CHAPTER I.

INTRODUCTION.

I.A. General.

Heterogeneous catalysis forms the cornerstone for many industrial processes. The most important catalysts are the metal oxide catalysts. A proper understanding of the processes taking place on the surface of the catalyst, and the factors determining the rate of the reaction has been the main aim of many research workers.

The metal oxide catalysts include insulators such as alumina and silica-alumina catalysts, or semiconductor oxides such as chromia, nickel oxide, zinc oxide, etc. The explanations of the catalytic behavior of the insulators have been restricted mainly to their acid-base properties. For the semiconductor oxides a number of theories have been proposed to account for their catalytic behavior. The most well known of these are the electronic theories put forward by Hauffe and Wolkenstein. Balandin has sought to explain the behavior of catalysts in terms of a general multiplet theory.
The catalysts chosen for study in this thesis are alumina and chromia. Previous investigations carried out with respect to their physico-chemical and catalytic properties are reviewed in sections I.B. and I.C. of this chapter, respectively.

I.B. Alumina.

Alumina is widely used as a catalyst for alcohol dehydration, olefin isomerisation, and hydrocarbon cracking reactions. In industry it is mainly used as a support for metal or metal oxide catalysts. The activity of the alumina catalyst or support depends primarily on the method of its preparation and activation, and various factors have to be considered in selecting the most active catalyst.

I.B.1. Crystal structure and texture. A comprehensive account of the crystal structure and texture of alumina can be found in the thesis submitted by Lippens and the reports of the Alcoa Co.

Alumina can be prepared by the dehydration of its hydroxide or by the decomposition of its salts. Of these, the former is more important, as the catalyst thus obtained is more active and has a higher surface area.

I.B.1.1. The aluminium hydroxides may be obtained in an amorphous form, as a gel, or as crystalline mono- or trihydrates. The hydrates chiefly used in the preparation of catalysts are bayerite, gibbsite and boehmite. Alumina gels have also been used.

The trihydrates of alumina (bayerite, gibbsite and norstrandite) have similar cell dimensions except for the length
of the c axis. This has been rationalised by considering the trihydrates as being built out of layer lattices loosely stacked in the c direction. Gibbsite is generally associated with sodium or some other alkali metal ions. Bayerite is reported to be converted into gibbsite in the presence of alkali metal ions. Saalfeld has discussed the stabilising influence of impurity ions on the gibbsite lattice. Wefers considers the growth of the gibbsite crystal and the brucite structure of bayerite and the monoclinic structure of gibbsite on the basis of an incorporation of sodium ions in vacancies in the hydroxyl network of the layer lattice and the consequent distortion of the lattice. Lippens, however, considers the different structures of the trihydrates as being due to the different sequence of stacking of the double layers in the various hydrates.

The monohydrates are considered to have a double-chain structure. Similarly, the structure of the sheet-like gelatinous boehmite gel is considered to be similar to that of the monohydrates, except that the chain-like structure is converted into a sheet-like structure by hydrogen bonding between the chains and some incorporated water molecules.

I.B.1.2. The dehydration of the aluminium hydroxides give α-alumina as the final product. The α-alumina is catalytically inactive. The catalytically active aluminas are generally obtained by heating the hydroxides to a temperature between 500° and 600° C.

The hydrates or gels of alumina have six hydroxyl groups octahedrally surrounding the aluminium ion.
As dehydration takes place the aluminium ions become tetrahedrally coordinated. It is for this reason, perhaps, that the initial products of dehydration resemble cubic spinel structures, with the aluminium ions occupying both octahedral and tetrahedral holes. As the dehydration temperature is increased, the crystal structure of the intermediate phases resemble those of the hexagonal corundum-like structures with the aluminium ions occupying octahedral holes.

The generally accepted dehydration sequence of bayerite, boehmite and gibbsite are given below:

\[
\begin{align*}
\text{Gibbsite} & \quad 270^\circ \rightarrow x \quad 970^\circ \quad k \\
\downarrow & \\
\text{Boehmite} & \quad 450^\circ \rightarrow y \quad 750^\circ \rightarrow 900^\circ \rightarrow \Theta \rightarrow \alpha \\
\text{Bayerite} & \quad 230^\circ \rightarrow \eta \quad 850^\circ \rightarrow \Theta \quad 1100^\circ \rightarrow \alpha
\end{align*}
\]

This sequence depends on the original nature of the hydrate. Laubengayer et al. has shown that all the hydrates may be converted into boehmite under hydrothermal conditions. It is, therefore, difficult to obtain an alumina without it being contaminated with the decomposition product of boehmite, namely, \(\gamma\)-alumina.

Catalytically the most active forms of the various aluminas are \(\eta\) - and \(\gamma\) - alumina. The \(\eta\) - and \(\gamma\) -aluminas have very similar structures, resembling a deformed cubic spinel. The difference between \(\eta\) - and \(\gamma\) -alumina has been attributed to the predominant exposure of the (111) plane by the \(\eta\) -alumina and the (110) or the (100) plane.
by the $\gamma$-alumina. Fripiat et al consider that the difference between these two aluminas is due to the presence of more loosely bound oxygen on the surface of the $\eta$-alumina than on the $\gamma$-alumina.

I.B.1.3. Johnson et al have characterised the porous texture of alumina obtained by the dehydration of boehmite or bayerite into three types. They are (a) the micropores of about 10Å width obtained from the tri-hydrates, (b) boehmite pores from a gel-like structure and (c) interparticular pores dependent on the particle size of the hydrate.

An initial increase in the surface area of the tri-hydrates of alumina has been attributed to the evaporation of water molecules from between the layer lattices in the tri-hydrate. For the monohydrates of alumina and the alumina gels the initial increase in the surface area has been attributed to the breakdown of the structure to give microcrystallites. The subsequent decrease in the surface area is due to the sintering of the small pores or due to the sintering of the small crystallites. The trihydrates also undergo a hydrothermal transformation within the pores of the larger crystals to boehmite, and this gives rise to the formation of 'ink-bottle' type of pores.

I.B.2. Dehydration of alcohols. Perhaps the earliest reaction in which alumina was consciously used as a catalyst for any reaction was the dehydration of alcohols. A large number of papers have been published on these dehydration reactions which have been reviewed by Winfield and by Pines and Manassen.
I.B.2.1. The most widely studied alcohol is ethyl alcohol which gives rise to ethylene and diethylether as the main products. The early workers had suggested the intermediate formation of ether in the formation of ethylene, while others considered the ether and olefin to be formed by parallel paths. Balaceanu and Jungers suggest a primary ether formation with possible equilibration with the alcohol, and secondary olefin formation of the ether with the formation of alcohol.

The necessity of an ether intermediate is now rejected from a number of considerations. First, most of the secondary alcohols do not give ethers although they give olefins. Secondly, radioactive tracer studies carried out with ethanol and ether mixtures by Isagulyants et al showed that the alcohol and ether quickly achieve a dynamic equilibrium, and the subsequent olefin formation can take place from either the ether or the alcohol. The reaction sequence for alcohol dehydration as proposed by Knözinger et al, and outlined below, is essentially similar to that proposed by Balandin and co-workers.

\[
\begin{align*}
2 \text{ Alcohol} & \xrightarrow{\text{Ether + Water}} \text{Alcohol + Olefin + Water} \\
& \xrightarrow{2 \text{ Olefin} + 2 \text{ Water}} \text{2 Alcohol}
\end{align*}
\]

I.B.2.2. Although the question of the reaction sequence for alcohol dehydration has been more or less settled, the exact mechanism of the reaction and the part played by the
catalyst is still uncertain.

The early workers had proposed a radical inter-
mediate to account for the dehydration of alcohols
Whitmore suggested a carbonium ion mechanism brought about by a Bronsted acid site. Brey and Kreiger and others have suggested similar carbonium ion mechanisms.

Adkins and Watkins found a greater activity with alumina catalysts prepared by the hydrolysis of an aluminium alcoholate compared to commercial alumina catalysts. Using the results of Peacem and Swallow they suggested that the increased activity was due to an increase in the aprotic acidity because of the absence of sodium ions in the alumina catalysts prepared by the hydrolysis of the alcoholates.

Pines and Haag carried out a detailed study of the differences in the activity of alumina catalysts prepared by the hydrolysis of aluminium isopropanoxide and by the neutralization of sodium aluminate solutions. The latter catalysts are less active. They, therefore, postulated an intrinsic acidity for alumina, which is poisoned by the presence of sodium ions. They also showed by titrations with typical Lewis acid indicators, that the acid sites of alumina resemble Lewis acids. The alcohols are adsorbed on these sites by an oxonium-carbonium ion mechanism. Krylov suggested a similar mechanism after a consideration of the thermochemical factors involved in the adsorption and desorption of the reactant and products from acid sites of various strengths.
I.B.2.3. Kochloeff et al. 47,48, working with substituted cyclohexanols so as to distinguish between double bond isomerisations and dehydration, found that the double bond isomerisation reaction is forty times slower than the dehydration reaction, and that the dehydration reaction is not poisoned by pyridine. They, therefore, postulated that the dehydration reaction did not require acid sites. Vasserberg et al. found strong support for a non-ionic mechanism when they observed a para-ortho hydrogen conversion during alcohol dehydration over alumina which was absent in the absence of alcohol. Based on their work on conjugate dehydration of ethanol and isopropanol and on the influence of various alcohol-ether mixtures on each other during dehydration, they have postulated a polymolecular complex formation on the surface interactions between which leads to the products of dehydration.53

With the advances in infra-red spectrophotometric techniques, the chemical species formed on the surface of alumina on alcohol adsorption could be studied. Thus, coordinated or hydrogen-bonded alcohol or ether molecules could be detected which on heating gave rise to species with alkoxide or a carboxylate structure.

Topchieva et al. were among the first to propose an alkoxide intermediate in the formation of ethers and olefins from alcohols. Although an alkoxide-like species is accepted as an intermediate in the formation of ethers from alcohols, its intermediacy in olefin forming reactions has been doubted mainly on the basis that certain alcohols which give olefins on dehydration do not form an alkoxide structure.63,64,65
I.B.2.4. The presence of an alkoxide intermediate suggests an interaction between the alcohol molecule and a hydroxyl group or an oxide ion on the surface. Kagel has found evidence for an interaction with the oxide ion, as shown below:

\[ \text{ROH} + \text{AlO} \xrightarrow{\text{Al}} \text{RO} + \text{AlOH} \]

Adkins and Watkins suggested that the hydrogen on the \( \beta \) carbon atom is involved in a hydrogen bond with a surface oxygen while the alcoholic hydroxyl group was coordinated to an aluminium ion. Pis'man et al. have also considered a similar mechanism involving the oxide ion on the surface and the carbon atom, the dehydration taking place by a Baker-Nathan effect. Trambouze et al., on the basis of the poisoning influence of tetracyanoethylene on the dehydration reaction, consider the basic sites as being important in dehydration reactions. Knözinger has proposed a mechanism involving the basic oxide or hydroxyl groups on the surface of alumina, on the basis of deuterium exchange studies and consideration of the shifts in the hydroxyl group absorption band in the infra-red spectra of adsorbed alcohol molecules on alumina with temperature.

I.B.2.5. From what has been discussed so far in this section, one is yet to be convinced of the actual nature of the active site for alcohol dehydration on the surface of alumina. The activity of the catalyst is, furthermore, determined by the nature of the substrate molecule. Kochloeff has found a dependence on the geometry of the substrate and Pines et al. have shown a
change from Saytzeff to Hoffman elimination for various alcohols with increased branching.

The important factor in olefin formation seems to be the acidity of the catalyst. Pines and Pillai have shown a poisoning influence of bases such as ammonia, triethyl amine, and piperidine on the dehydration of menthols. Ross and Bennett have observed that sodium impregnation poisons the dehydration activity. Jain and Pillai have proposed a carbonium ion mechanism on an acid site for olefin formation and an alkoxide formation on a basic site for ether formation on the basis of their studies with alcohol, in which they found that an acidic compound like phenol poisons the ether formation and a basic compound like pyridine poisons the olefin formation. Pines et al. have proposed a synchronous trans-elimination reaction, involving acid and basic sites, operating synchronously from opposite walls of a micropore, on an alcohol molecule "solvated" within it.

I.B.3. The Carboxylate species observed in the IR on alcohol adsorption. Although Babushkin et al. had observed the formation of an alkoxide surface species in the infra-red spectra of alcohols adsorbed on alumina, there was no mention of an acetate or carboxylate species. The latter species were reported later by several workers and was obtained by heating the sample containing the adsorbed alcohol to a higher temperature. The exact part played by this species in the reactions of alcohols over alumina is not clear.

Makarov and Shchekochikhin have observed both
alkoxide and acetate species on the adsorption of ethanol on alumina. On the basis of the influence of sodium addition on the acetate species, they have suggested that the acetate structure may be directly or indirectly responsible for olefin formation.  

Yakerson et al consider the acetate or carboxylate species as arising from side reactions not associated with olefin formation. Further, while the alkoxide structure could be easily influenced by the adsorption of water and ammonia, the acetate or carboxylate species was quite stable to such treatment.

Kagel has considered the origin of the carboxylate species as due to a dehydrogenative reaction leading to a structure shown below:

$$R-CH_2 \xrightarrow{\text{A1}} H + \frac{1}{2} H_2$$

They have observed the evolution of hydrogen. Fink, however, considers that the acetate or carboxylate structure is due to the conversion of the alcohol molecule to a carbonyl molecule, and the further saponification of this molecule to get the carboxylate species. Their arguments were based on their observations of the infra-red spectra of carbon dioxide adsorbed on alumina.

Krylov et al have measured the heats of adsorption of isopropanol on alumina and the desorption products of the adsorbed alcohols corresponding to various heats of adsorption. The alcohols adsorbed with a heat of adsorption greater than 40 to 50 kcal/mole — which according to Egorov is due to
adsorption of aluminium ions with uncompensated charge do not desorb till above 300°C. The desorption products are not olefin and water, but methane and carbon monoxide. Hence it is quite likely that the alcohols which are adsorbed with a high heat of adsorption form an acetate-like species on the surface. The site for such an adsorption is probably an aluminium ion with an uncompensated charge, which would be expected to have strong oxidative properties. The mechanisms proposed by Kegel and Fink involve dehydrogenation reactions. Knözinger has suggested that the carboxylate species is associated with the dehydrogenation reactions of alcohols.

I.B.4. Red-ox centres on alumina. Egorov, proposing a model for γ-alumina, which has a structure similar to spinel (MgAl2O4), suggested that the aluminium ions, which occupy the tetrahedral holes occupied by magnesium in spinel, would have one of its charges uncompensated. As mentioned above, such aluminium ions may be associated with red-ox reactions on the catalyst surface.

Flockhart et al. have observed the formation of radical cations or radical anions on alumina catalysts. They have suggested that different, mutually dependent, surface sites are responsible for reduction or oxidation. These authors have proposed, on the basis of Peri's model, an over exposed aluminium ion which acts as an acceptor centre for adsorption of donor molecules such as polynuclear hydrocarbons. A powerful donor site associated with the acceptor site converts
acceptor molecules such as trinitrobenzene to the radical-anion form. These authors have sought to distinguish red-ox reactions from Lewis acid-Lewis base reactions. Brouwer has suggested one electron transfer reactions for the formation of radical anions or cations.

Golubev and Ebreinov have attributed a wide and a narrow signal in the ESR spectrum on the adsorption of quinones on alumina to the presence of Lewis acid centres such as the aluminium atom on the surface and to radical ions respectively. Kotel'nikov and Tarenin, studying the photochemical dissociation of water and the photosorption of hydrogen, oxygen, and ammonia, have also found evidence for electron acceptor centres on alumina.

I.B.5. Reactions of Hydrocarbons. Hydrocarbons can undergo a number of reactions on alumina such as double bond isomerisation, skeletal isomerisation, and cracking. It is generally agreed that double bond isomerisation reactions require weaker acid sites than skeletal isomerisation reactions, which in turn require weaker acid sites than cracking reactions.

I.B.5.1. The products of alcohol dehydration can undergo double bond isomerisation. Pires et al. have proposed that the dehydration and double bond isomerisation proceed through a common carbonium ion intermediate. Dzis'ko et al. on the basis of sodium poisoning studies that alcohol dehydration and isomerisation take place on the same centres. Balandin et al. suggested that the dehydration of an alcohol
such as 2-butanol to the three isomeric butenes, 1-butene, and cis- and trans-2-butene, takes place on the same site and that the subsequent isomerisation of these olefins takes place after desorption of the olefins and their readsorption.

I.B.5.2. Although the necessity of acid sites for isomerisation reactions is undisputed, the exact nature of the acid site is still a matter of controversy.

Oblad et al. proposed a Bronsted acid mechanism for olefin isomerisation. Medema and Houtman consider two types of Bronsted acid sites - water molecules and hydroxyl groups - for the isomerisation of 1-butene to cis- and trans-2-butene.

Hall et al. have rejected mechanisms involving Bronsted acid sites on the basis that the rate of isomerisation is not connected with the hydrogen content of the surface. Addition of water has also been found to poison the isomerisation reaction. Knözinger and Spanheimer have found that on adsorption of water the Lewis acid sites are poisoned and there is a loss in the specific interaction between π-electron containing organic compounds and the Lewis acid sites.

Lewis acids as active sites for double bond isomerisation reactions have been proposed by a number of workers on the basis of both catalytic and spectroscopic studies.

I.B.5.3. An interesting aspect of double bond isomerisation is the fact that the thermodynamically less stable
cis-2-butene preponderates over trans-2-butene during the isomerisation of 1-butene. Hall et al. have found that the activation energy for cis-2-butene formation from 1-butene is lower than that for trans-2-butene. Various mechanisms have been proposed to account for the preponderance of cis-2-butene.

Pines et al. and Lucchesi et al. have proposed a carbonium ion stabilised by a \( \pi \) complex to account for the high cis-/trans-2-butene ratio over pure alumina. On the other hand, an allyl carbonion stabilised by a cyclic structure has been proposed for the formation of cis-2-butene over sodium-impregnated alumina. Similar allyl carbonion mechanisms have been proposed by Peri and by Cvetanovic and Foster. An allyl carbonium ion mechanism has been proposed by Leftin and Hermana.

Perhaps the most interesting mechanism for the preponderance of cis-2-butene over trans-2-butene is that by Hall et al. On the basis of Peri's evidence that adsorbed 1-butene resembles liquid cis-2-butene, they proposed the adsorption of 1-butene on two aluminium ions across the 1- and 4- positions of 1-butene. The aluminium ions are on the opposite sides of an oxide ion, and the distance between them is sufficient to satisfy the geometrical requirements of an adsorption of 1-butene by the 1- and 4- carbon atoms. The oxide ion, which is now able to span across three carbon atoms, transfers a hydrogen atom from the 3- position to the 1-position, thus giving cis-2-butene. Hall et al. have shown that the rate determining step in the isomerisation of 1-butene involves a
C-H bond breakage in the transition state. 103

I.B.5.4. The above mechanism gives an importance to the oxide ion which had not been considered previously. A strong interaction between acetylene and hydroxyl groups was shown by Yates and Lucchesi, who studied by infra-red methods the adsorption of acetylene on alumina. These authors also showed a slow interaction between ethylene and the hydroxyl groups of alumina with the formation of a -C₂H₅ group. 106

The importance of basic sites is also seen if comparisons with liquid phase base-catalysed reactions are made. 96, 103 Thus, the mechanism proposed by Hall et al. for 1-butene isomerisation over alumina is almost identical with that proposed by Lucchesi for the liquid phase base catalysed isomerisation of 1-pentene. Similarly, the results of Hall et al. concerning the rate of vinyl exchange over alumina bear a striking resemblance to the results of Cram et al. 108

The necessity of both acid and basic sites is apparent. Hall et al. have suggested that the dual acid-base sites proposed by Peri, which are responsible for NH₂₂ formation, are also responsible for the isomerisation reactions. These authors have also suggested that the dual acid-base sites are also responsible for vinyl exchange, although they were not able to come to a definite conclusion regarding the modus operandi of these sites.

I.B.5.5. From a comparison of the activities of
various alumina catalysts for skeletal isomerisation reactions, it has been found that strong acid sites are necessary. Hall et al have shown that the isomerisation of cyclopropane requires Bronsted acid sites. Tung and McInnich have proposed a passive Bronsted site which becomes activated at temperatures higher than 400°C for cracking reactions, in analogy with silica-alumina catalysts which are good cracking catalysts.

I.B.6. Influence of crystal structure and texture.
Although it is recognised that the catalytic activity of a solid depends on its crystal structure and texture, not much work has been done on these lines.

Uvarov et al who investigated the adsorption of alcohols on various γ-aluminas and θ-alumina, attributed the difference in the adsorptive and catalytic properties of these solids to the difference in the number of tetrahedrally and octahedrally coordinated aluminium ions. They attributed the greater activity of θ-alumina to the larger number of tetrahedrally coordinated sites, which have been considered to be catalytically active by Egorov et al.

Wade et al have studied the influence of the surface areas of various aluminas including α-alumina on alcohol adsorption. They found a maximum in the specific adsorption capacity with α-alumina. Only methanol had a cross-sectional area for a saturated monolayer that corresponded with the values obtained for tightly packed alcohol molecules on a homogeneous liquid surface. They attributed the larger cross-sectional area of the other alcohol molecules to an autopobicity. Similar observations by
Vasserberg et al. were, however, attributed by them to perpendicular and parallel modes of adsorption of the alcohol molecules on the surface, the parallel mode of adsorption increasing the cross-sectional area of the adsorbed alcohol molecule.

Wade et al. have also found that the catalyst with the maximum surface area has the maximum dehydration activity per unit surface area. Simon et al., however, have found that the activity of some alumina catalysts are the same for alcohol dehydration, in spite of their different surface areas. They have attributed this behaviour to the insufficient access within the pores of the catalysts of high surface area. Evidence for diffusion controlled reactions for aluminas with narrow pores have been reported.

Dzis'ko et al. working under conditions in which the reaction was not diffusion controlled, found a constancy in the activity of \( \gamma \) - and \( \theta \) - alumina samples for the dehydration of isopropanol. Sato et al. have found that \( \gamma \) - and \( \alpha \) - alumina are more active than \( \gamma \) -alumina for isopropanol dehydration, 1-butene isomerisation and iso-butane cracking. \( \delta \) - \( \delta \) - and \( \kappa \) -alumina are still less active.

De Boer et al. have found, that all other factors being equal, \( \gamma \) -alumina is more active than \( \gamma \) -alumina for the dehydration of alcohols. McIver et al. have also found a greater activity with \( \gamma \) -alumina compared to \( \gamma \) -alumina.
for double bond isomerisation, skeletal isomerisation, and cracking reactions. The greater activity of $\gamma$-alumina is in agreement with the earlier observations by Pines et al.

I.C. Chromia.

I.C.1. Preparation and properties.

I.C.1.1. The catalytically active chromia catalyst is usually obtained by the dehydration of the chromium hydroxide and activation by heating to about 500°C, or by the decomposition of its salts $^{123,124}$. The catalysts thus obtained have an $\alpha$-chromia structure. A stable, active catalyst can be obtained from chromium hydroxide gel $^{124}$. Such gels are obtained by the slow hydrolysis of a chromium salt solution - usually a nitrate - either by the dropwise addition of ammonia $^{124}$, or by the in situ production of ammonia by the hydrolysis of urea $^{125}$. The activation of these catalysts $^{124,125}$ has to be carried out carefully.

I.C.1.2. The decomposition of the chromium hydroxide gel or chromium trioxide to give chromia has been the subject of a number of papers. Deren et al. have suggested the intermediate formation of a trihydrate which decomposes further to a monohydrate, which is stable in the temperature range 280 to 370°C. The monohydrate could have the structure $^{127}$ $\text{CrO}_2\cdot\text{H}_2\text{O}$. Sing et al. have suggested a structure corresponding to the formula $\text{CrO(OH)}$. At about 400°C to 410°C an exothermic peak is obtained in the DTA and this is attributed to crystallisation.
The region at 400 to 410°C during the decomposition of chromium hydroxide gel corresponds to a "glow phenomenon" reportedly discovered as early as 1818 by Berzelius. The mechanism of the "glow phenomenon" as a precursor to the stable Cr₂O₃ phase has recently been discussed by Sing, Carruthers and Fenerty. Deren et al. have suggested that the exothermic peak at 400°C corresponds to the decomposition of CrO₂·H₂O or to a phase which is a mixture of Cr₂O₃ and CrO₃. Kesavulu et al. have found that the rate of oxygen evolution is a maximum at 360 to 380°C during the heating of a fresh chromium hydroxide gel.

Balandin et al. studying the decomposition of chromium hydroxide in various atmospheres, have found that heating in hydrogen leads to the antiferromagnetic form of α-chromia, while air produces a ferromagnetic form attributable to the presence of CrO₂. A ferromagnetic phase has been isolated in the decomposition products of chromium trioxide. Chromium dioxide, CrO₂, is unstable above 400°C and in the presence of Cr₂O₃ and exists only under high oxygen pressure during the decomposition of chromium trioxide.

I.C.1.3. Emmett et al. have attributed small discrepancies observed in the adsorption of gases by chromia prepared by various methods to differences in the porous texture of the solid. Burwell et al. have studied the pore size distribution of several chromia catalysts prepared
by several methods. They have found the presence of micro-
porous in the catalysts prepared by the gel method. Similar
results have been reported by Rode et al. Sing et al.
have suggested that the decomposition of the monohydrate
leads to the formation of micropores. These pores may be
active in catalysis.

The surface area of the chromia gels if care-
fully prepared may be quite high. Heating of the freshly
activated to gels at high temperatures leads to a decrease in
the surface area by sintering. The chromia gel catalysts
which are activated at low temperatures have a high concen-
tration of Cr(VI) ions on the surface. On sintering, the concentra-
tion of Cr(VI) ions on the surface is decreased.

I.C.2. Chromia gel is considered to be a p-type
semiconductor, at low temperatures in the presence of oxy-
gen. Anderson et al. considered chromia to be an oxygen
excess p-type semiconductor. Hauffe and Block considered
that the dependence of electrical conductivity of the
chromia on the partial pressure of oxygen was less than that
expected for an oxygen excess p-type semiconductor. Voltz and
Weller have, however, rejected this argument. Lorenz
et al. have shown that single crystal Cr2O3 are p-type
solids, the resistivity being independent of the oxygen pressure.
Jaffray and Beaufort have considered the conductivity of
crystalline and amorphous chromia to be due, principally, to
the presence of adsorbed water.
The activation energy of electrical conductivity is dependent on the atmosphere. The activation energy for electrical conductivity in various atmospheres increases in the order: oxygen < air < nitrogen < hydrogen. The electrical conductivity of the chromium hydroxides become important only after crystallisation. With increasing sintering temperature, the electrical resistance and the activation energy also increase. Garcia de la Banda et al. have attributed the decrease in the electrical conductivity and the increase in the activation energy of electrical conduction, to the concentration of oxygen at grain boundaries, which decreases with increased sintering. These authors have also found that the electrical resistance of chromia increased with time at a particular temperature and attributed this increase to an increase in the oxygen-to-chromium ions ratio on the surface by diffusion from the bulk or by the readsoption from the walls of the apparatus.

Anderson et al. have observed a break in the Arrhenius plot of the electrical resistance of chromia in an atmosphere of hydrogen. They have attributed this break to a change in the semi-conductor type of the catalyst, i.e., from p-type to n-type at high temperatures. Several similar observations have since been reported. Lorenz et al. have shown that the incorporation of TiO₂ changes the conductivity type of single crystal chromia from p- to n-type. Garcia de la
Banda et al. have shown that the temperature of the p-type to n-type transition is dependent on the hydrogen partial pressure.

The change in the conductivity type at high temperatures in a reducing atmosphere led Voltz and Weller to suggest that the change may be due to the formation of Cr(II) species. 

Cr(II) ions have been shown on chromia- and chromia-alumina catalysts by van Reijen et al. using ESR techniques. Rubinshtein et al. have also demonstrated the presence of Cr(II) ions by showing that the gas evolved on the addition of water to a reduced chromia catalyst is completely hydrogen. The Cr(II) ions are unstable in the presence of water. This suggests that Cr(II) species need not be responsible for the change in the conductivity type, at least for conditions in which water is present, as during the reactions of alcohols. Kazanskii et al. consider that the ESR signals attributed by van Reijen et al. to Cr(II) ions are due to strained, coordinatively unsaturated Cr(III) ions, although such a consideration had been rejected by van Reijen et al.

I.C.3. Reactions over chromia. The surface area of chromia especially after use is low, and it is usually supported on a material of high surface area such as alumina or silica. Pines et al. and MacIver et al. have shown that the activity of a supported chromia catalyst is determined to a certain extent by the nature of the support itself.
I.C.3.1. In industry, chromia is used mainly as a polymerisation catalyst. The polymerisation activity of chromia has been attributed to the presence of Cr(V) ions on the basis of a correlation between the polymerisation activity and the intensity of a sharp band in the ESR spectrum attributed to the presence of Cr(V) ions. Although such a species may not be stable under the reaction conditions the catalytic activity may arise out of a sort of organo-metallic complex on the surface arising out of a reduction of the Cr(V) ion.

I.C.3.2. Unlike alumina, chromia can give rise to both dehydration and dehydrogenation reactions with alcohols. The products may include ethers, olefins, aldehydes or ketones. For ethanol, the reaction is complicated, and a number of compounds are formed such as ether, ethylene, acetaldehyde, acetone and ethylacetate. The production of symmetrical ketones from alcohols form the basis of a number of papers published by Komarewsky et al.

The main interest in studying the reactions of alcohols seems to be theoretical at present. Urged by the electronic theories of catalysis, a large amount of work has been carried out to correlate catalytic activity with electrical conductivity. A number of workers have found a p- to n-type change at high temperatures with chromia catalysts in the presence of alcohol, similar to the p- to n-type change observed in the presence of hydrogen. At the same time, a break in the Arrhenius plot for the
dehydrogenation reactions of alcohols was observed, corresponding to the region of the break in the Arrhenius plot for conductivity. The correlation between catalytic activity and electrical conductivity, therefore seemed to be eloquently proved. However, there does not seem to be any agreement whether the electron rich $n$-type chromia, or the electron deficient $p$-type chromia is responsible for dehydrogenation. Thus, Garcia de la Banda considers that the $n$-type catalyst is more active, on the basis of comparisons with the catalytic activity of $\text{ZnO-Cr}_2\text{O}_3$ catalysts. Szabo and Solymosi studied the behaviour of $\text{NiO}$ and $\text{Cr}_2\text{O}_3$ towards the dehydration and dehydrogenation of formic acid, and have found that lowering the conductivity of $p$-type catalysts promoted dehydration, and increasing the conductivity promoted dehydrogenation. Kuriacose et al. consider that the $p$-type conductivity leads to a greater activity for dehydrogenation. Krylov has proposed a mechanism for dehydrogenation of alcohols, common to all catalysts, and he has suggested that all sites responsible for chemisorption and electrical conductivity need not necessarily contribute to the catalytic activity of the catalysts. A $p$- to $n$-type change has been observed for a number of systems such as $\text{ZnO-K}_2\text{CrO}_4-\text{Cr}_2\text{O}_3$, Pt-alumina. In our laboratory, a reduction to the metallic phase occurred with $\text{NiO}$ at high temperatures.

A dependence on the structure of the substrate molecule of the selectivity for dehydration and dehydrogenation
has been noted by Kuriacose and co-workers. Kuriacose et al. have also noted a dependence of selectivity for dehydration and dehydrogenation on the contact time of the alcohol. An interesting proposal put forward by Kuriacose et al. is that during the reaction of alcohol, another compound such as acetic acid can change the activity of the catalyst by getting adsorbed on the surface and increasing the concentration of charge carriers. Swaminathan and Kuriacose have found that acetic acid can poison both dehydration or dehydrogenation activity of the alcohols depending on the nature of the alcohol substrate and the catalyst.

Garcia de la Banda et al. have suggested that possibly two oxygen atoms are responsible for the surface reactions of the adsorbed alcohol and other molecules. Teremin et al. have found evidence for an alkoxide species on the chromia surface on the adsorption of methanol or ethanol. No mention seems to have been made in the literature concerning the formation of a carboxylate species on the chromia surface although a carboxylate species has been observed on nickel oxide. Krylov considers that the carboxylate species may be responsible for the dehydrogenation activity.

I.C.4. Reactions of hydrocarbons. Chromia can be used for a number of reactions involving hydrocarbons. Burwell et al. on the basis of deuterium exchange studies with a number of hydrocarbons, came to the conclusion that a carbanion-like species is involved in the reactions of hydrocarbons. Using these results van Reijen et al.
have suggested that Cr(II) ions are the active species for
the reactions of hydrocarbons. Weisz et al have found an
inversion in the conductivity of chromia catalysts and they
have attributed this to the formation of Cr(II) species.
There does not seem to be any report in the literature of a
break in the Arrhenius plot for the dehydrogenation of hydro-
carbons similar to that found for the dehydrogenation of alco-
hol. The reason may lie in the fact that the dehydrogenation
reactions of hydrocarbons over chromia catalysts require a
higher activation energy than the dehydrogenation of alcohols.
In our laboratory, a break in the Arrhenius plot for the dehydro-
genation of a bicyclic terpene, 3-carene, was observed over
a non-reduced chromia catalyst corresponding to the break in
the Arrhenius plot for electrical conductivity in a hydrogen
atmosphere. However, no such break was found when the reaction
was carried out with a reduced catalyst.

Burwell et al who studied the deuterium exchange
and hydrogenation of benzene, and Balandin et al who studied the
deuterium exchange and dehydrogenation of cyclohexane found similar
results with chromia. The deuterium exchange takes place at
lower temperatures than the hydrogenation-dehydrogenation reactions.
Burwell et al have attributed the exchange reaction to the
presence of OH groups on the surface, and hydrogenation to
the removal of that group.

I.D. Aldol Reactions in the Gas Phase

Although the aldol reaction in the gas phase is well
known, systematic work has been carried out only by Malinowski and coworkers. These workers have used silica catalyst either by itself or modified with sodium and other ions. These workers have found a linear increase in the aldol condensation activity of silica catalysts with incorporation of sodium ions up to an unimolecular coverage of the surface after which the activity of the catalyst decreases. They have therefore attributed the catalytic activity to the presence of Si-O-Na sites. These authors have also found an induction period over silica catalysts for the formation of the aldol condensation product, associated with the formation of a polymeric layer on the surface of the catalyst. Malinowski et al. have shown that while the determination of the alkalinity of the catalysts by conventional adsorption indicators did not give a proper correlation with the activity, a correlation was found between the ammonia adsorption capacity of these catalysts and the catalytic activity.

I.E. Reactions of ketones over alumina and chromia.

Very little work has been done on the reactions of ketones over alumina or chromia catalysts.

A systematic investigation of the conversion of straight chain ketones into olefins was carried out recently by Blouri and Ahmadi over alumina catalysts prepared by two methods: by the hydrolysis of aluminium isopropoxide and by the neutralisation of sodium aluminate solution. The former catalyst was more active than the latter.
These authors have not studied the composition of the products having a boiling point higher than the starting ketone. Adkins and Watkins investigated the dehydration of ketones on the basis of Newton and Coburn's conversion of pinacolone to 2,3-dimethylbutadiene. They have reported the conversion of various ketones to olefins. Condensation reactions of ketones over alumina catalysts have not been studied in a detailed manner. Scheidt has reported the conversion of various ketones and aldehydes over alumina catalysts, but they did not observe the formation of any olefinic products. Acetone has been found to give, besides the condensation products, such as mesityl oxide, isocorone, and mesitylene, sizeable amounts of isobutene also.

Fujii has studied the condensation of ketones over chromia catalysts. They have observed that acetone besides giving mesitylene, and mesityl oxide, also gave rise to the formation of iso-butene. Similar observations have been recorded by Kuriacose et al.

Cyclohexanone has been reported to be converted over alumina to cyclohexene by several workers. They have attributed the formation of cyclohexene by a disproportionation reaction of cyclohexanone to phenol and cyclohexanol, and the subsequent dehydration of cyclohexanol to cyclohexene. Scheidt has been the only worker to report a condensation reaction of cyclohexanone over alumina in the vapour phase. Gusev has reported the disproportionation of cyclohexanone over chromia above 400°C.
I.F. Purpose and scope of the present investigation.

The above literature survey shows that the oxygen atoms on the surface of metal oxide catalysts have an important role to play. The study of typical base-catalysed reactions such as the aldol condensation reactions of ketones, therefore, would give an idea of their importance. At the same time Blouri and Ahmadi have shown that the formation of olefins from ketones depends on the acidic character of the catalyst employed. Thus, by studying the behaviour of catalysts towards the aldol condensation and olefin-forming reactions of ketones one could arrive at some conclusions regarding the importance of basic and acidic sites, respectively. No such systematic work seems to have been carried out so far.

In our laboratory, parallel studies are in progress on the vapour phase dehydrogenation and hydrogenation reactions of cyclohexanone and phenol, respectively. The catalysts used are alumina supported metal catalysts. Since cyclohexanone is an intermediate in the above reactions, the behaviour of cyclohexanone over alumina catalysts was thought to be of interest in analysing and improving the behaviour of the metal catalysts.

The condensation products of cyclohexanone are also of wide use in industry. They have been used as stabilizers and plasticisers of polyvinylchloride resins, and as solvents for the manufacture of artificial resins. Determination of optimum conditions for the condensation reaction was of interest.
In this thesis the reaction of cyclohexanone over alumina and chromia catalysts was investigated. For the alumina catalysts the investigations were carried out in the temperature range 250°C to 410°C, while for the chromia catalysts the investigations were carried out in the temperature range 250 to 450°C.

In Chapter II, the experimental procedure employed for this study is given. Chapter III gives the results of the investigations into the physico-chemical properties of the catalysts and some of the conclusions that could be derived from them.

Chapters IV and VI contain the results on the reaction of cyclohexanone under various conditions over alumina and chromia catalysts, respectively. Chapters V and VII give the discussion of these results, respectively.

Chapter VIII gives a summary of the findings and the conclusions drawn.