SURFACE PROPERTIES AND CATALYTIC ACTIVITY OF SULPHATE MODIFIED METAL OXIDES

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By
KUMAREE SEENA C. R.

DEPARTMENT OF APPLIED CHEMISTRY
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
KOCHI - 682 022, INDIA

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CERTIFICATE

This is to certify that the thesis bound herewith is the authentic record of research work carried out by the author under our supervision in partial fulfilment of the requirements for the Degree of Doctor of Philosophy and no part thereof has been presented before for any other degree.

Dr. V.N.Sivasankara Pillai
Professor
School of Environmental Studies
Cochin University of Science and Technology

Dr. S.Sugunan
Professor
Department of Applied Chemistry
Cochin University of Science and Technology

Kochi 682 022
7th January, 1998

CONTENTS

Chapter I

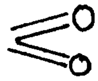
INTRODUCTION

Chapter I

INTRODUCTION

The name "superacid" was first suggested by Hall & Conant [1,2] for strongly acidic non-aqueous solutions. The term superacid is reserved for an acidic media which exhibits an acidic strength higher than that of 100% sulfuric acid [3].

The study of sulfated metal oxides was first reported in 1976 [4,5]. It has become an active area of research because of the high catalytic activity for carbocation reactions. The significantly higher activity over that of the untreated metal oxides has been ascribed to the presence of sulfur (VI) species. It was shown that the surface of the activated oxides is modified by sulfate ions [6,7]. The SO_4^{2-} groups were described as covalently bonded to the metal oxide lattice [7,8].

It was reported that the single sulfide species which is formed via oxidation of H_2S or SO_2 on Al_2O_3 or TiO_2 via impregnation of these oxides with $(NH_4)_2SO_4$ or H_2SO_4 followed by activation at 450°C had a structure $(MO)_3S = 0$ and that the intense high wave number band near 1400 cm^{-1} could be assigned to the S=O, stretching mode [8]. A similar band for sulfated SiO_2 was assigned to a surface $(MO)_2$ S  species [9]. Sulfation by means of the incipient wetness technique was also reported [10]. The catalytic activity of these materials depends upon the sulfur content. Therefore, in order to control the structure and activity of these catalysts it is highly desirable that the amount of sulfate ions deposited on the surface can be controlled in the preparation.

Liquid superacids [11] combinations of Bronsted and Lewis acids such as HF + SbF_5, are active catalysts for alkane conversions at low temperature, but they are not applied industrially because they are corrosive and lack stability.

Researchers have long sought to replace the liquid superacids with solids having the same chemical properties while also being stable and noncorrossive [12]. Examples include sulfonated polymers combined with $AlCl_3$ or SbF_5 [13] sulfated zirconia, titania and Fe_2O_3 [14–16].

In recent years interest has grown in the unique properties of anion modified oxides, among these sulfate doped zirconia is particularly interesting due to their superacid properties [14] and catalytic activity in several important acid-catalysed reactions. Despite considerable research, the origin and nature of superacid sites in sulfated zirconia are still not understood. A detailed interpretation of the acid properties of these materials is required to develop further their high potential for heterogenously catalyzed hydrocarbon transformations, particularly for skeletal isomerizations of aliphatic compounds [17].

The acidity of solids used as catalysts or catalyst carriers has been the subject of numerous investigations and reviews [18] for a long time. In the beginning, the acidity was considered as ionic property of catalysts responsible for their activity in hydrocarbon conversion, in particular in the processes of petrochemical industry. Today it is well established that the acidity plays an important role in virtually all organic reactions occurring over solid catalysts. Many solids which exhibits acidic sites on their surface are used either as catalyst or catalyst carriers. The acidity may influence the properties of a catalyst by interaction with the active components (support effect) or by providing acidic sites which may make the catalyst bifunctional.

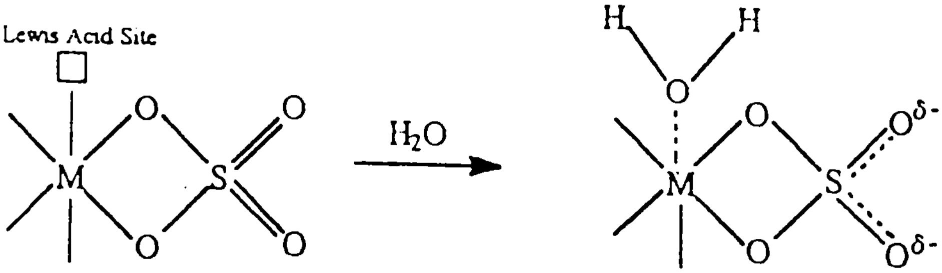
Acid sites on metal oxides are believed to be ascribed to surface hydroxyl groups or a charge imbalance localized on the surface. Localization of deficient amounts of electrons result from a local imbalance between positive and negative charges of the constituents and act as a Lewis acid for catalytic reactions. Since a charge imbalance can be expected by substituting the metal ion with other metal ions possessing different charges, new acid sites could be designed on the surface of doped and or mixed metal oxides [19–21].

It is well known that some sulfated metal oxides lead to superacid materials with surface acidity and surface areas much larger as compared with those oxides without sulfate [14]. Both features, acidity and surface area make many of these superacid compounds very active as catalysts when used in reactions that generally are catalyzed by strong acids. A similar enhancement in catalytic activity is also shown by non-metal sulfated materials [22]. According to Salmones *et al.* [22], the enhanced catalytic properties of platinum are improved by using a sulfated mixture of silica and zirconia as support. This is due to the fact that the new system can be considered as a bifunctional catalyst, with enlarged acid surface properties that come from the sulfation process as well as the existence of two metals that are able to absorbs H_2. Surface acidity of sulfated TiO_2—SiO_2 was also reported [23].

The surface properties of titania strongly depend on the presence of impurities [24]. Thus a Lewis type of acidity is characteristic of a pure surface. Sulfated surface has strong Bronsted sites and belongs to the small number of known superacid sites [25].

Doping of metal oxides by sulfate ions, enhances their acidity. In particular Fe_2O_3, TiO_2 and ZrO_2 doped with SO_4^{2-} have been described as superacidic solids [26,27]. Sulfation enhances the strength of the weakest Lewis acid sites but poisons the strongest. It also creates Bronsted acidity in the case of highly loaded samples [28].

Factors such as formation of oxide solid solutions and enhancement of the quantity and bonding of the sulfate groups on the oxide surface will retard the phase transformation of ZrO_2, whereas they may cause an increase in superacidity and catalytic activity at the same time [29]. IR spectra of sulfated zirconia solid superacids after evacuation at 300°C for 3 hour display four adsorption bands at 1390, 1190, 1020 and 930 cm^{-1} [28]. The former two bands are assigned to the asymmetric and the latter two bands are assigned to the symmetric stretching frequencies of the O=S=O and O—S—O groups respectively. The 1390 cm^{-1} band representing the asymmetric stretching frequency of S=O double bond is often regarded as characteristic band of SO_4^{2-} promoted superacids. The same author reported that the electronic structures of the surface sulfur complex before and after water adsorption may be illustrated as follows [Scheme I].



Scheme I

Crystallinity and morphological features of the sulfated ZrO_2 systems are found to vary with preparative and activation conditions. Type and relative concentrations of surface acidic sites (both Bronsted and Lewis centres) turn out to depend primarily on the type and relative concentration of surface sulfates [29]. The UV Raman Spectra indicate that the surface phase of sulfated zirconia changed during the deactivation process from the tetragonal phase of the fresh sample to the monoclinic phase of the deactivated samples, even though the bulk phase maintain the tetragonal phase before and after the reaction test. Surface tetragonal phase together with the sulfate groups is associated with the catalytic activity [31].

It is known that the activity of a catalyst is greatly influenced by the method of catalyst preparation and the conditions of pretreatment [32–38]. This is illustrated by the fact that the physical or chemical structure of a catalyst varies with the method of preparation and that chemical species adsorbed on the surface affect the catalytic activity profoundly. It has been shown that NiO–ZrO_2 and ZrO_2 modified with sulfate ion are very active for acid catalysed reactions even at room temperature [39–42]. The high catalytic activities in the above reactions were attributed to the enhanced acidic properties of the modified catalysts, which originate from the inductive effect of S=O double bond of the complex formed by the interaction of oxides with sulfate ion.

According to Tanabe [43], a surface is known to have oxidizing sites, if it is able to abstract an electron from a suitable molecule to form a paramagnetic radical cation. Yamaguchi *et al.* [44] reported that the adsorption of perylene on sulfated zirconia (SZ) gave the typical EPR signal of the corresponding radical cation, whereas no signal was observed on non-sulfated ZrO_2 indicating that the oxidising property of ZrO_2 is generated by the introduction of sulfate ions.

In the esterification of carboxylic acids, with alcohols, homogeneous catalysts such as H_2SO_4 and HCl are usually used. These methods however need tedious work up procedures in the isolation of the products. Recently, heterogeneous catalysts such as Nafion–H, the ZrO_2–sulfate ion, the TiO_2—SO_4^{2-} ion heteropoly acids supported on carbon, silica alumina, zeolite HY, cation exchanged resin and niobic acid have been reported to be effective catalysts for esterification [45].

In 1979, Arata and coworkers [46] reported that Zirconia, upon proper treatment with H_2SO_4 or $(NH_4)_2SO_4$, exhibits extremely strong acidity and is capable of catalyzing the isomerisation of n-butane to isobutane at room temperature. This catalytic performance is unique compared to typical solid acid catalysts, such as zeolites, which show no activity for the reaction at such low temperatures. The strength of an acid can be characterized by the so called Hammett acidity function, Ho. The greater the value of the function, the weaker the acid.

Using Hammett indicators, Hino and Arata [46] claimed that sulfated zirconia is an acid 10^4 times stronger than 100% H_2SO_4. Sulfated titania and zirconia have been proposed as superacids with Ho values –14.6 for TiO_2/SO_4^{2-} and –16.0 for ZrO_2/SO_4^{2-}.

Several authors [47–50] showed that, sulfated zirconia is a strong solid acid with an acid strength comparable to that of H_2SO_4 or some acidic zeolites. Since the discovery of its strong acidity it has attracted much attention as a potential process catalyst [51]. The main reason is associated with the increasing need for environmentally benign processes and for producing environmentally friendly fuels and chemicals. The study of this type of materials is now one of the fastest developing areas of catalysis research, and has generated a great deal of concepts as well as controversies.

Current technology to produce gasoline alkylates uses HF or H_2SO_4 as catalysts, which suffer many drawbacks such as high toxicity and extreme corrosivity in addition to the inherent risk of handling large amounts of hazardous acids. The development of new processes based on strong solid acid catalysts to replace HF and H_2SO_4 is strongly needed for environmental as well as safety considerations [51].

Among solid superacids studied so far [14,52] sulfate supported zirconia is highest in acid strength. SO_4^{2}/ZrO_2 materials impregnated with noble metal salts were also reported [53,54]. Sulfated binary and binary oxide solid superacids were prepared and characterized. The incorporation of Cr, Fe, Mn and V in to sulfated zirconia increases its superacidity [29].

It is worth noting that, since the nature of acid sites (Bronsted or Lewis) on sulfated zirconia depends critically on its water contents, which in turn depends on the history of pretreatment of the sample, the choice of appropriate pretreatment conditions is extremely important in controlling the nature of the acidity of sulfated zirconia [55]. Bronsted/Lewis acidity ratio depends not only on sulfate loading but also on the surface hydration degree [30], surface dehydration does not produce any protonic acidity. In fact upon hydration, there is only the desorption of some of the Lewis co-ordinated species and the conversion of part of the Lewis co-ordinated species into Hydrogen bonded one due to the partial rehydroxylation of the catalyst surface.

It was reported that [30] sulfate doped zirconia systems with medium-high sulfur loadings and activated at medium temperature possess both Bronsted (few) and Lewis sites. The sulfur content of a sulfated Zirconia catalyst strongly depends on its calcination temperature. Increasing calcination temperature usually results in the gradual removal of sulfur from the catalyst surface. The most common calcination temperature ranges from 550-650°C [51]. The calcination temperature significantly affects the catalytic performance of sulfated zirconia catalysts. It is inferred that calcination at an appropriate temperature results in the formation of S species with a proper configuration that generates strong acidity.

Arena *et al.* studied the effect of chloride ion on the surface acidity of γ-Al_2O_3 system [56]. Catalytic activity of Fe_2O_3 modified with sulfate ions are also reported [57]. Metal oxides (ZrO_2, Fe_2O_3, TiO_2, SnO_2 etc.) modified by SO_4^{2-} anions [14,35,41] have been shown to be the most promising superacidic catalysts for the low temperature processes of isomerisation, alkylation and cracking of paraffins.

Pure zirconia was less acidic than alumina or anatase but that after sulfation showed acidity comparable to that of anatase [55]. The actual seat of this activity lies in the exposure of highly co-ordinatively unstructured Zr^{4+} ions, as suggested by Tanabe *et al.* [58].

The catalyst texture may have some role to play in the catalytic behaviour. But it is felt that this is probably of secondary importance and it is difficult to attribute the very marked difference in catalytic activity of ZrO_2 and ZrO_2/SO_4^{2-} to difference in texture alone [59]. Sulfation of crystallized zirconium oxide does not produce strong acidity [60,61]. Studies on γ-alumina modified by the introduction of small amount of SO_4^{2-}, PO_4^{3-}, Cl^-, F^-, Mg^{2+} and Na^+ are also reported [62]. Seiyame *et al.* [63] found that the surface acidity of bismuth and tin oxide increased upon introduction of more electronegative elements into their lattices.

Bronsted acidity on sulfated oxides was also observed by NMR techniques, but the exact location of Bronsted sites could not be determined [51].

Morterra *et al.* [30] have shown that pyridine adsorbed on Lewis acid sites dominated the spectra of samples degassed in vacuo at 400°C. The addition of water at 27°C, however, significantly increased the amount of Bronsted acidity.

A comparison of the solid state NMR spectra of adsorbed TMP (trimethyl phosphine) with the activity for the alkylation of isobutane with 2–butane suggests that the strong acidic protons on sulfated zirconia are responsible for the catalysis. But the strong acidity requires the presence of adjacent Lewis acid centres. That is, through an inductive effect, electrons are withdrawn from O-H bonds by co-ordinatively unsaturated Zr, thus giving rise to more acidic protons [64]. Pure and phosphate modified titanium dioxide (anatase) have been studied by IR spectroscopy of probe molecules, X-ray photoelectron spectroscopy, X-ray phase analysis, electron microscopy etc. It is established that the phosphate anions are strongly bonded to the anatase surface and are stable even at the temperature of anatase-rutile transition [65]. The phosphate cannot be removed by washing with water or diluted acids, but are extracted by basic solutions. The active sites for phosphate adsorption are hydroxyl groups and Lewis acid sites on the anatase surface.

The effect of the sulfate depends upon the nature of the metal oxide and the sulfate amount. On ZrO_2 and both samples of TiO_2 (Rutile and anatase) addition of SO_4^{2-} increases the conversion of methanol. Sulfation tends to decrease the very high activity of alumina. The active species are stable at 300°C on alumina and zirconia but are quickly decomposed on TiO_2 samples [28].

For sulfate doped ZrO_2 catalysts capable of carrying both Bronsted (B) and Lewis (L) acidity, the B/L ratio is not an absolute parameter. It depends reversibly on the surface hydration/dehydration degree of the system (the higher the hydration, the higher the B/L ratio) and irreversibly on the highest temperature reached by the catalyst in any stage of its activity, in that sulfates responsible for Bronsted acidity are the thermally most labile fraction of the surface sulfate layer [66].

The strong acidity of sulfated zirconia was attributed to the electron withdrawing anion groups which lead to co-ordinatively unsaturated and electron deficient metal centres, that behave as strong Lewis acid sites [67]. Such Lewis acid sites predominate in the absence of water vapour and after calcination at high temperature [68]. Water vapour titrates such Lewis sites and converts them to Bronsted acids with very reactive protons.

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Chapter II

SURFACE ELECTRON PROPERTIES

Chapter II

SURFACE ELECTRON PROPERTIES OF METAL OXIDES

2.1 ELECTRON DONOR ACCEPTOR PROPERTIES

The electron donor strength on metal oxides can be defined as the conversion power of an electron acceptor adsorbed on the surface into its anion radical. The formation of negative radicals on the surface of various oxides have been demonstrated [1–6]. It is known that when strong electron acceptors or donors are adsorbed on metal oxides, the corresponding radicals are formed as a result of electron transfer between the adsorbate and the metal oxide surface. On the other hand, if a weak electron acceptor is adsorbed, the formation of anion radical will be expected only at the strong donor sites. Finally in the case of very weak electron acceptor adsorption, its anion radical will not be formed even at the strongest donor sites [7].

Flockhart *et al.* [8] obtained experimental evidence for the presence of electron donor sites on the surface of alumina by electron spin resonance technique. When tetracyanoethylene and 2,3,5,6 tetra chloro-1,4-benzoquinone were adsorbed on activated samples of gibsite, γ-Al_2O_3 and η-Al_2O_3, corresponding anion radicals were formed.

The electron donating power of titania surface was evaluated by adsorption of electron acceptors with electron affinities ranging from 1.26 to 2.84 eV from acetonitrile solution onto a titania sample [9].

The electron donor strength of a metal oxide can be expressed as the limiting electron affinity value at which free anion radical formation is not observed at the metal surface [10]. The concentration of radical anions formed on the surface as a result of electron transfer from the surface of titania to the acceptor decreased with decreasing electron affinity of the acceptors. The decrease was steepest between 1.26 and 1.77 eV. These results suggest that the limit of electron transfer from the surface of titania to the acceptor ranged between 1.77 and 1.26 eV in terms of the electron affinity of the acceptor.

It has been shown that specific adsorption occurs on the surface silanol groups and the adsorption on silica has been measured, spectroscopically and heats of adsorption have been obtained [11,12].

M.L.Hair and W.Hertl measured the adsorption isotherms by volumetric, gravimetric and spectroscopic techniques, on silica surfaces which have been modified in a variety of ways. For most of the adsorbates, freely vibrating hydroxyl groups on silica surface is the strongest surface adsorption site [13].

Edlund *et al.* [14,15] observed the esr spectra of singly charged monomeric and dimeric cation radicals at 77K in a γ-irradiated C_6H_6–silica gel system. The formation of cation radical of triphenyl amine on surface of synthetic zeolites and anion radicals of naphthalene and biphenyl on silica gel have also been reported [16,17]. Kinell *et al.* [18] detected the cation radicals of naphthalene, anthracene, phenthrene and biphenyl adsorbed on silica gel by esr spectra.

The presence of electron deficient centres on strongly dehydrated alumina surfaces sufficiently powerful to promote the formation of positive radical ions from aromatic hydrocarbons has also been demonstrated [19–24]. The formation of cationic species adsorbed on the surface has been established by studies of the adsorption of hydrocarbons on silica alumina catalysts [25-29]. Chemisorption of O_2 on MgO was observed under conditions which involve different types of electron transfer processes, either from electron donor centres formed by irradiation or by addition of extrinsic impurity ions [30–33].

A.J.Tench and R.L.Nelson studied the adsorption of nitrocompounds on the surface of magnesium oxide powder by esr and reflectance spectroscopy [34]. The electron donor properties of several oxide powders (CaO, MgO, ZnO, Al_2O_3, SiO_2–Al_2O_3) activated at temperatures upto 1200 K, have been investigated using the esr spectra of adsorbed nitrobenzene radicals as a probe [35]. The results indicated that the existence of a correlation between electron donor activity of oxides and their Lewis base strength. The electron donocity of metal oxides were found to be enhanced by a low temperature plasma treatment. The electron donacity was found to increase by ammonia and nitrogen, plasma treatments [36–39].

The electron donor property of the zirconia-titania system was investigated by means of adsorption of TCNQ. The radical concentration on the zirconia-titania system was investigated by means of adsorption of TCNQ. The radical concentration on the zirconia–titania system decreased with an increase in the titania content, reached a minimum point at a titania content of 38% and then increased with further increase in the titania content. This behaviour can be explained by the relative amount of OH^- sites, which must be proportional to both or either one, the relative contents of the pure zirconia phase or the pure titania phase existing on the surface of the zirconia-titania system [40].

The electron donor properties of TiO_2 and MgO have been investigated by tetracyanoethylene and trinitrobenzene adsorption. The electron donor centres are associated with hydroxyl groups on the surfaces of the solids activated at low temperature (<300°C). During the dehydration of TiO_2 and MgO at higher temperature, weakly coordinated O^{2-} ions are formed on their surfaces and these are responsible for the reducing properties of these solids [41].

The active sites on the surface of silica alumina cracking catalysts are assumed to be either Bronsted or Lewis acid, which may be interconverted by addition or removal of traces of H_2O [42–47].

J.B.Peri *et al.* [48] proposed a semiquantitative model for surface of silica-alumina catalyst in which acid sites of various types are created by attachment and subsequent bridging reactions of Al–OH groups on a silica surface.

Fowkes *et al.* [49] have studied the interaction between inorganic solids and basic adsorbates by using the Drago-correlation of the heat of acid base interaction and have determined the Drago parameters for several solids such as silica, rutile and magnetite.

When catalytic aluminas are heated to a high temperature, sites are produced on the surface which are capable of oxidizing polynuclear aromatic hydrocarbons to the corresponding ion-radical at room temperature, provided oxygen is present [22].

It was observed that while γ-alumina supported palladium oxide showed better acceptor properties than donor properties, silica supported palladium oxide showed only electron acceptor properties [50]. K.A.Enriquiz and J.P.Fraissard carried out a comparable study of variation of surface properties and catalytic activity of TiO_2 samples with their in vacuo pre-treatment temperature [51]. The results showed that active sites are electron donor centres, number of which has been determined by adsorption of tetracyanoethylene and trinitrobenzene. These centres are Ti^{3+} ions and O-Ti-OH groups for higher and low pre-treatment temperature respectively.

The investigation of the strength and distribution of electron donor sites on several metal oxide surfaces by adsorption of some electron acceptors measured by means of ESR spectroscopy was reported [10]. Hosaka *et al.* [52] studied the electron donor properties of several metal oxides from TCNQ adsorption. The order of the TCNQ anion radical concentration per m^2 formed on the metal oxides was found to be as follows:

$MgO > ZnO > Al_2O_3 > TiO_2 > SiO_2 > NiO$

When the electron acceptors having different electron affinities were adsorbed on the metal oxides from their acetonitrile solutions, the surfaces of metal oxides developed characteristic coloration with each electron acceptor. The coloration of the metal oxide surface suggests that some new adsorbed species are formed on the surfaces. The coloured samples also showed ESR absorption [8].

The electronic state of adsorbed species was studied by UV-vis spectroscopy in addition to ESR Spectroscopy [53, 54,8]. The band near 600 nm was related to the dimeric TCNQ anion radical which absorbs light at 643 nm [55]. This tentative attribution was supported by the characteristic features that neutral TCNQ absorbs only at 395 nm, that TCNQ has a high electron affinity and TCNQ anion radicals are stable even at room temperature [56-59]. ESR and electronic spectra provided evidence that TCNQ anion radicals are formed as a result of electron transfer from metal oxide surface to adsorbed TCNQ.

The electron donor properties of two component metal oxide systems, SiO_2-Al_2O_3, SiO_2, TiO_2, Al_2O_3-TiO_2 and ZrO_2-TiO_2 were studied by means of TCNQ adsorption [60,61].

The steep fall in the activity between the silica-alumina system and the alumina suggests that only a little pure alumina phase is present on the silica-alumina surfaces [62].

Esumi *et al.,* [63,64] studied the solvent effect on the acid-base interaction of electron aceptors with metal oxides, Al_2O_3 and TiO_2. The limiting amount of TCNQ adsorbed decreased considerably with increasing basicity of solvent or acidity of solvent for both metal oxides. The results were interpreted in terms of acid-base theory by Drago equation [65]. TCNQ radical concentrations for both metal oxides decreased with increasing basicity of solvent. TCNQ adsorption on metal oxides was found to be strongly influenced by interaction between basic solvents and TCNQ or between acidic solvent and donor sites of metal oxides. Similarly acid-base interaction at solid-ligand interface has also been confirmed to be important for the adsorption of tetrachloro-p-benzoquinone from various solvents [66]. Solvent effect of several aromatic solvents on charge transfer adsorption of TCNQ onto metal oxides was also studied and found that TCNQ radical concentration depends on ionisation potential of solvent [67].

The adsorption of TCNQ anion radical salts on alumina from acetonitrile solution was studied by measuring the adsorption isotherm, esr and electronic spectra of adsorbed TCNQ anion radical salts [68]. The order of adsorbed amount at the same equilibrium concentration was Li^+ TCNQ– > Na^+ TCNQ– > K^+ TCNQ–. Applying the relationship between solubility and chemical potential expressed by Miller [69], it was found that adsorption of TCNQ anion radical salts on alumina is not affected by solubility, but depends on nature of cation.

The basicity of Al_2O_3, TiO_2 and ZrO_2–TiO_2 was also determined by titration and electron acceptor adsorption [70]. The distribution of sites having different basicity were similar for alumina and titania with respect to Lewis and Bronsted sites. In zirconia-titania binary system only Lewis sites existed. Esumi *et al.* [71] measured the zeta potentials of Al_2O_3 and TiO_2 by adsorption of TCNQ from organic solvents. They found that the zeta potential of oxide decreased with increasing concentration of TCNQ in acetonitrile.

It has been suggested that two types of donor sites exist on oxide surfaces responsible for electron transfer process [72]. The first type consists of a defect centre involving oxide ions and second in a hydroxyl ion on the oxide surface.

Femin *et al.* [73] have shown that electron transfer from hydroxyl ion can occur in certain solvent systems provided a suitable acceptor is present.

Lee and Weller [72] confirmed the existence of surface hydroxyl groups on Al_2O_3 which had been dedhydrated at 500°C. The existence of surface hydroxyl groups on MgO has also been observed [75]. Surface silanol groups are found to be more stable than Al-OH groups [76]. Differences in acidity between the hydroxyl groups on several oxide surfaces have been reported [77]. It has been suggested that hydroxyl ions of metal oxide surfaces have different electron donor properties.

The electron donating properties of ceria activated at 300, 500 and 800°C and its mixed oxides with alumina are reported [78]. Ceria promotes the electron donating properties of alumina without changing the limit of electron transfer.

The electron donating properties of La_2O_3 and its mixed oxides with alumina was also reported. The limit of electron transfer from the oxide to the electron acceptor is between 2.40 and 1.77 eV [79].

The electron donor properties of perovskite-type mixed oxides ($LaFeO_3$, $SmFeO_3$, $PrFeO_3$, $LaCoO_3$, $PrCoO_3$, $SmCoO_3$, $LaNiO_3$, $PrNiO_3$ and $SmNiO_3$) were studied based on the adsorption of electron acceptors of different electron affinity viz., TCNQ, chloranil, PDNB and MDNB [80]. Electron donating properties and catalytic activity of samaria and its mixed oxides with alumna was also reported. The catalytic activity parallels its electron donating capacity [81].

The limit of electron transfer from the oxide surface to the electron acceptor are reported from the adsorption of EA on mixed oxides of Dy_2O_3 with alumina and Dy_2O_3, mixed oxides of Y_2O_3 with γ-alumina. The extent of electron transfer is understood from magnetic measurement [82].

The electron donor properties of Pr_6O_{11} activated at 300, 500 and 800°C are reported from the studies on adsorption of electron acceptors of various electron affinity [83]. The extent of electron transfer during adsorption is understood from magnetic measurements and ESR spectral data.

Electron donor sites of titania have been associated with surface hydroxyl ions and Ti^{3+} ions [84,85]. Che *et al.* [84] have suggested that the Ti^{3+} ions on the surface of titania were formed at high temperature in vacuo. Ti^{3+} ions do not play a predominant part in the electron donor sites of titania.

2.2 SOLID ACIDS AND BASES

Solid acid in general terms is a solid on which a base is chemically adsorbed. More strictly speaking, following both the Bronsted and Lewis definitions, a solid acid shows a tendency to donate a proton or to accept an electron pair, whereas a solid base tends to accept a proton or to donate an electron pair [86].

The acidic and basic properties of oxide catalysts are very important for the development of scientific criteria in catalyst application. The methods for determination of surface acidity were critically reviewed by H.A.Benesi and B.H.C.Winquist [87]. Surface acidic and basic sites of oxides are involved in the catalytic activity for various reactions such as cracking, isomerization and polymerization [86].

Acids and bases which exhibit zero activation energy in reaction [88] were termed primary acids or bases.

$$A + B: \rightarrow AB$$

The others possessing a measurable activation energy were termed secondary acids or bases.

Another classification, the "Hard Soft Acids and Bases" approach was introduced by Pearson [88–91]. Pearson formulated two principal rules, one of thermodynamic, the other of kinetic charactor. According to him, Hard acids prefer to associate with hard bases and soft acids prefer to associate with soft bases. Hard acids react readily with hard bases and soft acids react readily with soft bases.

The acid strength of a solid is the ability of the surface to convert an adsorbed neutral base into its conjugate acid as described by Walling [92]. If the reaction proceeds by means of proton transfer from the surface to the adsorbate, the acid strength is expressed by the Hammett acidity function, H_o [86],

$$H_o \equiv -\log a_{H+} f_B / f_{BH+}$$

or

$$H_o = pKa + \log [B] / [BH^+]$$

where a_{H^+} is the proton activity, [B] and $[BH^+]$ are the concentrations of the neutral base and its conjugate acid respectively and f_B and f_{BH^+} the corresponding activity coefficients.

If the reaction takes place by means of electron pair transfer from the adsorbate to the surface, H_o is expressed by,

$$H_o \equiv -\log a_A f_B / f_{AB}$$

or

$$H_o = pKa + \log [B] / [AB]$$

where a_A is the activity of the Lewis acid or electron pair acceptor.

The basic strength of a solid surface is defined as the ability of the surface to convert an adsorbed electrically neutral acid to its conjugate base. That is the ability of the surface to donate an electron pair to an adsorbed acid.

When an electrically neutral acid indicator is adsorbed on a solid base from a nonpolar solution, the colour of the acid indicator is changed to that of its conjugate base, provided that the solid has the necessary basic strength to impart electron pairs to the acid. It is possible to determine the basic strength by observing the colour changes of acid indicators, over a range of pKa values.

For the reaction of an indicator, AH with a solid base B,

$$AH + B \rightleftharpoons A^- + BH^+$$

The basic strength, H_o of B is given by the equation,

$$H_o = pKa + \log [A^-] / [AH]$$

where [AH] is the concentration of the acidic form of the indicator and $[A^-]$ the concentration of the basic form.

The initial colour change and the subsequent change in the intensity are observed at values of pKa ± 1. If we assume that the intermediate colour appear when the basic form reaches 50% ie., when $[A^-]/[AH] = 1$, we have $H_o = pKa$.

Solid acids and bases are characterised by amount, strength and nature of acid and base centres. The characterization not only depend upon the purity of the materials and the method of preparation but also upon the heat treatment, compression and irradiation.

The amount of base (basic sites) or acid (acidic sites) on a solid is usually expressed as the number of (or mmol) of base sites per unit weight or unit surface area of the solid.

The main method used for the determination of the acidic strength of a solid surface is the adsorption of an electrically neutral indicator and the observation of the colour appearing on the surface. The application of Hammett indicators for such determination was proposed by Walling [92]. The measure of the acidic strength of the surface is the pK_{BH^+} value of the weakest basic indicator which after adsorption exhibits the colour of the conjugated acid.

Using the acidity function of Hammett, one can state that the acidic strength H_o of the surface is less than or equal to the pK_{BH^+} of the indicator used, $(H_o = pK_{BH+})$.

Having a series of indicators with relatively small differences in pK_{BH^+} values, one can determine the acidic strength of a surface, placing it between

pK_{BH^+} of the last indicator, which changes its colour (pK'_{BH^+}) and the first which does not undergo any colour change after adsorption (pK_{BH^+}). For such a case

$$pK_{BH^+} < H_o < pK'_{BH^+}$$

Wail Malherbe and Weiss was the first to note that weakly basic indicators adsorbed on clays gave some colours as those formed when such indicators were added to concentrated sulfuric acid [93].

The indicator method is easiest and quickest way of screening surface acidities of solid catalysts, but it has two drawbacks. First of all, the number of suitable indicator is limited, because of the visual requirement that the colour of the acid form mask that of the basic form. Secondly, the acid colour of many of the Hammett indicators can be produced by processes other than simple proton addition.

After the acid strength of a catalyst surface has been bracketed by means of colours of adsorbed indicator, the next step in the determination of surface acidity is the measurement of number of acid groups. This is generally done by titrating a suspension of the catalyst with a solution of a suitable indicator in an inert solvent.

Hirschler [94] proposed the use of the acidity function H_R for the determination of protonic surface acidity. As indicators specific for acidic Bronsted sites, a series of arylmethanols and diphenyl methanes have been used. An advantage of the application of these indicators is the carbocationic character of their acidic forms. They are similar to intermediates occurring in catalytic reactions.

Leftin and Hall [95], who studied the chemisorption of triphenyl derivatives on commercial silica-alumina, have shown the presence of nearly the same number of sites active in adsorption of triphenyl methane and triphenyl carbinol. The adsorbed amount of both reagents could be taken as a measure of the total Lewis type acidity.

Transformation of an indicator into its conjugated acid form can also be detected spectrometrically. The spectroscopic method was introduced by Leftin and Hobson [96].

The amine titration method in the presence of Hammett indicators was proposed by Tamale [97] and further developed by Johnson [98] and Benesi [99]. Hirschler [94] introduced the titration with arylcarbinols as indicators. The measurement of the distribution of acid sites by the titration with bases has been discussed and reviewed several times [86].

The amine titration method is obviously limited to white or light coloured surfaces. Titration of dark coloured solids can be carried out by adding a small amount of white solid acid [100]. The end point of the titration is taken when the colour change is observed on white solid and a correction is made for the amount of n-butyl amine used for the added white material. Using this method, both acid amount and acid strength have been measured for titanium trichloride by employing silica-alumina as the white material.

There are many methods for the measurement of acid strength like visual colour change method [94], spectrophotometric method using fluorescent indicators [96] and gaseous adsorption method [101]. For basic strength, method using indicators [102], phenol vapour adsorption method [6] and temperature programmed desorption technique [103] are generally employed.

Steric effects can disturb the neutralization reaction during titration with indicator. Unger *et al.* [104] have shown the influence of the size of the amine molecule used on the measured total acidity for a series of silicas and zeolites with different pore sizes.

Parry showed that adsorption of pyridine on silica involved association through surface hydrogen bonds [105]. Basila *et al.* have gone one step further and have proposed that primary sites on silica alumina are of the Lewis type (centred on aluminium atoms) and that appreciably Bronsted sites are produced by a second order interaction between the molecule chemisorbed on a Lewis site and nearby surface hydroxyl groups [106].

To evaluate the catalytic activity of zeolite, it is necessary to determine the nature of strength and distribution of acid sites. Zeolite acidity can be determined by n-butylamine titration [107]. UV spectrophotometry has been applied for measurement of acid strength of silica-alumina catalysts using 4-benzene azodiphenylamine, 4-nitroaniline and 2,4-dinitroquinoline [108].

Yamanaka and Tanabe [109,110] have proposed a common scale for the determination of the distribution of surface acid-base strength. This scale takes into account the bifunctional character of solid surfaces. The experimental procedure involves the double titration of a given surface, firstly with n-butylamine and secondly with trichloroacetic acid as a titrant. The titration with n-butylamine yields the distribution of the acidic sites on the surface. For the titration with trichloroacetic acid Hammett indicators of decreasing basic strength are used, starting with the one which does not give colour change on the fresh catalyst surface. Since the weakest basic sites form stronger conjugated acids, H_0 of the conjugated acid of the weakest basic sites should be equal or greater than pK_{BH^+} of the indicator.

The curves of acidic and basic strength distribution intersect at the point where acidity = basicity = 0. Therefore, the strongest H_o value of the acidic sites is equal to the strongest H_o of the basic sites. Yamanaka *et al.* [110] defined $H_{o,max}$ as the H_o value at the point of intersection. This value may not be the exact value of the maximal H_o parameters. The acidic and basic sites of the same H_o do not coexist that, $H_{o,max}$ is lower than H_o for the case where the measured acidity is minimal, and higher than H_o when the measured basicity is minimal.

Yamanaka and Tanabe [110] have shown that the $H_{o,\ max}$ parameter is more useful than the zero point of charge (ZPC) determined for water solutions [111].

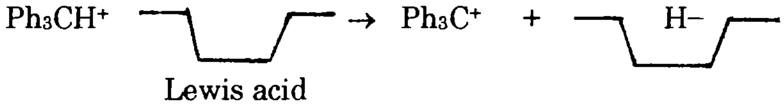
Quantitative information on the base strength distribution of solid base surfaces are essential for studies of solid base catalysts. The relative base strength of solid bases such as MgO and CaO was determined from the adsorption power for phenol vapour [112].

T.Yamanaka and K.Tanabe determined the basicity of a series of oxides and found that basicity at basic strength ($H_o \geq 1.5$) has the order ZnO > TiO_2 > γ Al_2O_3 > BaO > activated alumina > B_2O_3 > ZrO_2 > $MgSO_4$ > MoO_3 [109].

The amount of basic sites can be determined by titrating a suspension of a solid in benzene on which an indicator has been adsorbed its conjugate base form with benzoic acid dissolved in benzene [86]. The benzoic acid titres are a measure of the amount of basic sites having basic strength corresponding to the pKa value of the indicator. Malinowski and Sczepanska have devised titration methods for use with aqueous solutions and with anhydrous acetic acid [102].

J.Take, N.Kikuchi and Y.Yoneds developed a method for the determination of basic strength of solid surfaces which consists of titration of solids suspended in cyclohexane with benzoic acid using a series of Hammett indicators [113].

It is necessary to distinguish between Bronsted and Lewis acid sites for the catalytic action of solid acids. The number of Bronsted sites on a solid surface may be derived from the number of free protons in aqueous solution arising from the exchange of proton or hydrogen atom. Malinowski and sczepanska measured the amount of Bronsted acid by potentiometric titration of solid acid in anhydrous picoline with 0.1 N solution of sodium methoxide [102]. Leftin and Hall reported that the amount of Lewis acid can be determined from the amount of triphenyl carbonium ion formed, when the solid acid abstract a hydride ion from triphenyl methane as shown below [114].



Schwarz described a new method for the measurement of Lewis and Bronsted acid sites [115] from the infrared study of pyridine chemisorbed on silica-alumina catalysts of varying silica content.

Gay and Liang [116] have investigated the surface acidities of silica, alumina and silica-alumina by C^{13} NMR spectra of a variety of aliphatic and aromatic amines adsorbed on these solids. In the case of silica, only weak interactions of amines with surface hydroxyl groups are observed. Much stronger interactions are observed in the case of alumina. In silica-alumina, chemical shift due to protonation is observed. Yoshizumi *et al.* determined acid strength distribution on silica alumina catalyst calorimetrically by measuring the heat of adsorption of n-butylamine from benzene solution [117].

Shibata and Kiyoura measured surface acidities by the n-butylamine titration method of the TiO_2-ZrO_2 system as a function of composition and method of preparation. Highest titer of strong acid sites [$H_o \leq 5.6$] was obtained at a composition of 50% M (mole %) ZrO_2 [118]. Surface acidities of Al_2O_3—TiO_2, SiO_2—TiO_2 and TiO_2—ZrO_2 preparations heated at various temperatures have been reported by Walvekar and Halgeri [119]. Butylamine titres of each binary oxide increase as calcination temperature is increased, go through maximum value and finally decrease.

It was found that silica-titania is highly acidic and has high catalytic activity for phenol amination with ammonia and for double bond isomerization in butane [120,121]. The highest acidity per unit weight of catalyst was obtained when TiO_2—SiO_2 (1:1 molar ratio) was heated at 500°C.

Microcalorimetric measurement of the differential heat of pyridine adsorption were used to probe the distribution of acid strength on a series of silica supported oxide catalysts [122]. Depositing oxides of the following cation ie., Ga^{2+}, Zn^{2+}, Al^{3+}, Fe^{3+}, Fe^{2+}, Mg^{2+} and Sc^{2+} onto silica increased the acid strength of the catalyst. Gallium oxide is the most electronegative oxide and when it is added to silica strong acid sites are generated and that both Lewis and Bronsted acid sites are present on the surface [123,124].

Tanabe *et al.* [125] found that the acid base properties of mixed metal oxides can be varied by choosing different metal oxide composition at different concentrations and by changing the treatment of the sample [125].

Infrared spectroscopic studies of benzene adsorbed on several KH β zeolites, where the extent of potassium exchange, K/Al (%) varied from 0 to 88.32% have been undertaken under different conditions [126]. The bands of adsorbed benzene on KH β zeolites, is in the range 2050-1700 cm^{-1}. KH β zeolites, exhibit basicity when $K/Al \leq 88.32\%$ where its basicity is stronger and acidity is weaker.

The acid base nature and catalytic activity of rare earth oxides have been reviewed [127]. The rare earth oxides have been classified as base catalysts on the basis of the O_{1S} binding energy study of oxides [128]. Nakashima *et al.* [129] measured the basicity of samarium oxide by benzoic acid titration method.

V.H.Rane and V.R.Choudhary [103] compared the acid and base strength distribution of rare earth oxides by stepwise thermal desorption of CO_2 and temperature programmed desorption of carbon dioxide. Lanthanum oxide showed highest surface basicity and strong basic sites, whereas cerium oxide and samarium oxide catalysts showed lowest surface basicity. Lanthanum oxide catalyst also showed highest surface acidity but all of its acid sites are of intermediate strength. Both weak and strong acid sites were present on ytterbium oxide, europiun oxide, samarium oxide and cerium oxide catalysts. The stronger acid sites were observed on cerium oxide catalyst.

Pines *et al.* using a range of indicators concluded that alumina displayed Lewis acidity [130]. Experiments based on the infrared absorption bands of pyridine adsorbed on alumina provide additional very strong evidence that alumina acid sites are of the Lewis type.

The acidity of chromic oxide in its oxidized state is about twice that in the reduced state, and in both cases half (or more) of the total acid sites are strongly acidic. Hirschler *et al.* [131] suggested that the acid sites on oxidized chromic oxide are related to the defects which are also responsible for its semiconducting properties, but the nature of the acid sites on reduced chromic oxide remains obscure.

Ordinary metal sulfates and phosphates have no intrinsic surface acidity, and become solid acids only after appropriate physical treatment [86]. The acidic properties of metal sulfates can be changed by means other than heating, for example by inducing crystal imperfections through compression of the solid. Concentrations of Bronsted and Lewis acid sites on sulfated zirconia catalysts were determined using the ^{31}P MAS NMR spectra of adsorbed trimethyl phosphine [132]. A sample that had been calcined and exposed to air for a long period exhibited only Bronsted acidity. However, treatment of the sample at progressively higher temperatures resulted in the development of at least three types of Lewis acidity along with a decrease in the concentration of Bronsted acid sites.

It was reported that remarkable increase in the surface acidity and in the catalytic activity of Fe_2O_3 were caused by treatment with sulfate ion. The sulfate treated catalyst showed possibility for bearing the surface acidity higher than that of SiO_2—Al_2O_3, which is well known as one of the solid acid catalysts with the highest surface acidity [133].

Transition metal oxide promoters deposited on Rh can increase the overall activity of the metal by several orders of magnitude for reactions involving the hydrogenation of molecules such as CO, CO_2 and NO [134–144]. Several explanations for oxide promotion have been introduced. Sachtler, Ichikawa and co-workers [137,144] suggested that a Lewis acid/base bonding interaction occurs between the oxygen end of the adsorbed CO and the oxide promoter at the oxide/metal interface.

The increase in acidity and acid strength of the binary oxide, ZrO_2—SiO_2 was due to the new stronger acid sites formed by mixing the two oxides. The catalytic activities for 2-propanol dehydration and cumene dealkylation were correlated with both acidity and acid strength of the catalyst. Modification with H_2SO_4 enhanced the activities of the catalysts remarkably, being responsible for the superacidic properties of the modified catalysts [145].

The Lewis acidity of ZrO_2 and sulfated zirconia has been investigated by using the probe molecules CO, CO_2, CH_3SH and pyridine [146]. It was found that pure ZrO_2 was less acidic than alumina or anatase, but for that after sulfation, the acidity was comparable to that of anatase.

2.3 CATALYTIC ACTIVITY AND ACID BASE PROPERTIES

The simplest division of oxide surface reaction classes is into two groups: acid-base reactions and oxidation-reduction reactions. This is clearly a "broad brush" treatment [147]. The exposed cations and anions on oxide surfaces have long been described as acid base site pairs [148,149]. The oxygen anions can act as Bronsted or Lewis base sites; the metal cations are Lewis acid sites. Hydroxyl groups bound at certain oxide surfaces may exhibit considerable Bronsted acidity, but Bronsted acidity of oxide surfaces in surface science studies was neglected. Dissociation reactions of Bronsted acids were among the first to be examined in detail on high surface area materials by infrared spectroscopy.

Henrich and Cox [150] have compiled a list of studies of organic molecules on single crystal oxides through 1993 which includes examples on various crystal planes of MgO, ZnO, SnO_2, TiO_2, V_2O_5, NiO, MoO_3 and Cu_2O. Recent work has also been reported on ZrO_2 [151]. Oxygen anions on metal oxide surfaces can act as Lewis as well as Bronsted bases. As such they may oxidize adsorbed organics. The most common examples of such reactions in the metal oxide surface science literature are nucleophilic oxidations of carboxyl compounds. Aldehydes are oxidized to the corresponding carboxylates on a number of oxide surfaces.

The adsorption, whether dissociative or otherwise of molecules on the surface is usually but the first in a sequence of reactions that may be of interest. Indeed for a catalytic process, subsequent steps which regenerate the active sites must occur. The menu of feasible reactions for an adsorbate, eg., the conjugate base of a Bronsted acid, will depend not only upon its own structure, but also upon the availability of potential reaction patterns [147].

Good correlations have been found in many cases between the total amount of acid (Bronsted plus Lewis type usually measured by the amine titration method) and catalytic activities of solid acids. The rates of both the catalytic decomposition of cumene [97] and the polymerisation of propylene [97,98] over SiO_2, Al_2O_3, catalysts were found to increase with increasing acid amounts at strength $H_o \leq +3.3$.

Approximately linear relationship have however been demonstrated between the acid amount for SiO_2–Al_2O_3 catalysts as measured by the quinoline adsorption method and their cracking activity for volatile petroleum fractions [152–156]. A relationship has also been found to hold between acidity and activation energies.

Uchida and Imai have found that both the ethylene polymerization activity of SiO_2–Al_2O_3 and its acid amount are increased by the addition of Nickel oxide [157].

Morikawa, Shirasaki *et al.* [157] have shown that the catalytic activity and selectivity of SiO_2–Al_2O_3 catalysts can be enhanced by the adsorption of various cations [158,159]. In fact the catalytic activity of the nickel ion exchanged catalyst is far greater than that of the unexchanged catalyst in the disproportionation of toluene, the level of activity depending to a very large extent upon the kind and amount of the exchanged cations [159].

Alumina's catalytic activities in a range of reactions such as the isomerization of hydrocarbons, the polymerization of olefins etc. have all been attributed to the acidic properties of the surface [160–167].

Correlations have been established between the acidity at $H_o \leq +3.3$ of zoelite X exchanged with divalent cations such as Cd, Mg, Ca, Sr and Ba, and the catalytic activity in the decomposition of diisobutylene at 300°C and the polymerization of isobutylene at 350°C, by the studies of Matsumoto and Morita [168].

The pronounced catalytic activity displayed by zeolites in the cracking of cumene has been shown to depend upon the large number of acid sites, but not specifically upon their acid strength [169].

The catalytic activity of $Al_2O_3.B_2O_3$ in the transalkylation of aromatic compounds is found to be higher than that of $SiO_2.Al_2O_3$. The higher activity seems to be essentially due to the higher concentrations of acid sites on $Al_2O_3.B_2O_3$. It is also found that $Al_2O_3.B_2O_3$ shows high activity for the Beckmann rearrangement of cyclohexanone oxine [171].

Although the fundamental catalytic and surface properties of alkali, alkaline earth and other basic oxides have been extensively studied [86], equivalent information about the series of basic rare earth oxides is much less.

Empirical studies have demonstrated that following appropriate pre-treatment, rare earth oxides are active catalysts for a number of reactions.

Taylor and Diamond have shown that paramagnetic oxides, Gd_2O_3 and Nd_2O_3 are more active in catalyzing ortho para hydrogen conversion [172].

Hopkins and Taebel have measured the catalytic activity of rare earths for oxidation, hydrogenation, decomposition and synthesis of organic compounds [173]. Oxidation—Reduction reactions are important in organic chemistry. Rare earth oxides like La_2O_3 and Dy_2O_3 are effective in Meerwein–Ponndorf–Verley type reduction of ketones [174,175].

The reduction of multiple bonds using an organic molecule as a hydrogen donor in place of hydrogen gas or metal hydride is known as hydrogen transfer reactions [176]. Reduction of carboxyl groups is one of the most fundamental operations in organic chemistry. This was called Meerwein–Ponndorf–Verley Reduction. It was discovered in 1925 and has been used successfully in a number of instances [177].

Aluminium isopropoxide has been found to be the best reagent for this reaction. This method calls for both addition of at least 100–200% excess aluminium isopropoxide and neutralization of alkoxide salt with strong acid. Heterogeneous reactions for the reduction reactions are known [178]. The mechanism of the reduction reaction involves a hydride transfer from aluminium isopropoxide to the carbonyl carbon of the ketone. Kibby and Keithhall have reported on hydrogen transfer reaction over hydroxy apatite catalyst and proposed a mechanism similar to that of the Meerwein–Ponndorf–Verley reduction [179].

Shibagaki *et al.* [180] studied the liquid phase reduction of aldehydes and ketones with 2-propanol over hydrous zirconium oxide. Kinetic experiments have indicated that the reaction rate is of first order dependence on each of the concentration of the carbonyl compound, 2-propanol and the catalyst. An observation of the primary isotopic effect has suggested that a step of hydride transfer from adsorbed 2-propanol to adsorbed carbonyl compound constitute the rate determining step for the reduction.

Tin(IV) oxide is an effective catalyst in the vapour phase reduction of carboxylic acid with 2-propanol [181]. Tin(IV) oxide is analogous to hydrous zirconium(IV) oxide regarding its characteristic reactivity. The reverse reaction which is known as Oppenauer oxidation has been used for the oxidation of alcohols.

In 1937 Oppenauer showed that unsolvated steroid alcohols could be oxidized to the corresponding ketone in excellent yields through the use of aluminium tertiary butoxide in the presence of a large amount of acetone, that compound functioning as the hydrogen acceptor and the large excess serving to shift the equilibrium in the desired direction [182]. In view of the reversible nature of the reaction, many statements about the mechanism of the Meerwein–Poundorf–Verley reduction [177] are equally applicable to the Oppenauer oxidation. Activation of the alcoholic hydrogen atom by the aluminium resulting in hydrogen bonding has also been proposed by Woodward *et al.* [183].

The Oppenauer oxidation has not been used as a preparative method for the oxidation of primary alcohols to aldehydes because the aldehydes condensed with the hydrogen acceptor. Schinz and Lauehensuer have developed a general preparative method for the Oppenauer oxidation of low molecular weight primary alcohols to aldehydes. The procedure is essentially a reversal of the MPV reduction but does not require an excess of alcohol [184].

The three most common catalysts in the Oppenauer oxidation are aluminium t-butoxide, isopropoxide and phenoxide. Aluminium isopropoxide and in particular phenoxide are easier to prepare. Aluminium isopropoxide is the most powerful oxidising agent [185]. In the modified Oppenauer oxidation benzophenone was found to be satisfactory oxidising agent, since it cannot undergo condensation in the presence of a strongly basic catalyst.

The esterification of carboxylic acids is a straight forward reaction subjected to Bronsted acid catalysis. Conventional method used sulfuric acid as a catalyst. The yields are high but traces of sulfuric acid is detected along with the ester, which finds tedious procedures in the isolation of products. The use of heterogeneous catalysts for the esterification has been reported [186]. The presence of acid sites in the catalyst offer good potential for the application in Bronsted catalysis for esterification [187].

It was reported that strontium doping decreases the catalytic activity of lanthana towards the liquid phase reduction of cyclohexanone in isopropanol. This is because of the fact that, surface basicity of lanthana decreased due to strontium doping [188].

The activity of sulfated zirconia catalysts for the alkylation of isobutane with 2-butene was studied [133]. The aged catalyst was inactive, but activation of the material at 100°C resulted in the most active catalyst. Thermal treatment at higher temperatures resulted in a loss in activity which paralleled the decrease in the Bronsted acid sites. These results are consistent with a model in which strong Bronsted acidity is a result of the interaction between bisulfate groups and adjacent Lewis acid sites.

Although zirconium oxide is an active catalyst on its own for methanol and hydrocarbon synthesis [189–191], sulfated zirconia is reported to have superacid properties for the isomerization of hydrocarbons [192] or for the conversion of methanol to hydrocarbons [193].

The activity of SiO_2–ZrO_2 in the dehydration of alcohols and the cracking of cumene is directly proportional to the amount of acid on the surface [194].

Perincone *et al.* [195] mentioned the close correlation between the surface acidity of MoO_3–$Fe_2(MoO_4)_3$ catalysts at $H_0 \leq +4.0$ and their activity in the oxidation of methanol to formaldehyde.

Tani and Ogino, found that the activity of ZnO-Cr_2O_3-SiO_2-Al_2O_3 catalysts for the synthesis of methanol from carbon dioxide and hydrogen largely depends upon the amount of acid within a limited range of fairly low acid strength [196].

Certain reactions catalyzed by metal sulfates and phosphates have revealed good correlations between the acidity measured by amine titration and catalytic activity.

Tanabe and Ohnishi [197] found an excellent correlation between the acidity of nickel sulfates and their catalytic activity for the depolymerization of paraldehyde.

Usually, the high polymerization of aldehydes is catalyzed not only by bases but also by both Bronsted and Lewis acids. Takida and Noro have found that some metal sulfates do in fact catalyze this polymerization [198].

Measurement of the polymerization activity and acidic properties of solid sulfates of Fe(III), Cr, Zn, Ni, Mn, Mg, Cu, Fe(II) and Ca which had been heat treated at various temperatures revealed that those catalysis possessing acid sites with $H_o \leq +3.3$ are effective in the polymerization [86]. The low polymerization of propylene in the vapour phase was found to be catalyzed by sulfates of Ni, Co, Fe, Cu, Mn and Zn, by Tarama *et al.* [86] the catalytic activity increasing with increase in the number of acid sites having strength $H_o \leq +3.3$.

Various metal phosphates have been found effective as solid acid catalysts for the high polymerization of ethylene oxide [199], the cracking of volatile fractions of petroleum [44] and dehydration of isopropyl alcohol [200]. There is a good correlation between the amount of acid within a definite range of acid strengths and the catalytic activity for phosphate.

There are solid acids with only weak sites at $H_o > +3.3$ such as TiO_2 and ZnS, which do not show any catalytic activity for the polymerization of propylene [201], the isomerization of pinene [202] or the condensation of glucose with acetone [203].

Shephard *et al.* [204] studied the polymerization of propylene on a silica-alumina catalyst and found that the activity was drastically curtailed when surface hydrogen atoms of the catalyst were exchanged with sodium ions, suggesting that Bronsted acid sites are essential to the reaction.

Shiba *et al.* [205] have demonstrated a clear connection between the polymerization activity of silica-aluminas and Bronsted acidity, the latter being derived from the difference between the total acidity and Lewis acidity. The fact that the greater proportion of olefins is formed from propylene on silica alumina treated with perylene, which is thought to be adsorbed only on Lewis sites and not to any appreciable extent on Bronsted sites, suggests that Lewis sites may be responsible for those reactions which supply the necessary hydrogen for the conversion of olefins and carbonium ions to saturated compounds [204]. This conclusion is in conformity with the hypothesis that Lewis sites are active in the accumulation of aromatic compounds with coke.

MacIver *et al.* [206] observed that perylene which specifically poisons Lewis acid sites, had no effect on the activity or selectivity of SiO_2–Al_2O_3 and SiO_2–MgO for skeletal isomerization of 1–pentene. This suggests that the Lewis sites are inactive for these isomerization reactions.

It is known that perylene and anthracene are oxidized by BF_3, a typical Lewis acid and 98% sulfuric acid, but not by Bronsted acids such as HF in the absence of molecular oxygen [207].

A reliable method for the measurement of Bronsted or Lewis acidity is that based on the infrared spectrum of chemisorbed pyridine. A relationship that holds between the amount of Bronsted acid and the catalytic activity for o-xylene isomerization was determined by this method that was given by Ward and Hansford [208].

The activity of a partially halogenated porous glass catalyst for the cracking of cumene was shown to be due to Bronsted (and not Lewis) acid sites [209]. Both the amount and strength of Bronsted acid on silica gel is known to increase remarkably upon adsorption of a halogen [210].

Antipina *et al.* [211] have clearly shown the correlation between the amount of Bronsted acid as fluorided alumina and aluminium hydroxyfluorides and their cumene—cracking activity [211].

Ward has found that the cumene cracking activity of cation exchanged zeolite Y increases with increasing Bronsted acidity [212]. The high activity of zeolite and mordenite (NH_4^+ form) heat treated at 600~700°C in the disproportionation of toluene and the reaction of n-paraffins is assumed to be due to Bronsted acid sites [213].

In the case of alumina–boria catalysts, the activity for the disproportionation of toluene was found to correlate with the Bronsted acidity, but not significantly with either, the Lewis acidity or the total acidity [214].

In the case of silica-magnesia, Bremer and Steinberg [215] found that moderately strong Lewis type acid sites and weakly acidic isolated OH groups exist on the surface, and suggested that the catalyst acts as a bifunctional acid catalyst for the dehydration of isopropanol.

It was pointed out that the maximum rate of depolymerization of paraldehyde when catalyzed by solid nickel sulfate is considered to coincide with the maximum amount of (Lewis + Bronsted) acid as determined by amine titration. This reaction is known to be catalyzed not only by Bronsted acid (H_2SO_4, CCl_3COOH etc.) but also by Lewis acid ($TiCl_4$, $AlCl_3$, $SnCl_4$ etc.) [216].

Hydrolysis of methylene chloride by nickel sulfate at temperatures above 300°C is catalyzed by Lewis acid, whereas the isomerization of α-pinene and 1-butene are catalyzed by Bronsted acid sites [86].

The selectivity of a solid acid catalyst is influenced by its acidic properties and many other factors such as its geometric structure (particularly pore structure), the distribution of basic sites if present, the polarity of the surface etc. [86]. Selectivity is also governed by the strength and type of acid sites.

Several catalysts including $4MgCO_3.Mg(OH)_2.4H_2O$ [217], $Ce_2O.MnO.MgO$ [92] and $Fe_2O_3.ZnO$ [93] were found to show extremely high selectivity for the formation of 2,6-xylenol.

Rearrangements of olefins which proceed via primary carbonium ions are believed to progress with any great rapidity only on relatively strong acid sites, whereas those involving more stable secondary and tertiary carbonium ions can occur equally well on both strong and weak sites [160].

The oxides, carbonates and hydroxides of alkali metals and alkaline earth metals (MgO, CaO, SrO, Na_2CO_3, K_2CO_3, $SrCO_3$, NaOH, $Ca(OH)_2$ etc.) have been found active in the high polymerization of formaldehyde [218], ethylene oxide [219] propylene oxide [220], lactam [221] and β-propiolactone [222].

A solid base like Na/Al_2O_3 which has a large surface area is very active for the isomerization of olefins. Clark and Finch [223] on the basis of results from ammonia blocking, H-D exchange and radiochemical experiments using ^{14}C suggest that the isomerization of 1-butene over magnesium oxide may proceed by an anionic mechanism which is independent of catalyst acidity.

Olefin alkylation of aromatic compounds is also catalyzed by solid bases such as Na/Al_2O_3, NaH, K/graphite etc. The activities for aldol type formaldehyde and acetaldehyde condensation over NaOH/SiO$_2$, MgO, CaO and PbO correlate well with the basic properties of the surfaces.

In the reaction of acrolein with ethanol over various metal oxides, the catalytic activity is found to increase with increasing differences in electronegativities, an indication that the reaction proceeds accordingly to a base type mechanism [224].

Malinowski *et al.* [225–227] have investigated the reactions of formaldehyde with nitromethane, acetaldehyde, acetone and acetonitrile over silica gel catalysts containing various amounts of Na at 275^{0}C. They found a linear relationship between the apparent reaction rate constants and the amount of sodium, since the basic strength of the catalyst is directly proportional to the sodium concentration.

The first order rate constant for the formation of benzyl benzoate from benzaldehyde over calcium oxides calcined at various temperatures is found to change in parallel with the change in catalyst basicity [86].

In the reaction of acrolein with ethanol on basic metal oxides, Krylov and Fokins [224] have inferred from infrared studies that the alcoholate is first formed with the participation of metal and oxygen atoms on the solid bases.

Tanabe *et al.* [228] have found that the mutarotation of α-D-tetramethyl glucose in benzene which is thought to involve acid-base bifunctional catalysis is catalyzed by metal sulfates, silica alumina etc.

The elimination of hydrogen halide from alkyl halide in many cases is thought to proceed by a concerted mechanism with acid-base bifunctional catalysts [86].

The acceptor strength of the cation increases with increasing charge and decreasing size, while the donor strength of the anion may be related to the basicity of the ion in the liquid phase or to the acidity of the corresponding acid. Although it is possible to give figures for the basicity of anions in the crystal surface, it is likely that Cl^- is less basic than SO_4^{2-} and SO_4^{2-} considerably less than PO_4^{3-}, CO_3^{2-} and BO_2^- [86].

It was observed that the catalytic activity of cerium oxide and its mixed oxides with alumina towards the reactions such as oxidation of alcohols and reduction of ketones have been correlated with their surface electron donor properties, which in turn depend upon the surface acidity/basicity of the oxide [229].

The performance of Pt catalysts supported on sulfated zirconia-silica with different stoichiometries is investigated in the n-pentane hydroisomerization reaction. Comparatively, with respect to the $Pt/SO_4^{2-}-SiO_2$ or $Pt/SO_4^{2-}-ZrO_2$ catalysts, the sulfated mixed oxides show an enhancement of the catalytic activity that increases with the content of ZrO_2 reaching its maximum at values between 10 and 15 wt % zirconia. The characterization of the samples reveals that at this stoichiometry, the highest H_2-consumption of the samples as well as the top value of strong Bronsted acid sites occurs according to the TPD–H_2 and FTIR measurements of absorbed pyridine respectively [230].

The incorporation of Cr, Fe, Mn and V into sulfated zirconia increases its superacidity and catalytic activity for n-butane isomerization at 35°C significantly. The catalytic activity of sulfated oxides of Cr–Zr, Fe–Cr–Zr and Fe–V–Zr is 2–3 times greater than that of the well known sulfated Fe–Mn–Zr oxide. A negative effect was observed in the cases of sulfated Mn–Zr, Sn–Zr, W–Zr and Mo–Zr oxides. IR spectroscopic studies showed that the active sites for isomerization of n-alkane on superacid catalysts are the superacidic Bronsted acid sites produced via the adsorption of water on the strong Lewis acid sites [231].

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Chapter III

EXPERIMENTAL

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3.1 MATERIALS

3.1.1 Metal oxides

Aluminium oxide, zirconium oxide and rare earth oxides (Sm_2O_3 and CeO_2) were prepared by hydroxide method [1] from nitrate salt. Samarium nitrate and cerium nitrate (99.9%) were obtained from Indian Rare Earth Ltd., Udyogamandal, Kerala. Titanium dioxide from s.d Fine Chem Ltd. was used as such. SnO_2 was prepared from stannous chloride after oxidation with aqua regia.

Hydroxide Method

To the boiling nitrate solution of the sample, added 1:1 ammonium hydroxide dropwise with stirring until the precipitation was complete. Concentrated ammonium hydroxide solution (an amount equal to one tenth of volume of solution) was then added with stirring. It was then allowed to digest on a steam bath until precipitate was flocculated and settled. The precipitate was filtered on a Whatmann No.41 filter paper and washed until the precipitate was free from NO_3^-. The precipitate was kept in an air oven at 110^0C for overnight and was ignited in a china dish at 300^0C for 2 hours. It was then powdered and seived to get samples below 75 micron mesh size. Stannic oxide was prepared from stannic chloride solution by using the same hydroxide method [1]. The precipitate was washed free from NO_3^- and Cl^- ions.

3.1.2 Sulfate modified oxides

Sulfated catalysts were prepared by a previously published procedure [2]. The metal oxides after heating in an electric furnace at 300°C for 2 hours were powdered and seived to get samples below 75 micron mesh size. Sulfation was carried out by impregnation of the oxides with 0.2 N ammonium sulfate solution for 4 hours using a magnetic stirrer. The precipitate was filtered without washing and dried and seived as above.

3.1.3 Electron acceptors

Electron acceptors employed for the study are 7,7,8,8–tetracyanoquinodimethane (TCNQ), 2,3,5,6–tetrachloro–p–benzoquinone (Chloranil), p–dinitrobenzene (PDNB) and m–dinitrobenzene (MDNB).

TCNQ was obtained from Merck Schuchandt and was purified by repeated recrystallisation from acetonitrile [3].

Chloranil was obtained from Sisco Research Laboratories Pvt. Ltd., and was purified by recrystallisation from benzene [4].

p-Dinitrobenzene was supplied by Kochlight Laboratories Ltd. and was purified by recrystallisation from chloroform [5].

m-Dinitrobenzene was obtained from Loba Chemie Industrial Company and was purified by recrystallisation from CCl_4 [6].

3.1.4 Solvent

Acetonitrile

SQ grade acetonitrile obtained from Qualigens Fine Chemicals was first dried by passing through a column filled with silica gel (60-120 mesh) activated at 110°C for 2 hours. It was then distilled with anhydrous phosphorous pentoxide and the fraction between 79-82°C was collected [7].

3.1.5 Reagents used for acidity/basicity measurements

Benzene

Benzene used for acidity and basicity measurements was purified by the following procedure [8].

SQ grade benzene obtained from Qualigens Fine Chemicals was shaken repeatedly with about 15% of the volume of concentrated sulphuric acid in a stoppered separating funnel until the acid layer was colourless on standing. After shaking, the mixture was allowed to settle and lower layer was drawn off. It was then washed twice with water to remove most of the acid, then with 10% sodium carbonate solution, and finally with water. It was dried with anhydrous $CaCl_2$. It was filtered and distilled and the distillate was kept over sodium wire for one day. It was then distilled and fraction boiling at 80°C was collected.

Hammett Indicators

Hammett indicators used for the study are the following:

Neutral red [Romali]

Methyl red [E.Merck India Pvt. Ltd.]

Crystal violet [Romali]

Dimethyl yellow [Loba Chemie Industrial Company]

Thymol blue [Qualigens Fine Chemicals]

Bromothymol blue [Qualigens Fine Chemicals]

4-Nitro aniline [Indian Drug and Pharmaceuticals Ltd.]

Trichloroacetic acid (SQ Grade) obtained from Qualigens Fine Chemicals and n-butylamine (s.d Fine Chemicals Pvt. Ltd.). They were used without further purification.

3.1.6 Reagents used for activity measurements

Cyclohexanone

Commercial cyclohexanone obtained from BDH was purified through the bisulphite method [9]. A saturated solution of sodium bisulphite was prepared from 40 gm of finely powdered sodium bisulphite. The volume of the resulting solution was measured and it was treated with 70% of its volume of rectified spirit. Sufficient water was added to dissolve the precipitate which was separated. 20 g of cyclohexanone was introduced into the aqueous alcoholic bisulphite solution with stirring and the mixture was allowed to stand for 30 minutes. The crystalline bisulphite compound was filtered off at the pump and washed it with a little rectified spirit.

The bisulphite compound was transferred to a separating funnel and decomposed with 80 ml of 10% NaOH solution. The liberated cyclohexanone was removed. The aqueous solution layer was saturated with salt and extracted it with ketone layer and dried with 5 gm of anhydrous magnesium sulfate. The dried etherial solution was filtered into a 50 ml distilling flask, attached with a condenser and distilled off the ether using a water bath. The resultant cyclohexanone was distilled and the fraction at 153°C was collected.

Benzophenone

Benzophenone was supplied by Sisco Research Laboratories Pvt. Ltd. and was purified by recrystallisation from ethanol [10].

2-Propanol

LR grade reagent obtained from Merck was further purified by adding about 200 g of quick lime to 1 litre of 2-propanol. It was kept for 3-4 days, refluxed for 4 hours and distilled. The fraction distilling at 82°C was collected [11].

Xylene

Extra pure quality xylene obtained from Merck was used as such.

Cyclohexanol

Cyclohexanol obtained from Merck was refluxed with freshly ignited CaO and then fractionally distilled. The fraction distilling at 161.1°C was collected [12].

Toluene

SQ grade toluene obtained from Qualigens Fine Chemicals was shaken twice with cold concentrated H_2SO_4 (100 ml of acid for 1 litre of toluene), then with water, 5% aq. $NaHCO_3$ and again with water. Then it was dried successively with $CaSO_4$ and P_2O_5, distilled and fraction distilling at 110°C was collected [13].

n-Decane

LR grade reagent obtained from s.d Fine Chemicals Pvt. Ltd., was further purified by shaking with conc. H_2SO_4. It was washed with water and aq. $NaHCO_3$. Finally it was washed with more water. Then it was dried with $MgSO_4$, refluxed with sodium and distilled. The fraction distilling at 174°C was collected [14].

1-Butanol

LR grade reagent obtained from Merck was further purified by drying with anhydrous potassium carbonate and fractionally distilled. The fraction distilling at 116.5°C was collected [17].

Acetic Acid

LR grade reagent obtained from Merck was purified by adding some acetic anhydride to react with the water present. It was then heated for 1 hour just below boiling in the presence of 2 g of Cr_2O_3 per 100 ml and then fractionally distilled. The fraction distilling at 116–118°C was collected [18].

3.2 METHODS

3.2.1 Adsorption studies [19]

The oxides were activated at a particular temperature for 2 hrs, prior to each experiment. The oxide (0.5 g) was placed in a 25 ml test tube and outgassed at 10^{-5} Torr for 1 hour. In to the test tube which was fitted with a mercury sealed stirrer, 20 ml of a solution of an electron acceptor in acetonitrile solvent was then poured. After the solution had subsequently been stirred for 3 hours at 28°C in a thermostated bath, the oxide was collected by centrifuging the solution and dried at room temperature in vacuo. The reflectance spectra of the dried samples were recorded on a Shimadzu 160A UV-visible spectrophotometer with a 200-0531 reflectance attachment.

The ESR spectra were measured at room temperature using Varian E-112 X/Q band ESR spectrophotometer. Radical concentrations were calculated by comparison of areas obtained by double integration of the first derivative curves for the sample and standard solutions of 1,1-diphenyl-2-picryl hydrazyl in benzene. The amount of electron acceptor adsorbed was determined from the difference in concentration before and after adsorption. The absorbance of electron acceptors was measured by means of a Shimadzu 160A UV-vis spectrophotometer at the λ_{max} of the electron acceptor in the solvent. The λ_{max} values of TCNQ, Chloranil PDNB and MDNB were 393.5 nm, 288 nm, 262 nm and 237 nm respectively in acetonitrile.

Infrared spectra of oxides were taken Shimadsu IR 470 Spectrophotometer.

Surface areas of oxides were determined by BET method using Carlo Erba Strumentazone Sorptomatic Series 1800 and mercury porosimetry using Quantachrome Corporation.

3.2.2 Acidity/basicity measurement [20]

The catalysts were sieved to prepare powders below 75 micron mesh size. The acidity at various acid strengths of a solid was measured by titrating 0.1 g of solid suspended in 5 ml of benzene with a 0.1 M solution of n-butyl amine in benzene. At the end point, the basic colour of indicators appeared.

The basicity was measured by titrating 0.1 g of solid suspended in 5 ml of benzene with a 0.1 M solution of trichloroacetic acid in benzene using the same indicators as those used for acidity measurement. The colours of indicators on the surface at the end points of the titration were the same as the colours which appeared by adsorption of respective indicators on the acid sites. The colour of the benzene solution was the basic colour of the indicator at the end point but it turned to be the acidic colour by adding an excess of the acid. As the results for a titration lasting 1 hr were the same as those for a titration lasting 20 hrs, 1 hr was taken for titration.

3.2.3 Magnetic susceptibility measurements

Magnetic moments of the oxides before and after the adsorption of electron acceptors were determined by magnetic susceptibility measurements.

The magnetic susceptibility measurements were done at room temperature on a simple Guoy type balance. The Guoy tube was standardised using [Hg(Co(CNS)$_4$)] as recommended by Figgs & Nyholm [21]. The effective magnetic moment μ_{eff} was calculated using the equation,

$$\mu_{eff} = 2.8\ (\chi_M \text{ corr. } T)^{1/2}$$

where T is the effective temperature and χ_M corr. is the corrected molar susceptibility [22].

3.2.4 Catalytic activity measurements

Oxidation of Cyclohexanol [23]

In a round bottomed flask equipped with a reflux condenser were placed 0.5 gm catalyst (below 75 micron mesh size), 10 cc of a toluene solution of cyclohexanol (0.25 mmol), benzophenone (14.6 mmol) and n-decane (0.20 mmol) as an internal standard. The contents were heated under gentle reflux at 110°C for 2 hrs. The reaction was followed by product analysis by means of a CHEMITO-8510 Gas Chromatograph by comparison of its retention time with that of the standard samples. From the peak area of the product, the concentration of the product formed was calculated with reference to that of the internal standard.

Reduction of Cyclohexanone [24]

To 0.5 gm of the catalyst placed in a round bottomed flask equipped with a reflux condenser, 5 mmol of ketone, 10 cc of 2-propanol and 0.5 mmol of xylene were added. The contents were heated under gentle reflux at 80°C for 10 hours. The reaction was followed by product analysis by means of a CHEMITO-8510 Gas Chromatograph, by comparison of its retention time with that of the standard samples. From the peak area of the product, the concentration of the product formed was calculated with reference to that of the internal standard.

Esterification of Acetic Acid using 1-butanol [25]

The esterification was carried out in a 25 ml round bottomed flask equipped with a reflux condenser in which the catalyst (1 gm), acetic acid (2 mmol) n-butanol (32 mmol) and n-decane (0.2 mmol) was used as the internal standard. The reaction temperature was maintained at 98^{o}C and stirred continuously on a magnetic stirrer for 5 hours.

The reaction was followed by product analysis by means of a CHEMITO-8510 Gas Chromatograph, by comparison of its retention time with that of the standard samples. From the peak area of the product, the concentration of the product was calculated with reference to that of the internal standard.

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Chapter IV

ACIDITY/BASICITY, ELECTRON DONOR PROPERTIES AND CATALYTIC ACTIVITY OF SULFATED ZIRCONIA

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ACIDITY/BASICITY, ELECTRON DONOR PROPERTIES AND CATALYTIC ACTIVITY OF SULFATED ZIRCONIA

4.1 INTRODUCTION

The use of sulfated zirconia is of increasing interest in the literature because of the superacidic properties induced in these materials by the presence of SO_4^{2-} that have been exploited in a variety of reactions giving interesting results particularly in the hydroisomerisation of alkanes. It has also been observed that the addition of metals such as Fe, Mn, or Pt greatly enhances the activity and stability of these catalysts on stream [1]. Unlike other sulfated oxides, sulfate doped zirconia possess enhanced surface acidity and possibly superacid catalytic properties and their surface and catalytic features have attracted a great deal of interest [2].

Arata and co-workers [3] reported that zirconia upon proper treatment with sulfuric acid or ammonium sulfate exhibits extremely strong acidity and is capable of catalyzing the isomerization of n-butane to isobutane at room temperature.

Numerous studies have been devoted to the preparation of sulfated zirconia and to the characterization of its physicochemical properties and catalytic performance in various chemical reactions. Sulfur content of a sulfated zirconia catalyst strongly depend on its calcination temperature. Increase in calcination temperature usually results in the gradual removal of sulfur from the catalyst surface. The most common calcination temperature ranges from 550°C to 650°C [3]. The calcination temperature significantly affects the catalytic performance of sulfated zirconia catalysts.

Sulfated zirconia shows very high initial activity for alkane isomerization and has been designated as a superacid catalyst. Unfortunately this catalyst deactivates very rapidly. Possible mechanisms of deactivation of sulfated oxide catalysts can be summarized as follows:

1. Coke formation
2. Reduction of S(VI) to lower oxidation state
3. Sulfur migration into the bulk of metal oxides.

Depending on the deactivation process, catalyst may or may not be regenerated by high temperature calcination [4].

Compared to other solid-acid catalysts sulfated zirconia has a relatively low surface area. Tanabe and co-workers [5] made an effort to increase the apparent surface area by dispersing the sulfated zirconia in SiO_2.

Recent experimental evidence as well as theoretical calculations suggested the existence of bisulfate on sulfated zirconia [6]. Lavalley *et al.* [7] found that impregnation with a high amount of sulfate creates Bronsted acidity and inferred that this acidity was generated by surface bisulfate ion.

It is worth noting that, since the nature of acid sites (Bronsted or Lewis) on sulfated zirconia depends critically on its water content, which in turn depend on the history of pre-treatment of the sample, the choice of appropriate pre-treatment conditions is extremely important in controlling the nature of the acidity of sulfated zirconia [4]. Since the discovery of its strong acidity, sulfated zirconia has found a number of potential applications as a process catalyst. Hydroisomerization and hydrocracking of straight chain hydrocarbons to produce branched ones are among the most promising catalytic applications. Compared to currently used zeolite catalysts, the more active sulfated zirconia catalysts allow the use of lower reaction temperature. Some other applications such as acylation, esterification etc. were also reviewed by Arata [8].

Though a number of studies have so far been reported about sulfated zirconia, no studies have been made about the electron donor properties of sulfated zirconia. The aim of present work is to understand the sources of increased acidity after modification with sulfate ion. That is to find out whether the increase in acidity due to sulfation is at the expense of basic sites already present on the surface or it can be due to the generation of new acid sites.

Esterification of acetic acid using n-butanol, reduction of cyclohexanone in 2-propanol and oxidation of cyclohexanol with benzophenone are the test reactions selected for finding catalytic activity.

4.2 EXPERIMENTAL

Zirconia was prepared from zirconium nitrate by hydroxide method. Sulfation was carried out by impregnation of oxide with ammonium sulfate solution. The detailed procedure was described in chapter III.

The samples activated at different activation temperatures of 300, 500 and 700°C were used. The surface area of samples were determined by BET method using Carles Erba Strucmentazone Sorptomatic Series 1800. The surface area of samples are given in Table 4.1.

Table 4.1: Surface area of zirconia and sulfated zirconia at different activation temperatures

Catalyst	Activation temperature (^{C}C)	Surface area $(m^2 g^{-1})$
ZrO_2	300	151.85
ZrO_2	500	62.28
ZrO_2	700	49.52
SO_4^{2-}/ ZrO_2	300	145.57
SO_4^{2-}/ ZrO_2	500	192.98
SO_4^{2-}/ ZrO_2	700	81.43

The acidity and basicity was determined by the standard procedure by titrating the solid suspended in benzene against n-butylamine/trichloroacetic acid for acidity/basicity respectively, using a set of Hammett indicators. The detailed procedure was described in chapter III.

The strength and distribution of electron donor sites on the oxide surface were determined by the adsorption of different electron acceptors from acetonitrile solution, which is a very weak base. The amount of electron acceptor adsorbed was determined by means of UV-vis spectrophotometry and adsorbed state of electron acceptor was studied by ESR and electronic spectra.

The catalytic activities of zirconia and sulfated zirconia for the esterification, reduction and oxidation reactions are determined in liquid phase. The descriptive procedures for these reactions are given in chapter III. IR spectra of both modified and unmodified samples were taken using a Shimadsu IR-470 spectrophotometer.

4.3 RESULTS AND DISCUSSION

4.3.1 Acidity/Basicity

The colour of the adsorbed indicators can give a measure of the acid base strength. The indicators used are given in Table 4.2. Among them, SO_4^{2-}/ZrO_2 responded only to 4 indicators. They are crystal violet, dimethyl yellow, methyl red and bromothymol blue. The acidity and basicity was determined on a common H_0 scale. The results of acid base strength distributions at different activation temperatures are given in Table 4.3.

Table 4.2: Hammett indicators used

Indicator	pKa values	Colour change	
		Acid	Base
Crystal violet	0.8	White	Blue
Dimethyl yellow	3.3	Yellow	Red
Methyl red	4.8	Yellow	Red
Neutral red	6.8	Yellow	Red
Bromothylmol blue	7.2	Yellow	Blue
4-nitroaniline	18.4	Yellow	Red

Table 4.3: Acid-base strength distribution of zirconia and sulfated zirconia at different activation temperatures

Catalyst	Activation Temp. °C)	Basicity (10^{-3} mmol m^{-2})			Acidity (10^{-3} mmol m^{-2})			
		$H_o \geq 3.3$	$H_o \geq 4.8$	$H_o \geq 7.2$	$H_o \leq 0.8$	$H_o \leq 3.3$	$H_o \leq 4.8$	$H_o \leq 7.2$
ZrO_2	300	3.56	1.24	0.18	--	--	--	--
ZrO_2	500	2.60	0.87	--	--	--	--	0.44
ZrO_2	700	2.18	0.55	--	--	--	--	1.65
SO_4^{2-}/ZrO_2	300	--	--	--	--	0.76	0.56	2.43
SO_4^{2-}/ZrO_2	500	--	--	--	0.04	0.84	1.12	3.37
SO_4^{2-}/ZrO_2	700	--	--	--	0.09	2.66	3.34	8.01

Acidity at an H_o value shows the number of acid sites whose acid strength is equal to or less than the pKa value of the corresponding indicator and the basicity at an H_o value shows the number of basic sites, whose conjugate acid has strength equal to or greater than the H_o value. The acid base properties of the oxides are expressed by $H_{o,\,max}$ values. It was found that the strongest H_o

value of acid sites was approximately equal to the strongest H_0 value of the basic sites and is termed as $H_{0,\,max}$. It is obtained from the point of intersection of acid-base strength distribution curve at a point on the abscissa where acidity = basicity = 0. $H_{0,\,max}$ value is considered as a practical parameter to represent the acid base properties of a solid surface [9] which is very sensitive to the surface structure. A solid with a high $H_{0,\,max}$ value possess strong basic sites and weak acidic sites and vice-versa.

The acid-base distribution curves are given in Figure 4.1. From this, it can be inferred that, ZrO_2 shows acidic sites at H_0 value 7.2. The $H_{0,\,max}$ values are given in Table 4.4. It was reported that ZrO_2 shows both acidic and basic behaviour. The acid sites was reported as Lewis acid and partially Bronsted sites [10].

Table 4.4 $H_{0,\,max}$ values of zirconia and sulfated zirconia at different activation temperatures

Catalyst	Activation temperature (°C)	$H_{0,\,max}$
ZrO_2	300	7.45
ZrO_2	500	6.50
ZrO_2	700	5.45
SO_4^{2-}/ZrO_2	300	--
SO_4^{2-}/ZrO_2	500	0.25
SO_4^{2-}/ZrO_2	700	0.45

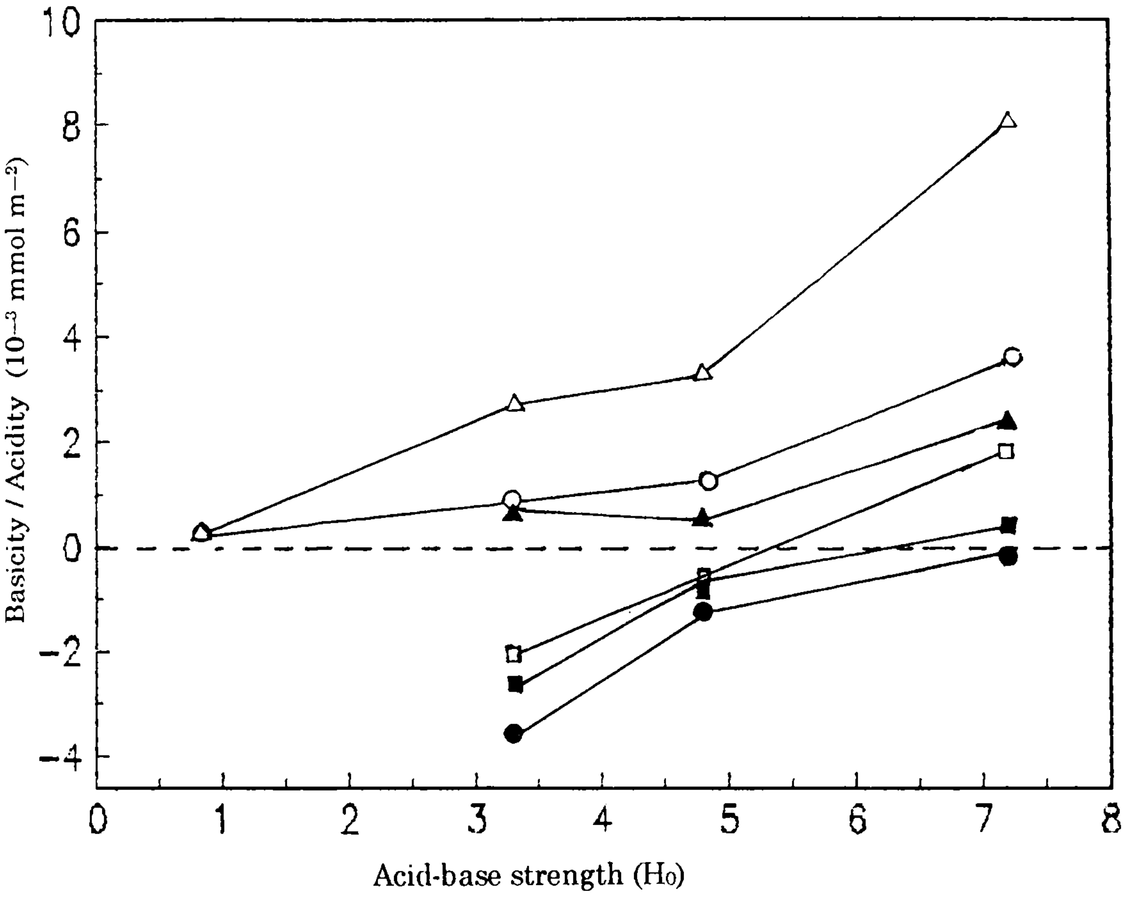


Figure 4.1: Acid-base strength distribution curves for zirconia and sulfated zirconia at different activation temperatures (°C)

●	ZrO_2 300	▲	SO_4^{2-}/ZrO_2 300
■	ZrO_2 500	○	SO_4^{2-}/ZrO_2 500
□	ZrO_2 700	△	SO_4^{2-}/ZrO_2 700

It has already been reported that ZrO_2 possess a low but definite basicity and is confirmed by the studies on the adsorption of CO [11]. ZrO_2 itself has both weakly acidic and basic properties which sometimes result in intriguing acid base bifunctional catalysis [12]. The basicity of ZrO_2 decreases with increasing temperature after 500°C. It may be due to the change in crystallinity from amorphous to monoclinic form.

Sulfated zirconia generates acidic site at H_0 value 0.8, which is comparable to acidity of 0.1 N H_2SO_4. Hino and Arata claimed that sulfated zirconia is an acid 10^4 times stronger than 100% H_2SO_4 [13] using 1 N sulfuric acid solution. The lower acidity with our samples compared to the reported value may be ascribed to the nature of zirconia, and the concentration of ammonium sulfate used for sulfation and the condition under which sulfation was carried out. It was reported that crystallinity and morphological features of the sulfated ZrO_2 systems vary with preparative and activation conditions. Type and relative concentrations of surface acidic sites (both Bronsted and Lewis centres) turn out to depend primarily on the type and relative concentration of surface sulfates, which in turn depend on several of the preparative parameters [14].

It was reported that IR spectra of sulfated zirconia solid superacids after evacuation at 300°C for 3 hrs display four adsorption bonds at 1390, 1190, 1020 and 930 cm^{-1}. The former two are assigned to the bulk sulfates and the latter two bands are assigned to the asymmetric and symmetric stretching frequencies of the O=S=O and O–S–O groups respectively. The 1390 cm^{-1} band representing the asymmetric stretching frequency of S=O double bond is often regarded as characteristic band of SO_4^{2-} promoted super acids [15]. Our results are in agreement with reported values. IR spectra of sulfated zirconia and zirconia are given in Figure 4.2.

The nature of surface acidity in anion-modified oxides remains controversial. Their catalytic properties however clearly reveal the strong effect of surface modification of the metal oxides by electron rich anions. The superacidity is considered to be generated by the interaction between the oxide and sulfate ion. It has been shown that $NiO-ZrO_2$ and ZrO_2 modified with sulfate ion are very active for acid catalyzed reactions even at room temperature. The high catalytic activity can be attributed to the enhanced acidic properties, which originate from the inductive effect of S=O double bond of the complex formed by the interaction of oxides with the sulfate ion. Both Lewis and Bronsted acid strengths increase due to the inductive effect of S=O double bond in the complex [16]. According to Kustov [17], sulfation leads to an enhancement of the acid strength of surface OH groups. However, the Bronsted acidity of sulfated zirconia (SZ) is weaker than that of acidic zeolites. Based on this, he came to the conclusion that SZ cannot be considered as a superacid.

Riemer *et al.* [18] reported a H MAS NMR study of Bronsted acid strength on SZ. It was observed that SZ has stronger acid sites than H-ZSM-5. Babou *et al.* [19] carried out theoretical calculations for Bronsted and Lewis

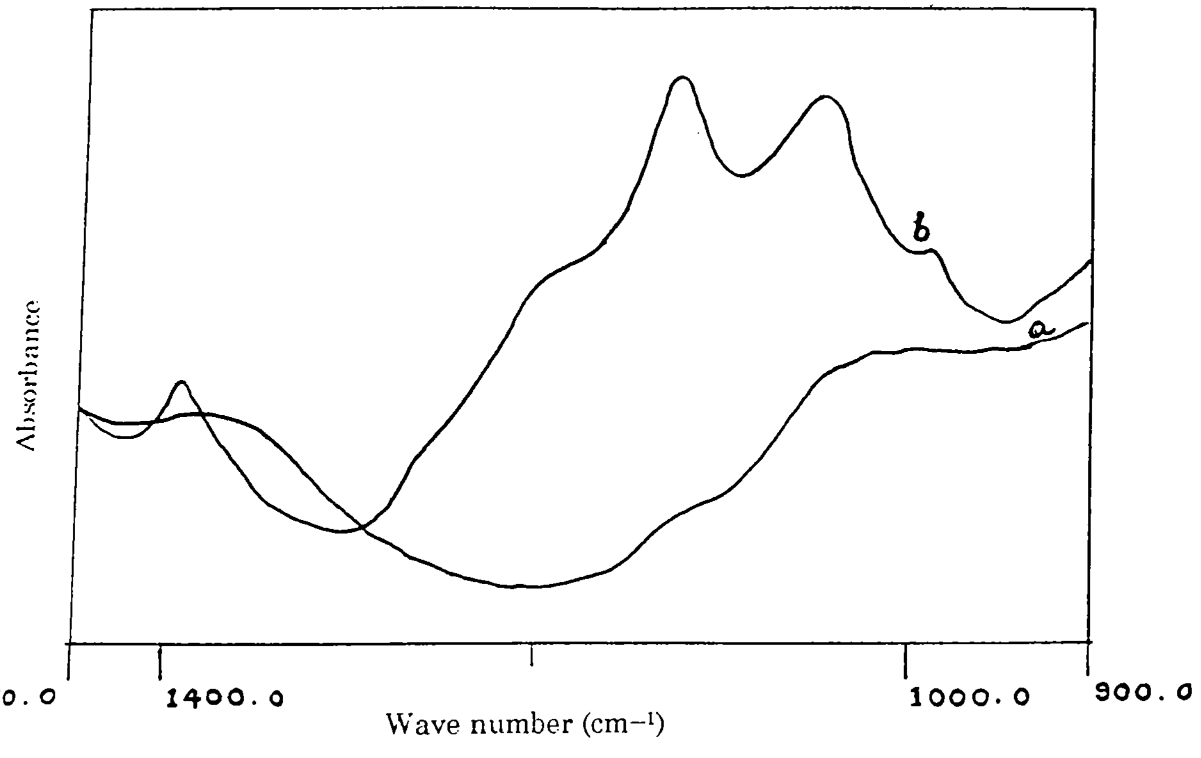


Figure 4.2: IR Spectra of zirconia and sulfated zirconia activated at 500°C

(a) ZrO_2 (b) SO_4^{2-}/ZrO_2

acidities respectively. They found that SZ behaves like H_2SO_4 grafted onto zirconia surface, and its acid strength is close to that of pure H_2SO_4, implying that SZ is a strong acid but not a superacid.

XPS data revealed that the oxidation state of sulfur in catalysts showing high catalytic activity in acid catalyzed reactions was S^{+6}. Catalysts containing S in a lower oxidation state were inactive [20].

The strong acidity was attributed to the electron withdrawing anion groups, which lead to co-ordinatively unsaturated and electron deficient metal centres that behave as strong Lewis acid sites. Such Lewis acid sites predominate in the absence of water vapour and on calcination at high temperature. Water vapour converts such Lewis sites to Bronsted acids with very reactive protons [21].

4.3.2 Electron donor properties

The surface electron donor properties of ZrO_2 and SO_4^{2-}/ZrO_2 have been determined by the adsorption of four electron acceptors with electron affinity values ranging from 1.26 to 2.84 eV on the surface, to form corresponding anion radicals. Since electron donating property varies with activation temperatures, the oxides activated at different activation temperatures of 300, 500 and 700°C were studied. The list of electron acceptors used are given in Table 4.5.

Table 4.5: Electron acceptors used for adsorption studies

Electron acceptor	Electron affinity values (eV)
m-dinitrobenzene (MDNB)	1.26
p-dinitrobenzene (PDNB)	1.77
2,3,5,6-tetrachloro-1,4-benzoquinone (chloranil)	2.40
7,7,8,8-tetracyanoquinodimethane (TCNQ)	2.84

In the case of PDNB and MDNB, the adsorption was found to be so negligible at all activation temperatures that the amount could hardly be detected. TCNQ and chloranil gave adsorption with characteristic results. The adsorption isotherms of TCNQ and chloranil from acitonitrile can be classified as Langmuir adsorption isotherms. It is obtained by plotting the amount of the electron acceptor adsorbed (Cads) against equilibrium concentration (Ceq). From such plots the limiting amount of electron acceptor adsorbed can be calculated. The data given in Table 4.6.

Table 4.6: Limiting amount of electron acceptor adsorbed on zirconia and sulfated zirconia at different activation temperatures

Catalyst	Activation temp. (°C)	Limiting amount of electron acceptor adsorbed (10^{-5} mol m^{-2})	
		Chloranil	TCNQ
ZrO_2	300	11.35	15.70
ZrO_2	500	39.78	51.76
ZrO_2	700	17.85	24.99
SO_4^{2-}/ZrO_2	300	2.49	7.44
SO_4^{2-}/ZrO_2	500	1.11	2.87
SO_4^{2-}/ZrO_2	700	0.77	1.44

It was verified by the linear form of Langmuir isotherm, where Ceq/Cads was plotted against equilibrium concentration (Ceq). The Langmuir adsorption isotherm obtained by the adsorption of chloranil and TCNQ are given in Figures 4.3 and 4.4. The linear form of Langmuir isotherm is given in Figure 4.5.

When electron acceptors are adsorbed from the solution, the surface developed remarkable coloration characteristic of each electron acceptor adsorbed owing to the interaction between electron acceptor adsorbed and the oxide surface [22]. Chloranil gave pink colour and TCNQ gave a greenish yellow colour. The coloration indicate the formation of new adsorbed species on the surface. It was confirmed by the evidence that these samples showed esr absorption indicating the formation of new free radical species. Figure 4.6 shows the esr spectrum of the sample adsorbed with TCNQ (Cads = 7.04×10^{-5} mol m^{-2}) on the surface. The radical concentrations were calculated by comparing the areas obtained by double integration of the first derivative curve for the sample and standard solution of 2,2-diphenyl-1-picrylhydrazil in benzene. The plot of radical concentration against equilibrium concentration of electron acceptor in solution also corresponds to the Langmuir adsorption isotherm (Figure 4.7). From such plots, the limiting radical concentrations of electron acceptor adsorbed can be estimated (Table 4.7).

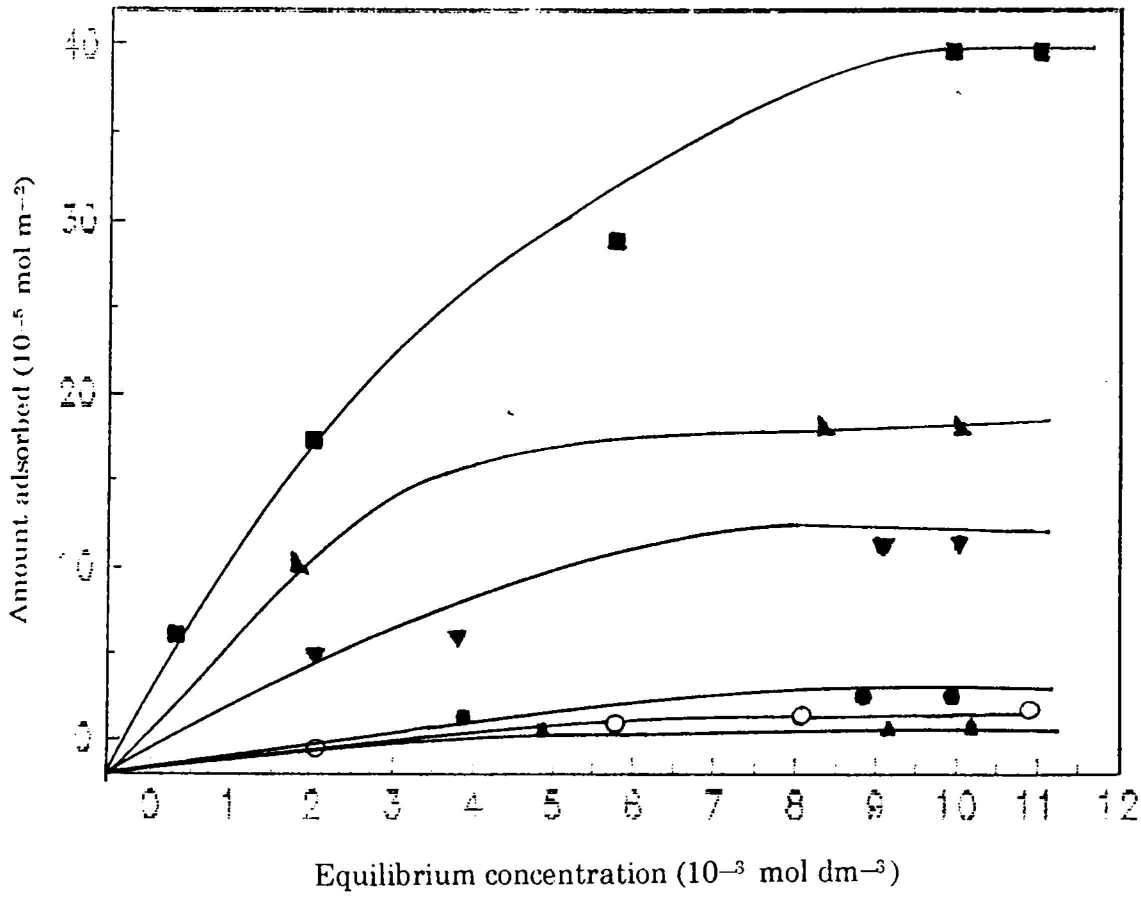


Figure 4.3: Langmuir adsorption isotherms of chloranil adsorbed on zirconia and sulfated zirconia at different activation temperatures (°C)

▼	ZrO_2 300	●	SO_4^{2-}/ZrO_2 300
■	ZrO_2 500	○	SO_4^{2-}/ZrO_2 500
◣	ZrO_2 700	▲	SO_4^{2-}/ZrO_2 700

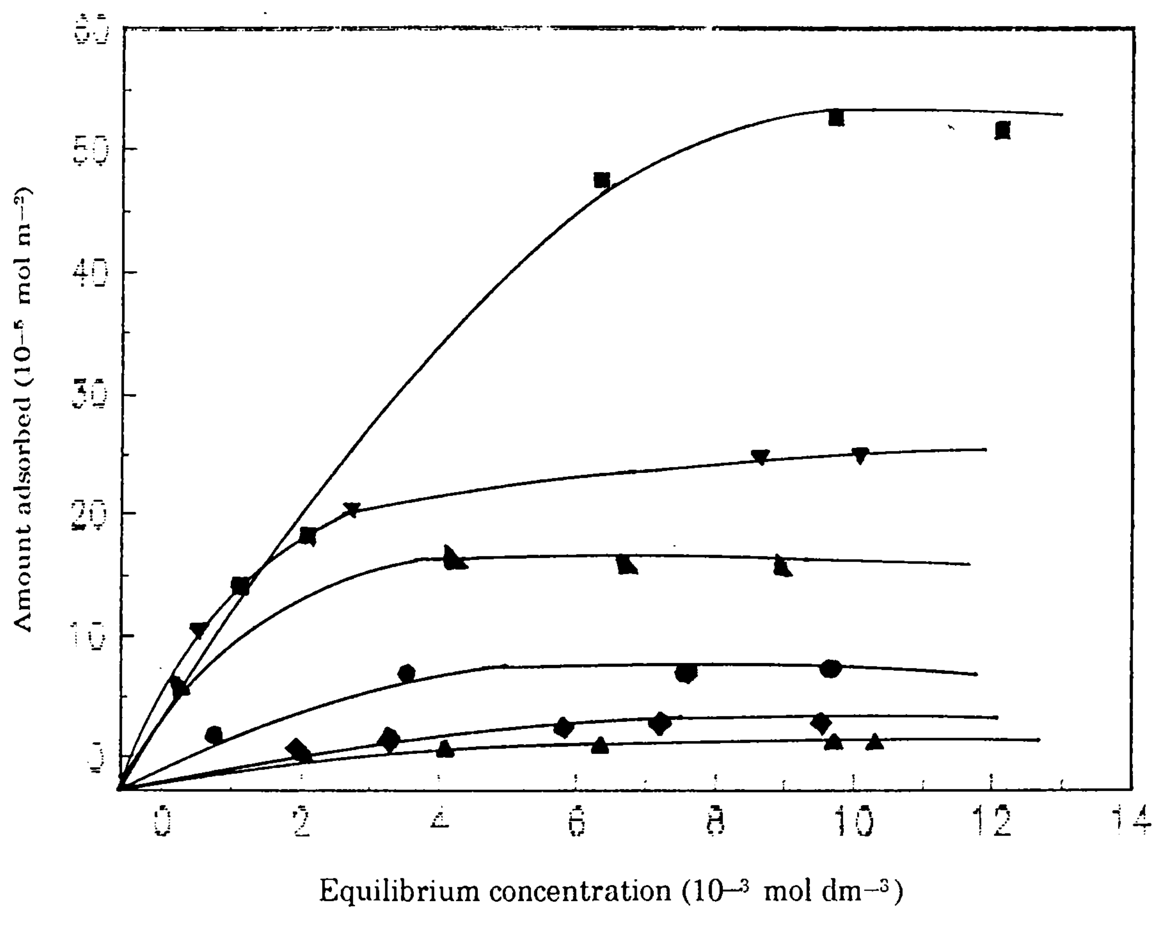
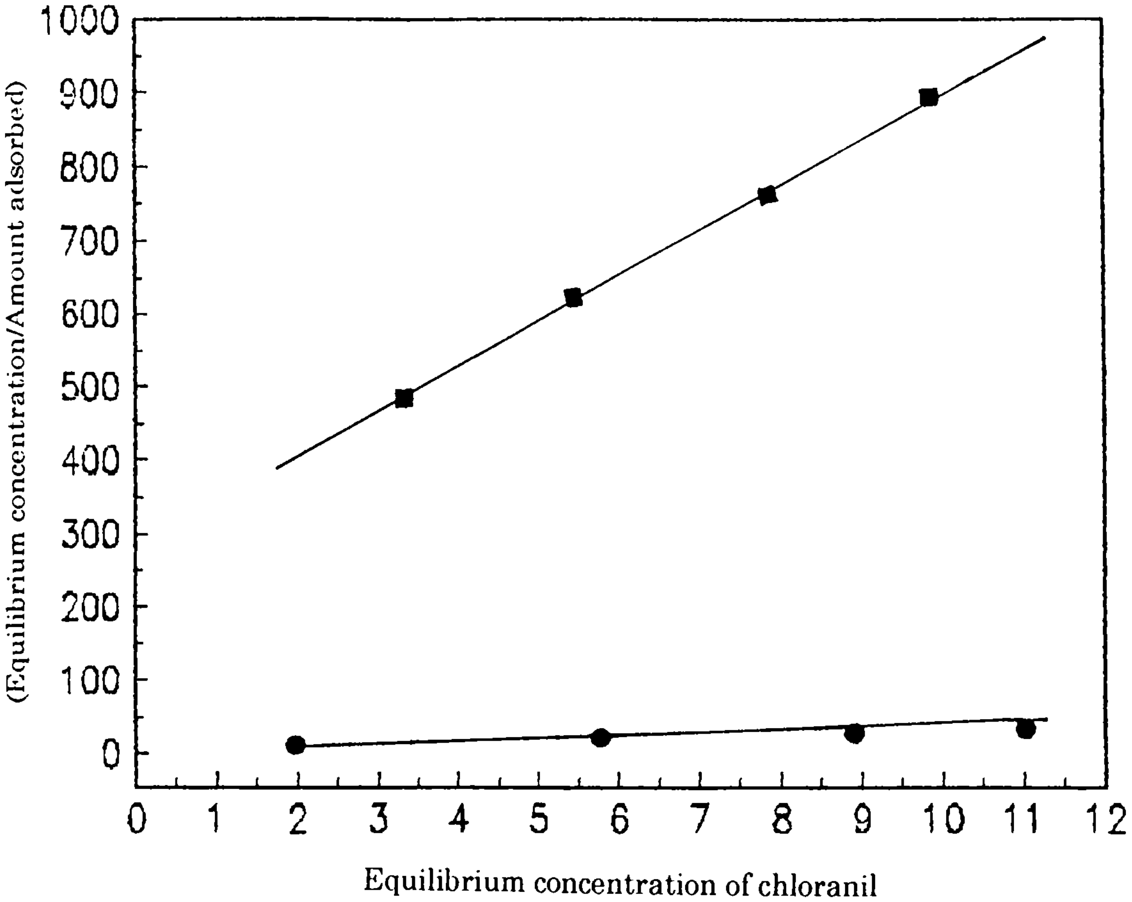


Figure 4.4: Langmuir adsorption isotherms of TCNQ adsorbed on zirconia and sulfated zirconia at different activation temperatures (°C)

◣	ZrO_2 300	●	SO_4^{2-}/ZrO_2 300
■	ZrO_2 500	◆	SO_4^{2-}/ZrO_2 500
▼	ZrO_2 700	▲	SO_4^{2-}/ZrO_2 700



(Equilibrium concentration in 10^{-3} mol dm^{-3} and amount adsorbed in 10^{-5} mol m^{-2})

Figure 4.5: Linear form of Langmuir isotherm obtained for adsorption of chloranil on zirconia and sulfated zirconia

● ZrO_2 ■ SO_4^{2-}/ZrO_2

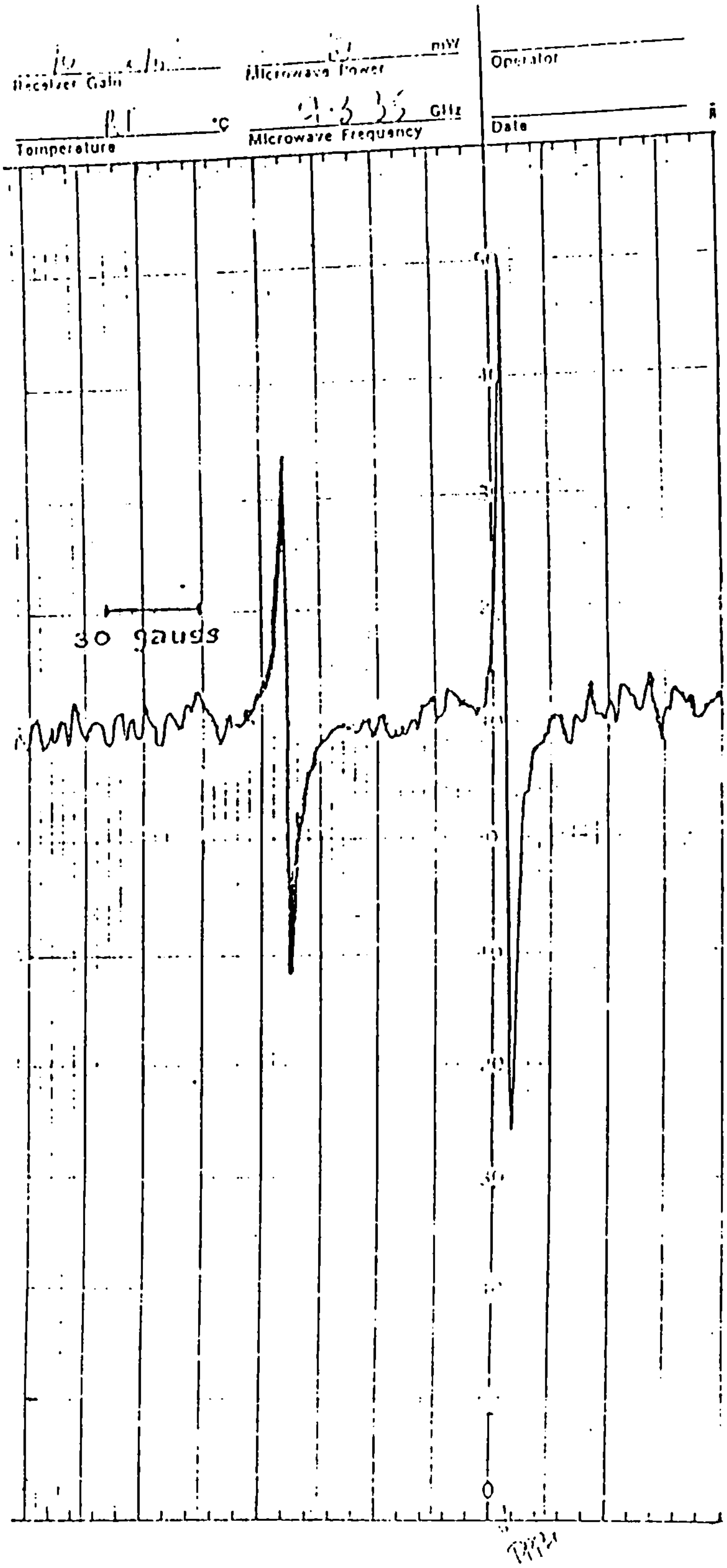


Figure 4.6: ESR spectrum obtained from the adsorption of TCNQ on zirconia

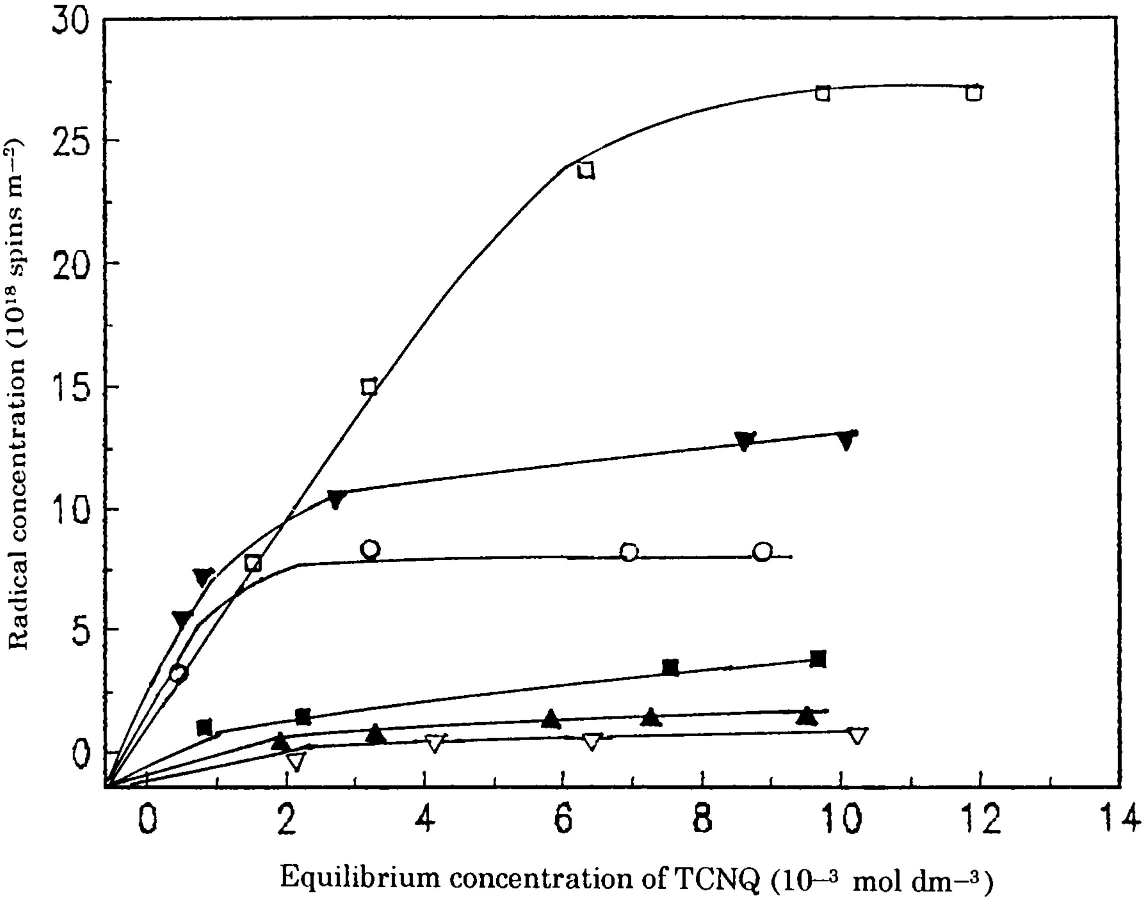


Figure 4.7: Radical concentration of TCNQ vs. its equilibrium concentration on zirconia and sulfated zirconia at different activation temperatures (^{o}C)

○	ZrO_2 300	■	SO_4^{2-}/ZrO_2 300
□	ZrO_2 500	▲	SO_4^{2-}/ZrO_2 500
▼	ZrO_2 700	▽	SO_4^{2-}/ZrO_2 700

The samples coloured by TCNQ adsorption gave an unresolved esr spectra with a g value of 2.003. These spectra have been identified as due to TCNQ anion radicals [23]. The coloured samples obtained by the adsorption of chloranil gave an unresolved esr spectra with a g value of 2.011 [24].

Table 4.7: Limiting radical concentration of electron acceptors adsorbed on zirconia and sulfated zirconia at different activation temperatures.

Catalyst	Activation temp. (°C)	Limiting radical concentration (10^{18} spins m^{-2})	
		Chloranil	TCNQ
ZrO_2	300	0.34	8.11
ZrO_2	500	1.21	26.72
ZrO_2	700	0.54	12.90
SO_4^{2-}/ZrO_2	300	0.08	3.84
SO_4^{2-}/ZrO_2	500	0.03	1.48
SO_4^{2-}/ZrO_2	700	0.02	0.74

In order to study the nature of interaction during adsorption electronic spectra of these samples were measured. The spectrum gave bands appearing at 400 nm corresponding to physically adsorbed state of neutral TCNQ which has an adsorption band at 395 nm [25] and near 600 nm corresponding to the dimeric TCNQ radical which adsorb at 643 nm [26]. In the case of chloranil, a broad band extending up to 700 nm was observed. It is in agreement with the reported results [27]. Figure 4.8 shows the reflectance spectrum.

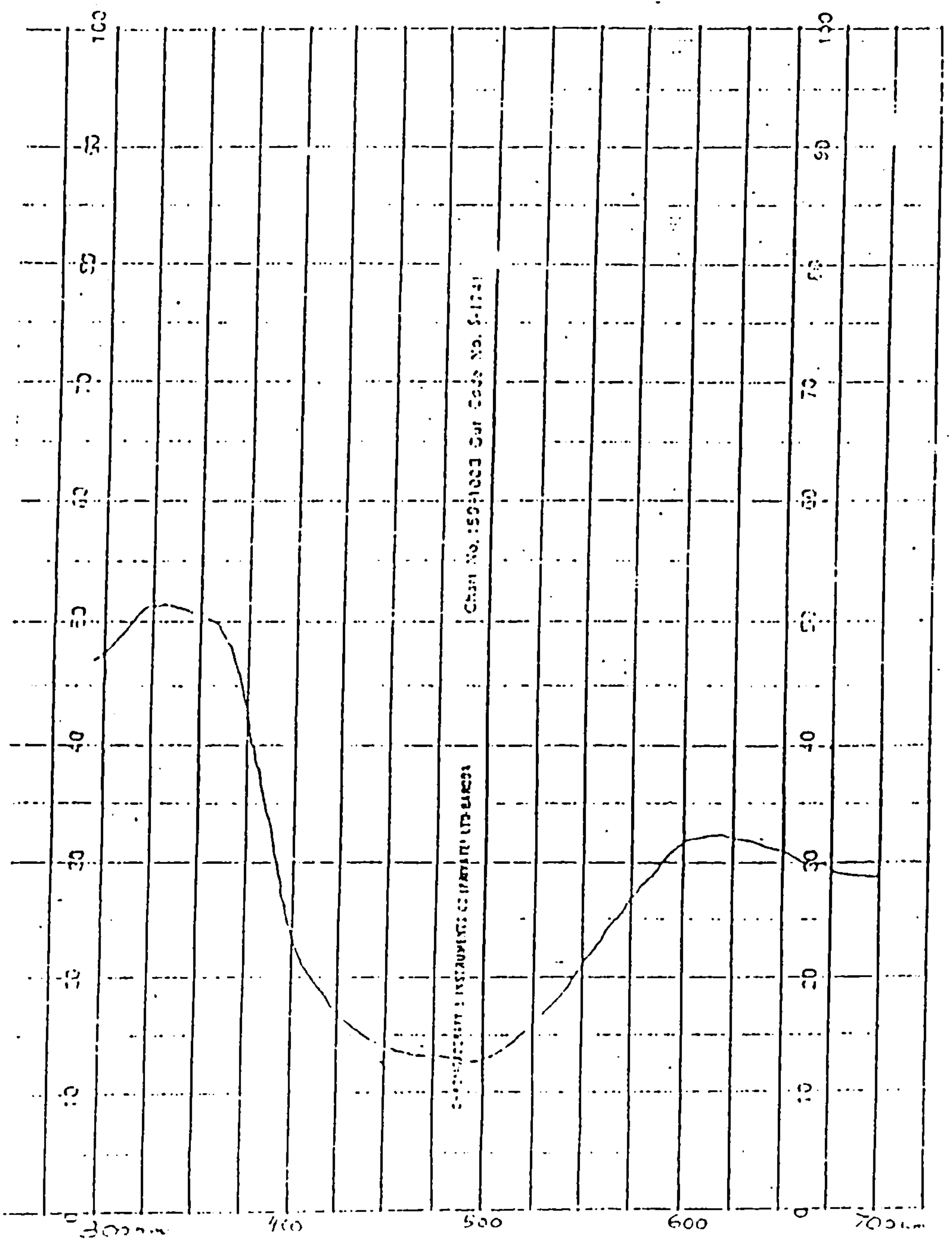


Figure 4.8: Reflection spectrum obtained from the adsorption ofTCNQ on zirconia

The limiting radical concentration of electron acceptors on the surface is a measure of the number of electron donor sites on the surface. The electron donor strength of a metal oxide surface can be defined as the conversion ratio of an electron acceptor adsorbed on the surface into its anion radical. The electron donocity depend upon the electron affinity of the electron acceptors adsorbed. The amount of electron acceptors adsorbed or the radical concentrations on the surface increased with increasing electron affinity of the electron acceptor.

TCNQ can form anion radicals even at weak donor sites. But very weak electron acceptors like MDNB and PDNB are capable of forming anion radicals only at strong electron donor sites. Hence the limiting radical concentration of the weak electron acceptor is a measure of the number of stronger donor sites on the surface and that for a strong electron acceptor is a measure of the total number of both weak and strong donor sites on the surface. It was found that the limiting amount and limiting radical concentration of electron acceptors adsorbed decreases with decreasing electron affinity values for both oxides. Thus the electron donor strength can be expressed as the limiting electron affinity value at which free anion radical formation is not observed on the surface. The limit of electron transfer in terms of electron affinity of the acceptors is between 1.77 and 2.40 for ZrO_2 and SO_4^{2-}/ZrO_2.

From the data it can be observed that the electron donor property of both zirconia and sulfated zirconia decreases after 500°C. This may be due to the change in crystallinity from amorphous to monoclinic form at about 500°C and is confirmed by DSC experiment [28]. In the case of sulfated zirconia, there is a sharp decrease in electron donocity compared to the unmodified ones. In general, two types of sites are responsible for the electron donocity of metal oxides. One of these is electron trapped in intrinsic defect sites and the other is surface hydroxyl groups [29]. Surface O^{2-} can also act as electron donor sites at high temperature. The decrease in electron donocity on sulfation may be due to the conversion of some of the basic sites to acidic sites.

Navarrete and co-workers [30] observed that sulfation is an anion exchange mechanism between OH^- ions and SO_4^{2-} ions. This explains why electron donocity decreases upon sulfation at low temperature. As temperature increases the number of OH groups decreases and desorption of water molecules from adjacent sites occur. But at high temperature, there is no OH^- for exchanging with SO_4^{2-} ions. The variation of limiting amount of electron acceptor adsorbed with temperature is given in Figure 4.9.

4.3.3 Catalytic activity

4.3.3.1 Esterification of Acetic Acid using 1-Butanol

Esterification reaction is a typical acid catalyzed reaction. The heterogeneous catalysis for esterification of carboxylic acids have been

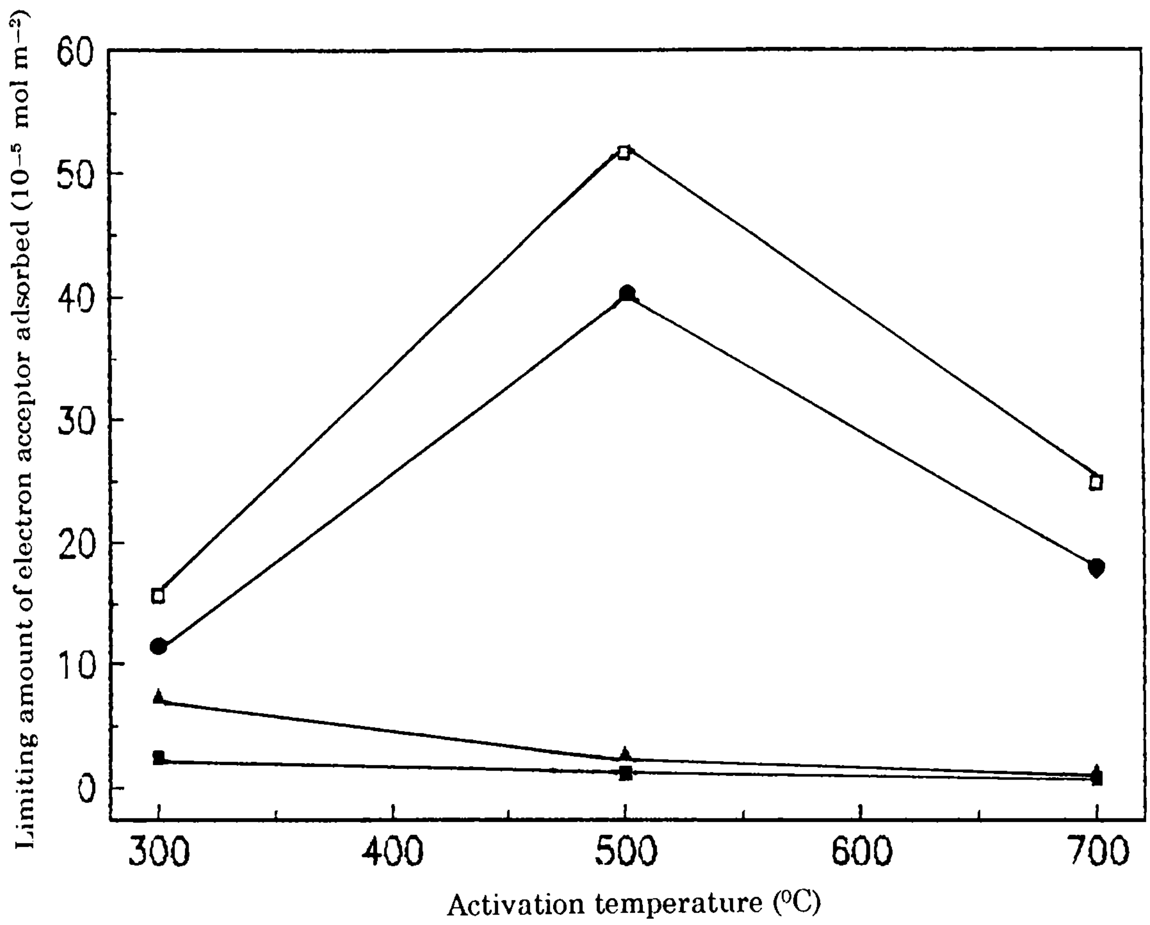


Figure 4.9: Limiting amount of electron acceptor adsorbed as a function of activation temperature

●	ZrO_2 Chloranil	■	SO_4^{2-}/ZrO_2 Chloranil
□	ZrO_2 TCNQ	▲	SO_4^{2-}/ZrO_2 TCNQ

reported [31]. To evaluate the acidity of acid sites, the esterification of acetic acid with n-butanol has been selected as a test reaction. The results for esterification reaction are given in Table 4.8. From the data it is clear that sulfated zirconia catalyzes the esterification more effectively than the unmodified ones. The higher catalytic activity of the modified catalyst may be accounted for by the greater acidity and higher acid strength of sulfated zirconia as compared with the unmodified catalyst.

Table 4.8 Catalytic activity for esterification of acetic acid using n–butanol using zirconia and sulfated zirconia at different activation temperatures.

Catalyst	Activation temperature (°C)	Percentage conversion	Rate constant (10^{-7} s^{-1} m^{-2})
ZrO_2	300	46.51	2.29
ZrO_2	500	44.33	5.23
ZrO_2	700	72.45	14.47
SO_4^{2-}/ ZrO_2	300	79.34	6.07
SO_4^{2-}/ ZrO_2	500	98.99	13.23
SO_4^{2-}/ ZrO_2	700	99.17	32.70

As temperature increases, the activity for esterification increases for both ZrO_2 and SO_4^{2-}/ZrO_2. This is in accordance with the acid-base properties. The variation of catalytic activity for esterification with temperature is given in Figure 4.10.

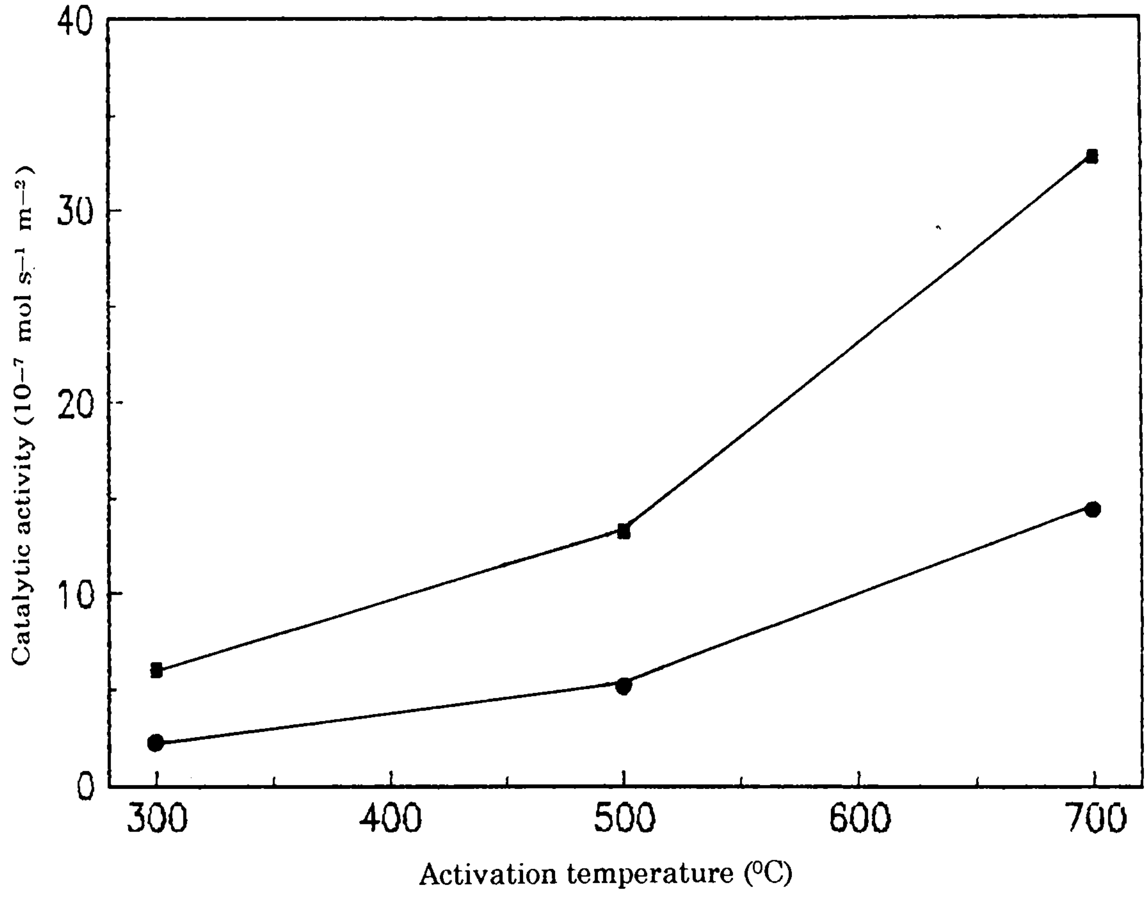


Figure 4.10: Catalytic activity for esterification as a function of activation temperature

● ZrO_2 ■ SO_4^{2-}/ZrO_2

ZrO_2 has been recognized as a refractory oxide, which possess both acidic and basic sites. Due to the presence of acidic sites, zirconia catalyzes the esterification reaction even without modification with sulfate ion. The increase in activity on sulfate modification may be attributed to the increase in both Lewis and Bronsted acidic sites. At high temperature there is not only Lewis acidic sites but also acidic sites generated due to change in crystallinity.

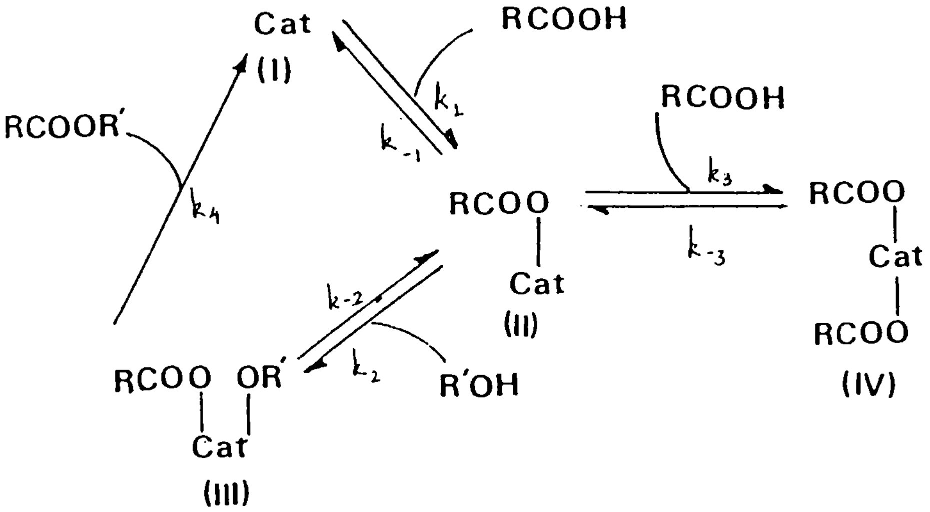
The mechanism of esterification reaction is given in Scheme 1 [32]. The reaction follows first order kinetics. The rate determining step is the step subsequent to the adsorption of carboxylic acid and alcohol on the surface. The kinetic results shows that the last step constitute the rate determining step.

4.3.3.2 Reduction of Cyclohexanone in Isopropanol

The data are given in Table 4.9.

Table 4.9: Catalytic activity for reduction of cyclohexanone in isopropanol using zirconia and sulfated zirconia at different activation temperatures

Catalyst	Activation temperature (^0C)	Percentage conversion	Catalytic activity 10^{-7} $m^{-2}s^{-1}$
ZrO_2	300	72.92	2.39
ZrO_2	500	56.60	3.72
ZrO_2	700	27.63	1.79
SO_4^{2-}/ZrO_2	300	29.71	0.67
SO_4^{2-}/ZrO_2	500	29.90	0.51
SO_4^{2-}/ZrO_2	700	12.93	0.47

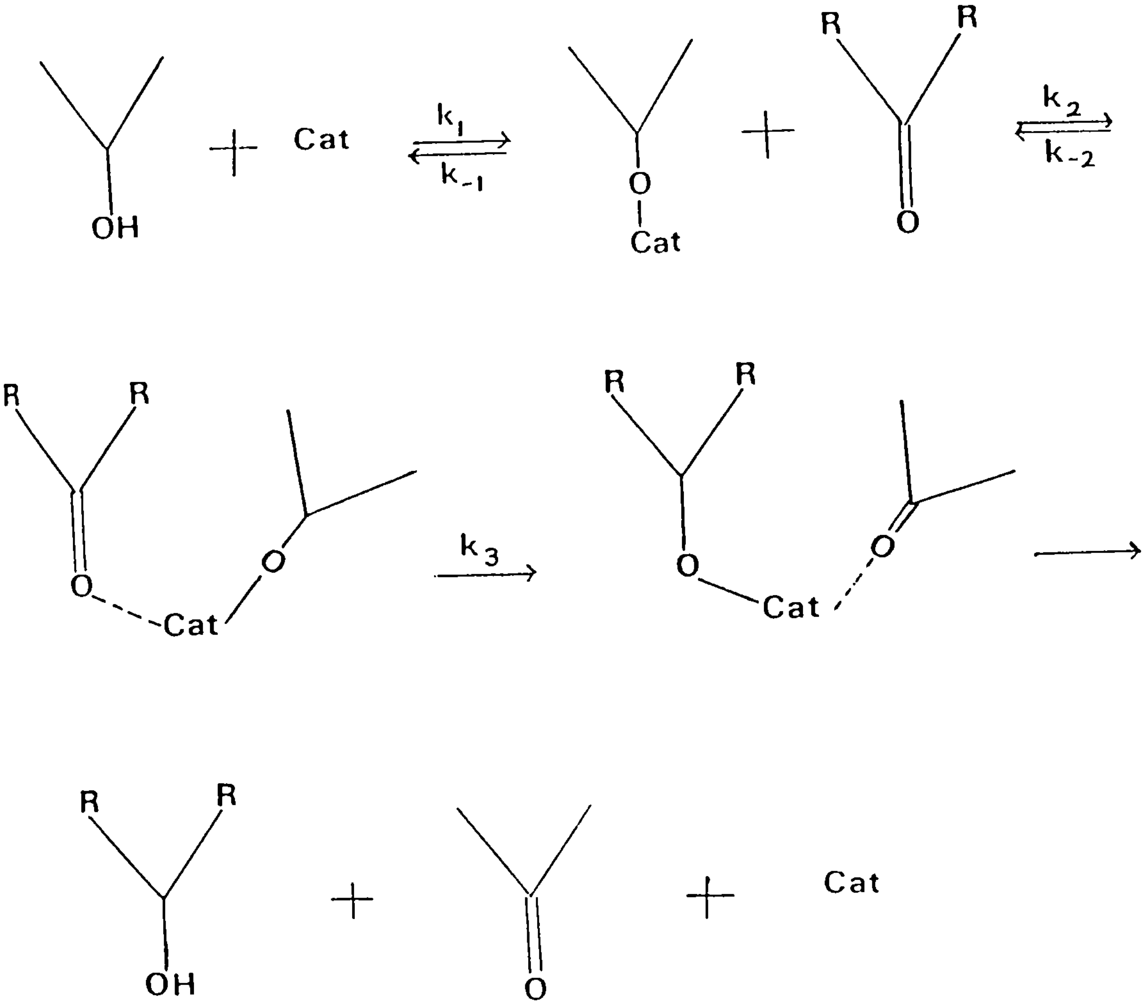

Cat
(I)
RCOOH
k_1
k_{-1}
RCOOR′
k_4
RCOOH
k_3
k_{-3}
RCOO
Cat
(II)
RCOO
Cat
RCOO
(IV)
k_{-2}
k_2
R′OH
RCOO OR′
Cat
(III)

Scheme 1

The reaction is analogous to the well known MPV reduction. The reaction shows a first order kinetics with respect to the ketone, isopropanol and the catalyst. Kibby *et al.* [33] proposed a mechanism for the heterogeneous catalysis, which is similar to the MPV reduction. Shibagaki *et al.* [34] have also reported a reaction mechanism for the reduction of cyclohexanone over ZrO_2 which follows the conventional mechanism of MPV reduction. An observation of kinetic isotopic effect suggested that a step of hydride ion transfer from adsorbed isopropanol to the adsorbed carbonyl group constitute the rate determining step. The catalytic activity can be rationalized in terms of the mechanism (Scheme 2) proposed by Shibagaki *et al.* for reduction. k_3 is the rate determining step. That is the step subsequent to the adsorption of 2-propanol and carbonyl compound on the catalyst. The mechanism of the reaction involves the hydride ion transfer from alcohol to the carbonyl carbon of the ketone. Basic sites favour the hydride transfer. The activity parallels with the basicity of the oxides.

From the data it is clear that unmodified zirconia catalyzes the reduction reaction more effectively than the modified ones. For zirconia as temperature increases, the number of basic sites increases upto 500°C and then decreases. The catalytic activity for reduction also follows the same pattern.

In the case of sulfated zirconia, as temperature increases, the electron donocity decreases ie., basicity decreases due to the conversion of basic sites to acidic sites. IR spectroscopic studies of the H_2 and CH_4 adsorption, probing



Scheme 2

Lewis acid-base pair polarizations, reveal that zirconia on sulfation reduces its Lewis basicity which is in good agreement with the experimental results. Catalytic activity also follows the same pattern. The variation of catalytic activity with activation temperature is given in Figure 4.11.

The electron donor properties of the oxides are discussed in Section 4.2. The decrease in activity for reduction upon modification with sulfate ions is due to the generation of new and strong acid sites. The formation of acid sites have been confirmed by titration method (see section 4.1). For ZrO_2 and SO_4^{2-}/ZrO_2, the highest activity was found at 300°C.

4.3.3.3 Oxidation of Cyclohexanol with Benzophenone

The amphoteric character of alcohol permits their interaction with the acids and bases. The ability of oxide catalysts to dehydrogenation activity has also been reported.

The oxidation of cyclohexanol over metal oxides is analogous to Oppenauer oxidation, where alcohols oxidized using metal alcoxides in presence of hydrogen acceptor. This is an example of hydrogen transfer reaction, which is the reverse of MPV reduction. Hence the same mechanism (Scheme 2) has been suggested for oxidation of alcohols. Benzophenone is used as the hydrogen acceptor. The data are given in Table 4.10.

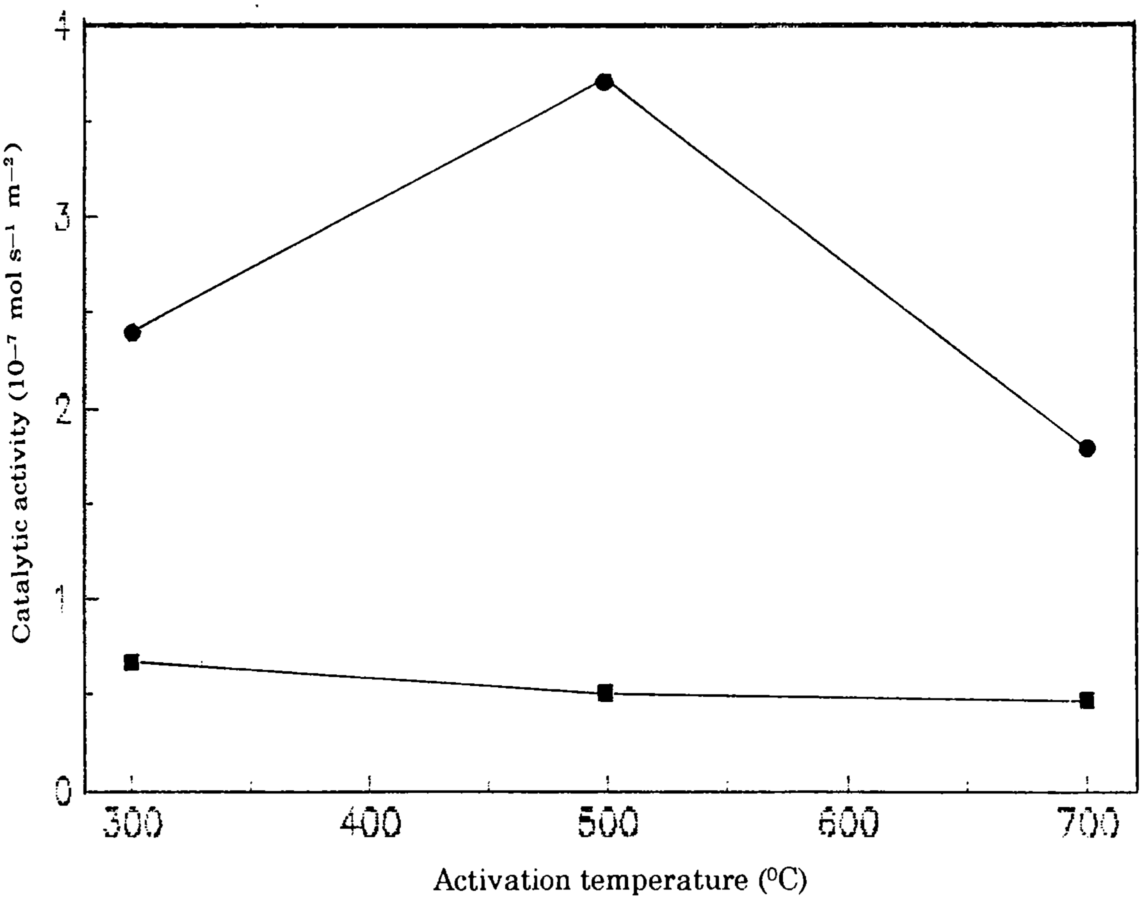


Figure 4.11: Catalytic activity for reduction as a function of activation temperature

● ZrO_2 ■ SO_4^{2-}/ZrO_2

Table 4.10: Catalytic activity for oxidation of cyclohexanol with benzophenone using zirconia and sulfated zirconia at different activation temperatures

Catalyst	Activation temperature (°C)	Percentage conversion	Catalytic activity $10^{-6}\,m^{-2}\,s^{-1}$
ZrO_2	300	68.42	1.05
ZrO_2	500	66.98	2.47
ZrO_2	700	70.88	3.43
SO_4^{2-}/ZrO_2	300	84.42	1.77
SO_4^{2-}/ZrO_2	500	99.98	6.13
SO_4^{2-}/ZrO_2	700	99.95	12.96

The activity is reported as the first order rate coefficient for the conversion of cyclohexanol per unit area of the catalyst surface. From the data it was found that, catalytic activity for oxidation increases on modification with sulfate ion. This indicate that presence of acid sites are very significant in determining activity. The presence of acid base sites have been confirmed by titration method. The high activity for oxidation can be attributed to the acid base bifunctional catalysis.

According to Bezouhanove and Echiyoga [35], the ability of the oxide catalysts to dehydrogenation activity has also been related to the existence of basic sites originating from the oxygen in the oxide lattice. Eventhough oxidation is a base catalyzed reaction, the presence of acid sites could be a factor of importance. The increase in catalytic activity of several transition metal oxides for the selective oxidation reactions have been considered in the light of their acid-base properties. High valent incompletely co-ordinated metal ions or anionic vacancies on oxide surface can be considered as acidic sites. A significant influence of the acid-base properties of the transition metal oxides in their selectivity in the oxidation reactions have been reported [36]. It has been reported that the presence of acid sites of moderate strength favour the deep oxidation of acrolien [37].

A surface is said to have oxidizing property if it is able to abstract an electron from a suitable molecule to form the cation radical. A surface is said to have reducing property, if it is capable of donating an electron from a suitable molecule to form the anion radical [38]. That means oxidizing ability is enhanced if the surface become more acidic. Yamaguchi *et al.* [39] reported that the oxidizing property of ZrO_2 is generated by the introduction of sulfate ion. It has also been reported that the co-operation of acid sites with basic sites causes surprisingly high catalytic activity and selectivity. Not only the acid and base strengths but also, their orientation are important for the catalytic activity and selectivity [38].

According to Anthonella Gervasini and Aline Auroux [40], the dehydrogenation is catalyzed by both acid and basic sites through a concerted mechanism.

It has also shown that SZ based catalysts not only have strong acidity but exhibits strong oxidizing ability at elevated temperature [4].

As temperature increases the catalytic activity for oxidation also increases for both ZrO_2 and SO_4^{2-}/ZrO_2 catalysts. The variation of activity with temperature is given in Figure 4.12.

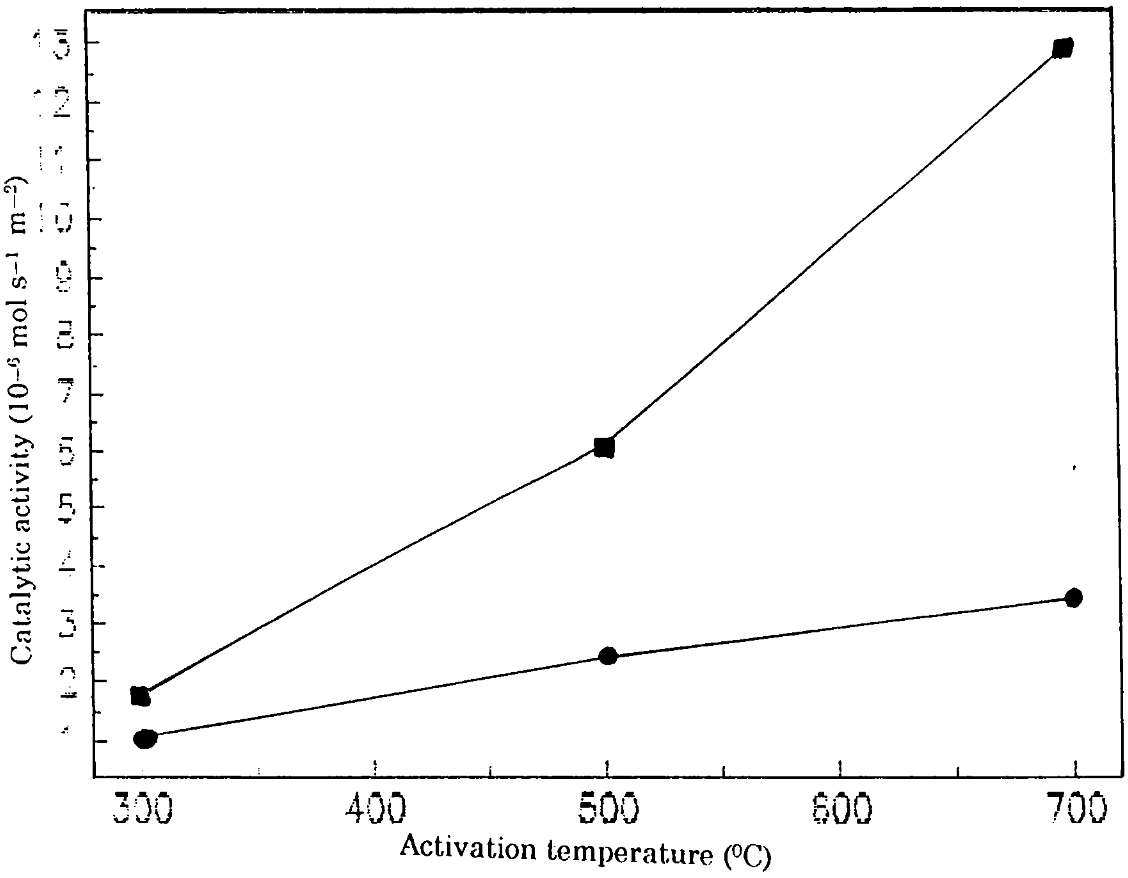


Figure 4.12: Catalytic activity for oxidation as a function of activation temperature

● ZrO_2 ■ SO_4^{2-}/ZrO_2

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Chapter V

ACIDITY/BASICITY, ELECTRON DONOR PROPERTIES AND CATALYTIC ACTIVITY OF SULFATED TITANIA

Chapter V

ACIDITY/BASICITY, ELECTRON DONOR PROPERTIES AND CATALYTIC ACTIVITY OF SULFATED TITANIA

5.1 INTRODUCTION

In the 1970's a TiO_2 based catalyst was first applied commercially in air pollution control equipment and became a subject of many scientific studies. Thermal stability of a TiO_2 support is usually lower than that of γ-Al_2O_3, since sintering is accompanied by the titration of anatase to rutile at about 700^{0}C [1].

Surface chemistry of anatase, in particular acidity, greatly depend on the preparation of the sample, both through the resulting morphology and the presence of surface impurities. Different morphology may result in different types of Lewis acid sites. If pure, anatase does not show Bronsted acidity. Very strong Bronsted acidity is generated by the presence of sulfate impurities [2]. The presence of strong Bronsted acidity on sulfate containing samples was already reported by Morterra *et al.* [3], even if OH group responsible for this behaviour was not identified. It was shown that, for TiO_2, the acidic OH group corresponding to the υOH band at 3690 cm^{-1} seems too high to be assigned to a S-OH group which is expected to absorb near 3600 cm^{-1} [4]. Therefore it was considered by Busca *et al.* that it is due to a perturbed Ti-OH group, whose acidity would be greatly enhanced by the closeness of the sulfate ion [2].

Methanol dehydration was used as a test reaction and CO and pyridine adsorption studied by infrared spectroscopy, allow comparison of the acidity of pure and sulfated metal oxides such as ZrO_2, TiO_2–anatase, TiO_2–rutile and Al_2O_3. It was found that sulfation enhances the strength of the weakest Lewis acid sites but poisons the strongest [5].

The strength and distribution of electron donor sites on TiO_2 was studied by the adsorption of TCNQ, 2,5-dichloro-p-benzoquinone (DCQ), PDNB and MDNB [6,7]. But the electron donor property of sulfate modified TiO_2 is not yet reported. We have attempted to study the electron donor property of sulfated titania. The influence of sulfation on basic sites can be understood from the studies on the electron donating properties.

Esterification of acetic acid using n-butanol, reduction of cyclohexanone in 2-propanol and oxidation of cyclohexanol with benzophenone are the reactions selected for determining catalytic activity.

5.2 EXPERIMENTAL

Titanium dioxide (Rutile form) from s-d Fine Chemicals Ltd. was used as such. Sulfation was carried out by impregnation with ammonium sulfate solution. The detailed procedure was given in chapter III. The samples activated at different temperatures of 300, 500 and 700°C were used.

The surface areas of the samples were determined by BET method. Results are given in Table 5.1.

Table 5.1: Surface area of titania and sulfated titania at different activation temperatures

Catalyst	Activation temperature (^{o}C)	Surface area $(m^2 g^{-1})$
TiO_2	300	15.05
TiO_2	500	15.62
TiO_2	700	19.29
SO_4^{2-}/TiO_2	300	11.54
SO_4^{2-}/TiO_2	500	11.98
SO_4^{2-}/TiO_2	700	14.80

The acidity/basicity was determined by standard procedure by titrating the solid suspended in benzene against n-butyl amine/trichloroacetic acid for acidity/basicity respectively using a set of Hammett indicators. IR spectra of titania and sulfated titania were taken using a Shimadsu IR-470 spectrophotometer.

The strength and distribution of electron donor sites on the surface of oxides were determined by the adsorption of different electron acceptors from acetonitrile solution.

The catalytic activities of titania and sulfated titania for the oxidation, reduction and esterification reactions are done in liquid phase. The detailed experimental procedure was given in chapter III. The activity is expressed as the first order rate constant for the conversion of reactants per m^2 of the catalyst surface.

5.3 RESULTS AND DISCUSSION

5.3.1 Acidity/basicity

The results of acid-base strength distributions at different activation temperatures are given in Table 5.2. The $H_{0,\,max}$ value obtained at different activation temperatures are given in Table 5.3. The acid-base distribution curves are given in Figure 5.1.

Table 5.2: Acid-base strength distribution of titania and sulfated titania at different activation temperatures

Catalyst	Activation Temp. °C)	Basicity (10^{-3} mmol m^{-2})	Acidity (10^{-3} mmol m^{-2})		
		$H_0 \geq 3.3$	$H_0 \leq 3.3$	$H_0 \leq 4.8$	$H_0 \leq 7.2$
TiO_2	300	0.18	--	0.27	2.53
TiO_2	500	0.22	--	0.17	2.17
TiO_2	700	0.14	--	0.14	1.41
SO_4^{2-}/TiO_2	300	--	0.12	0.47	4.00
SO_4^{2-}/TiO_2	500	--	0.16	0.50	4.05
SO_4^{2-}/TiO_2	700	0.09	--	0.28	2.02

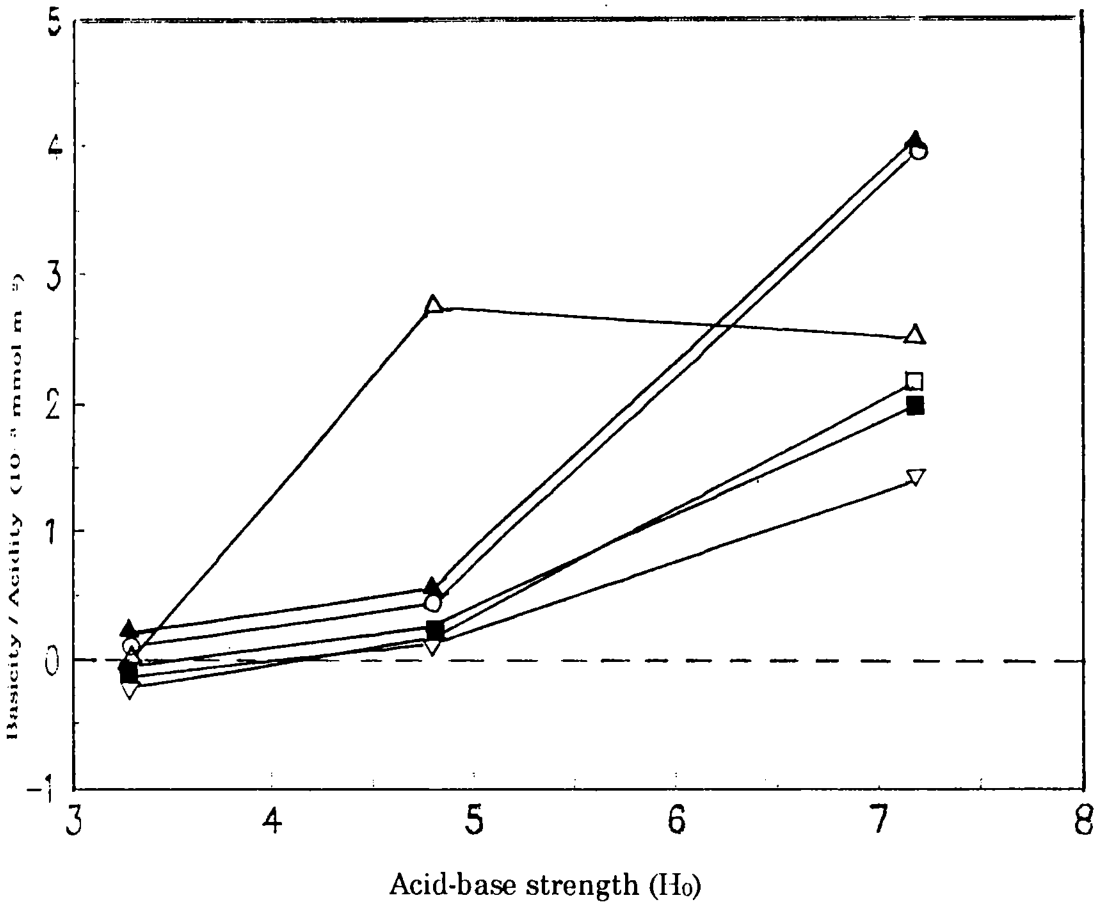


Figure 5.1: Acid-base strength distribution curves for titania and sulfated titania at different activation temperatures (°C)

■	TiO_2 300	○	SO_4^{2-}/TiO_2 300
□	TiO_2 500	▲	SO_4^{2-}/TiO_2 500
▽	TiO_2 700	△	SO_4^{2-}/TiO_2 700

Table 5.3 $H_{0,\,max}$ values of titania and sulfated titania at different activation temperatures

Catalyst	Activation temperature (°C)	$H_{0,\,max}$
TiO_2	300	3.90
TiO_2	500	3.60
TiO_2	700	4.25
SO_4^{2-}/TiO_2	300	--
SO_4^{2-}/TiO_2	500	--
SO_4^{2-}/TiO_2	700	4.00

From the data it is clear that for unmodified titania, the maximum number of acid sites is at $H_0 = 7.2$ and maximum number of basic sites is at $H_0 = 3.3$. This implies the presence of weak acid and base sites on the surface. $H_{0,\,max}$ values shows that activation temperature has not much influence on acidity and basicity of titania.

During sulfation of titania, acidity is generated at H_0 value of 3.3, 4.8 and 7.2. It was reported that surface chemistry of titania, particularly acidity depend on the method of preparation and the amount of impurity present. Eventhough sulfated titania exhibit superacid nature [8], the sample used for our study is not having such superacidic nature, since we have used aq. 0.2 N ammonium sulphate for modification.

IR spectra of sulfated titania after activation at 500^{0}C gave an intense band at 1400 cm^{-1}. This is due to the presence of sulfate ions (Figure 5.2). The behaviour of this band is similar to that already discussed by Morterre *et al.* [9].

According to Jin Yamaguchi and Tanabe [10] the strong acidity on sulfate modification was attributed to the electron withdrawing anion groups, which lead to coordinatively unsaturated and electron-deficient metal centres, that behave as strong Lewis acid sites. Such Lewis acid sites predominate in the absence of water vapour. In presence of water vapour, Lewis sites are converted to Bronsted acid sites with very reactive protons.

Using X-ray photoelectroelectron spectroscopy, (XPS) and infrared, Tanabe and co-workers [11] first studied the structure of acid sites in several sulfated metal oxides (Fe_2O_3, ZrO_2, TiO_2), which exhibit strong acidity or high catalytic activity for acid catalyzed reactions. The XPS data revealed that the oxidation state of sulfur in catalysts showing high activity in acid catalyzed reactions was S^{+6}. Catalysts containing S in a lower oxidation state were inactive [12]. All these sulfated oxides were found to have the same characteristic IR spectrum. The most probable structure of this species was proposed as model 1 in scheme 1 where M denotes Fe, Zr or Ti. Removal of water results in the formation of an organic like sulfate with a stronger

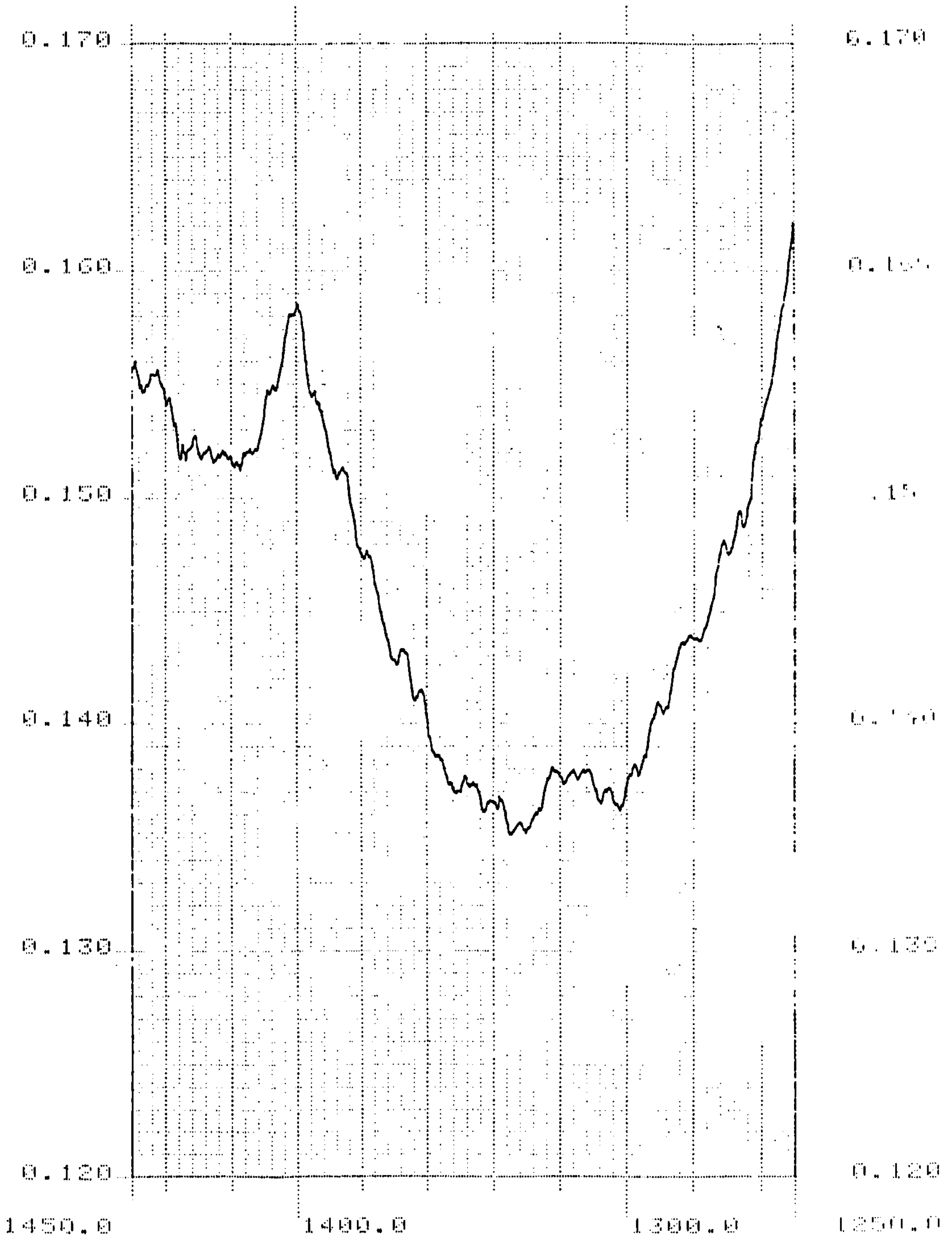
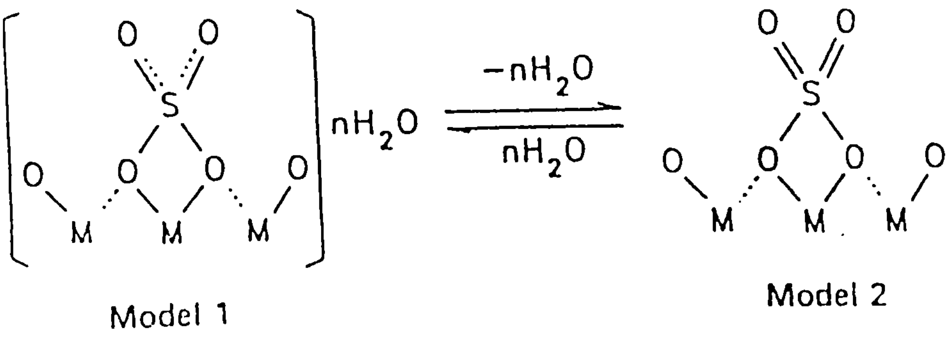


Figure 5.2: IR spectra of sulfated titania activated at 500°C

covalent character to the S=O double bond (model 2). Tanabe *et al.* proposed that the strong acidity is generated by the inductive effect of the S=O double bonds, which increases the electron deficient nature of the metal atom attached to the sulfate group, thus strengthening its Lewis acid character.



Scheme 1

5.3.2 Electron donor properties

The surface electron properties of the titania and sulfated titania have been determined by the adsorption of four electron acceptors with electron affinity values varying from 1.26 to 2.84 eV, on the surface to form corresponding anion radicals. The list of electron acceptors used as given in Table 4.1.

The limiting amount of electron acceptor adsorbed calculated from Langmuir adsorption isotherms (Figures 5.3 and 5.4) is given in Table 5.4. The linear form of Langmuir adsorption isotherm is given in Figure 5.5.

The colour of oxide after chloranil and TCNQ adsorption for titania and sulfated titania are light yellow and pink respectively. The detailed study about the coloured samples (esr spectra and electronic reflection spectra) were already discussed in chapter IV. The radical concentration is calculated from esr spectra.

The plot of radical concentration against equilibrium concentration of electron acceptor in solution also corresponds to the Langmuir adsorption isotherm (Figure 5.6). From such plots, the limiting radical concentration of the EA adsorbed can also be estimated. The data given in Table 5.5.

Table 5.4: Limiting amount of electron acceptor adsorbed on TiO_2 and SO_4^{-2} / TiO_2 at different activation temperatures

Catalyst	Activation temp. (°C)	Limiting amount of electron acceptor adsorbed (10^{-5} mol m^{-2})	
		Chloranil	TCNQ
TiO_2	300	5.89	9.34
TiO_2	500	4.75	8.15
TiO_2	700	6.12	10.57
SO_4^{2-}/ TiO_2	300	2.05	2.21
SO_4^{2-}/ TiO_2	500	1.66	1.72
SO_4^{2-}/ TiO_2	700	5.20	10.21

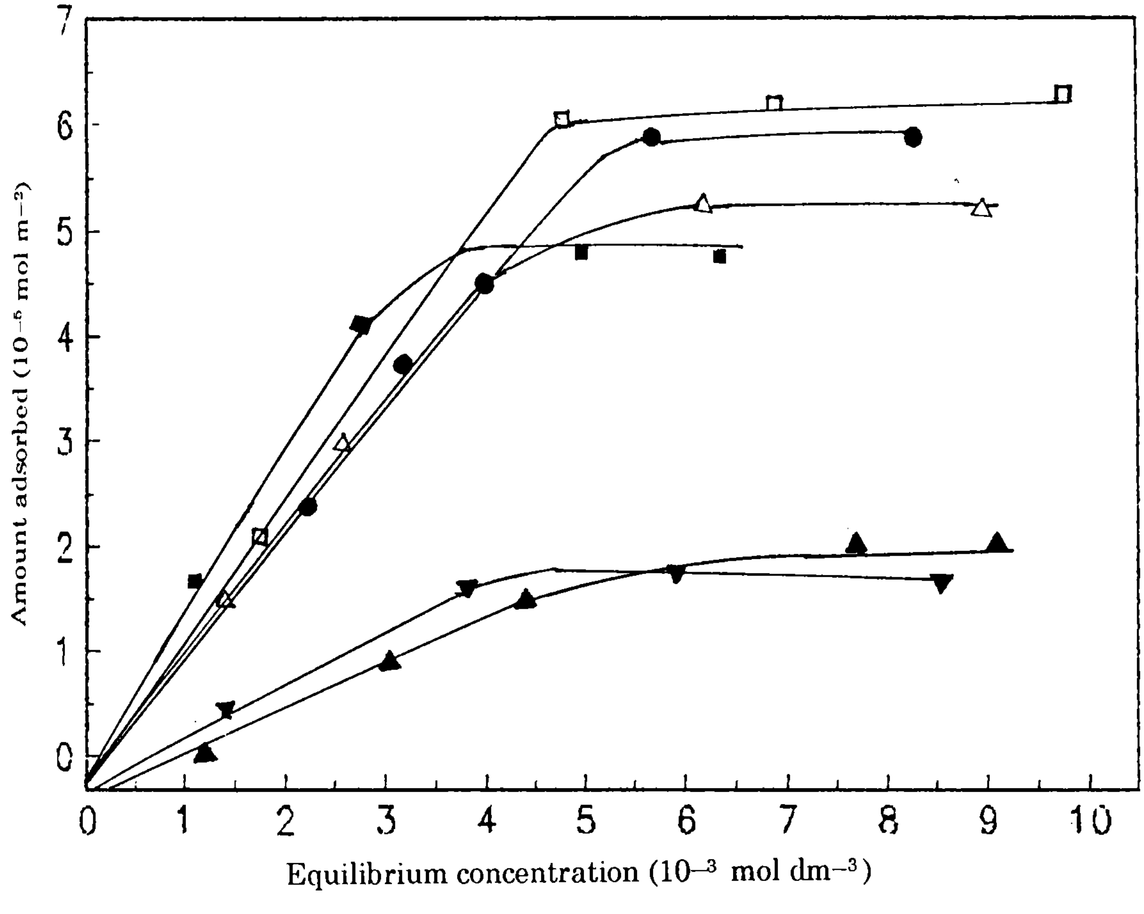


Figure 5.3: Langmuir adsorption isotherms for the adsorption of chloranil on titania and sulfated titania at different activation temperatures (°C)

△	TiO_2 300	▲	SO_4^{2} /TiO_2 300
■	TiO_2 500	▽	SO_4^{2} /TiO_2 500
□	TiO_2 700	●	SO_4^{2-}/TiO_2 700

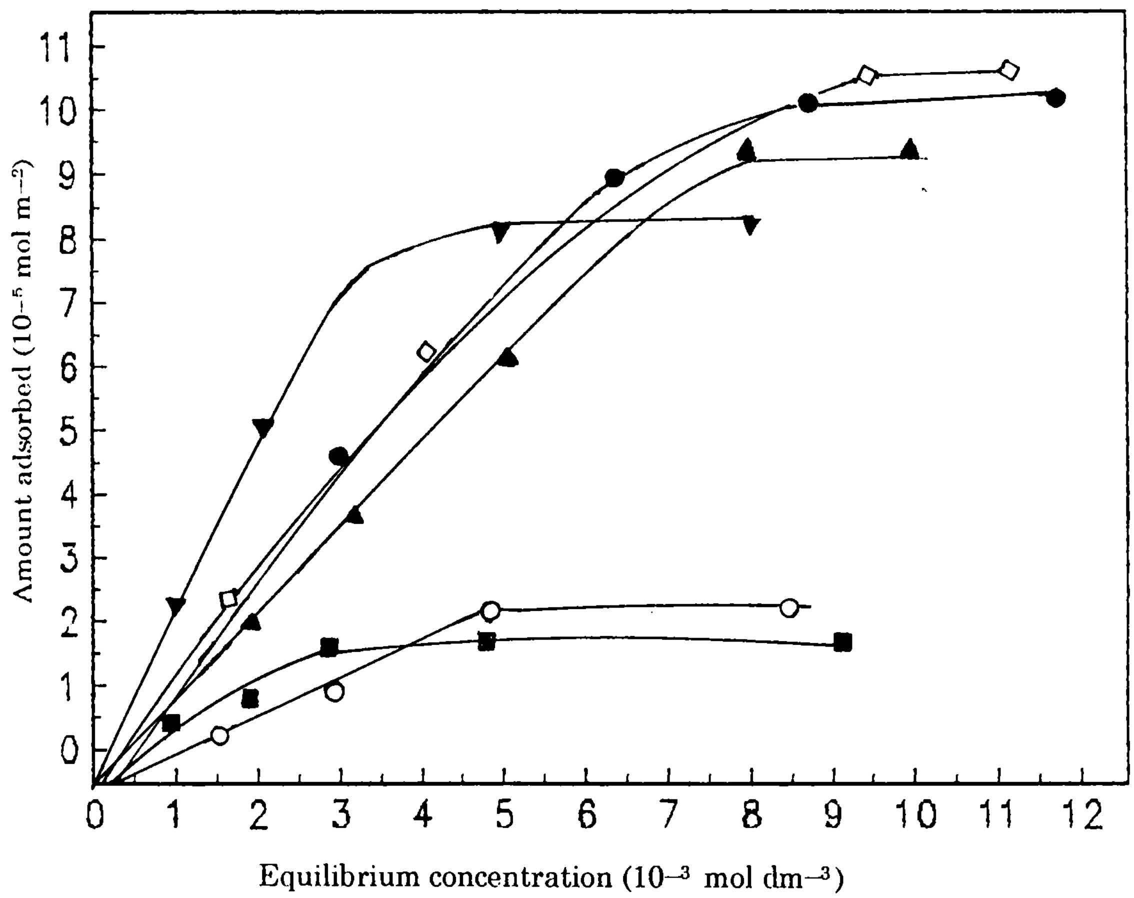


Figure 5.4: Langmuir adsorption isotherms for the adsorption of TCNQ on titania and sulfated titania at different activation temperatures (°C)

▲	TiO_2 300	○	SO_4^{2-}/TiO_2 300
▼	TiO_2 500	■	SO_4^{2-}/TiO_2 500
◇	TiO_2 700	●	SO_4^{2-}/TiO_2 700

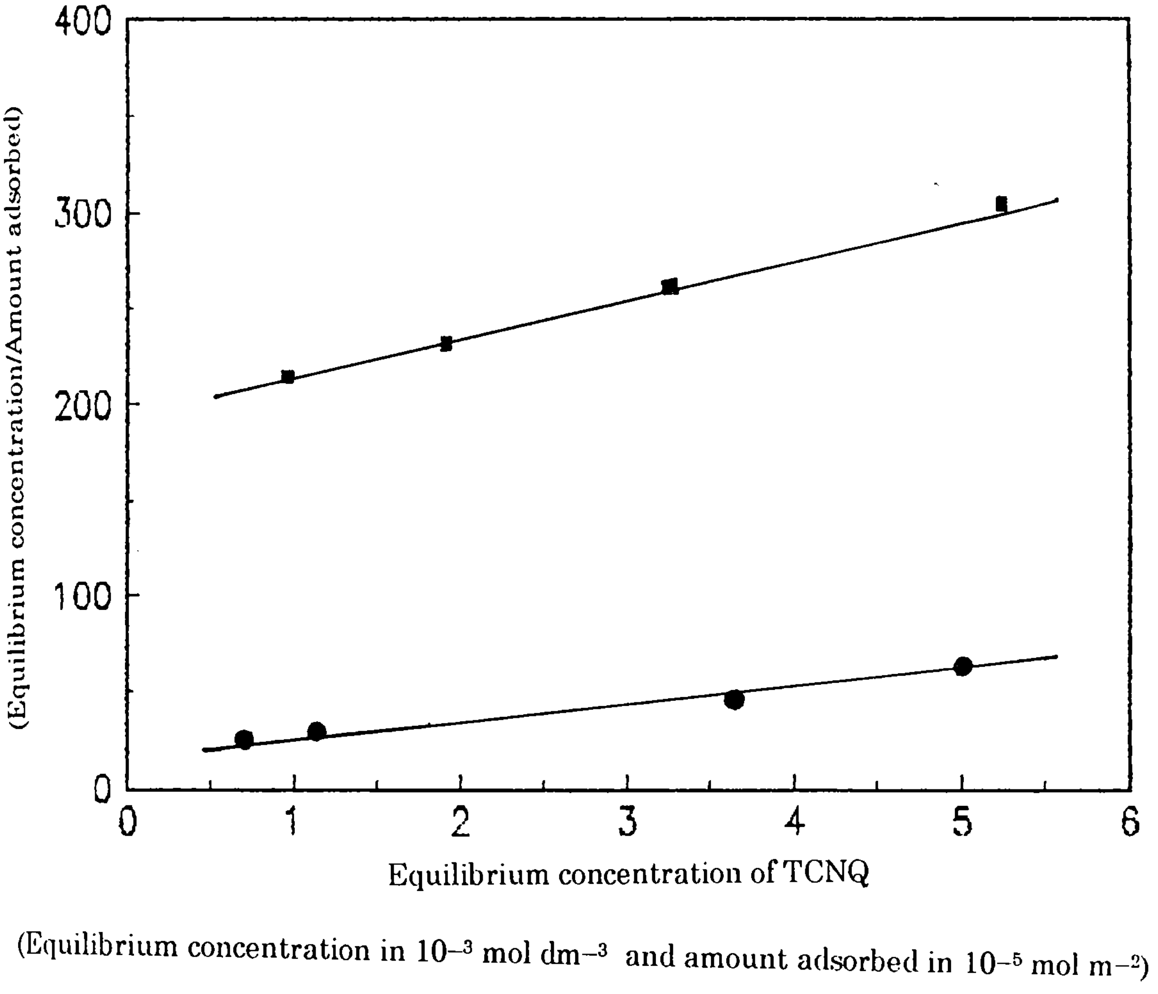


Figure 5.5: Linear form of Langmuir adsorption isotherm obtained for adsorption of TCNQ on titania and sulfated titania

■ TiO_2 ● SO_4^{2-}/TiO_2

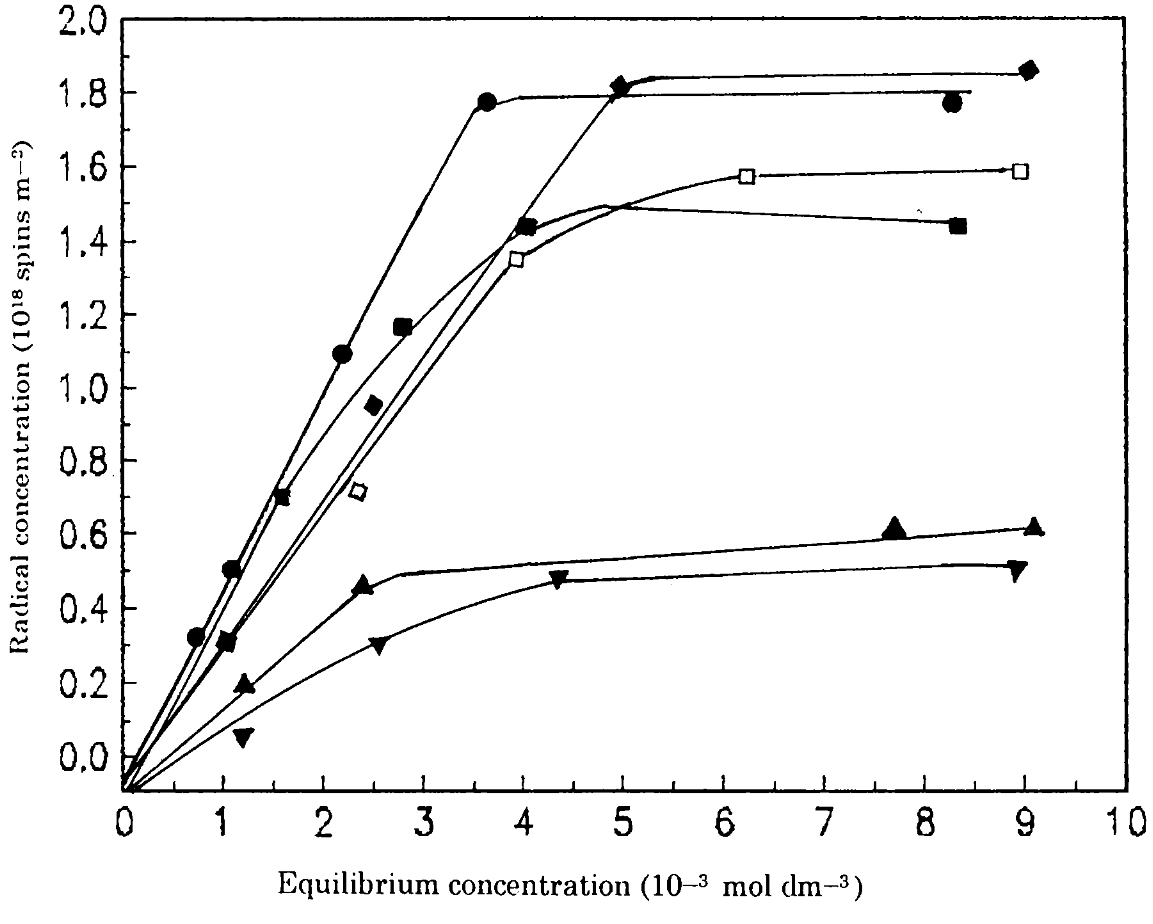


Figure 5.6: Radical concentration of chloranil vs. its equilibrium concentration on titania and sulfated titania at different activation temperatures (°C)

●	TiO_2 300	▲	SO_4^{2-}/TiO_2 300
■	TiO_2 500	▼	SO_4^{2-}/TiO_2 500
◆	TiO_2 700	□	SO_4^{2-}/TiO_2 700

Table 5.5: Limiting radical concentration of electron acceptors adsorbed on TiO_2 and SO_4^{-2} / TiO_2 at different activation temperatures.

Catalyst	Activation temp. (°C)	Limiting radical concentration (10^{18} spins m^{-2})	
		Chloranil	TCNQ
TiO_2	300	0.18	4.82
TiO_2	500	0.14	4.21
TiO_2	700	0.19	5.46
SO_4^{2-}/ TiO_2	300	0.06	1.14
SO_4^{2-}/ TiO_2	500	0.05	0.89
SO_4^{2-}/ TiO_2	700	0.16	5.27

The significance of limiting amount of EA adsorbed and limiting radical concentration are discussed previously in chapter IV. The limit of electron transfer in terms of electron affinity (eV) of the acceptors is between 1.77 and 2.40 for TiO_2 and SO_4^{2-}/ TiO_2.

Metal oxides show electron donor properties because of the presence of two types of sites. One of these is electron trapped in intrinsic defect sites and the other in surface hydroxyl groups. Surface O^{2-} can also act as electron donor sites at high temperature. From the data, in Table 5.4 and 5.5, it is seen that the electron donocity of both titania and sulfated titania decreases at 500°C, and then increases on heating to 700°C. The increase in electron donocity at 700°C is due to the electrons trapped in intrinsic defect sites. Surface O^{2-} can also be taken into account for the basicity. The decrease in the limiting amounts of EA adsorbed at 500°C is due to the decrease in number of hydroxyl groups.

The variation of limiting value of electron acceptor adsorbed with activation temperature is given in Figure 5.7.

On modification with sulfate ion, the electron donor property decreases, implying that some of the basic sites are converted to acidic sites on modification with sulfate ion.

It was reported that the mechanism of sulfation is an anion exchange between SO_4^{2-} and OH^- ions [13] which give an additional proof for the decrease in electron donocity on sulfate modification. The electron donocity of sulfated titania is almost equal to that of unmodified one when the activation temperature was 700°C, which indicate that surface O^{2-} and trapped electrons are responsible for basicity at high temperature. Moreover, there is no OH^- ions for exchange with SO_4^{2-} ion at high temperature.

5.3.3 Catalytic activity

5.3.3.1 Esterification of Acetic Acid using n-Butanol

The mechanism of esterification reaction is described in chapter IV.

The data for esterification of TiO_2 and SO_4^{2-}/TiO_2 are given in Table 5.6. The data indicate that sulfate modified titania catalyzes the esterification

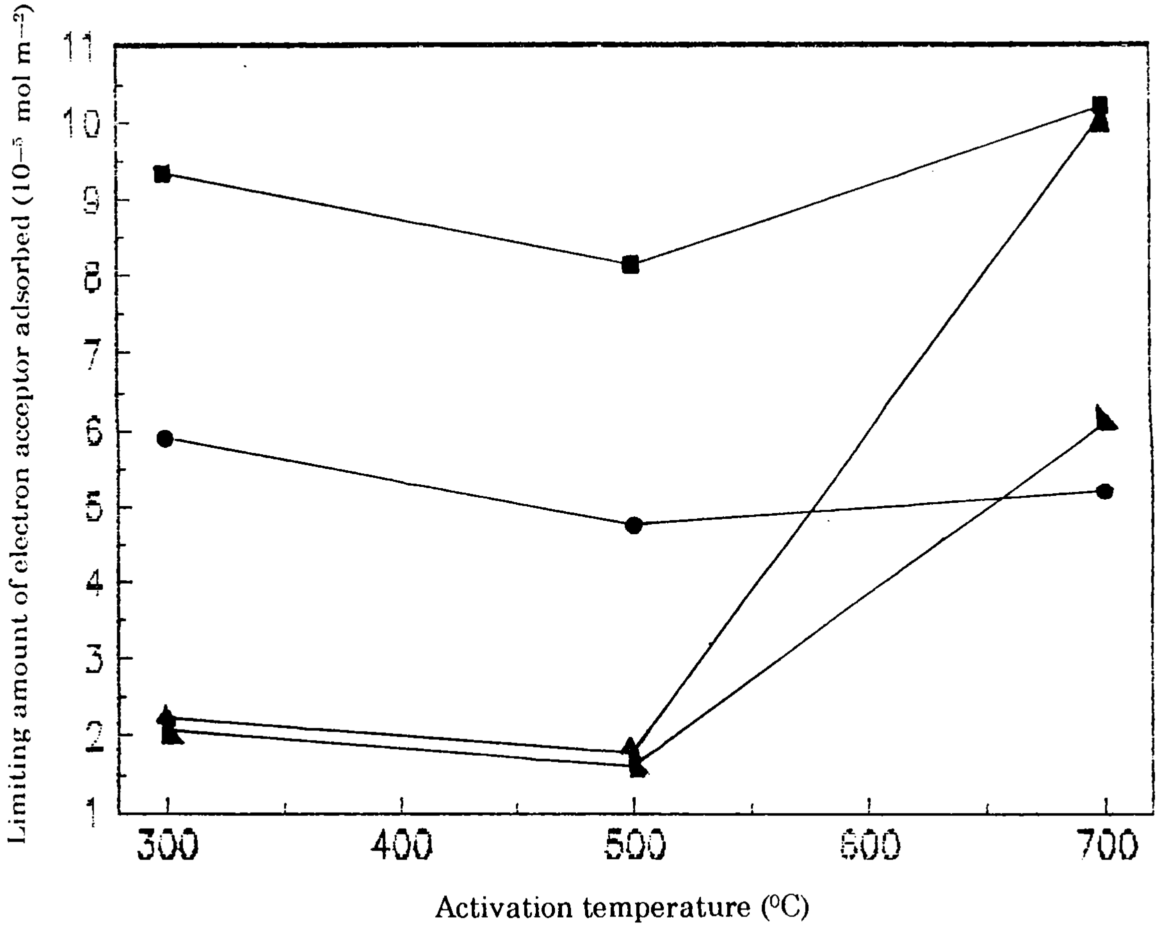


Figure 5.7: Limiting amount of electron acceptor adsorbed as a function of activation temperature

● TiO$_2$ Chloranil
▲ SO$_4^{2-}$/TiO$_2$ Chloranil
■ TiO$_2$ TCNQ
◣ SO$_4^{2-}$/TiO$_2$ TCNQ

reaction more effectively than the unmodified one. The higher the catalytic activity of the modified catalyst may be accounted for by the greater acidity and acid strength as compared with unmodified catalyst. The catalytic activity for these oxides decreases when the activation temperature is 700°C. This is in accordance with the acid base properties. It was reported that after heating TiO_2 at 750°C, the mass of the sample was the same as it was before sulfation, by using McBain Balance. This means that all sulfate had been removed after heating at 700°C [14]. The catalytic activity of both the samples at 700°C is nearly the same, which can also be understood in the same line. At 500°C sulfated titania showed more activity (more than 5 times increase). Esterification reaction parallels with the acid base properties.

Table 5.6: Catalytic activity for esterification of acetic acid using n-butanol at different activation temperatures.

Catalyst	Activation temperature (°C)	Percentage conversion	Rate constant ($10^{-6}\,s^{-1}\,m^{-2}$)
TiO_2	300	64.01	3.77
TiO_2	500	71.30	4.44
TiO_2	700	29.64	1.01
SO_4^{2-}/TiO_2	300	66.35	5.24
SO_4^{2-}/TiO_2	500	99.42	23.9
SO_4^{2-}/TiO_2	700	30.72	1.38

The variation of catalytic activity with activation temperature is given in Figure 5.8.

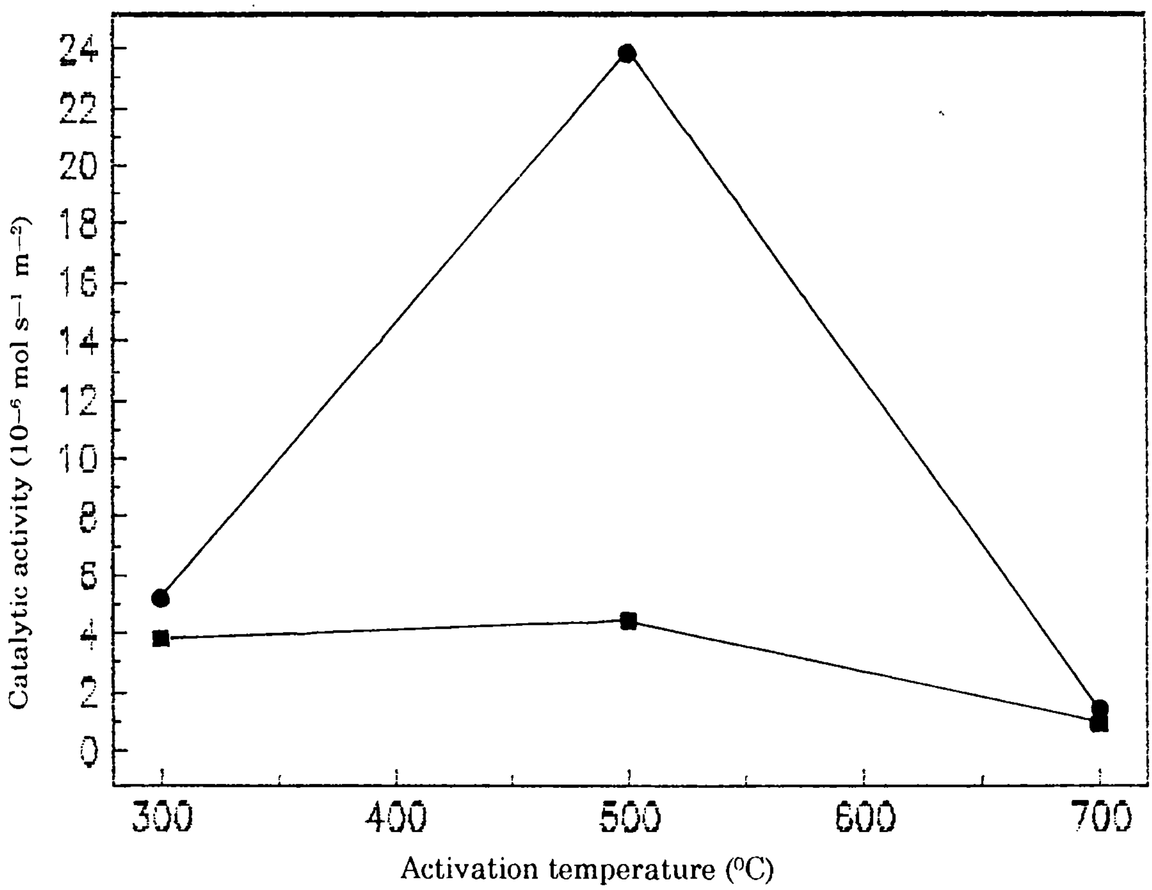


Figure 5.8: Catalytic activity for esterification as a function of activation temperature

■ TiO_2 ● SO_4^{2-}/TiO_2

5.3.3.2 Reduction of Cyclohexanone in Isopropanol

The detailed mechanism for reduction is described in chapter IV. The data given in Table 5.7.

Table 5.7: Catalytic activity for reduction of cyclohexanon in isopropanol using TiO_2 and SO_4^{2-}/TiO_2 at different activation temperatures

Catalyst	Activation temperature (°C)	Percentage conversion	Catalytic activity 10^{-6} m^{-2} s^{-1}
TiO_2	300	70.57	2.26
TiO_2	500	70.02	2.14
TiO_2	700	80.91	2.39
SO_4^{2-}/TiO_2	300	12.67	0.33
SO_4^{2-}/TiO_2	500	0.83	0.02
SO_4^{2-}/TiO_2	700	35.28	0.82

From the data it is clear that reduction proceeds effectively over pure TiO_2 due to its high basicity than sulfated titania. For the reduction reaction to take place, there is the transfer of hydride ion from adsorbed isopropanol to adsorbed carbonyl group. Basic sites favour the hydride transfer. Catalytic activity parallels with the basicity of oxides. The lower catalytic activity of sulfated titania is attributed to the conversion of basic sites to acidic sites on sulfation. The data have been correlated with the surface electron properties (see section 5.3.2). The catalytic activity parallels with the electron donating capacity.

Variation of catalytic activity with activation temperature is given in Figure 5.9. The results are in accordance with the acid base properties.

5.3.3.3 Oxidation of Cyclohexanol using Benzophenone

The data given in Table 5.8. The detailed mechanism is discussed in chapter IV.

Table 5.8: Catalytic activity for oxidation of cyclohexanol with benzophenone using TiO_2 and SO_4^{2-}/TiO_2 at different activation temperatures.

Catalyst	Activation temperature (°C)	Percentage conversion	Rate constant ($10^{-6} s^{-1} m^{-2}$)
TiO_2	300	8.11	0.78
TiO_2	500	16.06	1.56
TiO_2	700	--	--
SO_4^{2-}/TiO_2	300	24.01	3.31
SO_4^{2-}/TiO_2	500	27.97	3.80
SO_4^{2-}/TiO_2	700	1.84	0.17

The mechanism of oxidation is discussed in chapter IV.

The data show that catalytic activity for oxidation increases on modification with sulfate ion. For a catalyst to be active in oxidation reactions, it must participate in the following two processes: (1) Activation of reactant molecules and (2) Activation of O_2 when a catalyst is potent in the activation of oxygen i.e., it has an oxidizing power which depend on two factors; (a) the number of oxidizing sites and (b) mobility of oxygen at a site [15]. TiO_2 was

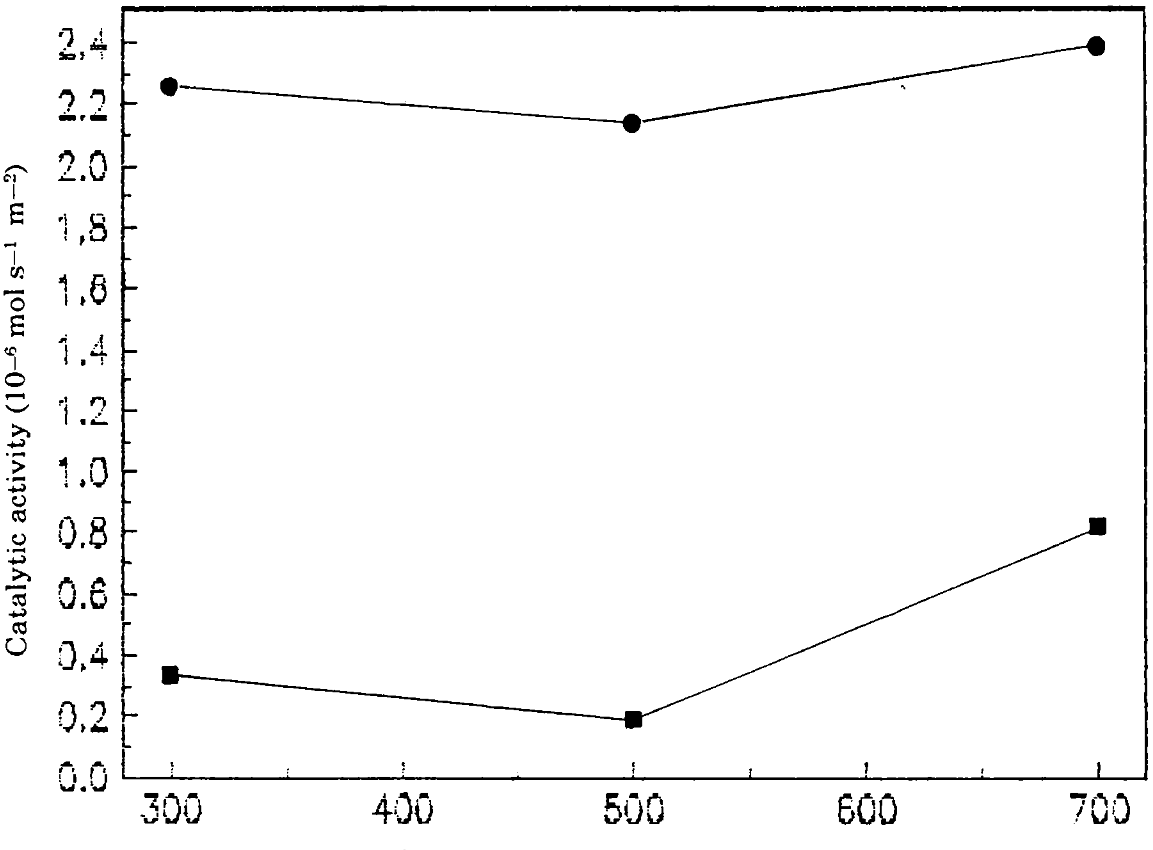


Figure 5.9: Catalytic activity for reduction as a function of activation temperature

● TiO_2 ■ SO_4^{2-}/TiO_2

reported to have only weak acidic property [16]. The higher catalytic activity for oxidation of modified catalyst may be accounted for by the greater acidity and higher acid strength as compared with the unmodified catalyst which is in accordance with the acid-base properties. Explanation was similar to that given in chapter IV. The dehydrogenation is catalyzed by both acidic and basic sites through a concerted mechanism. It has been reported that in the dehydrogenation of isopropanol to acetone, the activity of the catalysts takes place through a concerted mechanism involving both acid and base sites. Also in this case the number and nature of the sites influence mainly the entropic term, but the activation energy is independent of the strength of both the acid and basic sites [17]. Variation of catalytic activity with temperature is given in Figure 5.10.

The pronounced changes in catalytic activity with temperature suggest that the number of the most active sites used for the reaction changes with the activation temperature. The observed effect may be due to one or more of several possible thermally induced phenomenon including crystallographic transformation of residual surface hydroxyl groups or fundamental alterations in the chemical or structural nature of the active sites.

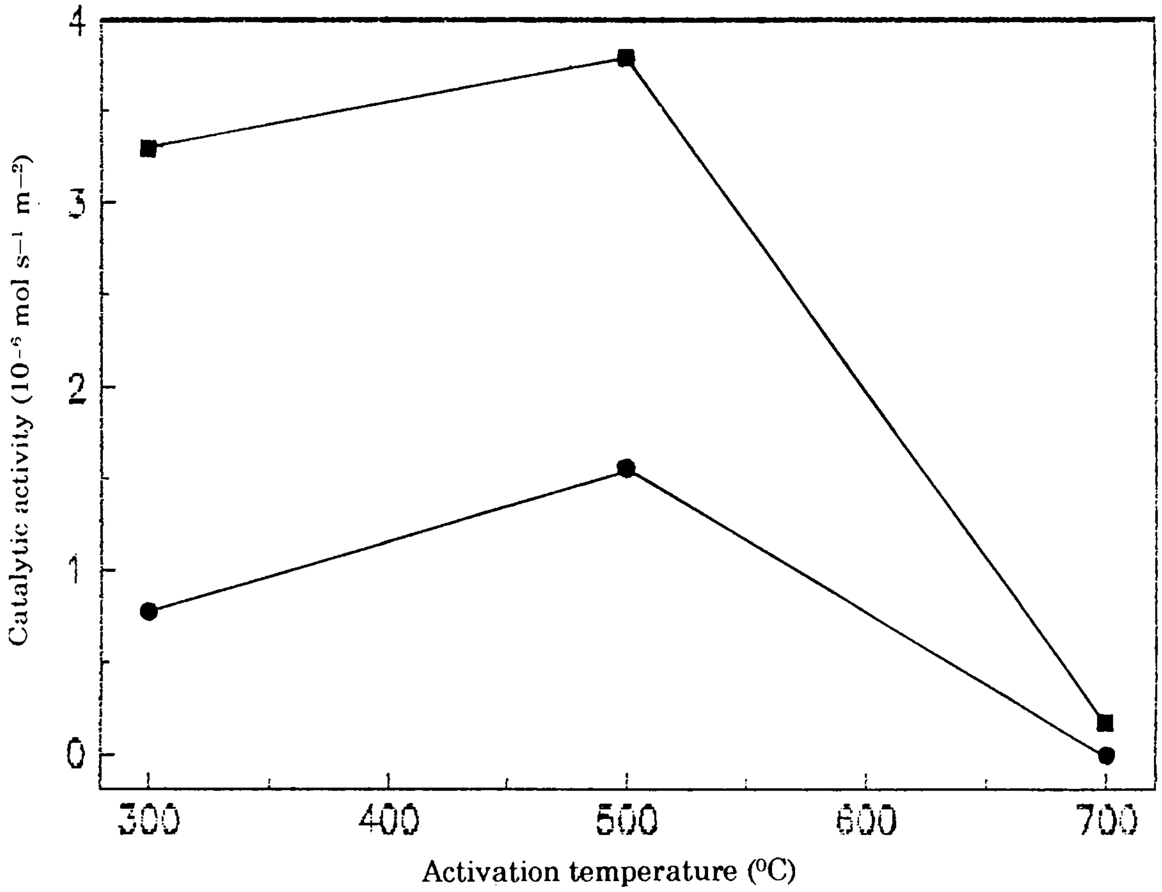


Figure 5.10: Catalytic activity for oxidation as a function of activation temperature

● TiO_2 ■ SO_4^{2-}/TiO_2

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Chapter VI

ACIDITY/BASICITY, ELECTRON DONOR PROPERTIES AND CATALYTIC ACTIVITY OF SULFATED SAMARIA

Chapter VI

ACIDITY/BASICITY, ELECTRON DONOR PROPERTIES AND CATALYTIC ACTIVITY OF SULFATED SAMARIA

6.1 INTRODUCTION

Although the fundamental catalytic and surface properties of alkali, alkaline earth and other basic oxides have been extensively studied [1] equivalent information about the series of basic rare earth oxides is much less. Systematic correlations between surface basicity and catalytic activity among rare earth oxides have been explored to only a limited extent. Hopkins and Taebel have summarized the catalytic activity of rare earths for oxidation, hydrogenation, decomposition and synthesis of organic compounds [2]. McGougu and Houghtow evaluated the effects of paramagnetism, crystal structure and crystal field on catalytic activity of lanthanides for dehydrogenation of cyclohexane [3].

The use of rare earth oxides as promoters or supports in catalytic reactions has grown extensively due to interesting properties encountered in pollution control by catalysis or syngas conversion [4]. In pollution control, the reducibility of some rare earth oxides has been put forward to explain the increase in performance of rare earth modified catalysts [5]. In syngas conversion, both reducibility and basicity of rare earth oxides have been invoked [6].

Nakashima *et al.* [7] investigated the isomerization of butane over samarium oxide and found that rate of reaction was proportional to the concentration of reactants. Osuka *et al.* [8] observed that among rare earth oxides, Sm_2O_3 shows highest activity and selectivity for C_2-hydrocarbons in oxidative coupling of methane. It was pointed out that relative activities of rare earth metal oxides parallels their basicities [9].

Though a number of studies have so far been reported about sulfate modified metal oxides no studies have been made to gain information about the acidic and catalytic properties of sulfate modified rare earth oxides. We have studied the influence of sulfate ion on the acidity/basicity of samarium oxide. We have attempted to study the electron donor properties of samaria. The purpose of this study is to find out whether the increase in acidity due to sulfation can be at the expense of basic sites already present on the surface or it can be due to the generation of new acidic sites.

Esterification of acetic acid using n-butanol, reduction of cyclohexanone in 2–propanol and oxidation of cyclohexanol with benzophenone are the reactions selected for determining catalytic activity.

6.2 EXPERIMENTAL

Samarium oxide was prepared from samarium nitrate by hydroxide method. Sulfation was carried out by impregnation of oxide with ammonium sulfate solution. The detailed procedure was described in chapter III.

The samples activated at different temperatures of 300, 500 and 700°C were used. The surface area of samples were determined by BET method. The data are given in Table 6.1

Table 6.1 Surface area of samaria and sulfated samaria at different activation temperatures

Catalyst	Activation temp. (°C)	Surface area ($m^2\ g^{-1}$)
Sm_2O_3	300	30.40
Sm_2O_3	500	29.13
Sm_2O_3	700	26.16
SO_4^{2-}/Sm_2O_3	300	28.43
SO_4^{2-}/Sm_2O_3	500	27.45
SO_4^{2-}/Sm_2O_3	700	25.91

The acidity/basicity was determined by the standard procedure by titrating the solid suspended in benzene against trichloroacetic acid/n-butyl amine for basicity/acidity respectively using a set of Hammett indicators. The detailed procedure was given in chapter III.

The strength and distribution of electron donor sites on the oxide surface were determined by the adsorption of different electron acceptors from acetonitrile solution, which is a very weak base. The amount of electron acceptor adsorbed was determined by means of UV-vis Spectrophotometry and adsorbed state of electron acceptor was studied by ESR and electronic spectra. The detailed experimental procedures are given in chapter III.

The catalytic activities of samaria and sulfated samaria for the esterification, reduction and oxidation reactions are studied in liquid phase. The descriptive procedures for these reactions are given in chapter III.

6.3 RESULTS AND DISCUSSION

6.3.1 Acidity/basicity

The Hammett indicators used are given in Table 4.2. Among them samaria and sulfated samaria responded only to three indicators. They are dimethyl yellow, methyl red and bromothymol blue.

The results of acid-base strength distribution at different activation temperatures are given in Table 6.2. $H_{0,\ max}$ values obtained at different activation temperatures are given in Table 6.3. The acid base strength distribution curves are given in Figure 6.1.

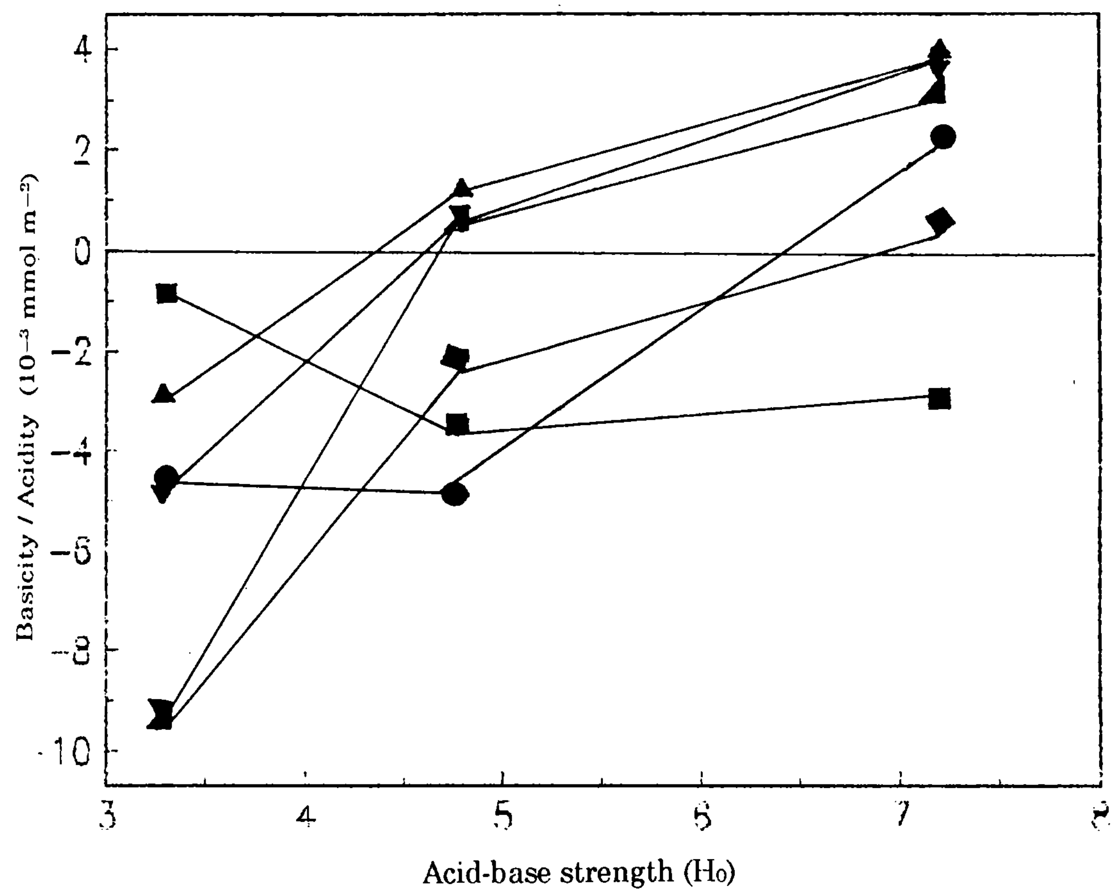

Figure 6.1: Acid-base strength distribution curves for samaria and sulfated samaria at different activation temperatures (^0C)

●	Sm_2O_3 300	▲	SO_4^{2-}/ Sm_2O_3 300
◆	Sm_2O_3 500	▼	SO_4^{2-}/ Sm_2O_3 500
■	Sm_2O_3 700	◢	SO_4^{2-}/ Sm_2O_3 700

Table 6.2: Acid-base strength distribution of samaria and sulfated samaria at different activation temperatures

Catalyst	Activation Temp. ^0C)	Basicity (10^{-3} mmol m^{-2})			Acidity (10^{-3} mmol m^{-2})	
		$H_0 \geq 3.3$	$H_0 \geq 4.8$	$H_0 \geq 7.2$	$H_0 \leq 4.8$	$H_0 \leq 7.2$
Sm_2O_3	300	4.64	0.49	--	--	0.89
Sm_2O_3	500	9.30	2.09	--	--	0.48
Sm_2O_3	700	0.84	3.52	2.94	--	--
SO_4^{2-}/ Sm_2O_3	300	2.85	--	--	1.20	3.83
SO_4^{2-}/ Sm_2O_3	500	4.92	--	--	0.51	3.46
SO_4^{2-}/ Sm_2O_3	700	9.38	--	--	0.54	3.16

Table 6.3 $H_{0,\,max}$ value of samaria and sulfated samaria at different activation temperatures

Catalyst	Activation temperature (^0C)	$H_{0,\,max}$
Sm_2O_3	300	5.95
Sm_2O_3	500	6.85
Sm_2O_3	700	--
SO_4^{2-}/ Sm_2O_3	300	4.35
SO_4^{2-}/ Sm_2O_3	500	4.63
SO_4^{2-}/ Sm_2O_3	700	4.70

The basicity of rare earth oxides increases with activation temperature. This increase has been ascribed to the removal of trace surface contaminants such as carbonate ion, OH species or adsorbed water [10] and to the generation of stoichometric and/or structural defects such as anion vacancies and exposed metal ions that serve as catalytic sites [11]. Increasing temperature undoubtedly leads to the formation of various surface defect structures on rare earth oxides.

Regarding sulfated samaria maximum acidity is shown at activation temperature of 300°C. On increasing temperature, the increase in basicity is quite negligible which shows that eventhough the acidity of unmodified samaria depends on activation temperature, the acidity and acid strength ($H_{0,\,max}$ value) of sulfated samaria are independent of activation temperature.

For sulfated samaria, acidity was generated at H_0 value of 4.8 and 7.2. But unmodified samaria shows acidity only at H_0 value of 7.2. No acid sites are reported at H_0 value of 3.3 for both modified and unmodified Sm_2O_3. It shows that sulfated samaria does not have as strong acid sites as other solid acid catalysts. It was reported that the nature and relative concentration of surface acidic sites (both Bronsted and Lewis centres) depend upon the type and relative concentration of surface SO_4^{2-} which in turn depend on many of the preparative parameters [12].

$H_{0,\,max}$ values show that pure samaria is more basic in nature, whereas sulfated samaria is more acidic in nature. The nature of surface acidity in anion-modified oxides remain controversial. Their catalytic properties however clearly reveal the strong effect of surface modification of these metal oxides by electron rich anions. Superacidity is generated by the interaction between the oxide and sulfate ion.

IR spectra of sulfated samaria showed a strong absorption band at 1380 cm^{-1}, which is attributed to an assymmetric vibrational mode of a S=O double bond [13]. The enhanced acidic property of sulfated samaria originate from the inductive effect of S=O bonds of the complex formed by the interaction of oxides with the sulfate ion. Both Lewis and Bronsted acid strength increases due to the inductive effect of S=O bond in the complex [14]. The surface species, SO_4^{2-} in the highest oxidation state is responsible for the superacidic property of sulfated oxide as evidenced by IR and X-ray photoelectron spectra [15]. The strong acidity was attributed to the electron withdrawing anion groups, which leads to co-ordinatively unsaturated and electron deficient metal centres that behave as strong Lewis acid sites.

It was reported that modification of ZrO_2 with SO_4^{2-} anion results in a strengthening of Lewis acid sites represented by low-coordinate zirconium ions and in a weakening of the polarizability of Lewis acid base pairs [16].

Navarrete *et al.* [17] reported that the fixation of sulfate species was made at the expense of the OH species. This suggests that mechanism of sulfation is an anion exchange between these two species.

6.3.2 Electron donor properties

The surface electron donor properties of samaria and sulfated samaria have been determined by the adsorption of four electron acceptors with electron affinity values ranging from 1.26 to 2.84 eV to form corresponding anion radicals. Since the electron donating properties vary with the activation temperature, the oxides activated at different temperatures of 300, 500 and 700°C were studied. The list of electron acceptors are given in Table 4.1. The data are given in Table 6.4.

Table 6.4: Limiting amount of electron acceptor adsorbed on Sm_2O_3 and SO_4^{2-}/Sm_2O_3 at different activation temperatures

Catalyst	Activation temp. (°C)	Limiting amount of electron acceptor adsorbed (10^{-5} mol m^{-2})	
		Chloranil	TCNQ
Sm_2O_3	300	1.32	2.58
Sm_2O_3	500	2.17	2.77
Sm_2O_3	700	2.87	4.11
SO_4^{2-}/Sm_2O_3	300	0.56	1.19
SO_4^{2-}/Sm_2O_3	500	0.73	1.64
SO_4^{2-}/Sm_2O_3	700	0.83	1.88

The isotherms obtained by the adsorption of chloranil and TCNQ are given in Figures 6.2 and 6.3.

When the electron acceptors are adsorbed from solution, the oxide with chloranil gave a pink colour and that with TCNQ gave light green colour which

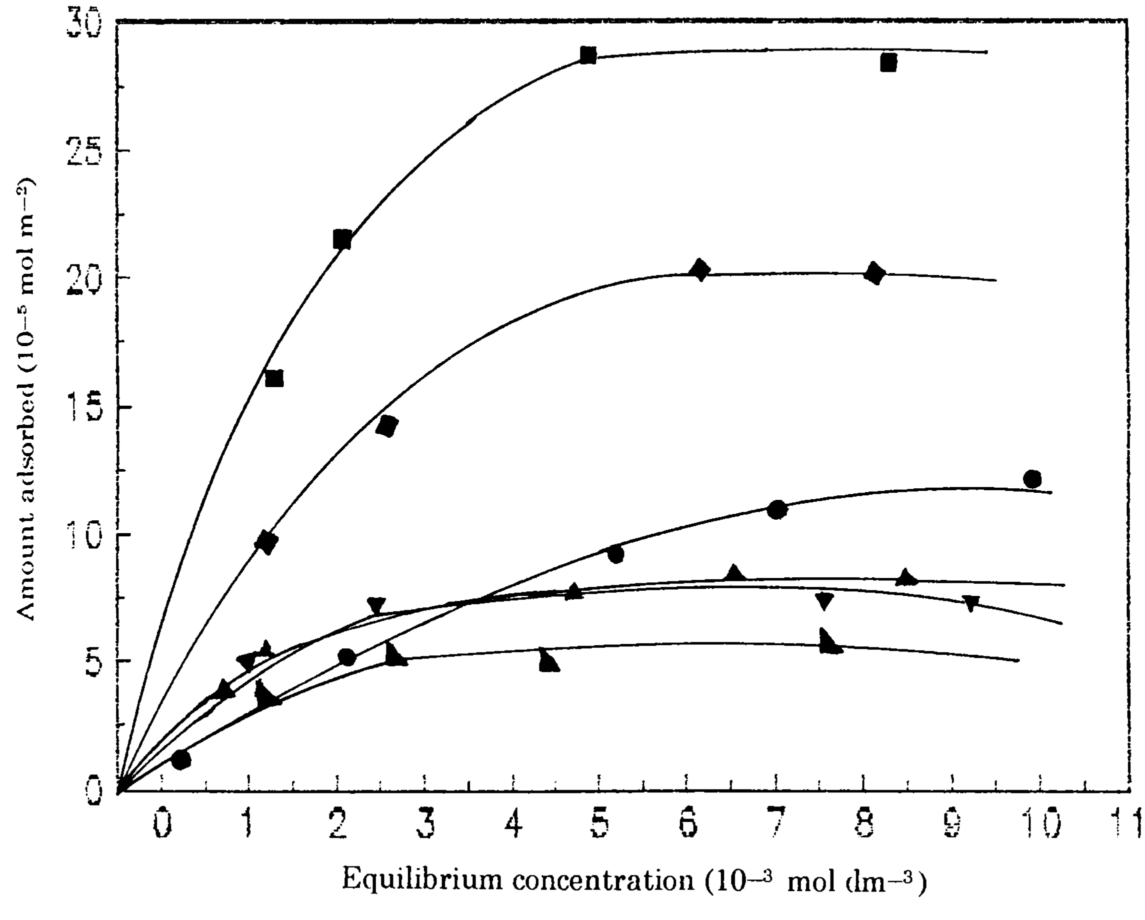

Figure 6.2: Langmuir adsorption isotherms of chloranil adsorbed on samaria and sulfated samaria activated at different activation temperatures (°C)

● Sm_2O_3 300 ◣ SO_4^{2-}/Sm_2O_3 300

◆ Sm_2O_3 500 ▼ SO_4^{2-}/Sm_2O_3 500

■ Sm_2O_3 700 ▲ SO_4^{2-}/Sm_2O_3 700

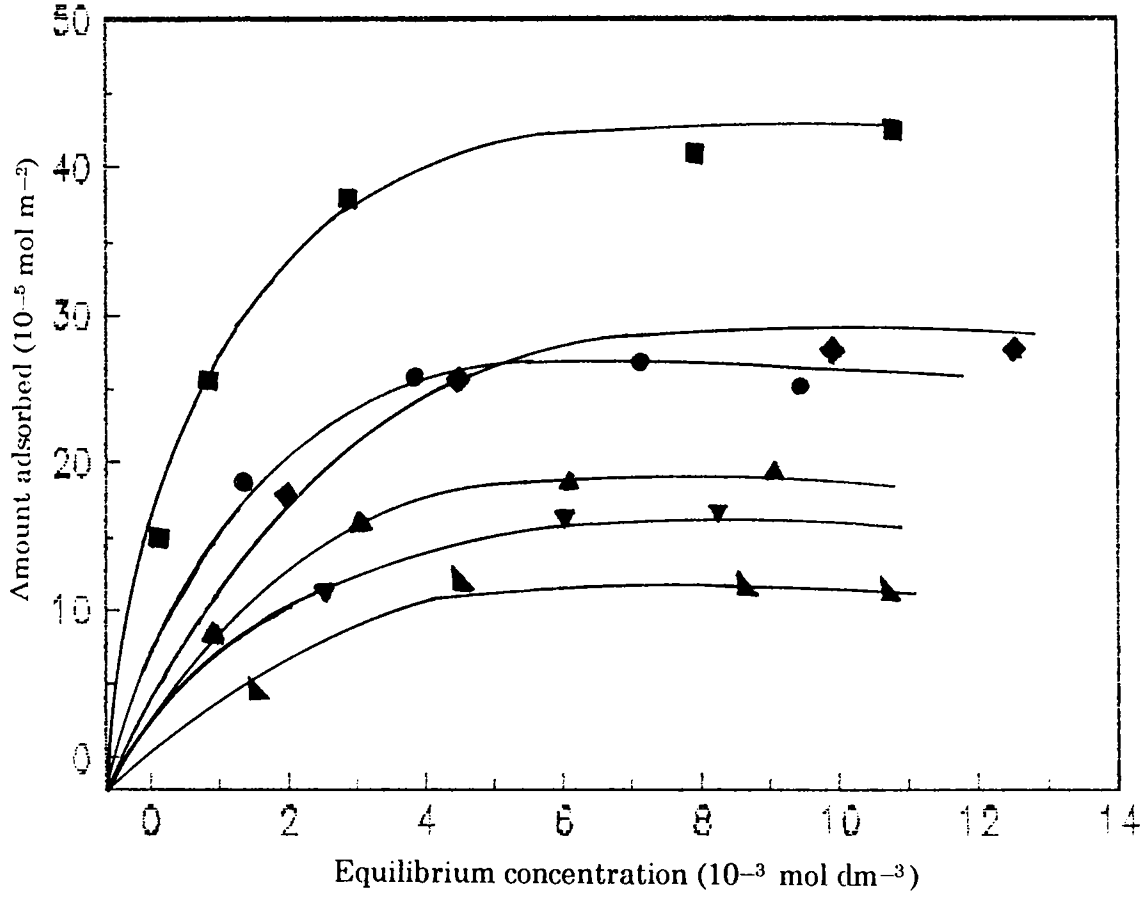

Figure 6.3: Langmuir adsorption isotherms of TCNQ adsorbed on samaria and sulfated samaria activated at different activation temperatures (°C)

●	Sm_2O_3 300	◣	SO_4^{2-}/Sm_2O_3 300
◆	Sm_2O_3 500	▼	SO_4^{2-}/Sm_2O_3 500
■	Sm_2O_3 700	▲	SO_4^{2-}/Sm_2O_3 700

indicate the formation of new adsorbed species. The detailed study about the esr spectra of oxides coloured due to adsorption were given in chapter IV. The radical concentration calculated from esr spectra is plotted against equilibrium concentration of the electron acceptor, in solution, which also corresponds to the Langmuir adsorption isotherm. From such plots, the limiting radical concentration of the electron acceptor adsorbed can be estimated (Table 6.5).

Table 6.5: Limiting radical concentration of electron acceptors adsorbed on Sm_2O_3 and SO_4^{2-}/Sm_2O_3 at different activation temperatures.

Catalyst	Activation temp. (°C)	Limiting radical concentration (10^{17} spins m^{-2})	
		Chloranil	TCNQ
Sm_2O_3	300	0.40	13.30
Sm_2O_3	500	0.65	14.28
Sm_2O_3	700	0.86	21.19
SO_4^{2-}/Sm_2O_3	300	0.17	6.16
SO_4^{2-}/Sm_2O_3	500	0.22	8.45
SO_4^{2-}/Sm_2O_3	700	0.25	9.68

In order to study the nature of interaction during adsorption, the electronic spectra of the coloured samples were measured. It has already been explained in chapter IV.

The difference in limiting amount of TCNQ and chloranil adsorbed on the surface would give an estimate of the stronger donor sites. The limit of electron transfer in terms of electron affinity (eV) of the acceptors is between 1.77 and 2.40 for Sm_2O_3 and SO_4^{2-}/Sm_2O_3.

In general, two types of surface sites are responsible for the electron donor properties of metal oxides. One of these is electron trapped in intrinsic defect sites and the other is surface hydroxyl groups [18]. Surface O^{2-} can also act as electron donor sites of higher temperatures. From the data given in Tables 6.4 and 6.5, it is clear that as temperature increases, surface electron donor property increases. Surface hydroxyl groups are responsible for basicity at low temperature. As temperature increases, the number of OH ions decreases and desorption of water molecules from adjacent sites occur.

It may be concluded that the basicity at higher temperature depend upon the availability of trapped electrons. The variation of limiting value of electron acceptor adsorbed with activation temperature is given in Figure 6.4.

From the data given in Tables 6.4 and 6.5, it is clear that, on modification with sulfate ion, the electron donocity decreases. The decrease in electron donocity of sulfated samaria must be attributed to the decrease in basicities. From the data, it can be observed that electron donocity of sulfated samaria is almost independent of the activation temperature. It can be inferred that some of the surface OH groups are converted to acid sites by sulfation. The Decrease in electron donocity on sulfation can be attributed to the conversion of some of the basic sites to acidic sites.

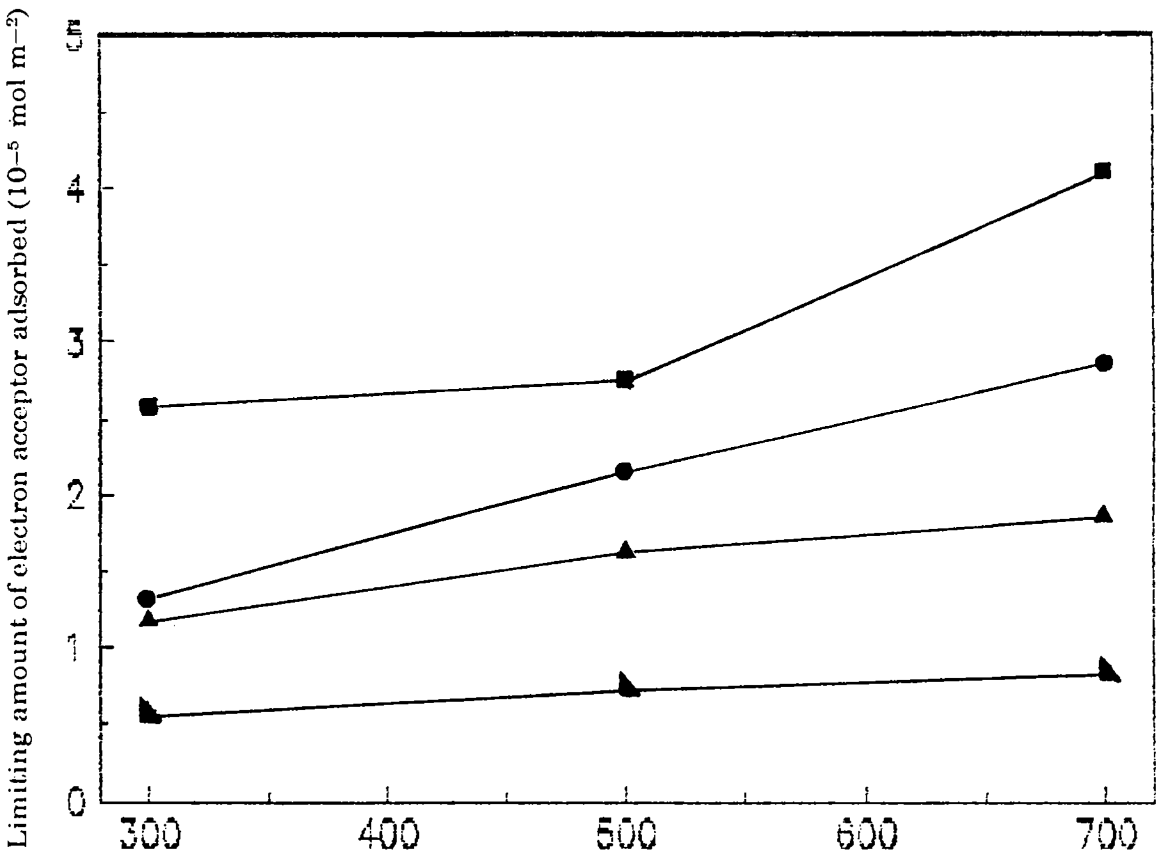

Figure 6.4: Limiting amount of electron acceptor adsorbed as a function of activation temperature

● Sm_2O_3 Chloranil ◣ SO_4^{2-} / Sm_2O_3 Chloranil

■ Sm_2O_3 TCNQ ▲ SO_4^{2-} / Sm_2O_3 TCNQ

During adsorption of electron acceptor on samaria and sulfated samaria, the magnetic moment of oxide decreases and reaches a limiting value, at the same concentration at which the limiting amount of electron acceptor is adsorbed. The plot of magnetic moment (BM) as a function of equilibrium concentration of the electron acceptor is given (Figure 6.5).

6.3.3 Catalytic activity

6.3.3.1 Esterification of Acetic acid using n-Butanol

Esterification is an acid catalysed reaction. The mechanism of esterification reaction is described in detail in chapter IV.

The data for esterification reaction of Sm_2O_3 and SO_4^{2-}/Sm_2O_3 are given in Table 6.7. The catalytic activity is expressed as first order rate coefficient for the conversion of acetic acid per unit area of the catalyst. The data indicate that unmodified samaria did not have enough acid strength to catalyze the esterification reaction. When samarium oxide is modified with sulfate ion, acidity and acid strength increases resulting in higher catalytic activity for esterification. It may be noted that while surface properties of oxide depend on activation temperature, acidity and acid strength of sulfated samaria ($H_{0,\ max}$ value) are independent of activation temperature. Catalytic activity is also in agreement with the observations. Samarium oxide owing to its basicity and low acidity is not at all catalyzing the reaction. But sulfated samaria catalyzes the esterification reaction effectively. Activation temperature has not much effect

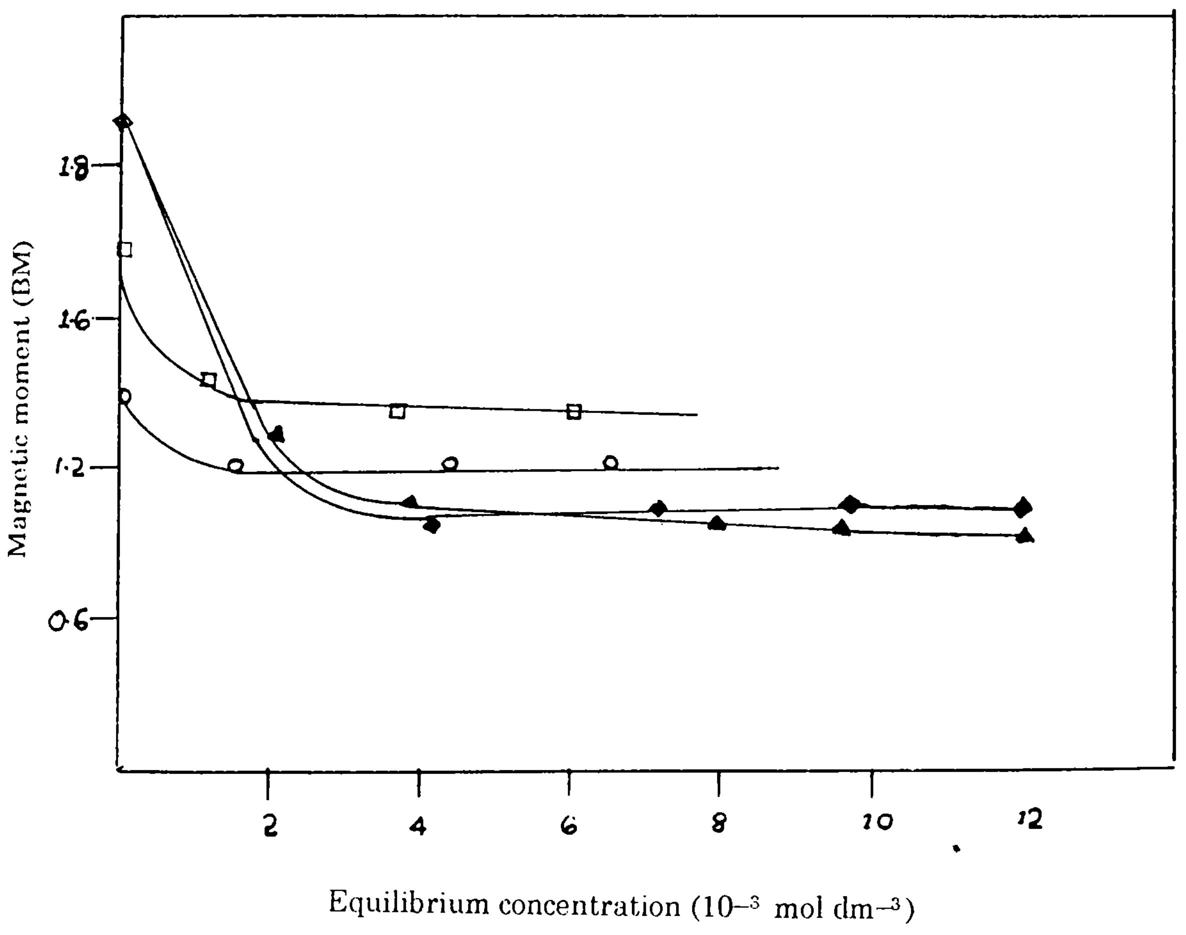

Figure 6.5: Magnetic moment of samaria and sulfated samaria activated at 500°C as a function of equilibrium concentration of electron acceptor

◆ Sm_2O_3 Chloranil □ SO_4^{2-}/Sm_2O_3 Chloranil

▲ Sm_2O_3 TCNQ ○ SO_4^{2-}/Sm_2O_3 TCNQ on catalytic activity of sulfated samaria. Catalytic activity as a function of activation temperature is given in Figure 6.6.

Table 6.7: Catalytic activity for esterification of acetic acid using n-butanol at different activation temperatures

Catalyst	Activation temperature (°C)	Percentage conversion	Rate constant (10^{-5} $m^{-2}s^{-1}$)
Sm_2O_3	300	--	--
Sm_2O_3	500	--	--
Sm_2O_3	700	--	--
SO_4^{2-}/ Sm_2O_3	300	15.25	1.94
SO_4^{2-}/ Sm_2O_3	500	11.98	1.55
SO_4^{2-}/ Sm_2O_3	700	10.22	1.39

6.3.3.2 Reduction of Cyclohexanone in Isopropanol

The liquid phase reduction of cyclohexanone in isopropanol proceed very well over the catalyst. Data are given in Table 6.8. The detailed mechanism is described in chapter IV. The activity is expressed as first order rate coefficient for the conversion of cyclohexanone per unit area of the catalyst surface.

From the data it is clear that the reduction reaction proceeds effectively over pure samaria, owing to its high basicity than sulfated samaria. It was suggested that a step of hydride ion transfer from adsorbed isopropanol to the adsorbed carbonyl group constitute the rate determining step for the reduction of cyclohexanone. Basic sites favour the hydride ion transfer. Catalytic

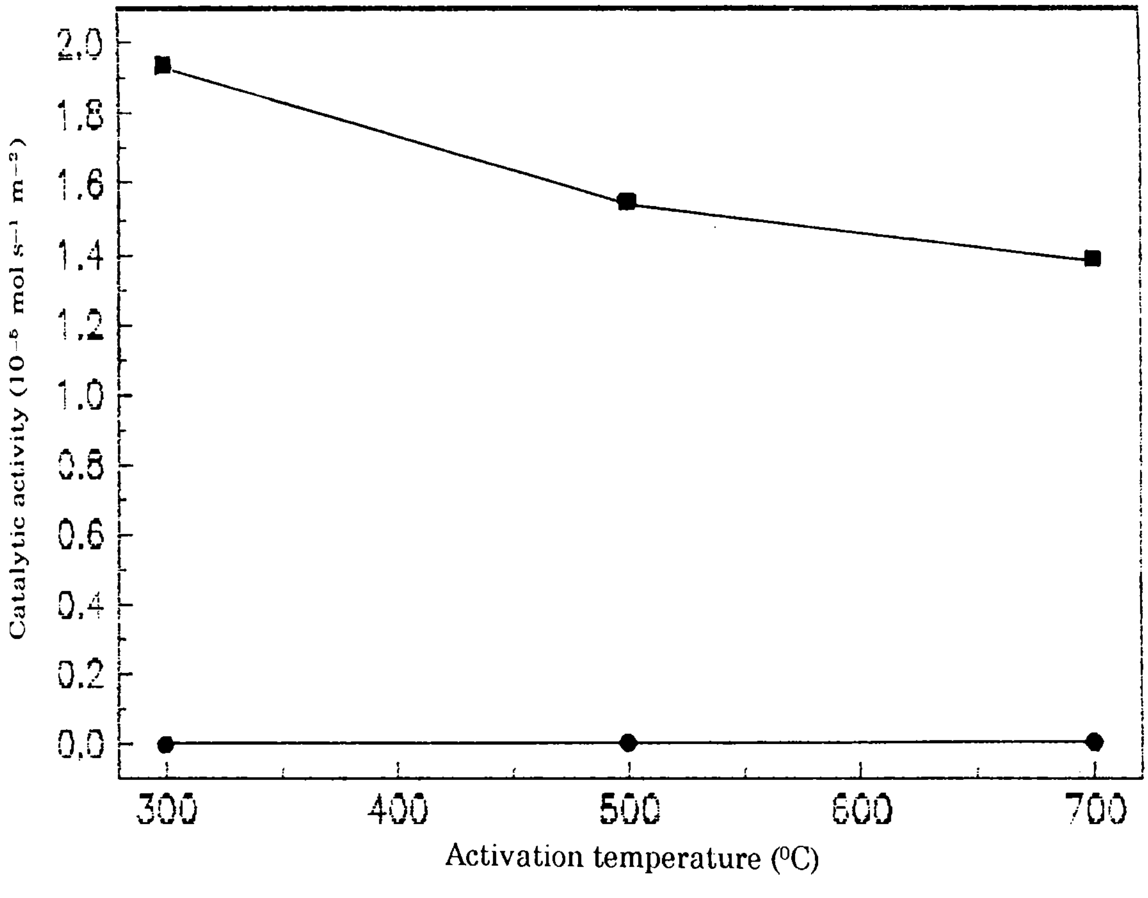

Figure 6.6: Catalytic activity for esterification as a function of activation temperature

● Sm_2O_3 ■ SO_4^{2-}/Sm_2O_3

activity parallels with the basicity of oxides. The lower catalytic activity of sulfated samaria is attributed to the conversion of some of the basic sites to acidic sites. The data have been correlated with the surface electron donor properties of these oxides (discussed in section 6.3.2). The catalytic activity parallels with the electron donating capacity. It is also observed that the catalytic activity increases with increasing activation temperature, due to increase in basic nature. Variation of catalytic activity with activation temperature is given in Figure 6.7. For sulfated samaria, the increase in activity with activation temperature is small which is in agreement with the electron donor property.

Table 6.8: Catalytic activity for reduction of cyclohexanone in isopropanol using Sm_2O_3 and SO_4^{2-}/ Sm_2O_3 at different activation temperatures.

Catalyst	Activation temperature (°C)	Percentage conversion	Rate constant ($10^{-7} s^{-1} m^{-2}$)
Sm_2O_3	300	31.39	3.44
Sm_2O_3	500	85.94	18.71
Sm_2O_3	700	86.94	21.62
SO_4^{2-} / Sm_2O_3	300	21.12	2.32
SO_4^{2-} / Sm_2O_3	500	39.42	5.07
SO_4^{2-} / Sm_2O_3	700	51.23	7.70

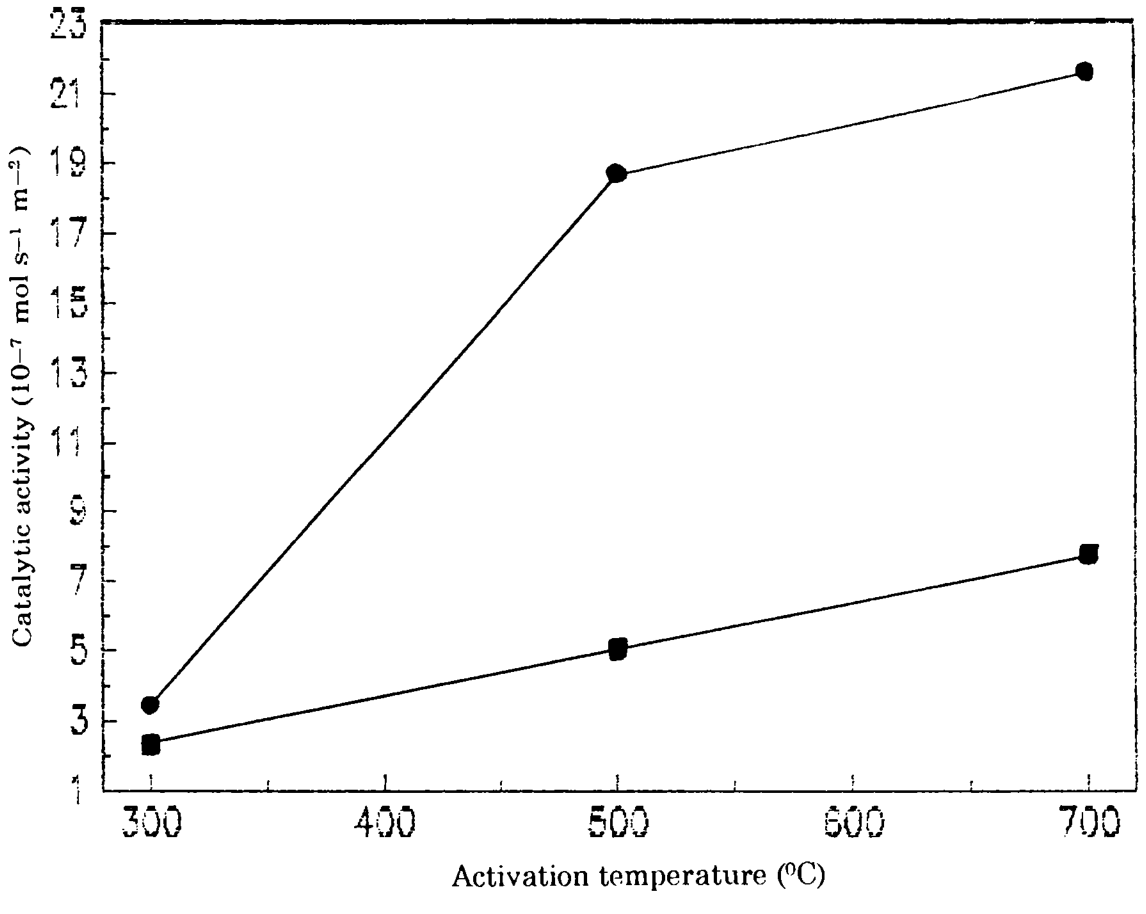

Figure 6.7: Catalytic activity for reduction as a function of activation temperature

● Sm_2O_3 ■ SO_4^{2-}/ Sm_2O_3

6.3.3.3 Oxidation of Cyclohexanol using Benzophenone

The results are given in Table 6.9. The detailed mechanism is described in chapter IV. The oxides show high catalytic activity. The ability of oxide catalysts to dehydrogenation activity has been related to the existence of basic sites originating from the oxygen in the oxide lattice [19].

Table 6.9: Catalytic activity for oxidation of cyclohexanone with benzophenone using Sm_2O_3 and SO_4^{2-}/ Sm_2O_3 at different activation temperatures.

Catalyst	Activation temperature (°C)	Percentage conversion	Rate constant ($10^{-7} s^{-1} m^{-2}$)
Sm_2O_3	300	88.00	5.81
Sm_2O_3	500	89.77	6.52
Sm_2O_3	700	88.99	7.02
SO_4^{2-} / Sm_2O_3	300	80.12	4.74
SO_4^{2-} / Sm_2O_3	500	82.58	5.30
SO_4^{2-} / Sm_2O_3	700	83.00	5.70

The unmodified samaria exhibit good catalytic activity for the oxidation of cyclohexanol just like reduction of cyclohexanone, where both reactions are favoured by basic sites. Higher activity is found in the case of oxidation. The activity for oxidation decreased on modification with sulfate ion. This may be due to the increase in acidity on modification. In both cases, catalytic activity increases on increasing activation temperature, which is in accordance with the acid-base properties. The variation of catalytic activity with temperature is given in Figure 6.8. The mechanism involves hydride transfer from alcohol to the carboxyl carbon of ketone. Lewis basicity of catalyst surface favours the hydride transfer. Unmodified samaria, owing to its high basicity favours the oxidation reaction of cyclohexanol effectively. Catalytic activity parallels the electron donor properties.

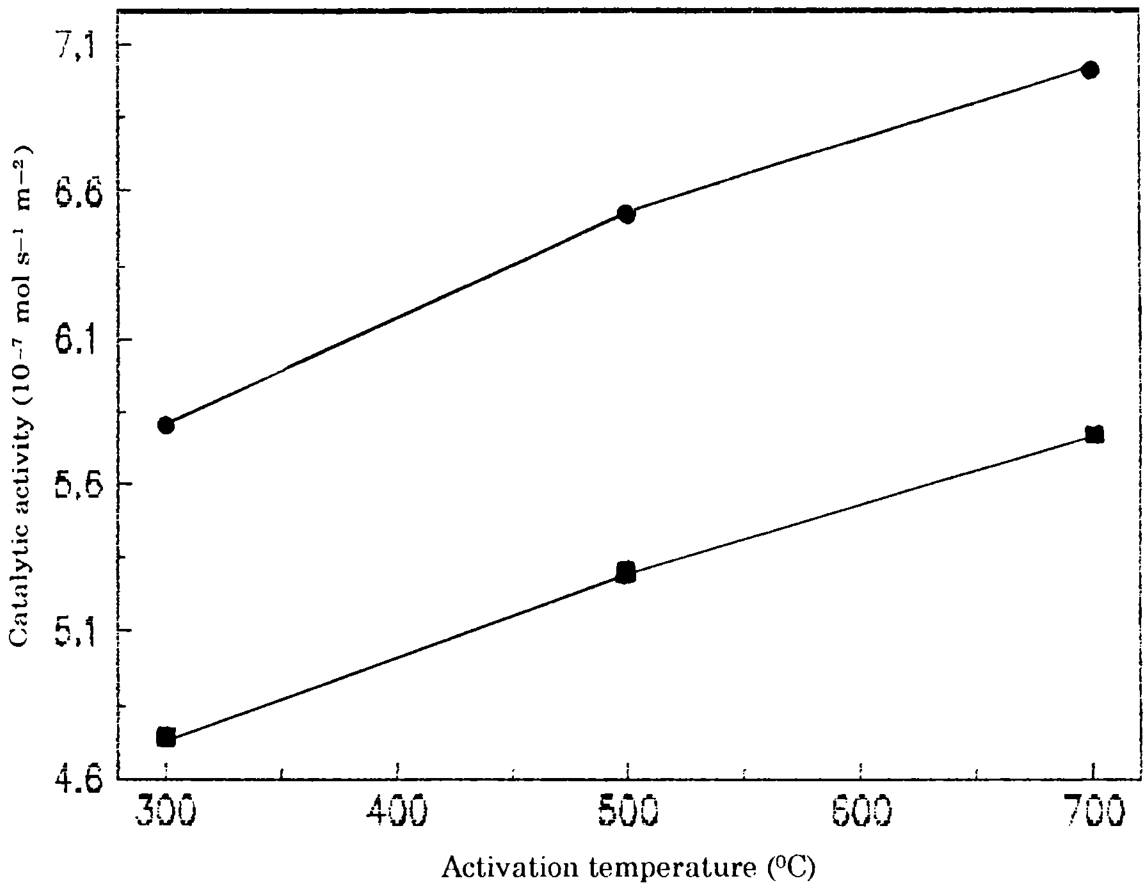

Figure 6.8: Catalytic activity for oxidation as a function of activation temperature

● Sm_2O_3 ■ SO_4^{2-}/Sm_2O_3

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Chapter VII

ACIDITY/BASICITY, ELECTRON DONOR PROPERTIES AND CATALYTIC ACTIVITY OF SULFATED CERIA

Chapter VII

ACIDITY/BASICITY, ELECTRON DONOR PROPERTIES AND CATALYTIC ACTIVITY OF SULFATED CERIA

7.1 INTRODUCTION

We have investigated the changes in surface acidity/basicity, and catalytic activity of cerium oxide due to surface modification by sulfate ion. In order to find out whether the increase in acidity on sulfation is due to the generation of new acidic sites or they are formed at the expense of some of the basic sites to acidic sites, we have carried out the study of electron donor properties of both modified and unmodified oxides using electron acceptors of various electron affinity values.

Esterification of acetic acid using n-butanol, reduction of cyclohexanone in 2-propanol and oxidation of cyclohexanol with benzophenone are the reactions selected for determining catalytic activity.

7.2 EXPERIMENTAL

The detailed procedure for the preparation of cerium oxide and sulfated cerium oxide was described in chapter III.

The samples activated at different temperatures of 300, 500 and 700°C were used for the study. The surface area of samples were determined by BET method. The values are given in Table 7.1.

Table 7.1: Surface area of ceria and sulfated ceria at different activation temperatures

Catalyst	Activation temperature (°C)	Surface area ($m^2 g^{-1}$)
CeO_2	300	49.48
CeO_2	500	44.81
CeO_2	700	31.18
SO_4^{2-}/ CeO_2	300	40.64
SO_4^{2-}/ CeO_2	500	30.15
SO_4^{2-}/ CeO_2	700	18.68

7.3 RESULTS AND DISCUSSION

7.3.1 Acidity/basicity

The list of Hammett indicaters used for acidity/basicity measurements are given in chapter IV (Table 4.2). Among them, ceria and sulfated ceria responded only to three indicators. They are dimethyl yellow, methyl red and bromothymol blue. The results of acid-base strength distribution at different activation temperatures are given in Table 7.2. The acid-base strength distribution curves are given in Figure 7.1. $H_{0,max}$ values at different activation temperatures are given in Table 7.3.

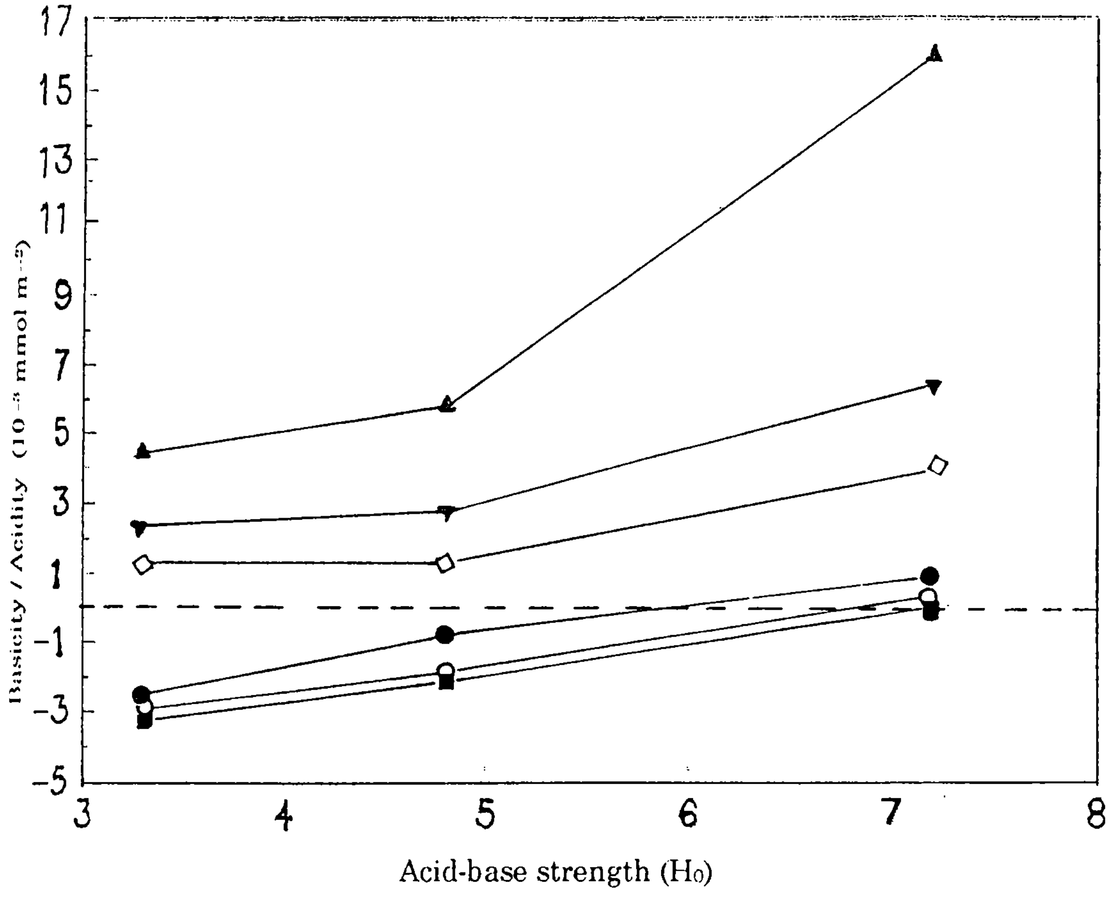

Figure 7.1: Acid base strength distribution curves for ceria and sulfated ceria at different activation temperatures (°C)

■ CeO$_2$ 300
○ CeO$_2$ 500
● CeO$_2$ 700
◇ SO$_4^{2-}$/ CeO$_2$ 300
▼ SO$_4^{2-}$/ CeO$_2$ 500
▲ SO$_4^{2-}$/ CeO$_2$ 700

Table 7.2: Acid-base strength distribution of ceria and sulfated ceria at different activation temperatures

Catalyst	Activation Temp. ^{o}C)	Basicity (10^{-3} mmol m^{-2})		Acidity (10^{-3} mmol m^{-2})		
		$H_0 \geq 3.3$	$H_0 \geq 4.8$	$H_0 \leq 3.3$	$H_0 \leq 4.8$	$H_0 \leq 7.2$
CeO_2	300	3.27	2.18	--	--	0.14
CeO_2	500	3.01	1.81	--	--	0.34
CeO_2	700	2.60	0.86	--	--	0.87
SO_4^{2-}/ CeO_2	300	--	--	1.34	1.33	4.01
SO_4^{2-}/ CeO_2	500	--	--	2.26	2.72	6.30
SO_4^{2-}/ CeO_2	700	--	--	4.39	5.84	16.01

Table 7.3 $H_{0,\,max}$ values of ceria and sulfated ceria at different activation temperatures

Catalyst	Activation temperature (^{o}C)	$H_{0,\,max}$
CeO_2	300	7.3
CeO_2	500	6.8
CeO_2	700	6.1
SO_4^{2-}/ CeO_2	300	--
SO_4^{2-}/ CeO_2	500	--
SO_4^{2-}/ CeO_2	700	--

From the data it can be observed that as the activation temperature increases the acidity increases for both cerium oxide and sulfate modified cerium oxide. It is impossible to find $H_{0,max}$ value of sulfate modified cerium oxide, even by extrapolation method. Unmodified cerium oxide is weakly acidic as acidic sites are present only at H_0 value of 7.2. But for sulfate modified cerium oxide acidity is generated at H_0 value of 3.3, 4.8 and 7.2. From this, it is clear that on modification with sulfate ion, the acidity and acid strength increases. Eventhough the acidity of cerium oxide increases by modification with sulfate ion, it is not considered as a superacid (A substance with acid strength more than that of sulfuric acid). The nature and relative concentration of surface acidic sites (both Lewis and Bronsted centres) depend upon the type and relative concentration of surface sulfate ions which in turn depend on many of the preparative parameters [1].

Infrared spectra of sulfated ceria shows a strong absorption band at 1400 cm^{-1} like other sulfated metal oxides, which corresponds to the asymmetric stretching frequency of S=O double bond is regarded as characteristic band of SO_4^{2-}. The IR spectra of sulfated ceria is given in Figure 7.2.

The calcination temperature affects the catalytic performance of sulfated ceria. At high temperature the increase in acidity may also be due to change in crystallinity.

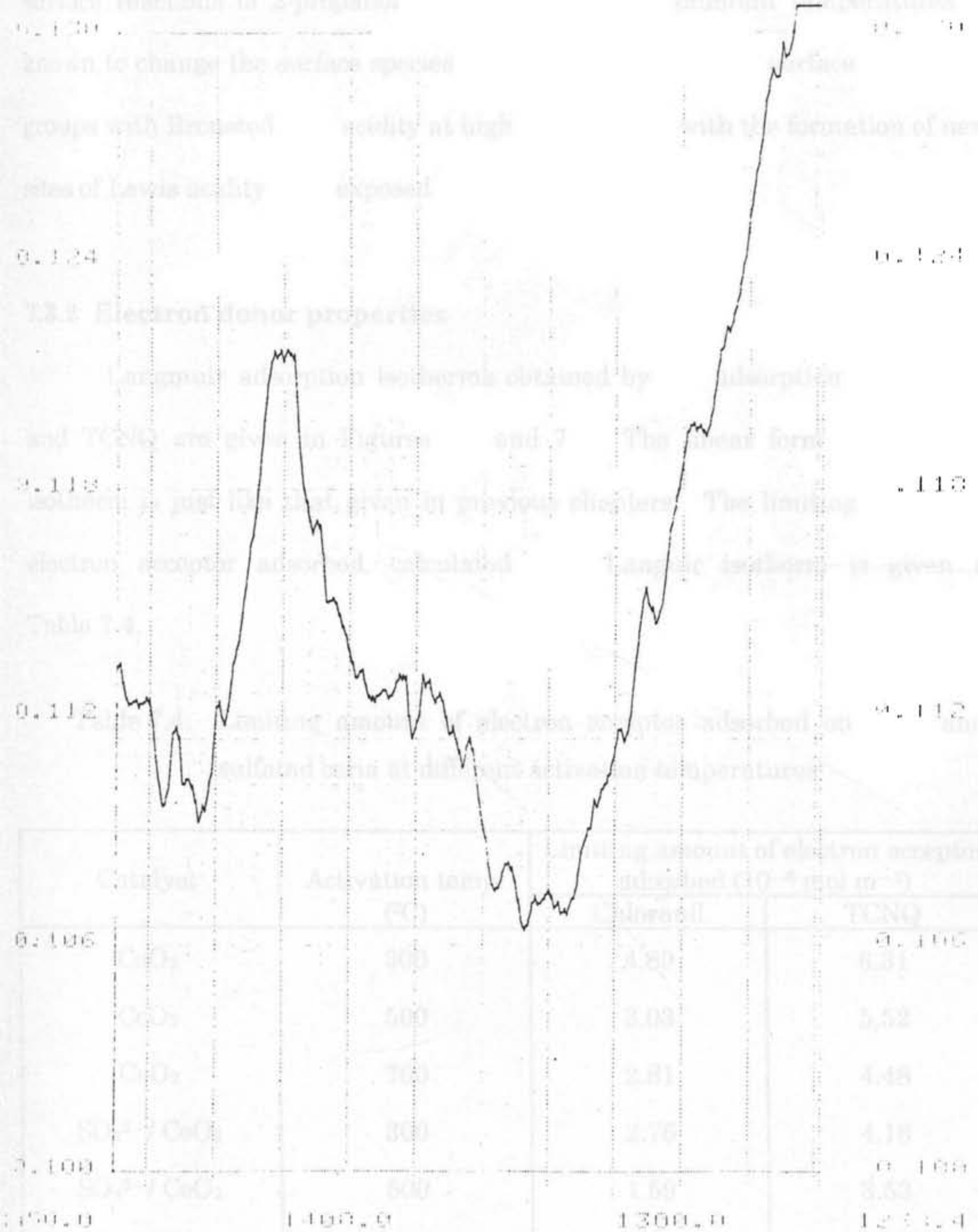

Figure 7.2: IR spectra of sulfated ceria activated at 500°C

According to Zaki and Sheppard, the adsorption and mechanism of surface reactions of 2-propanol on ceria calcined at different temperatures is known to change the surface species on the oxide and remove surface bound OH groups with Bronsted type acidity at high temperature with the formation of new sites of Lewis acidity from exposed metal cations [2].

7.3.2 Electron donor properties

Langmuir adsorption isotherms obtained by the adsorption of chloranil and TCNQ are given in Figures 7.3 and 7.4. The linear form of Langmuir isotherm is just like that given in previous chapters. The limiting amount of electron acceptor adsorbed, calculated from Languir isotherm is given in Table 7.4.

Table 7.4: Limiting amount of electron acceptor adsorbed on ceria and sulfated ceria at different activation temperatures

Catalyst	Activation temp. (^oC)	Limiting amount of electron acceptor adsorbed (10^{-5} mol m^{-2})	
		Chloranil	TCNQ
CeO_2	300	4.89	6.31
CeO_2	500	3.03	5.52
CeO_2	700	2.81	4.48
SO_4^{2-}/ CeO_2	300	2.76	4.18
SO_4^{2-}/ CeO_2	500	1.59	3.53
SO_4^{2-}/ CeO_2	700	1.44	3.34

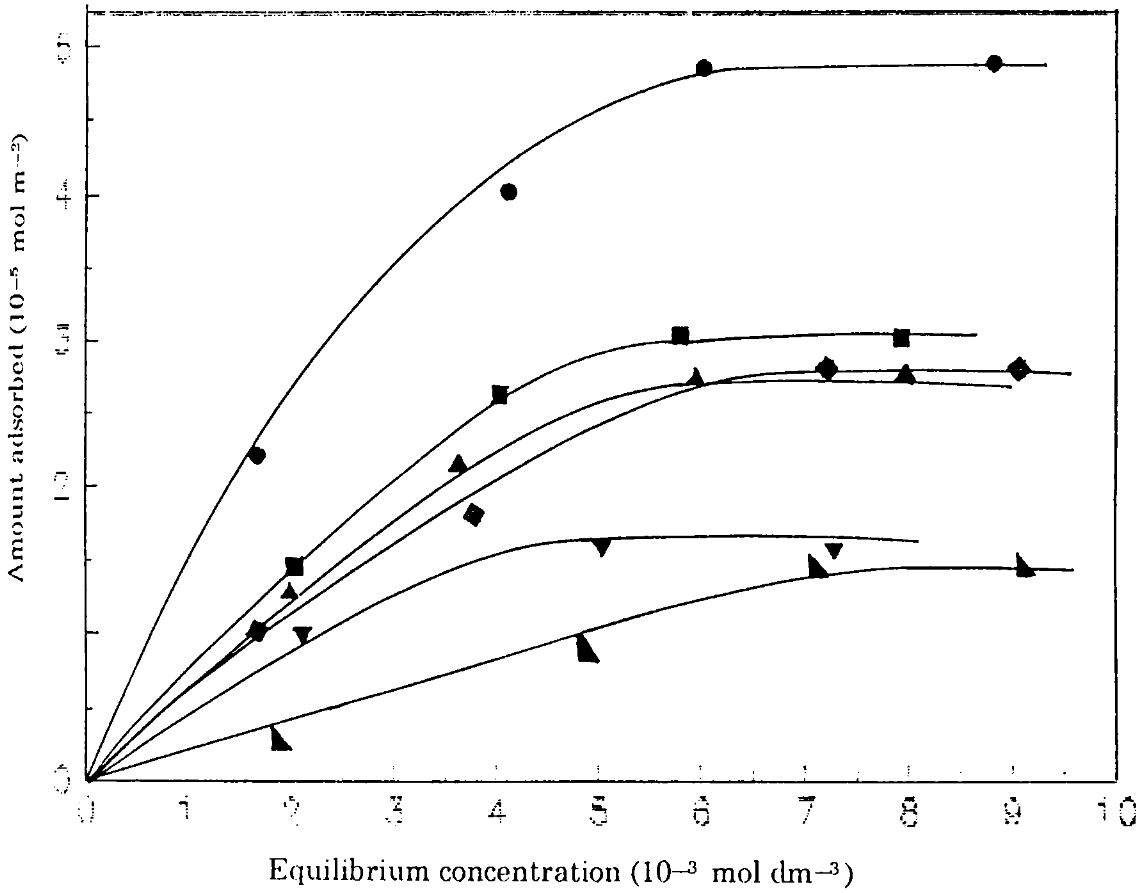

Figure 7.3: Langmuir adsorption isotherms of chloranil adsorbed on ceria and sulfated ceria at different activation temperatures (°C)

●	CeO_2 300	▲	SO_4^{2-}/CeO_2 300
■	CeO_2 500	▼	SO_4^{2-}/CeO_2 500
◆	CeO_2 700	◣	SO_4^{2-}/CeO_2 700

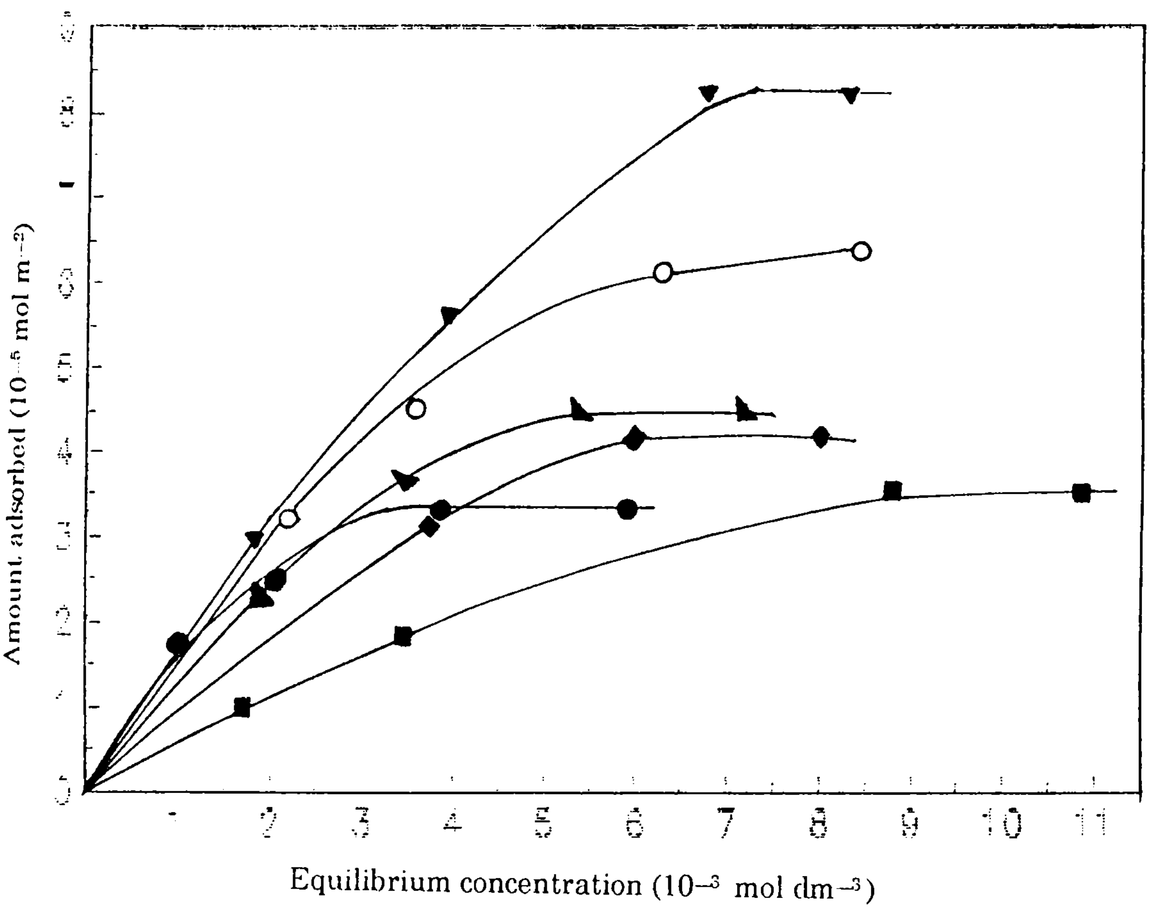

Figure 7.4: Langmuir adsorption isotherms of TCNQ adsorbed on ceria and sulfated ceria at different activation temperatures (°C)

○	CeO_2 300	◆	SO_4^{2-}/CeO_2 300
▼	CeO_2 500	■	SO_4^{2-}/CeO_2 500
◣	CeO_2 700	●	SO_4^{2-}/CeO_2 700

The limiting radical concentration of the electron acceptor are given in Table 7.5.

Table 7.5: Limiting radical concentration of electron acceptors adsorbed on ceria and sulfated ceria at different activation temperatures.

Catalyst	Activation temp. (°C)	Limiting radical concentration (10^{18} spins m^{-2})	
		Chloranil	TCNQ
CeO_2	300	0.15	3.26
CeO_2	500	0.09	2.85
CeO_2	700	0.08	2.31
SO_4^{2-}/ CeO_2	300	0.08	2.16
SO_4^{2-}/ CeO_2	500	0.05	1.82
SO_4^{2-}/ CeO_2	700	0.04	1.72

The difference in limiting amount of TCNQ and chloranil adsorbed on the surface would be an estimate of the stronger donor sites. The limit of electron transfer in terms of electron affinity is between 1.77 and 2.40 for CeO_2 and SO_4^{2-}/CeO_2.

As discussed in previous chapters, the electron donor properties arises from surface O^{2-}, electrons trapped in intrinsic defect sites and surface hydroxyl groups. In the case of both ceria and sulfated ceria, as temperature increases electron donocity decreases. Therefore, it is inferred that surface OH groups are responsible for basicity in the case of both ceria and sulfated ceria. As temperature increases, the number of OH groups decreases due to desorption of water molecules by the dehydroxylation process from adjacent OH groups. According to Bluementhal, Lee and Panlener [3] as activation temperature increases electronic mobility is decreased for ceria. The decrease in electron donocity on increasing activation temperature may be attributed to the decrease in number of OH groups and electronic mobility. For sulfated ceria, the electron donocity is further decreased. The decrease may be attributed to the increase in acidity on modification with sulfate ion. Study of electron donor properties revealed that, by sulfation, acidic sites are enhanced at the expense of basic sites. The variation of Limiting amount of the electron acceptor adsorbed with activation temperature is given in Figure 7.5. This aspect has already been explained in section 7.3.1.

7.3.3 Catalytic activity

7.3.3.1 Esterification of Acetic acid using n-Butanol

In order to evaluate the increase in acidity on modification with sulfate ion, esterification of acetic acid with n-butanol has been selected as a test reaction.

The mechanism of esterification is described in chapter IV. The data for esterification reaction are given in Table 7.6.

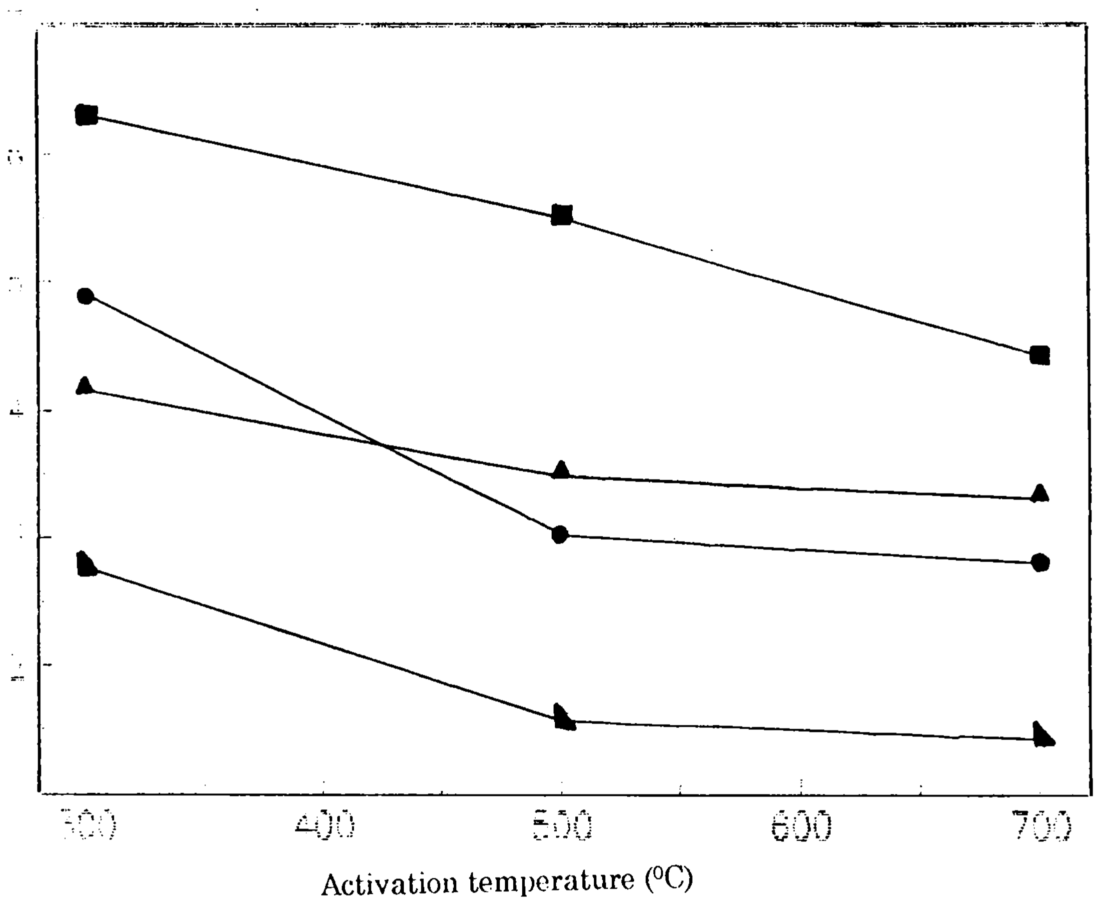

Figure 7.5: Limiting amount of electron acceptor adsorbed as a function of activation temperature

●	CeO_2 Chloranil	◣	SO_4^{2-}/CeO_2 Chloranil
■	CeO_2 TCNQ	▲	SO_4^{2-}/CeO_2 TCNQ

Table 7.6: Catalytic activity for esterification of acetic acid using n-butanol at different activation temperatures.

Catalyst	Activation temperature (°C)	Percentage conversion	Rate constant ($10^{-7} s^{-1} m^{-2}$)
CeO_2	300	13.39	1.61
CeO_2	500	16.64	2.26
CeO_2	700	17.11	3.34
SO_4^{2-} / CeO_2	300	40.30	7.05
SO_4^{2-} / CeO_2	500	37.04	8.53
SO_4^{2-} / CeO_2	700	28.76	10.09

The data indicate that sulfate modified ceria catalyzes the esterification reaction more effectively than the unmodified ones. On modification with sulfate ion, both acidity and acid strength increases resulting in higher catalytic activity. The catalytic activity is found to be in agreement with the acid-base properties. The variation of catalytic activity with temperature is given in Figure 7.6.

7.3.3.2 Reduction of Cyclohexanone in Isopropanol

The mechanism for reduction is described in chapter IV. The data given in Table 7.7.

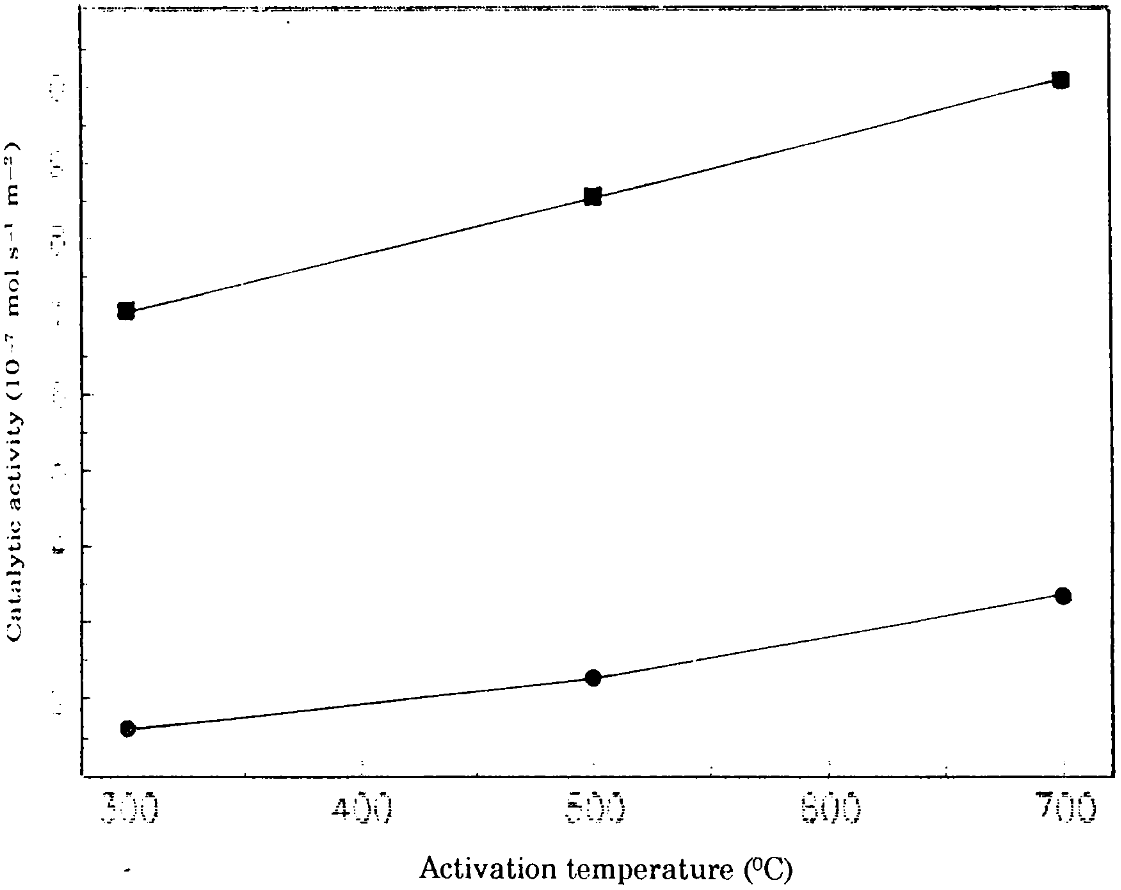

Figure 7.6: Catalytic activity for esterification as a function of activation temperature

● CeO_2 ■ SO_4^{2-}/CeO_2

Table7.7: Catalytic activity for reduction of cyclohexanon in isopropanol using ceria and sulfated ceria at different activation temperatures

Catalyst	Activation temperature (°C)	Percentage conversion	Catalytic activity $10^{-7}\ m^{-2}s^{-1}$
CeO_2	300	26.19	17.10
CeO_2	500	22.28	15.60
CeO_2	700	10.91	10.20
$SO_4^{2-}/\ CeO_2$	300	0.32	0.22
$SO_4^{2-}/\ CeO_2$	500	0.17	0.16
$SO_4^{2-}/\ CeO_2$	700	0.11	0.03

The data indicate that reduction reaction proceeds effectively over unmodified ceria owing to its higher basicity. Due to the enhanced acidic property of sulfated ceria, the percentage conversion is negligible.

The data have been correlated with the surface electron donor property of the oxides which is in agreement with the acid base properties. Variation of catalytic activity with temperature is given in Figure 7.7.

7.3.3.3 Oxidation of Cyclohexanol using Benzophenone

The mechanism is described in chapter IV. Data are given in Table 7.8. Catalytic activity is expressed as first order rate coefficient per unit area of the catalyst.

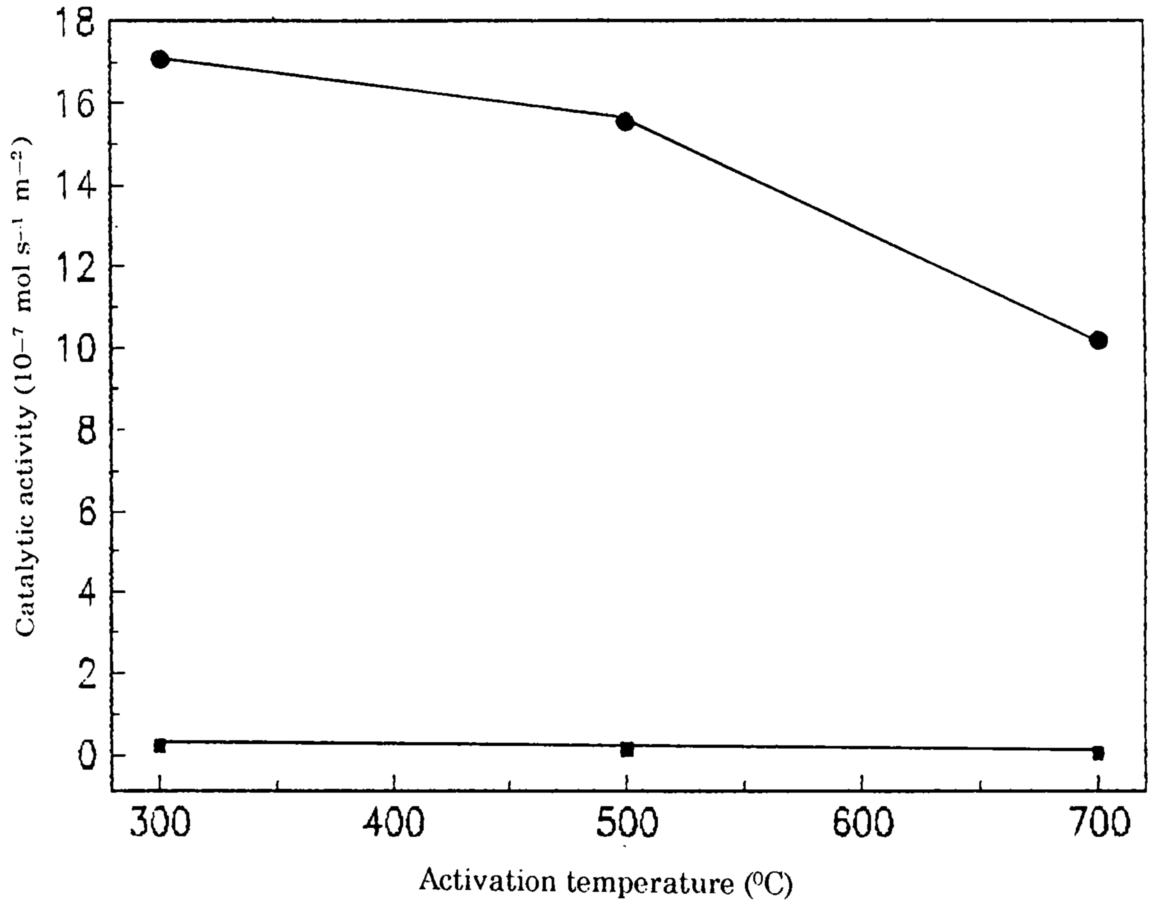

Figure 7.7: Catalytic activity for reduction as a function of activation temperature

● CeO_2 ■ SO_4^{2-} / CeO_2

Table 7.8: Catalytic activity for the oxidation of cyclohexanol with benzophenone using ceria and sulfated ceria at different activation temperatures

Catalyst	Activation temperature (°C)	Percentage conversion	Catalytic activity (10^{-6} s^{-1} m^{-2})
CeO_2	300	85.39	5.40
CeO_2	500	76.97	4.55
CeO_2	700	48.09	2.92
SO_4^{2-}/ CeO_2	300	41.55	1.83
SO_4^{2-}/ CeO_2	500	28.55	1.56
SO_4^{2-}/ CeO_2	700	15.42	1.26

The data indicate that oxidation reaction takes place effectively over unmodified ceria than modified ones which may be attributed to the increase in acidity on modification with sulfate ion. The activity has been correlated with the acid base property. As discussed in chapter VI, the ability of the catalysts to dehydrogenation activity has been favoured by basic sites. As activation temperature increases catalytic activity decreases for both modified and unmodified oxides which parallels the electron donor properties. Catalytic activity as a function of activation temperature is given in Figure 7.8. The mechanism involves hydride transfer from alcohol to the carbonyl carbon of ketone. Lewis basicity of catalyst surface favours the hydride transfer. Unmodified ceria owing to its high basicity favours the oxidation reaction.

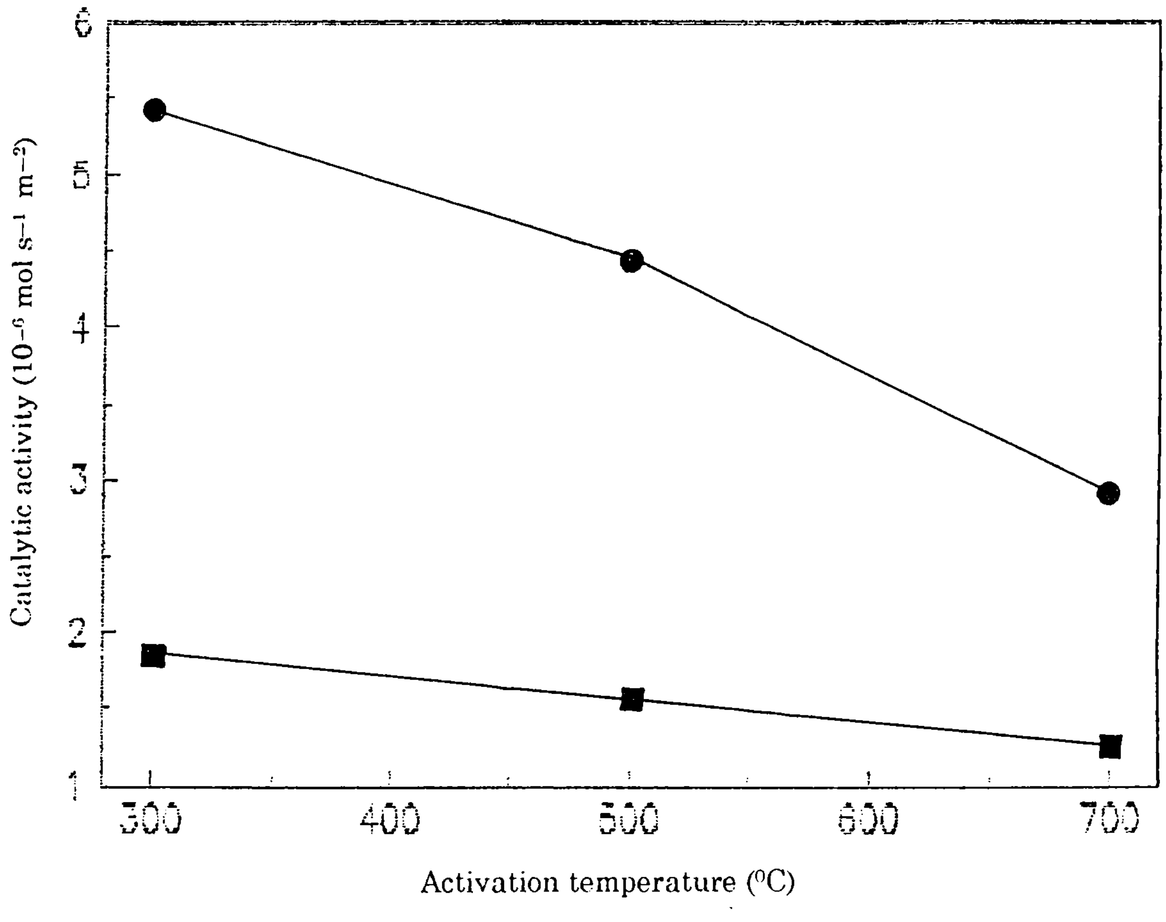

Figure 7.8: Catalytic activity for oxidation as a function of activation temperature

● CeO_2 ■ SO_4^{2-}/CeO_2

On modification with sulfate ion, some of the basic sites are converted to acidic sites and hence catalytic activity also decreases which is in agreement with the acid base properties. According to Navarrete, Lopez and Gomez mechanism of sulfation is an anion exchange between SO_4^{2-} and OH^- species, which give an additional proof for the enhancement of acidity at the expense of basicity [4].

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Chapter VIII

ACIDITY/BASICITY, ELECTRON DONOR PROPERTIES AND CATALYTIC ACTIVITY OF SULFATED TIN OXIDE

Chapter VIII

ACIDITY/BASICITY, ELECTRON DONOR PROPERTIES AND CATALYTIC ACTIVITY OF SULFATED TIN OXIDE

8.1 INTRODUCTION

The oxidation of CO has been investigated on catalysts obtained by thermal activation of granular hydrous tin(IV) oxide gel in the temperature 200–500°C [1]. Determination of the strength of acidic sites exposed on the solid surface as well as their distribution is necessary to understand the catalytic properties of acidic solids. The selectivity and yield for methacrolein in the oxidation of isobutane over pure SnO_2 and Sb_2O_4 can be improved dramatically by impregnating the oxides with a small amount of the cation belonging to the other oxide (Sb for SnO_2 and Sn for Sb_2O_4) [2].

The recent breakthrough in the chemistry of catalysis by nonzeolitic solid superacids is related, in particular to the problem of activation and utilization of paraffins as well as to new applications of superacids for the production of fine chemicals. Solid superacids have been synthesized by the addition of sulfate ion to Fe_2O_3 [3], TiO_2 [4] ZrO_2 [5,6] and HfO_2 [7]. The activity enhancement of metal oxides by sulfate addition was not observed for MgO, CaO, CuO, NiO, ZnO, CdO, Al_2O_3, La_2O_3, MnO_2, ThO_2, Bi_2O_4 and CrO_3 [8]. For SnO_2, acidity and activity are remarkably enhanced by sulfate addition, though its highest acid strength was not superacidic, $H_o = -8.2$ [9]. It was shown that for the surface of activated oxides modified by sulfate ion, the sulfate groups were described as covalently bonded to the metal oxide lattice [6,10,11]. Among the solid superacids studied so far [12-14] sulfate supported zirconia is highest in acid strength ($H_o \leq -16.04$). Sulfated ternary oxide containing Fe, Mn and Zr has recently been developed, by Hsu et al. [15] and has shown higher superacidity than SO_4^{2-} / ZrO_2.

In this work, we have investigated the changes in surface acidity/basicity and catalytic activity of tin oxide when it is modified with sulfate ion. We have attempted to study the electron donor properties of SnO_2 and SO_4^{2-} /SnO_2. The purpose of this study is to find out whether the increase in acidity due to sulfation can be at the expense of basic sites already present on the surface, or it can be due to the generation of new acidic sites.

In order to correlate, the acidity/basicity with catalytic activity, esterification of acetic acid using n-butanol, reduction of cyclohexanone in 2-propanol and oxidation of cyclohexanol with benzophenone are the selected reactions.

8.2 EXPERIMENTAL

Tin oxide prepared from stannous chloride after oxidation with aquaregia. Sulfation was carried out by impregnation with 0.2 N ammonium sulfate solution. The samples activated at different activation temperatures of 300, 500 and 700°C were used. The surface area of the samples were determined by BET method. The surface area of the samples are given in Table 8.1

Table 8.1: Surface area of SnO_2 and SO_4^{2-}/SnO_2 at different activation temperatures

Catalyst	Activation temperature (°C)	Surface area ($m^2 g^{-1}$)
SnO_2	300	122.33
SnO_2	500	31.72
SnO_2	700	13.68
SO_4^{2-}/ SnO_2	300	133.77
SO_4^{2-}/ SnO_2	500	54.30
SO_4^{2-}/ SnO_2	700	22.22

8.3 RESULTS AND DISCUSSION

8.3.1 Acidity/Basicity

The Hammett indicator used for acidity/basicity studies are given in Table 4.2. Among them SnO_2 and SO_4^{2-}/SnO_2 responded only to three indicators. They are dimethyl yellow, methyl red and bromothimol blue.

Table 8.2: Acid-base strength distribution of SnO_2 and SO_4^{2-}/SnO_2 at different activation temperatures

Catalyst	Activation Temp. ^oC)	Basicity (10^{-3} mmol m^{-2})	Acidity (10^{-3} mmol m^{-2})		
		$H_0 \geq 3.3$	$H_0 \leq 3.3$	$H_0 \leq 4.8$	$H_0 \leq 7.2$
SnO_2	300	0.66	--	1.99	2.89
SnO_2	500	0.85	--	2.57	12.80
SnO_2	700	1.97	--	3.90	13.90
SO_4^{2-}/SnO_2	300	--	0.61	2.43	3.34
SO_4^{2-}/SnO_2	500	--	2.50	4.00	9.01
SO_4^{2-}/SnO_2	700	--	2.45	6.11	23.23

The results of acid-base strength distribution at different activation temperatures are given in Table 8.2. The acid base strength distribution curves are given in Figure 8.1. $H_{0,\ max}$ values obtained at different activation temperatures are given in Table 8.3.

Table 8.3 $H_{0,\ max}$ values of SnO_2 and SO_4^{2-}/SnO_2 at different activation temperatures of 300, 500 and 700°C

Catalyst	Activation temperature (^oC)	$H_{0,\ max}$
SnO_2	300	3.72
SnO_2	500	3.74
SnO_2	700	3.85
SO_4^{2-}/SnO_2	300	--
SO_4^{2-}/SnO_2	500	--
SO_4^{2-}/SnO_2	700	--

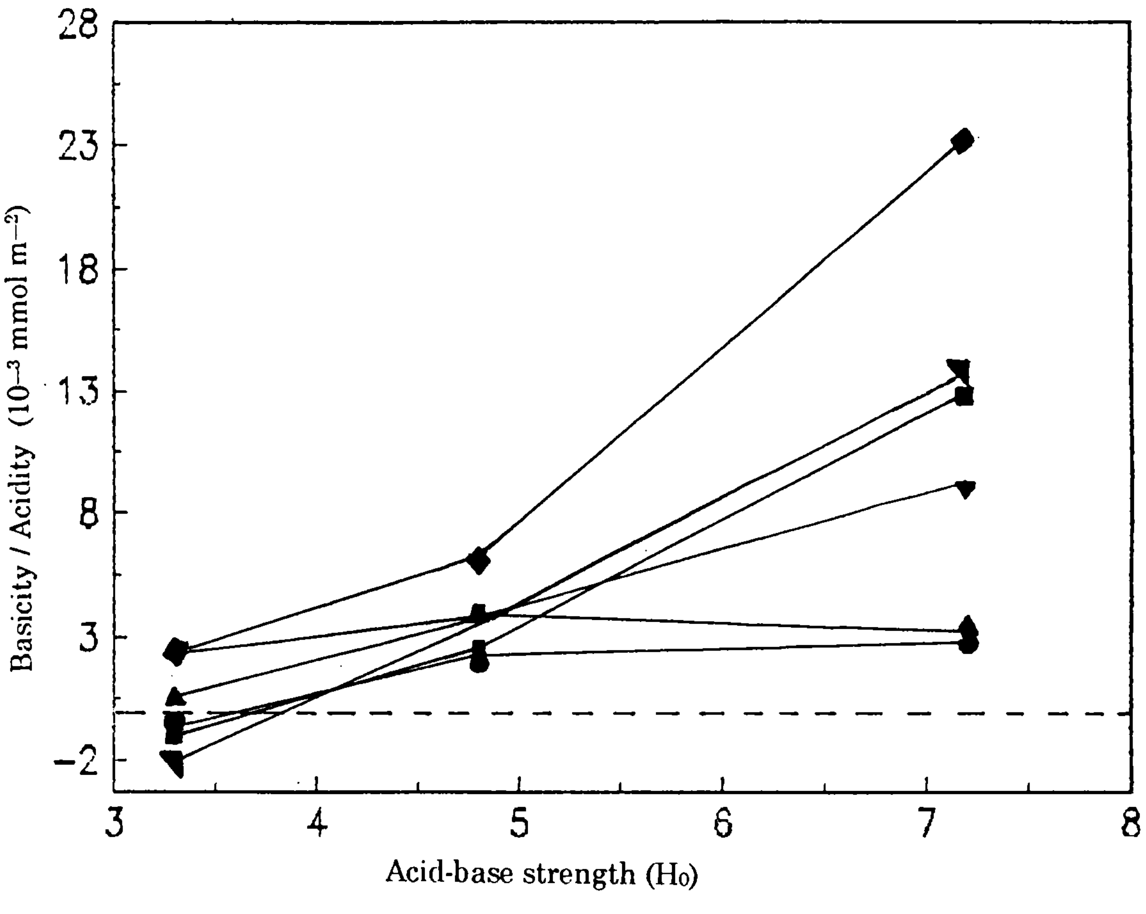


Figure 8.1: Acid base strength curves for tin oxide and sulfated tin oxide at different activation temperatures (°C)

●	SnO_2 300	▲	SO_4^{2-} / SnO_2 300
■	SnO_2 500	▼	SO_4^{2-} / SnO_2 500
◥	SnO_2 700	◆	SO_4^{2-} / SnO_2 700

From the data it was found that unmodified SnO_2 shows maximum acidity at H_0 value 7.2. SnO_2 shows very weak basicity at H_0 value 3.3. This implies the presence of weak acidic and basic sites on the surface. As activation temperature increases, $H_{0,\,max}$ value decreases which indicates that the acidity also increases.

Regarding sulfate modified tin oxide acidity was generated at H_o value of 3.3, 4.8 and 7.2. In the case of SnO_2/SO_4^{2-}, it is impossible to find out $H_{o,\,max}$ values, even by extrapolation. This itself indicate that sulfated SnO_2 is more acidic than unmodified ones. H_o values show that sulfated SnO_2 does not have as strong acid sites as other solid superacids. It may be due to the nature of SnO_2 used for the study and also due to the concentration of sulfate ions present on it, which in turn depend on many of the preparative parameters [16]. From $H_{0,\,max}$ values, it can be seen that, as activation temperature increases, acidity increases for both SnO_2 and SO_4^{2-}/SnO_2. An increase in temperature causes change in crystallinity from amorphous to monoclinic form of SnO_2. As discussed in chapter VII, calcination at an appropriate temperature results in the formation of sulfur species with a proper configuration that generates strong acidity. At high temperature lattice distortion can also contribute to an increase in acid sites. Activation at higher temperature facilitates the crystallisation, resulting in the stabilized surface states and decreasing the surface area leading to a decrease in number and strength of the active sites.

8.3.2 Electron donor properties

As discussed in chapter IV, the electron donor properties of SnO_2 and SO_4^{2-}/SnO_2 have been determined. Langmuir adsorption isotherms obtained by the adsorption of chloranil and TCNQ are given in Figures 8.2 and 8.3. Limiting amount of electron acceptors adsorbed calculated from Langmuir adsorption isotherms are given in Table 8.4.

When the electron acceptors are adsorbed from solution chloranil gave a light yellow colour and TCNQ gave an ash colour for both SnO_2 and SO_4^{2-}/SnO_2, which indicate the formation of new adsorbed species. The electronic state of adsorbed species was studied by esr spectroscopy in addition to electronic spectroscopy (chapter IV).

Plot of radical concentration against equilibrium concentration are of Langmuir type and are of the same shape as shown in Figures 8.2 and 8.3. Limiting radical concentration of the electron acceptor adsorbed calculated from such plots are given in Table 8.4.

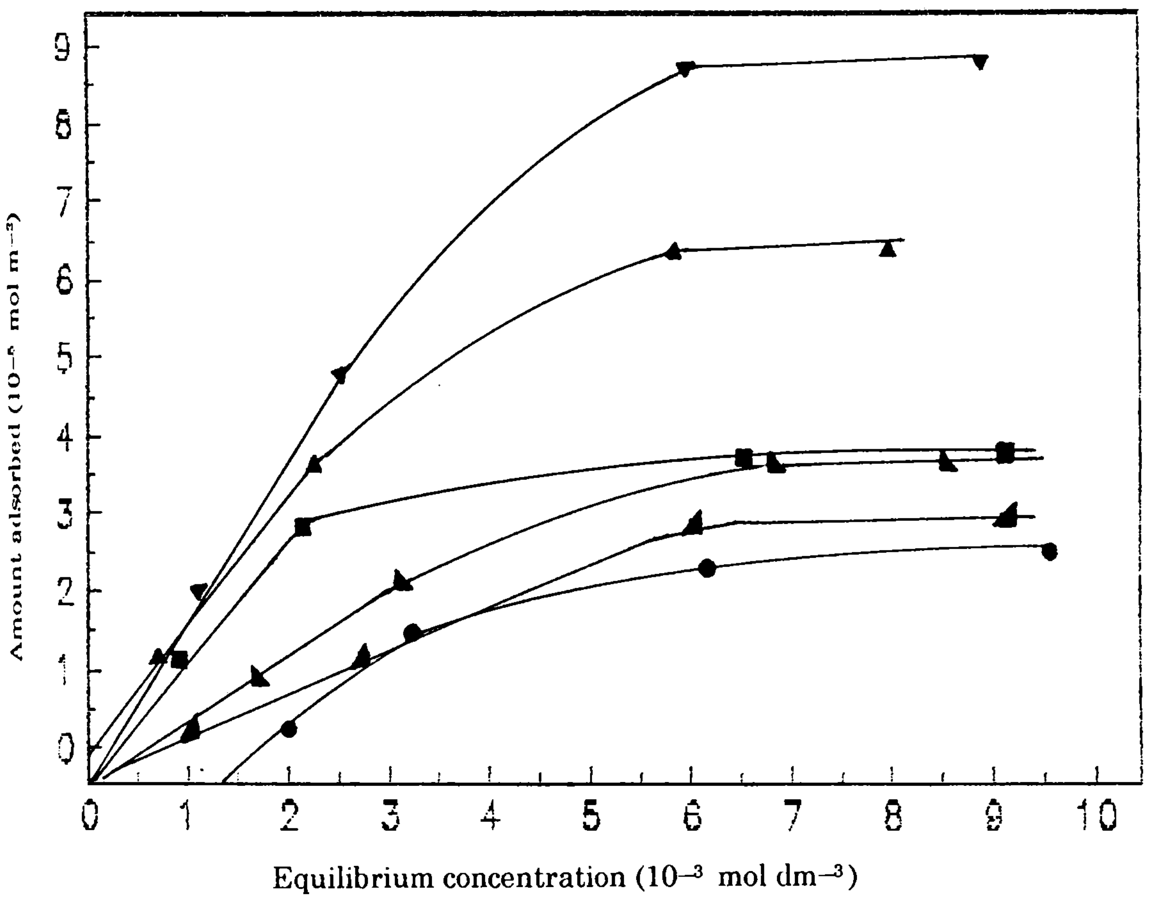
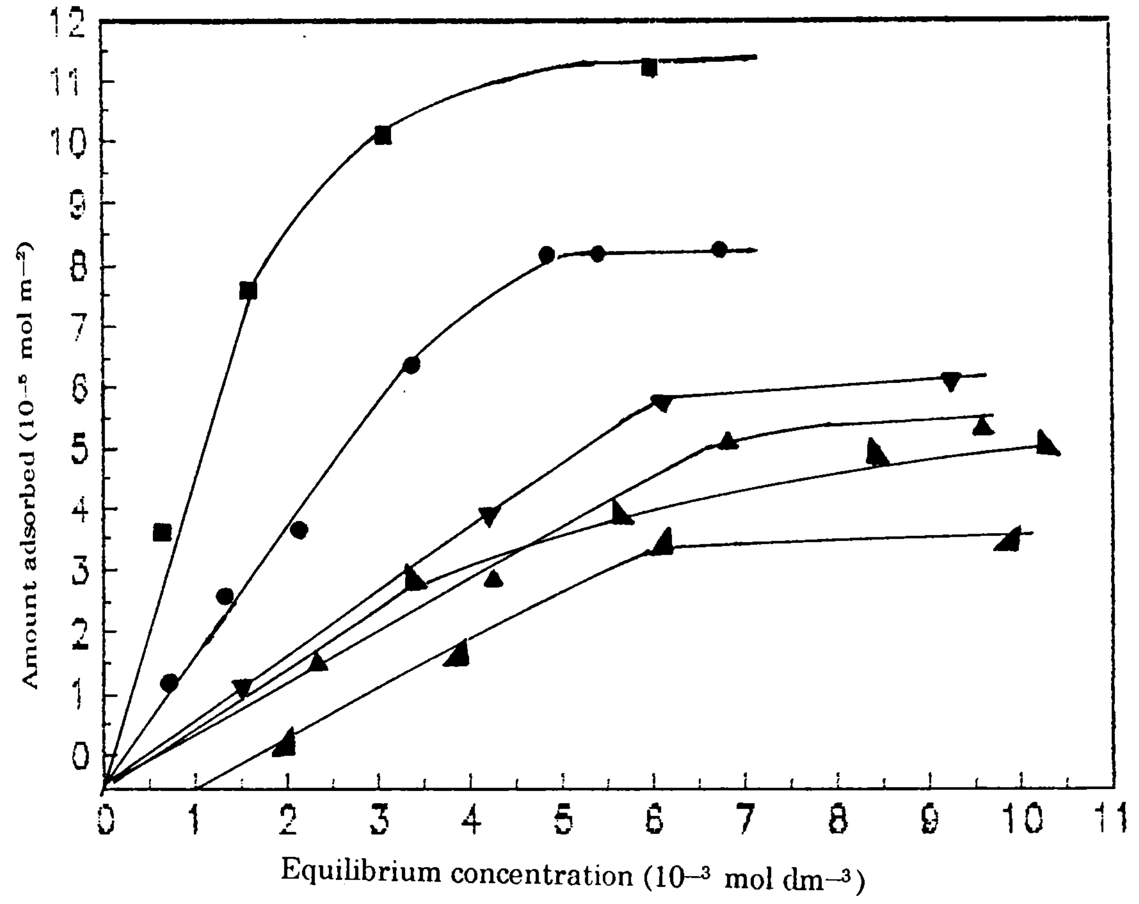


Figure 8.2: Langmuir adsorption isotherms of chloranil adsorbed on tin oxide and sulfated tin oxide at different activation temperatures (°C)

▲ SnO_2 300
▼ SnO_2 500
◣ SnO_2 700

◢ SO_4^{2-}/ SnO_2 300
■ SO_4^{2-}/ SnO_2 500
● SO_4^{2-}/ SnO_2 700



igure 8.3: Langmuir adsorption isotherms of TCNQ adsorbed on tin oxide and sulfated tin oxide at different activation temperatures (°C)

● SnO_2 300

■ SnO_2 500

◢ SnO_2 700

▲ SO_4^{2-}/SnO_2 300

▼ SO_4^{2-}/SnO_2 500

◢ SO_4^{2-}/SnO_2 700

Table 8.4: Limiting amount and limiting radical concentration of electron acceptors adsorbed on SnO_2 and SO_4^{2-}/SnO_2 at different activation temperatures

Catalyst	Activation temp. (°C)	Limiting amount of electron acceptor adsorbed (10^{-5} mol m^{-2})		Limiting radical concentration of electron acceptor adsorbed (10^{18} spin m^{-2})	
		Chloranil	TCNQ	Chloranil	TCNQ
SnO_2	300	6.40	8.20	0.19	4.23
SnO_2	500	8.76	11.27	0.27	5.82
SnO_2	700	3.74	5.05	0.11	2.61
SO_4^{2-}/SnO_2	300	2.95	5.38	0.09	2.78
SO_4^{2-}/SnO_2	500	3.81	6.09	0.12	3.14
SO_4^{2-}/SnO_2	700	2.52	3.49	0.08	1.80

The difference in limiting amount of chloranil and TCNQ adsorbed on the surface would be an estimate of the stronger donor sites. The limit of electron transfer in terms of electron affinity is between 1.77 and 2.40 for SnO_2 and SO_4^{2-} / SnO_2.

From the data it is clear that as temperature increases, surface electron property increases up to 500°C for both SnO_2 and SO_4^{2-}/SnO_2. The decrease in electron donocity after 500°C may be attributed to the change in crystallinity from amorphous to monochlinic form.

From the data it has been found that the electron donocity of SnO_2 decreased by modification with sulfate ion. This decrease may be attributed to the increase in acidity on modification with sulfation. The study of electron donor properties revealed that, some of the basic sites are converted to acidic sites on modification with sulfate ions. Limiting amount of the electron acceptor adsorbed as a function of activation temperature is given in Figure 8.4.

8.3.3 Catalytic activity

8.3.3.1 Esterification of Acetic acid using n-Butanol

In order to evaluate the increase in acidity on modification with sulfate ion, esterification of acetic acid with n-butanol has been selected as a test reaction. The mechanism is described in chapter IV. As in previous chapters, the activity is expressed as 1st order rate coefficient for the conversion of acetic acid per unit area of the catalyst surface. The data for esterification reaction are given in Table 8.5. The data indicate that sulfate modified tin oxide catalyzes the reaction more effectively than the unmodified ones. Esterification is a typical Bronsted acid catalyzed reaction. On modification with sulfate ions both acidity and acid strength increases resulting in higher catalytic activity, which is found to be in agreement with the acid-base properties. Detailed explanation given in section 8.3.1. Catalytic activity as a function of activation temperature is given in Figure 8.5.

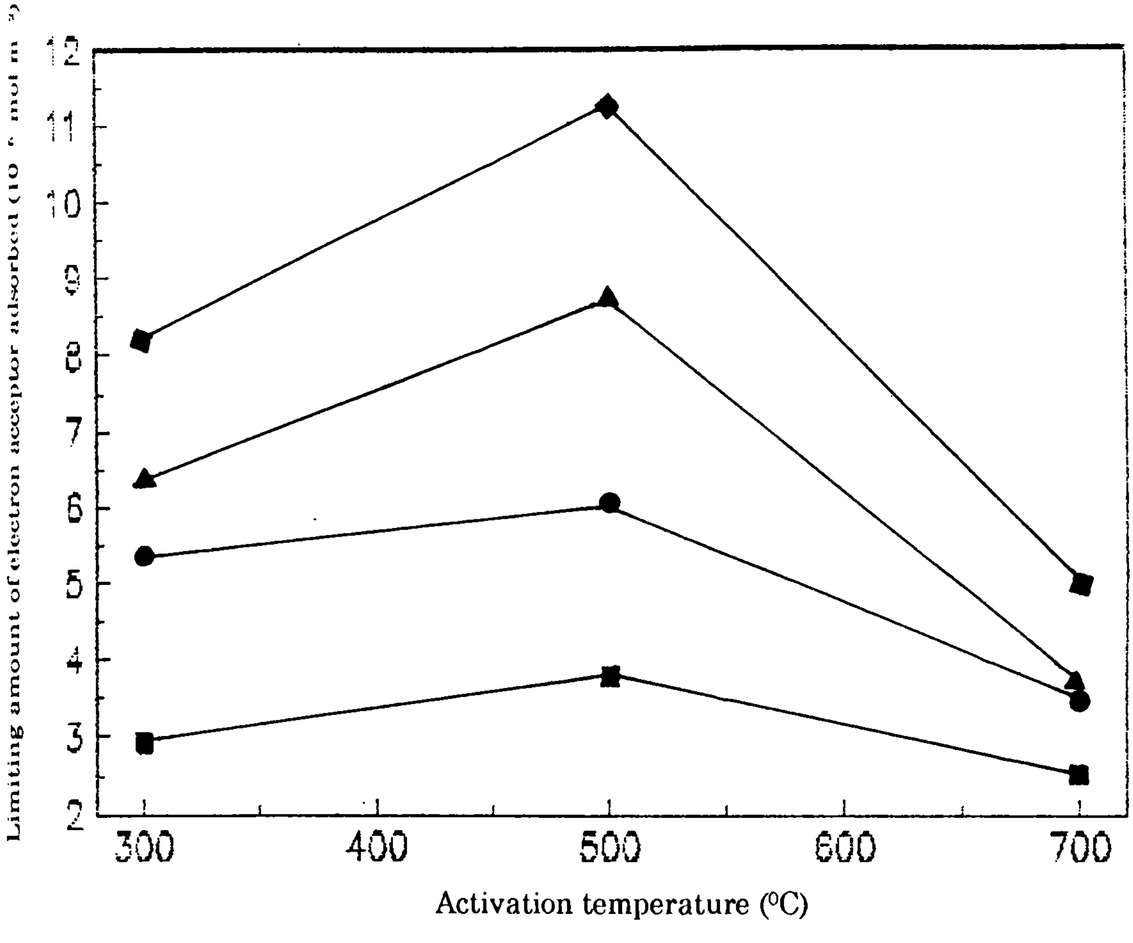


Figure 8.4: Limiting amount of electron acceptor adsorbed as a function of activation temperature

▲ SnO_2 Chloranil ■ SO_4^{2-}/SnO_2 Chloranil

◆ SnO_2 TCNQ ● SO_4^{2-}/SnO_2 TCNQ

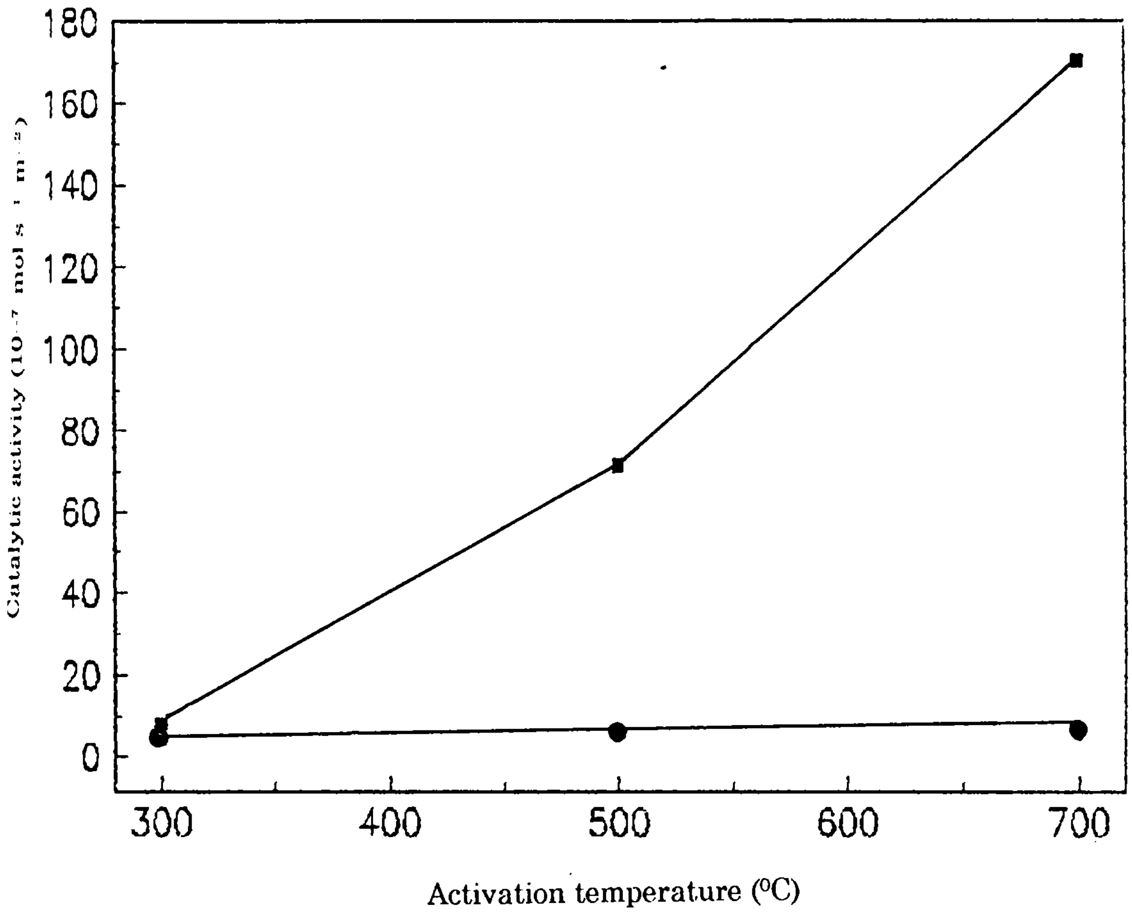


Figure 8.5: Catalytic activity for esterification as a function of activation temperature

● SnO_2 ■ SO_4^{2-}/SnO_2

Table 8.5: Catalytic activity for esterification of acetic acid with n-butanol using SnO_2 and SO_4^{2-}/SnO_2 at different activation temperatures.

Catalyst	Activation temperature (°C)	Percentage conversion	Rate constant ($10^{-6}\,s^{-1}\,m^{-2}$)
SnO_2	300	64.03	0.46
SnO_2	500	28.15	0.58
SnO_2	700	14.18	0.62
SO_4^{2-}/SnO_2	300	85.77	0.81
SO_4^{2-}/SnO_2	500	99.91	7.17
SO_4^{2-}/SnO_2	700	99.89	17.04

8.3.3.2 Reduction of Cyclohexanone in Isopropanol

Mechanism for the reaction is discussed in chapter IV. The data given in Table 8.6.

Table 8.6: Catalytic activity for reduction of cyclohexanone in 2-propanol using SnO_2 and SO_4^{2-}/SnO_2 at different activation temperatures

Catalyst	Activation temperature (°C)	Percentage conversion	Catalytic activity ($10^{-7}\,m^{-2}\,s^{-1}$)
SnO_2	300	30.35	0.82
SnO_2	500	12.72	1.19
SnO_2	700	2.10	0.43
SO_4^{2-}/SnO_2	300	29.78	0.73
SO_4^{2-}/SnO_2	500	18.83	1.02
SO_4^{2-}/SnO_2	700	2.36	0.30

Catalytic activity is expressed as first order rate coefficient for the conversion of cyclohexanone per unit area of the catalyst surface. From the data, it is clear that reduction reaction proceeds effectively over pure SnO_2 owing to its high basicity compared to SO_4^{2-}/ SnO_2. As discussed in chapter IV, a step of hydride transfer from adsorbed isopropanol to the adsorbed carboxyl groups constitute the rate determining step. Basic sites favour hydride transfer. Catalytic activity parallels with the basicity of oxides. The lower catalytic activity of sulfated SnO_2 is attributed to the conversion of some of the basic sites to acidic sites. The data have been correlated with the surface electron properties. (See section 8.3.2). The catalytic activity parallels with the electron donocity. Variation of catalytic activity as a function of activation temperature is given in Figure 8.6.

8.3.3.3 Oxidation of Cyclohexanol using Benzophenone

The mechanism for oxidation of cyclohexanol with benzophenone was described in chapter IV. The data are given in Table 8.7.

The activity is expressed as first order rate coefficient for the conversion of cyclohexanol per unit area of the catalyst surface. Unmodified tin oxide exhibit good catalytic activity for the oxidation of cyclohexanol compared to modified ones. Both modified and unmodified catalysts show maximum

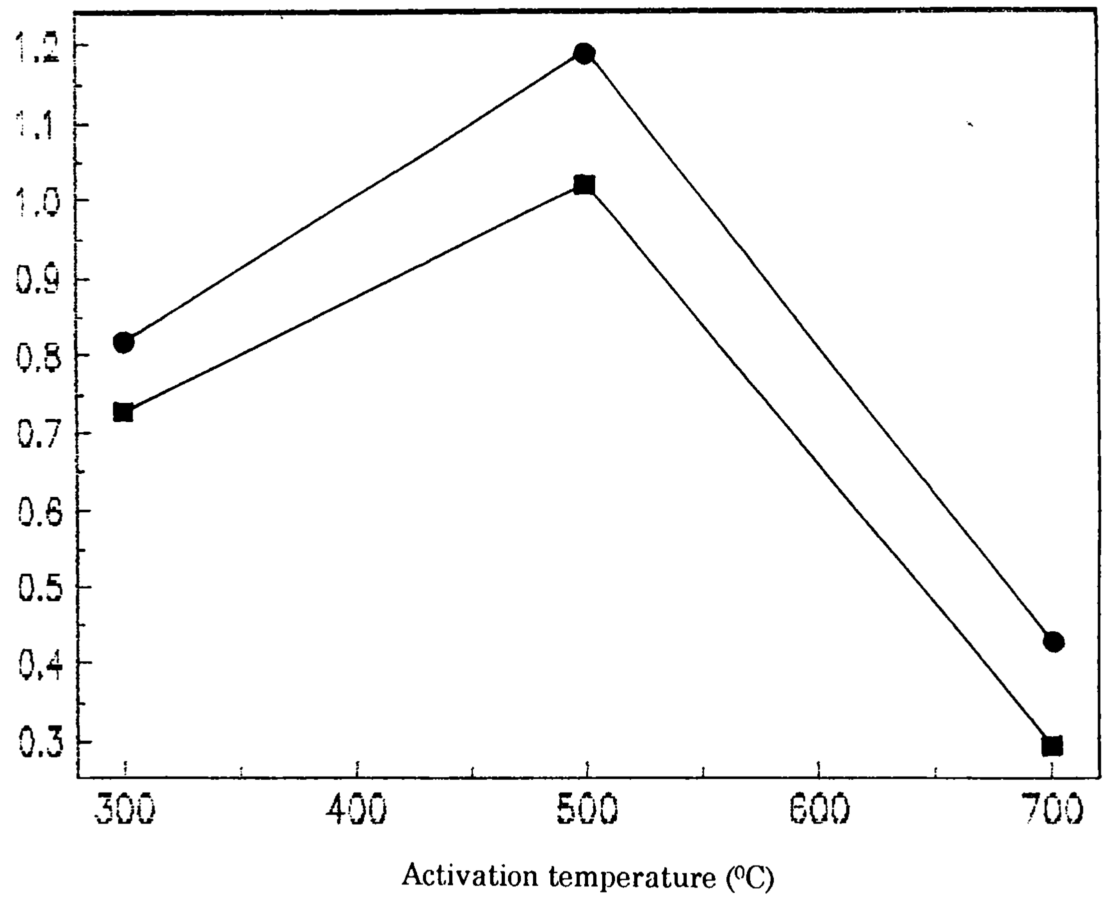


Figure 8.6: Catalytic activity for reduction as a function of activation temperature

● SnO_2 ■ SO_4^{2-}/SnO_2

Table 8.7: Catalytic activity for oxidation of cyclohexanol with benzophenone using SnO_2 and SO_4^{2-}/SnO_2 at different activation temperatures

Catalyst	Activation temperature (°C)	Percentage conversion	Catalytic activity (10^{-6} $s^{-1} m^{-2}$)
SnO_2	300	94.6	3.31
SnO_2	500	87.78	9.21
SnO_2	700	19.43	2.19
SO_4^{2-}/SnO_2	300	92.67	2.71
SO_4^{2-}/SnO_2	500	96.26	8.48
SO_4^{2-}/SnO_2	700	26.15	1.89

activity at 500°C. The presence of acidic sites are very significant in determining activity. The variation of catalytic activity with temperature is given in Figure 8.7.

Unmodified tin oxide exhibits good catalytic activity for the oxidation of cyclohexanol just like reduction of cyclohexanone, where both reactions are favoured by basic sites. The activity for oxidation decreased on modification with sulfate ion. This may be due to the increase in acidity on modification. In both cases, catalytic activity increases upto 500°C and then decreases, which is in accordance with the acid base properties. The mechanism involves hydride

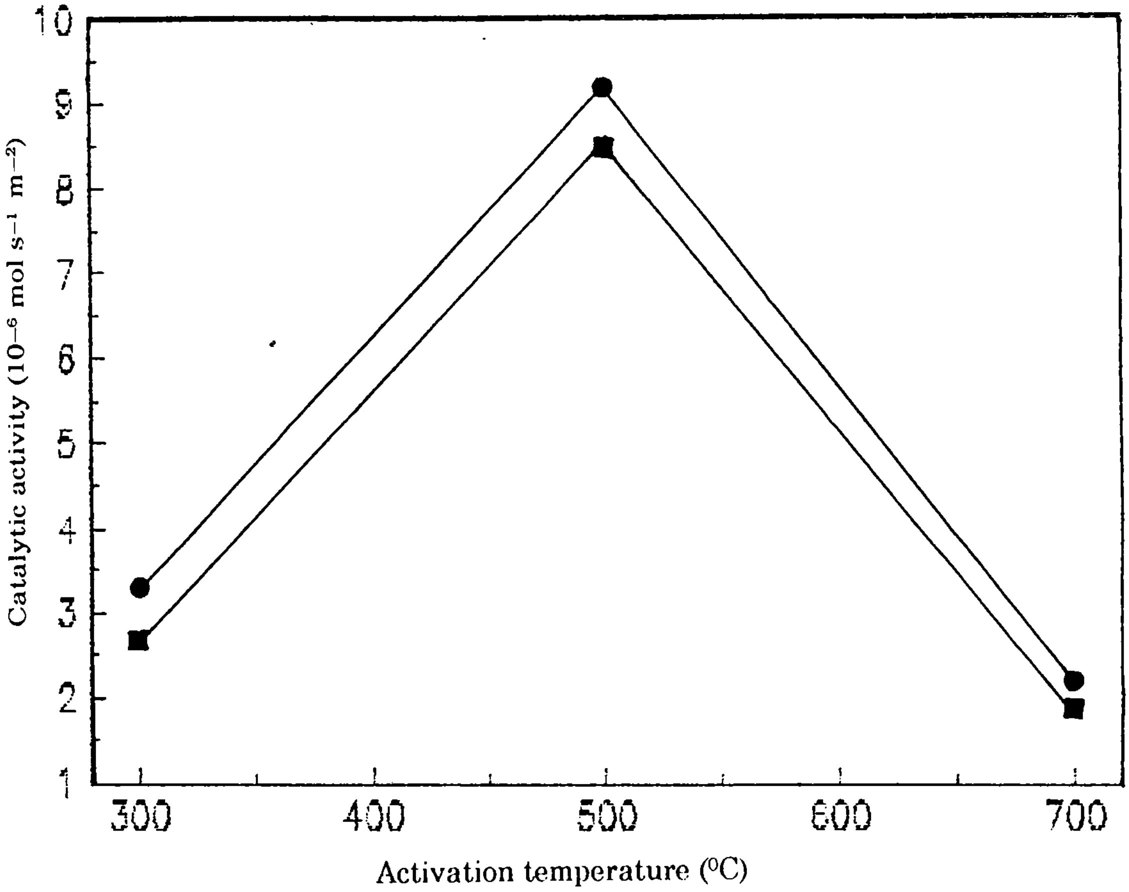


Figure 8.7: Catalytic activity for oxidation as a function of activation temperature

● SnO_2 ■ SO_4^{2-}/SnO_2

ion transfer from alcohol to the carbonyl carbon of ketone. Lewis basicity of catalyst surface favours the hydride transfer. Unmodified tin oxide, due to its high basicity favours oxidation reactions of cyclohexanol effectively. Catalytic activity parallel the electron donocity.

Ai *et al.* [17] assumed that dehydrogenation is catalyzed by both acidic and basic sites through a concerted mechanism. All catalysts active in the selective oxidation of hydrocarbons contain transition metal cations d^0 or d^{10}, configuration. The interaction of weakly basic unsaturated hydrocarbons with transition metal ions can be considered as weak base – strong acid (d^0 cations) or weak base – weak acid (d^{10} cations) interactions [18]. Keeping in mind that the bond between a strong acid and a weak base cannot be strong, it seems clear that an increase in the acidic properties of a cation leads to a weakening of the interaction with a hydrocarbon. The selectivity of the oxidation is thus likely to be improved.

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Chapter IX

ACIDITY/BASICITY, ELECTRON DONOR PROPERTIES AND CATALYTIC ACTIVITY OF SULFATED ALUMINA

Chapter IX

ACIDITY/BASICITY, ELECTRON DONOR PROPERTIES AND CATALYTIC ACTIVITY OF SULFATED ALUMINA

9.1 INTRODUCTION

Among Al_2O_3, ZrO_2, and TiO_2, Al_2O_3 possesses the strongest Lewis acid sites. ZrO_2 and TiO_2 have comparable acid strength. Impregnation with high amount of SO_4^{2-} generally creates Bronsted acidity on all the oxides [1]. Alumina surface exhibits a remarkable chemical heterogeneity and can be considered as a typical amphoter. The few important types of active sites which exists on alumina surfaces are surface hydroxyls and aluminium cations embedded in a specific neighbourhood. The existence of these sites depends on the calcination temperature of aluminium hydroxide or oxide.

We have attempted to study the changes in surface acidity/basicity and catalytic activity of aluminium oxide due to surface modification by sulfate ion. We have also carried out the study of electron donor properties to find out whether the increase in acidity by sulfation is due to the generation of new acidic sites or they are formed by the conversion of some of the basic sites to acidic sites. We have carried out the study of electron donor properties of both modified and unmodified oxides with electron acceptors of various electron affinity values.

In order to correlate, acidity/basicity with catalytic activity, esterification of acetic acid using 1–butanol, reduction of cyclohexanone in 2–propanol and oxidation of cyclohexanol with benzophenone are the reactions selected.

9.2 EXPERIMENTAL

The detailed procedure for the preparation of alumina and sulfated alumina was given in chapter III. The samples activated at different temperatures of 300, 500 and 700°C were used for study. Surface area of the samples were determined by mercury porosimetry. The values are given in Table 9.1.

Table 9.1: Surface area of alumina and sulfated alumina at different activation temperatures

Catalyst	Activation temperature (°C)	Surface area ($m^2 g^{-1}$)
Al_2O_3	300	84.87
Al_2O_3	500	177.70
Al_2O_3	700	150.51
SO_4^{2-}/Al_2O_3	300	134.54
SO_4^{2-}/Al_2O_3	500	183.65
SO_4^{2-}/Al_2O_3	700	156.53

9.3 RESULTS AND DISCUSSION

9.3.1 Actidity/basicity

The list of Hammett indicators used for acidity/basicity measurements are given in chapter IV (Table 4.2). Among them, alumina and sulfated alumina responded only to three indicators. They are dimethyl yellow, methyl red and bromothymol blue. The results of acid base strength distribution at different activation temperatures are given in Table 9.2.

Table 9.2: Acid-base strength distribution of alumina and sulfated alumina at different activation temperatures

Catalyst	Activation Temp. (°C)	Basicity (10^{-3} mmol m^{-2})			Acidity (10^{-3} mmol m^{-2})	
		$H_0 \geq 3.3$	$H_0 \geq 4.8$	$H_0 \geq 7.2$	$H_0 \leq 4.8$	$H_0 \leq 7.2$
Al_2O_3	300	5.09	1.59	2.86	--	--
Al_2O_3	500	1.98	0.76	1.52	--	--
Al_2O_3	700	3.77	1.79	1.26	--	--
SO_4^{2-}/Al_2O_3	300	1.20	--	--	0.61	3.03
SO_4^{2-}/Al_2O_3	500	1.17	--	--	1.48	3.40
SO_4^{2-}/Al_2O_3	700	1.21	--	--	0.87	3.99

The acid base strength distribution curves are given in Figure 9.1. The $H_{0,max}$ values are given in Table 9.3.

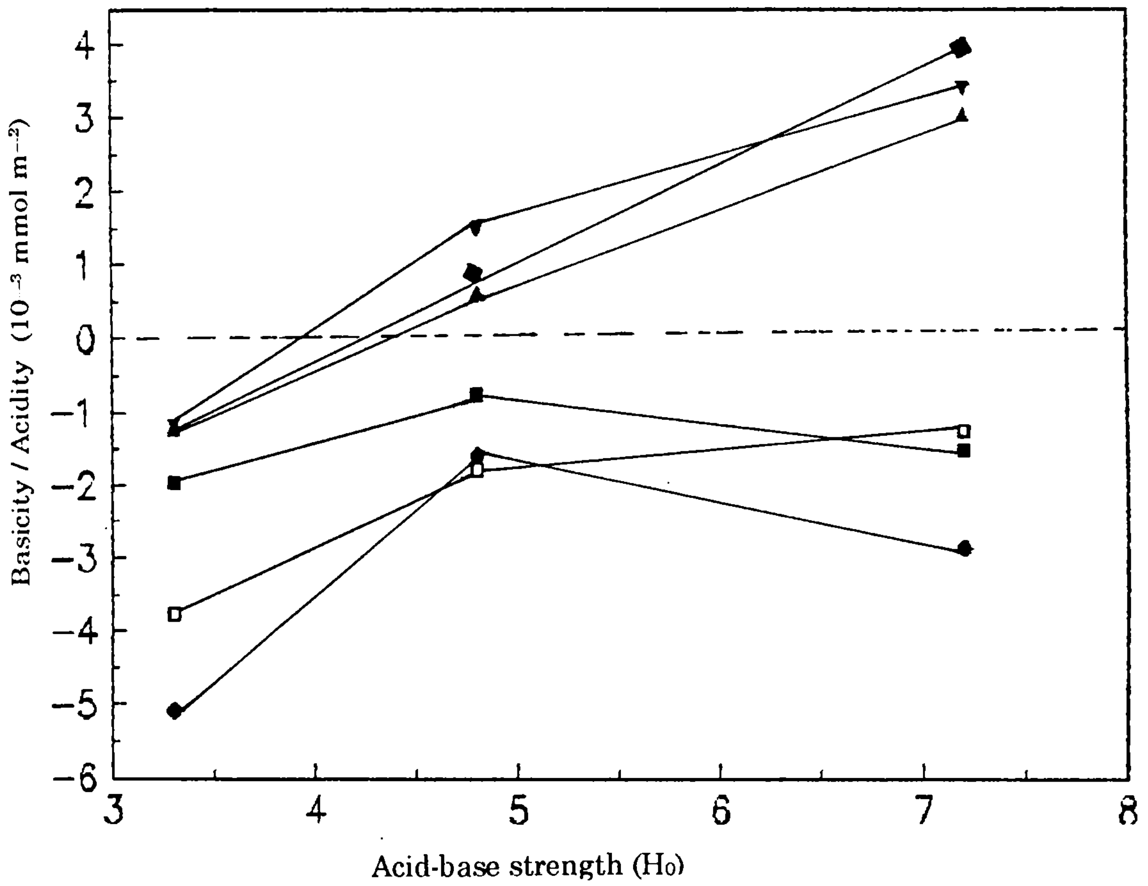

Figure 9.1: Acid base strength distribution curves for alumina and sulfated alumina at different activation temperatures (°C)

● Al_2O_3 300
■ Al_2O_3 500
□ Al_2O_3 700
▲ SO_4^{2-}/ Al_2O_3 300
▼ SO_4^{2-}/ Al_2O_3 500
◆ SO_4^{2-}/ Al_2O_3 700

Table 9.3 $H_{0,\ max}$ values of alumina and sulfated alumina at different activation temperatures

Catalyst	Activation temperature $({}^{0}C)$	$H_{0,\ max}$
Al_2O_3	300	--
Al_2O_3	500	--
Al_2O_3	700	--
$SO_4^{2-}/\ Al_2O_3$	300	4.21
$SO_4^{2-}/\ Al_2O_3$	500	3.90
$SO_4^{2-}/\ Al_2O_3$	700	4.15

From the data, it can be observed that as the activation temperature increases, the acidity increases for both alumina and sulfated alumina. Data show that Al_2O_3 is basic in nature. But on modification with sulfate ion, acidity is generated at H_o values of 4.8 and 7.2. It shows basicity only at H_o value 3.3 implying that it is weakly basic.

The infrared spectra of sulfated alumina shows a strong adsorption band at 1380 cm^{-1}, which is in agreement with literature values. Both alumina and sulfated alumina show maximum acidity at $500^{0}C$.

In general, alumina shows strong surface acidity when heated to temperature above $470^{0}C$ in a vacuum [4]. Pine et al. using a range of indicators concluded that alumina displayed Lewis acidity [5]. Pine et al., have carried out a series of interesting stereochemical studies which strongly suggest that alumina contains intrinsic basic sites as well as acid sites, and acts as an acid-base bifunctional catalyst [6].

9.3.2 Electron donor properties

Langmuir adsorption isotherm obtained by the adsorption of chloranil and TCNQ are given in Figures 9.2 and 9.3. The limiting amount of electron acceptor adsorbed, calculated from Langumir isotherm is given in Table 9.4. Limiting radial concentration of the electron acceptor are given in Table 9.5.

Table 9.4: Limiting amount of electron acceptor adsorbed on alumina and sulfated alumina

Catalyst	Activation temp. (°C)	Limiting amount of electron acceptor adsorbed (10^{-5} mol m^{-2})	
		Chloranil	TCNQ
Al_2O_3	300	11.94	28.86
Al_2O_3	500	7.84	14.11
Al_2O_3	700	8.17	16.09
SO_4^{2-}/ Al_2O_3	300	4.16	9.97
SO_4^{2-}/ Al_2O_3	500	3.28	3.84
SO_4^{2-}/ Al_2O_3	700	5.34	9.78

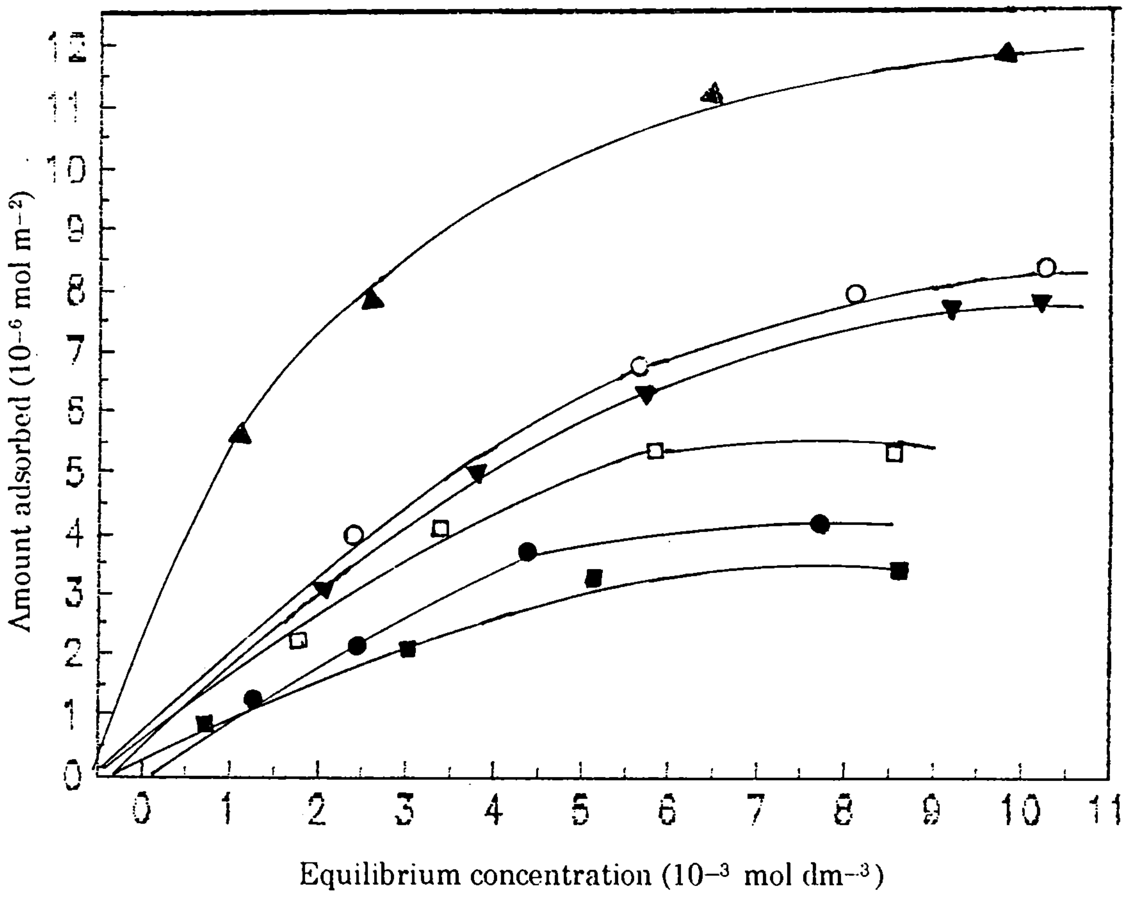

Figure 9.2: Langmuir adsorption isotherms of chloranil adsorbed on alumina and sulfated alumina at different activation temperatures (°C)

▲	Al_2O_3 300	□	SO_4^{2-}/ Al_2O_3 300
▼	Al_2O_3 500	■	SO_4^{2-}/ Al_2O_3 500
○	Al_2O_3 700	●	SO_4^{2-}/ Al_2O_3 700

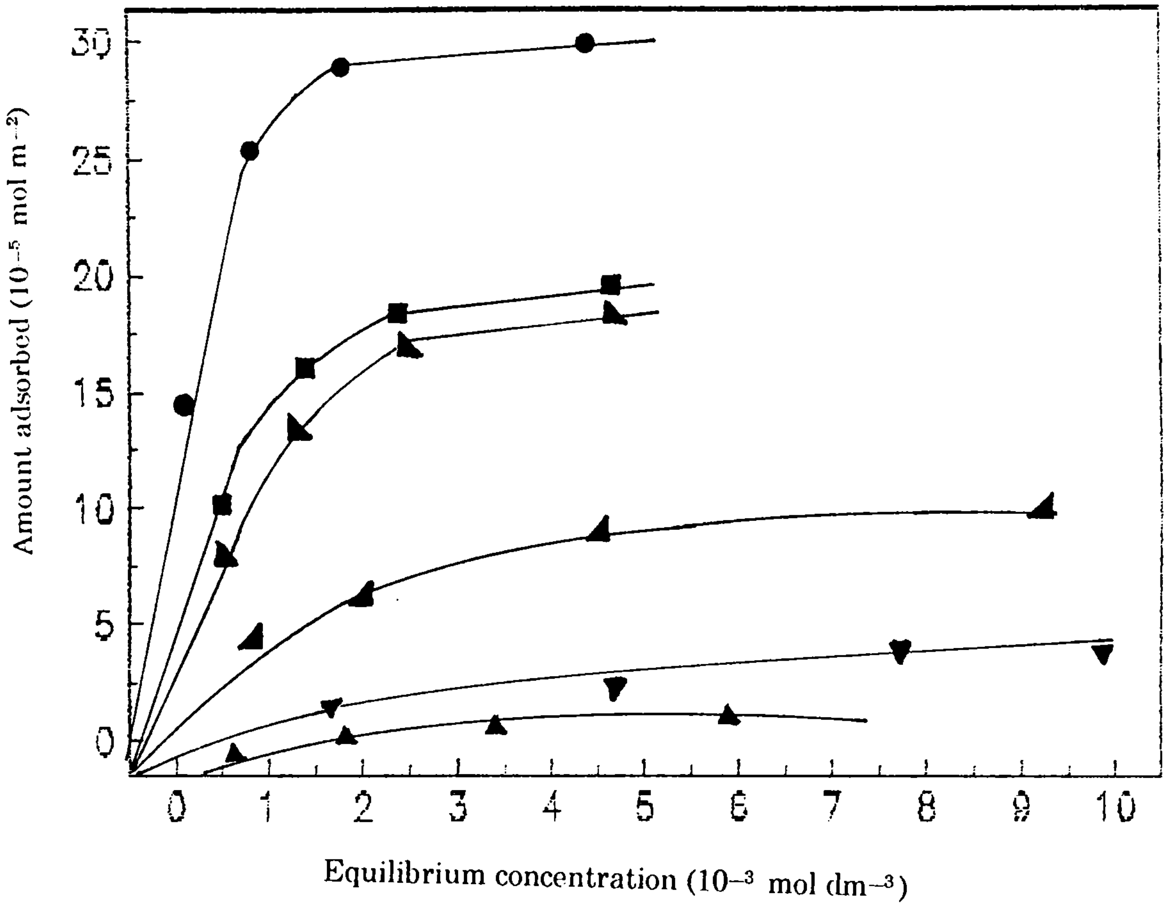

Figure 9.3: Langmuir adsorption isotherms of TCNQ adsorbed on alumina and sulfated alumina at different activation temperatures (°C)

●	Al_2O_3 300	◢	SO_4^{2-}/ Al_2O_3 300
◣	Al_2O_3 500	▲	SO_4^{2-}/ Al_2O_3 500
■	Al_2O_3 700	▼	SO_4^{2-}/ Al_2O_3 700

Table 9.5: Limiting radical concentration of electron acceptor adsorbed on alumina and sulfated alumina at different activation temperatures

Catalyst	Activation temp. (°C)	Limiting radical concentration (10^{18} spin m^{-2})	
		Chloranil	TCNQ
Al_2O_3	300	0.36	14.90
Al_2O_3	500	0.24	7.28
Al_2O_3	700	0.25	8.31
SO_4^{2-}/ Al_2O_3	300	0.13	5.15
SO_4^{2-}/ Al_2O_3	500	0.01	1.98
SO_4^{2-}/ Al_2O_3	700	0.16	5.05

The difference in limiting amount of TCNQ and chloranil adsorbed on the surface would be an estimate of the stronger donor sites. The limit of electron transfer in terms of electron affinity is between 1.77 and 2.40 for Al_2O_3 and sulfated alumina.

For both alumina and sulfated alumina, as temperature increases electron donocity decreases up to 500°C and then increases. As temperature increases, the number of OH groups decreases due to desorption of water molecules by the dehydroxylation process from adjacent OH groups and hence electron donocity decreases. After 500°C, the electron donocity increases which may be due to the availability of trapped electrons in defect sites.

For sulfated alumina, the electron donocity is further decreased. This decrease may be attributed to the conversion of some of the basic sites into acidic sites during sulfation. The variation of limiting amount of the electron acceptor adsorbed with activation temperature is given in Figure 9.4.

9.3.3 Catalytic activity

9.3.3.1 Esterification of Acetic acid using n-Butanol

The data for esterification reaction are given in Table 9.6.

Table 9.6: Catalytic activity for esterification of acetic acid with n-butanol using alumina and sulfated alumina at different activation temperatures.

Catalyst	Reaction Time (hrs)	Activation temperature (°C)	Percentage conversion	Rate constant (10^{-6} s^{-1} m^{-2})
Al_2O_3	5	300	28.50	2.19
Al_2O_3	5	500	62.06	2.86
Al_2O_3	5	700	24.28	1.03
SO_4^{2-}/Al_2O_3	1	300	42.45	11.4
SO_4^{2-}/Al_2O_3	1	500	64.60	15.7
SO_4^{2-}/Al_2O_3	1	700	16.13	3.12

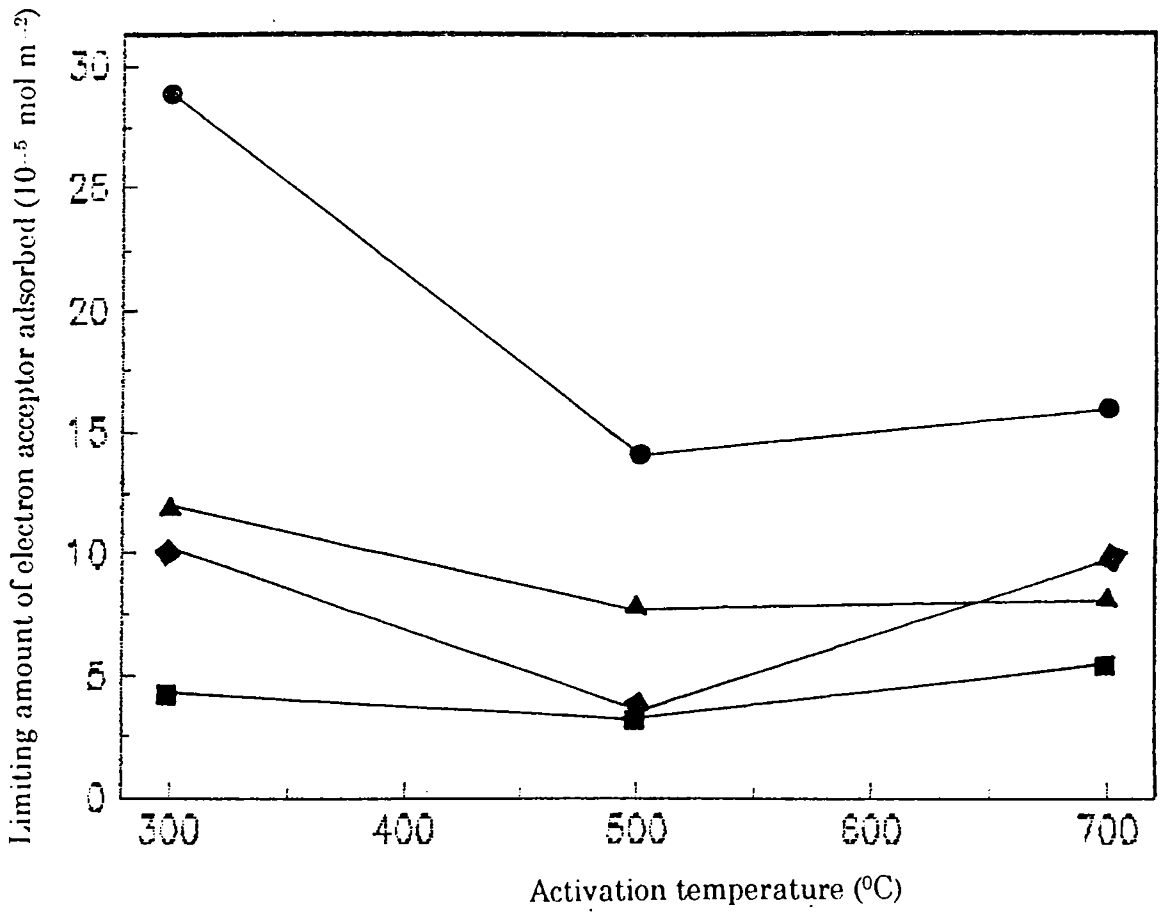

Figure 9.4: Limiting amount of electron acceptor adsorbed as a function of activation temperatures

▲	Al_2O_3 Chloranil	◆	SO_4^{2-} / Al_2O_3 Chloranil
●	Al_2O_3 TCNQ	■	SO_4^{2-} / Al_2O_3 TCNQ

Due to the high catalytic activity of sulfated alumina, data after one hour is taken to calculate the activity. In the case of unmodified alumina, reaction was studied up to 5 hours to get appreciable percentage conversion.

The data indicate that sulfate modified alumina catalyses the esterification reaction effectively than the unmodified ones. On modification with sulfate ion, both acidity and acid strength increases resulting in higher catalytic activity. The catalytic activity is found to be in agreement with the acid base properties. The variation of catalytic activity with temperature is given in Figure 9.5.

9.3.3.2 Reduction of Cyclohexanone in Isopropanol

The mechanism for reduction is described in chapter IV. The data given in Table 9.7.

Table 9.7: Catalytic activity for the reduction of cyclohexanone in isopropanol using alumina and sulfated alumina at different activation temperatures

Catalyst	Activation temperature (°C)	Percentage conversion	Catalytic activity (10^{-7} m^{-2} s^{-1})
Al_2O_3	300	67.06	3.60
Al_2O_3	500	59.33	1.47
Al_2O_3	700	58.44	1.62
SO_4^{2-} / Al_2O_3	300	71.22	2.57
SO_4^{2-}/ Al_2O_3	500	49.02	1.02
SO_4^{2-}/ Al_2O_3	700	53.33	1.35

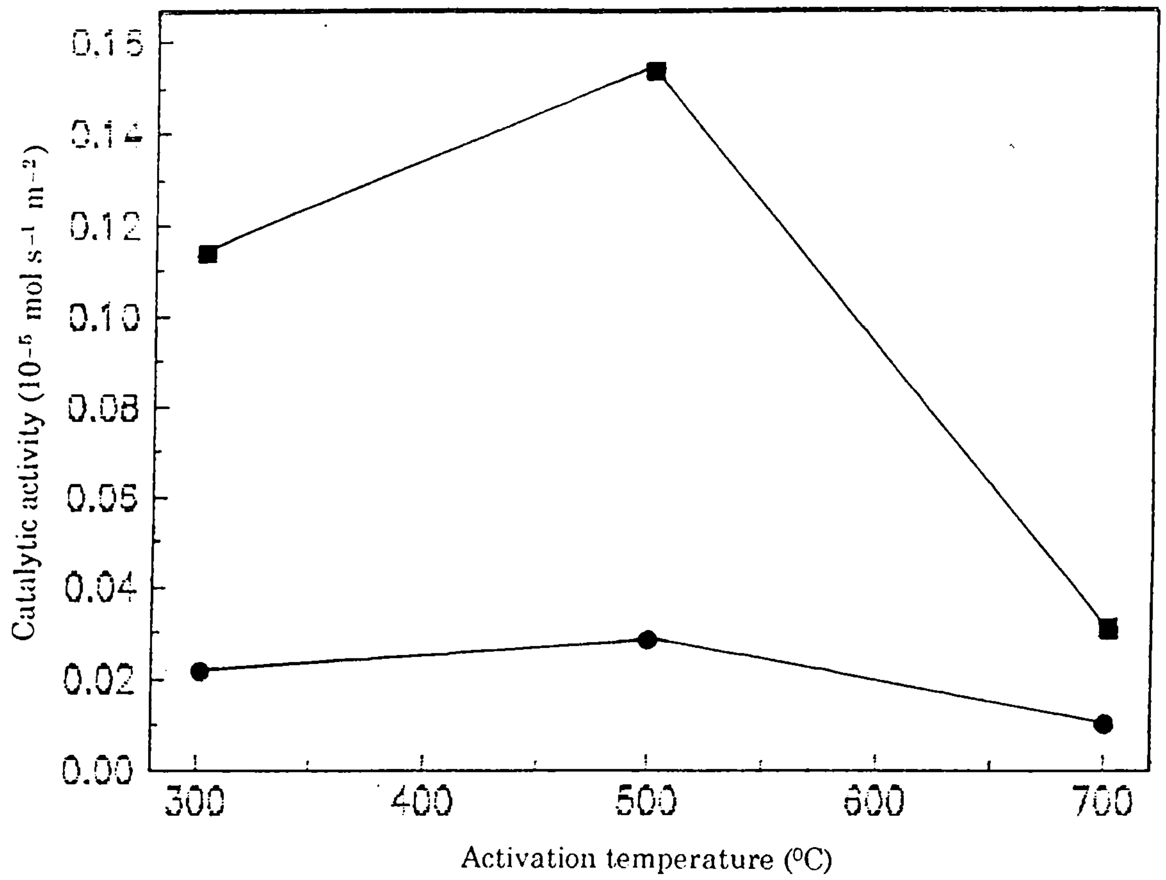

Figure 9.5: Catalytic activity for esterification as a function of activation temperature

● Al_2O_3 ■ SO_4^{2-}/Al_2O_3

The data indicate that the reduction reaction proceeds effectively over unmodified alumina owing to its higher basicity. The data have been correlated with the surface electron donor property of the oxides, which is in agreement with the acid-base properties. Variation of catalytic activity with temperature is given in Figure 9.6.

9.3.3.3 Oxidation of Cyclohexanol using Benzophenone

The mechanism is described in chapter IV. Data are given in Table 9.8.

Table 9.8: Catalytic activity for oxidation of cyclohexanol with benzophenone using alumina and sulfated alumina at different activation temperatures

Catalyst	Activation temperature (°C)	Percentage conversion	Catalytic activity (10^{-6} $s^{-1}m^{-2}$)
Al_2O_3	300	82.21	2.83
Al_2O_3	500	85.48	1.51
Al_2O_3	700	39.25	0.46
SO_4^{2-}/Al_2O_3	300	83.01	1.83
SO_4^{2-}/Al_2O_3	500	14.76	0.12
SO_4^{2-}/Al_2O_3	700	67.93	1.01

The data indicate that oxidation reaction takes place effectively over unmodified alumina than modified ones, which may be attributed to the

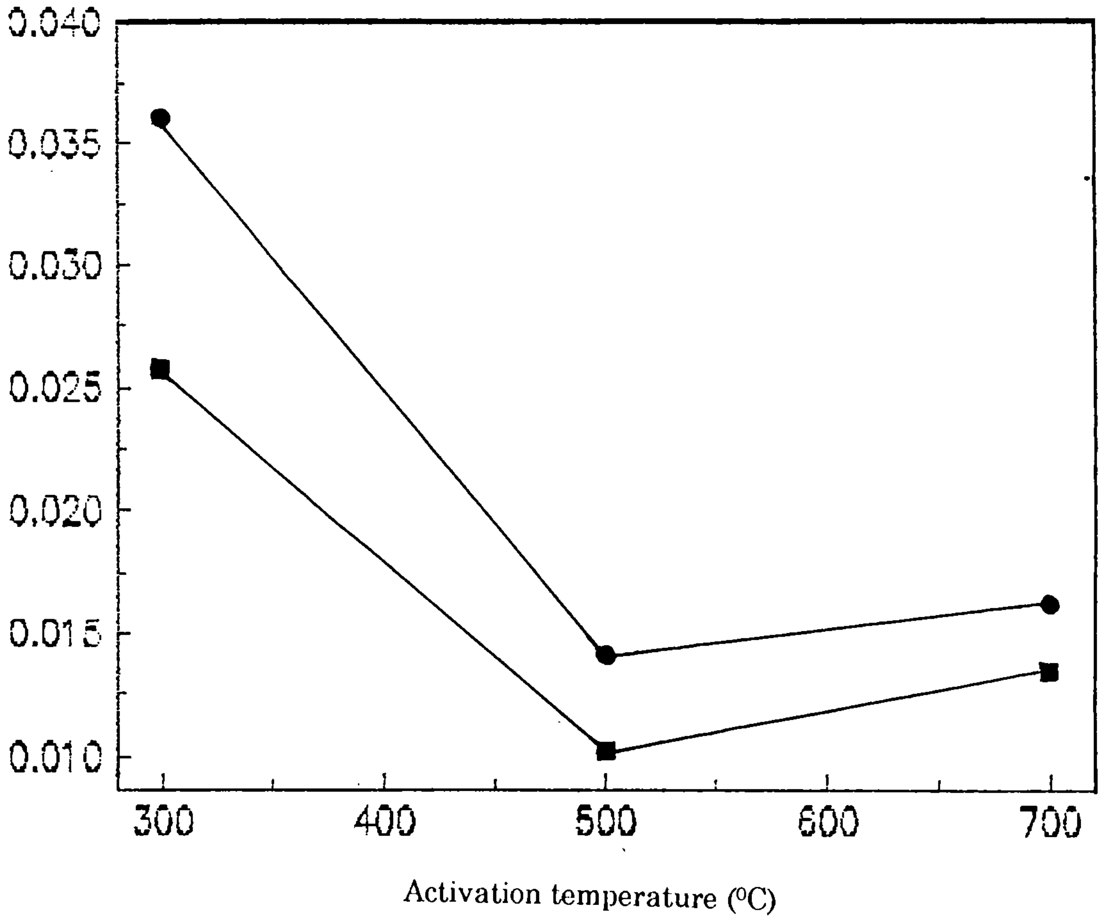

Figure 9.6: Catalytic activity for reduction as a function of activation temperature

● Al_2O_3 ■ SO_4^{2-}/Al_2O_3

increase in acidity on modification with sulfate ion. The catalytic activity can be correlated with the acid-base property. The ability of the catalyst to dehydrogenation activity has been favoured by basic sites which is in accordance with the electron donating property. The variation in catalytic activity as a function of activation temperature is given Figure 9.7.

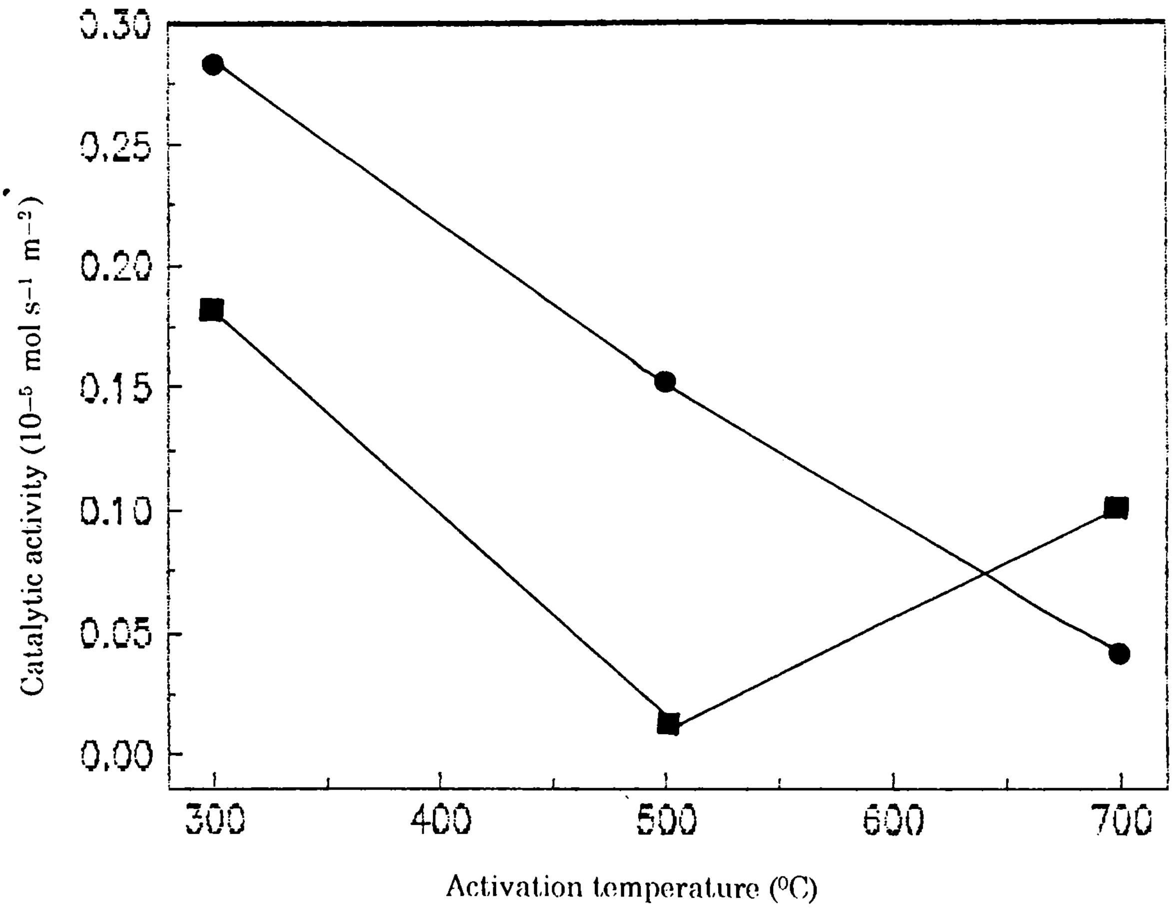

Figure 9.7: Catalytic activity for oxidation as a function of activation temperature

● Al_2O_3 ■ SO_4^{2-} / Al_2O_3

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CONCLUSION

The investigations were carried out to study the acidity/basicity, electron donor properties and the catalytic activity of sulfate modified metal oxides (ZrO_2, TiO_2, Sm_2O_3, CeO_2, SnO_2 and Al_2O_3) along with the unmodified oxides. It lead to the following conclusions.

1. Both acidity and acidic strength increase on modification with sulfate ion.
2. Electron donor properties decrease on modification with sulfate ion.
3. Electron donocity depends upon electron affinity of the electron acceptor and the activation temperature.
4. Study of electron donocity reveals that, some of the basic sites are converted to acidic sites on modification with sulfate ion.
5. Catalytic activity for esterification increases on modification with sulfate ion which parallels the acid/base properties.
6. Catalytic activity for reduction decreases on modification with sulfate ion which parallels the electron donor properties which in turn depends upon basicity.
7. In the case of zirconia and titania, catalytic activity for oxidation increases by sulfation.
8. In the case of alumina, tin oxide, samaria and ceria, the catalytic activity for oxidation decreases by sulfation.

LIST OF PUBLICATIONS

1. S.Sugunan and C.R.Kumaree Seena; "Surface acidity and catalytic activity of sulfated samaria", Indian J. Chem., (In press).
2. S.Sugunan and C.R.Kumaree Seena; "Electron donor properties and catalytic activity of sulfated samaria", Collect. Czech. Chem. Commun., (In press).
3. S.Sugunan and C.R.Kumaree Seena; "Surface properties and catalytic activity of sulfated titania (Communicated to J.Mater. Sci. Technol).
4. S.Sugunan and C.R.Kumaree Seena; "Electron donor properties and catalytic activity of sulfated zirconia", (Communicated to React. Kinet. Catal. Lett.).
5. S.Sugunan and C.R.Kumaree Seena; "Acidity/basicity, electron donor properties and catalytic activity of sulfate modified tin oxide (Under preparation).
6. S.Sugunan and C.R.Kumaree Seena; "Acidity/basicity, electron donor properties and catalytic activity of sulfated ceria", (Under preparation).
7. S.Sugunan and C.R.Kumaree Seena; "Acidity/basicity, electron donor properties and catalytic activity of sulfate modified alumina" (Under preparation).