AN INVESTIGATION OF SUPPORTED HETEROGENEOUS DISPROPORTIONATION CATALYSTS

by

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TO

MUM AND DAD
Abstract

A study has been made of alumina and silica supported molybdenum hexacarbonyl olefin disproportionation catalysts which have been prepared by a variety of techniques. The measurement and analysis of the volume of non-condensable gas liberated by each catalyst during activation at high temperatures has been carried out by means of a Töpler pump and spectroscopic techniques respectively, with the intention that this information would improve the present knowledge of the nature of the catalytically active species. An attempt was made to study semi-quantitatively the rate at which non condensable carbon monoxide was evolved during activation, and to determine if the pressure equilibrium level in a closed system was temperature dependent for similar sample weights.

An analytical method was developed in order to determine the molybdenum content of the catalysts by atomic absorption spectrophotometry. Verification of this technique by a colourimetric method showed that the original work had failed to account for certain ionic interferences during the analysis of alumina supported catalysts. Consequently a correction factor was calculated for the catalysts which were no longer available for further analysis. The true molybdenum content of each catalyst was determined and from this CO:Mo molar ratios were calculated.

Although the results of the work presented in this thesis were in rough agreement with other results in the
literature, they mainly served to indicate how irreproducible these catalyst systems were. The possible nature of the catalyst is discussed but only qualitatively because a complete determination of the active species was not possible from the data obtained.
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CHAPTER I
INTRODUCTION TO CATALYSIS

1.1 Definition

A catalyst is a substance which increases the rate at which a chemical reaction reaches equilibrium. That is, a catalyst will decrease the activation energy of a chemical reaction or increase the pre-exponential factor. The species can only be used for reactions which are thermodynamically feasible, not for ones which are thermodynamically unfavourable. It must be stipulated that the position of the equilibrium for the reaction must remain constant, as though the catalyst had not been used, and consequently, any change in the rate of the forward reaction must be equivalent to the change in the back reaction. There are two different broad classifications of catalysts, homogeneous, and heterogeneous. Homogeneous catalysts are ones which function in the same phase as the reactants. Heterogeneous catalysts promote chemical reactions by means of the presence of an interface between two phases. Generally, this involves a gaseous or liquid reactant passing over a solid catalyst.

The bulk of the work presented in this thesis is concerned with the physical and chemical properties of a heterogeneous olefin disproportionation or dismutation catalyst, molybdenum hexacarbonyl supported on silica or gamma alumina. Consequently this introductory section will emphasize those theories which are generally common to studies of heterogeneous catalysts.
1.2 Physical Adsorption

As the name implies, physical adsorption is concerned with weak Van der Waals, dipolar, quadrupolar interactions between adsorbant and adsorbate. It is characterized by low heats of adsorption which are usually near or below the boiling point of the adsorbate. No activation energy is required for physical adsorption which usually occurs rapidly, depending on the porosity of the solid adsorbant. Physical adsorption is significant in surface area determinations (1) or pore size distribution studies (2).

1.3 Chemical Adsorption

This second and more important form of adsorption is more complex than physical adsorption because it is associated with the rearrangement of electrons on or near the surface of the adsorbant and those within the valence shell of the adsorbed gas molecules. This results in the formation of a chemical bond between the surface and the gas, mainly because unsaturation is such that the valency requirements of surface atoms would not be fulfilled by bonding with adjacent atoms on the surface.

Heats of chemisorption are usually high (~80 KJ mol⁻¹), though lower values have been reported. It is not necessarily accurate to say that chemisorption involves high activation energies, because clean surfaces can undergo rapid chemisorption even at low temperatures, such that activation energies may approach zero. Because chemisorption is more specific than physical adsorption, reaction surfaces must be clean. Whether or not chemisorption will be possible is
determined chiefly by the chemical potentials of the adsorbant and the adsorbate. Once a monolayer has been formed on the surface of a heterogeneous catalyst, chemisorption will cease. It is this layer of chemisorbed species which forms the intermediates of a heterogeneously catalyzed reaction. If held on the surface too strongly the adsorbate may poison the catalytic reaction, but should the bond be too weak, the adsorbate may not be on the surface long enough to react.

1.4 Mechanism of Surface Reactions

Reaction on the surface of a heterogeneous catalyst is known to consist of five consecutive steps.

1. Diffusion of reacting molecules to the surface.
2. Adsorption to the surface.
3. Reaction on the catalyst surface. This may be the adsorbed species reacting with each other, with physically adsorbed species, or with molecules colliding with the surface.
4. Desorption of products.
5. Diffusion of products away from the surface.

Anyone of the above steps might be the rate determining step of the reaction. However, except in the case of porous catalysts or solutions involved in the reaction, it is quite unlikely that the diffusion steps will be rate determining. Diffusion in the gaseous state normally requires little activation energy, therefore it will be faster than the overall surface reaction which usually involves appreciable activation energy.
1.5 The Catalyst Support

By means of impregnating catalyst supports such as gamma alumina or silica with solutions containing catalyst precursors, active catalysts are created. The catalyst support can serve two purposes; it might increase the surface area available for adsorption and hence for reaction, or it might increase the catalytic activity per unit surface area. For a given catalyst, the greater the amount of active surface available to the reacting gas, the rate of the conversion to products is improved.

Supports can affect the mechanical strength of a catalyst, impose restraints on the rate of recrystallization and grain growth, or improve its packing characteristics. In addition they might affect the life of the catalyst as well as exerting some promoter effects, which could be due to an alteration in the atomic spacing of the support or modification of the valency of the atoms in the lattice because of incorporation in the crystal field. Because of any alteration in the catalyst surface, physical features such as porosity, that is size and distribution of pores and their stability, must be taken into account.

Heterogeneity in a (silica or alumina) support will be induced by the presence of molybdenum hexacarbonyl. The effect of this is to render certain areas more active than others. In such an event the activity of a catalyst is not directly proportional to the surface area of the support, but is more dependent on the manner in which the activity is distributed over the available surface area. Catalyst activity can concomitantly decrease with a decrease
in support surface area, but should this not be the reason, catalyst poisoning may be suspected.

1.6 Geometric and Electronic Factors related to Catalytic Activity.

1.6.1 The Geometric Factor

This factor is very much concerned with the geometric spacing or disposition of the support atoms within a catalyst. Adsorption energy will be controlled by the magnitude of lattice spacings. If this separation is small, adsorption energy will increase because of repulsion between neighbouring adsorbate species. It is frequently the case that adsorbed molecules will be forced to split due to large values of the lattice spacing. This often results in an apparent increase in the energy of adsorption over the values normally associated with adsorption onto unstrained support surfaces.

1.6.2 The Electronic Factor

The "electronic factor" is an approach to the study of catalytic activity that seeks a relationship between this and the electronic structure of the bulk solid. Schwab's (3) work showed that the greater the concentration of electrons in an alloy catalyst, the greater would be the activation energy for a catalyzed decomposition reaction. Kemball (4) indicated that there exists a rough correlation between the nature of the chemical bond in transition metals and the activation energy of deuterium exchange with ammonia over a series of metal surfaces. Beeck (5) plotted rate measurements against interatomic spacing and found a maximum at the
same point for a plot of "d"-character versus interatomic spacing. His work emphasized that if the surface states are qualitatively related to the electron configuration of the bulk of the metal, it may be expected that metals with a large d-character of their metallic bond will have less orbitals available for bonding with the adsorbate than those with a small d-character. In this light the geometric factor is very much controlled by the electronic factor.

1.7 Surface Structure and Dehydration

Alumina is commercially available in one of four forms, boehmite, bayerite, hydrargillite (6) and gibbsite. In each of these crystal structures the aluminium atom has a coordination number of six (7), sharing valence bonds with six oxygen atoms. The ability, nevertheless, of aluminium atoms in crystalline solids to shift from the \( \{\text{six}\} \) to the \( \{\text{four}\} \) coordinate state is related to the ionic radius of 0.5Å, which is small enough to allow an aluminium ion to fit between four or six closely packed oxygen atoms. Therefore the various crystalline forms of alumina are simply atomic rearrangements which include either one of the possible coordination states of aluminium. The gamma (γ) alumina structure which was used in the work presented in this thesis is formed by the dehydration of boehmite at above 623K. It is a metastable form which changes with increases in temperature. Intermediate forms of the structure which appear in the 673-973K range are of value in hydrocarbon catalysis and catalytic transformations.
At room temperature the surface of uncalcined gamma alumina is saturated with adsorbed water molecules, the majority of which are physically adsorbed and can be removed by gentle heating. Also there exists across the surface an unevenly distributed monolayer of hydroxyl groups (8) which are chemically bonded to aluminium atoms and cannot be removed without excessive heating. Extreme outgassing conditions could lead to sintering of the alumina and undesirable changes in the nature of the catalyst. Evacuation at 298K for twenty-four hours is a condition for the removal of most physically adsorbed water (9).

Outgassing of alumina at temperatures greater than 573K might follow the mechanism:

\[
\begin{align*}
\text{H}_2\text{O} & \text{H}_2\text{O} \quad \text{H}_2\text{O} \\
\text{Al} & \text{Al} \quad \text{Al} \\
\text{H}_2\text{O} & \text{H}_2\text{O} \quad \text{H}_2\text{O} \\
\text{Al} & \text{Al} \quad \text{Al} \\
\text{Al} & \text{Al} \quad \text{Al} \\
\end{align*}
\]

\[\text{+ H}_2\text{O}\]

**Mechanism 1.1**

The removal of water on heating occurs through the reaction of two immediately adjacent hydroxyl groups and this leaves the "odd" oxide ion in the outermost layer and an exposed aluminium ion in the next lower layer (10).
Although the removal of hydroxyl pairs occurs randomly it does so in such a way that the residual oxide ions on the surface layer form a regular cubic lattice with no two oxide ions on immediately adjoining sites. Oxide ions on the surface lattice thus normally alternate with depressed aluminium ions in incomplete octahedral sites in the next lower layer (11).

Water that is evolved from alumina upon evacuation at temperatures greater than 298K may be considered as having originated in one of the following sources:
1. the condensation of surface hydroxyl groups,
2. molecular water bound to the surface by forces strong enough to prevent desorption at 298K,
3. chemically bound water incorporated into the bulk lattice as internal hydroxyl groups.

The strong dependence of such surface properties as acidity and heat of immersion on the water or hydroxyl group content of alumina would suggest that chemisorbed water is associated with the surface rather than the bulk of the material.

1.8 Catalytic Activity in Relation to centres of acidity on Alumina

It has been suggested (12) that the high catalytic activity of alumina is associated only with the surface of this support which will be partially covered with hydroxyl groups. Low activity may be due to the saturation of the surface with water if the calcination temperature is low. Sites of structural strain will normally be formed at 673-773K and at higher temperatures approaching 1173K these
sites will most likely anneal.

The acidity of the surface is considered (13-18) responsible for the catalytic activity of alumina supports. Protonic Brönsted and aprotic Lewis acid sites on the surface, enhance activity via various mechanisms. At a Brönsted site aluminium might be bound to four oxygen atoms in the lattice. Because its natural valence is three, a proton is required to balance the charge. This proton is therefore considered available to take part in chemical reactions. At Lewis acid sites aluminium is bound to three oxygen atoms leaving an electron pair vacancy in its valence shell. This vacancy can therefore be filled by sharing an electron pair from a base that is chemisorbed onto the surface, subsequently fulfilling the coordination requirements of the exposed aluminium ion. There also exists the possibility that hydrated Lewis acid sites will promote catalytic activity. The electron pair vacancy in aluminium will be filled by sharing the free electron pairs of oxygen in molecular water, thus allowing a proton from the chemisorbed water to be readily ionizable, leaving a hydroxyl group on the surface.

1.9 Determination of Acid Sites

A variety of techniques have been used (19-24) to characterize and measure the strengths of acid sites on catalyst support surfaces. These techniques often give very different results for the same support, but according to several authors it is infra-red studies of pyridine (25) or ammonia (13, 26) adsorption which enables one to
distinguish between Lewis and Brønsted sites. The spectrum of pyridine coordinately bonded to the surface is markedly different from that of the pyridinium ion. This permits the differentiation of acid type on the surface of acid solids. From the frequency shift of one of the bands of coordinately bonded pyridine over that found in the liquid phase, and from the retention of the band upon evacuation and heating, a very rough estimate of the strength of surface Lewis sites can be inferred.

1.10 Deactivation or Neutralization of The Support Surface

Solid acid surfaces can be neutralized by addition of an amine (19) or ammonia in the vapour phase or in an inert solvent such as benzene or iso-octane. With the loss of its acid sites the oxide catalyst is no longer capable of functioning. When alumina is impregnated with sodium hydroxide the total number of acid sites is reduced without there being any appreciable effect on the overall acidity of the remaining sites. Employing sodium chloride in the same capacity apparently reduces the acidity of the remaining sites.

When the surface of the support is rehydrated (10) the activity gained by removal of a given weight of water is lost by addition to the dried catalyst of a much smaller amount. At high temperatures redistribution of water to sites of highest activity will cause greater poisoning than that caused by the non specific adsorption of water at low temperatures.
1.11 Dehydration of Silica

Various techniques have been used to study the dehydration of the surface of silica. Shapiro and Weiss (27) used a method involving diborane in order to make a distinction between hydroxyl groups and adsorbed water by studying the hydrogen-diborane ratio as a function of the outgassing temperature. McDonald (28) also made an infra-red study and found that hydroxyls on the surface exist in several different states which can absorb at distinct frequencies. The destruction of silanol groups during outgassing produced active surface sites which reacted rapidly with water vapour at room temperature to regenerate hydrogen bonded silanol groups.

All physically adsorbed bulk water can be removed by evacuation of silica at room temperature. On activation above 453K (29) the silanol groups will condense to form siloxane groups and water.

\[
\begin{align*}
\text{Si-OH} + \text{H}_2\text{O} &\rightarrow \text{Si-O-Si} \\
\text{low heat} &\rightarrow \text{high temp}
\end{align*}
\]

Mechanism 1.2

At low temperatures the surface can be reversibly dehydrated but not if maintained at over 673K. This would suggest that there has been a change in the surface structure during activation between 453K and 673K. Should the two silicon atoms in the above scheme not be the appropriate distance apart, the Si-O-Si group would be under considerable strain.
Surface hydroxyl groups may be geminal as well as single, and a suggested mechanism for the removal of these geminal groups is as follows;

\[
\begin{align*}
\text{HO}_2\text{SiOH} + \text{HO}_2\text{SiOH} & \xrightleftharpoons{\text{low temp}} \text{HO}_2\text{SiOSiOH} \\
& \xrightarrow{\text{high temp}} \text{HO}_2\text{SiOSiOSiOH}
\end{align*}
\]

Between 673 and 773K more water will be removed from the surface with increasing time and temperature of calcination. At high temperatures there will be insufficient hydroxyl groups remaining on the surface to fulfil the valency (30) requirements of surface silicon atoms, consequently a portion of the surface will be in a state of strain and no less active. Oxygen atoms at siloxane bridges could be quite reactive due to probable distortion of the normal unit cell. A lot of work (31-33) has been carried out to study the removal of hydroxyl groups over a range of temperatures. The amount of either single or geminal type present depends on a number of factors (34) including the method of preparation, the impurity content, the heating and vacuum conditions employed, and the extent of annealing prior to any rehydration process that the silica may finally undergo. Silica is usually annealed
at 723K and carries only single hydroxyl groups at this temperature.

Possibly the most reasonable mechanism (35) for the dehydration of silica involves surface silicon \( b \) atoms carrying geminal hydroxyl groups, interacting with a second layer of silicon \( a \) atoms carrying one hydroxyl group.

\[
\text{Further heating to 673K completely removes the geminal hydroxyl groups and allows relaxations to occur so that the Si-O-Si bridges become unstrained and unreactive to water, therefore preventing the successful rehydration of silica so treated. Silica that has been annealed prior to rehydration will subsequently have only one hydroxyl group per silicon atom and dehydration is by the following mechanism (35):}
\]

\[
\text{For rehydration of the surface to occur a particular water molecule must remain in contact with a particular strained surface Si-O-Si bridge long enough for reaction to}
\]
occur between them. Therefore resistance to rehydration at low vapour pressures may be due to the surface mobility of weakly sorbed water molecules.

1.12 Areas of Reactivity and Adsorption

By means of infra-red and deuterium exchange studies of surface and bulk hydroxyl groups, researchers (36) have pin-pointed the most active centers of specific adsorption on dehydrated silica as being the surface hydroxyl groups of which there are two types; free ones (37), and ones bound by a mutual hydrogen bond. The principle role in specific adsorption is played by the free hydroxyl groups. This point is substantiated by infra-red studies (37). These groups are energetically non-uniform and are therefore expected to possess different reactivities. The strength of an adsorption site on silica towards an adsorbate such as benzene or fluoranthene is determined by two factors.

1. The relative availability of hydroxyl groups in the required region for hydrogen bonding to the adsorbate. Free hydroxyls will have greater availability than bound ones.

2. The relative number of hydroxyl groups in the region of adsorption. The greater this number is, the greater will be the adsorption energy.
The field of olefin disproportionation was pioneered by Banks and Bailey (38). Using alumina supported molybdenum hexacarbonyl, tungsten hexacarbonyl or molybdenum trioxide as heterogeneous catalysts, linear olefins were converted to homologs of shorter and longer carbon chains. These catalysts were prepared by means of impregnating the preactivated alumina in vacuo with a molybdenum or tungsten precursor in a cyclohexane solution. This technique was frequently used with little variation by others working in the same field.

Davie et al. (39) describe attempts to show that carbon monoxide was liberated from the catalyst during activation, by using a mass spectrometer connected to the gas handling apparatus. An activation temperature of 523K was required before carbon monoxide showed up at mass number 28 on the spectrometer output. Although no quantitative measurement of carbon monoxide was possible by this method, Davie postulated that the catalytic species was Mo(CO)$_2$.

Whan et al. (40) studied the disproportionation catalyst by noting a major shift of ca. 1 e.v. in molybdenum binding energy as indicated by x-ray photo electron spectroscopic studies. Such a shift is too large and too discrete to be due to the acidity of the support and might possibly indicate a change in the oxidation state of molybdenum. This theory was further substantiated by e.p.r. studies (41) which provide evidence to suggest that the catalytically active species is Mo(IV) (42).
The decomposition of the molybdenum hexacarbonyl supported on silica, alumina and magnesia has been followed by infra-red spectroscopy (42). The rate of decomposition is greatest for the silica supported catalyst because this support is unable to stabilize intermediate sub-carbonyl species. Variations in catalytic activity have been discussed (43) in terms of the sites on the supports which are available for interaction with molybdenum hexacarbonyl, and also the possible state of molybdenum in the active catalyst. The role of the support has been considered two fold; initially to disperse the molybdenum hexacarbonyl and then to assist the oxidation of the molybdenum to form the active species. Maximum activity will be achieved on any particular support when both of these conditions are optimized.

1.14 The Purpose of the Present Investigation

There are no results in the chemical literature which suggest that a rigorous characterization and quantitative measurement of the carbon monoxide liberated from the supported disproportionation catalyst, activated at different temperatures, has been made. With infra-red and photo electron spectroscopy as the available tools such a study was begun. A simple and reproducible method of determining the molybdenum content of the catalyst must be developed in order that CO:Mo molar ratios could be calculated. With this latter information it was hoped that one would be able to understand the nature of intermediate sub-carbonyl species and study the speed at which they decompose when subject to high activation temperatures.
CHAPTER II

EXPERIMENTAL APPARATUS AND TECHNIQUE

2.1 Apparatus

2.1.1. Activation of each alumina supported catalyst was carried out in a cylindrical pyrex vessel 15 x 1.25 cm in size. This was attached to the main body of the pyrex gas handling vacuum line by either a ground glass joint sealed with Apiezon 'L' grease, or by a glass blown seal.

2.1.2. Impregnation apparatus.

Certain silica supported molybdenum hexacarbonyl catalysts were prepared by means of impregnation which is discussed in section 2.5. A special pyrex apparatus was designed and constructed to facilitate this technique and is illustrated in Fig. 2.3. This device was attached to the gas handling line by means of a B-10 ground glass joint sealed with Apiezon 'L' grease, and employed a Rotaflo greaseless tap to allow entry of the catalyst solution into the activation chamber.

The pressure within the gas-handling line was maintained at approximately $1.33 \times 10^{-3} \text{Nm}^{-2}$ by a mercury diffusion pump and a rotary back-up pump. A liquid nitrogen 'muck' trap was located in a suitable position. The presence of gas molecules in the line was monitored by a Pirani deflection gauge, via a tungsten filament head open to the system. The volumes of non-condensable gases evolved during catalyst activation were accurately measured ($\pm 0.2 \text{ cm}^3$) by means of a Töpler pump the top of which could be opened via a 4 mm. stopcock to an attached pyrex infra-red cell which was always pre-evacuated to approximately $1.33 \times 10^{-3} \text{Nm}^{-2}$ by the gas.
handling line. The ends of the infra-red cell were fitted with potassium bromide windows.

2.1.3. Apparatus for Gas Identification

Identification of non-condensable gas evolved from the activated catalyst was facilitated by use of either a Perkin-Elmer PS-16 photo electron spectrometer or a Perkin-Elmer 457 infra-red spectrometer.

2.2 Reagents

Molybdenum hexacarbonyl was supplied by B.D.H. Ltd., and used without further purification. The γ-alumina support was prepared by calcining a high purity boehmite (Johnson and Matthey Chemicals Ltd.) at over 900K in air for twenty-four hours. Surface area determinations were not made. The silica was a Fisher grade 923 (100-200 mesh) silica gel calcined in air at over 900K for twenty-four hours.

2.3 Experimental Procedure

2.3.1. Dry mixing

A ten percent by weight ratio of molybdenum hexacarbonyl to alumina or silica support was ground together to a fine powder at room temperature in air. The sample was weighed (+ 0.05 mg) then poured into the clean dry activation vessel.

2.3.2. Sublimation

The apparatus used for this technique has been diagrammatically represented in Fig. 2.1. Both the molybdenum hexacarbonyl in the side-arm and the pre-ground alumina or silica support in the bottom of the vessel were evacuated at 77K. The carbonyl complex was allowed to warm
Fig. 2.1. Sublimation Apparatus
up to room temperature and by means of a heat gun at approximately 430K, was sublimed onto the support. Every effort was made to ensure that an excess amount of molybdenum hexacarbonyl went onto the support without subliming onto cooler parts of the activation vessel.

2.3.3. Activation procedure

All catalysts which had been prepared by either method described in the previous sections were evacuated at 77K prior to activation for at least one minute, or until the Pirani gauge open to the vacuum line registered its original deflection at low pressure. A glass wool plug had been fixed above the dry mixed catalyst in order to prevent fine powder from getting into any ground-glass connections during evacuation. The sample was activated by immersing it in an oil bath, the temperature of which was maintained at ± 0.5 °K of the pre-set value by means of a thermistor control, connected to a variac power supply. A thermometer attached to the outside of the activation vessel indicated the approximate temperature of the sample. In later experiments this was more carefully performed by a thermocouple connected to a recording unit.

Catalyst activation was carried out for a pre-determined time because of interest in the possible time dependency of carbon monoxide evolution. Upon removal of the heat source from the sample the apparatus was opened via a 4 mm stop cock to the Töpler pump and the volume of non-condensable gas was measured. The operation of this pump is discussed in section 2.4. After volume measurement the gas was pushed into the infra-red cell and its spectrum recorded.
2.4 The Töpler Pump

This apparatus is diagrammatically represented in Fig. 2.2. A water pump controlled by a three-way greased tap reduced the atmospheric pressure on the mercury in the conical flask exposed to the atmosphere. Pressure on the closed side of the mercury was reduced to ca. $1.33 \times 10^{-3} \text{Nm}^{-2}$ by means of the gas-handling vacuum line. The mercury in the conical flask, freshly distilled and therefore free of volatile impurities could be pushed into the burette C, by opening the three-way tap B, to the atmosphere. When B was opened to the water pump the pressure on the open side of the mercury was reduced, causing the mercury to return to the conical flask. Non-condensable gas could be let into the pump and then trapped when the 4 mm tap was shut. The mercury via B was opened to the atmosphere thus forcing most of the gas into the burette, where it could be held by means of a greased tap. The bulk of the mercury was returned to the conical flask, and the pump then opened to the gas-handling system. The procedure of trapping the gas in the burette was repeated until a constant volume was indicated. The actual volume of the gas at atmospheric pressure was determined by closing E and opening F then the levels of the mercury in the burette and the side-arm reservoir were equilibrated at room temperature.

2.5 Catalyst Preparation by Impregnation of Silica

Catalyst samples supported on silica were prepared by dry-mixing, sublimation and impregnation. The first two methods have already been discussed in sections 2.3.1
Fig. 2.2  Töpler Pump
and 2.3.2. A diagram of the apparatus used throughout sample preparation by impregnation and activation is indicated in Fig. 2.3. A certain weight (± 0.05 mg) of finely ground silica was spread across the bottom of the activation vessel. Prior to use as a catalyst support it was evacuated in situ at 573°K for over 1 hour.

Molybdenum hexacarbonyl, 10% of the support weight was warmed in a beaker with a minimum volume of cyclohexane to 333K. This solution was then poured into the reservoir attached to the activation vessel via a Rotaflo tap which was shut while the apparatus was evacuated to 1.33 x 10⁻³ Nm⁻².

Nitrogen, which had been dried and purified through three columns containing sodium hydroxide, phosphorus pentoxide and BASF catalyst R3-11, was used to flush both the activation vessel and the cyclohexane solution in the reservoir. A nitrogen atmosphere prevented the solution from spattering onto the walls of the vessel when it was dripped onto the support by opening the Rotaflow tap. The resulting slurry was left for approximately 30 minutes in order that impregnation of the support was reasonably complete. It was cooled to 77K then allowed to warm up slowly under vacuum to remove cyclohexane and nitrogen which were subsequently trapped in a liquid nitrogen trap in the gas handling line.

The solid sample was then activated in an electric muffle. Carbon monoxide volumes were determined by means of the Töpler pump and infra-red spectroscopy facilitated the final identification of this gas. Further Mo(CO)₆-SiO₂ catalysts were prepared by dry-mixing and sublimation, and
Fig. 2.3.  Impregnation Apparatus
these were activated in the apparatus used for activation of Mo(CO)\(_6\)-Al\(_2\)O\(_3\) samples.

2.6 Rate of Carbon Monoxide Evolution

During the activation of the alumina and silica supported molybdenum hexacarbonyl catalysts, an effort was made to determine semi-qualitatively the rate at which carbon monoxide was evolved. The gas handling apparatus was operated in two ways.

1. open system: after each measurement of the pressure exerted by the non-condensable gas in the apparatus, this volume of gas was tripled in order to reduce the pressure in the apparatus. Each time a measurement was made the activation vessel was shut-off from the gas handling apparatus.

2. closed system: the gas evolved during activation was allowed to remain within the vicinity of the catalyst in order that a state of equilibrium would be established between the CO molecules still attached to the catalyst, and those in the gaseous state. Measurement of the gas pressure in the apparatus was made after suitable time intervals.

Change in time was measured by a stop-clock which was started when the catalyst came into contact with the heat source. Pressure readings were taken from a mercury manometer open to the gas handling apparatus.

2.7 Activation of Supported Molybdenum Hexacarbonyl Organic Derivatives

The derivatives of molybdenum hexacarbonyl that were examined in these gas evolution studies were: mesitylene
Fig. 2.4. Apparatus for Activation of Supported Organic Derivatives of Molybdenum Hexacarbonyl

to vacuum line

thermocouple wire

catalyst sample
tricarbonyl molybdenum, toluene tricarbonyl molybdenum, triphenylphosphine pentacarbonyl molybdenum, bis π-cyclopentadiene tricarbonyl molybdenum and norbornadiene tetracarbonyl molybdenum. Before use it was necessary to purify some of these compounds. The mesitylene tricarbonyl species was recrystallized from di-iso propyl ether and then washed in n-hexane. The triphenylphosphine derivative was washed in diethyl ether to remove excess triphenylphosphine. All catalyst samples were prepared by drymixing a 10:1 w/w ratio of support and molybdenum carbonyl species. The mesitylene and toluene derivatives were dry mixed with alumina in a nitrogen atmosphere in a glove bag as they are susceptible to rapid decomposition when exposed to air for a short period of time. The nitrogen used here was dried and purified in the same manner described in section 2.5.

The vessel used for the activation of these catalysts is diagrammatically represented in Fig. 2.4. A plug of glass wool was fitted into the neck of this apparatus to prevent fine dust particles from interfering with the greased ground-glass joint. A weighed (± 0.05 mg) amount of catalyst was poured into the vessel which was evacuated at 77K to $1.33 \times 10^{-3}$ Nm$^{-2}$. The heat source employed was an electric muffle and temperatures were monitored by a thermocouple using $T_1-T_2$ chromel-alumel thermocouple wire connected to a Servoscribe recorder. This latter piece of apparatus was calibrated with water at both 0°C and 100°C prior to use in each experiment. The length of activation times was measured by a stop-clock. The volumes of gases liberated by the samples after passing through a liquid-nitrogen trap
to remove organic impurities, were measured by a Töpler pump, adopting the "open system" technique described in section 2.6. These gases were then identified according to their infra-red spectra via a Perkin-Elmer A57 infra-red spectrometer.

2.8 Carbon Monoxide Evolved at Room Temperature

Experimental work was carried out in order to try to obtain comparative data concerning the possible evolution of carbon monoxide from silica and alumina supported molybdenum hexacarbonyl at room temperature. Three methods of sample preparation were used: dry mixing, pressed discs, and impregnation.

2.8.1. Dry mixing

The apparatus used is diagrammatically represented in Fig. 2.5. This pyrex vessel contained a finely ground support in the bottom section and molybdenum hexacarbonyl in the attached side arm. Initially the apparatus was evacuated with both support and hexacarbonyl complex at 77K, then the latter was sublimed onto the support at 433K. The catalyst sample was swirled by a magnetic stirrer at 291K and any gas evolved was tōpled to a constant volume, having passed through a liquid nitrogen trap. The sample was then heated and the gas evolved was tōpled to a constant volume. The volume of gas evolved on heating was not measured separately, but was obtained by subtracting the volume given off at room temperature from the combined volume. This gas was then trapped in a cell and identified by infra-red spectroscopy. The silica supported catalysts were analyzed by means of atomic absorption spectrophotometry for their molybdenum content.
Fig. 2.5. Dry Mixing Apparatus
2.8.2. Pressed discs

Experiments similar to those discussed in section 2.8.1. were carried out on wafer thin discs, 30 mm in diameter, and prepared in a stainless steel dye at $1.516 \times 10^5 \text{KNm}^{-2}$. Molybdenum hexacarbonyl was sublimed onto these supports and variable temperature gas evolution studies were made.

2.8.3. Impregnation

The purpose of this experiment was to prepare a catalyst sample at low temperatures and monitor any volume of carbon monoxide evolved as the sample temperature approached room temperature. This work involved an impregnation technique which employed solvents with high vapour pressures at temperatures below 273K.

To a fixed weight of molybdenum hexacarbonyl cooled to 77°K was added a minimum volume of dry acetone. An acetone-dry ice bath warmed this to 195°K. A 10:1 weight ratio of silica to molybdenum hexacarbonyl was added to this solution; it was hoped that the distribution of molybdenum hexacarbonyl over the support surface obtained in this way would be uniform. The solution was allowed to warm up and the acetone very slowly condensed into a liquid nitrogen trap. The sample approached room temperature overnight, and the volume of carbon monoxide liberated during this time was pumped and measured.

An identical experiment was performed with liquid butane substituting the acetone as solvent. The vapour pressure of butane is higher than that of acetone at low temperatures. The apparatus used had previously been
Fig. 2.6. Impregnation Apparatus: Measurement of Carbon Monoxide Evolved at Low Temperatures

butane gas

catalyst support

molybdenum hexacarbonyl
evacuated to $1.33 \times 10^{-3} \text{Nm}^{-2}$. Approximately 20 ml of butane were condensed into an impregnation apparatus at 77K containing a carefully weighed amount of molybdenum hexacarbonyl. The liquid nitrogen bath was replaced by a carbon tetrachloride/ice bath and the solution was allowed to warm up to 250K, and was maintained at this temperature until it was decided that all of the molybdenum carbonyl species had gone into solution. A carefully weighed amount of silica, situated in a side arm (see Fig. 2.6) was poured into the butane solution and the latter was allowed to impregnate the silica at 250K for approximately 30 minutes. The ice bath was removed, and butane having a vapour pressure of $1.01 \times 10^5 \text{Nm}^{-2}$ at 272.5K, was allowed to condense into a liquid nitrogen trap as the impregnation solution approached 273K. When the catalyst was apparently dry and free of butane, it was then warmed to room temperature, and any gas evolved was tópled. No measurable volume of gas did evolve during this procedure, which can imply one of three things; the molybdenum hexacarbonyl might not have gone into solution at 250K, the silica might not have been properly impregnated by the butane solution at 250K, or perhaps no carbon monoxide is evolved at these temperatures.
CHAPTER III
ANALYSIS OF SUPPORTED CATALYSTS FOR MOLYBDENUM

3.1 Atomic Absorption Spectrophotometry

3.1.1 History

The earliest observations of atomic absorption were made by Wollaston (44) who saw the "Fraunhofer lines" in the spectrum of the sun. In 1832 Brewster (45) suggested that these lines were due to the passage of white light through a hot absorbing vapour. Kirchhoff (46) studied reversal of spectral lines due to lithium, sodium, potassium, calcium, and strontium in the non-luminous flame of a burner. The basis of this technique is possibly as Brewster had considered it; when light is passed through a hot vapour, emission or absorption lines will appear, depending on whether the temperature of the light source does or does not exceed that of the flame containing the atomic vapour.

Walsh (47) was one of the first scientists to develop atomic absorption spectrophotometry for analytical purposes. Since that time the technique has advanced considerably to a point at which there are now approximately 3,000 references to it in the literature, including several books (48-54) and various reviews (55-68).

3.1.2 General Theory

When a standard or sample solution is aspirated into a flame, and the relevant metal atoms to be studied are free of any molecular bonding forces, and energy is supplied to this atomic vapour, then some of the atoms present will be excited to higher energy levels. When these atoms eventually
return to their lower energy levels, the energy acquired must be released. That portion of the released energy which appears as light is the emission spectrum for this particular atom. The number of atoms, however, which remain in the ground state (state of least energy) is up to $10^{16}$ times as great as the number in excited states. These unexcited atoms are then available to absorb radiation from a light source at the appropriate wavelength equivalent to the energy required to excite the atom to a higher energy level. Absorption can therefore be monitored by a light detector or monochromator situated on the opposite side of the atomic vapour to the light source.

Previous authors (57, 47) have derived a mathematical expression which enables one to calculate the ratio of atoms in the excited state $N_J$ to those in the ground state $N_0$:

$$\frac{N_J}{N_0} = \frac{P_J}{P_0} e^{-\frac{E_J}{kT}}$$  \hspace{1cm} (3.1)

$P_J$ and $P_0$ represent the statistical weights of the excited and ground states respectively. This is the statistical probability that a particular transition will take place. Walsh (77) gives the ratio $N_J/N_0$ for various metals over a range of temperatures.

<table>
<thead>
<tr>
<th>Element</th>
<th>$A^0$</th>
<th>$P_J/P_0$</th>
<th>$N_J/N_0$ @ 2000°C</th>
<th>3000°C</th>
<th>4000°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs</td>
<td>8521</td>
<td>2</td>
<td>$4 \times 10^{-4}$</td>
<td>$7 \times 10^{-3}$</td>
<td>$3 \times 10^{-2}$</td>
</tr>
<tr>
<td>Na</td>
<td>5890</td>
<td>2</td>
<td>$1 \times 10^{-5}$</td>
<td>$6 \times 10^{-4}$</td>
<td>$4 \times 10^{-3}$</td>
</tr>
<tr>
<td>Ca</td>
<td>4227</td>
<td>3</td>
<td>$1 \times 10^{-7}$</td>
<td>$4 \times 10^{-5}$</td>
<td>$6 \times 10^{-4}$</td>
</tr>
<tr>
<td>Zn</td>
<td>2139</td>
<td>3</td>
<td>$7 \times 10^{-15}$</td>
<td>$6 \times 10^{-10}$</td>
<td>$1 \times 10^{-7}$</td>
</tr>
</tbody>
</table>
The $P_J/P_0$ ratios are for the most populated energy states. At higher temperatures the excited state population has increased in every case illustrated in Table 3.1. Nonetheless, $N_0 > N_J$ irrespective of temperature. Wood (69) has drawn up an expression for the relationship between absorption and atomic concentration.

\[
\int Kd_\nu = \frac{\lambda^2}{8\pi} \frac{P_J}{P_0} \cdot N_\nu A_{J_0}
\]

(3.2)

where $\int Kd_\nu$ is the integrated absorption.

$N_\nu$ is the number of atoms per cm$^3$ capable of absorption in the range $\nu + d_\nu$ to $\nu$. $N_\nu$ will be greater than $N_J$.

$K$ is the absorption coefficient of the atomic vapour at frequency "$\nu"."

$\lambda$ is the wavelength at the centre of the absorption line.

$0$ is the lower or ground state.

$J$ is the excited state.

$A_{J_0}$ is the Einstein coefficient of spontaneous emission for the $J$ to $0$ transition.

From Table 3.1 it is noted that with increases in temperature there is a simultaneous exponential increase in the number of atoms which are capable of emitting light. However, expression 3.2 is independent of temperature and substantiates the hypothesis that in atomic absorption spectrophotometry it is the unionized, unexcited atoms which are of importance. Absorption techniques are not as sensitive to temperature changes as are emission methods. Should the flame temperature be too high, absorption could
hypothetically be affected by light emitted by atoms already excited in the flame.

The intensity of radiation transmitted through the flame is given by

\[ I_\nu = I_\nu^0 e^{-K_\nu L} \]  \hspace{1cm} (3.3)

\[ = I_\nu^0 10^{-0.43 K_\nu L} \]  \hspace{1cm} (3.4)

where \( I_\nu \) is the intensity of transmitted radiation,
\( I_\nu^0 \) is the intensity of the incident radiation,
\( \nu \) is the frequency of the incident and transmitted radiation,
\( L \) is the atomic absorption path length,
\( K_\nu \) is the absorption coefficient of the atomic vapour at frequency \( \nu \).

In an excited state an atom has a life time of approximately \( 10^{-8} \) seconds. It can undergo a) non radiational deactivation via collision with flame gas molecules, or b) radiational deactivation which is emitted isotropically and called fluorescence.

Winefordner and de Galan (70) reject the argument that flame temperature is immaterial in atomic absorption spectrophotometry. Even though a greater fraction of atoms remain in the ground state, absorption signals are not entirely independent of flame temperature. The Beer's Law expression
\[ A^0 = \log \left( \frac{I^0}{I_j} \right) = 0.43 \, K^0 L \]  
(3.5)

\[ = C_A N_0 \delta /\Delta \lambda_D \]  
(3.6)

will hold true if the spectral line emitted from the flame is very much narrower than the absorption line in the flame.

\( A^0 \) is the absorbance

\( K^0 \) is the atomic absorption coefficient in cm\(^{-1}\)

\( C_A \) includes factors such as wavelength, transition probability, statistical weights and the atomic partition function.

\( \delta \) accounts for the decrease in the absorption signal caused by broadening of the absorption line and finite width of the source line. In an ideal case \( \delta \) would equal 1. From this it is inferred that measurements are made at the wavelength peak of the spectral line, and Doppler broadening is the major source of absorption line broadening, and so any temperature dependence of \( \delta /\Delta \lambda_D \) will reduce to the Doppler half-width \( \lambda_D \) which is proportional to \( T^{\frac{1}{2}} \). Therefore \( A^0 \) becomes \( C_A N_0 T^{-\frac{1}{2}} \). This equation will only hold if the ground state concentration of atoms \( N_0 \) equals the total atom concentration \( N_T \) of an element in the flame.

### 3.1.3 The Selection of Spectral Lines

Absorption of energy need not necessarily result in a transition of an atom from the ground state to a higher excited state. Sometimes good results can be obtained by employing a spectral line which starts in absorption from a metastable state, not the ground state, but from which an atom cannot without breaking the selection rules go directly to the ground state. It must first be excited to some higher energy state from which it may then be dropped to the ground state. This can often occur
as a result of collisions with other atoms. Analysis might be more advantageous from a metastable state than from a ground state; and for a particular element flame conditions might be such that a considerable metastable population exists. It is occasionally worthwhile to measure absorption from several lines in order to determine which is the most advantageous for analytical purposes. For some elements the resonance lies outside the region in which the photo-cell is sensitive.

3.1.4 Profile of Atomic Absorption Lines

Spectral line profiles and half-widths are determined by certain broadening parameters. Much work has been carried out in an attempt to find out what parameters affect spectral line widths (71) and the effects that they have on the analytical sensitivity of atomic absorption spectrophotometry. In his initial work (71), Walsh assumed the breadth of a resonance emission line from a hollow cathode lamp to be extremely small, and that the central wave-length of the resonance emission line from the lamp corresponds to the central wavelength of the resonance absorption line. Also, he assumed that the breadth of the line is partially predetermined by the Doppler effect. Winefordner (72) showed that the absorbance is independent of the absorption line breadth as long as the breadth of the resonance emission line is much less than that of the resonance absorption line.

Yasuda (73) found that when working with calcium a decrease in the absorbance of this element in the flame, caused by an increase in the discharge current of the lamp, was due to self-absorption of the resonance emission line
from the lamp. In order to increase the absorption of atomic vapour in the flame, the atomic vapour temperature, gas pressure, and the degree of self absorption, all of which play a role in determining the breadth of the resonance emission line from a hollow-cathode lamp as the light source, must be of low value. Doppler broadening arises because the atoms in the vapour have different components of velocity along the line of observation. This breadth is represented by $D$;

$$D(\lambda) = \left(\frac{1.67 \lambda}{c}\right)\left(\frac{2RT}{m}\right)^{\frac{3}{2}} \quad (3.7)$$

$m$ is the atomic weight.

3.1.5 Types of Line Broadening

Collisional or Lorentz broadening: This is caused by the perturbation of the absorbing or emitting atoms by foreign gas molecules.

Resonance: This is similar to collisional broadening but it results from the collision between the absorbing or emitting atoms.

Natural broadening: This results from the finite lifetime of the atom (ca. $10^{-8}$ seconds) in its excited state.

Stark broadening: This type of broadening can also be considered as it involves the splitting of the atomic line on the application of an electric field. It is not entirely significant as far as the work presented in this thesis is concerned because a hollow cathode lamp was used for the analysis.
Natural broadening
Doppler broadening
Collisional broadening

Half Width
$10^{-5}$ nm
$8 \times 10^{-3}$ nm
$10^{-3} - 10^{-2}$ nm.

These parameters are added quadratically to give the entire half width of the line. In a flame of between 2000°C and 3000°C Doppler broadening will be the greatest contributor to line width at a low vapour pressure of the metal atoms.

A substantial amount of the fundamental theory behind atomic absorption spectrophotometry has been presented. It should nevertheless be emphasized that this technique is still largely empirical in its practical application.

3.1.6 Working Curves

If the profile of the absorption line remains constant, the analytical curve should be linear within an almost unlimited concentration range. Nevertheless, the shape of a working curve is not entirely predictable (59) for it depends on a variety of parameters; lamp characteristics, the nature and homogeneity of the flame, the entrance optics, spectral resolution, solvents used, and even the method of photometry. Therefore the non-linearity of analytical curves can be attributed to faults of the apparatus or the properties of the particular spectral line used (74, 75). These include; the hyperfine structure of the line, the ratio of the absorption and emission line widths, resonance line broadening, and the line shift in the absorbing media.
3.1.7 Sample Treatment Prior to Analysis

Sample attack with acids and bases has been reported (76, 81). Various authors have recommended the use of organic solvents for metal extraction prior to aspiration into the flame (77-81). Increases in sensitivity (82, 83) and independence from errors due to slight changes in acidity or the presence of certain interfering ions have been reported. Absorption signals in organic solutions are equal to or greater than the signal from an analogous aqueous solution. This is attributed to more efficient atom production (due to easier combustion of the organic solvent, and easier release of atoms from an organic product than from an inorganic salt) and higher flame temperature. Malissa and Schoffmann (84) found that successful separation of many heavy metals including molybdenum could be accomplished by means of chelation with ammonium pyrrolidine dithiocarbamate.

3.1.8 Comparison with other Analytical Techniques

This author has found that the analysis of the heterogeneous catalysts discussed for their molybdenum content by atomic absorption spectrophotometry is less sensitive and precise than colourimetry. However, on the grounds of rapidity and simplicity the former has proven itself superior to the latter.

3.1.9 Precision

Atomic absorption varies in precision from element to element, and depends on the stability of the light source, whereas flame emission is approximately constant for different elements, the precision of this technique being more dependent on flame stability. Gilbert (59) mentions
that the reproducibility of precision for atomic absorption is commonly no better than 1%.

3.1.10 Interferences

3.1.10.1 Chemical Interferences

This is also referred to as a condensed phase interference. This kind of interference occurs if the element which is studied (i.e. Mo) combines with some other cation or anion in solution to form a compound which influences the degree of reduction to neutral metallic atoms in the flame used. Therefore, the number of atoms in the flame capable of absorbing resonance radiation is changed, as is the atomic absorption sensitivity. Because the interferent is not usually present in the standard solution an error will result in the data from the analysis.

There are several ways of overcoming chemical interferences. One is to increase the temperature of the system, or else to add a releasing agent to the sample and standard solutions. The releasing agent is also a competing cation. Lanthanum ions when added to the solution will preferentially react with the interferent atom.

If a higher temperature is used this will provide additional energy to break down the compound formed which is at least partially stable in low temperature flames.

3.1.10.2 Matrix Interferences

These are also known as viscosity or bulk interferences. They occur when the physical characteristics (viscosity, surface tension, etc.) of the sample and standard solutions differ considerably. If the sample solution has a high concentration of dissolved salts or acid; when
different solvents are used for sample and standard solutions; or when the sample and standard solutions are at appreciably different temperatures, then matrix interferences will occur.

Matrix interferences can be controlled by dilution a level at which dissolved salts or acids are a problem and therefore become negligible. If dilution is not possible, then the matrix effects can often be controlled by matching the concentrations of major constituents in sample and standard solutions.

3.1.10.3 Ionization Interferences

These occur when the flame temperature is high enough to generate the removal of an electron from a neutral atom, giving a positively charged ion. Although the ion is capable of absorbing radiation, it does so at a different wavelength than the parent atom. As the number of neutral atoms in the flame is reduced, atomic absorption sensitivity will be depressed.

Ionization interference can easily be overcome or controlled by the addition to both sample and standard solutions of a large excess of an easily ionizable element. The alkali metals, for example; K, Na, have low ionization potentials and are duly ionized in the nitrous oxide-acetylene flame.

3.1.10.4 Spectral Interferences

Spectral interferences can occur when an element present in the sample solution, but not being determined, has an absorbing wavelength that falls within the width of the absorption line of the element of interest. Results of
determinations will be erroneously high due to the contribution of the interfering element to the atomic absorption signal. This can be controlled by altering the spectral slit width or using an alternate wavelength.

3.1.10.5 Background Absorption

This is a collective term used to describe the combined effects of flame absorption, molecular absorption, and "light scattering" in atomic absorption determinations. Flame absorption is significant at wavelengths below 250 nm and can be controlled by properly setting fuel and oxidant flow rates, or by using a flame with less absorption at the wavelength of interest. Molecular absorption is controlled by using a higher temperature flame - one with sufficient energy to break down the absorbing molecular species.

"Light scattering" can be compensated for by measuring the background absorption at a nearby non-absorbing line, and subtracting this value from the absorption at the line of interest.
3.1.11 Atomic Absorption Flame Conditions

The unseparated nitrous oxide-acetylene flame has been the principal atom reservoir employed in the analytical work presented in this thesis. This flame is of particular use in the determination by atomic absorption spectrophotometry of elements which form refractory compounds with high dissociation energies. Without an excessive burning velocity (85), and under fuel rich conditions, the nitrous oxide-acetylene flame exhibits the strong reducing properties necessary to support the existence of free atoms of many elements whose oxides are thermally stable. This flame was first studied by Parker and Wolfhard (86, 87), but it was not until Willis (85) in 1965 reported promising results from work with the nitrous oxide-acetylene flame using a special burner, that the value of its application to atomic absorption spectrophotometry was appreciated.

Much of the value of this flame has been its ability to reduce interferences, especially of the chemical type. Its high temperature, combined with the fact that only the smallest of droplets of sample solution actually reach the premixed flame, reduces the severity of chemical interferences compared with other commonly used flames. The ionization of the metal to be determined could present a problem if its first ionization potential (I.P.) were less than 6.5 volts (88). Molybdenum has an I.P. of 7.35 volts, furthermore, ionization interferences can be overcome by the addition of an alkali salt to the sample solution (see Section 3.1.10.3). Koirtyohann and Pickett (89) found a different type of
# TABLE 3.2.

Mechanism of Metal Atom Reduction in Flame (62)

<table>
<thead>
<tr>
<th>Part of Flame</th>
<th>Physical form of sample</th>
<th>Reaction</th>
<th>Factors controlling reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outer mantle</td>
<td>Oxide</td>
<td>Equilibrium with</td>
<td>Flame composition</td>
</tr>
<tr>
<td></td>
<td></td>
<td>metal atoms</td>
<td>stability of oxide</td>
</tr>
<tr>
<td>reaction zone</td>
<td>Atoms</td>
<td>oxidation</td>
<td>Keq</td>
</tr>
<tr>
<td>inner cone</td>
<td>solid particles</td>
<td>Disintegration to atoms</td>
<td>M + O$_2$ $\leftrightarrow$ Mox</td>
</tr>
<tr>
<td>base</td>
<td>droplets</td>
<td>evaporation</td>
<td>Flame temperature anion</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Droplet size flame temperature feed rate</td>
</tr>
</tbody>
</table>
interference when using the nitrous oxide-acetylene flame. Heavy particles will diffuse less rapidly than lighter ones formed in the absence of acid or salt, resulting in a higher concentration of sample near the centre of the flame at its base. Such an interference could possibly enhance the absorption values for a metal.

Amos and Willis (90) considered the combustion process in a stoichiometric nitrous oxide-acetylene flame to be;

\[
5 \text{N}_2\text{O} \rightarrow 5 \text{N}_2 + \frac{5}{2} \text{O}_2 \quad \Delta H_{298} = +101.5 \text{ Kcal}
\]

\[
\text{C}_2\text{H}_2 + \frac{5}{2} \text{O}_2 \rightarrow 2\text{CO}_2 + \text{H}_2\text{O} \quad \Delta H_{298} = -300.1 \text{ Kcal}
\]

As nitrous oxide decomposes the temperature of the flame is increased by the energy which is liberated by the decomposition. Marks and Welcher (91) discredit this theory and propose a different mechanism;

\[
3\text{N}_2\text{O} + \text{C}_2\text{H}_2 \rightarrow 2\text{CO} + 3\text{N}_2 + \text{H}_2\text{O}
\]

At the temperature of the flame carbon dioxide will be almost completely dissociated, and the maximum temperature is produced by a stoichiometry of three moles of oxidant to one mole of fuel. The actual ratio of oxidant to fuel used in flame spectrometry is less than the stoichiometric amount. This ratio is of prime importance in defining the temperature of the flame and gas composition. Other authors (92) have carried out much work to determine flame conditions.

Kirkbright et al. (93) attribute the high population of free atoms in the nitrous oxide-acetylene flame to the existence of sufficient free carbon atoms or species in the flame to provide reducing conditions to prolong the lifetime
of the larger atomic population produced by the higher temperature. The existence of free carbon atoms would subsequently aid the production of free metal atoms by the reaction:

\[
\text{MO + C} \leftrightarrow \text{M + CO}
\]

where MO denotes the refractory form of metal M.

Much work has been done to determine which part of the flame will give absorption of greatest intensity. Rann and Hambly (94) suggest that molybdenum atoms can be observed in a small region near the core of a stoichiometric air-acetylene flame. The work of Willis et al. (95) suggests that the temperature of the region of the flame for atomic absorption spectrophotometry lies about 350° lower than the 3228K which is quoted as (85) the maximum temperature of the nitrous oxide-acetylene flame. This value occurs, if at all, only in the primary reaction zone, where lack of thermal equilibrium makes the results of temperature measurement uncertain.

Kirkbright et al. (96) report significant improvements in detection limits and sensitivities in separated nitrous oxide-acetylene flames sheathed with argon or nitrogen. In comparison with conventional flames, the interconal zone of the hot, slightly fuel rich separated flames provides better conditions for the maintenance of free atoms of elements which form refractory oxides.
3.2 Experimental Procedure and Apparatus

3.2.1 Reagents

A stock solution of 1000 parts per million (p.p.m.) molybdenum was prepared by dissolving ca. 1.840359g of ammonium molybdate \((\text{NH}_4)_6\text{Mo}_7\text{O}_{24}(\text{H}_2\text{O})_4\) in water and 5 ml of concentrated hydrochloric acid and diluting this to 1 litre with distilled-deionized water. Dilute standard solutions were prepared from this solution by suitable dilution. All other reagents were analytical reagent grade. All water used in this experimental section was distilled-deionized.

3.2.2 Apparatus

A Varian Techtron AA-4 atomic absorption spectrophotometer was used and this was set at 313.26 nm, which is the most sensitive absorption line for molybdenum. Also, the following settings for operation of this instrument were used;

- Slit width: 100\(\mu\)
- Source: molybdenum hollow cathode lamp
- Lamp current: 8 mA
- Fuel: acetylene
- Oxidant: nitrous oxide
- Support gas: air, delivery pressure 21.5 p.s.i.
- Burner: type AB50 titanium-steel burner for high temperature work 5cm x 0.45mm slit.
- Aspiration rate: 1.7 ml per minute.

The system used in the analytical work presented for discussion in this thesis is indicated in Fig. 3.1. It consisted of a hollow cathode discharge tube (H.C.D.T.) which
Fig. 3.1. Techtron AA4 flame spectrophotometer

- Hollow cathode discharge tube
- nebulizer and burner
- lens
- optical bed
- entrance slit
- photomultiplier
- monochromator
- wavelength adjuster
- fuel and oxidant controls
- amplifier
- output recorder
emits narrow resonance lines, a flame into which the sample was aspirated, a lens for focusing radiation from the source onto the central part of the outer cone of the flame, a second lens for transmitting radiation onto the monochromator entrance slit, a monochromator with accompanying optics and slits, a photodetector, amplifier, and a digital read out system. The H.C.D.T. emits a line of intensity $I_v^0$ and the intensity of the transmitted radiation is $I_v$. Prior to use, the second lens was adjusted with respect to distance from the flame, until transmittance was at a maximum value.

3.2.3 Calibration

Initially the atomic absorption values for 0, 2.5, 5, 10 and 20 p.p.m. molybdenum solutions were measured and calibration curves were plotted. These solutions contained 10 ml of lanthanum chloride (from a 10% solution), 6 ml of hydrochloric acid (1+1), ca. 0.1g of sodium chloride; in a total volume of 100 ml. It was noted after several runs of these solutions, that the calibration curves were not entirely linear. It was therefore found to be more expedient to bracket sample solutions between close standards and to make p.p.m. calculations from the data. Prior to making any measurements, the height and angle of the burner were adjusted, as was the position of the light source, so as to give optimum absorbance conditions for the standard solutions. Fresh 1000 p.p.m. stock solutions were prepared for each set of samples to be analyzed, because it was found that standards which were several days old were very unstable, and rapidly went off.
3.2.4 Putting Sample into Solution

The sample initially examined by atomic absorption spectrophotometry was unactivated molybdenum hexacarbonyl supported on γ-alumina. Work was carried out to develop a series of steps by which any disproportionation catalyst containing molybdenum on this type of support could easily be analyzed. This section covers the methods by which attempts were made to get the sample into solution in order that it could be aspirated into a flame, and give an accurate quantitative indication of the number of moles of molybdenum present. The sample used was prepared by dry mixing a 10% by weight ratio of molybdenum hexacarbonyl to γ-alumina support. The amount of molybdenum present, assuming uniform homogeneity across the support surface was estimated to be approximately 3.6%.

3.2.4.1: 0.03g of sample were treated with boiling (ca 10%) caustic soda. This solution was neutralized with concentrated nitric acid. Upon cooling, a residue remained, and it was considered unlikely that all of the molybdenum had gone into solution.

3.2.4.2: Approximately 0.03g of γ-alumina and 0.2g of lithium borate were fused in a carbon crucible at 1373K for 10-15 minutes. The molten bead produced was poured into 40 ml of 3% nitric acid, and the solution was quantitatively transferred to a volumetric flask and the volume was made up to 100 ml with water. 0.03g of sample were treated in the same manner as the standard discussed above. The resulting clear solution and standard were aspirated into a nitrous oxide-acetylene flame.
P.p.m. molybdenum concentrations of the samples were determined from a calibration plot by bracketing absorbance values of the samples between those of the standards, but these values did not reflect the amount of molybdenum that was initially thought to be present in the sample when it was prepared.

A test was carried out to determine the loss, if any, of molybdenum due to volatilization in the electric furnace. Samples were fused with lithium borate for 5, 10, 15 and 20 minutes, but any loss of molybdenum that occurred was not time dependent. This was indicated by the % molybdenum values of 0.65, 0.97, 0.99 and 1.00 calculated from a calibration curve, for the fused samples. It was concluded that either not all of the molybdenum present had gone into solution, or that most was lost by immediate volatilization upon exposure to the temperature of 1373K. These results need not necessarily imply that this method of sample attack was inaccurate, but that the sample composition was not homogeneous or that it was not the same as first considered. Also, no attempt had been made to eliminate possible anionic or cationic interferences.

3.2.4.3: Approximately 0.02g of sample were carefully weighed into a clean platinum crucible. 6 ml of (1 + 1) sulphuric acid were added and this was allowed to evaporate to fumes at 611K (97) on a hot plate. This volume of sulphuric acid was used because it was a good excess to completely cover and destroy the sample in the crucible. Evidence for the presence of molybdenum was given by a dark blue stain at the center of the semi-dry cake in the crucible.
"Molybdenum blue" is a mixture containing varying proportions of the oxides of Mo (VI) and Mo (V), for example Mo₂O₅·2MoO₃ (98). The cake was probably "semi-dry" because of moisture adsorption from the atmosphere. 6 ml of (1+1) hydrochloric acid was added and the crucible was heated gently on a hot plate until a clear solution resulted, while ensuring that the loss of hydrochloric acid by evaporation was minimal, by addition of about 10 ml of water. This solution was quantitatively transferred to a P.T.F.E. beaker and ca. 0.1g of sodium chloride, 10 ml of 10% lanthanum chloride were added and the volume made up to 100 ml in a volumetric flask with water. All solutions, including the standards described in section 3.2.3 were aspirated into a nitrous oxide-acetylene flame and molybdenum concentrations were calculated from the calibration curve. The values calculated were 3.4 and 3.2% molybdenum. This method of putting the sample into solution was considered the most useful of those tried because of the similarity between the initial percent molybdenum content and the value determined. This method of sample attack was probably the best because it involved a low temperature. Potassium hydrogen sulphate fusion for example would have required a temperature of almost 1000K and lithium borate fusion around 1400K. The method was clean and avoided the introduction of possible interferences from potassium, lithium and boron.

Other catalyst samples were prepared by dry mixing molybdenum hexacarbonyl or its organic derivatives with γ-alumina. These were put into solution by the method
described above and then aspirated with standard solutions into a nitrous oxide-acetylene flame. In Table 3.3 are listed the catalyst samples that were analyzed by atomic absorption spectrophotometry.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Estimated % Mo content</th>
<th>Determined % Mo content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(Co)₆ - γAl₂O₃</td>
<td>3.3</td>
<td>3.4 3.2</td>
</tr>
<tr>
<td>para-xylene - Mo(Co)₃ - γAl₂O₃</td>
<td>3.2</td>
<td>3.5 3.3 3.4 3.5</td>
</tr>
<tr>
<td>mesitylene - Mo(Co)₃ - γAl₂O₃</td>
<td>3.0</td>
<td>3.2 3.2</td>
</tr>
</tbody>
</table>

These samples were prepared and analyzed only to check the method, and the accuracy of the results would suggest that the method described in section 3.2.4.3 is quite satisfactory.

Catalyst samples that were supported on silica were prepared for analysis by a similar method. 6 ml of 40% hydrofluoric acid, and 2 ml of (1+1) sulphuric were added to the catalyst (ca. 0.02g) in a platinum vessel. Both acids were evaporated to fumes and the silica was lost with the hydrofluoric acid as H₂SiF₆.

3.2.5 Elimination of Chemical Interferences

In section 3.2.4.3 it was mentioned that lanthanum had been added to all solutions in order to eliminate the possible chemical interference of aluminium ions present after the dissociation of aluminium sulphate. A further set of tests were carried out to determine quantitatively the suitability of lanthanum in overcoming this particular
problem. Table 3.4 indicates the absorbance values of various solutions when lanthanum was and was not present to counteract aluminium interference.

<table>
<thead>
<tr>
<th></th>
<th>without La$^{3+}$</th>
<th>with La$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10 p.p.m. Mo, 0.1427g Al(NO$_3$)$_3$·9H$_2$O</td>
<td>178</td>
</tr>
<tr>
<td>B</td>
<td>10 p.p.m. Mo</td>
<td>120</td>
</tr>
<tr>
<td>C</td>
<td>0.1427g Al(NO$_3$)$_3$·9H$_2$O</td>
<td>0</td>
</tr>
</tbody>
</table>

It is very apparent that aluminium, possibly in conjunction with the nitrate ion significantly enhanced the reading shown by molybdenum on its own. Ca. 10 ml of (10% w/v) lanthanum chloride were added to solutions A, B, and C and the absorbance readings were then listed in the right hand column of Table 3.4. In solution B it is noted that lanthanum chloride has caused a slight enhancement of the molybdenum absorbance values. Nevertheless, the good agreement between the values for solutions A and B in the second column substantiates the original premise that lanthanum chloride would successfully eliminate any chemical interference caused by aluminium ions.

3.2.6 Nitrous oxide-acetylene flame versus air-acetylene flame

Throughout the catalyst analysis by means of atomic absorption spectrophotometry only a nitrous oxide-acetylene flame had been used as a means of sample atomization. During preliminary investigations a brief study was made of the suitability of the lower temperature air-acetylene flame. Air pressure was maintained at 21.5 p.s.i. and the acetylene
flow rate was adjusted until optimum absorbance values were indicated for an aspirated standard solution. Sample and standard solutions were aspirated into this flame and the % molybdenum content of the samples were calculated to be 0.77, 0.72 and 0.77. There are not enough values here to consider calculating the standard deviation or the relative deviation.

The same catalyst sample was aspirated into a nitrous oxide-acetylene flame. Twelve values of its % molybdenum content were calculated. The mean value was $1.65\% \pm 0.148$. The relative standard deviation was $9.00\%$. Certainly this latter value is rather high, but the sample was analyzed over a period of one year, and also it is possible that the molybdenum was not evenly distributed across the entire surface. Nevertheless these results do point out that the sample was not satisfactorily atomized in the air-acetylene flame.
3.3 Verification of Atomic Absorption Results by Colourimetry

The choice to use atomic absorption spectrophotometry as the method of catalyst analysis was entirely arbitrary. The results discussed in section 3.2.6 referring to the analysis of the replicate sample would suggest that atomic absorption spectrophotometry is a relatively precise and straightforward technique once developed. However, the accuracy of the method had not been fully investigated, so it was considered an appropriate exercise to verify the previous results by analyzing the replicate sample by colourimetry.

3.3.1 History and General Theory: Thiocyanate Method

Molybdenum reacts with alkali thiocyanate to form an amber to orange-red complex. The oxidation state of molybdenum in this complex is five (99, 100, 101), although Groothamel and Johnson (101) report that sexivalent molybdenum forms a thiocyanate complex in acetone medium (60% by volume) with an absorption peak at 350 nm. A variety of formulae has been assigned to the molybdenum (V) complex (102, 103). Babko considered the complex formation to proceed as follows;

\[ \text{Mo}^{+5} + m \text{SCN}^- \leftrightarrow [\text{Mo(SCN)}_m]^{5-m} \text{ colourless} \]

\[ [\text{Mo(SCN)}_m]^{5-m} + (5-m)\text{SCN}^- \leftrightarrow \text{Mo(SCN)}_5 \text{ red} \]

Perrin (104) reported that the ratio of SCN$^-$/molybdenum in the red-coloured complex was 3:1. This complex is uncharged and most likely MoO(SCN)$_3$ as Sand (102) has suggested. Complexes with SCN/molybdenum ratios of 2:1 and 1:1 are yellow and colourless respectively.
Dick and Bingley (105) suggested that the complex used for analysis consisted of chromogenic and non-chromogenic entities, but Crouthamel and Johnson (101) found no evidence to support the mixed complex theory.

Hurd and Allen (106) investigated the optimum operating range of the concentrations of thiocyanate ion, stannous chloride, and hydrochloric and sulphuric acids. The colour intensity depends on acidity, concentration of thiocyanate, and the time of standing. The acidity of the solution in hydrochloric acid should be approximately 5%. At this acidity the colour remains nearly constant for the length of time required to measure the absorption of each solution. Acidities higher and lower than this give less colour and greater fading, which is especially marked in strongly acidic solutions. Fluctuations in the stannous chloride concentration had no effect on the speed of colour development or on the subsequent rate of fading.

Dick and Bingley (105) found absorption values were enhanced when one gram-atom of ferrous iron per gram atom of molybdenum was included in sample solutions. This author is unable to report any such enhancement of absorption signals when ferrous ammonium sulphate was added to sample solutions.

Grimaldi and Wells (107) recommended water miscible solvents such as acetone in the thiocyanate procedure. Acetone has a slight reducing effect and also assists in
stabilizing molybdenum (V).

3.4 Experimental Apparatus and Procedure

3.4.1 Reagents

A stock solution of 1000 p.p.m. molybdenum was prepared by dissolving ca. 1.84035g (carefully weighed) of brushed and finely ground crystals of ammonium molybdate with 1 litre of water. Dilute standard solutions of 1, 2, 3, 4 and 5 p.p.m. were prepared by suitable dilution of this stock solution. To each standard were added 10 ml (1+1) hydrochloric acid, 10 ml KSCN (10% w/v), 1 ml SnCl$_2$.2H$_2$O (10% w/v), and 25 ml of acetone. All volumes were made up to 100 ml with water. All chemicals used were of analytical reagent grade.

3.4.2 Apparatus

The absorption values of the sample and standard solutions were measured by a Pye Unicam SP600 spectrophotometer. Cells of length 1 or 2 cm., depending on the intensity of the colour of the solutions, were used.

3.4.3 Calibration

A standard solution of 3 mg of molybdenum was prepared in aqueous medium (the standards in 3.4.1 refer to those used in final colourimetric method). The absorption of this solution was measured after time intervals of approximately 3 minutes, and this value appeared to decrease after each reading taken, as indicated in Fig. 3.2. A set of molybdenum standards was then prepared in aqueous-acetone medium and the absorption was measured. A straight line calibration curve was obtained. The method finally used determined molybdenum directly from a thiocyanate complex in an acetone-aqueous medium, using molybdenum standards
Fig. 3.2. Calibration curves

parts per million of molybdenum

absorbance

aqueous medium

aqueous-acetone medium
made up in the same medium. According to Sandell (108) the intensity of the complex colour in aqueous medium will remain constant for less time than is necessary to study the samples.

3.4.4 Method

The sample for analysis had been analyzed in replicate by atomic absorption spectrophotometry (See 3.2.6 for mean value and standard deviation). The choice of colourimetric method to use was not easy to make. The sensitivity of the dithiol (109) method was greater than that required for this work, molybdenum isolation procedures such as precipitation as the sulphide, extraction of molybdenum cupferrate with chloroform, ether or iso amyl alcohol extraction (108) were unnecessary because a reliable method of sample attack had already been developed for the atomic absorption analysis. These would have been far too sensitive anyway, necessitating an undesirable reduction of the sample weight or an increase of dilution factors with associated problems of possible lack of replicate homogeneity. Therefore the procedure for putting the sample into solution for this colourimetric analysis was identical to that established in the previous atomic absorption analysis. It seemed prudent to continue to work with 20 mg. of sample, since it had not yet been established if any other elements or ions, alone or in conjunction with each other chemically interferred with the colourimetric method. Also, this weight was a very easy amount of sample to put into solution. Later work proved that certain foreign ions did not interfere and that a lower sample weight could have been used. 10 ml of (1+1) hydrochloric acid were added to the semi-dry cake in the
platinum crucible then warmed with approximately 5 ml of water to produce a clear solution. The solution was then transferred quantitatively to a 100 ml volumetric flask, to which were added 10 ml (10% w/v) KSCN, 1 ml (10% w/v) SnCl₃·2H₂O and 25 ml of acetone. At the final acid concentration (5%) the colour intensity of the thiocyanate complex remained fairly constant. Hurd and Allen (106) found that higher or lower acidities gave less colour intensity and greater fading.

3.4.5 Results

The first results obtained from calibration curves were 1.04, 1.12 and 1.14% molybdenum in the replicate sample. The discrepancy between the values obtained by colourimetry and atomic absorption (1.65%) becomes immediately evident and indicated that either one or the other, or both methods, had produced inaccurate results. Below are listed some possible explanations for this significant difference.

3.4.5.1: Dick and Bingley (105) found that when they employed an extraction procedure with iso amyl alcohol, trace amounts of iron facilitated greater colour development. Although solvent extraction had not been used in the analysis presented in this section, it is certainly conceivable that this, in conjunction with ferrous iron - capable of reducing Mo(VI) to Mo(V) - and present in the standard solutions and not in the sample, could have produced lower results for the replicate sample than for the standards. Therefore, the samples would appear to have lower molybdenum content than was actually present.
3.4.5.2: Emeleus and Anderson (110) state that molybdenum hexacarbonyl decomposes readily in nitric acid. It is possible that during the catalyst activation, not all of this complex on the alumina support decomposed to molybdenum metal or a non-carbonyl bearing species, but existed as a sub-carbonyl species somewhat resistant to attack by sulphuric acid. This probably would not be a problem during the analysis by atomic absorption spectrophotometry because the flame temperature would have been sufficient to break up any molybdenum sub-carbonyl compound, but it would be a problem for the colourimetric method because free molybdenum ions are necessary to form the coloured complex.

3.4.5.3: Possibly molybdenum in small quantities was lost by volatilization when treated with sulphuric acid at over 611K (97) on a hot plate. Rates of volatilization may have been different but this was highly unlikely because of the precision of the colourimetric results, and also the results for the replicate analyzed by atomic absorption were in good agreement.

3.4.5.4: The last possible explanation for the discrepancy in the results may have been the lack of suitability of the ammonium molybdate standards that were used. Molybdenum trioxide dissolved in caustic soda and neutralized with acid might have been preferable. The same type of standard solutions were used for both the atomic absorption and the colourimetric methods so it was unlikely that the standard solutions were at fault. Acid molybdate standard solutions rapidly deteriorate, and had this problem affected the colourimetric method, (this method only requires free
molybdenum ions in solution available to form a coloured complex), then the % molybdenum content determined by atomic absorption would have been lower than the colourimetric result, and this was not the case.

3.4.6 Examination of the Possible Reasons for the Difference in the Analytical Results.

3.4.6.1: A sample solution for colourimetric analysis was prepared by the method already described. In addition 1 ml of ferrous ammonium sulphate (1% w/v) and 2 ml of stannous chloride (10% w/v) were added. A 1 ml excess of the latter had been added in order to ensure that iron remained in the ferrous state having possibly assisted with the reduction of molybdenum (VI). Iron (III) forms a coloured species which absorbs at 480 nm, when complexed with thiocyanate, and might as a consequence enhance the absorption due to the molybdenum thiocyanate complex. From a calibration plot the % molybdenum content of the samples was determined to be 1.14, 1.06, and 1.07. These values are in good agreement with the results already obtained, thus indicating that the addition of ferrous iron to the sample solutions had not increased the number of molybdenum ions able to form a coloured complex with thiocyanate.

3.4.6.2: Approximately 20 mg of alumina supported catalyst sample were treated with a 1:1 mixture of (1+1) sulphuric acid and nitric acid. The former was added primarily to remove HNO₃ by evaporation to fumes and the nitric acid was present to assist the decomposition of any molybdenum carbonyl molecules present. Fresh standards were prepared and from a calibration curve the % molybdenum content of the
samples was calculated to be 1.13, 1.09 and 1.09. The standards did not contain nitric acid therefore this was removed from the test solution by fuming to prevent the oxidation of stannous chloride. From the results obtained it is apparent that nitric acid does not increase the molybdenum content of the solutions for analysis, and sulphuric acid heated to fumes leads to the complete recovery of molybdenum.

3.4.6.3: 1.53 mg of molybdenum hexacarbonyl were weighed into a clean pyrex dish. 3 ml each of concentrated sulphuric and nitric acids were added and the mixture fumed to dryness at 611K on a hot plate, and the residue was dissolved in 10 ml of 1+1 hydrochloric acid, then diluted further with 5 ml of water. 10 ml (10% w/v) of KSCN, 1 ml (10% w/v) SnCl₂·2H₂O, and 25 ml of acetone were added. This solution was quantitatively transferred to a 100 ml volumetric flask and the volume was made up with water. Fresh molybdenum standards were prepared to match the sample solutions, and from the calibration plot the amount of molybdenum in the sample was calculated at 36.7%. The theoretical value was 36.3%.

Molybdenum hexacarbonyl or some sub carbonyl species, may or may not have been present in the catalyst samples supported on alumina, but the above results prove that if it is still present after catalyst activation then none is lost during sample treatment. Also, the validity of the colourimetric method was proven, but in the absence of sulphate and aluminium ions.

3.4.6.4: Approximately 1.84060g of ammonium molybdate were
dissolved in one litre of water. 1.51511 g of molybdenum trioxide were dissolved in a minimum of caustic soda, neutralized with a small amount of hydrochloric acid and made up to one litre in a volumetric flask with water. To aliquots of each were added 10 ml of KSCN, 1 ml of SnCl₂·2H₂O, and 25 ml of acetone, and the volumes made up to 100 ml, thus creating two 3 p.p.m. molybdenum solutions. Both solutions were examined colourimetrically using 2 cm cells and the absorption values were 0.150 and 0.148 for the molybdate and oxide solutions respectively. The significance of these results is that the discrepancy between the colourimetric and atomic absorption results was not due to the standards.

The results presented in section 3.4.6 would therefore suggest that the colourimetric method was entirely in order and that further investigation would be required of the preliminary atomic absorption analysis. Unfortunately none of the catalyst samples analyzed by atomic absorption were available for colourimetric analysis, and so the replicate sample was used in further studies. The mean value of ten colourimetric determinations of the replicate was 1.11% ± standard deviation 0.03. The relative deviation was 2.70%. It must be emphasized that these were obtained at different times using different methods.

3.4.7 Reinvestigation of Anionic and Cationic Interferences

Because no systematic error in the colourimetric analysis could be established, earlier investigations discussed in section 3.2.5 were repeated. Included in this work were tests for interferences caused by sulphate in
addition to aluminium and nitrate ions in the atomic absorption of molybdenum. A fresh 1000 p.p.m. stock solution was prepared, and from this, solutions to be aspirated into the nitrous oxide-acetylene flame.

3.4.8 Results and Discussion

The solutions aspirated and the atomic absorption values are presented in Table 3.5. It will be noted that the results for solutions 2 and 6 agree quite closely with each other, and also with previous data presented in Table 3.4. of section 3.2.5. It was originally assumed that lanthanum successfully nullified aluminium interference and that anionic interferences were negligible. However it might be that the nitrate ion is exerting a depressing effect on molybdenum and that the addition of lanthanum does not completely remove aluminium interference which probably causes enhancement. The combined effect of aluminium and nitrate ions would therefore be zero.

The results for solutions 3 and 4 show that lanthanum has not very effectively removed the combined interference caused by aluminium and sulphate ions. During sample treatment with sulphuric acid the following reaction will take place:

$$\text{Al}_2\text{O}_3 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Al}_2(\text{SO}_4)_3 + 3\text{H}_2\text{O}$$

Excess sulphuric acid would have been fumed off and water lost by evaporation. The semi-dry cake in the crucible was therefore $\text{Al}_2(\text{SO}_4)_3$. When acidified and diluted with hydrochloric acid and water this substance would dissociate to aluminium and sulphate ions. The weight of catalyst used
<table>
<thead>
<tr>
<th>Solution*</th>
<th>Atomic Absorbance</th>
<th>Colourimetric Absorbance†</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 10 p.p.m. Mo</td>
<td>53</td>
<td>847×201*†</td>
</tr>
<tr>
<td>2. 10 p.p.m. Mo, 20 ml LaCl₃</td>
<td>76</td>
<td></td>
</tr>
<tr>
<td>3. 10 p.p.m. Mo, Al₂(SO₄)₃·16 H₂O</td>
<td>123</td>
<td>213</td>
</tr>
<tr>
<td>4. 10 p.p.m. Mo, &quot; &quot;&quot; &quot; , LaCl₃</td>
<td>126</td>
<td></td>
</tr>
<tr>
<td>5. &quot; &quot; Al(NO₃)₃·9 H₂O</td>
<td>105</td>
<td>833</td>
</tr>
<tr>
<td>6. &quot; &quot; &quot; &quot; , LaCl₃</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>7. Al₂(SO₄)₃·16 H₂O</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8. Al(NO₃)₃·9 H₂O</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>9. Al₂(SO₄)₃ 16 H₂O, LaCl₃</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>10. Al(NO₃)₃ 9 H₂O, LaCl₃</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

* All solutions contained 0.1g NaCl, 3 ml conc. HCl
† 3 p.p.m. Mo solutions
* no SO₄²⁻ present
x no NO₃⁻ present
in every analysis was kept constant at $20 \pm 0.5$ mg, therefore one only need consider interference from an equivalent weight of aluminium sulphate. It was the combined interference of aluminium and sulphate ions that caused the discrepancy between the colourimetric and atomic absorption results. It should be possible to apply a correction factor to the % molybdenum values obtained by atomic absorption in order to determine the correct % molybdenum content of these alumina supported catalysts.

3.4.9 Chemical Interferences in the Colourimetric Method

From the data presented in the right hand column of Table 3.5 it is evident that aluminium in conjunction with sulphate or nitrate ions does not interfere with the absorption of the coloured molybdenum complex.

Fig. 3.3 represents the absorption values of two sets of molybdenum solutions analyzed colourimetrically, one containing a fixed weight of sulphate and the other without. The closeness of the two lines suggest that sulphate ions do not interfere of their own accord. Two alumina supported catalyst samples were prepared for colourimetric analysis and their % molybdenum contents were determined from the calibration plots in Fig. 3.3.

<table>
<thead>
<tr>
<th></th>
<th>without $\text{SO}_4^-!!!!_2$</th>
<th>2.22</th>
<th>2.23</th>
<th>2.36</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>with $\text{SO}_4^-!!!!_2$</td>
<td>2.17</td>
<td>2.18</td>
<td>2.33</td>
</tr>
</tbody>
</table>

3.4.10 Determination of a Correction Factor

Two sets of molybdenum standards were prepared from a 1000 p.p.m. stock molybdenum solution. These solutions covered the parts per million working range that had been used during the atomic absorption method of analysis. All
Fig. 3.3. Colourimetric comparison of standards with and without sulphate ions present.

Absorbance

Parts per million of molybdenum

Sulphate present

No sulphate present
contained 20 ml (5% w/v) lanthanum chloride, 3 ml concentrated hydrochloric acid, and approximately 0.1g of sodium chloride. One set of standards was mixed with a fixed weight of aluminium sulphate (the weight of aluminium present in a 20 mg catalyst sample). Both sets of standards were aspirated in the nitrous oxide flame of the atomic absorption spectrophotometer. The ratio of the absorption readings of each solution without sulphate present to each with, was plotted against the parts per million concentration of each. These points have been plotted in Fig. 3.4. The mean value of this "correction factor" is $0.64 \pm 0.054$.

3.4.11 Verification of the Correction Factor

A fresh catalyst sample was prepared by dry mixing 1.0962g of Laport Boehmite $\gamma$-alumina with 0.1099g of molybdenum hexacarbonyl. This sample was heated in vacuo to 438K. The sample was analyzed by atomic absorption spectrophotometry and from a standard calibration curve the % molybdenum content was determined to be 3.17. By application of the correction factor the % molybdenum content was 2.05. Reanalysis of the same sample colourimetrically gave a value of 2.17% molybdenum which is in good agreement with the calculated value. Originally 3.31% molybdenum had been dry-mixed with the Boehmte support and almost certainly some molybdenum hexacarbonyl would have been lost by volatilization.

3.4.12 Chemical Interference caused by increasing Sulphate Ion Concentration

A check was made to determine whether or not an increase in the sulphate ion concentration in the solutions prepared
Fig. 3.4. Least-squares fit of line through points representing the correction factor.

\[
y = \text{intercept} \quad 0.6495
\]

\[
\text{gradient} \quad -0.0003129
\]
for analysis by atomic absorption affected their absorption values. Five samples of approximately the same weight of an alumina supported catalyst were prepared in the manner previously described (3.2.4.3). The volume of sulphuric acid used for sample decomposition ranged from 1 to 5 ml. In Table 3.6 are listed the absorption readings when the solutions were aspirated into a nitrous oxide-acetylene flame.

<table>
<thead>
<tr>
<th>vol. $\text{H}_2\text{SO}_4$(ml)</th>
<th>Absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>49</td>
</tr>
<tr>
<td>4</td>
<td>49</td>
</tr>
<tr>
<td>5</td>
<td>49</td>
</tr>
</tbody>
</table>

According to these results the volume of sulphuric acid used was in excess of the amount required to decompose the samples.

3.4.13 Conclusion

The colourimetric method for molybdenum appeared to be more precise than the atomic absorption method, probably because of greater sensitivity. It is therefore a much more versatile method because sample weights could have been varied widely. Aluminium and sulphate ions do not interfere with the molybdenum colourimetric method, and it is to be recommended in preference to the atomic absorption method for the molybdenum analysis of catalysts of this type.
CHAPTER IV
THE PRESENTATION OF RESULTS

4.1 Study of the Activated Mo(CO)$_6$–$\gamma$Al$_2$O$_3$ Catalyst

4.1.1 Changes in Catalyst Colour

At room temperature, prior to outgassing and activation, the dry mixed catalyst sample was cream-white in colour. Outgassing of the catalyst at room temperature for any extended period of time caused it to take on a lemon-yellow appearance. Activation in vacuo at temperatures approaching 373K resulted in a rapid change to dark yellow and further heating caused the product to turn dark grey or brown. At room temperature when exposed to air after activation it slowly reverted to its original cream colour, very similar to that of calcined alumina. Catalysts which had been prepared by sublimation of the molybdenum hexacarbonyl precursor onto $\gamma$-alumina were also lemon-yellow after being outgassed, and behaved much as the dry mixed catalyst when activated at temperatures above room temperature. If however, the sample was stored in vacuo, reversal of colour characteristics was not noticeable unless the storage vessel developed a slow leak.

4.1.2 Analysis of Gas Evolved

The volume of gas not condensable at 77K, which had evolved from the catalyst during the activation procedure, was measured by means of a Töpler pump which was further used to push some of this gas into an evacuated infra-red cell approximately 8 cm in length and equipped with potassium bromide windows. All infra-red spectra were run on a Perkin-
Photo Electron Spectrum of gas from catalyst GDS

CO  3000 counts per second
N₂  25
H₂O  25
CO₂  0
Photo Electron Spectrum of gas from catalyst GD9

CO  > 5000 counts per second
N$_2$  25
H$_2$O  0
CO$_2$  0

Electron  Volts
Photo Electron Spectrum of gas from catalyst GD10

- CO: 3000 counts per second
- Ar: 15
- O₂: 0
- H₂O: 100
- CO₂: 10

Electron Volts
Elmer 457 grating spectrometer. A Perkin-Elmer PS-16 photo electron spectrometer was occasionally used to provide supporting qualitative evidence to the infra-red data for the presence of carbon monoxide.

4.1.3 Study of CO:Mo Molar Ratios

Because of significant losses of catalyst during outgassing procedures (finely ground particles of catalyst were trapped in the glass wool plugs during outgassing), sample weights were usually determined after the activation procedure. These samples were then analyzed by atomic absorption spectrophotometry for their molybdenum content and from the available data CO:Mo molar ratios were calculated. In Tables 4.1 and 4.2 are presented some of the numerical details pertaining to each catalyst sample after it was activated. The carbon monoxide volumes were corrected for standard temperature and pressure. The temperatures presented are those of the heat source as recorded on a thermometer, and not necessarily those of the samples themselves. It was not until an activation study of alumina supported organic derivatives of molybdenum hexacarbonyl was carried out, that temperatures were determined more accurately by means of a thermocouple.

The data of Tables 4.1 and 4.2 are discussed in the order of the restricted temperature ranges at which the catalyst samples were activated, followed by the measurement of the volumes of non-condensable gas evolved.

4.1.3.1. 403-433K

This range of temperatures is very uncertain, but this reason alone cannot account for the lack of reproducibility
of the CO:Mo molar ratios. Volume measurements were not
started until each catalyst had been activated for
approximately 60-70 minutes. During the activation of
GD-2 it was noted that a significant amount of molybdenum
hexacarbonyl crystals had sublimed onto the cool, upper
part of the reaction vessel. The product of the decompo-
sition of molybdenum hexacarbonyl which had remained on
the alumina support surface was pale yellow with dark brown
areas unevenly distributed across the visible surface. Such
evidence emphasized how poor a method of sample preparation
sublimation was because there was no guarantee that molyb-
denum hexacarbonyl would be homogeneously distributed across
the surface. There was no evidence to suggest that any of
the molybdenum hexacarbonyl on the vessel walls from GD-2
had decomposed to carbon monoxide and molybdenum subcarbonyl
molecules. No molybdenum mirror was seen at the coolest
upper surface of the reaction vessel. If any molybdenum
hexacarbonyl had remained undecomposed on the surface after
activation, it is quite possible that it would have been
included in the analysis of the sample. However, any such
compound retained on the surface of the glass reaction
vessel would not have been included, because in each
experiment the section of the vessel containing the catalyst
was cut away from the rest of the apparatus in order to
prevent excess molybdenum hexacarbonyl from being present.

4.1.3.2. 363-395K

The majority (GD-5A, 6A, 10B, A-4, A-5) of the CO:Mo
molar ratios for catalysts activated in this temperature
range are in good agreement with each other. All of the
<table>
<thead>
<tr>
<th>Sample</th>
<th>Method of preparation</th>
<th>Temp. K</th>
<th>Volume of CO(ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GD-1</td>
<td>sublimation</td>
<td>413-423</td>
<td>4.7</td>
</tr>
<tr>
<td>A</td>
<td>GD-2</td>
<td>413-433</td>
<td>1.1</td>
</tr>
<tr>
<td>A</td>
<td>GD-3</td>
<td>403-413</td>
<td>1.9</td>
</tr>
<tr>
<td>A</td>
<td>GD-7</td>
<td>376</td>
<td>1.1</td>
</tr>
<tr>
<td>A</td>
<td>GD-8</td>
<td>393</td>
<td>1.7</td>
</tr>
<tr>
<td>A</td>
<td>GD-11</td>
<td>394</td>
<td>1.9</td>
</tr>
<tr>
<td>B</td>
<td>GD-5A</td>
<td>394</td>
<td>1.0</td>
</tr>
<tr>
<td>B</td>
<td>GD-6A</td>
<td>394</td>
<td>1.0</td>
</tr>
<tr>
<td>B</td>
<td>A-4</td>
<td>395</td>
<td>4.3</td>
</tr>
<tr>
<td>B</td>
<td>A-5</td>
<td>363</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>GD-10B</td>
<td>373</td>
<td>2.1</td>
</tr>
<tr>
<td>C</td>
<td>GD-9</td>
<td>425</td>
<td>3.4</td>
</tr>
<tr>
<td>C</td>
<td>GD-10</td>
<td>424</td>
<td>3.2</td>
</tr>
<tr>
<td>C</td>
<td>GD-4A</td>
<td>423</td>
<td>3.3</td>
</tr>
<tr>
<td>C</td>
<td>GD-8B</td>
<td>423</td>
<td>5.8</td>
</tr>
<tr>
<td>D</td>
<td>GD-1A</td>
<td>458</td>
<td>5.9</td>
</tr>
<tr>
<td>D</td>
<td>GD-2A</td>
<td>455</td>
<td>4.6</td>
</tr>
<tr>
<td>D</td>
<td>GD-3A</td>
<td>456</td>
<td>4.2</td>
</tr>
<tr>
<td>D</td>
<td>GD-5B</td>
<td>673</td>
<td>3.3</td>
</tr>
<tr>
<td>Sample</td>
<td>% Mo prior to activation</td>
<td>% Mo det'd by A.A.</td>
<td>Corrected % Mo</td>
</tr>
<tr>
<td>---------</td>
<td>--------------------------</td>
<td>--------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>GD-1</td>
<td>-</td>
<td>1.22</td>
<td>0.78</td>
</tr>
<tr>
<td>GD-2</td>
<td>-</td>
<td>2.23</td>
<td>1.44</td>
</tr>
<tr>
<td>GD-3</td>
<td>2.05</td>
<td>1.52</td>
<td>0.98</td>
</tr>
<tr>
<td>GD-7</td>
<td>4.81</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>GD-8</td>
<td>3.54</td>
<td>2.14</td>
<td>1.38</td>
</tr>
<tr>
<td>GD-11</td>
<td>4.08</td>
<td>4.21</td>
<td>2.71</td>
</tr>
<tr>
<td>GD-5A</td>
<td>3.14</td>
<td></td>
<td>2.02</td>
</tr>
<tr>
<td>GD-6A</td>
<td>4.29</td>
<td>2.68</td>
<td>1.73</td>
</tr>
<tr>
<td>A-4</td>
<td>-</td>
<td>3.76</td>
<td>2.41</td>
</tr>
<tr>
<td>A-5</td>
<td>-</td>
<td>1.39</td>
<td>0.89</td>
</tr>
<tr>
<td>GD-10B</td>
<td>3.35</td>
<td>1.59</td>
<td>1.02</td>
</tr>
<tr>
<td>GD-9</td>
<td>3.73</td>
<td>3.02</td>
<td>1.95</td>
</tr>
<tr>
<td>GD-10</td>
<td>3.81</td>
<td>3.21</td>
<td>2.07</td>
</tr>
<tr>
<td>GD-4A</td>
<td>4.29</td>
<td>3.94</td>
<td>2.54</td>
</tr>
<tr>
<td>GD-8B</td>
<td>3.42</td>
<td>4.36</td>
<td>2.81</td>
</tr>
<tr>
<td>GD-1A</td>
<td>4.29</td>
<td>5.25</td>
<td>3.39</td>
</tr>
<tr>
<td>GD-2A</td>
<td>4.29</td>
<td>4.56</td>
<td>2.95</td>
</tr>
<tr>
<td>GD-3A</td>
<td>4.29</td>
<td>4.42</td>
<td>2.85</td>
</tr>
<tr>
<td>GD-5B</td>
<td>-</td>
<td>2.05</td>
<td>1.33</td>
</tr>
</tbody>
</table>
carbon monoxide volume measurements were made, with the exception of A-4 and A-5, after the samples had been activated, rather than during this process. The time dependence of CO:Mo for GD-1OB, 8, 5A, and 6A was studied for 28, 60, 95, and 250 minutes respectively, and there appears to be very little effect caused by varying the length of the activation time. In the case of catalysts A-4 and A-5 the non-condensable gas was continually topped during activation, with no pronounced effect on the total volume of gas liberated.

4.1.3.3. 423-425K

The CO:Mo molar ratios for catalysts activated in this temperature range are in good agreement with each other. However the CO:Mo molar ratio for GD-8B is higher than those of the other catalysts present in this range, suggesting that the decomposition of molybdenum hexacarbonyl occurred more readily. It is also quite possible that the amount remaining on the support surface during the initial stages of activation was greater. During the activation of GD-8B the non-condensable gas evolved was continually topped to a constant volume. The equilibrium for the decomposition of molybdenum hexacarbonyl in this reaction would therefore be pushed more to the right, and one would expect a higher CO:Mo molar ratio for this catalyst. A high pressure of carbon monoxide above the catalyst in a closed system would also reduce the chances of unreacted Mo(CO)\(_6\) subliming onto the vessel walls.

4.1.3.4. 456-458K

The agreement between CO:Mo molar ratios presented indicates that the evolution of carbon monoxide at these
temperatures is not time dependent, because catalysts 1A, 2A and 3A were activated for 60, 125, and 246 minutes respectively. The CO:Mo molar ratios for catalysts activated at 458K approach and in some instances exceed 6.00. This is in agreement with infra-red spectroscopic studies (42) which suggest that catalyst activation at temperatures approaching 473K causes almost complete disappearance of carbonyl species.

In the second column of Table 4.2 are listed the molybdenum content values of each catalyst prior to activation. This figure represents the initial amount of molybdenum present during dry-mixing and only serves to give a rough indication of the amount of molybdenum hexacarbonyl lost by volatilization during catalyst activation.
4.2. Study of Supported Molybdenum Hexacarbonyl Organic Derivatives

4.2.1. Changes in Catalyst Colour

<table>
<thead>
<tr>
<th>Prior to Activation</th>
<th>After Activation</th>
<th>Exposed to Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>A  lemon yellow</td>
<td>dark brown</td>
<td>light brown</td>
</tr>
<tr>
<td>B  lemon yellow</td>
<td>dark brown</td>
<td>light brown</td>
</tr>
<tr>
<td>C  very pale yellow</td>
<td>greenish brown</td>
<td>light yellow</td>
</tr>
<tr>
<td>D  dark pink</td>
<td>dark brown</td>
<td>off-white</td>
</tr>
<tr>
<td>E  lemon yellow</td>
<td>dark brown</td>
<td>greenish grey</td>
</tr>
</tbody>
</table>

In Tables 4.3 and 4.4 are presented the observations and resulting calculations relevant to the study of these heterogeneous disproportionation catalysts.

4.2.2 Analysis of Gas Evolved

Infra-red spectra of each sample of non condensable gas (at 77K) were run on a Perkin-Elmer 457 spectrometer. All spectra contained peaks attributable to carbon monoxide and no C-H or O-H stretching peaks were present. Any organic ligand that had been lost during the activation procedure had successfully condensed in the liquid nitrogen trap. No attempt was made to separate, analyze or measure the volumes of these condensed materials.

4.2.3 Study of the CO:Mo Molar Ratio

For every catalyst studied, the carbon monoxide which evolved during activation was continually topped, therefore encouraging the evolution of the greatest possible volume of gas under the prevailing reaction conditions. In Tables 4.3 and 4.4 are presented the results of the experiments carried out.
Infra-red spectra of non-condensable gas from:
1 toluene tricarbonyl molybdenum - Al₂O₃
2 norbornadiene tetracarbonyl molybdenum - Al₂O₃
3 mesitylene tricarbonyl molybdenum - Al₂O₃
4 triphenylphosphine pentacarbonyl molybdenum - Al₂O₃
<table>
<thead>
<tr>
<th>Sample</th>
<th>Method of preparation</th>
<th>Temp. K</th>
<th>Vol. of CO (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mesitylene-Mo(CO)$_3$-Al$_2$O$_3$</td>
<td>dry mixing in N$_2$</td>
<td>483</td>
<td>3.7</td>
</tr>
<tr>
<td>A</td>
<td></td>
<td>491</td>
<td>7.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>499</td>
<td>13.1</td>
</tr>
<tr>
<td>toluene-Mo(CO)$_3$-Al$_2$O$_3$</td>
<td>dry mixing in N$_2$</td>
<td>493</td>
<td>6.1</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>498</td>
<td>7.5</td>
</tr>
<tr>
<td>(C$_6$H$_5$)$_3$P-Mo(CO)$_5$-Al$_2$O$_3$</td>
<td>dry mixing in air</td>
<td>480</td>
<td>1.9</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td>499</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>516</td>
<td>3.7</td>
</tr>
<tr>
<td>[π-C$_5$H$_5$-Mo(CO)$_3$]$_2$-Al$_2$O$_3$</td>
<td>dry mixing in air</td>
<td>483</td>
<td>3.6</td>
</tr>
<tr>
<td>D</td>
<td></td>
<td>493</td>
<td>6.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>503</td>
<td>2.3</td>
</tr>
<tr>
<td>D$_1$</td>
<td>-SiO$_2$</td>
<td>493</td>
<td>5.1</td>
</tr>
<tr>
<td>norbornadiene-Mo(CO)$_4$-Al$_2$O$_3$</td>
<td>dry mixing in air</td>
<td>488</td>
<td>6.1</td>
</tr>
<tr>
<td>E</td>
<td></td>
<td>493</td>
<td>6.2</td>
</tr>
</tbody>
</table>
The data presented in Table 4.4 is insufficient for one to be able to draw conclusions about the relative abilities of each catalyst to give up molecules of carbon monoxide, especially if one attempts to explain gas evolution in terms of the possible influence of the organic ligands on the strength of the molybdenum-carbon monoxide bond.

It is noted that the CO:Mo molar ratios for the silica supported catalyst D₁ and the alumina supported catalysts D closely agree. With only one result for the silica supported catalyst it is difficult to say if this is an established trend. It does suggest however that the change in support has not caused any difference in the amount of carbon monoxide evolved under identical reaction conditions.


<table>
<thead>
<tr>
<th>Sample</th>
<th>% Mo det'd by A.A.</th>
<th>Corrected % Mo</th>
<th>Corrected CO:Mo molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>mesitylene-Mo(CO)$_3$-Al$_2$O$_3$</td>
<td>3.42</td>
<td>2.21</td>
<td>3.3 ± 0.3</td>
</tr>
<tr>
<td>A</td>
<td>3.72</td>
<td>2.40</td>
<td>3.7 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>5.70</td>
<td>3.68</td>
<td>3.7 ± 0.3</td>
</tr>
<tr>
<td>toluene-Mo(CO)$_3$-Al$_2$O$_3$</td>
<td>6.55</td>
<td>4.22</td>
<td>1.7 ± 0.1</td>
</tr>
<tr>
<td>B</td>
<td>3.63</td>
<td>2.34</td>
<td>3.3 ± 0.3</td>
</tr>
<tr>
<td>(C$_6$H$_5$)$_3$P-Mo(CO)$_5$-Al$_2$O$_3$</td>
<td>0.68</td>
<td>0.44</td>
<td>6.8 ± 0.5</td>
</tr>
<tr>
<td>C</td>
<td>0.936</td>
<td>0.60</td>
<td>5.4 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>2.18</td>
<td>1.41</td>
<td>5.8 ± 0.5</td>
</tr>
<tr>
<td>[$\pi$-C$_5$H$_5$-Mo(CO)$_3$]$_2$-Al$_2$O$_3$</td>
<td>3.84</td>
<td>2.48</td>
<td>2.3 ± 0.2</td>
</tr>
<tr>
<td>D</td>
<td>4.05</td>
<td>2.61</td>
<td>2.9 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>1.91</td>
<td>1.23</td>
<td>2.6 ± 0.2</td>
</tr>
<tr>
<td>D$_1$</td>
<td></td>
<td></td>
<td>2.4 ± 0.2</td>
</tr>
<tr>
<td>norbornadiene-Mo(CO)$_4$-Al$_2$O$_3$</td>
<td>9.71</td>
<td>6.26</td>
<td>1.9 ± 0.2</td>
</tr>
<tr>
<td>E</td>
<td>10.06</td>
<td>6.48</td>
<td>1.9 ± 0.2</td>
</tr>
</tbody>
</table>
4.3 Study of the Activated Mo(CO)$_6$-SiO$_2$ Catalyst

4.3.1 Change in the Catalyst Colour

All samples, when outgassed or activated at temperatures greater than room temperature, demonstrated the same colour changes that have been described for the Mo(CO)$_6$-γAl$_2$O$_3$ in section 4.1.1.

4.3.2 Analysis of the Gas Evolved

Samples GD-Si-Mo 1, 2, and 3 had been prepared by impregnating the silica support with a cyclohexane solution of molybdenum hexacarbonyl at room temperature, under an atmosphere of dry nitrogen. The gas evolved from GD-Si-Mo 1 and 3 was left in the vicinity of the catalyst for the duration of the activation process before being passed through a liquid nitrogen "muck" trap and measured in the Töpler pump. The gas from GD-Si-Mo 2 was tøpled during the activation of the catalyst. The infra-red spectrum of the gas from GD-Si-Mo 2 showed strong peaks at 2940, 2865, 2665, 2170, 2125, 1455, 1260, 1040, and 863 cm$^{-1}$. The stretching mode of carbon monoxide is indicated by P and R branches at 2125 and 2170 cm$^{-1}$, and the rest of the spectrum can be attributed to the C-H stretches and other vibrational modes of a cyclic organic compound. The infra-red spectrum of GD-Si-Mo 3 contained peaks at 2930 and 800 cm$^{-1}$ despite attempts to remove all gases with the exception of carbon monoxide by condensation into a liquid nitrogen trap. Severe contamination of the carbon monoxide measured may well be the principle reason that the CO:Mo molar ratios presented in Table 4.5 lack precision for catalysts activated within the same temperature range. Because these results are not in
Table 4.5
Evaluation of CO:Mo ratio: Mo(CO)$_6$-SiO$_2$ catalyst system

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method of preparation</th>
<th>Temp. K</th>
<th>Volume of CO(ml)</th>
<th>CO:Mo molar ratio</th>
<th>Apparatus</th>
</tr>
</thead>
<tbody>
<tr>
<td>A GD-Si-Mo-13</td>
<td>dry mixing</td>
<td>370</td>
<td>16.9</td>
<td>5.5 ± 0.4</td>
<td>open</td>
</tr>
<tr>
<td>B A-2</td>
<td>sublimation</td>
<td>401</td>
<td>4.1</td>
<td>1.8 ± 0.1</td>
<td>closed</td>
</tr>
<tr>
<td>B A-3</td>
<td>dry mixing</td>
<td>400</td>
<td>3.7</td>
<td>1.4 ± 0.1</td>
<td>closed</td>
</tr>
<tr>
<td>C GD-Si-Mo-8</td>
<td>dry mixing</td>
<td>393</td>
<td>4.5</td>
<td>2.1 ± 0.2</td>
<td>closed</td>
</tr>
<tr>
<td>C GD-Si-Mo-9</td>
<td>dry mixing</td>
<td>393</td>
<td>6.5</td>
<td>4.0 ± 0.3</td>
<td>open</td>
</tr>
<tr>
<td>D GD-Si-Mo-12</td>
<td>dry mixing</td>
<td>423</td>
<td>6.9</td>
<td>1.2 ± 0.1</td>
<td>closed</td>
</tr>
<tr>
<td>D GD-Si-Mo-5</td>
<td>dry mixing</td>
<td>423</td>
<td>3.5</td>
<td>1.1 ± 0.1</td>
<td>open</td>
</tr>
<tr>
<td>D GD-Si-Mo-3</td>
<td>impregnation</td>
<td>423</td>
<td>14.3</td>
<td>2.7 ± 0.2</td>
<td>closed</td>
</tr>
<tr>
<td>D A-8</td>
<td>sublimation</td>
<td>430</td>
<td>13.8</td>
<td>3.4 ± 0.3</td>
<td>closed</td>
</tr>
<tr>
<td>E GD-Si-Mo-6</td>
<td>dry mixing</td>
<td>453</td>
<td>5.7</td>
<td>1.3 ± 0.1</td>
<td>closed</td>
</tr>
<tr>
<td>E GD-Si-Mo-7</td>
<td>dry mixing</td>
<td>453</td>
<td>19.4</td>
<td>2.9 ± 0.2</td>
<td>open</td>
</tr>
<tr>
<td>E GD-Si-Mo-10</td>
<td>dry mixing</td>
<td>453</td>
<td>7.5</td>
<td>2.3 ± 0.2</td>
<td>closed</td>
</tr>
<tr>
<td>E GD-Si-Mo-11</td>
<td>dry mixing</td>
<td>453</td>
<td>13.5</td>
<td></td>
<td>closed</td>
</tr>
<tr>
<td>F GD-Si-Mo-1</td>
<td>impregnation</td>
<td>473</td>
<td>10.8</td>
<td>3.3 ± 0.3</td>
<td>closed</td>
</tr>
<tr>
<td>F GD-Si-Mo-2</td>
<td>impregnation</td>
<td>473</td>
<td>8.7</td>
<td>3.3 ± 0.3</td>
<td>open</td>
</tr>
</tbody>
</table>
good agreement with each other a thorough interpretation
is difficult. It is also impractical to attempt to compare
and contrast the CO:Mo molar ratios of silica supported
catalysts with those of alumina supported catalysts.

Howe (42) has found that upon activation, silica
supported molybdenum hexacarbonyl gives up molecules of
carbon monoxide far more readily and to a greater extent than
the alumina supported analogue. The CO:Mo molar ratios in
Table 4.5 do not in themselves suggest this, however it is
possible that carbon monoxide might be released by the silica
supported catalyst at room temperature. In Table 4.6 are
presented the results of experiments to measure carbon
monoxide volumes released at and above room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time of study (mins)</th>
<th>Temp. K</th>
<th>Vol. of CO(ml)</th>
<th>% of total</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-2</td>
<td>10</td>
<td>291</td>
<td>1.9</td>
<td>46.3</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>401</td>
<td>2.2</td>
<td>53.6</td>
</tr>
<tr>
<td>A-3</td>
<td>18</td>
<td>291</td>
<td>1.8</td>
<td>48.6</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>400</td>
<td>1.9</td>
<td>51.4</td>
</tr>
<tr>
<td>A-4</td>
<td>10</td>
<td>291</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>394</td>
<td>4.3</td>
<td>100</td>
</tr>
<tr>
<td>A-5</td>
<td>11</td>
<td>291</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>363</td>
<td>2.9</td>
<td>100</td>
</tr>
</tbody>
</table>

The results in Table 4.6 confirm the infra-red study
made by Howe of silica and alumina supported catalysts.
Samples A-2 and A-3 were analyzed for the % molybdenum content
by atomic absorption spectrophotometry and the calculated CO:Mo molar ratios were $1.8 \pm 0.1$ and $1.4 \pm 0.1$ respectively, not 6.00 as predicted. These values might well have been increased had the gas evolved been continuously topped during the increase in temperature of the catalyst, rather than when the sample reached room temperature and again when the catalyst activation was terminated.
4.4 Rate of Carbon Monoxide Evolution

The results presented in sections 4.1, 4.2 and 4.3 give a rough estimate of the amount of carbon monoxide which is evolved when the supported catalysts are activated at certain temperatures and prepared by different techniques. However, so far no evidence has been presented in this thesis which might suggest the rate at which non-condensable gas is evolved, and what parameters affect the establishment or the position of the kinetic equilibrium of the reaction.

\[ \text{Mo(CO)}_6 \rightleftharpoons \Delta \rightarrow \text{Mo(CO)}_{6-x} + x\text{CO} \]

4.4.1 Silica and Alumina Supported Molybdenum Hexacarbonyl

The manner in which this study was carried out and the results presented do not permit the determination of a numerical rate constant for the above reaction, but it was hoped that one might be able to determine any possible difference in the rate of gas evolution from different supports. The terms 'open' and 'closed' systems used to describe the apparatus have already been discussed in section 2.6. The total volume of the apparatus was kept constant at 225 ± 10 ml. The sample weights were not uniform but the weight ratio of molybdenum hexacarbonyl to support was kept constant at approximately 1:10. From Figs. 4.4.2, 4.4.3 and 4.4.5 it is apparent that when carbon monoxide was left in the vicinity of the catalyst for the entire duration of the activation process the increase in the total pressure exerted by the carbon monoxide evolved, approached zero. The equipment used to measure pressure changes was not sufficiently sensitive to allow a thorough study of pressure changes at
Fig. 4.4.1. Open System.

- 373K
- 423K

Total pressure \( \times 10^3 \text{ N m}^{-2} \)

Total time (mins.)
Fig. 4.4.2. Closed System

- $373K$
- $423K$

Time (mins.)

Total pressure $\times 10^2$ Nm$^{-2}$

Silica supported
Fig. 4.4.3. Closed System

- θ 423K
- φ 453K
- • 673K
Fig. 4.4.4. Open System

- 393K
- 423K
- 473K

Time (mins.)

Total pressure x 10^2 Nm^-2 vs. time (mins.)

Silica supported
Fig. 4.4.5. Closed System

- 393K
- 423K
- 453K

Silica supported
fractions of a minute. Nevertheless the results roughly indicate that for the times at which pressure measurements were made, there was no noticeable difference in the initial rate of carbon monoxide evolution from the silica or alumina supported catalysts. The plots in Figs. 4.4.1 and 4.4.4 indicate that the carbon monoxide was evolved during a reduction of its partial pressure above the catalyst. An increase of this partial pressure caused the decomposition of molybdenum hexacarbonyl to cease, so that an equilibrium gas pressure was established. There was no indication of a decrease of the partial pressure in closed systems, caused by the adsorption of carbon monoxide onto the support. Such a reaction was unlikely because the calcined supports would have been rehydrated upon cooling to room temperature in air after initial calcination, and carbon monoxide is not adsorbed onto 'wet' surfaces. There was no sign of carbon dioxide condensed in the liquid nitrogen 'muck' trap.

There is not sufficient data in Figs. 4.4.2, 4.4.3 and 4.4.5 to indicate if the position of the equilibrium level is temperature dependent.
4.4.2 Silica supported Organic derivatives of Molybdenum Hexacarbonyl

Figs. 4.4.6 to 4.4.9 indicate that for the same weight of silica supported catalysts, an equilibrium pressure is established and in each case is at approximately the same value for catalysts activated at different temperatures in 'closed' systems. The data in Table 4.7 shows that although the equilibrium pressure remains constant, the temperature at which this is achieved does not, and is most likely due to inconsistent rates of sample heating.
Fig. 4.4.6. Pentacarbonyl triphenylphosphine molybdenum – SiO₂

♀ 0.6140g  443K
♀ 0.6757g  410K

Total pressure x 10² Nm⁻²

(time (mins.))
Fig. 4.4.7. Tricarbonyl mesitylene molybdenum - SiO$_2$
Fig. 4.4.8. Bis tricarbonyl π-cyclopentadiene molybdenum - SiO₂

- 1.0392g  443K
- 1.0520g  393K
- 1.0275g  413K

Time (mins.)
Fig. 4.4.9. Tetracarbonylnorbornadiene molybdenum - SiO$_2$

- $\phi$ 0.6240g 383K
- $\triangle$ 0.7002g 408K
- $\bigcirc$ 0.6921g 433K
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Equilibrium Pressure</th>
<th>Temp K at Equilibrium Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>mesitylene-Mo(CO)$_3$-SiO$_2$</td>
<td>A 13.3</td>
<td>386</td>
</tr>
<tr>
<td></td>
<td>B 13.3</td>
<td>450</td>
</tr>
<tr>
<td>[(\pi)-C$_5$H$_5$ Mo(CO)$_3)]$_2$-SiO$_2$</td>
<td>A 6.0</td>
<td>440</td>
</tr>
<tr>
<td></td>
<td>B 6.6</td>
<td>364</td>
</tr>
<tr>
<td></td>
<td>C 6.6</td>
<td>333</td>
</tr>
<tr>
<td>(C$_6$H$_5$)$_3$ Mo(CO)$_5$ - SiO$_2$</td>
<td>A 4.0</td>
<td>340</td>
</tr>
<tr>
<td></td>
<td>B 5.5</td>
<td>368</td>
</tr>
<tr>
<td>C$_7$H$_8$ Mo(CO)$_4$ - SiO$_2$</td>
<td>A 10.0</td>
<td>368</td>
</tr>
<tr>
<td></td>
<td>B 12.5</td>
<td>391</td>
</tr>
<tr>
<td></td>
<td>C 12.5</td>
<td>425</td>
</tr>
</tbody>
</table>
4. The activity of the catalyst depends on the temperature of activation after addition of Mo(CO)₆ to the support.

Molybdenum hexacarbonyl is sufficiently volatile that any excess not interacting with the support will be rapidly removed from the support surface on evacuation at room temperature. The results of analysis for % molybdenum content of the different catalysts presented in this thesis indicate a fairly high degree of precision for samples of the same catalyst, analyzed by the same method. This suggests that during the catalyst preparation, molybdenum hexacarbonyl is evenly dispersed across the support surface.

Via kinetic studies Smith et al. (43) have found that maximum catalytic activity for olefin disproportionation is obtained on silica supported molybdenum hexacarbonyl. The silica was outgassed at room temperature prior to addition of the Mo(CO)₆, this temperature being sufficient to remove most bulk water but not to remove strongly bonded hydroxyl groups. Consequently, throughout the interaction of the molybdenum hexacarbonyl with the silica support there was a maximum involvement of hydroxyl groups. Such was not the case for γ-alumina supported catalysts. Kinetic studies (43) have shown that maximum catalytic activity for the disproportionation reaction occurs when the support has been outgassed at 573K at which temperature dehydroxylation will be extensive.

Alumina supported catalysts pretreated above 673K show a decrease in catalytic activity as well as an increase (43) in the extent of surface dehydroxylation. This is not due to a decrease in the amount of molybdenum retained on the
support, thus confirming that there is no direct relationship between catalytic activity and % molybdenum content. Mild activation of supported Mo(CO)$_6$ produced Mo(CO)$_5$ (III) as indicated by the colour change from "off-white" to yellow. Measurement of the volume of carbon monoxide evolved and the subsequent calculation of CO:Mo molar ratios indicates that alumina supported molybdenum hexacarbonyl has completely decomposed releasing all of its carbon monoxide when activated at approximately 460K.

The results presented in Table 4.5 for the silica supported catalysts are less reliable than the CO:Mo molar ratios in Table 4.2. It would therefore be rather presumptuous to contradict more reliable infra-red data which indicates that all of the carbon monoxide is released from silica supported catalysts activated at high temperatures.

The data presented in Tables 4.2 and 4.5 suggest that at low activation temperatures sub-carbonyl species of molybdenum exist both on alumina and silica. At temperatures greater than 450K alumina-supported molybdenum hexacarbonyl is completely decomposed, whereas the silica supported analogue is unaccountably stable. Slow activation of the alumina supported catalyst results in the evolution of carbon monoxide at 313-320K with four new bands being produced in the infra-red spectrum of the catalyst. From this data, Howe (42) has concluded that there are three and possibly four different subcarbonyl species present: species A, in which $\nu$(10) appears at 1790 and 1725 cm$^{-1}$; species B, at 1935 cm$^{-1}$; and species C, at 2020 cm$^{-1}$. CO:Mo molar ratios of catalysts activated at low temperatures support the possible existence
of sub-carbonyl species of the type Mo(CO)$_x$ where $x = 2, 3$ or $4$. Infra-red studies (42) have shown that the decomposition of molybdenum hexacarbonyl on dehydrated alumina is not retarded by surface hydroxyl groups.

Silica supported molybdenum hexacarbonyl activated at 373K or higher has no bands in the carbonyl region. Howe et al. (42) have determined spectroscopically that the decomposition of Mo(CO)$_6$ on this support is almost complete after evacuation for several hours at 318K, and that above 373K this is no longer reversible. Results presented in Table 4.6 for this catalyst activated at 370K suggest that at least 50% of the total volume of carbon monoxide evolved did so at room temperature. The CO:Mo molar ratios for examples A-2 and A-3 fail to support the spectroscopic evidence in the literature, because in both cases these values are less than 6.00, and perhaps the amounts of CO evolved at these temperatures from silica-supported catalysts are large enough to account for the discrepancies.

The possible adsorption of carbon monoxide onto the high surface area silica must be ignored as Howe et al. have failed to observe carbonate species on silica supported catalysts. It has been suggested (42) that metallic molybdenum on the surface of silica, might be capable of readabsorbing carbon monoxide after catalyst evacuation at 318K, resulting in the formation of a band at 1985 cm$^{-1}$. However, because molybdenum species activated at 373K or greater do not reversibly adsorb carbon monoxide, then metallic molybdenum must not be involved in the active species. This band at 1985 cm$^{-1}$ is common to all catalysts discussed in this
thesis and is not strong enough to account for the CO:Mo molar ratios less than 6.00 for silica supported catalysts.

A photo electron spectrum of all gas evolved from decomposed Mo(CO)₆ on alumina revealed that approximately 1% was carbon dioxide. This result disagrees with a value of 15% reported by Wharton (112) who apparently measured the volume of CO₂ evolved in a Töpler pump and identified it by infra-red spectroscopy. The degree of accuracy of the 1% result presented in this work was greatly affected by machine noise at high levels of sensitivity, but it is very difficult to reconcile these results especially as the CO₂:CO volume ratio reported by Wharton is so high. Had a significant volume of carbon dioxide been present in the gas samples analyzed by photoelectron spectroscopy, then interference from machine noise would have been irrelevant.

Previous work carried out by this author involved the activation of a 1:1 by weight ratio of molybdenum hexacarbonyl and potassium fluoride on alumina. A photoelectron spectrum of the gas evolved indicated the possible formation of CO₂ but once again identification of the gas was not conclusive because of high noise levels.

The quantity of molybdenum retained on the support after activation is greater at high activation temperatures such as 455 or 460K, compared with 370 or 390K. Upon exposure to temperatures greater than room temperature, supported Mo(CO)₆ can do one of two things; it can sublime to a cooler part of the reaction vessel or it may decompose. It has already been mentioned that Mo(CO)₆ is volatile at room temperature and will therefore sublime
easily, but possibly, upon exposure to much higher temperature, sufficient activation energy has been provided to cause decomposition before sublimation. Catalyst temperature studies which employed a thermocouple attached to a Servo-scribe recorder indicate that the rate of temperature rise is greater for samples placed in an electric muffle preset at a high temperature than at a low temperature. Fig. 5.2 substantiates this statement. Unfortunately there was not sufficient data available to study the amount of molybdenum retained on the silica support after catalyst activation.

Possible Nature of the Catalyst

The reaction between molybdenum hexacarbonyl and alumina can perhaps be considered to proceed via the following steps.

1. Following catalyst preparation the sample was heated in vacuo. Just above room temperature some of the molybdenum hexacarbonyl sublimed onto the cooler parts of the reaction vessel, and that which remained on the support, decomposed.

2. Above a certain activation temperature, the decomposition of the molybdenum carbonyl species is no longer a reversible process. Subcarbonyl species of the type Mo(CO)$_x$ where $x = 2, 3$ and $4$, exist on the surface, even though infra-red data would suggest that decomposition was complete at 373K.

3. Molybdenum in its zero oxidation state will be free to react with surrounding hydroxyl groups on the hydrated surface. Alumina appears (113) to have the special property of stabilizing intermediate molybdenum valence states,