ESTER HYDROLYSIS BY HIGH SILICA ZEOLITES

By

James William Gordon (B.Sc. Edinburgh)

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degree of Doctor of Philosophy from the
University of Edinburgh
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Declaration

I declare that this thesis is of my own composition and is an accurate account of research which I carried out at the University of Edinburgh between October 1982 and September 1985.
To Helen
Acknowledgements

I am greatly indebted to Dr. B.M. Lowe for his conscientious supervision of this work and for his advice and guidance.

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Lecture Series and Courses

I attended the following lecture series and courses during my period of study for a Ph.D.

Courses

Fortran 77 computing course
Edinburgh Regional Computing Centre

Lecture Series

Colloid Chemistry
Dr. W.D. Cooper (University of Edinburgh)

Modern Liquid Phase Separation Techniques
Professor J.H. Knox (University of Edinburgh)

The Chemistry of Photographic Processes
Dr. L.A. Williams (Kodak Ltd.)

Aspects of Structural Chemistry
Dr. C. Glidewell (St. Andrews University)

Least Squares Analysis
Professor J. Tellinghuisen (Vanderbilt University, Tennessee)

Molecular Electronics
Professors R.W. Munn and J.O. Williams (UMIST)

Microcomputers and Instrumentation
Dr. A. Rowley and Mr. A. King (University of Edinburgh)
Chemical Technology and Industrial Chemistry
Drs. A.J.S. Nicoll, L.H. Mustoe and R.S. Sinclair (Paisley College of Technology)

X-Ray Diffraction Techniques
Drs. R.O. Gould, B.M. Lowe and A. Blake (University of Edinburgh)

Seminars
Research group and Departmental seminars were also attended.
Abstract

This thesis reports an investigation into the use of aqueous dispersions of high silica zeolites to catalyse the hydrolysis of esters. The general principles underlying this process were established with ethyl acetate and the commercially important zeolite ZSM-5. The reaction was studied by a specially developed titration procedure in which the pH of the dispersion was kept constant so as to minimise the homogenous background reaction. The reaction was found to be catalysed by intracrystalline zeolitic Bronsted acid sites and was found to be directly proportional to the amount of H-ZSM-5 present. With ester hydrolysis the reaction was first order in ester concentration, and it appeared that the limiting step is a chemical process and that the reaction is not diffusion controlled.

An ion-exchange procedure in which the hydrogen ions in the acid zeolite are exchanged for alkali metal ions was used to provide an independant measure of zeolite acidity. The results complemented those of the ester hydrolysis work and confirmed that steric restrictions prevented H-Ferrierite from acting as a catalyst for the hydrolysis of ethyl acetate; and H-ZSM-5, H-Mordenite and H-EU-1 from acting as a catalyst for the hydrolysis of ethyl benzoate.

Each of the steps involved in the conversion of the 'as made' zeolite to the catalytically active hydrogen form were investigated. It was shown that the calcination to remove the organic template species should be carried out at as low a temperature as possible, and
that the acid form of the zeolite is best prepared by ion-exchange with hydrochloric acid. An investigation into the preparation of the H-zeolite by ammonium exchange followed by calcination showed that the optimum temperature for deammoniation was 400°C. The catalytic properties of acid zeolites are very dependant on the methods used in their synthesis. Accordingly a large part of this investigation was devoted to a study of the hydrothermal synthesis of ZSM-5. The effects of temperature, free base content, SiO₂/Al₂O₃, organic and cationic species were studied and the optimum conditions for particular products were identified. These studies also led to the discovery of a good route for the synthesis of the novel lithium silicate EU-8, and two derivative phases EU-8B and EU-8C.
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Introduction

1.1 Background

A zeolite is "a crystalline alumino-silicate in which each
tetrahedrally co-ordinated aluminium or silicon atom is linked by
oxygen to four others, such that the (Si + Al)/O ratio is 1/2,
giving a framework which encloses cavities occupied by cations and
water molecules, both of which have considerable freedom of movement
permitting cation exchange and reversible dehydration". This
definition by Casci [1] is a modification of previous definitions [2-4]
and should also be expanded to include analogous species such as
zeolitic gallogermates [5]. Silica molecular sieves, aluminium
phosphates (ALPOS) and silicon aluminium phosphates (SALPOS) [6-8],
have framework structures analogous to those of zeolites, but
in their 'ideal' forms they do not contain cations and hence unlike
zeolites they do not undergo cation exchange.

Zeolites may be represented by the formula:

\[ M_{x/n} \left( (AlO_2)_x (SiO_2)_y \right)_n \cdot H_2O \]

in which M is a cation of valence n (e.g. group I, group II, rare
earth, organic) which balances the anionic charge carried by the AlO_4
tetrahedra. The framework composition (enclosed in [ ] in the formula)
is characterized by the ratio Si/Al = y/x, which in accordance
with Lowenstein's rule [9] is always greater than or equal to unity.
The sum of x + y is equal to the total number of tetrahedra in the
unit cell. Zeolitic channel systems are referred to by the number of tetrahedral (T) atoms surrounding them; hence a 10 T-atom channel is one surrounded by ten tetrahedrally co-ordinated $\text{SiO}_4$ and $\text{AlO}_4$ units. The intracrystalline zeolitic water (w mole per unit cell) can, in most cases, be reversibly removed, and is dependant on the number and type of charged species in the zeolite. $M$ may denote a mixture of cations, e.g. in their 'as made' form many synthetic zeolites contain alkali metal and tetra-alkyl ammonium ions, and many natural zeolites contain mixtures of alkali metals and alkaline earth ions. In some synthetic zeolites, framework aluminium may be substituted by boron, iron, chromium or gallium ions and silicon by germanium or phosphorus.

The study of zeolites began with the discovery of the mineral stilbite by Cronstedt in 1756 [10]. Since then there have been innumerable publications describing the occurrences and mineralogy of natural zeolite minerals, and 29 structure types have been identified [3]. These materials fall into two categories: igneous zeolites and sedimentary zeolites. Igneous zeolites are believed to form from aqueous solutions in the cavities and basaltic fractures of volcanic lava flows. As this material cools, successive growths of different zeolites are formed in conjunction with other minerals such as calcite and quartz. Sedimentary zeolites are more common than igneous zeolites and can occur in beds up to several hundred metres thick. The mechanisms involved in forming sedimentary zeolites are not fully understood but a possible explanation is that water reacts with volcanic glass to form alkaline potassium and sodium solutions that can then dissolve silica, and from which the zeolites eventually crystallize. The extent and purity of some sedimentary deposits has led to their
commercial exploitation in Japan, U.S.A., Italy, Bulgaria, Yugoslavia, Germany, Korea, Cuba and Mexico. More information can be found in a number of detailed reviews on both the occurrence and commercial applications of natural zeolites [11-15].

The first report of a synthetic zeolite was that of levynite in 1862, followed by analcime in 1882 [16]. These early synthesis experiments were based on the then current ideas about how igneous zeolites were formed and involved the use of very high temperatures and pressures. The results were interpreted in terms of phase equilibrium diagrams and were considered from a geological viewpoint. Attempts to repeat these experiments have often failed because a lack of analytical data, especially X-ray powder diffraction patterns, prevents substantiation of the original observations. With the discovery of sedimentary zeolites came the realisation that zeolites could be made at lower temperatures and pressures, making their synthesis more commercially attractive. The new approaches to zeolite synthesis have been very successful, and have led to the discovery of many new zeolitic materials with exciting chemical properties.

The market for zeolites was estimated [15] to have grown from 9000 tons in 1960 to 248,000 tons in 1978 with major industrial applications as catalysts, sorbents, dessicants and ion-exchangers. Scientific publications numbered about 25,000 up to 1978 and have increased steadily since then [17]. This success prompted one leading researcher to write "rarely in our technological society does the discovery of a new class of inorganic materials result in such a wide scientific interest and kaleidoscopic development of applications as has happened with the zeolite molecular sieves" [18].
1.2 Structure and Classification

The 29 natural and 12 synthetic zeolite structures, discovered so far, constitute the largest known group of aluminosilicates. As such zeolites do not comprise of an easily definable family and early workers, limited by the lack of suitable single crystals, classified aluminosilicates according to their morphology, i.e. three-dimensional network structures with uniform bonding; lamellar type structures consisting of weakly bonded aluminosilicate sheets; and fibrous networks consisting of weakly cross-lined aluminosilicate chain units. However, as all zeolites are three-dimensional, framework aluminosilicates they could not be readily classified according to their morphology. Furthermore, many natural zeolites are misleadingly fibrous. Because most synthetic zeolites are only readily synthesised as small crystals, unsuitable for single crystal X-ray diffraction studies, their structures cannot be easily determined. Consequently it is all too easy for researchers to give different names to the same zeolite, e.g. zeolites B and P have the same structure, as do THETA-1, Nu-10 and KZ-2. This problem is exacerbated by the eagerness of research workers to secure proprietary rights on a potentially valuable zeolite structure. Attempts have been made to standardise zeolite nomenclature and there now exists a set of IUPAC recommendations [19].

The elucidation of the structure of faujasite [20] and zeolite A [21] was followed by the first classification of zeolites on the basis of common structural units such as parallel six-rings [2]. There are three types of framework building unit: primary, secondary and tertiary.
The primary building units are the $\text{TO}_4$ tetrahedra, where T is a silicon or aluminium atom tetrahedrally bonded to four oxygen atoms that act as bridges to neighbouring T atoms. The T-O-T bond angle is usually 140-180° and very seldom 180° [22].

The most common method for classifying zeolite structure types is based on secondary building units (SBU). These consist of rings or other assemblages of primary building units, from which a complete zeolite framework can be constructed. It was found that any zeolite structure can be made up using only one type of SBU, and it proved possible to classify all the known zeolite structures into seven groups, according to their unique SBU [3]. It has been suggested recently that in addition to the SBU's shown in Figure 1.1 that 3 and 9 rings should be added and that the classification into seven groups be extended to nine, by inclusion of the melanophlogite and lovdarite groups [23].

Tertiary building units are polyhedra of different shapes and sizes, that stack or join together to build framework structures which occupy all the available space or create the zeolite channel systems that surround the polyhedra. The advantage of using tertiary building units is that they make it easier to visualise the zeolitic void structure. The classic example of this approach is the construction of the sodalite, zeolite A and faujasite structures from the truncated octahedron ($\beta$-cage) illustrated in Figure 1.2.

Although forty-one zeolite structure types have been recognised so far, numerous zeolite-like models have been built and hundreds more structures postulated. The feasibility of some of these hypothetical models is currently being studied by considering
Figure 1.1  Secondary building units identified in zeolite structures [3]. Each straight line represents a T-O-T linkage.
Figure 1.2 Formation of different zeolite structures from the truncated octahedron (β-cage).

A β-cage; B sodalite; C zeolite A; D faujasite.
bond angle and symmetry constraints [22,24]. The use of computers to facilitate the elucidation of zeolite structures is changing the basic approach to discovering new zeolites; the new trend is to predict a feasible structure before attempting to synthesise it [25].

Further information on the structure, classification and nomenclature of zeolites may be found in several excellent reviews which provide a comprehensive coverage of this subject [24, 26-31].

1.3 Synthesis

The first systematic studies in the field of synthetic zeolite chemistry were carried out in the 1940's. Heating analcitem in water, in the presence of an excess of salt, at 180-220°C for 2-6 days gave the first novel zeolites: P (using barium chloride) and Q (using barium bromide) [32-33]. The first substantiated synthesis of mordenite was made in 1948 by Barrer [34]. This was followed by the development in the 1950's of a new approach that involved using very reactive components in closed systems at relatively low crystallization temperatures. A schematic example of gel preparation and crystallization in the Na₂O-SiO₂-Al₂O₃-H₂O system is shown in Figure 1.3:

\[
\begin{align*}
\text{NaOH(aq)} & + \text{NaAl(OH)₄(aq)} + \text{Na₂SiO₃(aq)} \\
& \Downarrow T_1 \quad 25°C \\
[\text{Na}_d(\text{AlO}_2)_b(\text{SiO}_2)_c \cdot \text{NaOH} \cdot \text{H}_2\text{O}] \text{ gel} \\
& \Downarrow T_2 \quad 25-175°C \\
\text{Na}_x[(\text{AlO}_2)_x(\text{SiO}_2)_y] \cdot x\text{H}_2\text{O} + \text{solution} \\
\end{align*}
\]

zeolite crystals

Figure 1.3 Gel synthesis method
The major advantage of this technique is that short crystallization times are achieved while working at relatively low temperatures. Three of the most commercially valuable zeolites; zeolites A [35-36], X [37] and Y [38] are made by this method.

The crystallisation of zeolites from reactive gels can be interpreted in terms of free energies (see Figure 1.4). It is found that the products of these hydrothermal crystallizations obey Ostwald's rule of successive transformations, i.e. the least stable phase crystallizes first and is then replaced by more stable forms. For example, for the system shown in Figure 1.4, at low temperatures the metastable phase A would be successively replaced by phases B, and then by phase C. This tendency towards more ordered states is consistent with the 'simplicity' principle.
The growth of zeolites requires the formation of nuclei of a critical size. In a high-simplexity, i.e. high entropy, system the structurally disordered forms will attain critical size before more complex zeolite structures, and consequently it is expected that the metastable forms will crystallize first.

Thermodynamic variables do not necessarily determine which product is formed as nucleation is kinetically controlled. Typical plots of zeolite formation against time are sigmoidal and described by:

\[ Z = \frac{Z_t}{Z_f} = 1 - \exp(-kt^n) \]  

(1.1)

where Z is the ratio of mass of crystals formed in the gel to their mass in the final crystallization product; \( k \) and \( n \) are constants with \( n \) related to the rate of nucleation. Crystal growth may be followed by a variety of analytical techniques, e.g. X-ray diffractometry [39,40], sorption measurements [41] and changes in the pH of the solution phase [41]. \(^{29}\)Si, \(^{27}\)Al and \(^{23}\)Na n.m.r. spectroscopic techniques have provided evidence for intermediate phases that cannot be detected by X-ray techniques [42-45]. Studies using Raman spectroscopy challenged the proposed theory of zeolite growth via a solution phase ion transport mechanism [39, 46-48]. Instead it was postulated that zeolite growth occurred by a solid phase transformation mechanism [49-52]. A third proposal put forward is that the type of mechanism occurring, i.e. solution or solid phase, is dependant on the silica source and gel formulation used [42]. Recent experiments using Raman spectroscopy have provided evidence for changes in the solution phase during
crystallization [53-55] and the prevalent view is that zeolite growth occurs by a solution phase mechanism [53-57]. Further information on phase metastability [14, 58-60], multinuclear n.m.r. spectroscopy [61-66], together with more general reviews may be found in the literature [4,12,14,67-71].

Studies on systems containing organic molecules were first carried out in the early 1960's [72] and led to the 'nitrogenous' analogues of zeolites A, X and Y, designated N-A [38], N-X and N-Y [73] respectively. Important differences in the X-ray diffraction patterns were found between zeolite A and N-A, and these were attributed to differences in cation content and Si/Al ratios. The fact that the Si/Al ratio of N-A is higher than that of zeolite A may be explained by observing that the tetramethylammonium ion is larger than the sodium ion, and that its occlusion into the zeolite means that there should be fewer anionic $\text{AlO}_4^-$ species present in the framework. The use of organic molecules in reaction mixtures led to the discovery of high silica zeolites, i.e. new materials with Si/Al greater than ten - the third generation zeolites. Zeolite $\beta$ was the first of the high silica zeolites and its discovery was followed by that of ZSM-5 by Argauer and Landolt [74] and ZSM-11 by Chu [75]. These zeolites were synthesised with symmetrical, tetraalkylammonium cations: tetraethylammonium (TEA) for $\beta$, tetrapropylammonium (TPA) for ZSM-5 and tetrabutylammonium (TBA) for ZSM-11.

The patent literature now abounds with preparations for many different zeolites. The formulations include the use of: symmetric singly charged organic cations, e.g. tetramethylammonium (TMA) for Nu-1 [76], Fu-1 [77]; tetraethylammonium for ZSM-8 [78]
and ZSM-12 [79]; asymmetric singly charged organic cations, e.g. benzyltrimethyl ammonium for erionite [80]; multiply charged organic cations, e.g. hexamethonium for EU-1 [81,82], 1,4-dimethyl-1,4-diazabicyclo[2,2,2]octane (DDO) for ZK-5 [83,84] and ZSM-10 [85]; polymeric organic cations for mordenite [86]. Uncharged organic molecules also work, e.g. 1,4-diazabicyclo[2,2,2]octane (DABCO) for ZSM-4 [87]; various amines for THETA-1 [88] (also known as Nu-10 [89-91] and KZ-2 [92]) and ZSM-39 [93]. There are several excellent reviews which give a more comprehensive listing of nitrogenous zeolites which have been made [94,95].

A close relationship between the size and shape of cations and the zeolite structure has often been observed and this has led to the suggestion that the cations act as templates. This has been the subject of much debate [51,96] although it is now, in principle, accepted [96-98]. The fit of TPA into the ZSM-5 structure makes it easy to envisage that the molecule is indeed acting as a template. If a cation does act as a template then:

- either (a) a zeolite different from that which would form in its absence is obtained,
- or (b) a zeolite crystallizes from a reaction mixture that would otherwise remain amorphous,
- or (c) the zeolite produced is the same as that which would form in its absence, but possesses an altered chemical composition.

There are many variables that can effect the type of product obtained in the hydrothermal synthesis of zeolites. The effects of some of these variables are summarised in Table 1.1.
Table 1.1  Effect of reaction mixture composition

<table>
<thead>
<tr>
<th>Mol. ratio</th>
<th>Primary influence</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂/Al₂O₃</td>
<td>Framework composition</td>
</tr>
<tr>
<td>H₂O/SiO₂</td>
<td>Rate, crystallisation mechanism, viscosity</td>
</tr>
<tr>
<td>OH⁻/SiO₂</td>
<td>Silicate molecular weight, OH⁻ concentration</td>
</tr>
<tr>
<td>Na⁺/SiO₂</td>
<td>Cation distribution</td>
</tr>
<tr>
<td>R₄N⁺/SiO₂</td>
<td>Framework aluminium content</td>
</tr>
</tbody>
</table>

1.4 Ion-Exchange

Although ion-exchange processes were used in biblical times [99], the first investigation into the use of zeolites as ion-exchangers was in 1858 when chabazite and natrolite were used by Eichorn [100] to reversibly exchange sodium and calcium ions from dilute solutions. This led to the term zeolite being used to include all inorganic materials that exhibited ion-exchange properties, and thereby added to the confusion over the definition of zeolites.

The ion-exchange properties of zeolites are associated with the tetrahedrally co-ordinated aluminium in the framework. The framework is anionic and cations are required to balance the charge. These cations are mobile within the lattice and may participate in exchange reactions. The ion-exchange process for a simple binary ion system is given as follows:

\[
\frac{Z}{A}B(Z) + \frac{Z}{B}A(S) \leftrightarrow \frac{Z}{A}B^+(S) + \frac{Z}{B}A^+(Z)
\]  \hspace{1cm} (1.2)
where $Z_A$, $Z_B$ are the valencies of cations A and B; the subscripts $Z$ and $S$ refer to the zeolite and solution phases respectively [101-102]. The equivalent fractions of the exchanging cation in the zeolite and solution are defined by:

$$A_S = \frac{Z_A M_A^S}{Z_A^S + Z_B^S}$$

(1.3)

$$A_Z = \frac{\text{number of equivalents of exchanging cation A}}{\text{total equivalents of cations in the zeolite}}$$

(1.4)

where $M_A^S$ and $M_B^S$ are the molalities of ions A and B at equilibrium in the solution. The selectivity of a zeolite for one of two ions can be expressed by a separation factor $\alpha_A^B$, defined by:

$$\alpha_A^B = \frac{A_Z B_S}{B_Z A_S}$$

(1.5)

An ion-exchange isotherm is produced by plotting $A_Z$ against $A_S$ for a given temperature and solution concentration. Deviation from $\alpha_A^B = 1$ indicates that the zeolite has a preference for one of the two ions. In all five types of ion-exchange isotherm have been recognised. It is possible from these to make deductions about the ionic environments and to determine the thermodynamic parameters of the ion-exchange reaction. Extensive studies have been carried out on both binary and multicomponent systems [103-107] and several reviews are available in the literature [102,108-116].

Zeolites are not the only silicate species that display ion-exchange properties. Layer silicate minerals such as montmorillonite have their anionic aluminosilicate sheets bound together by their inter-layer cations. On wetting, these layers
move apart and allow the cations to become mobile. However, zeolites with their rigid three-dimensional framework, do not swell on addition of water and this gives them different properties from clays. Careful choice of cation can result in some 'fine-tuning' of the ion-exchange properties of a zeolite. This is illustrated for analcine and zeolite X in Table 1.2.

Table 1.2 Ion-sieving properties of some zeolites [112]

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Exchange Proceeds Cation</th>
<th>Diameter (Å)</th>
<th>Negligible Exchange Cation</th>
<th>Diameter (Å)</th>
<th>Size of largest Pore Opening (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analcine</td>
<td>Rb⁺</td>
<td>2.96</td>
<td>Cs⁺</td>
<td>3.38</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>Rb⁺ (hydrated)</td>
<td>6.58</td>
<td>Cs⁺ (hydrated)</td>
<td>6.58</td>
<td></td>
</tr>
<tr>
<td>Zeolite X</td>
<td>N(CH₃)₄⁺</td>
<td>6.94</td>
<td>N(CH₃)₄⁺ (hydrated)</td>
<td>7.34</td>
<td>7.4</td>
</tr>
<tr>
<td></td>
<td>N(CH₃)₄⁺ (hydrated)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Despite the possibility of synthesising zeolitic ion-exchangers with very specific ion-exchange properties, zeolites are confined to a few specialised markets, leaving the more expensive organic ion-exchangers to dominate the major areas. Two reasons for this are:

(a) Aluminous zeolites, i.e. low Si/Al ratio, are unstable in even mildly acidic solutions. Improvements in acid resistance require higher Si/Al ratios and a consequent decrease in cation exchange capacity.
(b) In order to maintain satisfactory throughput rates in ion-exchange columns, zeolites have to be pelletised and this leads to a drop in the exchange rate to such an extent that they are significantly inferior to ion-exchangers.

The first commercial ion-exchange application of zeolites arose in 1960 when clinoptilolite was used to selectively remove $^{137}\text{Cs}$ and $^{90}\text{Sr}$ from low level radioactive waste generated by nuclear reactors [117-118]. However, the most important industrial use has been as water softeners in detergents, replacing the tripolyphosphate builders and preventing eutrophication which is a problem in closed water systems [119-120]. This market for zeolite A is alone worth several hundred million dollars.

1.5 Sorption

Although the ability of zeolites to sorb small molecules other than water was first reported in 1924 [121], it was not until the 1940's that they were applied as selective sorbents [122-124]. Zeolites with the most open framework structures have the highest sorption capacities although framework density (i.e. the number of T-atoms per unit volume) does not necessarily reflect the openness of a zeolite structure for a particular sorbate. Access to the intracrystalline void space and channels is controlled by the size of the windows, that is the smallest cross-sectional area of the channels. As zeolites are crystalline the shape and dimensions of the channels are uniform throughout the zeolite. The relationship between the window size and number of constituent T-atoms $n$, is shown in Table 1.3.
Table 1.3 Theoretical dimensions of "circular" pore openings

<table>
<thead>
<tr>
<th>n</th>
<th>Free diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1.1</td>
</tr>
<tr>
<td>5</td>
<td>1.9</td>
</tr>
<tr>
<td>6</td>
<td>2.8</td>
</tr>
<tr>
<td>8</td>
<td>4.3</td>
</tr>
<tr>
<td>10</td>
<td>6.3</td>
</tr>
<tr>
<td>12</td>
<td>8.0</td>
</tr>
<tr>
<td>18 (to be made)</td>
<td>15.0</td>
</tr>
</tbody>
</table>

The diameter of the ring openings can also vary depending on the distortion of the framework oxygen atoms, e.g. large-pore mordenite has elliptical 12-T atom channels and cannot sorb \((C_4H_9)_3N\), whilst zeolite Y which has circular 12-T atom channels can. Although many zeolite frameworks contain large polyhedral voids access to these voids may often be controlled by the type of cation present. The classic example is the sorption of n-paraffins by zeolite A. In the sodium form, the eight ring windows of zeolite A are blocked and there is no sorption of n-paraffins. On replacing sodium ions with calcium ions, the window size increases from approximately 4 Å to 5 Å and allows n-paraffins to be sorbed. This fine tuning of the window size is the basis of a commercial process in which n-paraffins are separated from branched chain hydrocarbons, with a product purity of over 98%. Temperature is another important variable as thermal vibrations of the aperture oxygens can change the window size [125]. The lower the temperature, the more sensitive the molecular sieving process becomes.
Molecular sieving ability of a zeolite is not just dependant on the accessibility of its channel system. Physical bonding between the zeolite sorbent and the sorbate molecules is also important, and is for example used as the basis for the separation of nitrogen (3.64 \(\text{Å}\)) from oxygen (3.46 \(\text{Å}\)) in air [126]. Nitrogen is preferentially sorbed by many zeolites because of the strong interactions between its quadrupole moment and the electric field gradients in the zeolitic void space. The strength of the interaction between the zeolite and the sorbate molecule is reflected in the heat of adsorption. This may be determined experimentally, or estimated theoretically by summing the energy contributions of the following: dispersion forces; close-range repulsion forces; polarisation effects; electrostatic interactions with sorbate dipoles; and electric quadrupole moment interactions with electric fields [127]. The sorption isotherms, plots of sorbate uptake (weight sorbate per unit weight of dry zeolite) as a function of sorbate pressure, are usually of the type I or Langmuir type. At higher uptakes, interactions between sorbate molecules are also important in the interpretation of the sorption isotherms [128].

The electric fields set up within zeolites are due to the charged species present, i.e. the cations and the tetrahedrally co-ordinated framework aluminium. The strength of these fields is dependant on both the type and distribution of the cation and on the aluminium content of the framework. The ability of zeolites to sorb polar molecules diminishes as the aluminium content of the framework is decreased [126,129-132]. Consequently, synthesis of the hydrophobic, aluminium-free silica molecular sieves, e.g.
silicalite-1, was clearly an important development in molecular sieve technology as they offer the opportunity to selectively sorb non-polar molecules.

It has been found that the results for the sorption of non-polar molecules from the gas phase usually fit type I isotherms in Brunauer's classification, e.g. hexane in ZSM-5 [133]. However, temperature, sorbate condensibility and sorbate molecule-molecule interactions all influence the type of isotherm obtained. Many equilibrium and kinetic studies have been carried out and the various types of isotherm obtained and the rates of equilibration are well documented [134-140].

The similar size of zeolite pores and many simple organics means that a molecule diffusing through a zeolite crystal is constantly under the influence of the zeolite surface. This leads to non-classical diffusion and a new type of diffusion regime called 'configuration' diffusion. The rates of diffusion of both the reactants and products in zeolite catalysts is very important in shape selective catalysis [141].

1.6 Catalysis

The break through in the large scale industrial application of zeolites came with their use in cracking catalysts in the petroleum industry. Although Rabo [142] showed in 1960 that zeolite Y could catalyse the cracking of hydrocarbons, their commercial application only became possible when rare earth ions were used to stabilise zeolite Y against steam and heat sintering. The replacement of
amorphous silica-alumina catalysts, which had been used since the 1940's, was as a result of the ability of zeolites, specifically rare earth zeolite Y, to yield 10% more petrol per barrel of crude oil. Since then there have been continuous improvements in catalyst design. Modern cracking catalysts comprise 40% rare earth exchanged H-Y zeolite dispersed in a silica-alumina or clay matrix. Although catalytic cracking is still the most important catalytic application of zeolites there are three other main areas:

1. Hydrocracking. This process utilises the acidic properties of zeolite catalysts in combination with the hydrogenation properties of noble metal catalysts.

2. Selecto-forming. This process makes use of the shape selective effects of zeolite cages in addition to their hydro-cracking properties to obtain C₅-C₉ n-paraffins from naptha.

3. Oil Dewaxing. This uses shape selectivity in the hydro-cracking of n-paraffins.

Zeolite acidity can be of two types: Brønsted acidity in which the zeolite acts as a proton donor and Lewis acidity in which the zeolite abstracts a hydride ion from the guest molecule. Brønsted acid sites are associated with the tetrahedrally co-ordinated framework aluminium (see Figure 1.5). The acidic protons are free to jump to neighbouring sites, their mobility being dependent

Figure 1.5 Brønsted acid sites

\[
\begin{align*}
\text{Si} & \quad \text{Al} \quad \text{Si} \\
\text{Si} & \quad \text{Al} \quad \text{Si} + \text{H}_2\text{O}
\end{align*}
\]
Dehydration of Brønsted acid sites at high temperature will give rise to Lewis acidity [146,147] (see Figure 1.6).

Figure 1.6  Lewis acid sites

\[
\begin{array}{c}
\text{O} \\
\text{Si} \\
\text{Al} \\
\end{array} \quad +\begin{array}{c}
\text{O} \\
\text{Si} \\
\text{Al} \\
\text{Si} \\
\end{array}
\]

However, Barrer and Klinowski [148] thought that a reaction that produced \( ^+\text{Si} \equiv \) was unlikely to occur. They showed that high temperatures dislodged aluminium from the zeolite framework, which then healed to produce 'true' Lewis acid sites (see Figure 1.7).

Figure 1.7  'True' Lewis acid sites

\[
\begin{array}{c}
\text{O} \\
\text{Si} \\
\text{Si} \\
\text{Al} \\
\text{Si} \\
\end{array} \quad (+\text{AlO})
\]

Both Brønsted and Lewis acidity can be generated by:

1. Direct calcination, provided the zeolite contains only organic or ammonium cations [149,150].
2. Calcination (if necessary) followed by hydrogen exchange. This can only be done with high silica zeolites.
3. Calcination (if necessary) followed by treatment with an ammonium salt, washing and thermal decomposition of the ammonium ions. This is a milder procedure than acid treatment and is used mainly with aluminous zeolites such as
zeolites X and Y [142,151,152], although it has also been used with mordenite [148] and ZSM-5 [153].

4. Ion-exchange with a polyvalent cation [154]. Hydrolysis of highly charged cations such as lanthanum, generates acid sites by:

\[
\text{M}^+_{\text{2} \text{O}}^n \xrightarrow{\text{H}_2\text{O}} \text{M}^+(\text{n-x})^x + x\text{H}^+
\]

There are a number of techniques that may be used to characterize catalytic sites in zeolites. Unfortunately no single method provides information on the nature, number, strength, environment, location and mean life-time of these sites. Coloured dyes, used to determine the acid strength distribution of other solid acids, are of limited use with zeolites because many of these relatively large molecules are excluded from the zeolite channels. The method also fails to give information on the precise nature of acid centres. Despite these limitations, the technique is widely used [155-157] and has been improved to reduce equilibration times [158] and minimise contamination [159].

The most widespread analytical technique used to characterize acid sites in zeolites is infra-red spectroscopy. There are two types of hydroxyl groups in acid zeolites: one gives a peak at about 3740 cm\(^{-1}\) and is due to terminal silanol hydroxyls whilst the other gives a peak at 3550-3650 cm\(^{-1}\) and is due to bridged hydroxyls. Brønsted acidity is associated with the peak due to the bridged hydroxyls and their lower vibrational frequencies reflect their greater acid strength. Infra-red studies on the interactions of bases sorbed by zeolites are usually carried out
using pyridine, methyl and ethyl substituted pyridines or ammonia
and allow both qualitative and semi-quantitative determinations
of Brønsted acidity to be made [160,161]. The competitive
replacement of pyridine by 2,6-di-t-butyl pyridine (which is
specific to Brønsted acid sites), has been used to study H-Fu-1
[162]. Other studies have investigated the frequency shift of
hydroxyl groups upon interaction with hydrogen bond acceptor
molecules, e.g. benzene [163]. I.R. spectroscopy has also been
used in conjunction with calorimetric measurements [164] and
temperature programmed desorption [165,166], both techniques giving
a direct determination of acid strength and distribution. Other
spectroscopic techniques that have been used have included U.V.
spectroscopy [167], proton n.m.r. spectroscopy [143,144]. A recent
review describes these techniques in more detail [168].

One of the chief aims of research in this area is to find
a unifying principle that relates acidity and catalytic activity
of zeolites to their structure and composition. Theoretical models
used to explain the catalytic properties of zeolites have included
analogies with ionising solvents [169], crystalline liquids [170,171],
and even transition metal complexes [172]. Amongst the more important
experimental observations is the fact that the number of acid sites
in H-ZSM-5 is proportional to its hexane cracking activity [130]
whereas the acid strength is determined by the framework Si/Al
ratio. A plot of hydroxyl vibration frequency against the
aluminium content of different H-zeolites shows that the hydroxyl
frequency decreases and the acidity increases as the Si/Al ratio of
the lattice increases up to Si/Al ≈ 5-6 [170]. Thereafter, the
hydroxyl vibration frequency remained constant as the Si/Al → ∞,
and it was suggested this was due to a lack of interactions with other framework atoms. However, this discontinuity was not found when the square of the hydroxyl vibration frequency was plotted against a pseudo electric field parameter (E) defined \[173\] as:

\[
E = \left( \frac{\text{Al}}{\text{Al} + \text{Si}} \right)^{4/3} C \quad \text{(1.6)}
\]

in which C is the number of T atoms per \(\text{nm}^3\). This discontinuity was predicted by the Sanderson electronegativity equilisation principle, which showed it to be a result of differences in the amount of residual cations that were not ion-exchanged during the preparation of the acid forms of the zeolites.

The principle states that in a molecule that contains atoms with different electronegativities the electrons will be redistributed in such a way that they will be equally attracted to the nuclei in the bond. The Sanderson electronegativity (\(S\)) for a compound \(A_aB_b\) where the component atoms have electronegativity \(S_A\) and \(S_B\) is given by:

\[
S = \left( \frac{S_A}{S_B} \right)^{1/(a+b)} \quad \text{(1.7)}
\]

The partial charge \((\Delta S_A)\) on atom A, that arises when the atom loses or gains one electron, is given by:

\[
\Delta S_A = \frac{(S - S_A)}{2.08 S_A^{1/4}} \quad \text{(1.8)}
\]

The principle gives correlations with catalytic properties for reactions that involve all the hydroxyl groups, e.g. dehydration of isopropanol or reactions which involve a constant fraction of hydroxyl groups, e.g. hydroconversion of n-decane. Also its
structural insensitivity is useful in comparing structurally
dissimilar zeolites. However, its use is limited to zeolite
crystals with a homogenous chemical composition. The concept of
superacidity, in which Bronsted acid sites have enhanced acidity
due to inductive effects associated with dislodged aluminohydroxyl
species and framework hydroxyls, can neither be predicted nor
explained in terms of overall chemical composition [174].
Improvements have been made to the principle and these are detailed
in reviews by Jacobs [173] and Barthomeuf [175].

The effects of increasing the Si/Al ratio not only changes
a zeolite's sorption properties but also its catalytic properties
because it results in fewer catalytic sites of increased strength.
Jacobs [152] has classified reactions over zeolite H-Y according
to the acid strength required to catalyse them. These are given
in Table 1.4 together with the equivalent strength of sulphuric
acid that would be required.

Table 1.4 Correlation between catalytic activity and acid
strength [152]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Acid Strength (% $\text{H}_2\text{SO}_4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Dehydration of alcohols</td>
<td>$3 \times 10^{-4}$</td>
</tr>
<tr>
<td>2. Isomerisation of olefins</td>
<td>$3 \times 10^{-4}$</td>
</tr>
<tr>
<td>3. Alkylation of aromatics</td>
<td></td>
</tr>
<tr>
<td>4. Isomerisation of aromatics</td>
<td></td>
</tr>
<tr>
<td>5. Transalkylation of alkylaromatics</td>
<td></td>
</tr>
<tr>
<td>6. Cracking of alkylaromatics</td>
<td>70</td>
</tr>
<tr>
<td>7. Cracking of paraffins</td>
<td>88</td>
</tr>
</tbody>
</table>
The isomerisation of butenes illustrates the effect of acid strength on product formation:

\[
\text{trans-2-butene} \rightleftharpoons [\text{carbocation intermediate}]^+ \rightarrow 1\text{-butene} \\
\downarrow \\
\text{cis-2-butene}
\]

The isomerisation of trans-2-butene is an acid catalysed reaction which obeys first order kinetics, with the product ratio of cis-2-butene/1-butene being dependant on the acid strength [176]. Using faujasite catalysts it has been found that increasing the Si/Al ratio results in an increase in cis-2-butene formation [177].

A lot of work has been carried out with the aim of optimising the catalytic activity of acid zeolites by careful modification of the framework composition. The controlled de-alumination of zeolites has been carried out by many different methods. Some of these are harsher versions of the hydrogen exchange process used to prepare the catalyst and usually incorporate treatment with steam [129]. However treatment with acid or ammonium chloride can result in the collapse of the zeolite framework and other milder approaches have been used. These include the use of complexing agents such as ethylenediaminetetraacetic acid (EDTA), direct fluorination [178], chromic salts [179], silicon tetrachloride [180,181], or a combination of treatments that includes a high temperature thermal treatment stage [182] amongst others [183].

Modifications to the zeolite structures are not only confined to their production with preferred acidic properties; they also include attempts to improve the shape selectivity of zeolites.
There are three types of shape selectivity:

1. Reactant selectivity will take place if the reactants can be divided into two or more classes of molecules, of which one, at least, will not be able to diffuse through the catalyst pores because of diffusion constraints, selective sorption or molecular sieving effects. Selecto-forming, hydro-cracking and molecular shape-selective cracking all take advantage of this property.

2. Product selectivity occurs when similar restrictions apply to the product molecules. The molecules are either converted to less bulky molecules (e.g. by equilibrium) or eventually deactivate the catalyst by blocking the pores. The selective production of para-aromatic compounds over ZSM-5 zeolite is based on this property.

3. Restricted transition-state, molecular shape selectivity occurs when local configurational constraints, acting in the direct environment of the catalytically active sites, will prevent or decrease the occurrence probability of a given transition state. Reactions that require smaller transition states proceed unhindered. An example of this is the acid catalysed transalkylation of dialkyl-benzenes.

Shape selectivity is dependant on the crystal size as larger crystals offer less external surface effects in combination with longer diffusional paths. Effects due to active sites on the crystal surface can be reduced by coking which is caused by the formation of carbonaceous residues during hydrocarbon transformations.
Although coking can rapidly block the channels of uni-
dimensional pore systems, zeolites with tri-dimensional channel
systems can tolerate higher levels of coking. In the latter
situation, selectivity is improved due to smaller pores and increased
diffusional path lengths [184]. The effects of coking in the
transformation of dimethylether into light olefins by different
zeolite types has also been studied [185]. Rollman [186] has
found that the number of active sites on the outer surface of
crystallites can be reduced by decreasing the aluminium content in
the last stage of crystallization of ZSM-5. Kaeding and co-workers
[187,188] have shown that the impregnation of zeolites with
phosphorus compounds can improve the selectivity of H-ZSM-5 in
the production of p-xylene from toluene and methanol. Shape
selective catalysis in zeolites is comprehensively covered by
recent reviews [189-195].

All of the foregoing catalytic studies refer to gas phase
reactions. There have been few investigations into zeolite catalysis
of liquid phase reactions, despite the fact that homogenous acid
catalysed reactions often occur under mild conditions. Ruddlesden
and Stewart [196] have shown that zeolite Y is efficient, relative
to enzyme catalysts, in producing d-mannitol from d-glucose. It
has also been reported that it can catalyse the hydrolysis of methyl
(or ethyl) acetate although H-ZSM-5 was found to be much more
active [197].
1.7 **The Aims of this Work**

The aim of this work was to investigate the catalytic properties of zeolites dispersed in an aqueous solution. Virtually all the work that has been carried out on zeolite catalysis has concentrated on gas phase reactions and little is known about those in which the reactants are in the liquid phase. Accordingly, it was decided to investigate the hydrolysis of ethyl acetate as it is an acid catalysed reaction that is well documented in the literature. Although it has been claimed that zeolites Y, ZSM-5 and mordenite can catalyse this reaction, the work [197] was considered to be unreliable and open to many criticisms. Foremost amongst these was the use of an unsatisfactory experimental method in which the pH was not kept under control. For the work in this thesis a novel technique, which utilises the molecular sieving properties of zeolites was used to follow the reactions.

The initial objective of obtaining unambiguous evidence that such catalysis is indeed possible was achieved early in the investigations and work then concentrated on the use of the hydrolysis reaction to study the nature of the catalytic sites. This work required an independent measure of zeolite acidity and for this an ion-exchange procedure, similar to that developed by Breck and Skeels [198] was used. The effect of zeolite structure, morphology and the variables associated with the preparation of acid zeolites was investigated. The aim of this work was to prepare acid zeolites that were highly efficient catalysts for acid catalysed reactions such as the hydrolysis of esters in the liquid phase.
1.8 Layout of Thesis

Chapter 1 gives a general introduction to zeolite chemistry and highlights areas of research that are currently the subject of intensive investigations. In addition there is also a section in which the aims of this work are clearly defined.

Chapter 2 describes those analytical techniques which were used to characterize and identify the zeolites.

The zeolite samples used were all made to exact specifications and their synthesis and characterization is detailed in Chapter 3. In addition, separate investigations were undertaken on two of the most topical subjects, namely synthesis of organic free ZSM-5 and the templating role of uncharged organic molecules such as amines and alcohols. Studies were also carried out on the effect of temperature, inorganic cation and free base content in high silica zeolite systems.

Chapter 4 describes the novel technique that was used to follow the catalysis of ester hydrolysis by zeolites. Evidence is given to show that zeolites, and in particular ZSM-5, do possess catalytic properties. The kinetics, mechanism and activation energy for the reaction are all discussed in detail. The efficiency of acid zeolites as catalysts for the hydrolysis of esters is compared to that of other acid catalysts such as hydrochloric acid and cation-exchange resins.

The ion-exchange procedure that was used as a measure of zeolite acidity is described in Chapter 5. The complementary nature of the ion-exchange procedure and the hydrolysis reaction are used
to study the nature of the catalytic sites in acid zeolites in more detail.

In Chapter 6, the use of both techniques to investigate all of the variables associated with the preparation of acid catalysts is described. This work concentrates mainly on the way in which heat treatment effects the catalytic activity of ZSM-5.
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2.1 Introduction

The analytical techniques described in this chapter are those which were used to characterise and identify the zeolites. They were used extensively throughout the course of this research and are introduced to avoid repetition in the chapters that follow. The procedures that were employed to synthesise and evaluate the catalytic activity of zeolites are described and discussed in the appropriate chapters.

The importance of thorough characterisation of zeolites was emphasised in Chapter 1 and indeed much of the early synthetic work is unsatisfactory because the zeolites were not properly characterised. For example, Baur reported the synthesis of a potassium "faujasite" which was later shown to be the compound $\text{K}_2\text{SiF}_6$ [1]. The identification and characterisation of the catalytic sites in zeolites is difficult, and no single technique can provide all the necessary information.

2.2 X-Ray Powder Diffraction (XRD)

Introduction

Zeolites are crystalline materials and as such they diffract X-rays according to the Bragg condition:

$$n\lambda = 2d \sin \theta$$

which relates the wavelength ($\lambda$) and angle of incidence ($\theta$) of the radiation to the interplanar spacing ($d$). $n$ is an integer which
represents the order of reflection from an atomic plane. Although most of the monochromated X-rays pass through the powdered sample some are reflected by the lattice planes and it is these diffracted X-rays that characterise the crystal. The two main applications of X-ray powder diffraction in zeolite chemistry are (i) to monitor the progress of crystallisation and (ii) to characterise the final crystal product - the peak heights and positions of maximum intensity are used as "fingerprints" and compared against known diffraction patterns.

Experimental

A Philips semi-automatic X-ray powder diffractometer was used. It consisted of a PW1965/60 goniometer mounted on a PW1730 stabilised X-ray generator, fitted with a fine focus copper X-ray tube that provided CuKα₁,₂ radiation (mean \( \lambda = 1.5418 \) Å). A graphite monochromator was mounted between the sample and the detector. Samples were loaded by a PW1170 automatic sample changer and scanning was controlled with a PW1394 control unit. Output was analysed by a PW1390 single channel control unit and fed into a PM8203 pen recorder to give continuous mode scanning. Peak heights and positions of maximum intensity were converted into relative intensities and d-spacing values for comparison with standard patterns contained in files.

Samples were initially ground to a fine powder form and carefully packed into diffractometer slides. Standard operating conditions used throughout this work were as follows:
The percentage crystallinity was determined from the integral peak intensities (I) by the equation

\[
\text{% crystallinity} = 100 \cdot \frac{I}{I_o}
\]  

(2.2)

where \( I_o \) is the integral peak intensity of a standard sample chosen for its high crystallinity and purity. The ratio \( I/I_o \) is given by [2]:

\[
\frac{I}{I_o} = \frac{w \cdot H}{w_o \cdot H_o}
\]  

(2.3)

where \( I/I_o \) is the ratio of integral intensities which are calculated by multiplying together the peak height (H) and the peak width at half the peak height (w). The subscripts refer to use of a standard sample. The equation assumes that both \( I \) and \( I_o \) are obtained using the same operating conditions. Correction factors must be applied if \( I \) and \( I_o \) are obtained using different operating conditions. The standard samples that were used are given in Table 2.1.

A peak summation method that included the use of several of the most intense diffraction lines was felt to be the most accurate way to represent the % crystallinity of a sample. It was felt that its use could reduce the errors associated with water content variations and the presence of different organic molecules. The % crystallinities
Table 2.1  Standard zeolite and silicate samples used

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Code</th>
<th>Relevant Chapter</th>
<th>Peak positions (2θ)</th>
<th>$I_0$ cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5</td>
<td>T49</td>
<td>3.3</td>
<td>7.98, 8.85, 23.10, 23.93, 24.41</td>
<td>27.0</td>
</tr>
<tr>
<td>Mordenite</td>
<td>J19</td>
<td>3.5</td>
<td>6.65, 9.88, 19.81, 27.84</td>
<td>13.4</td>
</tr>
<tr>
<td>Ferrierite</td>
<td>J68</td>
<td>3.5</td>
<td>9.34, 25.23, 25.64</td>
<td>15.7</td>
</tr>
<tr>
<td>Magadiite</td>
<td>B5</td>
<td>3.6</td>
<td>5.84</td>
<td>4.5</td>
</tr>
<tr>
<td>Kenyaiite</td>
<td>b</td>
<td></td>
<td>4.55</td>
<td>3.6</td>
</tr>
</tbody>
</table>

a  Applicable to standard operating conditions.
b  Supplied by Dr. K.R. Franklin

determined in this way are subject to an error of ±10% of crystallinity. This is partly due to the sources of error already mentioned and also because it is difficult to pack the samples reproducibly. Other errors include that associated with the measurement of peak heights and widths, and that which arise from fluctuations in the X-ray tube intensity.

2.3  X-Ray Fluorescence Spectroscopy (XRF)

Introduction

The chemical composition of the zeolite samples was obtained by X-ray fluorescence analysis.

Experimental

Analyses were carried out on a Philips PW1450 sequential automatic X-ray spectrometer fitted with a chromium tube. Instrument calibration and sample analysis were carried out by the Department of Geology, Edinburgh University.

The help of Dr. J.G. Fitton in obtaining the XRF analyses is gratefully acknowledged.
Fused glass discs were prepared by adding to 1 - 1.2 g of anhydrous zeolite exactly 5x as much (by weight) of Johnson Matthey lithium borate spectroflux 105. The mixture was melted in a platinum-gold crucible and mixed thoroughly before being poured into a graphite mould and allowed to cool slowly. The procedure followed was identical to that described in the instruction manual [3].

The raw data was obtained in the form of weight % of the following main group metal oxides: SiO₂, Al₂O₃, Fe₂O₃, MgO, CaO, Na₂O, K₂O, TiO₂, MnO and P₂O₅. These results were then converted into the required molar ratios.

2.4 Thermal Gravimetric Analysis (TG)

Introduction

Thermal gravimetric analysis measures the weight of a sample as a function of temperature. Zeolite weight losses due to the loss of water and organic material are observed. Provided these processes occur over separate temperature ranges both can be accurately measured.

Experimental

Analyses were carried out on a Stanton-Redcroft TG770 thermal balance connected to a Kipp & Zonen BD9 twin-channel chart recorder. About 6 mg of sample was used. Prior to analysis each sample was equilibrated with water vapour by standing over a solution of saturated sodium chloride at 25°C for at least 24 hours (p/p° = 0.753). The standard operating conditions used throughout this work were as follows:
Heating Rate  
10°C min\(^{-1}\)

Temperature Range  
Room temperature → 1000°C

Air Flow  
4.5 cm\(^3\) min\(^{-1}\)

Chart Speed  
2 mm min\(^{-1}\)

Temperature  
10 mV full-scale deflection

Weight Loss  
50% full-scale deflection

2.5 **Differential Thermal Analysis (DTA)**

*Introduction*

In DTA the difference between the temperature of the sample under investigation and a thermally inert reference sample, when both are heated under identical conditions, is observed. To achieve this similar quantities of sample and reference material are placed in matched crucibles which are mounted on thermocouples which are placed symmetrically in a vertical tube furnace. If an endothermic process occurs in the test sample its temperature will lag behind that of the reference material. The reverse occurs for an exothermic process. In some cases the exothermic and endothermic peaks observed as a function of temperature by DTA can be related to the weight changes observed by TGA. In other cases, peaks for which there is no corresponding weight loss are observed. For example, phase transitions usually give rise to sharp endothermic peaks.

*Experimental*

Differential thermal analyses of samples were carried out on a Stanton-Redcroft DTA674 differential thermal analyser connected to a Kipp & Zonen BD9 twin-channel chart recorder. About 0.06 g of sample was used. Before analysis each sample was equilibrated with water vapour by standing over a solution of saturated sodium chloride at 25°C
for at least 24 hours (p/p° = 0.753). The standard operating conditions used throughout this work were as follows:

- **Heating Rate**: 10°C min⁻¹
- **Temperature Range**: Room temperature → 1000°C
- **Air Flow**: Static
- **Reference Material**: Alumina
- **Amplification**: 50
- **Chart Speed**: 2 mm min⁻¹
- **Temperature (T)**: 10 mV full scale deflection
- **ΔT**: 10 mV full scale deflection

### 2.6 Optical Microscopy

#### Introduction

Optical microscopy was used to provide a very quick method for following the crystallisation and had the additional advantage that it required a very small amount of sample.

#### Experimental

Analyses of samples taken during the course of the crystallisation were carried out on a Vickers model M41 Photoplan optical microscope fitted with a 20x oculars and the following lenses:

<table>
<thead>
<tr>
<th>Lens</th>
<th>Magnification</th>
<th>Numerical aperture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vickers Microplan Y8959</td>
<td>10 x</td>
<td>0.25</td>
</tr>
<tr>
<td>Vickers Microplan Y2910</td>
<td>4 x</td>
<td>0.12</td>
</tr>
<tr>
<td>Vickers Microplan Y3686</td>
<td>2.5 x</td>
<td>0.08</td>
</tr>
<tr>
<td>W. Watson &amp; Sons, London, 1/8</td>
<td>60 x</td>
<td>-</td>
</tr>
</tbody>
</table>
This system allowed 0.5 μm crystals to be observed. Crystal size determination was possible by estimation against a 1 μm background grid. Only a small amount of sample was required and this was sandwiched between a glass slide and a cover slip. Photographs could be taken using a Pentax ME Super 35 mm camera which was connected to the binocular viewing head and lit by means of a beam splitter.

2.7 Scanning Electron Microscopy (SEM)

Introduction
Accurate determinations of crystal sizes and morphology were made using scanning electron microscopy. In comparison to optical microscopy, SEM has superior magnification capabilities and 3-D vision (as opposed to 2-D vision) as it has a greater depth of field.

Experimental
Scanning electron micrographs were obtained using a Cambridge Instruments type 604 Stereoscan scanning electron microscope which provided up to 50,000 x magnification. Photographs of the crystals were taken with a Practica L2 35 mm camera. A micron marker facility on the SEM enabled crystal sizes to be accurately determined. Typical operating conditions used throughout this work were as follows:

<table>
<thead>
<tr>
<th>Magnification</th>
<th>500 - 50,000 x</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shutter Speed</td>
<td>10, 20, 50 seconds</td>
</tr>
<tr>
<td>Working Distance</td>
<td>10 mm</td>
</tr>
<tr>
<td>Definition</td>
<td>spot size 3</td>
</tr>
</tbody>
</table>

The samples were mounted on to aluminium pegs as follows. A small quantity of sample was placed on a clean stub, one drop of
arklone was added, and the mixture stirred to ensure separation of the crystals. After the arklone had evaporated off, the stub was placed on a Polaron Equipment Ltd. scanning electron microscope coating unit E5100 fitted to an Edwards high vacuum pump. The sample was pumped down and twice flushed with nitrogen before being coated with a thin film of gold by the procedure described in the instruction manual [4].

2.8 pH Measurements

Introduction

The crystallisation of zeolites from alumino-silicate gels is usually accompanied by a sharp increase in pH; and hence pH measurements of samples taken from reaction mixtures can be used as a simple, rapid method for monitoring the crystallisation process [5]. The method is particularly suitable for following crystallisations from reaction mixtures with relatively low pH values, such as those used in the synthesis of high silica zeolites. Although other quantitative methods can be used to follow the crystallisation process, e.g. sorption, X-ray powder diffraction, they all require the solid phase to be separated from a sample of the reaction mixture and then washed, dried and equilibrated with vapour prior to analysis. These preparative steps are all time consuming and are inappropriate if the aim is to prevent reaction over-run.

The pH rise arises as follows:

(1) Amorphous silica is more soluble than crystalline zeolite. Hence for a given level of base there is more silica in solution in the presence of amorphous silica than in the presence of zeolite.
(2) Amorphous silica, being more soluble, continues to control the silica level in solution until it is nearly all consumed. At this point control is transferred from the amorphous silica to the zeolite.

This may be represented by the following equations:

\[
\begin{align*}
\text{H}_2\text{O} + \text{SiO}_2\text{ amorphous} + \text{NaOH} & \rightarrow \text{Na}^+ + (\text{HO})_3\text{SiO}^- \\
\text{Na}^+ + (\text{HO})_3\text{SiO}^- & \rightarrow (\text{SiO}_2\text{) zeolite} + \text{H}_2\text{O} + \text{NaOH}
\end{align*}
\]

Dissolution of amorphous silica consumes base and formation of zeolite releases it. There is no nett change until the amorphous silica is used up. Obviously the situation is much more complicated than that represented above and the pH is controlled by the buffering action of many different anionic species present in the reaction mixture.

**Experimental**

pH measurements were made with an EIL plastic bodied combination pH electrode type 1180/200/UKP connected to a Philips PW9422 pH meter. Automatic temperature compensation was used and for this the laboratory temperature was monitored with a Pt100 resistance thermometer. The electrode was standardised in pH = 7.00 and pH = 9.20 reference buffer solutions (BDH tablets).

Measurements were carried out on samples that had been taken from reaction mixtures and allowed to cool to room temperature. Each sample (ca. 8 cm³) was stored in a stoppered glass bottle. Stable pH readings were obtained after 10 minutes and the pH electrode was carefully washed with distilled water between measurements. After a series of measurements had been made the pH of the pH = 9.20 buffer solution was re-checked. If the pH drift was found to be greater
than ±0.1 then the samples were re-measured. If possible all the samples
taken from a particular reaction were re-measured after the reaction
had finished so that electrode errors could be minimised. The
uncertainty in the absolute accuracy of measurements made in this
work is believed to be less than 0.1 pH units with differences of
0.03 or more between pH readings taken at different times on different
is
samples considered to be significant.
Chapter 2 - References

[1] M. Schlaepfer and P. Niggli


"A Users' Guide to the X-Ray Fluorescence Analysis of Rock
Samples", Grant Institute of Geology, Edinburgh University, 1984.

[4] W.D. Cooper
"A Users' Guide to the Scanning Electron Microscope",
Department of Chemistry, Edinburgh University, 1982.

CHAPTER 3

Synthesis of Zeolite ZSM-5

3.1 Introduction

It was explained in Chapter 1 that zeolites can have a framework Si/Al ratio of between one and infinity, and that the Si/Al ratio affects their sorption and catalytic properties. These can be altered within limits by adjustment of the Si/Al ratio. The principle requirement of the zeolites used in this work was that they should be able to sorb a non-polar ester molecule from a polar solvent, protonate it and desorb the relatively more polar hydrolysis products. Whilst the sorption/desorption stages require a hydrophobic zeolite with a low aluminium content, the catalytic sites required to protonate the ester molecule, are associated with aluminium in the zeolite framework. The zeolite ZSM-5 was chosen as the catalyst because it can be made over a large range of framework Si/Al ratios and has already been intensively studied by many research groups since it was first reported in 1972 by Argauer and Landolt [1].

Zeolite ZSM-5 is a member of the pentasil family [2]. Its structure can be derived from 5-1 SBU's [3] and it has apparent orthorhombic symmetry P\textsubscript{nma}. Olson et al [4,5] reported that the unit cell parameters were: a = 20.07 Å, b = 19.92 Å and c = 13.42 Å. The intracrystalline pore system consists of two 10 T-atom channels, one straight channel parallel to [010] of 5.4 x 5.6 Å and one sinusoidal channel of 5.1 x 5.5 Å that goes along [100]. The channel system is effectively three dimensional as diffusion in the [001] direction can take place by movement between the two...
channels. A diagrammatical representation of the ZSM-5 channel system is shown in Figure 3.1 together with a cross-sectional view along [010].

---

**Figure 3.1**  
(a) Skeletal diagram of ZSM-5 viewed along [010]  
(b) Diagrammatic representation of the ZSM-5 channel system

Zeolite ZSM-5 is usually synthesised from reaction mixtures which contain tetrapropyl ammonium cations. These ions act as templates for the ZSM-5 structure and occur intact at the channel intersections [6]. About 3.3–3.8 TPA molecules are usually found per unit cell and these all have tetrahedral symmetry [7]. Boxhoorn et al [8] have shown by nmr studies that weak interactions exist
between the organic and the zeolite framework. In accordance with
the original patent ZSM-5 is usually made from a reaction composition
that contains sodium and TPA ions. As already stated, ZSM-5 can be
made over a wide range of Si/Al ratios. An aluminium free analogue
of ZSM-5 has also been made and has been designated silicalite-1 [9].
Olson et al [10] showed that the "ion-exchange capacity, catalytic
activity and water sorption (at P/P_0 = 0.006) of ZSM-5 varied
linearly with aluminium content and extrapolated smoothly to the
end member of the series, a pure silica ZSM-5". These together with
other similarities between ZSM-5 and silicalite-1 led them to suggest
that silicalite-1 "appears to be a member of the ZSM-5 substitutional
series". Whether or not silicalite-1 can be regarded as "a member
of the ZSM-5 substitutional series" is the subject of much debate
at present [11,12].

Studies carried out on zeolite formation favour a solution phase
ion transportation mechanism (see Chapter 1.3). An adaptation of
the scheme proposed by Chao et al [13] for the formation of ZSM-5
by a solution phase mechanism, is given in Figure 3.2. As can be
seen the aluminosilicate or polysilicate hydrogel is attacked by
strong bases such as NaOH or TPAOH to form soluble silicalite and
aluminate species in solution. These can condense to form soluble
polymeric aluminosilicate and silicate species. There then exists
a quasi-equilibrium between the gel, dissolved species and zeolite
nuclei. As the ZSM-5 nuclei grow they become less soluble in solution.
It is the relative insolubility of zeolite crystals that forces the
reaction and causes the growing zeolite crystals to be fed with zeolite
building units. These units are formed for as long as the equilibrium
between gel, dissolved species and zeolite nuclei is maintained.
Figure 3.2  Schematic representation of ZSM-5 formation by a solution phase mechanism

amorphous aluminosilicate gel $\xrightarrow{\text{OH}^-} \xrightarrow{\text{H}_2\text{O}}$ monomeric silicate and aluminate species

$\xrightarrow{\text{OH}^-} \xrightarrow{\text{H}_2\text{O}}$ polymeric aluminosilicate and silicate species

$\xleftarrow{\text{TPA}^+ \xrightarrow{\text{OH}^-}}$ ZSM-5 nuclei crystal growth $\rightarrow$ ZSM-5 crystals

However, there are many uncertainties associated with the formation of ZSM-5, especially as to the nature of the species that act as building blocks to the growing zeolite crystals. Possible ZSM-5 precursors include the double five-ring silicate. $^{29}\text{Si}$ n.m.r., mass spectroscopy and attenuated total reflection Fourier transform infra-red spectroscopy studies carried out by Boxhoorn et al [14] showed an enhancement of the peak attributed to the double five-ring silicate after the addition of methanol, ethanol and dimethylsulphoxide to the ZSM-5 synthesis mixture. An $\text{Al(OSiO}_3\text{)}_{13^-}$ aluminosilicate precursor has been postulated by Guth et al [15] for solutions which have a Si/Al ratio greater than 5. Roozeboon and co-workers [16,17] postulated a mechanism whereby the $\text{Al(OSiO}_3\text{)}_{13^-}$ species reacted with polysilicate species to form five-ring systems.
Derouane et al. [18] also postulated that this species is the one transported through the liquid phase of silicon rich gels.

Monomeric species certainly play an important role during the synthesis of ZSM-5. Monomeric silicate, i.e. \((\text{HO})_3\text{SiO}^-\) and \((\text{HO})_2\text{SiO}_2^2-\) are known to be present in large quantities in the solution phase [19,20]. The solubilities of these and other silicate species are well documented in the literature [21-24]. Lowe [25] proposed an equilibrium model that explained the pH change due to the crystallization of high silica zeolites and predicted the maximum yield of zeolite. The model is based on the equilibrium between the solid phase and soluble silicate anions.

Studies on the nature of the aluminium species in solution have shown that the aluminium is monomeric for reaction compositions with \(\text{Na/Al} > 2.5\) [15,26]. Chao et al. [13] showed that the presence of aluminium in the reaction mixture had an effect on the crystallization rate. The apparent activation energies for nucleation and crystal growth in the aluminium-free silicate system were found to be 38 and 46 kJ mol\(^{-1}\) respectively. These activation energies decreased to 25 and 29 kJ mol\(^{-1}\) respectively when the reactant composition had \(\text{SiO}_2/\text{Al}_2\text{O}_3 = 70\). Mostowicz and Sand [27] found that the activation energy for crystal growth is lower than that for nucleation. They obtained an activation energy for the nucleation of ZSM-5 of 36-134 kJ mol\(^{-1}\) and found that it was dependant on the \(\text{SiO}_2/\text{Al}_2\text{O}_3\) ratio of the reaction composition. The alkali metal cation used in the reaction mixture was also found to effect the growth rate of ZSM-5 crystals. For reactant compositions with \(\text{SiO}_2/\text{Al}_2\text{O}_3 = 90\), the apparent activation energies for nucleation
and crystallization in a sodium system were 36 kJ mol\(^{-1}\) and 84 kJ mol\(^{-1}\). The corresponding figures for lithium were 31 kJ mol\(^{-1}\) and 94 kJ mol\(^{-1}\) and for potassium, 63 kJ mol\(^{-1}\) and 98 kJ mol\(^{-1}\).

Crystal size and morphology are also dependant on the nature of the cationic species. Mostowicz and Sand [27] found that for the system 4.5(TPA)\(_2\)O 12X\(_2\)O Al\(_2\)O\(_3\) 90SiO\(_2\) 3000H\(_2\)O, where X is an inorganic cation, that crystal size decreased in the order Sr > Ba > K > Li > Na. Sand and co-workers have published a series of papers on the morphological effect of silica source [28] and inorganic cation [29].

Zeolite ZSM-5 can also be made from systems that do not contain group I and II species. Bibby et al [30] and Ghamami and Sand [31] both report the successful synthesis of ZSM-5 from ammonium systems. Other successful compositions have included those that contain transition metal complexes [32,33], boron [34] and iron [35]. Whether or not ZSM-5 can crystallize from mono-cation TPA systems is less clear as both amorphous [36] and ZSM-5 [37] products have been reported.

Zeolite ZSM-5 can also be made from organic free sodium systems [38,39]. In both of these investigations great care was taken to eliminate the possibility of seeded reactions. Perhaps not surprisingly the synthesis of ZSM-5 has also been reported from other TPA free systems. These have used primary amines [40,41] triethyl-n-propyl ammonium cations [42], sodium n-dodecyl benzene sulfonate [43], alkanolamines [44] and alcohols [45-47] as the organic species.
3.2 Experimental

3.2.1 Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Source</th>
<th>Purity/Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lithium hydroxide</td>
<td>Fisons Ltd.</td>
<td>SLR</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>Aldrich Ltd.</td>
<td>AR</td>
</tr>
<tr>
<td>Potassium hydroxide</td>
<td>Fisons Ltd.</td>
<td>SLR</td>
</tr>
<tr>
<td>Alumina trihydrate</td>
<td>B.A.C. Ltd.</td>
<td>Kaiser</td>
</tr>
<tr>
<td>Aluminium</td>
<td>B.D.H. Ltd.</td>
<td>AR</td>
</tr>
<tr>
<td>Silica</td>
<td>B.D.H. Ltd.</td>
<td>Cab-o-sil M5</td>
</tr>
<tr>
<td>Tetrapropylammonium bromide (TPABr)</td>
<td>Fluka Ltd.</td>
<td>Purum</td>
</tr>
<tr>
<td>Tetrapropylammonium hydroxide (TPAOH)</td>
<td>Fluka Ltd.</td>
<td>Pract.</td>
</tr>
<tr>
<td>Piperazine hexahydrate</td>
<td>Aldrich Ltd.</td>
<td>98%</td>
</tr>
<tr>
<td>Hexane-1,6-diol</td>
<td>Aldrich Ltd.</td>
<td>99%</td>
</tr>
<tr>
<td>1,4-diazobicyclo[2,2,2]octane</td>
<td>Aldrich Ltd.</td>
<td>97%</td>
</tr>
<tr>
<td>Pinacol</td>
<td>B.D.H. Ltd.</td>
<td>98%</td>
</tr>
<tr>
<td>Homopiperazine</td>
<td>Aldrich Ltd.</td>
<td>98%</td>
</tr>
</tbody>
</table>

3.2.2 Reaction Vessels

3.2.2.1 500 cm³ Autoclaves

Most of the zeolite samples made during the course of this work were prepared in one of three identical 500 cm³ autoclaves that were designed and built by Baskerville and Lindsay Ltd. A schematic drawing of a 500 cm³ autoclave is given in Figure 3.3. An external control console monitored the temperature, pressure and stirring speed. Temperature control was by a Gulton-West MC36 four term temperature controller connected to a thermocouple situated in a thermocouple pocket which projected into the reaction mixture. The pressure gauges used incorporated a reed switch which could automatically cut the power to the heating mantle if a pre-set pressure was exceeded. A bursting disc set to rupture at 45 atmosphere pressure was also fitted. Stirring speed was monitored by
Figure 3.3 Schematic representation of 500 cm$^3$ autoclave

a stirrer motor; b rotating external magnet; c sampling tube;
d pressure gauge; e high pressure $N_2$ inlet; f retaining studs;
g heating mantle; h reaction vessel. In the reaction vessel from
left to right: sample port, stirrer and thermocouple pocket.
the external control console and could be checked by a handheld Power Instruments digital tachometer Model 1891-M. A Comark digital thermometer was used for more accurate temperature measurements. Typical operating conditions were:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>150°C ± 1°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>autogenous</td>
</tr>
<tr>
<td>Stirring speed</td>
<td>300 rpm</td>
</tr>
<tr>
<td>Sample weight</td>
<td>440 g</td>
</tr>
</tbody>
</table>

A sampling port allowed easy removal of a small portion of reaction mixture for analysis. About 8 cm³ of sample was taken at regular intervals during the course of a reaction.

The autoclaves were always thoroughly cleaned between reactions with 4% aqueous sodium hydroxide solution. The standard procedure involved heating the sodium hydroxide in the reaction vessel up to 100°C and maintaining the temperature for three hours, before cooling and repeating the process. The sampling port was cleaned by the removal of a sample of sodium hydroxide when the solution was at 100°C. Sometimes unusually heavy deposits of mixture warranted repetition of the cleaning procedure. These thorough cleaning procedures were required to combat seeding effects.

3.2.2.2 1 Litre Autoclave

When large amounts of product were required or when a standard recipe, e.g. hexanediol-ZSM-5 and piperazine-ZSM-5 was used, then the reactions were carried out in a 1 litre stainless steel autoclave which was designed and built by Baskerville and Lindsay Ltd. The temperature, pressure and stirring speed controls as well as the safety devices were similar to those fitted to the 500 cm³ auto-
claves. The cleaning and operating procedures were the same as those for the 500 cm$^3$ autoclaves except that 800 g of reaction mixture was used. The usefulness of this autoclave was limited as it lacked a sampling facility and consequently it was only used with reactant compositions of known crystallization times.

3.2.2.3 30 cm$^3$ Bombs

These were used when it was necessary to investigate a large number of reaction mixtures (see Section 3.6 and 3.7), as they required less experimental time than the autoclaves. Basically the bombs, which were designed and built in the Chemistry Department, consisted of a teflon lining which slipped into a stainless steel casing. The lid was securely fastened by means of a screw thread. As these bombs were not fitted with any safety devices and were thus potentially dangerous, great care was taken in their use. An allowance for liquid expansion on heating was always made and at no time was more than 20 cm$^3$ of sample used.

As there was no sampling facility the reactions had to be stopped before any analyses, e.g. by optical microscopy or pH measurements, could be carried out. Typical operating conditions were:

- Temperature: 120, 150 or 180°C
- Agitation: none
- Pressure: autogenous
- Sample weight: <20g

The bombs were cleaned between reactions with 1M sodium hydroxide solution at 95°C for 24 hours.
3.2.2.4 1 Litre Plastic Bottle

Low temperature synthesis reactions which were carried out in the early stages of this work when no autoclaves were available, were done in 1 litre plastic bottles fitted with a stainless steel stirrer assembly. Each reaction contained 500 g of reactant. The bottles were placed in a 95°C temperature regulated water bath and the mixture was stirred at 150 rpm. Sampling was achieved by removal of 8 cm³ aliquots of reaction mixture via a hole in the lid of the bottle which was kept stoppered at all other times. The cleaning procedure was with 1M sodium hydroxide solution at 95°C for 24 hours.

Apart from long nucleation times, those reactions which were carried out in the plastic bottles suffered from contamination by lubricating oil from the stirrer assembly unit and poor control of water content due to continuous loss by evaporation.

3.2.3 Gel Preparation

The weight of the reactants had to be calculated from initial molar compositions. This was usually done using computer program RMIX1 (written by Mr. D.S. Sinclair) or JMIX3. Both programs allowed for water of hydration. JMIX3 calculated the required weight of aluminium in terms of both aluminium metal and alumina trihydrate.

The gel preparation procedure was as follows. Aluminium wire or alumina trihydrate was accurately weighed out and added to a warm solution of alkali metal hydroxide in a Pyrex beaker. This solution was heated and stirred until all the solid had dissolved.
Organic, if required, was weighed out and dissolved in warm water in a beaker. The weight of the mixing vessel, a 1 litre plastic bottle, was tared out on a top pan balance before the addition of the required amount of silica. Distilled water was then added to the silica so that it could be stirred into a homogenous paste. The alkali metal aluminate solution was added to the wet paste and stirred in thoroughly, before the addition of the aqueous solution of the organic species. The washings from the two empty beakers were then poured into the mixture which was made up to the correct weight by the addition of distilled water. The gel which formed was thoroughly stirred before being poured into the reaction vessel.

An adaptation of the above procedure was required for the preparation of the alkali metal-free T88 mixture. In this case the aluminium was dissolved in a hot solution of tetrapropylammonium hydroxide to form tetrapropylammonium aluminate. This solution was then added to the silica paste and mixed in as described above.

3.3 Synthesis and Characterization of Zeolite ZSM-5

3.3.1 Introduction

The aim of the work described in this section was to make good samples of ZSM-5 for the ester hydrolysis experiments discussed in Chapters 4, 5 and 6. The samples are classified into four groups: (a) Hexanediol-ZSM-5 (H-series); (b) Piperazine-ZSM-5 (P-series); (c) Sodium, TPA-ZSM-5 (T-series); and (d) TPA-ZSM-5 (T88). Most of the work concentrated on the sodium, TPA system. Although much work has been carried out on the synthesis of ZSM-5 details of the optimum synthesis conditions are not easily obtained
from the literature, especially when the organic species is other than TPA.

3.3.2 Experimental

The zeolites were made in the apparatus and in accordance with the procedures described in section 3.2 and were characterized by the techniques described in Chapter 2. Apart from sample T88 all the zeolites were made with alumina trihydrate as the source of aluminium.

3.3.3 Synthesis and Characterization of Hexanediol-ZSM-5 (Na, HEX-ZSM-5)

Introduction

Nine samples of ZSM-5 were made with the reaction mixture composition:

\[ 10Na_2O \quad 60SiO_2 \quad Al_2O_3 \quad 10 \text{Hexanediol} \quad 3000H_2O \]

Each sample was made in the 1 litre autoclave, using 793.3 g of reaction mixture stirred at 300 rpm at 150°C for 72 hours.

Characterization of the different samples showed that they were very similar and that the synthesis was reproducible. The (Na, HEX)-ZSM-5 samples were regarded as typical of those prepared from the reaction mixtures that contained hexanediol.

X-ray Powder Diffraction

The interplanar d-spacings and relative intensities for (Na, HEX)-ZSM-5 match the literature values for ZSM-5 very well. There was no evidence to suggest the presence of a second phase
in any of the samples. The peaks obtained were slightly broader than those of (Na, TPA)-ZSM-5. This may be due to the greater degree of twinning observed. The degree of crystallinity for (Na, HEX)-ZSM-5 samples (see Table 3.1) is (within experimental error) the same as that of ZSM-5 (T49).

*Morphology*

Scanning electron microscopy showed that the crystals were ellipsoidal, 2 μm long and 1 μm wide. The shape of the crystals together with their size distribution is shown in Figure 3.4. The twinning observed is typical of ZSM-5 crystals with SiO₂/Al₂O₃ = 60 [48].

*Thermal Analysis*

DTA and TG traces of (Na, HEX)-ZSM-5 are shown in Figure 3.5. These show that water corresponding to 6% w/w is lost at low temperatures. Removal of organic begins at about 250°C and is complete by 450°C. These temperatures are significantly lower than those required for the removal of other occluded organic species.
Figure 3.4  Electron micrographs of (Na, HEX)-ZSM-5 (H34)
The chemical compositions of 'as made' and calcined plus ion-exchanged samples of (Na, HEX)-ZSM-5 are given in Table 3.1. The Si/Al ratio of the product is similar to that obtained for 'inorganic' ZSM-5 crystallised from reaction mixture compositions with SiO$_2$/Al$_2$O$_3$ = 60. Casci [49] also observed that (Na, HEX)-ZSM-5 and 'inorganic'-ZSM-5 materials were similar. The Na/Al
ratio of the product is approximately one and indicates that sodium ions balance the charge associated with the framework aluminium. The H₂O/unit cell and HEX/unit cell ratios were estimated from the size of the weight losses recorded in the TG trace given in Figure 3.5. As will be shown later, both ratios are dependant on the extent to which the zeolite is washed.

3.3.4 Synthesis and Characterization of Piperazine-ZSM-5 (Na, PIP-ZSM-5)

Introduction

Four samples of ZSM-5 were made from the reaction mixture:

10Na₂O 60SiO₂ Al₂O₃ 10 Piperazine 3000H₂O.

Each sample was made in the 1 litre autoclave, using 800.2 g of reaction mixture stirred at 150°C for 72 hours.

Characterization of the different samples showed that although P22, P29 and P40 were similar, P18 contained significant amounts of ferrierite. Consequently this sample (P18) was not used in the work described in Chapters 4, 5 and 6.

X-ray Powder Diffraction

The interplanar d-spacings and relative intensities for (Na, PIP)-ZSM-5 match the literature values for ZSM-5 very well. Only sample P18 showed evidence of a second phase and this was identified as the zeolite ferrierite. The product composition of sample P18 was 82% ZSM-5 + 18% ferrierite. The probable reason for this anomalous result was that too much aluminium was inadvertently added to the reaction mixture. The degree of crystallinity of the (Na, PIP)-ZSM-5 (see Table 3.2) is (to within experimental error) the same as ZSM-5 (T49).
Figure 3.6  Electron micrographs of (Na, PIP)-ZSM-5

A = Run P40  B = Run P40  C = Run P18
Morphology

Scanning electron microscopy showed that the crystals were aggregates of 0.5 μm spheres. A picture of sample P18 is also included and the disc-shaped ferrierite crystals can be clearly seen.

Thermal Analysis

DTA and TG traces of (Na, PIP)-ZSM-5 are shown in Figure 3.7. These show that water corresponding to 6% w/w is lost at low temperatures. (Na, PIP)-ZSM-5 starts to lose organic at a lower temperature (150°C) than (Na, HEX)-ZSM-5 (250°C). The DTA trace shows no sharp peak corresponding to the exothermic oxidative degradation. Instead the organic material is steadily removed at temperatures up to 700°C

![Figure 3.7](image)

**Figure 3.7** Thermal analysis of (Na, PIP)-ZSM-5 (P40)
The broad peak centred at 630°C suggests that a significant proportion of the piperazine, or its oxidation products, is stabilised by the zeolite framework.

**Chemical Composition**

Table 3.2 Typical characteristics of (Na,PIP)-ZSM-5

<table>
<thead>
<tr>
<th>Code</th>
<th>Si/Al</th>
<th>Na/Al</th>
<th>H₂O/unit cell</th>
<th>PIP/unit cell</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P22</td>
<td>18.15</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>86</td>
</tr>
<tr>
<td>P29</td>
<td>17.18</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>90</td>
</tr>
<tr>
<td>P40</td>
<td>18.88</td>
<td>0.43</td>
<td>19.8</td>
<td>5.3</td>
<td>91</td>
</tr>
</tbody>
</table>

The chemical compositions of (Na, PIP)-ZSM-5 (P40) and H-ZSM-5 (P22 and P29) are given in Table 3.2. The Si/Al of these products is similar to those obtained for (Na, HEX)-ZSM-5 zeolites and is much lower than would be obtained if the system contained TPA cations. The Na/Al is less than one and suggests that 57% of the framework aluminium is associated with protonated piperazine molecules. The PIP/Al ratio obtained is approximately equal to one; this suggests that some of the trapped piperazine is protonated. The number of piperazine molecules per unit cell is greater than four. This indicates that piperazine is found in the 10 T-atom channels as well as being sited at the channel intersections. The water content of the unit cell is similar to that obtained for (Na, HEX)-ZSM-5.
3.3.5 Synthesis and Characterisation of (Na, TPA)-ZSM-5

Introduction

Most of the ZSM-5 samples prepared in this work were made using the conventional Na, TPA system, first reported in 1972 [1]. This system allows good ZSM-5 materials to be made over a wide range of reaction mixtures.

Crystallization of ZSM-5 in 1 litre plastic bottles

Initial work on the synthesis of ZSM-5 was carried out using 1 litre plastic bottles as the reaction vessels. As stated in Chapter 3.2 these proved to be unsatisfactory for serious studies on zeolite synthesis. Nevertheless six ZSM-5 samples were made using the reaction mixtures given in Table 3.3.

Table 3.3 ZSM-5 Reaction mixtures and product crystallinity

<table>
<thead>
<tr>
<th>Code</th>
<th>Na₂O</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>TPA Br</th>
<th>H₂O</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T9</td>
<td>2</td>
<td>20</td>
<td>0.1</td>
<td>4</td>
<td>1500</td>
<td>88</td>
</tr>
<tr>
<td>T10</td>
<td>2</td>
<td>10</td>
<td>0.1</td>
<td>2</td>
<td>1500</td>
<td>97</td>
</tr>
<tr>
<td>T11</td>
<td>2</td>
<td>40</td>
<td>0.1</td>
<td>2</td>
<td>1500</td>
<td>98</td>
</tr>
<tr>
<td>T13</td>
<td>3</td>
<td>15</td>
<td>0.1</td>
<td>2</td>
<td>1000</td>
<td>-</td>
</tr>
<tr>
<td>T17</td>
<td>1</td>
<td>8</td>
<td>0.1</td>
<td>1</td>
<td>750</td>
<td>110</td>
</tr>
<tr>
<td>T20</td>
<td>2</td>
<td>8</td>
<td>0.1</td>
<td>2</td>
<td>750</td>
<td>108</td>
</tr>
</tbody>
</table>

Comparison of the zeolites obtained in this way with those from other systems showed that the type of reaction vessel used did not effect the product.
pH Measurements

The pH changes that occur during the crystallization of (Na, TPA)-ZSM-5 are shown in Table 3.4. Although sampling was infrequent the effect of alkalinity on both the crystal size and crystallization is clear. The higher the alkalinity of the system the shorter the crystallization time. Each sample has a high degree of crystallinity which is consistent with the large rise in pH observed upon crystallization.

Table 3.4 Characteristics of ZSM-5 materials made in the 1 litre plastic bottle

<table>
<thead>
<tr>
<th>Code</th>
<th>Crystal size (μm)</th>
<th>pH Measurements [Time (days)]</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>T9</td>
<td>2.5 x 1.5 x 1.5</td>
<td>7</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>11.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12.22</td>
</tr>
<tr>
<td>T10</td>
<td>&lt;1</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>11.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12.90</td>
</tr>
<tr>
<td>T11</td>
<td>&lt;1</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>11</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12.35</td>
</tr>
<tr>
<td>T13</td>
<td>2.5 x 2.5 x 2.5</td>
<td>3</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>11.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12.84</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12.86</td>
</tr>
<tr>
<td>T17</td>
<td>3 x 3 x 3</td>
<td>11</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12.28</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>12.46</td>
</tr>
<tr>
<td>T20</td>
<td>1.5 x 1.5 x 1.5</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>
Crystallisation of ZSM-5 in 500 cm$^3$ autoclaves

Most of the ZSM-5 samples prepared in this work were made in the 500 cm$^3$ autoclaves. The molar compositions that were used and the crystallinities of the ZSM-5 materials obtained are given in Table 3.5. The results show that (Na, TPA)-ZSM-5 samples can be made from a range of reaction mixture compositions. Most samples had a degree of crystallinity that was close to that of the standard ZSM-5 (T49), although T80 and T83 were both somewhat less crystalline.

<table>
<thead>
<tr>
<th>Code</th>
<th>Na$_2$O</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>TPA Br</th>
<th>H$_2$O</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T24</td>
<td>3</td>
<td>60</td>
<td>1</td>
<td>3</td>
<td>3000</td>
<td>108</td>
</tr>
<tr>
<td>T25</td>
<td>3</td>
<td>30</td>
<td>1</td>
<td>3</td>
<td>3000</td>
<td>111</td>
</tr>
<tr>
<td>T28</td>
<td>3</td>
<td>40</td>
<td>1</td>
<td>3</td>
<td>3000</td>
<td>104</td>
</tr>
<tr>
<td>T32</td>
<td>4</td>
<td>80</td>
<td>1</td>
<td>4</td>
<td>3000</td>
<td>102</td>
</tr>
<tr>
<td>T33</td>
<td>3</td>
<td>60</td>
<td>0.75</td>
<td>3</td>
<td>3000</td>
<td>98</td>
</tr>
<tr>
<td>T37</td>
<td>10</td>
<td>60</td>
<td>1</td>
<td>10</td>
<td>3000</td>
<td>98</td>
</tr>
<tr>
<td>T38</td>
<td>3</td>
<td>50</td>
<td>1</td>
<td>3</td>
<td>3000</td>
<td>110</td>
</tr>
<tr>
<td>T41</td>
<td>3</td>
<td>60</td>
<td>0.2</td>
<td>3</td>
<td>3000</td>
<td>103</td>
</tr>
<tr>
<td>T42</td>
<td>3</td>
<td>60</td>
<td>0.1</td>
<td>3</td>
<td>3000</td>
<td>99</td>
</tr>
<tr>
<td>T43</td>
<td>3</td>
<td>60</td>
<td>0.4</td>
<td>3</td>
<td>3000</td>
<td>99</td>
</tr>
<tr>
<td>T44</td>
<td>3</td>
<td>60</td>
<td>0.05</td>
<td>3</td>
<td>3000</td>
<td>97</td>
</tr>
<tr>
<td>T49</td>
<td>3</td>
<td>60</td>
<td>1</td>
<td>3</td>
<td>3000</td>
<td>100</td>
</tr>
<tr>
<td>T80</td>
<td>3</td>
<td>25</td>
<td>1</td>
<td>3</td>
<td>3000</td>
<td>85</td>
</tr>
<tr>
<td>T83</td>
<td>3</td>
<td>70</td>
<td>1</td>
<td>3</td>
<td>3000</td>
<td>86</td>
</tr>
</tbody>
</table>

The molar composition of the former reaction mixture T80 marks a boundary for ZSM-5 formation. It was the most aluminous of a reaction series T24, T25, T28, T38 and T83. Scanning electron
microscopy showed that some amorphous gel was present in the product. This boundary for the Na, TPA-system was reported in the original patent [1] and by Olson et al [10]. Run T83 marks the upper limit for the above series as the TPA/Si ratio of the reaction mixture is equivalent to 4.1 TPA/unit cell. Any increase in the Si/TPA ratio of the reaction mixture will lower the TPA/unit cell ratio and give incomplete crystallization. The degree of crystallinity for T83 is a little lower than expected; this is probably due to the low alkalinity of the reaction mixture.

\textit{pH Measurements}

The pH changes that occur during the crystallisation of (Na, TPA)-ZSM-5 are shown in Table 3.6. The results obtained are in accord with those calculated for high silica zeolite systems [25] and as predicted a sharp rise in pH accompanied crystallization from the amorphous gel in most cases. A rise in pH due to zeolite crystallization was not observed for runs T80 and T83. This is probably because significant amounts of unreacted material remained and continued to control the pH. The results show that in general the higher the alkalinity of the system then the shorter the crystallization time. Reaction mixture compositions with Si/Al > 75 (runs T41-44) took considerably less time to crystallise than more aluminous samples. This suggests that the activation energies for the nucleation and crystallization of ZSM-5 decrease as the Si/Al of the gel is increased. This result supports the work of Mostowicz and Sand [27].
Table 3.6  pH measurements of samples taken during the synthesis of (Na, TPA)-ZSM-5

<table>
<thead>
<tr>
<th>Code</th>
<th>pH measurements [pH (hours)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>T24</td>
<td>24 48 68 71 72 89 92</td>
</tr>
<tr>
<td></td>
<td>11.20 11.71 12.01 12.04 12.04 12.04</td>
</tr>
<tr>
<td>T25</td>
<td>5   92 104 140 146</td>
</tr>
<tr>
<td></td>
<td>11.71 12.02 12.19 12.15 12.15</td>
</tr>
<tr>
<td>T28</td>
<td>48 70 94 118 142</td>
</tr>
<tr>
<td></td>
<td>12.14 12.21 12.21 12.21 12.18</td>
</tr>
<tr>
<td>T32</td>
<td>3   19 28 42 114 123 163 187</td>
</tr>
<tr>
<td></td>
<td>11.25 11.38 11.31 11.31 11.8 12.06 12.09 12.06</td>
</tr>
<tr>
<td>T33</td>
<td>4   21 28 .49 52 55</td>
</tr>
<tr>
<td></td>
<td>11.30 11.40 11.32 12.18 12.19 12.15</td>
</tr>
<tr>
<td>T37</td>
<td>2   21 28 33 46 70</td>
</tr>
<tr>
<td></td>
<td>11.80 12.89 12.94 12.95 12.96 12.96</td>
</tr>
<tr>
<td>T38</td>
<td>24 43 46 67 73</td>
</tr>
<tr>
<td>T41</td>
<td>4   21</td>
</tr>
<tr>
<td></td>
<td>11.59 11.85</td>
</tr>
<tr>
<td>T42</td>
<td>2   21</td>
</tr>
<tr>
<td></td>
<td>11.38 11.63</td>
</tr>
<tr>
<td>T43</td>
<td>21 24</td>
</tr>
<tr>
<td></td>
<td>11.71 11.79</td>
</tr>
<tr>
<td>T44</td>
<td>2   20 22</td>
</tr>
<tr>
<td></td>
<td>11.38 11.44 11.79</td>
</tr>
<tr>
<td>T49</td>
<td>4   69 93 117 141 165</td>
</tr>
<tr>
<td></td>
<td>11.33 11.30 11.71 11.84 12.06 12.04</td>
</tr>
<tr>
<td>T80</td>
<td>4   21 28 45 52 69 76</td>
</tr>
<tr>
<td></td>
<td>11.71 11.66 11.65 11.64 11.64 11.66 11.65</td>
</tr>
<tr>
<td>T83</td>
<td>4   21 28 45 52 69 168</td>
</tr>
<tr>
<td></td>
<td>10.98 10.95 10.72 11.00 11.01 11.01 11.03</td>
</tr>
</tbody>
</table>
Characterization Results

X-ray Powder Diffraction

The interplanar d-spacings and relative intensities for (Na, TPA)-ZSM-5 made in 1 litre plastic bottles and in 500 cm$^3$ autoclaves match the literature values for ZSM-5. There was no evidence to suggest the existence of a second phase in any of the samples. Sharp well defined peaks were obtained for all the samples except T80 and T83.

Morphology

Scanning electron microscopy showed that spherical crystals were obtained. These were usually small (< 1 μm) and the product had a narrow size distribution. Crystal sizes are given in Table 3.7 and typical electron micrographs are shown in Figure 3.8. The degree of twinning observed was found to be dependant on the SiO$_2$/Al$_2$O$_3$ of the reactant gel and in accordance with the results of von Ballmoos [48].

Table 3.7 Chemical composition of 'as made' and treated (Na,TPA)-ZSM-5

<table>
<thead>
<tr>
<th>Code</th>
<th>Si/Al</th>
<th>Na/Al</th>
<th>H$_2$O/unit cell</th>
<th>TPA/unit cell</th>
<th>Crystal size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T24</td>
<td>29.70</td>
<td></td>
<td></td>
<td></td>
<td>1 x 1 x 1</td>
</tr>
<tr>
<td>T25</td>
<td>13.23</td>
<td></td>
<td>16.9</td>
<td>3.64</td>
<td>&lt;1</td>
</tr>
<tr>
<td>T28</td>
<td>18.59</td>
<td></td>
<td></td>
<td></td>
<td>&lt;1</td>
</tr>
<tr>
<td>T32</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&lt;1</td>
</tr>
<tr>
<td>T33</td>
<td>35.90</td>
<td></td>
<td>11.3</td>
<td>4.19</td>
<td>&lt;1</td>
</tr>
<tr>
<td>T37</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&lt;1</td>
</tr>
<tr>
<td>T38</td>
<td>21.92</td>
<td></td>
<td></td>
<td></td>
<td>&lt;1</td>
</tr>
<tr>
<td>T41</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>T42</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>T43\textsuperscript{a}</td>
<td>64.33</td>
<td>0.24</td>
<td>2.5</td>
<td>3.99</td>
<td>1 x 1 x 1</td>
</tr>
<tr>
<td>T44\textsuperscript{a}</td>
<td>371.56</td>
<td>0.590</td>
<td>2.6</td>
<td>4.38</td>
<td></td>
</tr>
<tr>
<td>T49</td>
<td>24.08</td>
<td></td>
<td>7.3</td>
<td>4.00</td>
<td>1 x 1 x 1</td>
</tr>
<tr>
<td>T80</td>
<td>10.49</td>
<td></td>
<td></td>
<td></td>
<td>&lt;1</td>
</tr>
<tr>
<td>T83\textsuperscript{a}</td>
<td>20.87</td>
<td>0.54</td>
<td>17.4</td>
<td>3.23</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

\textsuperscript{a} 'as made'
Figure 3.8  Electron micrographs of Na, TPA-ZSM-5

A = Run T37   B = Run T20   C = Run T49
Thermal Analysis

DTA and TG traces of (Na, TPA)-ZSM-5 (T49) are shown in Figure 3.9. These show an endothermic loss of water at low temperatures that corresponds to 2.5% w/w of the total sample. This is less than observed for (Na, HEX)- and (Na, PIP)-ZSM-5 materials and is attributed to better packing of the TPA molecules in the intracrystalline channels. DTA shows that removal of TPA begins at about 400°C and is complete by 500°C. There are three clearly defined exothermic peaks centred at 425°C, 450°C and 475°C.

![Thermal analysis of (Na, TPA)-ZSM-5](image)

Figure 3.9 Thermal analysis of (Na, TPA)-ZSM-5

The fact that exothermic peaks are observed suggests that there are three different localised sites for TPA cations in ZSM-5. However without further studies using different sample sizes and heating rates it is not possible to be certain of this somewhat unlikely conclusion. Literature data are surprisingly rare although Romannikov et al [50] have reported that TPA removal under N₂ shows several endotherms.
Chemical Composition

The chemical composition of 'as made' and calcined plus ion-exchanged samples of (Na, TPA)-ZSM-5 are given in Table 3.7. The Si/Al ratio of the product shows a linear correlation when plotted against the initial Si/Al ratio (see Figure 3.10). The best fit line is:

\[ y = 0.854(\pm 0.03)x + 1.0(\pm 1.2) \]  

(3.1)
in which \( y \) is the Si/Al ratio of the product and \( x \) the Si/Al ratio of the reaction mixture. As expected the line goes through the origin. Equation 3.1 indicates that aluminium is preferentially incorporated into the zeolite phase. For systems other than those containing TPA (e.g. see Equation 3.3, section 3.4) the gradient is smaller; this indicates that preferential incorporation of aluminium also occurs in the absence of TPA but in these cases more silicon remains in solution, i.e. TPA reduces the solubility of the zeolite. Equation 3.1 is probably independant of sodium as sample T88, which was made in a sodium free system, was found to fit on the line represented by Equation 3.1.

Figure 3.11 shows a plot of Al/Si of the product against Al/Si of the reactant. The best fit line is:

\[ y = 1.17(\pm 0.04)x - 0.01(\pm 1.0) \]  

(3.2)
in which \( y \) is the Al/Si ratio of the product and \( x \) is the Al/Si ratio of the reactant. It should be noted that the results obtained
Figure 3.10 Product Si/Al against reaction mixture Si/Al for (Na, TPA)-ZSM-5

Figure 3.11 Product Al/Si against reaction mixture Al/Si for (Na, TPA)-ZSM-5
from reaction T83 were not used in either plot, because of the large amount of amorphous gel associated with the product.

The Na/Al of the product varied between 0.24-0.59. The fact that this is much less than unity indicates that TPA cations balance much of the anionic charge associated with the framework aluminium. The TPA/unit cell ratios were calculated from the relevant TG traces and the Si/Al and Na/Al ratios of the product. The Na/Al ratio of sample T43 was used for other samples in which only the chemical composition of the acid form was known. The TPA/unit cell ratios that were obtained are all very close to the ideal value of four. The experimental values are slightly higher than those reported by Nagy et al [6]. This is probably due to the different synthesis methods used and the limitations of the analytical procedure. The TPA/unit cell values for T25 and T83 are both significantly lower than four. The former has 6.75 Al per unit cell and so some of the anionic charge has to be balanced by sodium cations. Reaction T83 gave a less crystalline sample than expected and again some of the framework charge is balanced by sodium cations.

3.3.6 Synthesis and characterization of TPA-ZSM-5

Introduction

The preparation of H-ZSM-5 from inorganic cation-free reaction systems is advantageous as the ion-exchange stage is not required. Bibby et al [30] showed that ZSM-5 could be prepared in the ammonium system and that H-ZSM-5 could be obtained by calcination of the 'as made' zeolite. Nakamoto and Takahashi [37] followed
up the work of Erdem and Sand [36] and showed that a similar result could be achieved when ZSM-5 was prepared in the mono-
cation TPA system.

Experimental

Sample T88 was synthesised from the reaction mixture 3TPAOH 60SiO₂ Al₂O₃ 3700H₂O. The aluminium metal used in the preparation was added to a hot tetrapropylammonium hydroxide solution. The reaction (given below) is very slow and may be monitored by the evolution of hydrogen. The white precipitate formed was then added to a silica + water mixture. The reaction was carried out in a 500 cm³ autoclave at 159°C for 25 hours.

\[
\text{Al} + \text{TPAOH} + 2\text{H₂O} \rightarrow \text{TPA⁺Al(OH)₄}^{−} + 3/2 \text{H}_2
\]

Synthesis Results

pH Measurements

The pH values obtained for samples taken during the crystallization of TPA-ZSM-5 are shown in Table 3.8. These results are totally different to those usually observed in the synthesis of high silica zeolites. The pH of the reaction mixture is very low. This is because 2/3 of the base used reacts with the aluminium and results in a low ratio of free base to silica.

Table 3.8 pH measurements of samples taken during the synthesis of TPA-ZSM-5 (T88)

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>0</th>
<th>4</th>
<th>21</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>10.64</td>
<td>10.71</td>
<td>9.55</td>
<td>7.30</td>
</tr>
</tbody>
</table>
Nakamoto and Takahashi [37] claim that a (TPA)$_2$O/SiO$_2$ of 0.2 is necessary for the formation of ZSM-5 in this system. The present experimental results show that TPA-ZSM-5 can be made from reaction mixtures with (TPA)$_2$O/SiO$_2$ = 0.025. The probable reasons for the difference between this work and that of Nakamoto are (i) the lower H$_2$O/SiO$_2$ ratio used in this work (61.7 as opposed to 81), (ii) the different sequence used to prepare the reaction mixture and (iii) the slightly higher temperature used in this work.

The observed decrease in pH when TPA-ZSM-5 is formed is contrary to what is expected for high silica zeolites. Casci et al [51] and Lowe [25] have both shown that zeolite formation results in an increase in the alkalinity of the solution phase. This is not observed with reaction mixture TPA-ZSM-5 (T88). In fact the pH of the solution phase after TPA-ZSM-5 has crystallised is completely neutral. This indicates that the growing ZSM-5 crystals have used up virtually all of the soluble species that were initially present in the solution phase. The neutral pH of the product has obvious advantages if a continuous ZSM-5 synthesis process is desired.

**Optical microscopy**

Examination of samples, taken during the crystallization of TPA-ZSM-5, by optical microscopy show that ZSM-5 crystals had formed after 21 hours.
Characterization of TPA-ZSM-5

X-Ray Powder Diffraction

Inter-planar d-spacings and relative intensities for TPA-ZSM-5 and its calcined derivative H-ZSM-5 match the literature values for ZSM-5. Two extra peaks were observed in the diffraction pattern of T88. These weak peaks occurred at $d = 4.84 \, \text{Å}$ and $4.78 \, \text{Å}$, and both disappeared when the sample was calcined at 400°C for 72 hours. They are believed to arise from traces of TPA carbonate. These impurities were also detected by thermal analysis (see below). Some reversals in peak intensities were observed when the pattern of T88 was compared with those of other ZSM-5 samples. In particular the relative intensities of the peaks at $11.05 \, \text{Å}$ and $9.98 \, \text{Å}$ as well as those at $3.71 \, \text{Å}$ and $3.75 \, \text{Å}$ were found to be reversed. These reversals may be related to the absence of Na in sample T88. Nastro and Sand [29] report similar reversals for Li-ZSM-5.

The degree of crystallinity of sample T88 is 94% that of the standard ZSM-5 sample (T49). The peaks in the T88 pattern were the sharpest and most clearly defined that were obtained in this work.

Morphology

Scanning electron microscopy showed that the crystals were 10 μm long and 5 μm wide. The shape of the crystals together with their size distribution is shown in Figure 3.12. The crystals were always twinned and are identical to those obtained by von Ballmoos [48] with low Al ZSM-5 (0-2 Al/unit cell) systems.
Figure 3.12  Electron micrographs of TPA-ZSM-5 (T88)
However the product contains 3.3 Al/unit cell and the degree of twinning observed is much less than was obtained from similar compositions in the (Na, TPA)-ZSM-5 system. Thus it appears that sodium encourages twinning of ZSM-5 crystals. The crystals obtained from this preparation are much larger than the sub-micron spherulites obtained by Nakamoto and Takahashi [37]. Larger crystal size may be catalytically advantageous as it improves the shape selectivity of the zeolite by increasing the diffusional pathways and decreasing any effects due to catalytic sites on the crystal surface.

**Thermal Analysis**

DTA and TG traces for TPA-ZSM-5 (T88) are shown in Figure 3.13. These are similar to those obtained from (Na, TPA)-ZSM-5 although there are several important differences. Less water is lost from sample T88 due to (i) the absence of hydrophilic centres associated with sodium ions and (ii) less intercrystalline water because of the larger crystals. An endothermic weight loss centred at 285°C, was attributed to (TPA)$_2$CO$_3$ impurities. It should be noted that Erdem and Sand [36] went to great lengths to minimise the absorption of CO$_2$ by TPAOH.

Removal of TPA occurs between 400-600°C. Five distinct exothermic peaks centred at 425°C, 440°C, 470°C, 490°C and 580°C were observed. The reason for these separate exotherms is not understood, but it seems unlikely that it is associated with TPA ions in different sites within the lattice.
Figure 3.13 Thermal analysis of TPA-ZSM-5 (T88)
Chemical Composition

The composition of sample T88 is given in Table 3.9 and the Si/Al ratio is as expected for a ZSM-5 material synthesised in a TPA system. The TPA/Al ratio indicates that TPA cations balance all of the anionic charge of the framework aluminium. The TG trace indicates that there are 4.03 TPA ions per unit cell. This is expected if each channel intersection is occupied. This result suggests that strong aluminium zoning across the ZSM-5 crystal can be avoided if this preparation and composition is used. The \( \text{H}_2\text{O}/\text{unit cell} \) is lower than what would have been obtained if sodium had been used in the reaction mixture.

<table>
<thead>
<tr>
<th>Code</th>
<th>Si/Al</th>
<th>TPA/Al</th>
<th>TPA/unit cell</th>
<th>( \text{H}_2\text{O}/\text{unit cell} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>T88</td>
<td>28.02</td>
<td>1.22</td>
<td>4.03</td>
<td>3.8</td>
</tr>
</tbody>
</table>

3.3.7 Conclusions

Zeolite ZSM-5 can be readily made from the following reaction systems: sodium-hexanediol, sodium-piperazine, sodium-TPA and TPA. However the (Na, PIP)-ZSM-5 system was found to give small crystals and greater care had to be taken when preparing the initial gel as a significant amount of ferrierite was found in one batch. This system does not appear to have any advantages over the (Na, HEX)-ZSM-5 system which gives larger and more clearly defined crystals. The crystals from both systems were heavily twinned due to the high aluminium content of the product. Whilst the Na/Al of (Na, HEX)-ZSM-5 was found to be greater than unity the Na/Al of (Na, PIP)-ZSM-5
was only 0.43. This indicates that 57% of the framework aluminium is associated with protonated piperazine molecules. Thermal analysis showed that piperazine is more strongly held than hexanediol.

Most of the ZSM-5 materials were made from the (Na, TPA)-ZSM-5 system. Products were obtained from both low temperature reactions, which were carried out in a 1 litre plastic bottle, and high temperature reactions that were carried out in a 500 cm$^3$ autoclave. Zeolites could be made over a large range of initial Si/Al and Na/Al ratios. It was found that the Si/Al ratio of the product linearly related to the Si/Al ratio of the initial gel. DTA indicated that TPA may be at three distinct sites in the (Na, TPA-ZSM-5 lattice and TGA showed that there were four TPA per unit cell. In aluminous ZSM-5 samples and less crystalline samples it was found that a greater proportion of the anionic framework charge is balanced by sodium cations. TPA-ZSM-5 was synthesised using a novel procedure, and was found to be significantly different to zeolites prepared in the (Na, TPA)-ZSM-5 system. The growth of the TPA-ZSM-5 crystals was accompanied by a significant decrease in the pH of the reactant solution, and the final mother liquor was found to be neutral. This drop in pH was taken to indicate that the reaction mixture composition is ideal in that all the base was used up. The crystals were 10 µm long and 5 µm wide and are the largest crystals that have been made in a TPA-ZSM-5 system. Both X-ray powder diffraction and thermal analysis suggested that some TPA carbonate was present in the final product. The Si/Al ratio of the product is unaffected by the lack of sodium in the reaction mixture.
4.03 TPA ions were found per unit cell and the TPA/Al ratio of 1.22 indicates that the anionic framework charge is completely balanced by TPA cations.

3.4 Synthesis and Characterization of 'Inorganic'-ZSM-5

3.4.1 Introduction

Since the first reported synthesis of ZSM-5 from a sodium, TPA system [1] there have been numerous publications on the synthesis of ZSM-5 from organic containing systems. However there are only four publications [38,45,49,52] concerned with the synthesis of ZSM-5 from an organic free system. One of these [45] describes the use of seeding to promote ZSM-5 formation in the absence of organic species. To date there is no published work which investigates the Si/Al range over which inorganic-ZSM-5 can be made, nor any that identify the neighbouring phases. Therefore it was decided to investigate the following system at 150°C:

\[ 10\text{Na}_2\text{O} \ 60\text{SiO}_2 \ x\text{Al}_2\text{O}_3 \ 3000\text{H}_2\text{O} \]

where \(0 < x < 3\).

3.4.2 Experimental

Apart from runs J19 and J64, which were carried out in the 1 litre autoclave, all the reactions used the 500 cm\(^3\) autoclaves. Alumina trihydrate was used as the source of aluminium in all the reactions except J63 for which used pure aluminium was used. The zeolites were made using the procedures and apparatus described in section 3.2 and were characterized by the techniques listed in Chapter 2.
3.4.3 Results and Discussion

The experimental results given in Table 3.10 indicate that it is possible to make 'inorganic'-ZSM-5 over a wide range of initial Si/Al ratios. The degree of crystallinity of ZSM-5 obtained in this way is slightly less than that of (Na, TPA)-ZSM-5 and is related to unreacted amorphous gel material found in the product. However, Figure 3.14 shows that good quality ZSM-5 can be made from an inorganic system at 150°C. There are no differences in the peak positions or in their relative intensities when TPA is omitted from the reaction mixture. This suggests that 'inorganic'-ZSM-5 also has orthorhombic symmetry and belongs to the symmetry group Pnma.

Characterization of the 'inorganic'-ZSM-5 samples showed that they were very similar to (Na, HEX)-ZSM-5 with respect to morphology, Si/Al, Na/Al and degree of crystallinity (see Table 3.11). Crystal morphology is unaffected by the presence of hexanediol and the (Na, HEX)-ZSM-5 crystals shown in Figure 3.4 are identical to 'inorganic'-ZSM-5 crystals. The Na/Al of 'inorganic'-ZSM-5 is approximately one and this indicates that sodium cations balance the anionic framework charge associated with tetrahedrally coordinated aluminium. The ratio of (product Si/Al)/reactant (Si/Al) of J70 is similar to that obtained for the (Na, HEX)-ZSM-5 samples and not (Na, TPA)-ZSM-5. Thus 'inorganic'-ZSM-5 crystals probably grow by mechanisms that are similar to those of systems that do not contain TPA cations. The H₂O/unit cell of 'inorganic'-ZSM-5 (J70) was found to be 60 and this indicates that the intracrystalline channels are completely filled with water molecules. (Na, HEX)-ZSM-5 contains less water
Table 3.10  Synthesis of 'inorganic'-ZSM-5

<table>
<thead>
<tr>
<th>Code</th>
<th>Na₂O</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>H₂O</th>
<th>Product Si/Al</th>
<th>Crystallinity (%)</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>J55</td>
<td>10</td>
<td>60</td>
<td>2.4</td>
<td>3000</td>
<td>9.87</td>
<td>32</td>
<td>ZSM-5 (49%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>+ Mordenite</td>
</tr>
<tr>
<td>J52</td>
<td>10</td>
<td>60</td>
<td>2.0</td>
<td>3000</td>
<td>10.98</td>
<td>77</td>
<td>ZSM-5</td>
</tr>
<tr>
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<td>10</td>
<td>60</td>
<td>1.7</td>
<td>3000</td>
<td>11.95</td>
<td>75</td>
<td>ZSM-5</td>
</tr>
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<td>10</td>
<td>60</td>
<td>1.5</td>
<td>3000</td>
<td>13.30</td>
<td>85</td>
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</tr>
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<td>60</td>
<td>1.2</td>
<td>3000</td>
<td>16.87</td>
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<td>ZSM-5 (95%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>+ Magadiite</td>
</tr>
<tr>
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<td>10</td>
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<td>1.0</td>
<td>3000</td>
<td>17.90</td>
<td>86</td>
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</tr>
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<td>3000</td>
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<td>ZSM-5 (73%)</td>
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<td></td>
<td>+ Magadiite</td>
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<td>3000</td>
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<td>ZSM-5 (40%)</td>
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<td></td>
<td></td>
<td>+ Magadiite</td>
</tr>
<tr>
<td>J19</td>
<td>10</td>
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<td>1</td>
<td>3000</td>
<td>-</td>
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<td>Mordenite</td>
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<td>3000</td>
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<td>1</td>
<td>3000</td>
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<td>-</td>
<td>82</td>
<td>ZSM-5</td>
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</table>
Table 3.11  Comparison of chemical and physical properties of an inorganic ZSM-5 with (Na, HEX)-ZSM-5

<table>
<thead>
<tr>
<th>Code</th>
<th>Crystal size (µm)</th>
<th>Crystal morphology</th>
<th>Si/Al</th>
<th>Na/Al</th>
<th>H₂O/unit cell</th>
<th>Crystallinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>J70</td>
<td>2 x 1 x 1</td>
<td>heavy twinning spherulithic</td>
<td>17.64</td>
<td>0.98</td>
<td>60.36</td>
<td>86</td>
</tr>
<tr>
<td>H35</td>
<td>2 x 1 x 1</td>
<td>heavy twinning spherulithic</td>
<td>19.70</td>
<td>1.12</td>
<td>16.93</td>
<td>86</td>
</tr>
</tbody>
</table>
Figure 3.14 X-ray powder diffraction patterns of 'inorganic' ZSM-5 (J70) (top) and (Na, TPA)-ZSM-5 (T49) (bottom)
than 'inorganic'-ZSM-5 because of the presence of intracrystalline hexanediol molecules. These results are in good agreement with other studies on the sorption capacity of ZSM-5 [53]. The similarities found between the two ZSM-5 materials support the results of Casci [49] who found that hexanediol does not act as a template but as a void filler.

It can be seen from Figure 3.15 that the optimum reactant SiO$_2$/Al$_2$O$_3$ ratio for the synthesis of 'inorganic'-ZSM-5 at 150°C is between 40 and 60 although extrapolation of the two straight lines (see Figure 3.15) to their intersection suggests an optimum ratio of about 33. There is good agreement between those samples made in the 500 cm$^3$ autoclaves and those made in the 1 litre autoclave and this suggests that these observations are applicable to the synthesis of 'inorganic'-ZSM-5 on a larger scale. There is no difference in crystallinity when the aluminium source is changed from alumina trihydrate to the purer aluminium wire. The free base content of the mixture (defined as [Na$_2$-Al$_2$O$_3$]/SiO$_2$) does not appear to effect the crystallinity of the product. For example the degree of crystallinity of J64 and J45 (which both have SiO$_2$/Al$_2$O$_3$ = 40) is similar despite the fact that the free base content in the former is 1.6 x that of the latter. The SiO$_2$/Al$_2$O$_3$ boundaries for the synthesis of ZSM-5 appear from Figure 3.15 to be approximately 30 and 100. An increase in the concentration of aluminium in the reaction mixture, so that the SiO$_2$/Al$_2$O$_3$ ratio is less than 40, results in a less crystalline product that contains more amorphous material.
Figure 3.15 Effect of reaction mixture SiO$_2$/Al$_2$O$_3$ on the degree of crystallinity of the product.
When the SiO₂/Al₂O₃ ratio of the reaction mixture is 25 mordenite is the dominant phase. Extrapolation of the straight line drawn suggests that mordenite would be the only phase formed when SiO₂/Al₂O₃ < 20.

Reactant mixture compositions which have a SiO₂/Al₂O₃ greater than 60 also give a less crystalline product. Again there appears to be a linear correlation between the SiO₂/Al₂O₃ of the reactant gel and the crystallinity of ZSM-5 formed. Extrapolation of the straight line suggests that negligible ZSM-5 formation occurs when SiO₂/Al₂O₃ = 240. The dominant phases that are observed when high Si/Al compositions are used are the sodium silicates magadiite and kenyaiite [54,55]. These occur in natural deposits from systems with very low aluminium concentrations.

The sequence of formation for mixed phase systems is clearly illustrated in Figure 3.16 which shows that the crystallization of magadiite only starts after the crystallization of ZSM-5 has finished and has significantly reduced the aluminium concentration in the solution phase. These results are in contrast to those obtained with the same system at 180°C by Casci [49]. He found that kenyaiite and α-quartz co-crystallise with ZSM-5. Analcite and α-cristobalite were also observed although no evidence was found to suggest that any magadiite formed. These differences are probably due to the different reaction temperatures used (present work 150°C).

The experimental results obtained during run J48 suggest that 'inorganic'-ZSM-5 is similar to (Na, TPA)-ZSM-5 in that aluminium is preferentially incorporated into the zeolite phase.
Figure 3.16 Crystallization of ZSM-5 and magadiite as followed by the X-ray powder diffraction patterns of samples taken during Run J48. Time (t) is given in hours.
This is substantiated in Figure 3.17 and 3.18. Figure 3.17 shows that a linear correlation is obtained when the Si/Al ratio of the products is plotted against the Si/Al of the initial reaction mixture. The best fit line had the equation:

\[ y = 0.459(\pm 0.03)x + 8.0(\pm 0.5) \quad (3.3) \]

where \( y \) is the Si/Al ratio of the product and \( x \) the Si/Al ratio of the reaction mixture. Those points which lie above the line drawn were not used in its derivation as they are associated with silicate phases which co-exist with ZSM-5. The difference between the product Si/Al and that calculated with equation 3.3 is directly proportional to the amount of magadiite or kenyaiite formed. Both the gradient and intercept values obtained are different to those obtained for (Na, TPA)-ZSM-5 (equation 3.1). It is significant that equation 3.3 has a positive intercept and that the line does not go through the origin. The positive intercept suggests that the crystallization of ZSM-5 starts from a silicon rich species in the solution phase and that as the crystal grows aluminium is preferentially incorporated into the zeolitic phase. The experimental results agree with the scheme proposed by Derouane et al [18] for the formation of ZSM-5. They also suggest that there is strong aluminium zoning across the crystals in accordance with the findings of von Ballmoos and Meier [56] and Derouane et al [57].

The Al/Si ratio of the products is plotted against that of the reactant in Figure 3.18. The graph shows that preferential incorporation of aluminium into the zeolite phase. The extent by which the points deviate from the smooth curve drawn corresponds to the
Figure 3.17  Product Si/Al against reaction mixture Si/Al for 'inorganic' - ZSM-5

Figure 3.18  Product Al/Si against reaction mixture Al/Si for 'inorganic' - ZSM-5
degree of preferential incorporation of aluminium into the zeolite phase. The preferential incorporation of aluminium into the zeolitic phase cannot be explained by the presence of unreacted gel material in the product because no correlation is observed between the extent of preferential incorporation and the degree of crystallinity of ZSM-5 in the product.

The pH values of samples taken during the crystallization of 'inorganic'-ZSM-5 are shown in Table 3.12.

A plot of pH of the solution phase against time produces three different pH curves and a representative of each type is drawn in Figure 3.19. The type of pH curve observed is dependant on the initial reactant composition. Type (a) is the "classical" pH curve for high silica zeolites in which zeolite crystallization is accompanied by a sharp rise in pH [49,51]. This curve is applicable for inorganic systems in which the SiO₂/Al₂O₃ of the reactants is less than or equal to 45. Type (b) differs from type (a) in that it incorporates a sharp decrease in pH followed by a sharp increase in pH. It has been observed in an EU-i system by Casci [58]. However, he did not discuss its cause and it could possibly have been due to an incorrect pH measurement. Type (c) like type (b) cannot be used to predict when ZSM-5 has crystallised.

The most probable reason for the different curves is the different amounts of silicate species that are left in the solution phase after crystallization of ZSM-5 has finished. Equation 3.3 shows that when the SiO₂/Al₂O₃ ratio of the reactants = 50, then less than 40% of the total concentration of silicon species are incorporated
Table 3.12 pH of the reaction mixture during the crystallisation of 'inorganic'-ZSM-5

<table>
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<tr>
<th>Code</th>
<th>4</th>
<th>21</th>
<th>28</th>
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</tr>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.19 pH changes that occur during the crystallization of 'inorganic' - ZSM-5

a Run J55; b Run J70; c Run J46.
into the zeolite phase. The $\frac{Si_{\text{zeolite}}}{Si_{\text{total}}}$ ratio decreases as the initial $SiO_2/Al_2O_3$ increases. The obvious difference between Type (a) and Type (b) pH curves is the sharp drop in pH observed just prior to the rise in pH that is usually associated with crystal growth. This occurs after 75 hours into run J70. However, it cannot be used to predict the crystallization of ZSM-5 as X-ray powder diffraction shows that ZSM-5 crystallization had finished before (Run J70), at (Run J71) and after (Run J72) the drop. Since the drop in pH is independent of crystal growth it must therefore be associated with unreacted species in the solution phase. A drop in pH can be attributed to

(i) Uptake of base by the zeolite.

(ii) Neutralisation of base by a weak acid, e.g. silica

by

$$H_2O + NaOH + SiO_2 \rightleftharpoons Na^+[OSi(OH)_3]^-$$

In this case it is believed that (ii) is the dominant effect. It is only observed in systems where less than 60% of the initial silica is incorporated into the zeolitic phase. If these reactions are left long enough then the unreacted silicate species polymerise to form magadiite and/or kenyaitite (see Figure 3.16).

Type (c) pH curve is like type (b) in that it is only associated with low aluminium, inorganic systems in which a large amount of silica is not incorporated into the zeolitic phase. Its shape may be attributed to the buffering action of the silicate species that are at equilibrium with both the solid and liquid phases.
3.4.4 Conclusions

The results support the view of other workers [38,49] that ZSM-5 is a genuine product of the inorganic system and show that it can be made from a wide range of reactant compositions. In the system studied ZSM-5 was found to be the dominant phase in systems with \( \text{SiO}_2/\text{Al}_2\text{O}_3 = 30-100 \), with a preferred range of 40-60. Mordenite, magadiite and kenyaiite were found in some reactions to co-exist with 'inorganic'ZSM-5. The chemical composition of 'inorganic'ZSM-5 is similar to that of (Na, HEX)-ZSM-5 in that sodium ions balance the anionic charge of the zeolite framework. The crystal morphology was found to be unaffected by the lack of hexanediol in the reaction mixture. The Si/Al ratio of the products was found to be directly proportional to the Si/Al ratio of the reactants, but the equation that related products Si/Al to the reaction mixture Si/Al is different to that obtained for systems that contain TPA cations. The existence of magadiite or kenyaiite phases caused the experimental points to deviate from the equation and the extent of the deviation is proportional to the amount of magadiite or kenyaiite formed. The positive intercept found for 'inorganic'ZSM-5 indicates that ZSM-5 crystallization starts from a silicon rich species. As the crystal grows aluminium is preferentially incorporated into the zeolite phase. The proposed scheme supports the work of Derouane et al [18], and suggests strong aluminium zoning patterns across the crystals of 'inorganic' ZSM-5 in accordance with the findings of von Ballmoos and Meier [56] and Derouane et al [57]. The pH/(time) results showed three types of behaviour each related to the initial \( \text{SiO}_2/\text{Al}_2\text{O}_3 \) ratio.
3.5 Structure Directing Effects of Base Concentration and Uncharged Organic Molecules

3.5.1 Introduction

The majority of studies on the synthesis of high silica zeolites have concentrated on the use of charged molecules that usually contain a tetrahedrally coordinated nitrogen group. The ability of uncharged organic molecules to direct zeolite formation has received less attention. Recent work by Valyocsik and Rollman [40] shows that amines can act as templates and there are many other papers and patents that document the use of amines in high silica zeolite systems. Barri et al [59] used diethanolamine in the preparation of THETA-1. This structure has also been made with other amines [60-62].

The effects of alkalinity on the kinetics and product formation in ZSM-5 systems has been studied by Chao et al [13] and Romannikov et al [50]. However these studies concentrate on obtaining 'optimum' ZSM-5 compositions.

There have been no systematic studies on the effect of either uncharged organic molecules or alkalinity on the ZSM-5 phase boundary. Consequently it was decided to investigate the system:

\[ x\text{Na}_2\text{O} \ 60\text{SiO}_2 \ 2\text{Al}_2\text{O}_3 \ y\text{ Organic} \ 30\text{H}_2\text{O} \]

where \( x = 5, 10 \) or \( 15 \); \( y = 0 \) or \( 10 \).
The 'inorganic'-ZSM-5 system is an excellent base for the study of possible templating effects by uncharged organic molecules. The four organic compounds studied were pinacol, piperazine, homopiperazine and 1,4-diazobicyclo[2.2.2]octane (DABCO).

3.5.2 Experimental

The reactions were carried out in 500 cm³ autoclaves at 150°C using the procedures and materials described in section 3.2 and were characterized by the techniques listed in Chapter 2. Aluminium wire was used as the aluminium source except for runs J19 and J52 in which alumina trihydrate was used. The molecular diameters of the organic molecules used were obtained from models and were based on a molecular-kinetic diameter of cyclohexane of 6.0 Å.

3.5.3 Results and Discussion

Effect of Uncharged Organic Molecules

Table 3.13 lists the reaction compositions studied and Table 3.14 shows the structure directing effects of both base concentration and the organic components used. It is clear from Table 3.14 that piperazine shows clear ferrierite directing properties in that it leads to the formation of ferrierite rather than ZSM-5 or mordenite. Its structure directing properties are similar to those of the closely related species piperidine, which was found by Nanne et al [63] to direct to ferrierite in a more alkaline system over a SiO₂/Al₂O₃ range of 23-197. The fact that pinacol, which is of similar size and shape, does not effect product formation suggests that the ferrierite directing properties
<table>
<thead>
<tr>
<th>Code</th>
<th>Na₂O</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Organic</th>
<th>H₂O</th>
<th>ZSM-5</th>
<th>Mordenite</th>
<th>Ferrierite</th>
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<td>2</td>
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<td>2</td>
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<td>5</td>
<td>60</td>
<td>2</td>
<td>HOMOPIP</td>
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<td>84</td>
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<tr>
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<td>DABCO</td>
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<td>HOMOPIP</td>
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<td>DABCO</td>
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<td></td>
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<tr>
<td>J96</td>
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<td>60</td>
<td>2</td>
<td>HOMOPIP</td>
<td>3000</td>
<td>56</td>
<td>44</td>
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</tr>
</tbody>
</table>

*Pinacol added to the reaction mixture although not fully dissolved in cold water
HOMOPIP = homopiperazine
Table 3.14 Effect of base and organic on product formation

<table>
<thead>
<tr>
<th>Organic</th>
<th>Na₂O</th>
<th>None</th>
<th>Pinacol (a)</th>
<th>Piperazine (b)</th>
<th>DABCO (c)</th>
<th>Homopiperazine (d)</th>
</tr>
</thead>
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<tr>
<td>ZSM-5</td>
<td>5</td>
<td>ZSM-5 (100%)</td>
<td>ZSM-5 + tr. Ferrierite</td>
<td>ZSM-5</td>
<td>ZSM-5</td>
<td></td>
</tr>
<tr>
<td>ZSM-5</td>
<td>5</td>
<td>ZSM-5 (80%)</td>
<td>ZSM-5 + tr. Ferrierite</td>
<td>ZSM-5</td>
<td>ZSM-5</td>
<td></td>
</tr>
<tr>
<td>+ Mordenite</td>
<td>α-cristobalite</td>
<td>ZSM-5 + mordenite</td>
<td>ZSM-5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZSM-5</td>
<td>10</td>
<td>ZSM-5</td>
<td>Ferrierite</td>
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<tr>
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<td>Ferrierite</td>
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<td>Mordenite</td>
<td></td>
</tr>
<tr>
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<td>(83%) +</td>
<td>Ferrierite</td>
<td>(83%) + Mordenite</td>
<td>Ferrierite</td>
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</tbody>
</table>

(a) Pinacol

(b) Piperazine

(c) DABCO

(d) Homopiperazine
of piperazine are associated with the amine groups. The piperazine/Al and Na/Al ratios for (Na, PIP)-ZSM-5 were found to be 1.1 and 0.43 respectively (see section 3.3). This indicates that most of the anionic charge of the zeolite framework is balanced by protonated piperazine cations. A similar conclusion was also reached by Valyocsik and Rollman [40] for α,ω-diamines in ferrierite, ZSM-5 and ZSM-11. Thus it seems probable that piperazine is protonated and that it is the effective species that directs the reaction to ferrierite. Any increase in the amount of base in the reaction mixture not only increases the concentration of sodium cations in solution but it also reduces the proportion of protonated piperazine molecules. The balance point when sodium hydroxide concentration starts to have a structure directing effect and successfully competes with piperazine appears to be reached when the molarity of sodium hydroxide in the reaction mixture is 0.250 M. At this stage with the Na₂O/H₂O ratio = 15/3000, it is estimated that the concentration of protonated piperazine is 0.001 M. A further increase in the free base concentration would be expected to give mordenite as the sole product.

The reason why piperazine has ferrierite directing properties becomes clearer when its size and shape is compared to the dimensions of the ferrierite structure (see Table 3.15 and 3.16). It is clear that piperazine is too large to be situated in either the 8 T-atom or 10 T-atom channels. However, it could be situated at either the channel intersections or in the 7 Å cavities that are windowed by 8 T-atom rings. Figure 3.20 shows that piperazine
Table 3.15 Zeolite channel dimensions [3]

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>T-atoms in Channel</th>
<th>Channel Dimensions (Å)</th>
<th>Channel Dimensionality&lt;sup&gt;a&lt;/sup&gt;</th>
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<tbody>
<tr>
<td>ZSM-5</td>
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<td>5.4 x 5.6</td>
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<td>5.1 x 5.5</td>
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<td>6.7 x 7.0</td>
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<td></td>
<td>8</td>
<td>3.4 x 4.8</td>
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</tbody>
</table>

<sup>a</sup> Dependant on the size of sorbate molecule

Table 3.16 Molecular kinetic diameter of organic molecules used

<table>
<thead>
<tr>
<th>Organic</th>
<th>Kinetic diameter (Å)</th>
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</thead>
<tbody>
<tr>
<td>Cyclohexane</td>
<td>6.0 x 6.0 x 3.8</td>
</tr>
<tr>
<td>Piperazine</td>
<td>6.0 x 6.0 x 3.8</td>
</tr>
<tr>
<td>Pinacol</td>
<td>6.5 x 5.7 x 3.8</td>
</tr>
<tr>
<td>DABCO</td>
<td>6.0 x 6.0 x 4.7</td>
</tr>
<tr>
<td>Homopiperazine</td>
<td>6.8 x 6.0 x 3.8</td>
</tr>
</tbody>
</table>

can just fit into the space available at the channel intersections. Larger molecules, such as the bulkier DABCO molecule or homopiperazine, which contains an additional CH₂ group in the ring, are too large to be situated at the channel intersections although they could both fit into the 7 Å cavities. The fact that only piperazine shows strong ferrierite directing properties suggests that its incorporation into the channel intersections during crystallization is crucial.
Thermal analysis results for (Na, PIP)-Ferrierite are shown in Figure 3.21. The TG and DTA traces show that piperazine is strongly held and is situated inside the ferrierite crystals. As piperazine is too large to be sorbed by ferrierite its incorporation must occur during crystal growth. The maximum weight loss for (Na, PIP)-Ferrierite occurs at 435°C. This is 45°C higher than that observed for (Na, PIP)-ZSM-5. A comparison of the TG traces that were obtained for (Na, PIP)-Ferrierite and (Na, PIP)-ZSM-5 shows that the former contains 6% more organic per unit weight of zeolite. This is perhaps surprising as Valyocsik and Rollman [40] have shown that ZSM-5 has a higher sorption capacity for 3-methyl
pentane and n-hexane than has ferrierite. These results may be explained as being due to piperazine packing better into ferrierite. This is supported by the results given in Table 3.17 that show that (Na, PIP)-Ferrierite (J68) contains less water than (Na, PIP)-ZSM-5 (P40).

Table 3.17 Chemical composition of (Na, PIP)-Ferrierite and (Na, PIP)-ZSM-5

<table>
<thead>
<tr>
<th>Code</th>
<th>Crystal size (µm)</th>
<th>Crystal Morphology</th>
<th>Si/Al</th>
<th>Na/Al</th>
<th>H₂O/Al</th>
<th>Piperazine/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>J68</td>
<td>1 x 1 discs</td>
<td></td>
<td>10.08</td>
<td>-</td>
<td>3.2a</td>
<td>0.95a</td>
</tr>
<tr>
<td>P40</td>
<td>0.5x0.5x0.5 twinned spherulites</td>
<td>18.88</td>
<td>0.43</td>
<td>4.10</td>
<td>1.1</td>
<td></td>
</tr>
</tbody>
</table>

a Calculated assuming Na/Al = 0

Apart from piperazine only homopiperazine showed structure directing properties. It was found to direct away from mordenite during run J96 and favour ferrierite. The relative amounts of ferrierite and mordenite obtained in the product is similar to that obtained from the corresponding piperazine system. It is not clear why homopiperazine directs away from mordenite as the organic is not too large to fit in mordenite's 12 T-atom channels, and furthermore, it is too large to be situated in ferrierite's channels or channel intersections. It will however just fit into ferrierite's 7 Å cavities. It is unlikely that the high base content of the reaction system caused degradation of homopiperazine as the pH values of runs J84 and J86 (which gave ZSM-5 as the product) was the same as that of run J96.
Although pinacol and DABCO did not show any structure directing properties in the systems investigated, they improved the crystallinity of ZSM-5 in low base systems by 20%. This effect was also observed in the homopiperazine system. Although these molecules do not act as templates they act as void-fillers to stabilise the structure and suppress recrystallization in a manner similar to that reported by Casci [49] for ZSM-5 systems which contained hexanediol.

Thermal analysis results for (Na, PIN)-ZSM-5, (Na-DABCO)-ZSM-5 and (Na, HPIP)-ZSM-5 are given in Figures 3.22 - 3.24. The TG and DTA traces obtained show that the organic molecules are present inside the ZSM-5 crystals. As these molecules are too large to be sorbed by ZSM-5, they must be occluded during crystal growth. This is an important point and one which could not be ascertained for the sodium, hexanediol ZSM-5 system. The formation of α-cristobalite as a trace impurity during run J85 may be promoted by pinacol, as Boxhoorn et al [14] have shown that some alcohols favour the formation of certain intermediary silicate species.

The TG and DTA traces that were obtained for (Na, PIN)-Mordenite, (Na, DABCO)-Mordenite and (Na, HOM)-Mordenite + ferrierite are given in Figures 3.25 - 3.27. The thermal analyses given in Figures 3.21 - 3.27 are very similar, they all show an endothermic loss of water at low temperatures that varies from 5-8% of the sample weight. Organic removal begins at about 150°C with the maximum loss at approximately 400 ± 50°C. There are usually three exothermic peaks observed before total removal of organic at 550-850°C. Pinacol is the most weakly held of the organic molecules and is completely
Figure 3.21 Thermal analysis of (Na, PIP)-Ferrierite (J68)

Figure 3.22 Thermal analysis of (Na, PIN)-ZSM-5 (J66)
Figure 3.23 Thermal analysis of (Na, DABCO)-ZSM-5 (J75)

Figure 3.24 Thermal analysis of (Na, HOM)-ZSM-5 (J84)
Figure 3.25 Thermal analysis of (Na, PIN)-Mordenite (J69)

Figure 3.26 Thermal analysis of (Na, DABCO)-Mordenite (J97)
removed by 550°C. The TG traces of (Na, PIN)–ZSM–5 and (Na, PIN)–Mordenite both show poor resolution of the water and organic weight loss stages. Homopiperazine is the most difficult to remove and thermal analyses of (Na, HOM)–ZSM–5 and (Na, HOM)–Mordenite + ferrierite suggest that a calcination temperature of 800°C would be required for the complete removal of organic. The only material to show structure collapse was (Na, PIN)–Mordenite which started to decompose at 900°C.

Although it is clear that amines can act as templates for zeolite formation it does appear that an addition or source of alkalinity is required for crystallization to occur over comparable timescales. Two samples from the following system were placed in

\[60 \text{ Homopiperazine} \quad 60 \text{ SiO}_2 \quad 3000 \text{ H}_2\text{O}\]
30 cm³ bombs and left in ovens set at 120°C and 150°C. Despite being left for 35 days there was no evidence to suggest that any crystalline product had formed.

### Effect of Base Content

An increase in the amount of sodium hydroxide added to the reaction mixture results in an increase in both the cation concentration and the pH of the solution. The former effects both the cation distribution and the product obtained whilst the latter effects the relative solubilities of reacting species present in the mother liquor. The effect of free base content on the product is clearly shown in Table 3.18. The experimental results show that ZSM-5 is the dominant phase formed in this system when the free base content is less than or equal to 0.133. The co-formation of mordenite with ZSM-5 in run J62 occurs because of this system is on the boundary of ZSM-5 formation.

### Table 3.18 Effect of free base content on the formation of 'organic free' products

<table>
<thead>
<tr>
<th>Code</th>
<th>Initial SiO₂/Al₂O₃</th>
<th>Free base content⁴</th>
<th>Product</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>J62</td>
<td>30</td>
<td>0.067</td>
<td>ZSM-5 (80%) + mordenite</td>
<td>63</td>
</tr>
<tr>
<td>J77</td>
<td>30</td>
<td>0.067</td>
<td>ZSM-5</td>
<td>60</td>
</tr>
<tr>
<td>J52</td>
<td>30</td>
<td>0.133</td>
<td>ZSM-5</td>
<td>77</td>
</tr>
<tr>
<td>J63</td>
<td>30</td>
<td>0.133</td>
<td>ZSM-5</td>
<td>82</td>
</tr>
<tr>
<td>J59</td>
<td>30</td>
<td>0.266</td>
<td>mordenite</td>
<td>100</td>
</tr>
<tr>
<td>J19</td>
<td>32</td>
<td>0.281</td>
<td>mordenite</td>
<td>100</td>
</tr>
</tbody>
</table>

⁴ Free base content = [Na₂O] - [Al₂O₃]/[SiO₂]
However, an increase in the free base content in the reaction mixture gives a more crystalline ZSM-5 product. The degree of ZSM-5 crystallinity achieved in runs J52 and J63 is comparable to that of organic stabilised ZSM-5 materials (runs J73, J85 and J86). At some point when the free base content is between 0.133 and 0.266 there is a switch from ZSM-5 to mordenite formation. Further increase in the free base content results in the formation of pure mordenite. Work carried out on H-mordenite (see section 4.7) indicates that it was the large pore variety that formed. The chemical and physical properties of mordenite obtained from run J59 are given in Table 3.19. The Na/Al ratio of approximately one indicates that sodium balances the anionic framework charge associated with tetrahedrally coordinated aluminium. The water content of mordenite is slightly higher than that obtained for 'inorganic'-ZSM-5 having 69 water molecules per 96 T-atoms compared with 60 for mordenite. This is due to the more open structure of mordenite and the fact that it has a higher Al/Si ratio.

Table 3.19 Chemical and physical properties of 'inorganic'-mordenite

<table>
<thead>
<tr>
<th>Code</th>
<th>Crystal size (µm)</th>
<th>Crystal morphology</th>
<th>Si/Al</th>
<th>Na/Al</th>
<th>H₂O/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>J59</td>
<td>1 x 0.7</td>
<td>Ellipsoidal</td>
<td>7.60</td>
<td>1.02</td>
<td>6.2</td>
</tr>
</tbody>
</table>

The dependance of the rate of ZSM-5 formation on the pH of the reaction mixture has already been studied for ZSM-5 systems that contain TPA [13]. The effect of reaction mixture pH on the time taken for 'inorganic'-ZSM-5 to crystallise is shown in Table 3.20.
Table 3.20  Dependance of the crystallization time on the pH of the reaction mixture

<table>
<thead>
<tr>
<th>Code</th>
<th>Free base content&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Initial pH</th>
<th>Crystallization time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>J62</td>
<td>0.05</td>
<td>11.50</td>
<td>530</td>
</tr>
<tr>
<td>J63</td>
<td>0.13</td>
<td>11.80</td>
<td>45</td>
</tr>
<tr>
<td>J59</td>
<td>0.22</td>
<td>11.95</td>
<td>21</td>
</tr>
</tbody>
</table>

<sup>a</sup> Free base content = \([\text{Na}_2\text{O}]-[\text{Al}_2\text{O}_3]/[\text{SiO}_2]\)

The strong dependance found is more marked than Chao et al [13] observed for a (Na, TPA)-ZSM-5 system. The reactant pH is associated with an error of ±0.03 whilst the errors associated with the crystallisation time are dependant on the frequency sampling. Similar results were obtained for those systems which contain uncharged organic molecules. The pH of samples taken during the reaction is given in Table 3.21. The results show that (Na, PIP)-Ferrierite is formed in less time than might be expected from the data given in Table 3.20. This indicates that not only does piperazine have ferrierite directing properties but that it also reduces the crystallization time. It thus satisfies both of Rollman's [64] requirements for a template. Comparison of the pH values of the samples taken from the homopiperazine systems with those from inorganic systems shows that the organic acts as a buffer.
Table 3.21(a)  pH Measurements over 0 - 240 hours

<table>
<thead>
<tr>
<th>Code</th>
<th>TIME (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4</td>
</tr>
<tr>
<td>J62</td>
<td>11.50</td>
</tr>
<tr>
<td>J77</td>
<td>11.53</td>
</tr>
<tr>
<td>J85</td>
<td></td>
</tr>
<tr>
<td>J73</td>
<td>11.78</td>
</tr>
<tr>
<td>J82</td>
<td>11.66</td>
</tr>
<tr>
<td>J86</td>
<td>11.96</td>
</tr>
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<td>J52</td>
<td>11.80</td>
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<td>J63</td>
<td>11.79</td>
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<tr>
<td>J66</td>
<td>11.76</td>
</tr>
<tr>
<td>J68</td>
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<td>J84</td>
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<tr>
<td>J97</td>
<td>-</td>
</tr>
<tr>
<td>J96</td>
<td>12.07</td>
</tr>
<tr>
<td>Code</td>
<td>TIME (hours)</td>
</tr>
<tr>
<td>------</td>
<td>-------------</td>
</tr>
<tr>
<td></td>
<td>312</td>
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<tr>
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<td>J82</td>
<td>11.64</td>
</tr>
<tr>
<td>J86</td>
<td>12.28</td>
</tr>
</tbody>
</table>
For example, a threefold increase in the base concentration results in the pH increasing from 11.96 to 12.02 compared with 11.80 to 12.07 for the inorganic system. The average reactant pH for run J86, a homopiperazine-ZSM-5 system, is slightly higher than that of run J52, an 'inorganic'-ZSM-5 system. However the crystallization time for run J52 was about 1/5 that of run J86. This indicates that the concentration of sodium cations in the solution also has a strong effect on the crystallization time.

3.5.4 Conclusions

It was shown in section 3.4 that 'inorganic'-ZSM-5 can be synthesised over a wide range of SiO₂/Al₂O₃ ratios. Now it can also be seen that it is the genuine product over a range of free base contents from 0.067-0.133. Increasing the free base content of the reaction mixture results in mordenite formation. Addition of pinacol, piperazine, DABCO and homopiperazine to the reaction mixture gave different results. Whilst all four organic molecules are occluded during crystal growth only piperazine and homopiperazine showed structure directing properties. Piperazine was found to be a good template for ferrierite, directing away from both ZSM-5 and mordenite. The reason for its ferrierite directing properties is probably due to its size and shape. It just fits into the available space at the channel intersections and the 7R cavities. The piperazine/Al ratio obtained for (Na, PIP)-ZSM-5 suggests that piperazine is protonated inside the zeolite. Homopiperazine appeared to favour ferrierite formation at the expense of mordenite and must be sited in the 7R cavities in ferrierite. Like pinacol and DABCO it improved the crystallinity of ZSM-5 made in the low base
systems by about 20% and probably acts like hexane-1,6-diol to stabilize the ZSM-5 framework. Some α-cristobalite found in a low base pinacol mixture may be due to pinacol enhancing the formation of certain polymeric silicate species. The relationship between the reaction mixture pH and crystallization time was found to be stronger in the 'inorganic'-ZSM-5 system than when TPA was present. Not only was the crystallization time found to be dependant on alkalinity it was also related to the sodium ion concentration.

3.6 Product Dependence on Alkali Metal Cation in High-Silica Systems

3.6.1 Introduction

The ferrierite directing properties of piperazine were described in section 3.6. The aim of the work described in this section was to extend those investigations and find out over what temperature and \( \text{SiO}_2/\text{Al}_2\text{O}_3 \) range ferrierite can be formed. Lithium and potassium were used in place of sodium in order to discover if they would enhance or restrict the ferrierite directing properties of piperazine. To date the synthesis of ferrierite has not been reported in the lithium system although it has been made in the strontium [65], calcium [66], sodium [67] and potassium [68] systems. The system studied has the following molar composition:

\[
10\text{M}_2\text{O} \quad 60\text{SiO}_2 \quad x\text{Al}_2\text{O}_3 \quad 10 \text{ Piperazine} \quad 3000\text{H}_2\text{O}
\]

where \( \text{M} \) is lithium, sodium or potassium; \( x = 0, 0.5, 1, 2 \) or 4. The reactions were carried out in static systems at temperatures of 120°C, 150°C and 180°C.
3.6.2 Experimental

The 30 cm$^3$ bombs described in section 3.2 were used as the reaction vessels. The materials used were those listed in section 3.2, aluminium wire being used as the aluminium source. Characterization of the products was limited to X-ray powder diffractometry, (described in Chapter 2) because of the large number of products that were made and the fact that poor yields of zeolite and/or silicate product were usually obtained.

3.6.3 Results and Discussion

The product dependence on alkali metal cation, temperature and reactant SiO$_2$/Al$_2$O$_3$ ratio is shown in Table 3.22. Kinetic studies were not carried out because Sinclair [69] has shown that the sampling technique used for the 30 cm$^3$ bombs can induce nucleation. Since sampling was infrequent the crystallization times given are only approximate when the product contained more than one phase, or if significant amounts of amorphous material were found, then the products are listed in order of decreasing quantity as determined by X-ray powder diffractometry. In several reactions the product was found to contain large amounts of unreacted gel material and so the crystalline products were often of poor quality. Nevertheless, the results do indicate the dominant phases that occur and they do correlate well with results obtained from stirred systems. For example, run B7 and run J68 (see section 3.5) both indicate that ferrierite formation is preferred. Although in both of these examples the same product was obtained it was found that stirring reduced the crystallization time and gives a more crystalline product.
Table 3.22 Products obtained from the reaction mixture $10M_{2}O \times Al_{2}O_{3} \times 60SiO_{2} \times 10PIP \times 300H_{2}O$

<table>
<thead>
<tr>
<th>Alkali Metal</th>
<th>Temperature (°C)</th>
<th>15</th>
<th>30</th>
<th>60</th>
<th>120</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO$_2$/Al$_2$O$_3$</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>(°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>B1</td>
<td>Amorphous+ferrierite</td>
<td></td>
<td></td>
<td></td>
<td>B5</td>
</tr>
<tr>
<td>120</td>
<td>B2</td>
<td>Amorphous+ferrierite</td>
<td>(77)</td>
<td>(76)</td>
<td>(36)</td>
<td>(11)</td>
</tr>
<tr>
<td></td>
<td>B3</td>
<td>Analcite+ZSM-5 + ferrierite</td>
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<tr>
<td>Sodium</td>
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<td>(36)</td>
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<td>150</td>
<td>B5</td>
<td>Magadiite</td>
<td>(77)</td>
<td>(76)</td>
<td>(36)</td>
<td></td>
</tr>
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<td>(8)</td>
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<td>(6)</td>
<td>(8)</td>
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<td>(76)</td>
<td>(36)</td>
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<td></td>
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<tr>
<td></td>
<td>B9</td>
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<td>(76)</td>
<td>(36)</td>
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<td></td>
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<tr>
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<td>(36)</td>
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<td>(36)</td>
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<td>(16)</td>
<td>(6)</td>
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<td>(12)</td>
<td>(16)</td>
<td>(6)</td>
</tr>
<tr>
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<td>B23</td>
<td>Analcite + kenyaiite + ZSM-5</td>
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<td>(12)</td>
<td>(16)</td>
<td>(6)</td>
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<td>(6)</td>
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<td>(12)</td>
<td>(16)</td>
<td>(6)</td>
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<td>(6)</td>
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<td>(6)</td>
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<td>(6)</td>
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<td>Alkali Metal</td>
<td>Temperature (°C)</td>
<td>SiO$_2$/Al$_2$O$_3$</td>
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<tr>
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<td>30</td>
<td>60</td>
<td>120</td>
<td>150</td>
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<tr>
<td>B31</td>
<td>Amorphous+ZSM-5 + ferrierite (81)</td>
<td>B32</td>
<td>Amorphous+EU-8 (90)</td>
<td>B33</td>
<td>Amorphous+EU-8 (97)</td>
<td>B34</td>
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<td>B36</td>
<td>Ferrierite(75%)+ ZSM-5 (47)</td>
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<td>Amorphous+EU-8 (55)</td>
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<td>Amorphous+EU-8 (20)</td>
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</tbody>
</table>
This is because stirring increases the rate of transfer of nutrients to the growing crystals as well as facilitating the rate of dissolution of the aluminosilicate gel. The increase in product crystallinity when the reaction mixture is stirred and not static, is in contrast with the results of studies on the rate of formation of zeolite X [70]. However the results support those of Casci [71] who studied the effect of stirring speed on EU-1 crystallization.

Although observations on the kinetics are limited by the infrequency of sampling, it is clear from Table 3.22 that the crystallization time can be reduced by either reducing the aluminium content in the reactant gel or by increasing the reaction temperature. The latter is well known for high silica crystallization. The former has been reported for ZSM-5 by Chao [13] and is probably related to the free base content of the system, which is reduced by the addition of aluminium.

The results given in Table 3.22 show that the product and the crystallization time are dependent on the type of cationic species used. These observations are not unique to this system and have been reported elsewhere [29,64]. Of the three alkali metal cations tested the two which give the most similar results are sodium and potassium. A closer inspection shows that there are several important differences between these two systems. The experimental results indicate that the ferrierite directing properties of piperazine found in sodium systems are inhibited by potassium and lithium. In both of these systems ferrierite is only observed in systems with SiO$_2$/Al$_2$O$_3$ = 15 and which will not give ZSM-5 as the product in the corresponding inorganic reaction. Compared with potassium and lithium, sodium
enhances the formation of ferrierite. For example, no ferrierite formation is observed in the lithium and potassium systems from experiments that correspond to B2, B3, B7 and B12 in the sodium system. These results are unique to piperazine systems as Cormier and Sand [68] found that potassium is preferentially incorporated into ferrierite, at the expense of sodium during crystal growth in an inorganic system [66].

The crystallization time of ferrierite is also markedly less in the sodium system than in the potassium and lithium systems. This is in agreement with results given in section 3.5 in which it was reported that piperazine acts as a template for ferrierite in the sodium system. No mordenite formation was observed in any of the low SiO₂/Al₂O₃ systems and although blank piperazine-free compositions were not tested its formation could have been expected from low SiO₂/Al₂O₃ systems. Thus although piperazine does not direct away from ZSM-5 in either the potassium or lithium systems it probably directs away from mordenite.

In comparison with the formation of ferrierite that of ZSM-5 is less dependant on whether sodium or potassium are used. The main difference between the two systems is that whilst run B7 in the sodium system gave an amorphous + ferrierite product, the corresponding experiment in the potassium system gave an amorphous + ZSM-5 product. In addition, mixed ZSM-5 + ferrierite products were only obtained in sodium systems. The yield of silicates such as kenyalite were enhanced in the potassium system at the expense of ZSM-5. The crystallization time for ZSM-5 was found to be longer in the potassium system than in the sodium system. This result is
the opposite to that which Erdem and Sand [36] found for the growth of ZSM-5 from sodium+TPA and potassium+TPA systems. These results all indicate that piperazine strongly inhibits, and is inhibited by, potassium ions so that effects due to either species are not observed.

Although magadiite and kenyaiite are both naturally occurring sodium silicates, only kenyaiite was found to occur in the potassium system. Potassium-kenyaiite has not been reported in the literature. However experiments that were carried out to investigate the effect of hydrated alkali metal cations on the interplanar d-spacings of kenyaiite were inconclusive because of the large amounts of amorphous material in the product. The co-existence of magadiite and kenyaiite was not found in any of the systems studied. Whilst the formation of kenyaiite occurs in the sodium system when the reactions are carried out at 180°C, magadiite formation dominates at lower temperatures. Analcite and quartz were also observed. However, it is unlikely that piperazine is associated with either their formation or that of magadiite or kenyaiite.

The results obtained for the lithium system are different to those obtained for the sodium and potassium systems in that the dominant phase is a lithium-silicate designated EU-8. This species has been fully characterized and this work is described in section 3.7. The most crystalline samples were obtained from aluminium free compositions. The amorphous + EU-8 products obtained were found to be thermodynamically stable over the reaction timescales investigated. At SiO₂/Al₂O₃ = 15, ferrierite was observed to co-exist with EU-8. The X-ray powder diffraction pattern
which was obtained is given in Figure 3.28. The peak positions match those of the standard ferrierite sample. However the peak at \(2\theta = 9.5\) is enhanced in Li-ferrierite. Thermal analysis indicates

![X-ray powder diffraction of Li-Ferrierite + EU-8](image)

**Figure 3.28** X-ray powder diffraction of Li-Ferrierite + EU-8

X denotes major EU-8 peaks

that piperazine is strongly held inside the ferrierite crystals. The probable crystallization sequence is EU-8 and then ferrierite, however, kinetic studies would have to be carried out to verify this. The synthesis of Li-ZSM-5 which was made in run B31 has been reported before by Nastro and Sand [29].
3.6.4 Conclusions

The product dependence on the nature of the cationic species, \( \text{SiO}_2/\text{Al}_2\text{O}_3 \) ratio and temperature has been clearly shown for the system investigated. The results indicate that piperazine will only direct to ferrierite in sodium systems. Whilst ferrierite formation was favoured in the sodium system, ZSM-5 formation occurred without preference in both the sodium or potassium systems. Typical non-zeolite phases found in the sodium and potassium systems were magadiite, kenyaiite and quartz. In the lithium system the dominant phase was the lithium silicate designated EU-8.

3.7 Synthesis and Characterisation of EU-8 and Derivative Phases

3.7.1 Introduction

Although a lot of work has been carried out on the synthesis of zeolites from potassium and sodium systems, the synthesis of zeolites from lithium systems has received much less attention. Zeolites that have been made from lithium systems include Li-A, Li-H, ZSM-2, ZSM-5, bikitaite, Li-clinoptyilolite, Li-analcime, Li-mordenite and Li-phillipsite [29,72,73]. Other workers have reported the synthesis of Li-A, lithium metasilicate, lithium aluminate and an uncharacterised non-zeolitic material designated 'B' from lithium-sodium systems [74]. The solubility of lithium silicate has been extensively studied since the last century [75,76] and the X-ray powder diffraction patterns of all lithium silicates have been systematically catalogued [77,78].

Investigations on the system:

\[ 10\text{Li}_2\text{O} \ 60\text{SiO}_2 \ x\text{Al}_2\text{O}_3 \ 10 \text{Piperazine} \ 3000\text{H}_2\text{O} \]

with \( x = 0, 0.5, 1.0, 2.0, 4.0 \) in static systems at \( 120^\circ\text{C}, 150^\circ\text{C} \).
and 180°C (see previous section) led to the discovery of a material that had an X-ray powder diffraction pattern similar to that of EU-8 [79]. However its X-ray powder diffraction pattern showed broad, poorly resolved peaks which indicated very small crystals and that there was a lot of amorphous material present in the product.

The work now described covers the synthesis of pure EU-8, its X-ray powder diffraction pattern, morphology, thermal properties and ion-exchange properties. Related materials, designated EU-8B and EU-8C, are also characterized.

3.7.2 Experimental

Two samples of pure EU-8 were made from the following molar compositions:

<table>
<thead>
<tr>
<th>Code</th>
<th>Li₂O</th>
<th>SiO₂</th>
<th>Piperazine</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>B45</td>
<td>10</td>
<td>60</td>
<td>10</td>
<td>3000</td>
</tr>
<tr>
<td>J89</td>
<td>10</td>
<td>30</td>
<td>3000</td>
<td></td>
</tr>
</tbody>
</table>

The synthesis of sample B45 is described in the previous section. Sample J89 was made in a 500 cm³ autoclave at 150°C for 48 hours and was stirred at 300 rpm. The materials used and gel preparation are described in section 3.2. Products were analysed by the analytical techniques described in Chapter 2.

3.7.3 Characterization of EU-8

X-ray Powder Diffraction

X-ray powder diffraction data for samples B45 and J89 are given in Table 3.23. The diffraction patterns of samples that had the same molar composition as B45 but had been made at 120°C and 150°C are similar but indicate that a less crystalline product was obtained.
The inter-planar d-spacings and relative intensities of samples B45 and J89 indicate that both samples consist of the same crystalline phase. The main differences between the two patterns are in the relative intensities of the peaks centred at 3.00 Å and 4.07 Å. The similarity of the two diffraction patterns suggests that piperazine does not act as a template for EU-8 and its absence from the reaction mixture does not affect the structure of the product.

**pH Measurements**

A pH drop on formation of EU-8 was observed for both samples (Table 3.24). This indicates that EU-8 is not a zeolite because a rise in pH coincident with the crystallization, would be expected. The drop in pH indicates that a lithium silicate species was formed. The pH of the reaction mixture of sample B45 is higher than that of sample J89 because piperazine acts as a buffer.

**SEM Analysis**

Scanning electron microscopy of sample B45 showed that it consisted of irregularly sized balls of fibrous crystals together with some amorphous material which was probably unreacted silica gel. The largest of these fibrous crystals was about 4 μm long. Generally, the crystals were small and difficult to distinguish. SEM analysis of sample J89 showed that it consisted of 40 μm balls of 4 μm fibrous crystals. The balls and crystals are illustrated in Figure 3.29. The presence of a single crystal morphology in both samples indicates that they consist of only one phase.
Table 3.23 X-ray powder diffraction data for EU-8

<table>
<thead>
<tr>
<th>Sample</th>
<th>d-spacing (Å)</th>
<th>Peak height (cm)</th>
<th>Intensity I/I₀</th>
<th>d-spacing (Å)</th>
<th>Peak height (cm)</th>
<th>Intensity I/I₀</th>
<th>Error Δd (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B45</td>
<td>7.44</td>
<td>8.0</td>
<td>48</td>
<td>7.40</td>
<td>8.9</td>
<td>73</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>6.89</td>
<td>10.1</td>
<td>61</td>
<td>6.84</td>
<td>11.1</td>
<td>91</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>4.44</td>
<td>4.7</td>
<td>28</td>
<td>4.40</td>
<td>4.7</td>
<td>39</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>4.18</td>
<td>12.2</td>
<td>73</td>
<td>4.17</td>
<td>8.7</td>
<td>71</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>4.07</td>
<td>16.6</td>
<td>100</td>
<td>4.06</td>
<td>10.2</td>
<td>84</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>3.72</td>
<td>2.6</td>
<td>16</td>
<td>3.71</td>
<td>2.7</td>
<td>22</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>3.44</td>
<td>1.5</td>
<td>9</td>
<td>3.43</td>
<td>2.1</td>
<td>17</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>3.18</td>
<td>1.8</td>
<td>11</td>
<td>3.16</td>
<td>2.1</td>
<td>17</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>2.99</td>
<td>11.8</td>
<td>71</td>
<td>3.00</td>
<td>12.2</td>
<td>100</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>2.71</td>
<td>0.6</td>
<td>4</td>
<td>2.71</td>
<td>0.5</td>
<td>4</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>2.64</td>
<td>4.0</td>
<td>24</td>
<td>2.62</td>
<td>4.2</td>
<td>34</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>2.53</td>
<td>3.9</td>
<td>23</td>
<td>2.60</td>
<td>3.9</td>
<td>32</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>2.51</td>
<td>3.3</td>
<td>20</td>
<td>2.51</td>
<td>1.5</td>
<td>12</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>2.39</td>
<td>0.6</td>
<td>4</td>
<td>2.39</td>
<td>0.5</td>
<td>4</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>2.30</td>
<td>1.2</td>
<td>7</td>
<td>2.29</td>
<td>1.4</td>
<td>11</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table 3.24 pH measurements of samples taken from the reaction mixtures

<table>
<thead>
<tr>
<th>Code</th>
<th>pH after 0 hours</th>
<th>pH after 48 hours</th>
<th>ΔpH</th>
</tr>
</thead>
<tbody>
<tr>
<td>B45</td>
<td>11.956</td>
<td>11.721</td>
<td>-0.245</td>
</tr>
<tr>
<td>J89</td>
<td>11.745</td>
<td>11.510</td>
<td>-0.235</td>
</tr>
</tbody>
</table>
Figure 3.29  Electron micrographs of EU-8 and derivative phases.  A = EU-8;  B = EU-8;  C = EU-8B
Thermal Analysis

Thermal analysis of sample B45, shown in Figure 3.30 and tabulated in Tables 3.25 and 3.26 indicates that there are four distinct weight loss steps, all of which are endothermic. On heating EU-8 up from room temperature to 150 ± 10°C there is an endothermic loss of loosely held physi-sorbed water. Further heat treatment causes the loss of more strongly held water in three stages. These stages approximate to 1 : 2 : 1 in magnitude, and probably correspond to loss of water molecules associated with the hydration shell of lithium. The absence of any exothermic peak shows that no intra-crystalline piperazine is present. This supports the other analyses and measurements carried out which show that piperazine does not play a significant role in product formation.

Chemical Composition

X-ray fluorescence analysis of sample J89 gave the % SiO₂ in the product. The lithium content was obtained by difference measurement.

<table>
<thead>
<tr>
<th>%</th>
<th>Molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>82%</td>
</tr>
<tr>
<td>Li₂O</td>
<td>(98 - 82) = 16%</td>
</tr>
</tbody>
</table>

The total % composition was taken to be 98% as this was the average value obtained for zeolites. No evidence was found to suggest that any sodium, potassium or calcium was present in the product. However, a small amount of aluminium that corresponds to Al/Li = 0.0016 was detected. This was attributed to impurities in the silica used. TG analysis indicates a total loss of water corresponding to 15% of
Figure 3.30 Thermal analysis of Li-EU-8 (B45)
Table 3.25  TG analysis of EU-8 (sample B45)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>0-140</th>
<th>140-205</th>
<th>205-310</th>
<th>310-1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight Loss (%)</td>
<td>1.5</td>
<td>3.5</td>
<td>7.0</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Table 3.26  DTA of EU-8 (sample B45)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>0-160</th>
<th>160-310</th>
<th>310-350</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔT</td>
<td>Endothermic</td>
<td>Endothermic</td>
<td>Endothermic</td>
</tr>
<tr>
<td>Peak Maximum (°C)</td>
<td>broad</td>
<td>220</td>
<td>325</td>
</tr>
</tbody>
</table>

Table 3.27  X-ray powder diffraction data for EU-8 and related material

<table>
<thead>
<tr>
<th>EU-8</th>
<th>EU-8 treated with sodium chloride</th>
<th>Error Δd (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-spacing (Å)</td>
<td>Height (cm)</td>
<td>Intensity</td>
</tr>
<tr>
<td>7.40</td>
<td>8.9</td>
<td>73</td>
</tr>
<tr>
<td>6.84</td>
<td>11.1</td>
<td>91</td>
</tr>
<tr>
<td>4.40</td>
<td>4.7</td>
<td>39</td>
</tr>
<tr>
<td>4.17</td>
<td>8.7</td>
<td>71</td>
</tr>
<tr>
<td>4.06</td>
<td>10.2</td>
<td>84</td>
</tr>
<tr>
<td>3.71</td>
<td>2.7</td>
<td>22</td>
</tr>
<tr>
<td>3.43</td>
<td>2.1</td>
<td>17</td>
</tr>
<tr>
<td>3.16</td>
<td>2.1</td>
<td>17</td>
</tr>
<tr>
<td>3.01</td>
<td>12.2</td>
<td>100</td>
</tr>
<tr>
<td>2.71</td>
<td>0.5</td>
<td>4</td>
</tr>
<tr>
<td>2.62</td>
<td>4.2</td>
<td>34</td>
</tr>
<tr>
<td>2.60</td>
<td>3.9</td>
<td>32</td>
</tr>
<tr>
<td>2.51</td>
<td>1.5</td>
<td>12</td>
</tr>
<tr>
<td>2.39</td>
<td>0.5</td>
<td>4</td>
</tr>
<tr>
<td>2.29</td>
<td>1.4</td>
<td>11</td>
</tr>
</tbody>
</table>
the total weight of product. Thus the chemical composition of sample J89 at 25°C and equilibrated over saturated sodium chloride \((p/p_0 = 0.753)\) is:

\[
\text{Li}_2\text{O} \quad 2.7(\pm 0.2)\text{SiO}_2 \quad 1.88(\pm 0.2)\text{H}_2\text{O}
\]

3.7.4 Properties of EU-8

Ion-Exchange with NaCl

10 cm\(^3\) of 5 m NaCl solution was added to 0.2 g of sample J89 and the slurry left to stir overnight at room temperature. The slurry was filtered and washed with distilled water before being analysed by X-ray powder diffraction. The pattern obtained is compared with that of sample J89 in Table 3.27. Both X-ray powder diffraction patterns are similar. The minor peaks at 2.51 \(\AA\), 2.39 \(\AA\) and 2.29 \(\AA\) are not recorded in the sodium chloride exchanged sample because they are indistinguishable from the background noise. The broader peaks observed in the X-ray diffraction pattern of the sodium chloride exchanged sample indicates a loss of crystallinity. This broadening makes accurate peak measurements more difficult but there does appear to be a significant increase in some of the d-spacing values. For example, 6.84 \(\AA\) to 7.01 \(\AA\) and 3.16 \(\AA\) to 3.28 \(\AA\). This is probably due to the larger sodium ion ion-exchanging with some of the inter-planar lithium ions. This observation is supported by the increase in intensity of the peak centred at 4.92 \(\AA\) and suggests that prolonged ion-exchange treatment with sodium chloride would result in the formation of a sodium silicate species.
3.7.5 Synthesis and Characterization of EU-8B

Synthesis

0.2 g portions of sample J89 were calcined in a furnace under static air conditions at 200°C, 300°C, 400°C, 600°C and 800°C for 2 hours. Calcination at 800°C for 2 hours resulted in the complete transformation of EU-8 to a new material designated EU-8B.

X-Ray Powder Diffraction

The X-ray powder diffraction pattern of EU-8B is given in Table 3.28. The degree of crystallinity of EU-8 + EU-8B mixtures was calculated from equation 2.3. The representative peaks for both materials were chosen for their intensity and also for their position - they had to be clearly distinguishable and not overlap with corresponding peaks from the other pattern. The peaks at 7.40 Å, 6.84 Å, 4.40 Å and 3.00 Å were chosen to represent EU-8 whilst the peaks at 4.69 Å, 3.30 Å and 2.73 Å were chosen to represent EU-8B. The transformation of EU-8 to EU-8B is shown in Figure 3.31. EU-8 starts to lose crystallinity at temperatures >100°C and has completely disappeared by 300°C. Growth of EU-8B starts at temperatures >200°C (at which stage EU-8 has lost 50% of its crystallinity) and is complete at temperatures >625°C.

SEM Analysis

SEM analysis of 100% crystalline EU-8B showed that the thermal treatment did not result in changes in the crystal size and morphology. The crystals are shown in Figure 3.29 and consist of 4 μm needles that project out from the centre of 40 μm balls. The presence of only a single crystal morphology indicates that there is only one phase present and that EU-8B is a pure material.
### Table 3.28 X-ray powder diffraction data for EU-8B

<table>
<thead>
<tr>
<th>d-spacing (Å)</th>
<th>Peak Height (cm)</th>
<th>Intensity I/I₀</th>
<th>Error Δd (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.30</td>
<td>0.6</td>
<td>4</td>
<td>0.12</td>
</tr>
<tr>
<td>5.40</td>
<td>1.8</td>
<td>11</td>
<td>0.11</td>
</tr>
<tr>
<td>4.69</td>
<td>5.6</td>
<td>34</td>
<td>0.10</td>
</tr>
<tr>
<td>3.73</td>
<td>10.2</td>
<td>62</td>
<td>0.06</td>
</tr>
<tr>
<td>3.64</td>
<td>8.2</td>
<td>50</td>
<td>0.06</td>
</tr>
<tr>
<td>3.58</td>
<td>16.4</td>
<td>100</td>
<td>0.06</td>
</tr>
<tr>
<td>3.30</td>
<td>5.95</td>
<td>36</td>
<td>0.05</td>
</tr>
<tr>
<td>2.91</td>
<td>1.5</td>
<td>9</td>
<td>0.03</td>
</tr>
<tr>
<td>2.73</td>
<td>4.0</td>
<td>24</td>
<td>0.03</td>
</tr>
<tr>
<td>2.39</td>
<td>4.55</td>
<td>28</td>
<td>0.03</td>
</tr>
<tr>
<td>2.34</td>
<td>3.35</td>
<td>20</td>
<td>0.03</td>
</tr>
<tr>
<td>2.09</td>
<td>0.4</td>
<td>2</td>
<td>0.02</td>
</tr>
<tr>
<td>2.06</td>
<td>1.0</td>
<td>6</td>
<td>0.02</td>
</tr>
<tr>
<td>2.01</td>
<td>0.8</td>
<td>5</td>
<td>0.02</td>
</tr>
<tr>
<td>1.97</td>
<td>1.5</td>
<td>9</td>
<td>0.02</td>
</tr>
<tr>
<td>1.85</td>
<td>0.6</td>
<td>4</td>
<td>0.02</td>
</tr>
</tbody>
</table>

### Table 3.29 TG Analysis of EU-8, EU-8B and intermediate materials

<table>
<thead>
<tr>
<th>Temperature (°C) [Weight loss (%)]</th>
<th>0-140</th>
<th>140-205</th>
<th>205-310</th>
<th>310-1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcination Temperature (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1.5</td>
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<tr>
<td>200</td>
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<td>1.5</td>
<td>6.5</td>
<td>4.0</td>
</tr>
<tr>
<td>600</td>
<td>1.2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>800</td>
<td>0.5</td>
<td>0</td>
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<td>0</td>
</tr>
</tbody>
</table>
Figure 3.31 Thermal transformation of EU-8 to EU-8B
Thermal Analysis

TG analysis of EU-8, EU-8B and intermediate products given in Table 3.29 shows that EU-8B may be considered to be the anhydrous analogue of EU-8. Differential thermal analysis of sample B45 did not show a sharp endothermic peak that would have indicated a phase transformation. These facts indicate that the lithium silicate EU-8 loses water from the lithium solvation shell to form EU-8B.

Discussion

Table 3.30 shows that it is possible to partly re-construct the X-ray powder diffraction pattern of EU-8B from a combination of lithium silicate (Li$_2$O, 2SiO$_2$) and lithium metasilicate (Li$_2$O, SiO$_2$). However, there are a number of reasons that suggest EU-8B is in fact a new material. The reconstructed X-ray powder diffraction pattern does not exactly fit that of EU-8B. There is no corresponding peak at 2.09 \( \lambda \) and the intensity of the most intense peak at 3.58 \( \lambda \) is not fully accounted for. SEM showed the existence of only one phase. The chemical composition of the parent material has a Si/Li ratio higher than that of either lithium silicate or lithium metasilicate. The plot of crystallinity of EU-8 and EU-8B (Figure 3.31) suggests that EU-8B is a pure material as it is unlikely that two phases would grow at the same rate.

3.7.6 Synthesis and characterization of EU-8C

Synthesis

10 cm$^3$ of 1M hydrochloric acid was added to 0.2 g of sample J89 and left stirring overnight at room temperature. The slurry was filtered and washed with distilled water before being analysed by
Table 3.30  X-ray powder diffraction data for EU-8B and known lithium silicates

<table>
<thead>
<tr>
<th>EU-8B</th>
<th>Lithium silicate [77-78]</th>
<th>Lithium metasilicate [77-78]</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-spacing</td>
<td>Intensity</td>
<td>d-spacing</td>
</tr>
<tr>
<td>(Å)</td>
<td>I/I₀</td>
<td>(Å)</td>
</tr>
<tr>
<td>7.30</td>
<td>4</td>
<td>7.34</td>
</tr>
<tr>
<td>5.40</td>
<td>11</td>
<td>5.43</td>
</tr>
<tr>
<td>4.69</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>3.73</td>
<td>62</td>
<td>3.75</td>
</tr>
<tr>
<td>3.64</td>
<td>50</td>
<td>3.67</td>
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<tr>
<td>3.58</td>
<td>100</td>
<td>3.59</td>
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<td>3.30</td>
<td>36</td>
<td>3.30</td>
</tr>
<tr>
<td>2.91</td>
<td>9</td>
<td>2.20</td>
</tr>
<tr>
<td>2.73</td>
<td>24</td>
<td>2.70</td>
</tr>
<tr>
<td>2.39</td>
<td>28</td>
<td>2.40</td>
</tr>
<tr>
<td>2.34</td>
<td>20</td>
<td>2.36</td>
</tr>
<tr>
<td>2.09</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>2.06</td>
<td>6</td>
<td>2.06</td>
</tr>
<tr>
<td>2.01</td>
<td>5</td>
<td>2.02</td>
</tr>
<tr>
<td>1.97</td>
<td>9</td>
<td>1.97</td>
</tr>
<tr>
<td>1.85</td>
<td>4</td>
<td>1.85</td>
</tr>
</tbody>
</table>
X-ray powder diffraction. The product was found to have a different X-ray powder diffraction pattern and was designated EU-8C.

_X-Ray Powder Diffraction_

The X-ray powder diffraction pattern of EU-8C is given in Table 3.31 alongside that of a known alpha-hydrogen silicate species that has the molecular formula $\text{H}_2\text{O}.2\text{SiO}_2$. The pattern obtained for EU-8C showed poor peak resolution which indicated that amorphous material was present. Nevertheless there appears to be a good correlation between the peaks of EU-8C and alpha-hydrogen silicate. The peak at 3.77 Å is very poorly resolved and overlaps with that at 3.86 Å. However, its presence along with other peaks found at lower d-spacings does indicate that there is a second silicate species present. The peak at 3.77 Å does not match with any major peak of any known hydrogen silicate species. No peaks due to parent material were observed.

_SEM Analysis_

SEM analysis of EU-8C showed that, like the parent material, it consisted of 40 μm balls of crystals. Unlike the parent material the crystals were fibrous and varied in size. The largest crystals observed were fibres 4 μm in length, however smaller crystals were difficult to observe. Significant quantities of amorphous material was observed.
Table 3.31  X-ray powder diffraction data for EU-8C and alpha hydrogen silicate

<table>
<thead>
<tr>
<th>d-spacing (Å)</th>
<th>Error Δd (Å)</th>
<th>Peak height (cm)</th>
<th>Intensity I/I₀</th>
<th>d-spacing (Å)</th>
<th>Intensity I/I₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.58</td>
<td>0.12</td>
<td>4.2</td>
<td>38</td>
<td>7.69</td>
<td>50</td>
</tr>
<tr>
<td>5.67</td>
<td>0.12</td>
<td>1.1</td>
<td>10</td>
<td>5.67</td>
<td>50</td>
</tr>
<tr>
<td>3.86</td>
<td>0.07</td>
<td>11.0</td>
<td>100</td>
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<td>100</td>
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<td>3.77</td>
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<td>3.46</td>
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<td>1.3</td>
<td>12</td>
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</tr>
<tr>
<td>3.30</td>
<td>0.05</td>
<td>0.6</td>
<td>5</td>
<td></td>
<td></td>
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<tr>
<td>3.17</td>
<td>0.04</td>
<td>0.4</td>
<td>3</td>
<td></td>
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</tr>
<tr>
<td>3.07</td>
<td>0.04</td>
<td>0.3</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.71</td>
<td>0.03</td>
<td>0.3</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.53</td>
<td>0.03</td>
<td>0.3</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.49</td>
<td>0.03</td>
<td>0.3</td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.43</td>
<td>0.03</td>
<td>0.2</td>
<td>2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.42</td>
<td>0.03</td>
<td>0.5</td>
<td>5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.32  TG Analysis of EU-8C

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>0-170</th>
<th>170-240</th>
<th>240-1000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight Loss (%)</td>
<td>3.8</td>
<td>5.7</td>
<td>5.2</td>
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</table>
Thermal Analysis

TG analysis of EU-8C gives a trace similar to that of the parent material. However, it is less well resolved due to the presence of amorphous materials. Although the replacement of lithium ions by hydronium ions results in a phase change the new material has, like the parent material, waters of hydration associated with the cationic species.

3.7.7 Conclusions

EU-8 is a novel lithium silicate species with the molecular formula:

\[ \text{Li}_2\text{O} \cdot 2.7(\pm 0.2)\text{SiO}_2 \cdot 1.88(\pm 0.2)\text{H}_2\text{O} \]

It exists as a single phase and can be synthesised from reaction mixtures with different Li/Si ratios. Thermal analysis and pH measurements on samples taken at the start and finish of crystallization strongly suggests that EU-8 is a silicate species and not a zeolite. Loss of water upon heat treatment is irreversible and prolonged heat treatment leads to formation of EU-8B, the dehydrated analogue of EU-8. Calcination of EU-8 at temperatures \( >625^\circ\text{C} \) for 2 hours also results in formation of EU-8B. SEM analysis of EU-8B showed that it consisted of crystals that were identical in size and morphology to the parent EU-8 material. Both materials consist of 40 \( \mu \text{m} \) spherical balls of 4\( \mu \text{m} \) needle shaped crystals. Treatment of EU-8 with concentrated sodium chloride solution at room temperature led to a 40% loss of crystallinity. An increase in the d-spacing of some peaks suggests that some of the lithium is replaced by the larger sodium ions. Treatment of EU-8 with hydrochloric acid led
to the complete replacement of lithium by protons. This new material was designated EU-8C. SEM analysis showed that whilst it consisted of balls of crystals, the crystals were smaller and more fibrous than the parent material. A literature search for lithium silicate phases produced no single species comparable to EU-8, EU-8B or EU-8C. However, it was possible to partly reconstruct the X-ray powder diffraction patterns of both EU-8B and EU-8C from combinations of those for known silicate species. The results suggest that whilst EU-8 and EU-8B are novel species, EU-8C may be a combination of alpha hydrogen silicate plus an unknown species.
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CHAPTER 4

Catalysis of Ester Hydrolysis by Dispersions of
High Silica Zeolites in Water

4.1 Introduction

4.1.1 Background

The reactions of carboxylic acid derivatives such as esters, amides, acid halides and anhydrides have long been the subject of investigation. The catalytic action of dilute acids and alkali in the hydrolysis of carboxylic esters and the reverse reaction esterification were first studied in 1792 by Scheele [1]. Later studies carried out by Berthelot and Pean de Saint Gilles [2-4] on the esterification of acetic acid and the hydrolysis of ethyl acetate were used by Guldberg and Waage [5] in the derivation of the Law of Mass Action. When kinetic studies were applied to organic reactions both the hydrolysis and esterification reactions became the topic of intensive studies that produced a substantial accumulation of experimental results. These have been the subject of a number of comprehensive books and reviews which highlight the effect of structure on reactivity and detail the mechanism of the reactions [6-11].

The equilibrium which is set up when ester is added to water may be represented as:

\[ R_1\text{COOR}_2 + H_2O \rightleftharpoons R_1\text{COOH} + R_2OH \]
in which $R_1$ and $R_2$ denote alkyl groups. The rate law for the hydrolysis of an ester ($E$) is given by equation 4.1. This was first proposed by Wegscheider [12], and refers to specific acid or base catalysed reactions.

$$\frac{-d[E]}{dt} = (k_O + k_H[H^+] + k_{OH}[OH^-])[E] = k[E] \quad (4.1)$$

In equation 4.1, $k$ is the rate constant and $k_H$, $k_{OH}$ and $k_O$ are the respective catalytic coefficients for the hydronium ion, hydroxide ion and water catalysed reactions. Usually only one of the terms in equation 4.1 is dominant at a given pH. Since the rates are proportional to $[H^+]$ or $[OH^-]$ a plot of log $k$ versus log $[H^+]$ is formed of three linear parts with slopes 1, 0 and -1. This is illustrated in Figure 4.1.

![Figure 4.1](image)

**Figure 4.1** Rate profiles for various types of acid or base catalysis (see text).
In this figure curve (a) represents a reaction that is catalysed by an acid but not a base, the horizontal part corresponds to the uncatalysed or water catalysed reaction. Curve (b) shows a reaction that is catalysed by both an acid and a base. The observed solid line is a superimposition of the two straight line plots. In this example (which is applicable to the hydrolysis of ethyl acetate) the observed minimum lies on the acid side of neutral at about pH 5.5. At this point the two catalysed reactions are running at the same rate, i.e.

$$k_H[H_3O^+] = k_{OH}[OH^-]$$  \hspace{1cm} (4.2)

Thus,

$$\frac{k_{OH}}{k_H} = \frac{[H_3O^+]}{[OH^-]} = \frac{10^{-5.5}}{10^{-8.5}} = 1000$$

For the hydrolysis of ethyl acetate, the water catalysed reaction is exceptionally slow with an estimated half-life at 25°C of 75 years [13]. Curve (c) represents a two step reaction: one step is inhibited by acid whilst the other is enhanced. For example, the formation of oximes from ketones with hydroxylamine is retarded by acid because it inactivates the hydroxylamine by protonating it. The second step of the reaction is an acid catalysed dehydration which decelerates with increase in pH.

The mechanisms of ester hydrolysis and esterification have been classified according to the following criteria [14-16]: acid or base catalysis, denoted by 'A' or 'B'; whether the bond rupture takes place between ethereal oxygen and the acyl carbon atom (AC) or the alkyl carbon atom (AL); molecularity, 1 or 2. Although structural
evidence has been used to indicate the type of fission that occurs, tracer experiments are usually used to provide direct unambiguous evidence. For example, acyl-oxygen fission was proved when amyl acetate [17] was hydrolysed by base in water that was enriched in $^{18}O$. The resulting alcohol was found to have an excess of $^{18}O$ [18]. Of the eight possible combinations only six mechanisms have been identified experimentally and these are listed in Table 4.1.

Table 4.1 Ingold classification of ester hydrolysis reactions

<table>
<thead>
<tr>
<th>Acyl Fission</th>
<th>Alkyl Fission</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bimolecular Basic catalysis $B_{AC}^2$</td>
<td>Bimolecular Basic catalysis $B_{AL}^2$</td>
</tr>
<tr>
<td>Acidity catalysis $A_{AC}^2$</td>
<td></td>
</tr>
<tr>
<td>Unimolecular Acidic catalysis $A_{AC}^1$</td>
<td>Unimolecular Basic catalysis $B_{AL}^1$</td>
</tr>
<tr>
<td>Acidic catalysis $A_{AL}^1$</td>
<td></td>
</tr>
</tbody>
</table>

The $B_{AC}^2$ and $A_{AC}^2$ mechanisms written below, are by far the most common. The $A_{AC}^2$ mechanism is applicable to the acid catalysed hydrolysis of primary and secondary alkyl esters in solutions up to 80-88% sulphuric acid [19,20]. At these strong acid concentrations the activity of water is diminished and at stronger acid concentrations a unimolecular reaction ($A_{AL}^1$) takes over.
4.1.2 Ion-Exchange Resins as Catalysts

Although soluble inorganic acids and alkalis have been found to be very efficient catalysts for ester hydrolysis, they are not specific. Furthermore, they cannot be used with acid or base sensitive materials if secondary reactions are to be avoided. From a commercial point of view their removal from the product can be both expensive and time consuming. Consequently, there are good practical reasons for the investigation of other types of catalysts for ester hydrolysis. There are three possible alternatives to homogeneous acid-base catalysts: enzymes, ion-exchange resins and zeolites.
It has been shown that enzymes can act as very efficient and specific catalysts for ester hydrolysis and that with these some of the difficulties associated with homogenous acid-base catalysts can be avoided [9]. It is believed that the enzyme initially forms a complex with the ester which then reacts with the active sites in the enzyme. The latter step is usually rate-limiting and thus the process resembles an intramolecular reaction. The functional groups in the enzyme may be carboxylate ions, thiols, amines or even the -CO-NH- grouping of the peptide bond. However, many of the mechanistic details of the catalytic processes promoted by hydrolytic enzymes are still unknown. Like mineral acids and bases, unsupported enzyme catalysts are soluble and so their separation from the final product can present problems. Furthermore, they also have limited thermal stabilities.

Zeolites and ion-exchange resins have several advantages over enzymes and homogenous acid-base catalysts. As they are solids they may be removed from a reaction mixture by simple decantation or filtration and in principle they may be used repeatedly without regeneration. Acid-sensitive materials suffer considerably less decomposition if a solid catalyst is used rather than a mineral acid. In addition reaction mixtures can be circulated through an ion-exchange resin in a column and thus form a continuous process. This should also be possible with zeolite catalysts.

Most of the literature on the catalysis of ester hydrolysis by solid catalysts deals with the case in which the catalyst is an ion-exchange resin. The cation-exchange resins have been found to be
better than anion-exchange resins and so have commanded more attention. The first large scale esterification plant became operational in 1939. This plant used a phenol-sulphonic acid resin [21]. The use of other ion-exchange materials has been much less thoroughly investigated and is restricted to the use of acidified clay minerals [22].

When ion-exchange resins are used as acid catalysts it is important to establish whether they are more or less effective than mineral acids. This is done in terms of their catalytic efficiency \( q \) which is defined by the relation

\[
q = \frac{k_R}{k_H}
\]

(4.3)

where \( k_R \) is the second order rate constant for the hydrolysis of an ester catalysed by the resin and \( k_H \) is the corresponding rate constant for the same reaction catalysed by the soluble acid. Thomas and Davies [23] examined the hydrolysis of esters using a synthetic resin which contained sulphonic acid groups. They showed that the resin was more efficient than hydrochloric acid by 1.7\( x \) for methyl acetate, 2.3\( x \) for ethyl acetate and 9.8\( x \) for butyl acetate. However these results were found to be limited to water-acetone solutions that contained 0-35% acetone and are only applicable to some resin catalysts [24]. Davies and Evans [25] found that the catalytic efficiency of the resin in a mixed solvent, relative to hydrochloric acid, decreased with an increase in the chain length of the aliphatic ester. This result was supported for ester hydrolysis in other
mixed solvents by other researchers [26,27] and was also found to be true for the esterification reaction in solutions of alcohol [28,29]. Detailed studies carried out by Haskell and Hammett [30] on the acid catalysed hydrolysis of esters in 70% acetone showed that the enthalpies of activation for the hydrolysis of methyl acetate and ethyl n-butyrate were virtually identical and thus independant of chain length. However they found that the entropy changes that accompanied the formation of the transition state varied greatly with chain length, e.g. -23 JK\(^{-1}\) mol\(^{-1}\) with methyl acetate to -37.7 JK\(^{-1}\) mol\(^{-1}\) with ethyl n-butyrate. The entropy loss associated with the formation of the transition state was found to be the dominant factor and accounted almost entirely for the decrease in the rate of hydrolysis with chain length. This work was extended by Bernhard and Hammett [31] who found that for seven methyl esters of the type RCO\(_2\)CH\(_3\), the decrease in the rate of hydrolysis paralleled the entropy of the gaseous alkane RH. This was the only relationship to any obvious property of the esters. They defined the efficiency, q, of the catalyst for a particular reaction by the relation given in equation 4.3. The ratio of efficiencies for two esters, 1 and 2 are given by

\[-RT \ln \frac{q_2}{q_1} = (G^\#_{R_2} - G^\#_{H_2}) - (G^\#_{R_1} - G^\#_{H_1}) \tag{4.4}\]

where G\(^\#\) represents the free energy of the transition states. The subscript R refers to the resin whilst H refers to the homogenous system.
The degree of cross linking of a resin catalyst also effects the rate of hydrolysis: the higher the degree of crosslinking then the lower the catalytic efficiency [31]. Haskell and Hammett [30] explained this result by postulating that there are increased structural restraints imposed on the transition state. They also found that for the resins which they investigated, the rate of hydrolysis of methyl acetate was independant of the shaking rate and proportional to the concentration of catalyst used. Although the rate of ester hydrolysis was not dependant on the diffusion rate of the ester through the resin Bernhard and Hammett [31] found differences in the catalytic efficiency of surface and interior sites.

However, results obtained for ion-exchange resins dispersed in mixed solvents are inapplicable to systems that use water as the solvent. Although the earlier results on the relative efficiencies of resin and soluble acid catalysed systems were supported by the results of Bernhard and Hammett [32] they found that the efficiency of a resin catalyst was strongly dependant on the degree of cross-linking. Whilst strongly cross-linked resin catalysts gave results similar to those obtained from mixed solvent systems the activation energies and entropies of activation for lightly cross-linked resins were the same as those of aqueous hydrochloric acid. For example, the activation energies and entropies of activation for methyl acetate and ethyl acetate hydrolysis were found to be the same when a poly-styrene-sulphonic acid catalyst (a lightly cross-linked resin) and aqueous hydrochloric acid were used. They postulated that this was due to the increased solvation of the polar groups of the esters in water, as
opposed to mixed solvent systems, and that consequently there were no further restraints imposed on the ester by the solvation of the charged transition state. Strongly cross-linked resins could, even in water, impose additional restraints.

Although these investigations [30-32] showed beyond doubt that cation exchange resins can be efficient catalysts for ester hydrolysis, resins have nevertheless several drawbacks. They have limited thermal stability, high initial cost compared to dissolved electrolytes (although the running costs can be lower) and poor specificity. Attempts have been made to improve the latter deficiency. These have concentrated on replacing protons with ions that have features similar to the ester. For example, Riesz and Hammett [33] found for the hydrolysis of ethyl hexanoate, that the specific rate obtained with a resin containing hydrogen acetyl ions and trimethyl ammonium ions was 4.2x that for the same partially exchanged resin when it contained tetramethylammonium ions. They also found that partial proton replacement by methyltribenzylammonium ions gave a rate constant for the hydrolysis of methyl phenylacetate 3.5x that of ethyl hexanoate. The reason for these effects was believed to be an alteration of the environment of the transition state so as to reduce its standard free energy. However, Bernhard, Garfield and Hammett [34] found that the efficiency of the remaining hydronium ions of a lightly cross-linked ion-exchange resin for the hydrolysis of ethyl acetate and of ethyl hexanoate is reduced when the resin contains a considerable portion of ethylene diammonium ions. The catalytic efficiency is reduced by a factor which is twice as large for the hexanoate as
for the acetate. This work was continued by Tartarelli et al [35] who also studied solvent effects. More recent research with modern cation exchange resins is in general agreement with the earlier studies [36-38].

4.1.3 Catalysis by Aqueous Zeolite Dispersions

It is clear that there is commercial potential for an ester hydrolysis catalyst that can combine low cost, good thermal stability with high specificity. Preferably the catalyst should be the one that will allow the reactant to circulate through a catalyst column and be effective under mild reaction conditions so as to minimise unwanted side reactions such as the degradation of reactants.

Montmorillonite clays satisfy the above conditions and have been shown to catalyse the direct addition of ethene to acetic acid to produce ethyl acetate [39]. In this case the water consumed in the reaction was that associated with the interlamellar cations, e.g. Al\(^{3+}\). Clay minerals have also been used in ester hydrolysis [22]. Zeolite catalysts should satisfy the above conditions and should be an improvement over clay materials as they can offer better thermal stability and because their rigid framework does not swell in water they should provide much higher specificity. Perhaps surprisingly there have been few studies that involve the use of zeolites to catalyse liquid phase reactions and in particular ester hydrolysis. The intracrystalline channel system of zeolites is accessible to esters. It has been shown that ZSM-5 (silicalite-1) can sorb esters of long chain fatty acids and selectively separate them from solutions that also contain esters of resin acids [40]. A series of
studies carried out by Santacesaria et al [41,42] have shown zeolite Y is a very active catalyst for the esterification of acetic acid and ethanol in the vapour phase. They found that the reaction rate correlated well with the zeolite acidity, as measured by titration with n-butylamine in the presence of indicators, and saw no reason to suppose that the reaction mechanism was different to that which occurs under homogenous liquid-phase conditions.

The hydrolysis of methyl or ethyl acetate was found by Namba et al [43] to be catalysed by zeolites Y, mordenite and ZSM-5 as well as amorphous silica-alumina. The activities of the different zeolites were found to be markedly different. The most active zeolite catalyst used was a partly dealuminated ZSM-5 zeolite, which was found to be about 40% as active as a cation exchange resin and obeyed first order kinetics up to 30% hydrolysis of ethyl acetate. The activation energies that were determined for the zeolite catalysed reaction were found to be independant of zeolite structure and similar to those obtained for catalysis by hydrochloric acid. The first order rate constant $k_H$ for the hydrochloric acid catalysed reaction was expressed in terms of the concentration of acid ($C_H$) as follows:

$$k_H = 3.72 \times 10^{-2} C_H$$

(4.5)

where $k_H$ and $C_H$ have the units $\text{min}^{-1}$ and $\text{mol/dm}^3$ respectively.

They found that the rate constant was strongly dependant on the Si/Al ratio of the zeolite catalyst. Optimum activity of ZSM-5, mordenite and Y was observed when the Si/Al ratios were 47, 8 and 3 respectively. These results were explained in terms of (i) number of
available catalytic sites and (ii) the hydrophobicity of the zeolite framework. However, no adequate explanation was given as to the significance of the optimum Si/Al ratios observed. Nor was the difference in optimum Si/Al ratios explained. It was also reported that the degree of cation exchange did not effect the catalytic activity of zeolite Y; two H-Y zeolites with a Si/Al = 2.4 showed no difference in catalytic activity when 80% and 96% protonated. It was explained that "the activity was influenced less by the degree of cation exchange (probably in the region of high exchange degree) than by the Si/Al atomic ratio". These results indicate that zeolites can act in a different manner to both ion-exchange resins and homogenous catalysts and that the rate of reaction is not proportional to the concentration of catalytic sites. These apparently novel properties were not discussed [43].

4.2 Experimental

4.2.1 Materials

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Grade</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl acetate</td>
<td>Analar</td>
<td>BDH Ltd.</td>
</tr>
<tr>
<td>Methyl acetate</td>
<td>Analar</td>
<td>Aldrich Ltd.</td>
</tr>
<tr>
<td>Ethyl benzoate</td>
<td>SLR</td>
<td>Fisons Ltd.</td>
</tr>
<tr>
<td>Tetrabutylammonium hydroxide (TBAOH)</td>
<td>40% aqueous</td>
<td>Aldrich Ltd.</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>SLR</td>
<td>Fisons Ltd.</td>
</tr>
<tr>
<td>p-xylene</td>
<td>SLR</td>
<td>Fisons Ltd.</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>Analar</td>
<td>BDH Ltd.</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>Convol</td>
<td>BDH Ltd.</td>
</tr>
<tr>
<td>Ammonium chloride</td>
<td>Analar</td>
<td>Fisons Ltd.</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Oxygen free</td>
<td>British Oxygen Co.</td>
</tr>
</tbody>
</table>
The molecular dimensions of some of the organic materials used were estimated from molecular models and were based on a molecular diameter of cyclohexane of 6.0 Å.

Table 4.2 Molecular dimensions of organic molecules used in this work

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Molecular Dimensions (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl acetate</td>
<td>6.8 x 4.7 x 3.8</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>8.2 x 4.7 x 3.8</td>
</tr>
<tr>
<td>Ethyl benzoate</td>
<td>10.5 x 5.9 x 5.9</td>
</tr>
<tr>
<td>TBA OH</td>
<td>9.0 x 9.0 x 9.0</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>6.0 x 6.0 x 3.8</td>
</tr>
</tbody>
</table>

4.2.2 Experimental Procedure for Ester Hydrolysis Experiments

Before use zeolite samples were equilibrated with water vapour by standing over saturated sodium chloride solution at 25°C (p/p° = 0.753) in an evacuated dessicator. Unless otherwise stated, approximately 1 g of equilibrated zeolite was accurately weighed and placed in a 250 cm³ Quickfit round-bottomed, three-necked flask. To this was added 200 cm³ of distilled water. The reaction vessel was then partly immersed in a thermostat bath filled with polyethylene glycol. A stirrer rod was fitted with a Jencons B24 sleeve and attached to the central neck. The second neck of the reaction vessel was fitted with an EIL plastic bodied combination pH electrode type 1180/200/UKP connected to a Philips PW9409 pH meter. The neck was made airtight by a short length of a plastic tube which formed a sleeve
around the pH electrode stem. The third neck of the reaction vessel was fitted with a rubber seal. To avoid dissolution of atmospheric carbon dioxide into the unbuffered aqueous solution a nitrogen atmosphere was used. Nitrogen was fed through fine plastic tubing inserted into the rubber seal. A syringe needle, also inserted into the rubber seal allowed the nitrogen to escape and thus maintained atmospheric pressure within the reaction vessel. To compensate for the water lost from the reaction vessel as vapour and fine droplets in the nitrogen stream it was necessary to presaturate the nitrogen inflow to the reaction vessel. This was achieved by bubbling the nitrogen through two Dreschel bottles filled with water, one of which was immersed in the thermostat bath. The other was at room temperature and served as a pre-saturator and as a flow meter. The nitrogen was bubbled through the reaction mixture continuously throughout the experiment.

The zeolite/water slurry was stirred at 150 rpm by a PTFE stirrer blade 6.9 cm in diameter. As the viscosity of water ($\eta$) at 60°C is $4.66 \times 10^{-3}$ g s$^{-1}$ cm$^{-1}$ [44] and the density ($\rho$) 1 g cm$^{-3}$, the Reynolds number ($N_R$) can be calculated from equation 4.6.

$$N_R = \frac{N D^2 \rho}{\eta} \quad (4.6)$$

in which $N$ is the stirrer speed and $D$ is the diameter of the stirrer blade. This gave $N_R = 2.55 \times 10^4$ and thus the system satisfies the condition for turbulence ($N_R > 10^4$).
The slurry was equilibrated by being stirred for 16 hours at 60°C. The pH of the equilibrated slurry was noted and then adjusted to 6.0 with either hydrochloric acid or tetrabutylammonium hydroxide (TBAOH). Addition of $4.086 \times 10^{-2}$ moles ($4.0 \text{ cm}^3$) of ester to the slurry signified the start of an experiment. The time was monitored by use of a stopwatch. The continuously hydrolysis reaction was followed by the neutralisation of carboxylic acid, formed as a product of the reaction. TBAOH was used as the base as TBA$^+$ is too large to enter the intracrystalline channel systems of any of the zeolites studied. Each experiment lasted 90 minutes and unless otherwise stated was carried out at 60°C and at pH = 6.0. This reaction pH was chosen as the best compromise in view of the following constraints:

(i) the background, homogenous reaction for the hydrolysis of ethyl acetate is at a minimum at pH = 5.5,

(ii) the pH is most sensitive to changes in acid concentration at pH = 7.00 (i.e. well outside the region of maximum buffering pH = 4.76).

4.2.3 Preparation of Acid Zeolites

The synthesis of the zeolites used in this work is discussed in Chapter 3 and Appendices I and II. Unless a zeolite is made from a system that contains organic and/or ammonium hydroxide it has to undergo an ion-exchange stage in the preparation of the acid form. Whilst it was possible to convert TPA-ZSM-5 (T88) directly into the acid form by calcination all of the other zeolites used in this work had to undergo an ion-exchange stage to convert
them into the acid form. Acidification of the zeolites used in this work was achieved by the use of one of two methods:

(1) **HCl Treatment**

1M hydrochloric acid was added to an organic-free zeolite so that the resultant slurry contained 10 cm$^3$ acid per gram of zeolite. The slurry was stirred for four hours at room temperature. The zeolite was filtered off, then washed in distilled water, dried at 60°C and placed over saturated sodium chloride solution at 25°C.

(2) **NH$_4$Cl Treatment**

1M ammonium chloride solution was added to organic-free zeolite so that the resultant slurry contained 10 cm$^3$ solution per gram of zeolite. The slurry was stirred under reflux conditions for two hours. The zeolite was then filtered off and washed with distilled water. The process was repeated as before except that the slurry was refluxed for five hours. Finally a third treatment with ammonium chloride solution was carried out; this time at 50°C for 16 hours. The zeolite was then filtered and washed in distilled water before being dried in air at 60°C and placed over saturated sodium chloride solution. Unless otherwise stated the ammonium zeolites were calcined at 400°C for 24 hours in a shallow bed in the presence of air.

As can be seen from Table 4.3 both of these methods result in complete protonation of the zeolites with no sodium detected by XRF spectroscopy. However it should be noted that there is a 4% error in Na/Al attributed to the detection limits of the instrument used and it is conceded that 100% protonation is
unlikely. Table 4.3 also shows that the Si/Al ratio is unaffected by the acidification method employed. There is a 4% error associated with the Si/Al ratios quoted.

Table 4.3 Effect of pretreatment on the chemical composition of ZSM-5

<table>
<thead>
<tr>
<th>Code</th>
<th>Treatment</th>
<th>Si/Al</th>
<th>Na/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>H35</td>
<td>None</td>
<td>19.8</td>
<td>1.12</td>
</tr>
<tr>
<td>H35</td>
<td>HCl</td>
<td>19.8</td>
<td>0</td>
</tr>
<tr>
<td>H35</td>
<td>NH₄Cl</td>
<td>19.6</td>
<td>0</td>
</tr>
</tbody>
</table>

4.3 Treatment of Results

4.3.1 Theory

The equation for the hydrolysis of an ester may be represented as:

\[ R_1COOR_2 + H_2O \rightleftharpoons R_1COOH + R_2OH \]

where \( R_1 \) and \( R_2 \) are alkyl groups. It follows from this equation that the rate of hydrolysis of an ester is equal to the rate of formation of carboxylic acid. This rate can be measured by the frequent addition of known amounts of base (TBAOH) so as to neutralise the carboxylic acid formed by the hydrolysis reaction and keep the pH constant. Consequently the experimental data is of the form:

Volume of tetrabutylammonium hydroxide added versus time.

Let: \( C_{TBA} \) = molarity of tetrabutylammonium hydroxide
\( V_{TBA} \) = volume of tetrabutylammonium hydroxide added
\( C^o_E \) = original concentration of ester
\( C_E \) = concentration of ester at time \( t \) from the start of the reaction
\[ CA = \text{molarity of carboxylic acid} \]
\[ V^o = \text{original volume of water in reaction vessel} \]
\[ V = \text{volume of solution in reaction vessel at time } t. \]

It is known that:

\[ V = V^o + V_{TBA} \quad (4.7) \]
\[ V_{CA} = V_{TBA} \cdot C_{TBA} \quad (4.8) \]
\[ V_{CE} = V^o C^o_E - V_{CA} \quad (4.9) \]

Hence from equations 4.7 and 4.8,

\[ CA = C_{TBA} \cdot \frac{V_{TBA}}{(V^o + V_{TBA})} \quad (4.10) \]

and from equations 4.9 and 4.10,

\[ C_E = \left( \frac{V^o}{V^o + V_{TBA}} \right) C^o_E - \frac{C_{TBA} \cdot V_{TBA}}{V^o + V_{TBA}} \quad (4.11) \]

which may be rearranged to give

\[ C_E = \left( C^o_E V^o - C_{TBA} V_{TBA} \right)/(V^o + V_{TBA}) \quad (4.11a) \]

In all cases, \( V_{TBA} \ll V^o \) and \( C_{TBA} > C_A \). Provided the concentration of catalyst and water are taken to be constant, the reaction undergoes pseudo first order kinetics:

\[ \frac{-d(C_E)}{dt} = k_{obs} \cdot C_E \quad (4.12) \]

This equation can be integrated to give

\[ \ln C_E = -k_{obs} \cdot t + \ln C^o_E \quad (4.13) \]
Hence a plot of $\ln C_E$ versus time should give a straight line plot of slope $k_{\text{obs}}$. $k_{\text{obs}}$ is the pseudo first order rate constant and in this work it is reported in minutes$^{-1}$ (min$^{-1}$). To obtain a true rate constant for the zeolite catalysed reaction it was necessary to subtract the contribution of the background reaction due to $H^+$ and $OH^-$ species in aqueous solution. The true rate constant obtained is then divided by the weight of anhydrous zeolite used so that the rate constant is now given in min$^{-1}$ per gram of anhydrous zeolite (min$^{-1}$ g$^{-1}$). The subtraction of the pseudo first order rate constants is justified by equation 4.14.

$$\frac{dC_E}{dt} = k [C_E] + k_w [C_E]$$ \hspace{1cm} (4.14)

where $k$ and $k_w$ are the rate constants for the zeolite catalysed and homogenous catalysed reactions respectively. Hence from equations 4.12 and 4.14

$$k_{\text{obs}} = k + k_w$$ \hspace{1cm} (4.15)

The weight of anhydrous zeolite used could be calculated as the water content of the equilibrated zeolites was determined by thermal gravimetric analysis.

For an acid or base catalysed reaction $k_w$ is dependant on the acid or base concentration - whichever is dominant (see equation 4.1). The pseudo first order rate constant $k_H$ for an acid catalysed reaction may be calculated by:

$$k_H = k_w/[H_3O^+]$$ \hspace{1cm} (4.16)
The pseudo first-order rate constant \( k_H \) in this work is in \( \text{min}^{-1} \text{M}^{-1} \).

To determine the \([\text{H}_3\text{O}^+]\) associated with the acid zeolite it was necessary to:

(a) know the Si/Al ratio of the acid zeolite,

(b) assume that each aluminium was associated with a Brønsted acid site. For example, the Si/Al ratio of zeolite J45 was determined by XRF spectroscopy to be 13.3. Hence the weight of anhydrous sample J45 that will produce 1 mole of acid in 1 litre of water =

\[
\text{Mol.Wt. of H}^+ + \text{Mol.Wt. of Al} + (13.3 \times \text{Mol.Wt. of Si}) + ((13.3 + 1) \times \text{Mol.Wt. of O}_2) = 858.9 \text{ g}
\]

Hence 1 g of sample J45 is equivalent to \( 1/858.9 \) moles of acid.

In this work, 1 g of anhydrous zeolite is placed in 200 cm\(^3\) of water and hence for sample J45 the effective concentration of acid sites =

\[
[\text{H}_3\text{O}^+] = \frac{1000}{200} \times \frac{1}{858.9}
\]

\( k_{ZH} \), is given by: \( k_{ZH} = k/[\text{H}_3\text{O}^+] \) and has the units \( \text{min}^{-1} \text{M}^{-1} \). The efficiency of the zeolite catalysed reaction relative to the acid catalysed reaction is given by:

\[
q = \frac{k_{ZH}}{k_H}
\]

The value of \( k_H \) at 60°C was found to be 0.195 (±0.01) \( \text{min}^{-1} \text{M}^{-1} \).
4.3.2 Correction Factors

4.3.2.1 Potassium Exchange

XRF spectroscopy carried out on zeolites before and after an ester hydrolysis experiment showed that some of the acid sites in the zeolite catalyst had been replaced by potassium ions (see Table 4.4). The source of these potassium impurities is believed to be the TBAOH added throughout the course of each reaction.

Table 4.4 Extent of potassium uptake during an ester hydrolysis experiment by H-ZSM-5 (H53)

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>K₂O</th>
<th>K/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(moles)</td>
<td>(moles)</td>
<td>(moles)</td>
<td></td>
</tr>
<tr>
<td>Before</td>
<td>1.548</td>
<td>5.45x10⁻²</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>After</td>
<td>1.526</td>
<td>5.38x10⁻²</td>
<td>1.94x10⁻³</td>
<td>0.036</td>
</tr>
</tbody>
</table>

The uptake of potassium by an acid zeolite during an ester hydrolysis experiment has two effects on the amount of base added and hence the observed rate:

1. Additional acid is added to the solution by ion-exchange of acid zeolite with potassium by:

\[
\text{K}^+_{\text{soln}} + \text{H}^+ - \text{Zeolite} \rightarrow \text{K-zeolite} + \text{H}^+_{\text{soln}}
\]

This results in an excess of base added during a reaction.

2. Reduction in the number of catalytically active acid sites in the acid zeolite caused by ion-exchange with potassium.
Both of these effects are small (<2%) and since the first increases the amount of base required and the second reduces it, the nett effect is very small. A rough calculation indicates that the observed rate constant is typically 0.5% less than the true value and the correction factor of 1.005 has been used throughout. Although the true correction factor will differ for each reaction the variations are unlikely to have any bearing on the results obtained and indeed are unlikely to exceed the errors from other sources.

4.3.2.2 Incomplete Neutralisation of Carboxylic Acid

The hydrolysis reaction is monitored by the neutralisation of acid by base. For methyl acetate and ethyl acetate this may be represented as:

\[ \text{CH}_3\text{CO}_2\text{H} + \text{TBAOH} \rightarrow \text{CH}_3\text{CO}_2^- \text{TBA}^+ + \text{H}_2\text{O} \]

The amount of acetic acid that is neutralised is dependant on the equilibrium:

\[ \text{CH}_3\text{CO}_2\text{H} \rightleftharpoons \text{CH}_3\text{CO}_2^- + \text{H}^+ \]

\[ [\text{HA}] \quad [\text{A}^-] \quad [\text{H}^+] \]

\[ k_a = \frac{[\text{A}^-][\text{H}^+]}{[\text{HA}]} \tag{4.17} \]

neglecting activity coefficients,

\[ \text{pK}_a = \text{pH} - \log_{10}\frac{[\text{A}^-]}{[\text{HA}]} \tag{4.18} \]

The literature value for the \( \text{pK}_a \) of acetic acid at 60°C is 4.452 [45]. At \( \text{pH} = 6.0 \), \( \log_{10}(\frac{[\text{A}^-]}{[\text{HA}]})) = 1.548. \]
The total amount of acetic acid formed = [HA] + [A$^-$]

= [A$^-$] + [A$^-$]/10$^{1.548}$

= [A$^-$] (1 + 0.028)

Thus, at 60°C the experiment under-estimates the amount of base required by 2.8%. Consequently the amount of acid formed and hence the reaction rate are under-estimated by the simple treatment given earlier (equations 4.7 to 4.13). This can be allowed for by multiplying the rate constants by a factor of 1.028.

4.3.2.3 Conclusions

To obtain true rate constants for a zeolite catalysed reaction the observed rate constant must be multiplied by (1.005 x 1.028) = 1.033. The multiplication factor required for the background homogenous reaction at 60°C and pH = 6.0 is 1.028.

4.4 Hydrolysis of Ethyl Acetate in Water

4.4.1 Introduction

The object of this work was to study the background homogenous reaction of ethyl acetate hydrolysis in water. This was necessary so that accurate determinations of the rates of zeolite catalysed reactions could be made. Furthermore work on the homogenous system allowed evaluation of the novel experimental procedure by comparison with results reported in the literature. The effects of salts that form during the course of the experiment were also investigated.
4.4.2 Experimental

The experimental procedure that was used in these studies is as described in section 4.2, except no zeolite addition was made. The reagents used are described in section 4.2. Treatment of results is detailed in section 4.3.

4.4.3 Results and Discussion

Figure 4.2 shows that a plot of ln[Ester] against time gives a linear correlation and that the hydrolysis of ethyl acetate does undergo first order kinetics. The plot given is for the hydrolysis of ethyl acetate at pH 7.21 and is typical of both acid and base catalysed reactions in that the coefficient of determination obtained is greater than 0.99.

The relationship between the rate of hydrolysis of ethyl acetate at 60°C (represented by log₁₀ k) and the pH of the solution is shown in Figure 4.3. The minimum of the log₁₀ k/(pH) plot was observed at pH = 5.34. This is close to the literature value of pH 5.5 obtained for the hydrolysis of ethyl acetate at 25°C [11]. The observed shift to more acid solution with increase in temperature is due to the lower activation energy for the base catalysed reaction relative to the acid catalysed. Although there are no literature values at 60°C a comparison of the experimental rate for ethyl acetate hydrolysis at 60°C with literature values [11] obtained at 25°C indicates that the experimental values obtained are satisfactory. For example the rate of hydrolysis of ethyl acetate at pH 7 is reported [11] to be 7 x 10⁻⁷ min⁻¹. The value obtained in the present investigation at 60°C is
Figure 4.2  $\ln[\text{ester}]$ against time for the hydrolysis of ethyl acetate in water at pH = 7.21 and 60°C
Figure 4.3 \( \log_{10}(k/\text{min}^{-1}) \) against pH for the hydrolysis of ethyl acetate in water at 60°C
2.09 \times 10^{-5} \text{ min}^{-1} \text{ and corresponds to a } 2.7 \times \text{ increase in the rate of reaction per } 10^\circ\text{C rise in temperature. The gradients of the slopes of the two } \log_{10} k \text{ (pH)} \text{ lines, obtained by least mean squares procedure were } -1.04 \pm 0.05 \text{ and } 0.98 \pm 0.05. \text{ These are in excellent agreement with the expected values of } -1 \text{ and } +1 \text{ respectively. The first order rate constants } k_H \text{ and } k_{OH} \text{ for the acid and base catalysed reactions respectively were calculated to be } k_H = 0.195(\pm0.01) \text{ min}^{-1} \text{ M}^{-1} \text{ and } k_{OH} = 200(\pm10) \text{ min}^{-1} \text{ M}^{-1} \text{ at } 60^\circ\text{C. } k_{OH}/k_H = 1030 \text{ which indicates that base catalysis is much more effective than acid catalysis.}

The technique used to monitor the course of reaction was found to be applicable over the range pH 4.5-9.5. At pH values outside this range it was found that the pH changes produced by small increases in the acid concentration caused by the hydrolysis of the ester, were too small for the method to be used satisfactorily.

The effect of temperature on the base catalysed hydrolysis of ethyl acetate was studied. It was not possible to study the acid catalysed hydrolysis reaction because of (i) the large errors associated with the low observed rates and (ii) pH restrictions. The plot of \ln(k) against 1/T for ethyl acetate hydrolysis at pH 6.00 over the temperature range 20^\circ\text{C-80}^\circ\text{C is shown in Figure 4.4. It can be seen that the reaction satisfies the Arrhenius equation:}

\[ \ln k = \ln A - \frac{E_a}{RT} \]  

(4.19)

in which \( E_a \) is the activation energy after the reaction ( KJ mol\(^{-1}\)), \( A \) is the frequency factor (min\(^{-1}\)); \( R \) is the gas constant ( = 8.314 JK\(^{-1}\) mol\(^{-1}\)) and \( T \) is the temperature (Kelvin). The linear
Figure 4.4 Arrhenius plot for the hydrolysis of ethyl acetate in water at pH 6.0
correlation indicates that there is no change in mechanism over the temperature range investigated. The experimental results are compared with the literature values for both the acid ($A_{AC}^2$) and base ($B_{AC}^2$) mechanisms in Table 4.4. The experimental results are in good agreement with those obtained by Euranto [11] for the base catalysed reaction. Although it was not possible to verify this experimentally, it is assumed that the homogenous acid catalysed reaction, observed for the homogenous system, goes by an $A_{AC}^2$ mechanism.

Table 4.5 Comparison of Arrhenius parameters for the homogenous catalysed hydrolysis of ethyl acetate

<table>
<thead>
<tr>
<th>Source</th>
<th>Proposed Mechanism</th>
<th>Activation Energy (KJ mol$^{-1}$)</th>
<th>$\ln A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>$B_{AC}^2$</td>
<td>51.6 ± 5</td>
<td>3.2 ± 4</td>
</tr>
<tr>
<td>Euranto [11]</td>
<td>$B_{AC}^2$</td>
<td>47.57</td>
<td>7.38</td>
</tr>
<tr>
<td>Namba et al [43]</td>
<td>$A_{AC}^2$</td>
<td>63</td>
<td>-</td>
</tr>
<tr>
<td>Bernhard &amp; Hammett [32]</td>
<td>$A_{AC}^2$</td>
<td>71.7</td>
<td>19.77</td>
</tr>
</tbody>
</table>

Although Figure 4.2 indicates that the hydrolysis of ethyl acetate does undergo first order kinetics, it was decided to investigate possible salt effects. The results, given in Table 4.5, show that tetrabutylacetate, which is formed by neutralisation of acetic acid by TBAOH throughout each experiment, does not catalyse the hydrolysis of ethyl acetate. The use of sodium hydroxide as base instead of tetrabutylammonium hydroxide for the homogenous reaction
did not effect the observed rate. The salt, sodium acetate, formed by the neutralisation of acetic acid by sodium hydroxide did not effect the observed rate either. The results obtained are in good agreement with those in the literature [11]. However it has been reported that more concentrated salt solutions slightly increase the rate of the acid hydrolysis of ethyl acetate [46]. Although no salt effects were observed in this work their effect on the observed rate would be expected to be auto-catalytic.

Table 4.6 Effect of salt addition on the observed rate of ethyl acetate hydrolysis at 60°C and pH = 6.0

<table>
<thead>
<tr>
<th>Salt</th>
<th>Quantity (moles)</th>
<th>Change in observed rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH a</td>
<td>-</td>
<td>none</td>
</tr>
<tr>
<td>Na Acetate</td>
<td>4.0x10^-3</td>
<td>none</td>
</tr>
<tr>
<td>TBA Acetate</td>
<td>5.12x10^-3</td>
<td>none</td>
</tr>
</tbody>
</table>

a Used instead of TBAOH as base  
b Moles of salt added to standard reaction. These amounts are in excess of those formed by neutralisation in a typical reaction.

4.4.4 Conclusions

The novel technique used to monitor the rate of ethyl acetate hydrolysis gave results that are in good agreement with the literature. It is applicable over a wide pH and temperature range although the preferred pH range is 4.5 - 9.0. It was found that the base catalysed reaction is even more effective than the acid catalysed
reaction when higher reaction temperatures are employed. The observed minimum in the log k/(pH) plot for ethyl acetate hydrolysis at 60°C was at pH 5.34. However in practise the observed rate was constant over the pH range 5.04-5.74 to within experimental error. The rate of hydrolysis of ethyl acetate was found to obey first-order kinetics with respect to both the acid and base concentrations. The Arrhenius parameters for the base catalysed reaction were in good agreement with literature values. The effect of salt concentrations typical of those that might be produced in an ester hydrolysis experiment were investigated, and as expected they had no effect on the reaction rate.

4.5 Catalysis of Ethyl Acetate Hydrolysis by Dispersions of ZSM-5 in Water

4.5.1 Introduction

The use of zeolites as catalysts for organic reactions in the aqueous phase has received scant attention despite the fact that their use for gas phase reactions has received considerable attention. An aqueous process involves three stages, (i) adsorption of the reactant by the zeolite, (ii) conversion of the reactant to product over the catalytic sites and (iii) desorption of the product from the zeolite. In the case of ester hydrolysis by a high silica zeolite these three stages are:

(1) The sorption of a relatively non-polar ester molecule from a polar solvent.
(2) Catalytic conversion of the ester molecule into two organic molecules which are more polar and more hydrophilic than the ester.

(3) Desorption of the polar organic products from a hydrophobic environment into a polar solvent.

It has been shown that the hydrophobicity [47] and catalytic activity [48] of zeolites are both dependant on the Si/Al of the zeolite structure. Steps 1 and 3 are best satisfied by use of hydrophobic zeolites, i.e. those with a high Si/Al ratio. However the rate of ester hydrolysis is known to be proportional to the concentration of acid or base. This fact means that step 2 is best satisfied by an acid zeolite with a high concentration of acid sites, i.e. has a low Si/Al ratio. Obviously a compromise has to be reached. For example, the hydrophobic molecular sieve silicalite which contains no catalytic sites will be catalytically inactive although it will readily sorb ester from an aqueous solution. In contrast low silica zeolites that contain many catalytic sites are hydrophilic and do not readily sorb polar molecules from water. The only publication [43] in which the application of zeolites to the catalysis of aqueous ester hydrolysis is discussed states that zeolite ZSM-5 is a more efficient catalyst than mordenite or zeolite Y. The synthesis of zeolite ZSM-5 has been well documented and since it can be synthesised over a wide range of Si/Al ratios it appeared to be ideal material for the present investigation.
4.5.2 Experimental

The synthesis of zeolite ZSM-5 is described in detail in Chapter 3. The materials used and the experimental procedure for the hydrolysis of ethyl acetate is given in section 4.2. Details of the method used to prepare the acid form of the zeolites is also described in section 4.2. The method used to analyse the experimental results is given in section 4.3.

4.4.3 Results and Discussion

Figure 4.5 shows that a plot of ln[Ester] against time gives a linear correlation. This indicates that the zeolite catalysed hydrolysis of ethyl acetate in water obeys pseudo first order kinetics. The plot shown in Figure 4.5 is typical of those obtained for the zeolite catalysed hydrolysis of ethyl acetate. The coefficients of determination of the best fit lines were usually greater than 0.99. This result indicates that no autocatalytic or inhibition effects occur.

The error in the gradient obtained by plotting ln[Ester] against time was usually small. However this error did vary and was dependant on the magnitude of the observed rate. In practice an error of $\pm 2.0 \times 10^{-5} \text{ min}^{-1}$ was attached to the observed rate constant for reactions carried out at pH = 6.0 and 60°C.

Thus zeolites were judged to have an effect on the rate of hydrolysis of ethyl acetate if $k_{\text{ZEO}} > 2.0 \times 10^{-5} \text{ min}^{-1}$.

A plot of rate constant for the zeolite catalysed hydrolysis of ethyl acetate against % conversion of ester after 90 minutes is given in Figure 4.6. As expected a linear correlation is obtained
Figure 4.5  \( \ln[\text{ester}] \) against time for the H-ZSM-5 (T25) catalysed hydrolysis of ethyl acetate at 60°C
Figure 4.6  Rate constant (k) against % conversion of ester after 90 minutes for the hydrolysis of ethyl acetate in water at 60°C
with pseudo first order rate constant of $3.1 \times 10^{-4}\text{ min}^{-1}\text{ g}^{-1}$ corresponding to 2.8\% conversion of ethyl acetate after 90 minutes at 60\°C.

**Effect of Cation on the Rate of Hydrolysis of Ethyl Acetate**

The effect that the type of cation, used to balance the anionic framework charge, had on the catalytic activity of ZSM-5 was studied. The Na-, NH$_4$- and H-forms of ZSM-5 were investigated together with the cation free analogue, silicalite-1.

Table 4.7 Effect of charge balancing cation on the rate of ethyl acetate hydrolysis at 60\°C

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Weight anhydrous zeolite (g)</th>
<th>Rate constant (k) $10^6 \times k$ (min$^{-1}$ g$^{-1}$)</th>
<th>$k_{ZH}$ (min$^{-1}$ M$^{-1}$)</th>
<th>Efficiency (q)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0</td>
<td>2.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Na-ZSM-5 (P22)</td>
<td>0.9339</td>
<td>3.3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>NH$_4$-ZSM-5 (P22)</td>
<td>0.9402</td>
<td>2.7</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H-ZSM-5 (P22)</td>
<td>0.9342</td>
<td>80.6</td>
<td>0.018</td>
<td>0.095</td>
</tr>
<tr>
<td>H-Silicalite-1 (T50)</td>
<td>0.9659</td>
<td>2.6</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

ZSM-5 (P22) was calcined to the sodium form at 800\°C for 24 hours. The zeolite was then ion-exchanged into the ammonium form by repeated treatment with ammonium chloride. The acid form was obtained by calcination of the ammonium form at 400\°C for 24 hours. H-Silicalite was prepared by calcination at 600\°C for 72 hours followed by treatment with hydrochloric acid.
The results given in Table 4.7 show that whilst neither Na-ZSM-5 (P22) nor NH₄-ZSM-5 (P22) showed catalytic activity, H-ZSM-5 does. Experiments carried out with ZSM-5 (silicalite-1 (T50)) showed that the silanol groups were catalytically inactive. For ZSM-5 to show catalytic activity it is clear it must (i) contain aluminium and (ii) be in the acid form. There are three different types of aluminium associated with zeolites and hence three possible catalytic sites. Tetrahedrally co-ordinated framework aluminium can be associated with

(i) Brønsted acid sites:

\[
\begin{array}{c}
\text{H}_3\text{O}^+ \\
\text{O} \quad \text{O} \quad \text{O} \\
\text{Si} \quad \text{Al} \quad \text{Si}
\end{array}
\]

or (ii) Lewis acid sites

\[
\begin{array}{c}
\text{AlO}^+ \\
\text{O} \quad \text{O} \quad \text{O} \\
\text{Si} \quad \text{Al} \quad \text{Si}
\end{array}
\]

Aluminium can also exist as extra-framework octahedrally co-ordinated hydroxo-aluminium cations. The different properties of these aluminium sites for gas phase reactions are described in more detail in Chapter 1.6.

**Zeolites as Catalysts**

For a zeolite to be termed a catalyst it must be able to "increase the rate at which a chemical reaction approaches equilibrium, without being consumed in the process" [49]. To test that this condition is met for ZSM-5 catalysis of ester hydrolysis the following experiment was performed.
A sample of H-ZSM-5 (H54) was prepared by calcination at 600°C for 72 hours followed by treatment with hydrochloric acid. Samples of the catalyst were retained after an ethyl acetate hydrolysis experiment and divided into two portions. The first portion was re-equilibrated over saturated sodium chloride at room temperature before being re-used as a catalyst. The second portion was washed and treated with hydrochloric acid to remove any potassium ions that had been exchanged during the previous ethyl acetate hydrolysis experiment. The re-generated sample was again equilibrated over saturated sodium chloride before being re-used as a catalyst. The results obtained are given in Table 4.8. The efficiency of the zeolite catalysed reaction is given relative to the homogenous acid catalysed reaction.

Table 4.8 shows a 10% loss in catalytic activity when the zeolite is used without regeneration. Only some of this loss (4% at most) can be attributed to potassium uptake during the first experimental run. The difference is perhaps due to experimental error, although it seems more likely that it is due to some unidentified source of deactivation. It can be seen that regeneration of the zeolite catalyst is possible if the zeolite is again treated with hydrochloric acid. Care must be taken if a catalyst is to be fully regenerated. Similar regeneration experiments showed an increased loss of catalytic activity when the regeneration process included either (i) treatment with ammonium chloride or (ii) a calcination state. The results given in Table 4.8 show that H-ZSM-5 satisfies the conditions for a catalyst.
Table 4.8  Reuseability of ZSM-5 as a catalyst for the hydrolysis of ethyl acetate in water at 60°C

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Weight of anhydrous zeolite (g)</th>
<th>Rate Constant ($k_{10^4 \times k}$)</th>
<th>Rate Constant ($k_{10^4 \times k}$)</th>
<th>$k_{ZH}$ (min$^{-1}$ M$^{-1}$)</th>
<th>Efficiency (q)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H54 1st Run</td>
<td>0.8756</td>
<td>6.44</td>
<td>7.36</td>
<td>0.137</td>
<td>0.687</td>
</tr>
<tr>
<td>H54 re-used</td>
<td>0.8799</td>
<td>5.80</td>
<td>6.59</td>
<td>0.123</td>
<td>0.615</td>
</tr>
<tr>
<td>H54 re-generated</td>
<td>0.8827</td>
<td>6.53</td>
<td>7.40</td>
<td>0.138</td>
<td>0.691</td>
</tr>
</tbody>
</table>
Effect of Temperature on the Zeolite Catalysed Reaction

Samples of catalyst (ZSM-5 (H53)) were prepared by calcination at 600°C for 72 hours followed by treatment with hydrochloric acid. The zeolite catalysed reaction was studied over the same temperature range as used for the homogenous base catalysed reaction. The data obtained for the background base catalysed reaction were required so that true rate constants could be obtained for the zeolite catalysed reaction. The natural logarithm of the rate constants for the zeolite catalysed reaction were plotted against 1/T, in accordance with the Arrhenius equation (see equation 4.19). The experimental results are shown in Figure 4.7. The linear correlation observed shows that the zeolite catalysed reaction satisfies the Arrhenius equation. It also indicates that there is no change in mechanism over the temperature range investigated. The experimental values for the activation energy and the frequency factor are compared with the literature values in Table 4.9. The value obtained for the activation energy is in good agreement with the literature values for acid zeolites. However, with one exception the literature values for the cation exchange resins and hydrochloric acid are slightly higher. The reason for this could be because the acid sites in the zeolites are stronger than those in water. The acid sites in an ion-exchange resin is H₃O⁺(aq) and would be expected to have an acidity similar to that of water.
Figure 4.7  Arrhenius plot for the H-ZSM-5 (H53) catalysed hydrolysis of ethyl acetate in water
<table>
<thead>
<tr>
<th>Reference</th>
<th>Catalyst</th>
<th>Activation Energy (kJ mol(^{-1}))</th>
<th>ln A</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>H-ZSM-5 (H53)</td>
<td>65.1 ± 3</td>
<td>16.1 ± 1</td>
</tr>
<tr>
<td>43</td>
<td>H-ZSM-5</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>H-Mordenite</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>200 C</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>DVB-4</td>
<td>72.4</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>Dowex-50</td>
<td>72.8</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>HCl</td>
<td>71.7</td>
<td>19.77</td>
</tr>
</tbody>
</table>

However it is clear that the observed Arrhenius parameters are consistent with an acid catalysed \(A_{NC}^2\) mechanism. This involves the donation of a proton from an hydronium ion to the reactant ethyl acetate molecule (see Chapter 4.1) which is the rate limiting slow step. There is no reason to expect that the zeolite catalysed reaction proceeds other than by an \(A_{NC}^2\) mechanism but in a zeolite the acid site rather than the hydronium ion will be responsible for the initial proton transfer. This conclusion was also reached by Santacesaria et al [42] in their studies on the zeolite catalysed esterification of acetic acid and ethanol.
Effect of Zeolite Concentration on Rate of Hydrolysis

To show that the reaction rate was dependant on the amount of zeolite catalyst present and to find the order of reaction with respect to the solid catalyst a series of reactions in which only the amount of catalyst varied was carried out. The catalyst, H-ZSM-5 (H54), was prepared by calcination at 600°C for 72 hours followed by treatment with hydrochloric acid. The amount of zeolite per unit volume of solution was varied by changing the weight of catalyst added to 200 cm$^3$ of water. The results obtained are given in Table 4.10. The results clearly show that the rate constant of the zeolite catalysed reaction is proportional to the weight of zeolite used. This indicates that the rate limiting step in the zeolite catalysed reaction is a chemical step that occurs within the zeolite framework. If the reaction was diffusion controlled then the rate would not be linearly dependant on the amount of zeolite present.

The average efficiency of H-ZSM-5 (H54), relative to hydrochloric acid is 0.667 ± 0.03. If it is assumed that the catalytic activity of a Brønsted acid site in a zeolite is equal to that for the aqueous hydronium ion then this result indicates that 1/3 of the total amount of aluminium available is catalytically inactive. This could be due to either or both of the following:

(i) not all of the aluminium is accessible to the reactant,

(ii) not all of the aluminium is in a catalytically active form.
Table 4.10  Effect of zeolite weight/volume of solution for the hydrolysis of ethyl acetate at 60°C

<table>
<thead>
<tr>
<th>Weight of anhydrous zeolite (g)</th>
<th>Rate constant (k) $10^4 \times k$ (min$^{-1}$)</th>
<th>Rate Constant (k) $10^4 \times k$ (min$^{-1}$g$^{-1}$)</th>
<th>$k_{ZH}$ min$^{-1}$ M$^{-1}$</th>
<th>Efficiency q</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3211</td>
<td>2.29</td>
<td>7.12</td>
<td>0.133</td>
<td>0.664</td>
</tr>
<tr>
<td>0.7305</td>
<td>5.18</td>
<td>7.09</td>
<td>0.128</td>
<td>0.640</td>
</tr>
<tr>
<td>0.8756</td>
<td>6.44</td>
<td>7.36</td>
<td>0.137</td>
<td>0.687</td>
</tr>
<tr>
<td>1.2694</td>
<td>8.94</td>
<td>7.05</td>
<td>0.132</td>
<td>0.658</td>
</tr>
<tr>
<td>2.1239</td>
<td>15.67</td>
<td>7.38</td>
<td>0.138</td>
<td>0.688</td>
</tr>
</tbody>
</table>

Table 4.12b  Effect of calcination on the catalytic activity of (Na, PIP)-ZSM-5 (P40) and (Na, HEX)-ZSM-5 (H39)

<table>
<thead>
<tr>
<th>Code</th>
<th>Calcined treatment</th>
<th>Wash + HCl treatment</th>
<th>Rate Constant (k) $10^4 \times k$ (min$^{-1}$ g$^{-1}$)</th>
<th>$k_{ZH}$ min$^{-1}$ M$^{-1}$</th>
<th>Efficiency q</th>
</tr>
</thead>
<tbody>
<tr>
<td>P40</td>
<td>No</td>
<td>x 1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>P40</td>
<td>Yes</td>
<td>x 1</td>
<td>6.72</td>
<td>0.180</td>
<td>0.898</td>
</tr>
<tr>
<td>H39</td>
<td>No</td>
<td>x 1</td>
<td>1.90</td>
<td>0.039$^a$</td>
<td>0.196</td>
</tr>
<tr>
<td>H39</td>
<td>No</td>
<td>x 2</td>
<td>2.38</td>
<td>0.049$^a$</td>
<td>0.246</td>
</tr>
<tr>
<td>H39</td>
<td>No</td>
<td>x 3</td>
<td>2.76</td>
<td>0.057$^a$</td>
<td>0.285</td>
</tr>
<tr>
<td>H39</td>
<td>Yes</td>
<td>x 1</td>
<td>5.44</td>
<td>0.112$^a$</td>
<td>0.562</td>
</tr>
</tbody>
</table>

$^a$ Estimated taking average Si/Al for a Hexanediol-ZSM-5 to be 16.2
Comparison of the observed efficiency of H-ZSM-5 (H54) with that of H-ZSM-5 (P22) shows that the former is 35x more efficient than the latter. This fact illustrates just how crucial it is to control the preparation of an acid zeolite. In this case explanation (i) would be expected to have nearly the same effect for both zeolites. Explanation (ii) is the most likely cause of the difference between these zeolites, and is probably the reason for low efficiencies in general. Chapter 6 is devoted to the effect of catalyst preparation on the catalytic activity for ethyl acetate hydrolysis. Although most of the zeolite catalysts that were prepared in this work were found to have an efficiency of less than one, it was found that careful control of the catalyst pretreatment could result in efficiencies of close to unity (see section 4.8). The efficiencies for ZSM-5 found in this work are comparable with those given in reports by Namba et al [43]. These workers obtained a maximum rate constant for the hydrolysis of ethyl acetate of $1.75 \times 10^{-3} \text{ min}^{-1} \text{ g}^{-1}$. This was achieved with a H-ZSM-5 zeolite with Si/Al = 47. The exact details of their experiments are not reported but if it is assumed that they used 1 g of H-ZSM-5 in 10 cm$^3$ of solution then the catalytic efficiency of their zeolite is 1.262.

**Effect of Si/Al Ratio**

An alternative method of increasing the observed rate of hydrolysis is to increase the number of catalytic sites per gram of zeolite. Six zeolite catalysts were prepared from a series based on the reaction mixture:
where $x = 25, 30, 40, 50, 60$ and $70$. These zeolites were synthesised specifically for this particular investigation. The silica content in the reactant gel was varied instead of the aluminium content as it was hoped to differentiate between effects due to Si/Al and possible effects associated with the free base content of the reaction mixture per SiO$_2$. For example, in the series investigated, increase in Si/Al is associated with a decrease in the free base content per SiO$_2$ of the reaction mixture. The zeolites were converted to the acid form by calcination at 600°C for 72 hours followed by treatment with ammonium chloride solution and subsequent calcination at 400°C for 24 hours. All of the catalysts were prepared and activated in exactly the same manner. The experimental results are given in Table 4.11. Figure 4.8 shows a plot of the rate constant per gram of anhydrous zeolite against the aluminium content per unit cell. The linear relationship between the pseudo first order rate constant $k$ for the hydrolysis of ethyl acetate and the number of catalytically active sites is clearly shown in Figure 4.8. Hence it appears that for acid zeolite catalysts, that have undergone the same pretreatment and have nearly equal crystallinity, an increase in the aluminium content per gram of zeolite results in a corresponding increase in the rate of reaction. In the present example although the aluminium content was more than doubled the efficiency per aluminium remained constant (see Table 4.11). The Sanderson electronegativity principle predicts that the acid strength of the Brønsted acid sites will
Figure 4.8 Rate constant ($k$) for the H-ZSM-5 catalysed hydrolysis of ethyl acetate in water at 60°C against aluminium content.
Table 4.11  Dependence of rate of hydrolysis of ethyl acetate on the alumina content of H-ZSM-5 catalysts

<table>
<thead>
<tr>
<th>Code</th>
<th>Si/Al</th>
<th>Al per unit cell</th>
<th>Rate Constant (k) $10^4 \times k$ (min$^{-1}$ g$^{-1}$)</th>
<th>$k_{ZH}$ min$^{-1}$ M$^{-1}$</th>
<th>Efficiency q</th>
</tr>
</thead>
<tbody>
<tr>
<td>T80</td>
<td>10.49</td>
<td>8.355</td>
<td>3.21</td>
<td>0.044</td>
<td>0.222</td>
</tr>
<tr>
<td>T25</td>
<td>13.23</td>
<td>6.745</td>
<td>2.27</td>
<td>0.039</td>
<td>0.193</td>
</tr>
<tr>
<td>T28</td>
<td>18.59</td>
<td>4.901</td>
<td>2.06</td>
<td>0.047</td>
<td>0.236</td>
</tr>
<tr>
<td>T83</td>
<td>20.87</td>
<td>4.389</td>
<td>1.62</td>
<td>0.042</td>
<td>0.212</td>
</tr>
<tr>
<td>T38</td>
<td>21.92</td>
<td>4.188</td>
<td>1.44</td>
<td>0.040</td>
<td>0.198</td>
</tr>
<tr>
<td>T24</td>
<td>29.70</td>
<td>3.429</td>
<td>1.06</td>
<td>0.036</td>
<td>0.178</td>
</tr>
</tbody>
</table>
decrease with an increase in aluminium content [50]. However the experimental results obtained in the present case indicate the the acid strength of each site is independant of the Al content of the zeolite framework, at least over the Si/Al range studied. The linear relationship between the catalytic activity of this series of H-ZSM-5 zeolites and their aluminium content indicates that all the active acid centres of ZSM-5 are identical. A homogenous distribution of acid strength for ZSM-5 catalysts has been reported elsewhere. Olson et al [48] showed that the hexane cracking activity of H-ZSM-5 is a linear function of aluminium content. This result is in agreement with similar findings by Chen and Reagan [51] and Guisnet et al [52].

These experimental results are in contrast to the findings of Namba et al [43]. Their results, obtained for H-ZSM-5 zeolites with the same Si/Al compositions as those used in this work, showed that the rate of hydrolysis of methyl or ethyl acetate increased with a decrease in aluminium content. They proposed that this was due to the increased hydrophobicity of the zeolite. However, at Si/Al > 47 the requirement for catalytic sites became dominant and the rate decreased with decreasing aluminium content. Although it was not stated in the paper [43] the results suggest a heterogenous acid strength distribution. An increase in rate constant with decreasing aluminium content was not observed in the present work and it seems likely that the results of Namba et al are probably in error.

An increase in the free base content of the reactant gel is known to result in the formation of smaller crystals. There is a 2.8 fold decrease in the free base content per mole SiO₂ for T24
compared to that of T80. Although the crystal sizes obtained in this reaction series (Table 4.11) are small they do increase from sub-micron (ca. 0.5 μm) up to 1.2 microns in size with decrease in free base content. The consequent variation in the external crystal surface area and the diffusional path length does not appear to have any effect on the zeolite activity. Although the range in crystal size is small the experimental results suggest that all acid sites are equally accessible and provide no evidence to suggest that the rate is limited by diffusion.

**Relationship between the Catalytic Activity of H-ZSM-5 samples and their Water Content**

It is known that the water content of H-ZSM-5 is linearly related to its framework aluminium content. Chen [47] showed that, for zeolites with a low aluminium content, there were four water molecules associated with each hydrophilic centre. Since a linear relationship has been shown to exist between the catalytic activity of ZSM-5 and its aluminium content, the pseudo first order rate constant k for ester hydrolysis is expected to be linearly dependant on the equilibrium water content of the catalysts. These zeolites were synthesised with different Na/Al, Si/Al and TPA/Al ratios. They were all of a similar crystallinity and were all converted to the acid form by calcination at 600°C for 72 hours followed by treatment with ammonium chloride and subsequent calcination at 400°C for 24 hours. All of the water contents are for samples that had been equilibrated over saturated sodium chloride and were determined by thermal gravimetric analysis. The experimental results plotted in Figure 4.9
Figure 4.9 Rate constant ($k$) for the H-ZSM-5 catalysed hydrolysis of ethyl acetate in water at 60°C against water content.
show that, despite the differences in crystal size, there is indeed a linear relationship. This result agrees with earlier studies (see this section) on the absence of crystal size effects on the catalytic activity of H-ZSM-5. The non-zero intercept (Figure 4.9) is to be expected as the aluminium free analogue of ZSM-5, silicalite-1 (T50) which is not catalytically active contains about 0.035 g water per gram of anhydrous zeolite. The linear relationship obtained only applies to zeolites that have been converted to the acid form by the pre-treatment described. Different pretreatment procedures will give linear correlations with different gradients.

4.5.4 Conclusions

The hydrolysis of ethyl acetate in water has been shown to be catalysed by H-ZSM-5. The zeolite catalysed reaction has been shown to be first order in the ester concentration up to at least 7% conversion of ethyl acetate. The catalytic activity has been shown to be dependant on the acid sites associated with the framework aluminium atoms. Zeolites in the sodium and ammonium forms did not show any catalytic activity. The aluminium free analogue of ZSM-5, silicalite-1, did not display any catalytic activity either. Experiments showed that ZSM-5 could be considered to be a true catalyst. However regeneration after an ester hydrolysis experiment by treatment with hydrochloric acid was required as some acid sites were lost, due in part to uptake of potassium ions during the experiment. The zeolite catalysed reaction was found to obey the Arrhenius equation and the experimental activation energy of 65.1 ± 3 kJ mol\(^{-1}\) and \(\ln A\) of 16.1 ± 1 (\(A\) is in min\(^{-1}\) g\(^{-1}\)) compare well with literature values for an acid catalysed
reaction. The activation energy was slightly lower than the values obtained for cation exchange resins and aqueous hydrochloric acid, although the differences are small and might be due in part to experimental error. There is no reason to suppose that the zeolite catalysed hydrolysis of ethyl acetate proceeds by a mechanism other than the $\text{A}^2\text{C}$ reaction. This mechanism would involve the donation of a proton by an acid site in the H-zeolite to the reactant ethyl acetate molecule. The rate of reaction was found to be proportional to the weight of zeolite used. This fact suggests that the rate limiting step for the zeolite catalysed reaction involves a chemical step rather than a physical process such as diffusion. The rate of ethyl acetate hydrolysis was also shown to be directly proportional to the number of hydrophilic acid sites in ZSM-5. A linear relationship between the catalytic activity of a series of H-ZSM-5 zeolites and their aluminium content indicates a homogenous distribution of acid strength. This result is in agreement with similar findings with ZSM-5 catalysed reactions in the gas phase [48, 52, 53]. No evidence was found to support the hydrophobicity effect claimed by Namba et al [43] and the experimental results in this work are in opposition to their results. Variation in crystal size and consequent change in external surface area and diffusional path lengths did not have any effect on the catalytic activity of different H-ZSM-5 catalysts. As expected a linear relationship was found between the rate of hydrolysis of ethyl acetate catalysed by a series of H-ZSM-5 zeolites and their water content. This result agrees with other experimental results which indicated that the rate of reaction is dependant on the number of hydrophilic acid sites in the catalyst. It was also noted that the catalytic activity of H-ZSM-5
is strongly dependent on the pretreatment used. The effect of pretreatment methods on the catalytic activity of H-ZSM-5 is discussed in more detail in Chapter 6.

4.6 Evidence for Intra-Crystalline Catalysis by H-ZSM-5

4.6.1 Introduction

A practical requirement for catalysis by zeolites is that the catalysed reaction should occur inside the zeolite crystals. This enables the rigid crystalline zeolite framework to influence the reaction by (i) reactant selectivity, (ii) transition state selectivity and (iii) product selectivity. The molecular sieving properties of zeolites are discussed in detail in section 1.5 and section 1.6. Typical crystal sizes used in this work were about 1 µm. This means that the external surface of a crystal represents 0.5% of the total surface area presented to a reactant molecule. Recent studies by Cook et al [53] have shown the external crystal surface of the high silica zeolite H-Fu-1 to have catalytic properties. Therefore it is necessary to prove that the zeolite catalysed hydrolysis of ethyl acetate is catalysed by intra-crystalline rather than surface acid sites. If this is not shown then the efficiencies obtained for the zeolite catalysts become almost meaningless.

4.6.2 Experimental

The synthesis of zeolite ZSM-5 is described in detail in Chapter 3. The materials used and the experimental procedure for the hydrolysis of ethyl acetate is given in section 4.2. The method
used for the preparation of the acid form of the zeolites is also
given in section 4.2 whilst the treatment of results is given in
section 4.3.

4.6.3 Results and Discussion

It was decided that the best way to show that intracrystalline
acid sites of H-ZSM-5 catalyse the hydrolysis of ethyl acetate was
to compare an uncalcined sample of H-ZSM-5 with a calcined sample.
Two portions of sample T49 were used. One portion was calcined for
72 hours at 400°C before being acidified by treatment with hydro-
chloric acid. The second portion was not calcined, but merely
treated with hydrochloric acid. The experimental results obtained for
both portions are given in Table 4.12a.

Table 4.12a Effect of calcination on the catalytic activity of
(Na, TPA)-ZSM-5

<table>
<thead>
<tr>
<th>Code</th>
<th>Calcined</th>
<th>Rate Constant (k) 10^4 x k (min^-1 g^-1)</th>
<th>k_{ZH} (min^-1 M^-1)</th>
<th>Efficiency q</th>
</tr>
</thead>
<tbody>
<tr>
<td>T49</td>
<td>no</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>T49</td>
<td>yes</td>
<td>4.77</td>
<td>0.144</td>
<td>0.719</td>
</tr>
</tbody>
</table>

The results show that intracrystalline catalysis is observed when
ZSM-5 catalyses the hydrolysis of ethyl acetate. If the intra-
crystalline channels are not freed of organic then no catalytic
activity is observed. The acid sites on the external crystal surface
are too few to significantly raise the observed rate above background
levels. Removal of the intracrystalline TPA molecules by calcination
followed by treatment with hydrochloric acid results in a catalytically
active ZSM-5.
The above experiment with (Na, TPA)-ZSM-5 (T49) was repeated with (Na, PIP)-ZSM-5 (P40) and (Na, HEX)-ZSM-5 (H39). Sample preparation was similar to that for (Na, TPA)-ZSM-5, the only difference being that the (Na, HEX)-ZSM-5 (H39) was calcined for 72 hours at 600°C as opposed to 400°C for (Na, TPA)-ZSM-5 (T49) and (Na, PIP)-ZSM-5 (P40). In addition the zeolites were washed overnight in a Soxhlet extraction apparatus before treatment with hydrochloric acid. The effect of repeated washing and acid treatment was studied for the (Na, HEX)-ZSM-5 sample.

The experimental results given in Table 4.12 show that piperazine blocks the intracrystalline channels of ZSM-5 and that there is no catalytic activity associated with the uncalcined sample. However removal of the intracrystalline organic before treatment with hydrochloric acid results in a catalytically active zeolite with an efficiency comparable to that of hydrochloric acid. However the results obtained with (Na, HEX)-ZSM-5 (H39) are different. Unlike TPA or piperazine it is possible to remove intracrystalline hexanediol by simply washing the zeolite with hot water. Removal of intracrystalline hexanediol opens up the channel system so that ZSM-5 can sorb ethyl acetate and catalytically hydrolyse it. The experimental results show that a threefold wash-plus-acid treatment gives a catalyst that is 51% as efficient as when the same starting material is calcined for 72 hours at 600°C and then treated with hydrochloric acid. TG traces of the washed (Na, HEX)-ZSM-5 (H39) samples are shown in Figure 4.12. It can be seen from this figure that successive washing of (Na, HEX)-ZSM-5 (H39) increases the water content (low temperature weight loss) at the expense of the hexanediol content (high temperature weight loss), and the effect
Figure 4.10 TG analysis of washed (Na, HEX)-ZSM-5

a 'as made'; b wash + acid treatment;
c 2 x (wash + acid treatment);
d 3 x (wash + acid treatment). Note each trace is displaced by 3.0%

occurs with each successive wash. The interpretation of the TG traces for the washed samples is difficult as there are clearly several processes involved, however it appears that the wash plus acid treatment results in the loss of roughly 35% of the intracrystalline hexanediol. The experimental results obtained for (Na, PIP)-ZSM-5 and (Na, HEX)-ZSM-5 support those for (Na, TPA)-ZSM-5 in that they show that if the intracrystalline channel system is blocked, then no catalytic activity is observed.
Attempts to detect intracrystalline ethyl acetate in H-ZSM-5 after an hydrolysis experiment by DTA and TG analysis failed. This was presumably due to the high volatility of ethyl acetate.

The effect of adding a secondary organic during an experiment was also studied for acetate hydrolysis. The zeolite used, H-ZSM-5 (H53), was prepared by calcination for 72 hours at 600°C followed by treatment with hydrochloric acid. The experimental results showed that addition of either p-xylene or cyclohexane, up to an organic/ester ratio of unity did not alter the rate of hydrolysis of ethyl acetate. In this case thermal gravimetric analysis of the zeolite catalyst after the experiment had been completed showed no evidence to suggest that any organic had been sorbed. However, addition of benzyl alcohol during the hydrolysis experiment did retard the rate of hydrolysis of ethyl acetate. The relationship between the [benzyl alcohol]/[ethyl acetate] molar ratio and the rate of hydrolysis is illustrated in Figure 4.11. The experimental results suggest that addition of a small amount of benzyl alcohol has a marked effect on the rate of hydrolysis. Further additions of benzyl alcohol result in smaller decreases in the reaction rate. There appears to be a linear relationship when the [benzyl alcohol]/[ethyl acetate] mole ratio is greater than 0.5. The equation of the best fit least squares line was found to be:

\[ 10^4 k = -0.65(\pm 0.05) r + 5.13(\pm 0.2) \]  \hspace{1cm} (4.20)

where \( k \) is the specific rate of ethyl acetate hydrolysis (\( \text{min}^{-1} \text{g}^{-1} \)) and \( r \) represents the ratio of benzyl alcohol to ethyl acetate. The fact that benzyl alcohol does impair the efficiency of the catalyst whilst p-xylene and cyclohexane do not, despite being of similar size,
Figure 4.11  Rate constant (k) for the H-ZSM-5 (H53) catalysed hydrolysis of ethyl acetate against [Benzyl alcohol]/[Ethyl acetate] mole ratio.
is probably due to (i) the greater solubility of benzyl alcohol and (ii) it successfully competes with tetrabutyl ammonium hydroxide for acetic acid formed by the hydrolysis reaction to form benzyl acetate. It is believed that the sharp decrease in the reaction rate when the [benzyl alcohol]/[ethyl acetate] mole ratio is less than 0.5 is probably due to competitive sorption between benzyl alcohol and ethyl acetate. Thermal analysis shows that benzyl alcohol is sorbed by ZSM-5 during the timescale and under the conditions of the experiment. The linear relationship observed is probably due to the esterification reaction. The reason why benzyl alcohol does not entirely stop the sorption of ethyl acetate by ZSM-5 is not fully understood. However it does appear that its sorption is sufficiently limited so that the ester hydrolysis reaction continues.

4.6.4 Conclusions

These experimental results clearly show that the catalytic sites in H-ZSM-5 are situated in the intracrystalline channels. The lack of a calcination stage in the preparation of H-ZSM-5 from (Na, TPA)-ZSM-5 (T49) and (Na, PIP)-ZSM-5 (P40) resulted in no catalytic activity being observed. Any effect that might have been due to catalysis by acid sites on the crystal surface was too small to be detected. (Na, HEX)-ZSM-5 (H39) gave slightly different results to both (Na, TPA)-ZSM-5 (T49) and (Na, PIP)-ZSM-5 (P40). This is because it is possible to remove some of the intracrystalline hexanediol material by simply washing the zeolite. Approximately 35% of the total amount of intracrystalline hexanediol was lost when the uncalcined zeolite was washed overnight on a
Soxhlet extraction apparatus and then treated with hydrochloric acid. Loss of intracrystalline hexanediol was accompanied by a corresponding increase in catalytic activity. The possibility of aluminium zoning across the ZSM-5 crystals [54] makes studies on the correlation of the rate of ethyl acetate hydrolysis with the amount of intracrystalline hexanediol impossible to interpret. For such investigations it would be necessary to know the extent of any aluminium zoning.

Measurement of the rate of ethyl acetate hydrolysis in mixed solvents showed that neither p-xylene nor cyclohexane was sorbed within the timescale of the reaction. Thermal analysis supported these findings. However, addition of benzyl alcohol did have a marked effect on the rate of ethyl acetate hydrolysis. A plot of observed rate against the [benzyl alcohol]/[ethyl acetate] mole ratios showed a discontinuity when the [benzyl alcohol]/[ethyl acetate] mole ratio is about 0.5(±0.5). The dominant effect at low [benzyl alcohol]/[ethyl acetate] mole ratios was thought to be due to sorption of benzyl alcohol by ZSM-5. When this ratio is increased the dominant effect is probably the removal of acetic acid by esterification with benzyl alcohol. Thermal analysis again agrees with these findings in that it showed that benzyl alcohol was adsorbed by ZSM-5 during the timescale of an ester hydrolysis experiment.
4.7 Effect of Zeolite Framework Structure

4.7.1 Introduction

Whether or not sorption can occur depends on the size and shape of the channels and the size and shape of the sorbate molecule. Hence intracrystalline catalysis of the hydrolysis reaction will be dependant on the nature of the zeolite framework structure and on the molecular structure of the ester. Namba et al [43] found that zeolites H-ZSM-5, H-Mordenite and H-Y could catalyse the hydrolysis of either methyl acetate or ethyl acetate. However large differences in the efficiency of the different zeolite catalysts were reported although not understood. It was decided therefore to investigate the effects of channel and ester dimensions on the rate of the hydrolysis reaction. This work parallels similar research carried out by Bernhard and Hammett [32] on the relationship between the degree of cross-linking on the efficiencies of their cation-exchange resins for the hydrolysis of esters with different chain lengths. They found that lightly cross-linked ion exchange resins were better catalysts for the hydrolysis of aliphatic esters of low molecular weight than is hydrochloric acid, and that their effectiveness is greater for ethyl acetate than for methyl acetate. However, tightly cross-linked ion exchange resins were less effective than the homogenous strong acid, and the relative effectiveness of the resin decreases with increasing chain length of ester. It was hoped to be able to find out whether zeolites behave like lightly or strongly cross-linked ion-exchange resins.
4.7.2 **Experimental**

The synthesis of the zeolites used is described in detail in Chapter 3. The materials used and the experimental procedure for ester hydrolysis are given in section 4.2. The method used to prepare the acid form of the zeolites is also in section 4.2 whilst the treatment of results is described in section 4.3. The zeolites were converted to the acid form as follows. Zeolites H-ZSM-5 (J64) and H-Mordenite (J59) were treated with hydrochloric acid. No calcination stage was required as both were synthesised from inorganic systems. Zeolites H-ZSM-5 (T49), H-EU-I (J87) and H-Ferrierite (J68) were calcined for 72 hours at 450°C before being treated with hydrochloric acid.

4.7.3 **Results and Discussion**

Thermal analysis showed that the calcination treatment used resulted in the complete removal of any organic present in the as synthesised forms of the zeolites. The experimental results given in Table 4.13 show that the catalytic efficiency of acid zeolites is strongly dependant on the skeletal structure. Of the four acid zeolites tested H-ZSM-5, H-Mordenite and H-EU-I showed catalytic activity for the hydrolysis of ethyl acetate whilst H-Ferrierite was found to be catalytically inactive. The catalytic efficiency of 0.005 obtained for H-Ferrierite is probably due to catalysis by acid sites on the external surface of the ferrierite crystals. The lack of catalytic activity for H-Ferrierite is unlikely to be caused by the destruction of acid sites by the pretreatment method. Both H-ZSM-5 (T49) and H-EU-I (J87) had the same pretreatment and were found to be catalytically active for the hydrolysis of ethyl
Table 4.13a  Effect of zeolite structure on the rate of hydrolysis of ethyl acetate at 60°C

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Code</th>
<th>Channel system [55] (T-atoms)</th>
<th>Rate constant (k) (10^4 \times k) min(^{-1}) g(^{-1})</th>
<th>(k_{ZH}) min(^{-1}) M(^{-1})</th>
<th>Efficiency (q)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-ZSM-5</td>
<td>J64</td>
<td>10 x 10</td>
<td>8.30</td>
<td>0.138</td>
<td>0.688</td>
</tr>
<tr>
<td>H-ZSM-5</td>
<td>T49</td>
<td>10 x 10</td>
<td>3.73</td>
<td>0.112</td>
<td>0.562</td>
</tr>
<tr>
<td>H-Mordenite</td>
<td>J59</td>
<td>12 x 8</td>
<td>6.68</td>
<td>0.069</td>
<td>0.345</td>
</tr>
<tr>
<td>H-Ferrierite</td>
<td>J68</td>
<td>10 x 8</td>
<td>0.08</td>
<td>0.001</td>
<td>0.005</td>
</tr>
<tr>
<td>H-EU-1</td>
<td>J87</td>
<td>10  (^a)</td>
<td>2.00</td>
<td>0.058</td>
<td>0.291</td>
</tr>
</tbody>
</table>

\(^a\) Casci et al [56] report an entry port of slightly less than 6.0 Å which suggests that EU-1 has 10 T-atom windows

Table 4.13b  Molecular dimensions of channel systems of zeolites investigated [55]

<table>
<thead>
<tr>
<th>Zeolite structure</th>
<th>Channel system [55] (T-atoms)</th>
<th>Dimension (Å)</th>
<th>Direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZSM-5</td>
<td>10</td>
<td>5.4 x 5.6</td>
<td>[010]</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>5.1 x 5.5</td>
<td>[100]</td>
</tr>
</tbody>
</table>

| Mordenite         | 12                             | 6.7 x 7.0      | [001]     |
|                   | 8                              | 2.9 x 5.7      | [010]     |

| Ferrierite        | 10                             | 4.3 x 5.5      | [001]     |
|                   | 8                              | 3.4 x 4.8      | [010]     |
Acidity determination by an ion-exchange method (see section 5.5) showed that H-Ferrierite contained a large concentration of Brønsted acid sites. A comparison of the molecular dimensions of ethyl acetate (see Table 4.2) and the channel system of ferrierite (see Table 4.13b) indicates that steric restrictions are the reason for the lack of catalytic activity. The minimum kinetic diameter of ethyl acetate was found to be 4.7 Å. Meier and Olson [55] give the size of the 8 T-atom ferrierite channel as 3.4 x 4.8 Å and the 10 T-atom ring channel as 4.3 x 5.5 Å. The 8 T-atom channel found in mordenite (2.9 x 5.7 Å) is also too small to sorb ethyl acetate and probably accounts for the low efficiency of H-Mordenite (J59) relative to H-ZSM-5 (J64). The catalytic activity observed for H-EU-1 is consistent with the results published by Casci et al [56] who suggest that EU-1 probably contains 10 T-atom windows that are slightly less than 6.0 Å in diameter.

The catalytic activities of H-ZSM-5, H-Mordenite and H-EU-1 for the hydrolysis of methyl acetate, ethyl acetate and ethyl benzoate are given in Table 4.14. The experimental results show that H-EU-1 and H-Mordenite are less efficient catalysts for the hydrolysis of ethyl acetate than for methyl acetate. Both zeolites show an activity for the hydrolysis of ethyl acetate that is only 30% of the value obtained for the hydrolysis of methyl acetate. As the minimum kinetic diameter of both esters is the same then the acid sites of both zeolites should be equally accessible to them. The possibility of preferential sorption of ethanol rather than methanol, formed as products of the hydrolysis reaction, could
Table 4.14 Effects of zeolite structure on the rate of hydrolysis of different esters at 60°C

<table>
<thead>
<tr>
<th>Ester</th>
<th>Zeolite</th>
<th>Code</th>
<th>(10^4 \times k) (min(^{-1}) g(^{-1}))</th>
<th>(k_{ZH}) (min(^{-1}) M(^{-1}))</th>
<th>Efficiency q</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl</td>
<td>H-ZSM-5</td>
<td>J64</td>
<td>8.02</td>
<td>0.134</td>
<td>0.67</td>
</tr>
<tr>
<td>Acetate</td>
<td>H-Mordenite</td>
<td>J59</td>
<td>7.96</td>
<td>0.082</td>
<td>0.41</td>
</tr>
<tr>
<td></td>
<td>H-EU-1</td>
<td>J87</td>
<td>7.68</td>
<td>0.223</td>
<td>1.12</td>
</tr>
<tr>
<td>Ethyl</td>
<td>H-ZSM-5</td>
<td>J64</td>
<td>8.30</td>
<td>0.138</td>
<td>0.688</td>
</tr>
<tr>
<td>Acetate</td>
<td>H-Mordenite</td>
<td>J59</td>
<td>7.68</td>
<td>0.027</td>
<td>0.136</td>
</tr>
<tr>
<td></td>
<td>H-EU-1</td>
<td>J87</td>
<td>2.00</td>
<td>0.058</td>
<td>0.291</td>
</tr>
<tr>
<td>Ethyl</td>
<td>H-ZSM-5</td>
<td>J64</td>
<td>0.04</td>
<td>(7 \times 10^{-4})</td>
<td>0.004</td>
</tr>
<tr>
<td>Benzoate</td>
<td>H-Mordenite</td>
<td>J59</td>
<td>0.06</td>
<td>(6 \times 10^{-4})</td>
<td>0.003</td>
</tr>
<tr>
<td></td>
<td>H-EU-1</td>
<td>J87</td>
<td>0.03</td>
<td>(1 \times 10^{-4})</td>
<td>0.006</td>
</tr>
</tbody>
</table>
account for this result. However this possibility can be ruled out as it implies that non-first order kinetics would be observed, i.e. if the products formed inhibited the rate of hydrolysis then a plot of ln[Estern] against time would not be linear. The experimental results are similar to those of Bernhard and Hammett [32] for the hydrolysis of methyl acetate and ethyl acetate in the presence of strongly cross-linked ion-exchange resins. They postulated that the strongly cross-linked ion-exchange resins imposed restraints on the internal motions of the charged transition state. The resultant loss of entropy made the formation of the reaction intermediate less favourable.

Thus it is probable that H-EU-1 and H-Mordenite impose restraints on the transition state. It may be reasoned that if the larger mordenite channels impose restraints on the internal motions of the charged transition state then the same effect should be expected for the smaller ZSM-5 channels. The fact that this is not observed suggests that the acid sites in H-ZSM-5 are situated at the intersections of the two 10 T-atom channels. The experimental results for H-ZSM-5 are similar to those observed for lightly cross-linked ion-exchange resins [32].

It is unfortunate that the structure of EU-1 is not known. The present experimental results suggest that it does have windows of at least 10 T-atoms and that these are at least 4.7 Å in diameter. The observation that it behaves like a strongly cross-linked resin could imply that (i) the channel system is not analogous to that of ZSM-5 in that it does not have an intersection of two 10 T-atom channels or (ii) that the catalytic acid sites are situated in the 10 T-atom channels (or 10 T-atom windows if it has a cage structure).
The experimental results obtained for the hydrolysis of ethyl benzoate show no evidence for catalysis by H-ZSM-5, H-Mordenite or H-EU-1. However, the small efficiencies obtained suggest that catalysis only occurs at acid sites on the crystal surfaces. Thermal gravimetric analysis of H-Mordenite after the hydrolysis experiment showed some evidence for the intracrystalline sorption of organic material. However, it is not known if the organic species sorbed was ethyl benzoate or a product of the hydrolysis reaction. Consideration of the zeolite channel and ester sizes suggests that H-Mordenite should be able to sorb ethyl benzoate. It is possible that ethyl benzoate is sorbed by H-Mordenite but that the uptake is too slow to be observed over the duration of the experiment.

The efficiencies obtained for the zeolites investigated are compared with literature values for cation-exchange resins in Table 4.15. The table shows that the catalytic activity of acid zeolites is similar to that of cation-exchange resins and hydrochloric acid for the hydrolysis of methyl acetate and ethyl acetate in water.

4.7.4 Conclusions

Investigations into the effect of zeolite structure on the rate of ethyl acetate hydrolysis show that whilst H-ZSM-5, H-Mordenite and H-EU-1 all display catalytic activity, H-Ferrierite does not. This is considered to be because ethyl acetate is too large to enter the ferrierite channel system. The effect of ester chain length on its rate of hydrolysis catalysed by H-ZSM-5, H-Mordenite and H-EU-1 was also studied. The catalytic efficiency of H-Mordenite and H-EU-1 decreased when ethyl acetate was used instead of methyl
Table 4.15  Efficiencies for ester hydrolysis in water

<table>
<thead>
<tr>
<th>Source</th>
<th>Catalyst</th>
<th>Ester</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>H-ZSM-5 (J64)</td>
<td>Methyl acetate</td>
<td>0.67</td>
</tr>
<tr>
<td>This work</td>
<td>H-Mordenite (J59)</td>
<td>Methyl acetate</td>
<td>0.41</td>
</tr>
<tr>
<td>This work</td>
<td>H-EU-1 (J87)</td>
<td>Methyl acetate</td>
<td>1.12</td>
</tr>
<tr>
<td>[32]</td>
<td>DVB-4</td>
<td>Methyl acetate</td>
<td>1.23</td>
</tr>
<tr>
<td>[32]</td>
<td>IR-120</td>
<td>Methyl acetate</td>
<td>1.00</td>
</tr>
<tr>
<td>[32]</td>
<td>DVB-20</td>
<td>Methyl acetate</td>
<td>0.86</td>
</tr>
<tr>
<td>[23]</td>
<td>Phenol-formaldehyde resin</td>
<td>Methyl acetate</td>
<td>1.7</td>
</tr>
<tr>
<td>This work</td>
<td>H-ZSM-5 (J64)</td>
<td>Ethyl acetate</td>
<td>0.688</td>
</tr>
<tr>
<td>This work</td>
<td>H-Mordenite (J59)</td>
<td>Ethyl acetate</td>
<td>0.136</td>
</tr>
<tr>
<td>This work</td>
<td>H-EU-1 (J87)</td>
<td>Ethyl acetate</td>
<td>0.291</td>
</tr>
<tr>
<td>[32]</td>
<td>DVB-4</td>
<td>Ethyl acetate</td>
<td>1.29</td>
</tr>
<tr>
<td>[32]</td>
<td>IR-120</td>
<td>Ethyl acetate</td>
<td>1.01</td>
</tr>
<tr>
<td>[32]</td>
<td>DVB-20</td>
<td>Ethyl acetate</td>
<td>0.77</td>
</tr>
<tr>
<td>[23]</td>
<td>Phenol-formaldehyde resin</td>
<td>Ethyl acetate</td>
<td>2.3</td>
</tr>
<tr>
<td>[43]</td>
<td>H-ZSM-5</td>
<td>Ethyl acetate</td>
<td>0-1.262\textsuperscript{a}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Calculation based on the assumption that they used 1 g of H-ZSM-5 in 10 cm\textsuperscript{3} of water
acetate. This behaviour is analogous to that of a strongly cross-linked ion-exchange resin and is probably due to the zeolite structure imposing restraints on the internal motions of the charged transition state. H-ZSM-5 was found to behave like a lightly cross-linked ion-exchange resin and no decrease in its catalytic efficiency was observed when ethyl acetate was used instead of methyl acetate. This fact was taken to suggest that the catalytic activity of ZSM-5 is associated with acid sites at the intersection of the 10 T-atom ring channels. Zeolites H-EU-1, H-ZSM-5 and H-Mordenite did not catalyse the hydrolysis of ethyl benzoate. This is probably due to the size of ethyl benzoate relative to that of the zeolite channels. Although it is difficult to relate the effects of different zeolite structures to their catalytic activity the experimental results suggested that a significant proportion of Brønsted acid sites in H-Mordenite are situated at the 8 T-atom channels. The catalytic activity observed for H-EU-1 indicates that the minimum diameter of the entry ports is at least 4.7 Å. The efficiencies for ester hydrolysis obtained for H-ZSM-5, H-Mordenite and H-EU-1 are similar to the literature values for cation exchange resins.
4.8 Use of Ester Hydrolysis to Characterise 'Inorganic'-ZSM-5

4.8.1 Introduction

The work described so far has shown that the catalytic activity of ZSM-5 for the hydrolysis of ethyl acetate in the aqueous phase is associated with the hydrophilic acid sites. These hydrophilic centres are associated with protons that are required to balance the anionic charge of tetrahedrally coordinated framework aluminium. The ratio of the amount of aluminium associated with the zeolite, relative to that associated with amorphous gel material, can be estimated from the percentage crystallinity of the mixture. This in turn can be estimated from the areas of the X-ray powder diffraction peaks. As catalytic activity is associated with the zeolite phase, and not the amorphous gel, then provided that the zeolite can sorb the organic it should be possible to correlate the degree of crystallinity of a zeolite with their efficiency to catalyse organic reactions. It was decided to try to correlate the degree of crystallinity of the series of inorganic ZSM-5 materials with their catalytic activity for the hydrolysis of ethyl acetate.

4.8.2 Experimental

The synthesis of the 'inorganic'-ZSM-5 series is discussed in detail in section 3.4. The materials used and the experimental procedure for ester hydrolysis are given in section 4.2. Details of the methods used to prepare the acid form of the zeolites are also given in section 4.2 whilst the treatment of results is described in section 4.3. The zeolites were converted to the acid form by treatment with hydrochloric acid. No calcination stage was required as the zeolite channels did not contain any organic molecules.
4.8.3 Results and Discussion

The experimental results given in Table 4.16 show that there are marked differences in the efficiency of acid forms of 'inorganic'-ZSM-5 to catalyse the hydrolysis of ethyl acetate at 60°C. This large variation in efficiency from 0.17-1.0 cannot be attributed to pretreatment method used as this was kept constant. Nor can it be due to different degrees of cation exchange as XRF spectroscopy indicated that, within an instrumental error of 4%, there was complete removal of sodium from the gel + zeolite by ion-exchange. The reason for this variation in efficiency is amorphous material that co-exists with the zeolite phase in the product. The efficiency of a zeolite is calculated assuming that each aluminium present in the product can act as a Brønsted acid site and can catalyse the ester hydrolysis reaction. Von Ballmoos [57] has shown that the Si/Al ratio of amorphous gel is typically 3-4 and clearly large amounts of amorphous material will result in significantly reduced efficiencies. The presence of either amorphous silica or crystalline silicate phases such as magadiite will lower the specific rate observed but will leave the efficiency unchanged.

A plot of efficiency against the $\text{SiO}_2/\text{Al}_2\text{O}_3$ of the original gel is given in Figure 4.12. The curve shows similarity to that in Figure 3.15 in which the ZSM-5 crystallinity is plotted against the $\text{SiO}_2/\text{Al}_2\text{O}_3$ of the initial mixture. Although the % crystallinity decreases with increase in $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio (for ratios > 60) because of the presence of amorphous silica or crystalline silicates the efficiency remains constant. The low efficiency observed when $\text{SiO}_2/\text{Al}_2\text{O}_3 = 150$ is probably due to partial blockage of the
Table 4.16  Rates of hydrolysis of ethyl acetate using the acid form of inorganic ZSM-5

<table>
<thead>
<tr>
<th>Code</th>
<th>Al per unit cell</th>
<th>ZSM-5 Crystallinity (%)</th>
<th>Rate Constant (k) $10^4 \times k$ (min$^{-1}$ g$^{-1}$)</th>
<th>$k_{ZH}$ min$^{-1}$ M$^{-1}$</th>
<th>Efficiency q</th>
</tr>
</thead>
<tbody>
<tr>
<td>J55</td>
<td>8.829</td>
<td>32</td>
<td>2.61</td>
<td>0.034</td>
<td>0.171</td>
</tr>
<tr>
<td>J52</td>
<td>8.015</td>
<td>77</td>
<td>5.85</td>
<td>0.084</td>
<td>0.421</td>
</tr>
<tr>
<td>J47</td>
<td>7.412</td>
<td>75</td>
<td>8.07</td>
<td>0.126</td>
<td>0.628</td>
</tr>
<tr>
<td>J64</td>
<td>6.927</td>
<td>79</td>
<td>8.30</td>
<td>0.138</td>
<td>0.688</td>
</tr>
<tr>
<td>J45</td>
<td>6.716</td>
<td>85</td>
<td>8.63</td>
<td>0.148</td>
<td>0.741</td>
</tr>
<tr>
<td>J72</td>
<td>5.373</td>
<td>72</td>
<td>6.36</td>
<td>0.137</td>
<td>0.683</td>
</tr>
<tr>
<td>J70</td>
<td>5.080</td>
<td>86</td>
<td>8.36</td>
<td>0.184</td>
<td>0.918</td>
</tr>
<tr>
<td>J71</td>
<td>3.051</td>
<td>73</td>
<td>5.36</td>
<td>0.203</td>
<td>1.013</td>
</tr>
<tr>
<td>J46</td>
<td>2.948</td>
<td>59</td>
<td>4.96</td>
<td>0.194</td>
<td>0.970</td>
</tr>
<tr>
<td>J48</td>
<td>2.016</td>
<td>43</td>
<td>2.07</td>
<td>0.114</td>
<td>0.591</td>
</tr>
</tbody>
</table>
Figure 4.12 Efficiency of H-ZSM-5 for the hydrolysis of ethyl acetate against the reaction mixture SiO$_2$/Al$_2$O$_3$.

Figure 4.13 Efficiency of H-ZSM-5 for the hydrolysis of ethyl acetate against the aluminium content of H-ZSM-5.
entrances to the ZSM-5 channels by magadiite or other silicate phase.

Figures 4.12 and 4.13 show that there is a sharp decrease in efficiency when the SiO$_2$/Al$_2$O$_3$ of the reactant gel is less than 60. This is also observed when the % crystallinity is plotted against the SiO$_2$/Al$_2$O$_3$ of the reactant gel. A decrease in SiO$_2$/Al$_2$O$_3$ gives products that contain significant amounts of amorphous material. Extrapolation of the linear plot in Figure 4.13 beyond approximately 8 aluminium per unit cell is not possible as the mordenite formed is less efficient than ZSM-5 as a catalyst for the hydrolysis of ethyl acetate. The anomalous low crystallinity of sample J72, clearly apparent in Figure 3.8, is consistent with its low efficiency (Figure 4.13). The reason for the large amorphous content of sample J72 is unknown.

Namba et al [43] claim that amorphous silica-alumina can act as a catalyst for the hydrolysis of ethyl acetate. However the correlation between the crystallinity measurements and the correspondent efficiencies show no evidence to support this view, and it appears that catalysis by amorphous alumino-silicate material is very much less than that by zeolites.

The experimental results are consistent with the homogenous distribution of acid sites in H-ZSM-5 put forward by other research workers [48,52,53] and is supported by research reported elsewhere in this thesis. The observed variation in efficiencies is simply due to the amount of amorphous material that co-exists with 'inorganic'-ZSM-5.
4.8.4 Conclusions

The ability of the acid form of 'inorganic'-ZSM-5 to catalyse the hydrolysis of ethyl acetate at 60°C has been shown. Large variations in the efficiency of the H-ZSM-5 materials were attributed to the presence of significant quantities of amorphous alumino-silicate material. The rate of hydrolysis of ethyl acetate could be used to detect the presence of amorphous material and to estimate the quantity present. The experimental results correlated well with the degree of crystallinity of the product. It was found that the efficiency of the acid 'inorganic'-ZSM-5 materials made from reaction mixtures, with SiO_2/Al_2O_3 > 60 was approximately unity. However, large amounts of magadiite in the product would appear to block the entry ports to the ZSM-5 channels and reduce the observed catalytic activity. More aluminous H-ZSM-5 materials were found to contain significant amounts of amorphous alumino-silicate material. There is no evidence to support the claim made by Namba et al [43] that amorphous silica-alumina can act as a catalyst for the hydrolysis of ethyl acetate. The experimental results obtained with the acid form of 'inorganic'-ZSM-5 are concordant with a homogenous acid strength distribution.
Chapter 4 - References


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and K.J. Williams  
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5.1 Introduction

It was stated in Chapter 2 that there is no single ideal technique that will completely characterize a solid catalyst. The use of a single technique to characterize an acid zeolite is insufficient, and the results obtained are more likely to be wrongly interpreted if they are unsupported by other data. Thus a second technique was required to complement the ester hydrolysis work. An ion-exchange procedure, similar to that developed by Breck and Skeels [1] was used to measure the zeolite acidity. In this the acid zeolite is treated with a concentrated solution of sodium chloride and the acid species released are determined by potentiometric titration with sodium hydroxide. The procedure has many advantages; it is quick, requires little sample, and its chemistry has already been studied [2-4]. In addition, because the hydrated radius of a sodium ion (2.76 Å) [5] is much less than the minimum kinetic diameter of methyl acetate and ethyl acetate (4.7 Å), the technique should be able to determine whether a lack of catalytic activity shown by an acid zeolite, is due to steric restrictions or a lack of Brönsted acidity.

It was suggested in section 4.5 that the rate of an ester hydrolysis reaction catalysed by an acid zeolite, was directly proportional to the concentration of Brönsted acid sites available to the reactant ester. However it is not
possible to determine from the ester hydrolysis results alone whether Brönsted acid or Lewis acid sites are catalytically active.

Both types of acidity have received considerable attention since 1949 when Barrer [6] first prepared an acid zeolite by heating ammonium exchanged forms of certain zeolites in air (see section 1.6). The reactions that are associated with this type of procedure are given in equations 5.1-5.3. Equation 5.2 is referred to as the deammoniation stage and shows the formation of a classical Brönsted acid site (represented more fully by equation 5.3) that follows the oxidative removal of ammonia.

\[
\text{Na-Z + NH}_4^+ (aq) \rightleftharpoons \text{NH}_4^- Z + \text{Na}^+ (aq)
\] (5.1)

\[
\begin{array}{c}
\text{O} \\
\text{Al} \\
\text{O} \\
\text{Si} \\
\text{O}
\end{array}
\rightarrow_{\text{heat}}
\begin{array}{c}
\text{O} \\
\text{Al} \\
\text{O} \\
\text{Si} \\
\text{O}
\end{array} + \text{NH}_3 + \begin{array}{c}
\text{O} \\
\text{Al} \\
\text{O} \\
\text{Si} \\
\text{O}
\end{array}
\] (5.2)

\[
\begin{array}{c}
\text{O} \\
\text{Al} \\
\text{O} \\
\text{Si} \\
\text{O}
\end{array} \rightleftharpoons \begin{array}{c}
\text{O} \\
\text{Al} \\
\text{O} \\
\text{Si} \\
\text{O}
\end{array} + \text{H}_2\text{O}
\] (5.3)

The position of the equilibrium in equation 5.3 depends on the acidity of the site. For example, if the zeolite acid is a strong Brönsted acid the equilibrium will lie over to the left; for a weak acid it will lie to the right. Uytterhoeven et al [7] have shown from infra-red spectroscopy studies that equation 5.2 is reversible at room temperature, and that the presence of ammonia caused the equilibrium to lie over to the left. Barrer and Klinowski [3] thought that it seemed reasonable to assume that a similar reaction should occur in the presence of water,
i.e. the equilibrium of equation 5.3 would lie to the left if the zeolite came into contact with water.

Uytterhoeven et al also found that the deammoniation stage was accompanied by dehydroxylation (see equation 5.4) when the ammonium forms of zeolites X and Y were heated above 290°C. Bolton and Lanewala [8] found that although NH₄-Y could be completely deammoniated at 375°C, 25% dehydroxylation had occurred. Higher deammoniation temperatures resulted in more extensive dehydroxylation. The mechanisms by which dehydroxylation occurs have been the subject of much debate. Initial studies using infra-red spectroscopy and ion-exchange capacities [7,8] supported the mechanism given in equation 5.4 which was first proposed by Rabo et al [9]:

\[
2 \begin{array}{c}
\text{Al} \\
\text{Si}
\end{array} \rightarrow \text{H}_2\text{O} + \begin{array}{c}
\text{Al} \\
\text{Si}
\end{array} + \begin{array}{c}
\text{Al} \\
\text{Si}
\end{array}
\]

Equation 5.4 implies that dehydroxylation of a zeolite would result in up to 50% loss of ion-exchange capacity. This was confirmed [8] for an ammonium exchanged zeolite Y with SiO₂/Al₂O₃ = 5.0, which was calcined at 575°C. No loss of crystallinity was observed due to dehydroxylation which was found to occur at lower temperatures. Partial reconstitution of the exchanged sites was observed when zeolite Y was slowly cooled from 600°C in a nitrogen atmosphere that was saturated with water and ammonia.
Barrer and Klinowski [3] thought that a reaction which generated $^+\text{Si}$ was unlikely and that its stability in liquid water was even more improbable. They carried out a series of experiments on deammoniated mordenite using an ion-exchange procedure that was based on the fact that exchange with sodium chloride could be used to measure Brønsted acidity whilst exchange with sodium hydroxide gave a measure of the total acidity resulting from both Brønsted acid and Lewis acid sites. Their results showed that deammoniation of NH$_4$-mordenite at temperatures greater than 400°C resulted in the loss of framework aluminium and the formation of the following hydroxo-aluminium species: AlOOH, AlO$^+$, Al(OH)$^{2+}$ and Al$^{3+}$. These species can all act as Lewis acids and quantum mechanical calculations [10] have shown that their strength decreases in the order: Al$^{3+} >$ Al(OH)$^{2+} >$ AlO$^+ >$ AlOOH. The following reactions were postulated by Barrer and Klinowski [3] in order to explain their results:

\[
\begin{align*}
\text{H}_3\text{O}^+ \quad &\text{Si} \quad \text{O} \quad \text{Al} \quad \text{O} \quad \text{Si} \quad \text{H} \\
&\text{Si} \quad \text{O} \quad \text{Si} \\
&\text{Si} \\
\text{H}_2\text{O} \rightarrow 4 \quad &\text{Si} \quad \text{OH} \quad \text{AlOOH} \quad (5.5)
\end{align*}
\]

\[
\begin{align*}
\text{HO} \\
\text{A} \quad \text{Si} \\
\text{Si} \\
\text{AlOOH} \rightarrow &\quad \text{Al} \quad \text{O} \quad \text{Si} \quad \text{H} \\
&\text{Al} \quad \text{Si} \quad [\text{Al(OH)}_2]^+ \quad (5.6)
\end{align*}
\]
If reactions 5.5-5.8 are combined together, the result is:

$$4\left[ \begin{array}{c} \text{Al} \\ \text{Si} \end{array} \right] + [\text{Al(OH)}_2]^+ \rightarrow 3\left[ \begin{array}{c} \text{Al} \rightarrow \text{Si} \end{array} \right] + \text{Al}^3+ + 4\left[ \begin{array}{c} \text{Si} \rightarrow \text{OH} \end{array} \right]$$

Equation 5.9 accounts for dehydroxylation of an acid zeolite so that only 75% of the initial ion-exchange capacity is retained.

Additional reactions have been postulated by Barrer and Klinowski [3] and Kuhl [11] to account for complete dehydroxylation. Further information about evidence for the formation of hydroxyl nests (see equation 5.5) [12] and the loss of framework aluminium that accompanies dehydroxylation [13] may be found in the literature [14].

The changes in population of Brönsted acid sites and Lewis acid sites as a function of calcination temperature are found to be dependant on the zeolite structure. Ward [15] found that for zeolite Y, Lewis acidity is generated by the loss of Brönsted acidity. The latter was found to be constant for zeolites calcined at 350-550°C. Barrer and Klinowski [3] found that for mordenite,
both Brønsted acidity and Lewis acidity decrease together (although at different rates) when NH$_4$-mordenite is heated at temperatures greater than 400°C.

The effect of calcination temperature on the relative populations of Brønsted acid sites and Lewis acid sites has been studied by Skeels and co-workers for zeolites Y, ZSM-5 and mordenite [1,2]. Although they ion-exchanged acid zeolites with a concentrated solution of sodium chloride only, they were able to measure both Brønsted and Lewis acidity by exploiting the fact that the pH values which contain hydronium ions are typically nearly two orders of magnitude greater than those which contain a similar concentration of hydroxoaluminium cations. Their results showed that thermal treatment of NH$_4$-Y produced hydroxoaluminium cations whilst thermal treatment of NH$_4$-mordenite produced mainly hydronium ions, although hydroxoaluminium cations contributed 1/3 of the total acidity. The type of acidity obtained for H-ZSM-5 was found to be dependant on whether the zeolite was treated with NH$_4$Cl or HCl solutions.

However, work carried out by Elliot [4] using the same procedure as Skeels and co-workers cast doubt on the validity of the technique as a means of obtaining accurate quantitative determinations of the molar H$^+$/Al ratios of H-ZSM-5. It was found that the amount of acidity measured from titrations of the filtrate was dependant on the type of salt solution used. The acidity measured for H-ZSM-5 decreased in the following order CsCl > KCl > NaCl > LiCl. These results correlate
well with the ion-exchange selectivity of ZSM-5 for hydronium and alkali metal ions [16]. The acidity measured was also found to be dependant on the concentration of the solution used. Direct titrations of the zeolite slurry with base were very difficult to do as well as being very time consuming. Nevertheless the work showed that the technique could be used as a guide to the amount of Bronsted acidity in an acid zeolite.

5.2 Experimental

5.2.1 Materials

In addition to those materials listed in section 4.2, the following materials were used:

<table>
<thead>
<tr>
<th>Material</th>
<th>Source</th>
<th>Grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium chloride</td>
<td>Fisons Ltd.</td>
<td>SLR</td>
</tr>
<tr>
<td>Caesium chloride</td>
<td>BDH Ltd.</td>
<td>Analar</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>BDH Ltd.</td>
<td>Convol</td>
</tr>
</tbody>
</table>

5.2.2 Determination of Zeolite Acidity

The experimental technique that was used to measure the acidity of zeolites is similar to that developed by Skeels and co-workers [1,2].

Zeolite samples were equilibrated with water vapour by standing over saturated sodium chloride solution at 25°C (p/p° = 0.753). Approximately 0.3 g of zeolite was accurately measured in a 60 cm³ plastic bottle. To this was added 50 cm³ of 5 M sodium chloride solution. A stirrer bar was added and the bottle top was screwed on. The slurry was then left stirring overnight at room temperature to equilibrate. The
zeolite solid was filtered off and the filtrate plus washings placed in a modified 150 cm\(^3\) plastic bottle. The bottle top was modified so that it could be fitted with a pH electrode and a nitrogen leak. An opening was also required so that additions of base to the filtrate could be made. The filtrate was titrated with 0.01 M of NaOH solution to a pH of about 10. This had to be done under an inert nitrogen atmosphere to prevent the ingress of carbon dioxide. Changes in pH were monitored by an EIL combination pH electrode type 1180/200/UKP connected to a Pye Unicam model 290 pH meter.

5.2.3 Treatment of Results

The raw experimental data is in the form of base added against pH of the solution. The amount of acid present in the filtrate is initially expressed by the amount of base required for neutralisation. This is converted from base added (cm\(^3\)) to milli-equivalents of acid per gram of anhydrous zeolite (meg./g) by using equation 5.10,

\[
x = \frac{V_b M_b}{W_z} \times 10^{-3} \times 1000
\]

(5.10)

where \(x\) is the measurement of acid in meg./g and is obtained from the titration of \(V_b\) cm\(^3\) of base, of molarity \(M_b\), against the filtrate solution. The filtrate solution is obtained by the ion-exchange of \(W_z\) grams of anhydrous zeolite with a concentrated solution of sodium chloride.
5.3 Acidity Measurements by the Filtrate Titration Technique

5.3.1 Introduction

The aims of the work described in this section were to obtain a measure of the acidity of H-ZSM-5 by using the filtrate titration technique and to compare the experimental results with both literature values and the ester hydrolysis results.

5.3.2 Experimental

The synthesis of the zeolites that were used in this study is described in Chapter 3. The materials used and the experimental procedure for the hydrolysis of ethyl acetate is given in section 4.2. The zeolites were converted to the acid form by the use of the procedures described in section 4.2. The treatment of results for the ester hydrolysis work is given in section 4.3. The filtrate titration technique is described in section 5.2.

5.3.3 Results and Discussion

An example of an experimental potentiometric curve for H-ZSM-5 is shown in Figure 5.1. The shape of the curve matches those in the literature and shows that the zeolite contains both Brönsted acid sites and Lewis acid sites. There are two equivalence points in the curve. The first point corresponds to the neutralisation of acid that was produced as the result of sodium exchange at Brönsted acid sites. The second equivalence point is due to hydroxoaluminium cations which have been ion-exchanged and hydrolysed to produce acid and a soluble aluminium species [2]. Elliot [4] showed by analysis for aluminium that
Figure 5.1 Potentiometric titration curve for H-ZSM-5 (H54) at 25°C. a is the strong acid equivalence point and is measured of Brönsted acidity. b is the weak acid equivalence point and is due to hydroxo-aluminium cations. The zeolite had been calcined at 800°C for 24 hours to remove the intracrystalline organic material before being treated with hydrochloric acid.
these soluble aluminium species are indeed present in filtrate solutions.

The effect of using different salt solutions with which to measure the acidity of H-ZSM-5 was investigated by Elliot [4]. This was also studied in this work and the potentiometric curves that were obtained are shown in Figure 5.2. The experimental results obtained are summarised in Table 5.1. These results show that the salt solution used effects both the molar \( \text{H}^+ / \text{Al} \) ratios as well as the initial pH of the filtrate solution. Both initial pH values obtained are similar to the calculated values. However, there is nearly an order of magnitude difference between the two initial pH values and it is clear that these pH values are dependent on the salt solution used. The reason why the NaCl solution gives a lower initial pH than the CsCl solution, despite containing less acid

<table>
<thead>
<tr>
<th>Salt Solution</th>
<th>Titrated acidity (meg. g(^{-1}))</th>
<th>Molar ( \text{H}^+ / \text{Al} )</th>
<th>Observed initial pH</th>
<th>Calculated(^a) initial pH</th>
<th>Efficiency(^b) molar ( \text{H}^+ / \text{Al} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 M sodium chloride</td>
<td>0.615</td>
<td>0.55</td>
<td>1.93</td>
<td>2.40</td>
<td>1.16</td>
</tr>
<tr>
<td>1 M caesium chloride</td>
<td>0.700</td>
<td>0.63</td>
<td>2.71</td>
<td>2.40</td>
<td>1.02</td>
</tr>
</tbody>
</table>

\(^a\) calculated pH is obtained by assuming that each aluminium species that is detected by XRF spectroscopy will undergo ion-exchange with the salt solution. The relevant XRF data are given in section 3.3.

\(^b\) efficiency refers to the H-ZSM-5 (H53) catalysed hydrolysis of ethyl acetate at 60°C.
Figure 5.2 Potentiometric titration curve for H-ZSM-5 (H53) that had been exchanged with 5 M NaCl (O) and 1 M CsCl (●) solutions. The zeolite had been calcined at 60°C for 72 hours before being treated with hydrochloric acid.
could be due to activity coefficient effects arising from

(i) the difference in salt concentrations (different ionic strength), and

(ii) the difference in cation.

Both titration curves show that H-ZSM-5 (H53) contains only Brönsted acid sites. The measured acidity of H-ZSM-5 (H53) was 18% higher when 1 M CsCl solution was used instead of 5 M NaCl solution. Chu and Dwyer [17] have shown that the selectivity sequence for ZSM-5 is $\text{Cs}^+ > \text{H}_3^+ \text{O} >> \text{Na}^+$ and this accounts for the observed results.

The molar $\text{H}^+$/Al ratios given in Table 5.1 are calculated by assuming that each aluminium species detected by XRF spectroscopy is capable of ion-exchange with the salt solution. There are two reasons why the experimental values are not equal to unity. Firstly, the assumption that each aluminium is capable of ion-exchange with the concentrated salt solution used requires each aluminium to be situated at a Brönsted acid site. Any aluminium present as unreacted gel, Lewis acid or soluble hydroxo-aluminium species will lower the observed molar $\text{H}^+$/Al ratio. Secondly, even if all the aluminium is situated at Brönsted acid sites not all will undergo ion-exchange with the salt solution. The extent of ion-exchange is dependent on both the strength and type of salt solution used. It is considered that the latter explanation is of more importance in the interpretation of the molar $\text{H}^+$/Al values given in Table 5.1.
A comparison of these experimental results with those for the most similar sample used by Skeels and Flank [2], shows that the molar \( H^+/Al \) ratios obtained in this work are slightly higher. This is due to the more concentrated solution of sodium chloride used (5 molar as opposed to 3.4 molar) and the higher ratio of salt solution (moles) per gram of zeolite.

The experimental results discussed in section 4.5 show that the rate of hydrolysis of ethyl acetate is directly proportional to both the weight of H-ZSM-5 used and the aluminium content per unit weight of zeolite. These results are consistent with catalysis by zeolitic Brønsted acid sites. However, it was impossible to prove this theory by ester hydrolysis work alone. If the hydrolysis of esters is indeed catalysed by zeolitic Brønsted acid sites then the observed rate of hydrolysis should be directly proportional to the Brønsted acidity measured by the filtrate titration technique.

To test this the catalytic activity of a series of H-ZSM-5 zeolites for the hydrolysis of ethyl acetate in aqueous solution was determined and compared with their Brønsted acidity as measured by the filtrate titration technique. The zeolites chosen were of comparable crystallinity and each was calcined for 72 hours at 600°C before being treated with \( \text{NH}_4\text{Cl} \) and subsequently calcined at 400°C. A plot of the rate constant for the hydrolysis of ethyl acetate at 60°C against Brønsted acidity is given in Figure 5.3 and the numerical results are given in Table 5.2. The results show that the rate of hydrolysis of ethyl acetate is
Figure 5.3  Rate constant (k) for the H-ZSM-5 catalysed hydrolysis of ethyl acetate at 60°C against Brønsted acidity.
proportional to the number of Brønsted acid sites. The best fit straight line obtained had the equation:

\[ k = 7.62(\pm0.5) \times 10^{-4} x - 0.12(\pm0.2) \]  \hspace{1cm} (5.11)

where \( k \) is the first order rate constant for the hydrolysis of ethyl acetate at 60°C (min\(^{-1}\) g\(^{-1}\)) and \( x \) is the Brønsted acidity (meq. g\(^{-1}\)) that was measured by the filtrate titration technique. The line passes through the origin as expected. The weak acidity that was also measured does not correlate with the rate of hydrolysis of ethyl acetate. These results clearly show that Brønsted sites are the catalytic sites for the zeolite catalysed hydrolysis of ethyl acetate.

**Table 5.2** Comparison of measured acidity and the first order rate constant for the hydrolysis of ethyl acetate at 60°C by H-ZSM-5

<table>
<thead>
<tr>
<th>Code</th>
<th>Strong acidity (meq.g(^{-1}))</th>
<th>Weak acidity (meq.g(^{-1}))</th>
<th>Molar H(^+)/Al(^{a})</th>
<th>Rate Constant (k) (10^4 x k) (min(^{-1})g(^{-1}))</th>
<th>Efficiency molar (H(^+)/Al)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T80</td>
<td>0.426</td>
<td>0.010</td>
<td>0.29</td>
<td>3.21</td>
<td>0.222</td>
</tr>
<tr>
<td>T25</td>
<td>0.322</td>
<td>0.014</td>
<td>0.27</td>
<td>2.27</td>
<td>0.193</td>
</tr>
<tr>
<td>T28</td>
<td>0.306</td>
<td>0.065</td>
<td>0.23</td>
<td>2.06</td>
<td>0.236</td>
</tr>
<tr>
<td>T83</td>
<td>0.213</td>
<td>0.018</td>
<td>0.28</td>
<td>1.62</td>
<td>0.212</td>
</tr>
<tr>
<td>T38</td>
<td>0.200</td>
<td>0.030</td>
<td>0.28</td>
<td>1.44</td>
<td>0.198</td>
</tr>
<tr>
<td>T24</td>
<td>0.160</td>
<td>0.033</td>
<td>0.30</td>
<td>1.06</td>
<td>0.178</td>
</tr>
</tbody>
</table>

\(^{a}\) Based on strong acidity
A comparison of the data given in Tables 5.1 and 5.2 shows that the efficiency/molar \((H^+ / Al)\) ratio obtained for H-ZSM-5 (H53) treated with 5 M NaCl is significantly higher than corresponding values given in Table 5.2. Clearly equation 5.11 does not apply to H-ZSM-5 (H53). The low efficiency/molar \((H^+ / Al)\) ratios obtained for the zeolites in Table 5.2 suggests that the preparation processes used resulted in extensive dehydroxylation and it is possible that the hydroxoaluminium cations formed cause the partial blockage of some zeolite channels, i.e. the effective channel diameter is reduced so that its size is greater than that of a hydrated sodium cation \((2.76 \text{ Å})\) but less than the minimum kinetic diameter of ethyl acetate \((4.7 \text{ Å})\).

5.3.4 Conclusions

The experimental results obtained are in accordance with the results of Skeels and Flank [2] and Elliot [4]. The potentiometric titration curve that was obtained for a H-ZSM-5 sample which had suffered extensive dehydroxylation and lattice degradation during calcination showed significant quantities of both Brønsted acid sites and Lewis acid sites. The measured acidity of H-ZSM-5 was found to be markedly dependant on the type of salt solution used. The experimental results could be explained by the ion exchange selectivity coefficients of ZSM-5 for \(\text{Cs}^+\), \(\text{Na}^+\) and \(\text{H}_3^+\text{O}\) ions [16,17]. The rate constant obtained for the H-ZSM-5 catalysed hydrolysis of ethyl acetate was found to be directly proportional to the Brønsted acidity measured by the titration method. No correlation was found between the rate constant and Lewis acidity and this was
taken as being clear evidence that the Brönsted acid sites are the catalytic sites for the hydrolysis of esters by zeolites.

5.4 Correlation between Brönsted Acidity of Acid Zeolites and their Ability to Catalyse the Hydrolysis of Ethyl Acetate

5.4.1 Introduction

The aim of the work described in this section was to determine if the catalysis of the hydrolysis of ethyl acetate by zeolites H-ZSM-5, H-EU-1, H-Mordenite and H-Ferrierite is affected by steric restrictions. This was achieved by a comparison of the catalytic activity of these zeolites with their Brönsted acidity.

5.4.2 Experimental

The synthesis of the zeolites that were used in this study is described in Chapter 3 and Appendix 1. The materials used and the experimental procedure for the hydrolysis of ethyl acetate is given in section 4.2. The zeolites were converted from the sodium form to the acid form by treatment with hydrochloric acid as described in section 4.2. The nature of the pretreatment used is given in Table 5.3. The treatment of results for the ester hydrolysis work is given in section 4.3. The filtrate titration technique is described in section 5.2.
Table 5.3 Preparation of acid zeolites from "as made" form

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>Code</th>
<th>Temperature (°C)</th>
<th>Time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-ZSM-5</td>
<td>T49</td>
<td>450</td>
<td>72</td>
</tr>
<tr>
<td>H-ZSM-5</td>
<td>J64</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H-Mordenite</td>
<td>J59</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H-Ferrierite</td>
<td>J68</td>
<td>450</td>
<td>72</td>
</tr>
<tr>
<td>H-EU-1</td>
<td>J87</td>
<td>450</td>
<td>72</td>
</tr>
</tbody>
</table>

5.4.3 Results and Discussion

The experimental results for both the Brönsted acidity of the acid zeolites and their efficiency as catalysts for the hydrolysis of esters is shown in Table 5.4. The filtrate titration technique shows that each sample of acid zeolite contains large amounts of Brönsted acid sites and thus each zeolite could be expected to catalyse the hydrolysis of esters.

As two preparative processes were used the zeolites can be categorised according to the procedure used. The first group, which consists of H-ZSM-5 (T49), H-Ferrierite (J68) and H-EU-1 (J87), have similar molar H⁺/Al ratios. This suggests that the acid forms of these zeolites have similar selectivity coefficients for sodium ions and that their Brönsted acid sites are equally accessible to sodium ions. Despite being less crystalline the second group which consists of H-ZSM-5 (J64) and H-Mordenite (J59) have molar H⁺/Al ratios similar to those obtained for samples in
the first group. This is because neither sample required a calcination treatment to remove intracrystalline organic molecules. The molar $H^+/Al$ ratio for H-Mordenite is slightly higher than that obtained for H-ZSM-5. This was expected as Chu and Dwyer [17] have shown that the selectivity coefficient of Na-Mordenite for hydronium ions is lower than that of Na-ZSM-5.

The molar $H^+/Al$ ratio that was obtained for H-Mordenite is lower than 0.601 which was the value for H-Mordenite obtained by Kuhl [11]. This is because of the different experimental techniques which were used. Kuhl repeatedly treated H-mordenite with 2M sodium chloride solution until no more acid was produced. Whilst this technique is superior to that used in this work it is very time consuming.

The remaining six columns in Table 5.4 show how the efficiency of the acid zeolites, as catalysts for the hydrolysis of esters in the liquid phase, correlates with their Brönsted acidity. This correlation is expressed in terms of the efficiency of the catalyst, relative to hydrochloric acid, divided by its Brönsted acidity (efficiency/molar ($H^+/Al$)). For the hydrolysis of methyl acetate it was found that the efficiency/molar ($H^+/Al$) ratio of H-mordenite is lower than the experimental values obtained for H-ZSM-5 and H-EU-1. This is perhaps because the Brönsted acid sites are situated in the 8 T-atom channels of mordenite and are accessible to sodium cations but not to the larger methyl acetate molecules. Alternatively, the 12 T-atom channels may be blocked so as to obstruct the access of the ester molecule. The efficiency/molar ($H^+/Al$) ratio obtained for H-EU-1
Table 5.4  Bronsted acidity of acid zeolites and their activity in catalysing
the hydrolysis of esters at 60°C

<table>
<thead>
<tr>
<th>Code</th>
<th>Bronsted acidity (meq.g⁻¹)</th>
<th>Molar H⁺/Al</th>
<th>Methyl Acetate Efficiency</th>
<th>Methyl Acetate Efficiency/molar (H⁺/Al)</th>
<th>Ethyl Acetate Efficiency</th>
<th>Ethyl Acetate Efficiency/molar (H⁺/Al)</th>
<th>Ethyl Benzoate Efficiency</th>
<th>Ethyl Benzoate Efficiency/molar (H⁺/Al)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T49</td>
<td>0.330</td>
<td>0.498</td>
<td>-</td>
<td>-</td>
<td>0.562</td>
<td>1.13</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>J64</td>
<td>0.601</td>
<td>0.500</td>
<td>0.668</td>
<td>1.34</td>
<td>0.688</td>
<td>1.38</td>
<td>0.003</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>J59</td>
<td>0.888</td>
<td>0.558</td>
<td>0.411</td>
<td>0.74</td>
<td>0.136</td>
<td>0.24</td>
<td>0.003</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>J68</td>
<td>0.866</td>
<td>0.577</td>
<td>-</td>
<td>-</td>
<td>0.005</td>
<td>&lt;0.01</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>J87</td>
<td>0.292</td>
<td>0.552</td>
<td>1.117</td>
<td>2.02</td>
<td>0.291</td>
<td>0.53</td>
<td>0.006</td>
<td>&lt;0.01</td>
</tr>
</tbody>
</table>
is higher than that of H-ZSM-5, and this indicates that the former contains a higher proportion of Brönsted acid sites which are catalytically active.

The efficiency/molar \((H^+/Al)\) ratios that were obtained for the hydrolysis of ethyl acetate catalysed by the two samples of H-ZSM-5 are very similar. This result was expected as the Brönsted acid sites in both samples are equally accessible to both sodium cations and the reactant ester molecule. The effect of different organic molecules that were used to make zeolite ZSM-5, on its efficiency as a catalyst and its Brönsted acidity are dealt with in more detail in section 6.4. The low efficiency/molar \((H^+/Al)\) values that were obtained for both H-Mordenite and H-EU-1 are a result of the low efficiency values obtained. The reason for this result is discussed in section 4.7.

The efficiency/molar \((H^+/Al)\) value for H-Ferrierite is 0.01. This value indicates a lack of catalytic activity by the acid zeolite. Similar values were obtained for every reaction carried out with ethyl benzoate. There are two possible reasons for the lack of catalytic activity shown by H-Ferrierite. The first is that the zeolite does not contain any Brönsted acid sites and the second is that ethyl acetate is too large and cannot enter the intra-crystalline channels of ferrierite. The results obtained from the filtrate titration technique clearly show that H-Ferrierite contains a lot of Brönsted acid sites. Therefore, the reason for its inactivity as a catalyst must be due to it being unable to sorb ethyl acetate molecules from aqueous solution.
The inactivity of H-ZSM-5, H-Mordenite and H-EU-1 as catalysts for the hydrolysis of ethyl benzoate is also due to these zeolites being unable to sorb ethyl benzoate molecules from aqueous solution.

5.4.4 Conclusions

The Brönsted acidity measurements that were carried out on H-ZSM-5, H-Mordenite, H-Ferrierite and H-EU-1 complement the ester hydrolysis work. The filtrate titration technique provides unambiguous evidence on whether a lack of catalytic activity shown by an acid zeolite is due to its inability to sorb an ester from the aqueous phase or to a lack of Brönsted acid sites. The combined results obtained from both techniques show that steric restrictions prevent H-Ferrierite from acting as a catalyst for the hydrolysis of ethyl acetate. Similar results were obtained with H-ZSM-5, H-Mordenite and H-EU-1 for the hydrolysis of ethyl benzoate. The correlation between catalytic activity and Brönsted acidity was expressed as efficiency/molar (H+/Al). These results showed that a higher proportion of Brönsted sites in H-EU-1 compared to H-ZSM-5 are catalytically active for the hydrolysis of methyl acetate. H-Mordenite had the lowest proportion of catalytically active Brönsted acid sites. This could be due to blocked 12 T-atom channels or the fact that 8 T-atom channels are too small to sorb methyl acetate. The molar H+/Al ratio that was obtained for H-Mordenite was slightly higher than that obtained for H-ZSM-5. This is because H-Mordenite has a higher selectivity coefficient for sodium cations than H-ZSM-5 [17].
Chapter 5 - References


[4] L. Elliot
Fourth Year Honours Project, University of Edinburgh, 1984.


[14] R.M. Barrer
"Zeolites and Clay Minerals as Sorbents and Molecular Sieves",


[16] P. Chu and F.G. Dwyer

[17] P. Chu and F.G. Dwyer
CHAPTER 6

Effect of Preparation Procedure on the Acidity and Catalytic Properties of High Silica Zeolites

6.1 Introduction

There are few papers in the literature that deal with the effect of preparation procedure on the acidity and catalytic properties of zeolites and most of these study the deammoniation of NH$_4$-Y \[1-3\]. The deammoniation of NH$_4$-mordenite has been studied by Barrer and Klinowski \[4\] and Kuhl \[5\]. Nayak and Choudhary \[6\] have published a detailed report on the effects of temperature, time period, heating rate and atmosphere for the deammoniation of NH$_4$-ZSM-5. Skeels and Flank \[7\] have carried out studies on the ion-exchange of Na-ZSM-5 with hydrochloric acid and ammonium chloride.

The importance of preparation procedure and its effect on the catalytic properties of H-ZSM-5 was realised early on in this work. Consequently, experimental results obtained from different samples of ZSM-5 are only compared if each sample has undergone the same pretreatment as the rest.

Since this subject is inadequately covered by the literature and because of its importance in this work, it was decided to carry out a thorough investigation into the effects of all the variables which are associated with the preparation of an acid zeolite.
6.2 Effect of Preparation Technique used on the Acidity and Catalytic Properties of H-ZSM-5

6.2.1 Introduction

The two most common methods of preparing acid zeolites are (i) treatment with acid and (ii) treatment with an ammonium salt. The latter procedure requires a thermal treatment stage to deammoniate the zeolite, and is used in the preparation of the acid forms of zeolites with low Si/Al ratios, e.g. zeolite Y. This is because treatment of aluminous zeolites with acid causes dealumination to occur. Barrer and Klinowski [4] found that a Na-mordenite with Si/Al = 5.6 released aluminium into external solutions of pH < 3.1. However the deammoniation stage (see equation 5.2) is often accompanied by dehydroxylation. Thus the catalytic properties of acid zeolites are dependant on the procedure used in their preparation. Skeels and Flank [7] showed that the acidity of H-ZSM-5 was dependant on the nature of its preparation. They found that H-ZSM-5 prepared by treatment with hydrochloric acid, contained only Brönsted acid sites whilst treatment with ammonium chloride followed by deammoniation gave both Brönsted and Lewis acid sites.

As both hydrochloric acid and ammonium chloride treatments were used extensively in the present work it was decided to investigate their effect on the acidity and catalytic properties of H-ZSM-5.
6.2.2 Experimental

The synthesis of ZSM-5 (H35) is described in section 3.3. A description of the materials used, experimental procedure and treatment of results for the hydrolysis of ethyl acetate is given in section 4.2 and 4.3. The experimental procedure for the filtrate titration technique is described in section 5.2.

The 'as made' zeolite was calcined at 600°C for 72 hours to remove intracrystalline organic material. The experimental procedures that relate to treatment with hydrochloric acid and ammonium chloride are described in section 4.2. In addition to this the acid treated samples of ZSM-5 (H35) were thoroughly washed by Soxhlet extraction. A sample of zeolite was placed in an extraction thimble which was then fitted to the Soxhlet extraction apparatus. This meant that the zeolite could be washed in freshly distilled water at 95°C for 24 hours.

6.2.3 Results and Discussion

The experimental results obtained by treating Na-ZSM-5 (H35) with either hydrochloric acid or ammonium chloride are given in Table 6.1. It is clear that neither procedure used resulted in the extraction of framework aluminium. The small differences that are observed in the Si/Al ratios are due to instrument error. No sodium was detected in any of the samples that had been converted to the acid form. The results show that repeated treatment with hydrochloric acid does not remove any framework aluminium. The low temperature that was used in this work when treating ZSM-5 with acid is important as Skeels and Flank [7] found that treatment
Table 6.1  Acidity and catalytic activity of H-ZSM-5 (H35) that has been treated with hydrochloric acid and ammonium chloride.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Si/Al</th>
<th>Brønsted acidity (meq.g⁻¹)</th>
<th>Molar H⁺/Al</th>
<th>Rate Constant (k) $10^4 x k$ (min⁻¹.g⁻¹)</th>
<th>$k_zH$</th>
<th>Efficiency</th>
<th>Molar (H⁺/Al)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>19.70</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>None</td>
<td>19.80</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td>19.80</td>
<td>0.467</td>
<td>0.58</td>
<td>6.00</td>
<td>0.150</td>
<td>0.750</td>
<td>1.29</td>
</tr>
<tr>
<td>HCl + wash</td>
<td>19.70</td>
<td>0.475</td>
<td>0.59</td>
<td>6.68</td>
<td>0.166</td>
<td>0.831</td>
<td>1.41</td>
</tr>
<tr>
<td>2 x (HCl + wash)</td>
<td>19.43</td>
<td>0.490</td>
<td>0.60</td>
<td>6.08</td>
<td>0.149</td>
<td>0.747</td>
<td>1.24</td>
</tr>
<tr>
<td>3 x (HCl + wash)</td>
<td>19.92</td>
<td>0.451</td>
<td>0.57</td>
<td>6.44</td>
<td>0.162</td>
<td>0.809</td>
<td>1.43</td>
</tr>
<tr>
<td>NH₄Cl + heat</td>
<td>19.61</td>
<td>0.381</td>
<td>0.44</td>
<td>5.19</td>
<td>0.120</td>
<td>0.590</td>
<td>1.34</td>
</tr>
</tbody>
</table>
of Na-ZSM-5 with 1M hydrochloric acid (10 cm$^3$ acid/g zeolite) at 95°C for 1 hour followed by washing and drying at 100°C caused the Si/Al ratio to increase from 23.52 to 26.52.

Although treatment with ammonium chloride does not alter the Si/Al ratio of the zeolite, the measured Brønsted acidity and catalytic efficiency are both lower than if the samples had been treated with hydrochloric acid. The results obtained from the filtrate titration technique and the ethyl acetate hydrolysis work both indicate that a ZSM-5 sample that had been treated with ammonium chloride will contain 19% less Brønsted acid sites than if it had been treated with hydrochloric acid. This loss of Brønsted acidity is due to the dehydroxylation of Brønsted acid sites (see equations 5.5-5.9) and has been reported elsewhere [4,5]. Elliot [8] used 8-hydroxyquinoline to complex with hydroxo-aluminium species and found that framework aluminium was only lost from samples which had been treated with ammonium chloride. Thus, although no change in the zeolite composition was observed when Na-ZSM-5 was treated with ammonium chloride, dehydroxylation of some of the Brønsted acid sites does occur when the NH$_4$-ZSM-5 is decomposed at 400°C.

The average efficiency of H-ZSM-5 (H35), prepared by the hydrochloric acid method, was 0.78 and is less than unity because of the calcination temperature that was used in its preparation. The average efficiency/molar (H$^+$/Al) that was obtained was 1.34 ± 0.09. This value was also obtained for the sample that was treated with ammonium chloride and suggests that although some dehydroxylation occurred it was not severe enough to cause blockage of the ZSM-5 channels.
6.2.4 Conclusions

Of the two procedures for preparing H-ZSM-5, treatment with hydrochloric acid is preferable to treatment with ammonium chloride. Both Brønsted acidity measurements and the catalytic activity of H-ZSM-5 (H35) indicate that treatment with ammonium chloride causes the loss of 19% of the original number of Brønsted acid sites. Although dehydroxylation occurs it is not severe enough for the Al species released to block the channels, although in the NH$_4$-ZSM-5 case it seems likely that some Al is lost from the framework to the channels. The Si/Al ratio of H-ZSM-5 (H35) remained unchanged even after three treatments with hydrochloric acid.

6.3 Effect of Deammoniation Conditions of NH$_4$-ZSM-5 on the Catalytic Properties of the Acid Form

6.3.1 Introduction

The effect of deammoniation conditions of NH$_4$-ZSM-5 on the acidity and catalytic properties of H-ZSM-5 is already documented. Skeels and Flank [7] found that the maximum zeolite acidity was measured when the samples were calcined at 400°C. Any increase in the deammoniation temperature above 400°C was found to result in dehydroxylation of Brønsted acid sites. However they did not give details about either the heating rate or the deammoniation period used. Nayak and Choudhary [6] have carried out a more thorough investigation into the effects of deammoniation conditions. Their results agree with those of Skeels and Flank in that they found that Brønsted acidity decreased with calcination temperature. Whilst they found that the heating rate did not cause any significant change in either the acid strength distribution or catalytic
properties of H-ZSM-5 they found appreciable effects due to the deammoniation period and atmosphere used.

Due to the fact that there are several variables associated with the deammoniation of NH$_4$-ZSM-5 it was decided to find the optimum temperature with which to deammoniate NH$_4$-ZSM-5.

6.3.2 Experimental

The synthesis of the zeolites that are studied in this work is described in Chapter 3. A description of the materials used, experimental procedure and treatment of results for the hydrolysis of ethyl acetate is given in sections 4.2 and 4.3.

The calcination conditions used to remove organic material varied. Samples T24 and T33 were both calcined at 600°C for 72 hours and sample P22 was calcined at 800°C for 24 hours. The experimental conditions which were used for the ion-exchange of Na-ZSM-5 with 1M ammonium chloride is described in section 4.2.

6.3.3 Results and Discussion

The effect of deammoniation temperature on the activity (k/k$_{400}$) of H-ZSM-5 as a catalyst for the hydrolysis of ethyl acetate in an aqueous solution is given in Figure 6.1. The optimum deammoniation temperature was found to be 400°C and the catalytic activity for each zeolite is given relative to this temperature. This enables the effect of the deammoniation temperature used to be studied for all three zeolites.

Figure 6.1 shows that the results correlate very well and indicate that the graph is applicable to any ZSM-5 sample. The shape of the graph shows that deammoniation is the dominant reaction
Figure 6.1 Catalytic activity \(k/k_{400}\) of H-ZSM-5 against deammoniation temperature. 

- \(\bigcirc\) = H-ZSM-5 (P22);
- \(\square\) = H-ZSM-5 (T24);
- \(\triangle\) = H-ZSM-5 (T33);
- \(\bullet\) = common to all three zeolites
from 200°C-400°C. No catalytic activity is observed at temperatures less than 200°C. Increase in temperature results in the loss of ammonia and the formation of Brønsted acid sites according to equation 5.2. The best fit line that was obtained for this portion of the graph has the equation:

\[
\frac{k_T}{k_{400}} = 0.494(\pm0.04)T - 100(\pm14)
\]  

(6.1)

where \(k_T\) and \(k_{400}\) are the experimental rate constants (min\(^{-1}\)g\(^{-1}\)) which were obtained for the H-ZSM-5 catalysed hydrolysis of ethyl acetate at 60°C in which the deammoniation temperatures were \(T\) (°C) and 400°C respectively.

The effects due to deammoniation and dehydroxylation were found to be equal at 400°C, with the latter dominant at higher temperatures. The experimental data that were obtained at these temperatures do not fit a straight line because there are several dehydroxylation mechanisms. These were postulated by Barrer and Klinowski [4] (see equations 5.4-5.9). The results indicate that no catalytic activity would be observed at deammoniation temperatures greater than 850°C.

The experimental results are similar to those of Skeels and Flank and this indicates that the experimental procedures are also similar.

**6.3.4 Conclusions**

The optimum decomposition temperature was found to be 400°C. Deammoniation was found to occur at 200°C and a linear correlation was found to exist between the catalytic activity and the
deammoniation temperature over the range 200-400°C. This suggests that only deammoniation is dominant. At 400°C the effects due to deammoniation and dehydroxylation are equal with the latter dominant at temperatures greater than 400°C.

6.4 Effect of Organic Template used to make ZSM-5 on the Acidity and Catalytic Properties of H-ZSM-5

6.4.1 Introduction

The aim of the work described in this section was to investigate whether there were any mass transfer effects occurring at the zeolite/water interface. To do this six samples of ZSM-5 were prepared with different crystal morphologies. The zeolites were converted from the 'as made' to the acid form by identical methods. The Brønsted acidity of H-ZSM-5 was then compared with its efficiency, relative to hydrochloric acid, as a catalyst for the hydrolysis of ethyl acetate in water at 60°C. If there were effects due to mass transfer or the diffusional path lengths then the efficiency/molar (H⁺/Al) ratio obtained would be altered.

6.4.2 Experimental

The synthesis of the zeolites used in this work is described in Chapter 3. The materials used, experimental procedure and treatment of results for the hydrolysis of ethyl acetate is given in sections 4.2 and 4.3. The experimental procedure for the filtrate titration technique is described in sections 5.2.

The 'as made' zeolites were calcined at 400°C for 72 hours before being treated with hydrochloric acid according to the procedure described in sections 4.2. Sample T88 was not treated with hydrochloric acid as the acid form was obtained by calcination only.
Table 6.2  Effect of morphology on the acidity and catalytic properties of H-ZSM-5

<table>
<thead>
<tr>
<th>Code</th>
<th>Organic Used</th>
<th>Crystal Size (μm)</th>
<th>Brønsted Acidity (meq. g⁻¹)</th>
<th>Molar H⁺/Al</th>
<th>Rate Constant (k) 10⁴ x k (min⁻¹ g⁻¹)</th>
<th>kZH</th>
<th>Efficiency Molar (H⁺/Al)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T49</td>
<td>TPA Br</td>
<td>1 x 1 x 1</td>
<td>0.369</td>
<td>0.556</td>
<td>4.77</td>
<td>0.144</td>
<td>0.719</td>
</tr>
<tr>
<td>T88</td>
<td>TPA OH</td>
<td>10 x 5 x 5</td>
<td>0.004</td>
<td>0.007</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>P40</td>
<td>Piperazine</td>
<td>0.5x0.5x0.5</td>
<td>0.448</td>
<td>0.599</td>
<td>6.72</td>
<td>0.180</td>
<td>0.898</td>
</tr>
<tr>
<td>H54</td>
<td>Hexanediol</td>
<td>2 x 1 x 1</td>
<td>0.658</td>
<td>0.613</td>
<td>7.36</td>
<td>0.137</td>
<td>0.686</td>
</tr>
<tr>
<td>J70</td>
<td>Hexanediol</td>
<td>2 x 1 x 1</td>
<td>0.557</td>
<td>0.632</td>
<td>7.73</td>
<td>0.175</td>
<td>0.877</td>
</tr>
<tr>
<td>J84</td>
<td>Homopiperazine</td>
<td>0.5x0.5x0.5</td>
<td>0.651</td>
<td>0.607</td>
<td>6.56</td>
<td>0.147</td>
<td>0.735</td>
</tr>
</tbody>
</table>
The experimental results in Table 6.2 show how the organic used in the synthesis of zeolite ZSM-5 affects the Brønsted acidity and catalytic properties of H-ZSM-5. As expected there are large differences between the morphologies of the products with sample T88 containing the largest crystals. The results that are obtained from sample T88 are completely different from the rest. There is however a good correlation between the measured Brønsted acidity and the catalytic efficiency of H-ZSM-5 (T88) in that both sets of results indicate that the zeolite contains no Brønsted acid sites. This could be due to all the aluminium detected by XRF spectroscopy (see section 3.3.4) being concentrated in unreacted gel material. In support of this, von Ballmoos [9] has shown that the amorphous gel material is rich in aluminium relative to the zeolite phase. However scanning electron microscopy (see Figure 3.12) shows that the product contains very small amounts of gel and it is unlikely that this is sufficient to account for the observed results. The most likely explanation is that TPA-ZSM-5 was neither calcined for long enough nor at a high enough temperature and that the intra-crystalline channels are blocked by organic material. Thermal analysis of the calcined material showed that only 78% (by weight) of the TPA cations were removed during calcination. The fact that (Na, TPA)-ZSM-5 can be fully calcined at 400°C suggests that intra-crystalline sodium ions facilitate the removal of the intracrystalline TPA cations. Although only 22% (by weight) of the TPA cations are left after calcination it is possible that the cations have been broken down into smaller fragments, e.g. $\text{C}_3\text{H}_7\text{NH}_3^+$, $\text{C}_2\text{H}_5\text{NH}_3^+$, $\text{CH}_3\text{NH}_3^+$ etc., and that these balance all the anionic charge due to framework aluminium. The effect of calcination temperature on the Brønsted acidity and catalytic properties of TPA-ZSM-5 are discussed in section 6.5.
There are large variations in the Brønsted acidities obtained for the other ZSM-5 samples. This is due to differences in the Si/Al ratios of the samples as their molar $\text{H}^+/\text{Al}$ ratios are in excellent agreement. The average molar $\text{H}^+/\text{Al}$ ratio for ZSM-5 that has been ion-exchanged into the acid form using the procedure described is $0.60 \pm 0.05$.

The efficiencies that were obtained for the H-ZSM-5 catalysed hydrolysis of ethyl acetate at 60°C are in good agreement with the experimental results that were obtained by the filtrate titration technique. The average efficiency is $0.78 \pm 0.1$ and is less than unity because of (i) amorphous gel material in the product and (ii) calcination of the 'as made' zeolite results in the dehydroxylation at some of the Brønsted acid sites, e.g. the measured Brønsted acidity of H-ZSM-5 (J70) was 24% higher when the zeolite was not calcined at 400°C for 72 hours (see section 6.5).

Apart from sample T88, the efficiency/molar ($\text{H}^+/\text{Al}$) ratios are in good agreement and any differences can be attributed to experimental error. This suggests that mass transfer effects that might occur at the hydrophilic water/hydrophobic zeolite interface do not effect the rate of hydrolysis of ethyl acetate.

Although the range of crystal sizes studied is small the experimental results show no evidence to suggest that increased diffusional path lengths can cause a decrease in the rate of hydrolysis of ethyl acetate in H-ZSM-5. Although it was not possible to investigate whether aluminium zoning across the ZSM-5 crystals, as described by von Ballmoos and Meier [10] and Derouane et al [11], was present it is unlikely that the same aluminium zoning patterns
will apply to crystals obtained from different reaction mixtures. In any case it is unlikely that aluminium zoning would effect the rate of hydrolysis of ethyl acetate.

6.4.4 Conclusions

The experimental results show that the rate of hydrolysis of ethyl acetate in ZSM-5 is not diffusion controlled and that a chemical reaction is the rate limiting step. Thus the results support the ester hydrolysis work described in section 4.5. Although a change in the organic component used can cause changes to crystal morphology (and probably aluminium zoning distributions) it did not effect the molar $H^+/Al$ ratios obtained by the filtrate titration technique nor the efficiency of H-ZSM-5 as a catalyst for the hydrolysis of ethyl acetate. The experimental results from both techniques were found to be in good agreement.

The experimental results showed that calcination of TPA-ZSM-5 at 400°C for 72 hours is insufficient to remove all of the intra-crystalline organic species. Only 78% (by weight) of TPA cations were removed compared to 100% for (Na, TPA)-ZSM-5. This indicates that sodium facilitates the removal of the TPA cations and their oxidation products possibly by creating faults in the zeolite lattice.

6.5 Effect of Calcination Temperature on the Acidity and Catalytic Properties of H-ZSM-5

6.5.1 Introduction

The aim of the work described in this section was to investigate the effect of calcination temperature on the acidity and catalytic properties of ZSM-5. The following ZSM-5 materials were studied:
(Na, HEX)-ZSM-5 (H54), (Na, PIP)-ZSM-5 (P40), (Na, TPA)-ZSM-5 (T49), TPA-ZSM-5 (T88) and 'inorganic' ZSM-5 (J70).

6.5.2 Experimental

The synthesis of the zeolites used in this work is described in Chapter 3. The materials used, experimental procedure and treatment of results for the hydrolysis of ethyl acetate are given in sections 4.2 and 4.3. The experimental procedure for the filtrate titration technique is described in section 5.2.

The 'as made' zeolites were calcined for 72 hours except when temperatures were higher than 700°C, in which case the calcination period was reduced to 24 hours. The zeolites were treated with hydrochloric acid according to the procedure described in section 4.2. TPA-ZSM-5 (T88) was not treated with hydrochloric acid.

6.5.3 Results and Discussion

The effect of temperature used to calcine (Na, HEX)-ZSM-5 (H54), on the acidity and catalytic properties of its acid form are given in Table 6.3. The measured Brønsted acidities correlate well with the rate constants for the hydrolysis of ethyl acetate. Both sets of results show that calcining (Na, HEX)-ZSM-5 (H54) at 500°C instead of 400°C does not alter the number of Brønsted acid sites. However, loss of both acidity and catalytic activity is observed when the 'as made' zeolite was calcined at temperatures greater than 500°C. This is clearly demonstrated in Figure 6.2 in which the efficiency of H-ZSM-5 (H54), relative to the sample that was calcined at 400°C, is plotted against calcination
Table 6.3 Effect of calcination temperature on the acidity and catalytic properties of H-ZSM-5 (H54)

<table>
<thead>
<tr>
<th>Calcination Temperature (°C)</th>
<th>Brønsted Acidity (meq.g⁻¹)</th>
<th>Molar H⁺/Al</th>
<th>Rate Constant (k) 10⁴ x k (min⁻¹ g⁻¹)</th>
<th>kᵦH (min⁻¹ M⁻¹)</th>
<th>Efficiency Molar (H⁺/Al)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.658</td>
<td>0.613</td>
<td>7.36</td>
<td>0.137</td>
<td>0.686</td>
</tr>
<tr>
<td>500</td>
<td>0.654</td>
<td>0.609</td>
<td>7.39</td>
<td>0.138</td>
<td>0.689</td>
</tr>
<tr>
<td>600</td>
<td>0.594</td>
<td>0.553</td>
<td>5.70</td>
<td>0.106</td>
<td>0.531</td>
</tr>
<tr>
<td>800</td>
<td>0.265</td>
<td>0.247</td>
<td>2.30</td>
<td>0.043</td>
<td>0.214</td>
</tr>
</tbody>
</table>

Table 6.4 Effect of calcination temperature on the acidity and catalytic properties of H-ZSM-5 (P40)

<table>
<thead>
<tr>
<th>Calcination Temperature (°C)</th>
<th>Brønsted Acidity (meq.g⁻¹)</th>
<th>Molar H⁺/Al</th>
<th>Rate Constant (k) 10⁴ x k (min⁻¹ g⁻¹)</th>
<th>kᵦH (min⁻¹ M⁻¹)</th>
<th>Efficiency Molar (H⁺/Al)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.448</td>
<td>0.599</td>
<td>6.72</td>
<td>0.180</td>
<td>0.898</td>
</tr>
<tr>
<td>450</td>
<td>0.415</td>
<td>0.555</td>
<td>5.04</td>
<td>0.135</td>
<td>0.674</td>
</tr>
<tr>
<td>500</td>
<td>0.250</td>
<td>0.335</td>
<td>2.19</td>
<td>0.058</td>
<td>0.292</td>
</tr>
<tr>
<td>600</td>
<td>0.197</td>
<td>0.264</td>
<td>2.12</td>
<td>0.057</td>
<td>0.284</td>
</tr>
<tr>
<td>800</td>
<td>0.124</td>
<td>0.165</td>
<td>1.21</td>
<td>0.032</td>
<td>0.161</td>
</tr>
</tbody>
</table>
Figure 6.2 Catalytic activity \( \frac{k}{k_{400}} \) of H-ZSM-5 against calcination temperature.  
- \( \bigcirc \) H-ZSM-5 (H54);  
- \( \bullet \) H-ZSM-5 (J70);  
- \( \bigcirc \) common to both
temperature. The graph shows a linear correction between the catalytic activity of the zeolite and the calcination temperature for temperatures above 500°C. Extrapolation to higher temperatures indicates that complete loss of catalytic activity occurs on calcination at 930°C. The efficiency/molar (H⁺/Al) ratios that were obtained when (Na, HEX)-ZSM-5 (H54) was calcined at 600°C and 800°C are significantly lower than those obtained when the zeolite was calcined at 400°C or 500°C. This is probably due to partial blockage of the ZSM-5 channels at higher temperatures so that in some channels the effective channel diameter is less than the molecular kinetic diameter of ethyl acetate (4.7 Å) and greater than the hydrated radius of a sodium ion (2.76 Å). This result is similar to that observed by Nayak and Choudhary [6] for deammoniated ZSM-5. They found that extensive dehydroxylation caused a reduction in the effective channel diameters which resulted in an increase in the p- to o- and p- to m-xylene ratios obtained in xylene isomerisation reactions.

The results that were obtained with (Na, PIP)-ZSM-5 (P40) are similar to those obtained for (Na, HEX)-ZSM-5 (H54). Again there is a good correlation between the measured Brønsted acidity and the observed catalytic activity. However the acidity and catalytic activity both start to decrease at lower temperatures. This is clearly shown in Figure 6.3 in which catalytic activity is plotted against calcination temperature. The plot obtained can be split into two portions depending on whether the calcination temperature is greater than or less than 500°C. The efficiency/molar (H⁺/Al) ratios obtained at the different calcination
Figure 6.3  Catalytic activity \( \frac{k}{k_{400}} \) of H-ZSM-5 against calcination temperature.  
- \( \circ \) = H-ZSM-5 (T49);  
- \( \bullet \) = H-ZSM-5 (P40);  
- \( \bigcirc \) = common to both
temperatures indicate that extensive dehydroxylation and lattice degradation causes the partial blockage of the ZSM-5 channels.

The experimental results that were obtained for (Na, TPA)-ZSM-5 (T49) (see Table 6.5) are very similar to those of (Na, PIP)-ZSM-5 (P40). The effect of calcination temperature on the catalytic properties of ZSM-5 (T49) is shown in Figure 6.3. The only difference between the results for (Na, PIP)-ZSM-5 (P40) and (Na, TPA)-ZSM-5 (T49) is that the latter suffers more extensive dehydroxylation when the zeolite is calcined at temperatures up to 500°C. The dependence of the efficiency/molar (H⁺/Al) ratios on the calcination temperature used suggests that extensive dehydroxylation and lattice degradation causes partial blockage of the ZSM-5 channels.

The results which were obtained with TPA-ZSM-5 (T88) (see section 6.4) showed that it was more difficult to remove TPA cations from TPA-ZSM-5 (T88) than from (Na, TPA)-ZSM-5 (T49). The probable reason for this was thought to be that sodium ions caused faults in the zeolite lattice and facilitated the removal of the bulky TPA cations and their oxidation products. The experimental results for TPA-ZSM-5 (T88) (see Table 6.6) show that the highest Brønsted acid concentration was obtained when the zeolite was calcined at 600°C for 72 hours. The relationship between the catalytic activity of H-ZSM-5 (T88) and the calcination temperature used is clearly illustrated in Figure 6.4. Compared to the other samples of H-ZSM-5 that were studied, Brønsted acidity is only observed over a relatively narrow range of calcination temperatures.

The dominant effect at calcination temperatures less than 600°C is probably the incomplete removal of intracrystalline organic
Table 6.5 Effect of calcination temperature on the acidity and catalytic properties of H-ZSM-5 (T49)

<table>
<thead>
<tr>
<th>Calcination Temperature (°C)</th>
<th>Brønsted Acidity (meq. g⁻¹)</th>
<th>Molar H⁺/Al</th>
<th>Rate Constant (k) 10⁴ x k (min⁻¹ g⁻¹)</th>
<th>kZH (min⁻¹ M⁻¹)</th>
<th>Efficiency</th>
<th>Efficiency Molar (H⁺/Al)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.369</td>
<td>0.556</td>
<td>4.77</td>
<td>0.144</td>
<td>0.719</td>
<td>1.29</td>
</tr>
<tr>
<td>450</td>
<td>0.330</td>
<td>0.498</td>
<td>3.73</td>
<td>0.112</td>
<td>0.561</td>
<td>1.13</td>
</tr>
<tr>
<td>500</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.060</td>
<td>0.298</td>
<td>-</td>
</tr>
<tr>
<td>600</td>
<td>0.089</td>
<td>0.134</td>
<td>0.57</td>
<td>0.017</td>
<td>0.086</td>
<td>0.64</td>
</tr>
<tr>
<td>800</td>
<td>0.041</td>
<td>0.062</td>
<td>0.35</td>
<td>0.011</td>
<td>0.053</td>
<td>0.86</td>
</tr>
</tbody>
</table>

Table 6.6 Effect of calcination temperature on the acidity and catalytic properties of H-ZSM-5 (T88)

<table>
<thead>
<tr>
<th>Calcination Temperature (°C)</th>
<th>Brønsted Acidity (meq. g⁻¹)</th>
<th>Molar H⁺/Al</th>
<th>Rate Constant (k) 10⁴ x k (min⁻¹ g⁻¹)</th>
<th>kZH (min⁻¹ M⁻¹)</th>
<th>Efficiency</th>
<th>Efficiency Molar (H⁺/Al)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.004</td>
<td>0.007</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.0</td>
</tr>
<tr>
<td>500</td>
<td>0.038</td>
<td>0.007</td>
<td>0.14</td>
<td>0.005</td>
<td>0.026</td>
<td>0.4</td>
</tr>
<tr>
<td>600</td>
<td>0.048</td>
<td>0.084</td>
<td>0.77</td>
<td>0.027</td>
<td>0.135</td>
<td>0.6</td>
</tr>
<tr>
<td>700</td>
<td>0.016</td>
<td>0.028</td>
<td>0.33</td>
<td>0.012</td>
<td>0.058</td>
<td>2.1</td>
</tr>
<tr>
<td>800</td>
<td>0.001</td>
<td>0.002</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Figure 6.4 Catalytic activity ($k/k_{400}$) of H-ZSM-5 (T88) against calcination temperature.
material. Although thermal gravimetric analysis of TPA-ZSM-5 (T88) showed that the bulk of the organic had been removed only negligible Brønsted acidity and no catalytic activity was observed. This anomaly can be explained by the suggestion that the TPA cations are degraded rather than removed so that the anionic framework charge is balanced by species such as C\textsubscript{3}H\textsubscript{7}NH\textsubscript{3}, C\textsubscript{2}H\textsubscript{5}NH\textsubscript{3} etc. The experimental results indicate that temperatures >600°C are required for the complete removal of organic species. The molar H\textsuperscript{+}/Al ratio and catalytic activity of H-ZSM-5 (T88) is similar to that of H-ZSM-5 (T49) when both samples are calcined at 600° for 72 hours. However the former is more sensitive to dehydroxylation at high calcination temperatures and shows negligible Brønsted acidity and no catalytic activity when calcined at 800°C for 24 hours. The efficiency/molar (H\textsuperscript{+}/Al) ratios were found to vary over a larger range than normal. This is because the measured Brønsted acidity is low and is associated with large % errors.

The results that were obtained for 'inorganic' ZSM-5 (J70) are given in Table 6.7 and Figure 6.2. These show that the Brønsted acidity of a sample decreases by 24% if the 'as made' material is calcined at 400°C for 72 hours. This explains why the highest catalytic efficiencies for H-ZSM-5 are associated with the 'inorganic' series of ZSM-5 materials; 'inorganic' ZSM-5 does not require calcination and hence there is no associated degradation. The sample that was calcined at 800°C for 24 hours showed neither catalytic activity nor Brønsted acidity. X-ray powder diffraction showed that the crystalline structure had collapsed as a result of the calcination procedure. The results for 'inorganic' ZSM-5 (J70)
Table 6.7 Effect of calcination temperature on the acidity and catalytic properties of H-ZSM-5 (J70)

<table>
<thead>
<tr>
<th>Calcination Temperature (°C)</th>
<th>Brønsted Acidity (meq. g⁻¹)</th>
<th>Molar H⁺/Al</th>
<th>Rate Constant (k) (10^4 \times k) (min⁻¹ g⁻¹)</th>
<th>(k_{ZH}) (min⁻¹ M⁻¹)</th>
<th>Efficiency Molar (H⁺/Al)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.688</td>
<td>0.781</td>
<td>8.36</td>
<td>0.190</td>
<td>0.949</td>
</tr>
<tr>
<td>400</td>
<td>0.595</td>
<td>0.676</td>
<td>7.73</td>
<td>0.175</td>
<td>0.877</td>
</tr>
<tr>
<td>600</td>
<td>0.557</td>
<td>0.632</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>800</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>
were found to be similar to those obtained with (Na, HEX)-ZSM-5 (H54). The main differences between the two sets of results are that 'inorganic' ZSM-5 (J70) does not contain organic material and so does not have to be calcined, and that its structure collapses if it is calcined at 800°C for 24 hours. The similarity in the properties of the two materials is not surprising as Casci [12] has shown that hexanediol acts as an uncharged void filler and not as a template-like TPA⁺. The results for the five samples of ZSM-5 that were studied fall into three categories:

1. (Na, HEX)-ZSM-5, 'inorganic' ZSM-5
2. (Na, PIP)-ZSM-5, (Na, TPA)-ZSM-5
3. TPA-ZSM-5.

The difference between groups (2) and (3) is that TPA-ZSM-5 required harsher calcination conditions for the complete removal of all the intracrystalline organic material than did the materials in group (2). The results indicate that sodium ions facilitate the removal of intracrystalline TPA either by the formation of faults in the ZSM-5 lattice or by another mechanism.

Those ZSM-5 samples in groups (1) and (2) are easily categorised according to their catalytic activity/calcination temperature profiles. The difference between the profiles probably depends on whether or not the ZSM-5 material contains an organic cation. Chemical analysis of (Na, HEX)-ZSM-5 (H54) and 'inorganic' ZSM-5 (J70) (see section 3.3) shows that their Na/Al ratio is nearly unity. However those zeolites in group (2) have Na/Al ratios of 0.2-0.5 which indicates that most of the anionic framework charge is balanced by organic cations.
The experimental results may be explained as follows:

0-400°C

The results for 'inorganic' ZSM-5 showed that the catalytic activity was reduced by 8% and the Bronsted acidity by 24% if the preparation of the acid form required that the zeolite be calcined at 400°C for 72 hours. It is likely that the reactions that occur are similar to those reported by Barrer and Klinowski [4] and Kuhl [5] for deammoniated mordenite. However, the anionic framework charge is balanced by sodium ions so the reaction must be written as:

\[
\begin{align*}
\text{Na}^+ & \quad \text{Na-O} \\
\text{Al} & \quad \text{Al} \\
\text{Si} & \quad \text{Si}
\end{align*}
\]

(cf. 5.3)

\[
4 \left[ \begin{array}{c}
\text{Na-O} \\
\text{Al} \\
\text{Si}
\end{array} \right] \rightleftharpoons 3 \left[ \begin{array}{c}
\text{Al}-\text{O}-\text{Si}
\end{array} \right] + \text{Al}^{3+} + 4 \left[ \begin{array}{c}
\text{Si}-\text{ONa}
\end{array} \right]
\]

(cf. 5.9)

The reactions that occur at anionic framework aluminium sites are associated with organic cations and are given by equations 5.5-5.9, plus those postulated by Barrer and Klinowski [4] and Kuhl [5]. The extra-framework species formed do not effect the efficiency/molar (H⁺/Al) ratios and so the effective channel diameter is greater than the minimum kinetic diameter of ethyl acetate (4.7 Å).
The Bronsted acidity and catalytic activity of a sample of (Na, HEX)-ZSM-5, which had been calcined at 500°C, was found to be the same as the sample calcined at 400°C. Therefore no loss of framework aluminium is expected to occur at sites that are associated with sodium ions over the calcination temperature range of 400-500°C.

However, both (Na, PIP)-ZSM-5 and (Na, TPA)-ZSM-5 showed a large decrease in Bronsted acidity and catalytic activity when calcined at 500°C instead of 400°C. As this does not happen with samples that do not contain protonated organic molecules the only explanation is that framework aluminium is being lost at those sites which are associated with organic cations. Again the reactions that occur are expected to be similar to those postulated by Barrer and Klinowski [4] and Kuhl [5]. The efficiency/molar (H⁺/Al) ratio that was obtained when (Na, PIP)-ZSM-5 was calcined at 500°C for 72 hours suggests that some of the extra framework species that are formed are large enough to reduce the effective channel diameter to a value between the hydrated radius of a sodium cation (2.76 Å) and the minimum kinetic diameter of ethyl acetate (4.7 Å).

A sharp change in the catalytic activity/calcination temperature profiles for group (1) and (2) zeolites is observed at about 500°C. The dominant reaction is probably the loss of framework aluminium at sites associated with sodium cations. As group (1) zeolites contain more of these sites this accounts for
the large decrease in both Brønsted acidity and catalytic activity. The catalytic activity/calcination temperature profile for group (1) zeolites shows that the acid forms of samples which had been calcined at 800°C are only 0-30% as active as samples calcined at 500°C. The reactions that probably occur are given by equations 6.2-6.3 together with those given by Barrer and Klinowsk [4] and Kuhl [5]. The efficiency/molar \((H^+/Al)\) ratios for (Na, HEX)-ZSM-5 samples show that some of the extra-framework species that form at these calcination temperatures are large enough to reduce the effective channel diameters to between 2.76 Å and 4.7 Å.

The loss of framework aluminium at sites associated with sodium cations also occurs for the group (2) zeolites. In addition however there will also be the removal of strongly bound organic cations. The relative ease of removal of these cations plus probable difference in Na/Al ratios is thought to cause the different gradients obtained between 500°C and 800°C for (Na, PIP)-ZSM-5 and (Na, TPA)-ZSM-5. The efficiency/molar \((H^+/Al)\) ratios for both these zeolites indicate that some of the extra-framework species, that form as a result of the loss of framework aluminium, cause a partial blockage of some of the channels so that the effective channel diameter is reduced to between 2.76 Å and 4.7 Å.
6.5.4 Conclusions

The experimental results for (Na, HEX)-ZSM-5 (H54), (Na-PIP)-ZSM-5 (P40), (Na, TPA)-ZSM-5 (T49), TPA-ZSM-5 (T88) and 'inorganic' ZSM-5 (J70) show that calcination results in the loss of framework aluminium. The extent and nature of the loss of framework aluminium was found to depend on whether or not the organic species is charged, and the ease with which it is removed. The type of catalytic activity/calcination temperature profile obtained can thus be used to determine whether the intracrystalline organic material is charged or not. The reactions postulated by Barrer and Klinowski [4] and Kuhl [5] could be adapted to explain the experimental results.

The maximum Brønsted acidity and catalytic activity was found to occur when (Na, HEX)-ZSM-5 (H54), (Na, PIP)-ZSM-5 (P40) and (Na, TPA)-ZSM-5 (T49) were calcined at 400°C for 24 hours. The maximum activity for 'inorganic' ZSM-5 (J70) is found when it is not subjected to any thermal treatment. Because it is more difficult to remove TPA cations from TPA-ZSM-5 (T88) than from (Na, TPA)-ZSM-5 (T49) the maximum Brønsted acidity and catalytic activity for TPA-ZSM-5 (T88) was found when the zeolite was calcined at 600°C for 72 hours.

A comparison between the measured Brønsted acidity and the catalytic activity indicated that in all cases extensive dehydroxylation of ZSM-5 causes partial blockage of the channels.
6.6 Effect of Calcination Temperature on the Acidity and Catalytic Properties of H-Ferrierite and H-EU-1

6.6.1 Introduction

The aim of the work described in this section was to extend the investigations on ZSM-5 reported in section 6.5 to zeolites EU-1 and ferrierite.

6.6.2 Experimental

The synthesis of (Na, PIP)-Ferrierite (J68) is described in section 3.5 and the synthesis of (Na, HEXB)-EU-1 (J87) is described in Appendix 1. The experimental procedures that were followed for the hydrolysis of ethyl acetate and the filtrate titration technique are identical to those described in section 6.5.

6.6.3 Results and Discussion

The effect of calcination temperature on the acidity and catalytic properties of the acid form of (Na, PIP)-Ferrierite (J68) are given in Table 6.8. The results for the hydrolysis of ethyl acetate show that H-Ferrierite is inactive as a catalyst. This is discussed in section 4.7 and attributed to the fact that the entry parts of the ferrierite channel system are too small to allow the sorption of ethyl acetate. The catalytic activity observed when the 'as made' material is calcined at 400°C and 450°C is probably due to catalysis by acid sites situated on the surface of the ferrierite crystals. However, H-Ferrierite does undergo ion-exchange with sodium chloride solution and the Brönsted acidity measurements that were made are shown in Table 6.8 and Figure 6.5.
Table 6.8  Effect of calcination temperature on the acidity and catalytic properties of H-ferrierite (J68)

<table>
<thead>
<tr>
<th>Calcination Temperature (°C)</th>
<th>Brønsted Acidity (meq. g⁻¹)</th>
<th>Molar H⁺/Al</th>
<th>Rate Constant (k) 10⁴ x k (min⁻¹ g⁻¹)</th>
<th>kZH (min⁻¹ M⁻¹)</th>
<th>Efficiency Molar (H⁺/Al)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.893</td>
<td>0.595</td>
<td>0.17</td>
<td>0.002</td>
<td>0.011</td>
</tr>
<tr>
<td>450</td>
<td>0.866</td>
<td>0.577</td>
<td>0.08</td>
<td>0.001</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>500</td>
<td>0.167</td>
<td>0.111</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>600</td>
<td>0.154</td>
<td>0.102</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>800</td>
<td>0.101</td>
<td>0.067</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 6.9  Effect of calcination temperature on the acidity and catalytic properties of H-EU-1 (J87)

<table>
<thead>
<tr>
<th>Calcination Temperature (°C)</th>
<th>Brønsted Acidity (meq. g⁻¹)</th>
<th>Molar H⁺/Al</th>
<th>Rate Constant (k) 10⁴ x k (min⁻¹ g⁻¹)</th>
<th>kZH (min⁻¹ M⁻¹)</th>
<th>Efficiency Molar (H⁺/Al)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>0.251</td>
<td>0.365</td>
<td>0.90</td>
<td>0.026</td>
<td>0.131</td>
</tr>
<tr>
<td>450</td>
<td>0.292</td>
<td>0.425</td>
<td>2.00</td>
<td>0.058</td>
<td>0.291</td>
</tr>
<tr>
<td>500</td>
<td>0.045</td>
<td>0.065</td>
<td>0.20</td>
<td>0.006</td>
<td>0.029</td>
</tr>
<tr>
<td>800</td>
<td>0.028</td>
<td>0.041</td>
<td>0.05</td>
<td>0.001</td>
<td>0.007</td>
</tr>
</tbody>
</table>
Figure 6.5  Brønsted acidity (B.A.) of H-Porrierite (J68) against calcination temperature
The Brønsted acidity/calcination temperature profile for (Na, PIP)-Ferrierite (J68) is similar to that observed for group (2) ZSM-5 samples. This fact indicates that piperazine is protonated and balances some of the anionic charge of the zeolite framework. The Brønsted acidity/calcination temperature profile is composed of two parts and may be explained by those arguments used for (Na, PIP)-ZSM-5 (P40) and (Na, TPA)-ZSM-5 (T49). Calcination of (Na, PIP)-Ferrierite (J68) at 400-500°C causes extensive dehydroxylation at sites that are associated with protonated piperazine cations. Calcination of (Na, PIP)-Ferrierite (J68) at 500-800°C also causes loss of framework aluminium at sites that are associated with sodium cations. The mechanisms of these reactions are given in equations 6.2 and 6.3 and are expected to be similar to those proposed by Barrer and Klinowski [4] and Kuhl [5].

The experimental results for (Na, HEXB)-EU-1 (J87) are given in Table 6.9 and Figure 6.6. The catalytic activity/calcination temperature profile obtained shows that the maximum catalytic activity occurs when the zeolite is calcined at 450°C. TG analysis of the sample that was calcined at 400°C for 72 hours showed that 16% (by weight) of the organic component was not removed by the calcination procedure. Thus the limiting factor at calcination temperatures which are less than 450°C is removal of the hexamethonium cations (HEXB).

The rest of the profile suggests that the hexamethonium is charged as the profile is composed of two parts and is similar to that observed for group (2) ZSM-5 samples. Calcination of (Na, HEXB)-EU-1 (J87) at temperatures between 450-500°C causes
Figure 6.6 Catalytic activity ($k/k_{400}$) of H-EU-1 (J87) against calcination temperature
dehydroxylation to occur at 90% of the Brønsted acid sites. Higher calcination temperatures cause removal of framework aluminium at sites that are associated with sodium cations. Extrapolation of this part of the profile suggests that the zeolite will be catalytically inactive if it is calcined at 900°C. The mechanisms by which dehydroxylation and removal of framework aluminium occur are expected to be the same as those for (Na, PIP)-Ferrierite (J68).

The efficiency/molar (H⁺/Al) ratios for EU-1 show that dehydroxylation is also associated with obstruction of the catalytically active sites.

6.6.4 Conclusions

The experimental results which were obtained for zeolites EU-1 and ferrierite could be explained by the same mechanisms that were used for ZSM-5. The results indicated that piperazine in ferrierite and hexamethonium in EU-1 are both charged and balance the anionic charge of the zeolite framework. The maximum Brønsted acidity for H-Ferrierite was measured when the 'as made' material was calcined at 400°C. The maximum for EU-1 (J87) was found to be at 450°C as hexamethonium ions are not completely removed at lower temperatures.
Chapter 6 - References


Proceedings from 3rd International Conference on Molecular

[6] V.S. Nayak and V.R. Choudhary


[8] L. Elliot
Fourth Year Honours Project, University of Edinburgh, 1984.

Ph.D. Thesis, Institute of Crystallography & Petrography of the


and J. Verbist

Concluding Remarks

This work clearly illustrates the importance of the use of standard procedures for the preparation of acid zeolite catalysts. It also shows that acid zeolites, dispersed in an aqueous solution, can catalyse organic reactions. Although the hydrolysis of esters was studied in this work, the expertise developed could easily be applied to other organic reactions. Indeed it is hoped that these investigations provide the foundation required for further studies on the catalysis of liquid phase organic reactions by zeolites.
APPENDIX 1

Synthesis and Characterization of EU-1

Introduction

Zeolite EU-1 is a novel high silica zeolite that has been reported recently [1-3]. The conditions required for its synthesis are given in a patent [2] which also details its catalytic properties with respect to xylene isomerisation sorption studies carried out by Casci et al [3] on (Na, H)-EU-1 show that it can sorb 14 cm$^3$ of n-hexane per 100 g. The rapid sorption of p-xylene and the low capacity for cyclohexane was taken to indicate that EU-1 has an entry port slightly less than 0.60 nm and probably has 10 T-atom windows. These results suggest that it should be able to sorb ethyl acetate from aqueous solution. It was therefore decided to make a sample of EU-1 in accordance with the patent and investigate its catalytic properties with respect to the hydrolysis of esters. The sample made (Code: J87) was crystallised from the reaction mixture:

$$10\text{Na}_2\text{O} - 60\text{SiO}_2 - \text{Al}_2\text{O}_3 - 10 \text{hexamethonium bromide} - 3000\text{H}_2\text{O}$$

Experimental

Zeolite EU-1 was synthesised in a 500 cm$^3$ autoclave of the type described in section 3.2.1. The reaction was carried out at 167°C under autogenous pressure. The mixture was stirred at 300 rpm throughout the course of the reaction.
The reagents were: sodium hydroxide (AR grade; Fisons Ltd.), fumed silica (CAB-o-SIL M5; BDH Ltd.), aluminium (Analar; BDH Ltd.), hexamethonium bromide (purum; Fluka Ltd.) and distilled water. The reagents were mixed together in accordance with the technique described in section 3.2.3.

The acid form of EU-i was obtained by treatment with hydrochloric acid as described in section 4.2.3. The analytical techniques used to characterize EU-i are described in Chapter 2.

Characterization Results

X-ray Powder Diffraction

Interplanar d-spacings and relative intensities for 'as made' EU-i ((Na, HEX)-EU-1) and calcined EU-i ((Na, H)-EU-1) are given in Table 1 together with the literature values [4]. As can be seen from Table 1 the experimental values match those of the literature very well and show that sample J87 is zeolite EU-1. However a peak at d = 20.0 Å was observed in sample J87. This peak is characteristic of kenyaite. Although this peak is not mentioned in the patent for zeolite EU-i the only published X-ray powder diffraction patterns of EU-1 show a strong baseline drift at high d values. It is possible that this drift masks peaks due to kenyaite present as an impurity. The peak summation method described in Chapter 2 indicates that an accurate product composition of sample J87 is:

98% EU-1 + 2% kenyaite
Table 1  X-ray diffraction data for EU-1

<table>
<thead>
<tr>
<th>(Na, HEX) - EU-1</th>
<th>(Na, HEX) - EU-1</th>
<th>(Na, H) - EU-1</th>
<th>(Na, H) - EU-1</th>
<th>Error Δd (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>d (Å)</td>
<td>I/°</td>
<td>d (Å)</td>
<td>I/°</td>
<td>d (Å)</td>
</tr>
<tr>
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<td>13</td>
<td>19.95</td>
<td>15</td>
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</tr>
<tr>
<td>11.00</td>
<td>27</td>
<td>11.03</td>
<td>s-vs</td>
<td>11.07</td>
</tr>
<tr>
<td>10.01</td>
<td>26</td>
<td>10.10</td>
<td>m-s</td>
<td>10.11</td>
</tr>
<tr>
<td>9.73</td>
<td>12</td>
<td>9.78</td>
<td>w</td>
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</tr>
<tr>
<td>7.61</td>
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<td>7.62</td>
</tr>
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<td>w</td>
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<td>5</td>
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</tr>
<tr>
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<td>4</td>
<td>5.86</td>
<td>vw-w</td>
<td>5.74</td>
</tr>
<tr>
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<td>3</td>
<td>4.87</td>
</tr>
<tr>
<td>4.63</td>
<td>38</td>
<td>4.66</td>
<td>s-vs</td>
<td>4.61</td>
</tr>
<tr>
<td>4.29</td>
<td>100</td>
<td>4.31</td>
<td>vs</td>
<td>4.31</td>
</tr>
<tr>
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<td>56</td>
<td>4.00</td>
<td>s-vs</td>
<td>3.98</td>
</tr>
<tr>
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<td>34</td>
<td>3.82</td>
<td>s-vs</td>
<td>3.79</td>
</tr>
<tr>
<td>3.69</td>
<td>4</td>
<td>3.71</td>
<td>m-s</td>
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</tr>
<tr>
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<td>3.44</td>
<td>m</td>
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<tr>
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<td>22</td>
<td>3.38</td>
<td>m</td>
<td>3.34</td>
</tr>
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<td>50</td>
<td>3.26</td>
<td>s</td>
<td>3.27</td>
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<td>vw</td>
<td>3.15</td>
</tr>
<tr>
<td>3.08</td>
<td>6</td>
<td>3.11</td>
<td>vw</td>
<td>3.08</td>
</tr>
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<td>7</td>
<td>2.96</td>
<td>vw</td>
<td>2.94</td>
</tr>
<tr>
<td>2.69</td>
<td>5</td>
<td>2.71</td>
<td>vw</td>
<td>2.69</td>
</tr>
<tr>
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<td>9</td>
<td>2.55</td>
<td>vw</td>
<td>2.52</td>
</tr>
<tr>
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<td>3</td>
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<td>vw</td>
<td>2.45</td>
</tr>
<tr>
<td>2.40</td>
<td>6</td>
<td>2.42</td>
<td>vw</td>
<td>2.40</td>
</tr>
<tr>
<td>2.31</td>
<td>4</td>
<td>2.33</td>
<td>vw</td>
<td>2.32</td>
</tr>
<tr>
<td>2.29</td>
<td>4</td>
<td>2.30</td>
<td>vw</td>
<td>2.29</td>
</tr>
</tbody>
</table>
**Morphology**

Scanning electron microscopy showed that the EU-1 crystals were ellipsoidal. Most crystals were 2 μm long and 1 μm wide although some were 6 μm long and 4 μm wide. These are larger than those made by Casci et al [3].

**Thermal Analysis**

DTA and TG traces of 'as made' EU-1 are shown in Figure 1. These are very similar to published data and show an endothermic loss of water at low temperatures. Removal of organic begins at about 300°C and is virtually complete by 700°C. The main difference between the experimental and literature results is that the DTA trace for sample J87 shows a more pronounced and more clearly defined exotherm centred at 650°C. Differences in the position of the base line may be attributed to sample loading and "instrument effects".

**Chemical Composition**

The composition of a calcined sample of EU-1 that had been treated with hydrochloric acid was determined by XRF spectroscopy. The Si/Al ratio of the product was found to be 23.23 and is very similar to that obtained by Casci [5] who used an identical reaction mixture composition.
Synthesis Results

pH Measurements

The pH value of samples taken during the crystallization of EU-i are shown in Table 2. These results are in accordance with published data [6]. The pH of the solution phase shows a sharp rise in pH between 52 and 96 hours and this signifies completion of the crystallization of zeolite from the amorphous gel. The pH values obtained in this work are higher than those in the literature [6]; this may be because a lower reaction temperature was employed in the synthesis of sample J87.

Table 2 pH measurements of samples taken during the synthesis of EU-i

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>0</th>
<th>4</th>
<th>21</th>
<th>28</th>
<th>45</th>
<th>52</th>
<th>96</th>
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<tr>
<td>pH</td>
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<td>11.86</td>
<td>11.93</td>
<td>11.93</td>
<td>11.95</td>
<td>11.98</td>
<td>12.33</td>
</tr>
</tbody>
</table>

Crystallisation Time for EU-i

pH measurements indicate that the crystallization time for EU-i is between 52-96 hours at 167°C. The predicted crystallization time may be determined from the Arrhenius equation,

\[ CT^{-1} = A \exp(-E_a/RT) \]

in which CT is the total time (in hours) required at the reaction temperature (T) for complete crystallization, the activation energy \( E_a \) = 96.4 kJ mol\(^{-1}\) [3] and the pre-exponential factor is \( 3.96 \times 10^9 \) h\(^{-1}\) [3]. R is the gas constant. The predicted
crystallization time is 69.7 hours and is in excellent agreement with the experimental results. The fact that the reaction was allowed to over-run by 26 hours probably accounts for the formation of kenyaite.

Conclusions

A sample of EU-1 was prepared in accordance with the techniques covered in the patent [2]. Some kenyaite was observed as an impurity in the product. This is probably because the reaction over-ran by 26 hours.
Appendix 1 - References


APPENDIX 2

Additional Synthesis Reactions

Introduction

In addition to those reaction mixture compositions that are discussed in Chapter 3 and Appendix 1, several other systems were investigated.

Experimental

The synthesis procedures that are given in section 3.2 were used for the work described in this section. The materials that were used are listed in section 3.2. Aluminium was used in reactions J76 and J78 whilst alumina trihydrate was used in reaction J5. The products obtained were characterized by X-ray powder diffraction as described in Chapter 2.

Results and Discussion

The reaction mixture compositions which were used are given in Table 1 together with the products that were obtained. The fact that ZSM-5 was formed as a product in run J76 shows that not only can inorganic ZSM-5 be made at 150°C over a wide range of SiO$_2$/Al$_2$O$_3$ and Na$_2$O/SiO$_2$ ratios - it can also be made at other temperatures. This result agrees with work done by Casci [1] who found that inorganic ZSM-5 is a genuine product of the inorganic system. Compared with the results given in section 3.5 the ratio of ZSM-5/mordenite in run J76 suggests that higher temperature favours the formation of
mordenite at the expense of ZSM-5. No crystalline product was observed when the reaction temperature was reduced to 120°C.

Conclusion

Inorganic ZSM-5 can be made over the temperature range 150-180°C, and possibly outside this range.

Table 1 Reaction mixture compositions studied

<table>
<thead>
<tr>
<th>Code</th>
<th>Na₂O</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>TPABr</th>
<th>H₂O</th>
<th>Reaction Temp. (°C)</th>
<th>Reaction Vessel</th>
<th>Time (hrs)</th>
<th>Product</th>
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</thead>
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<td>300</td>
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<td>75</td>
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</tr>
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<td>20</td>
<td>-</td>
<td>2</td>
<td>1000PB</td>
<td>95  120</td>
<td>Silicalite-1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>J76</td>
<td>5</td>
<td>60</td>
<td>2</td>
<td>-</td>
<td>3000500A</td>
<td>180 552 47% ZSM-5 + mordenite</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>J78</td>
<td>5</td>
<td>60</td>
<td>2</td>
<td>-</td>
<td>3000500A</td>
<td>120 552 amorphous</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

PB 1 litre Plastic Bottle
500A 500 cm³ autoclave

Appendix 2 - Reference
