CHAPTER II
SURFACE ELECTRON PROPERTIES
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2.1 ELECTRON DONOR-ACCEPTOR PROPERTIES

Acid-base interactions during the adsorption of acidic and basic molecules on inorganic powders such as iron oxide, silica and titania have been studied by Fowkes et al [1-3]. They have also extended the acid-base interaction theory to polymer powder interfaces [4]. 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 [5-8]. Flockhart et al associated the electron donor sites with unsolvated hydroxyl ions and defect centers involving oxide ions [9]. Such electron donor-acceptor interactions at surfaces are quite important in elucidating the adhesion forces at these interfaces.

During the past decades there has been much discussion about the nature of the acid and base present on the metal oxide surfaces, and their relevance in catalysis has been extensively investigated. Spectroscopic studies have established the existence of strong electrophilic centers on the silica-alumina surface and formation of
cation radical from hydrocarbons at the same centers [10-12]. The nature of site responsible for electron transfer process is of wide interest [13].

The electron donor strength of metal oxide can be defined as the conversion power of an electron acceptor adsorbed on the metal oxide into its anion radical. If a strong electron acceptor is adsorbed on the metal oxide, the anion radical is formed at every donor site present on 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 site. Finally in the case of a very weak electron acceptor adsorption its anion radical will not be formed even at the strongest donor site. Therefore the electron donor strength of a metal oxide can be defined as the limiting electron affinity value of the electron acceptor at which free anion radical formation of the corresponding electron acceptor is not expected on the metal oxide surface [14].

It has been shown that dehydroxylation of a silica surface reduces the extent and heat of adsorption of aromatic and unsaturated hydrocarbons from the gas phase
Dehydration of surfaces (silica gel, aerosil, aerosillogel) is normally carried out at 900-1000°C. Sintering of the wide porous silica gel and aerosillogel does not occur at this temperature in vacuo. The effect of dehydroxylation of the silica surface on the state of the adsorbate is clearly seen in its heat of adsorption [15] and in the infrared spectra of silica surface on which various molecules have been adsorbed [16,17].

Terephthalic acid adsorbed on to alumina from alcohol solution was studied by using inelastic electron tunnelling spectroscopy [18]. A comparison with tunnelling spectrum of p-acetylbenzoic acid showed that terephthalic acid is adsorbed predominantly as a monocarboxylate ion on the alumina surface.

Flockhart et al [9] found that when catalytic aluminas are heated to a high temperature, sites are produced on the surface which are capable of oxidising polynuclear aromatic hydrocarbons to corresponding ion radical at room temperature provided O₂ is present.

Studies by Peri [19,20] have presented a clear picture of the surface of partially dehydrated catalytic
aluminas. During dehydration of alumina surface hydroxyl ions combine to form water molecules which are then desorbed leaving a surface lattice containing both hydroxyl and oxide ions. For each molecule of water formed one oxide ion is left in the top layer and one aluminium ion is left in an octahedral site in the next lower layer. The surface lattice develops in such a way as dehydration proceeds, that there are separate domains in each of which the oxide ions are regularly arranged. Remaining hydroxyl ions tend to concentrate in boundaries between these domains and isolated hydroxyl ions may occur within them.

Further dehydration of the surface results in the formation of two kinds of defects at domain boundaries. At one of these two or more immediately adjoining vacancies in the surface layer results in an abnormally exposed aluminium ion (site (a) in the Fig.1). The resultant

\[ \text{Fig.1 Electron acceptor defect site (a) and electron donor defect site (b) on the surface of alumina dehydrated above 500^°C.} \]
localised positive charge makes this site an electron acceptor and gives its oxidising character. At the second type of active site two or more oxide ions occupy immediately adjoining surface sites and a potential electron donor site is created.

The type of defect which may be regarded as an abnormally exposed \( \text{Al}^{3+} \) ion with resultant localised positive charge possesses the character of Lewis acid. The experiment in which an electron rich hydrocarbon is adsorbed on alumina surface, the potentially active adsorption site is clearly the defect which is electron deficient [6,12]. Interest in the nature of catalytic aluminas has centered mainly on the electron deficient sites on the alumina surface.

Flockhart et al described a detailed investigation of the reduction of tetracyanoethylene (TCNE) on the surface of alumina and silica-alumina catalysts [9]. They found that in the dehydration of catalytic aluminas, sites are formed on the surface which are capable of reducing TCNE to corresponding anion radical. Two different surface sites are responsible for reducing properties. One formed during dehydration at low temperatures (\(<350^\circ\text{C}\)) may be associated with the presence on the surface of unsolvated
hydroxyl ions. At higher temperature (>750°C) a different site is produced which is believed to be a defect centre involving oxide ions.

Fomin et al. have shown that electron transfer from the hydroxyl ions can and does occur in certain solvent systems provided a suitable acceptor molecule is present [21]. The steep fall in radical forming activity between 250 and 350°C corresponds to a reduction in the number of hydroxyl ions on the surface as dehydration proceeds. Above 500°C dehydration of the surface results in formation of two types of defects. As a result of oxide ion defect described by Peri [19] a potential electron donor site is created and this is mainly responsible for TCNE anion radical in the temperature range 500-1000°C.

A.J. Tench and R.L. Nelson studied the adsorption of nitro compounds on the surface of magnesium oxide powder by ESR and reflectance spectroscopy [7].

On studying the adsorption of TCNE on alumina, silica and silica-alumina it was observed that the electron donating sites decreased initially when silica was added to
alumina and passed through a minimum at about 50% silica [22]. It is interesting to note that the amount of electron donating sites present in silica-alumina is less than silica or alumina and are in the following sequence:

alumina > silica > silica - alumina.

H. Hosaka, T. Fujiwara and K. Meguro investigated the electron donor properties of metal oxides such as magnesia, alumina, silica, titania, zinc oxide and nickel oxide by 7,7,8,8-tetracyanoquinodimethane (TCNQ) adsorption [8]. They found that when TCNQ was adsorbed, the surface of metal oxides acquired the colouration characteristic of each electron acceptor. The colouration was caused by formation of TCNQ anion radicals on metal oxide surfaces. The order of radical forming activity determined by ESR spectroscopy was magnesia > zinc oxide > alumina > titania > silica > nickel oxide. Hosaka et al suggested that electron donor property of metal oxide surfaces depend on the nature of semiconductors and surface hydroxyl ions.

M. Che, C. Naccache and B. Imelik [23] investigated the electron donor properties of titanium dioxide and
magnesium oxide. They found that electron donor centers are associated with hydroxyl groups present on the surfaces of solids activated at low temperature (\(<300^\circ\text{C}\)), at higher temperatures weakly coordinated oxide ions are formed on their surfaces and these are responsible for the reducing property of these solids.

K.Meguro and K.Esumi have reported the adsorption of some electron acceptors having different electron affinity on alumina [24]. For this they employed electron acceptors such as 7,7,8,8-tetracyanoquinodimethane (TCNQ), 2,5-dichlorobenzoquinone (DCQ), p-dinitrobenzene (PDNB) and m-dinitrobenzene (MDNB). They found that when electron acceptors are adsorbed from solutions in acetonitrile, alumina surface showed remarkable colouration characteristic with the kind of acceptor. They suggested the possibility of its participation of an oxidation-reduction process which is of the type:

$$\text{OH}^- + A \rightarrow A^- + \text{OH}^-$$

where A is an electron acceptor.
M.A. Enriquez and J.P. Fraissard carried out a comparative study of variation of surface properties and catalytic activity of TiO$_2$ samples with pretreatment temperature in vacuo [25]. The results showed that active sites are electron donor centres, number of which has been determined by adsorption of tetracyanoethylene and trinitrobenzene. These centers are Ti$^{3+}$ ions and O-Ti-OH groups for high and low pretreatment temperatures respectively.

It has been shown that silica has stronger electron acceptor properties for phenothiazine than alumina [26]. Electron donor properties of these substances measured by the formation of anion radicals of tetracyanoethylene and 7,7,8,8-tetracyanoquinodimethane decreases in the opposite sequence.

K. Esumi and K. Meguro described an investigation of strength and distribution of electron donor sites on alumina, titania and zirconia-titania by adsorption of electron acceptors such as 7,7,8,8-tetracyanoquinodimethane (TCNQ), 2,5-dichloro p-benzoquinone (DCQ), p-dinitrobenzene (PDNB) and m-dinitrobenzene (MDNB) by means
of an ESR spectrophotometer [27]. They suggested that the electron donor sites of alumina, titania and zirconia-titania are mainly associated with surface hydroxyl ions.

The electronic state of adsorbed species was studied by UV-Visible spectroscopy in addition to ESR spectroscopy [8,14,24]. The observed bands near 600 nm were related to the dimeric TCNQ anion radical which absorbs light at 643 nm [28]. This tentative attribution was supported by the characteristic features that neutral TCNQ absorbs only at 395 nm. TCNQ has a high electron affinity and TCNQ anion radicals are stable even at room temperature [29-32]. 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.

On studying the adsorption of electron acceptors with electron affinities varying from 2.84 eV to 1.26 eV on the surface of titania Esumi and Meguro have shown that the limiting radical concentration decreases with decreasing electron affinity of the electron acceptor and steeply between PDNB and MDNB [33]. This suggests that adsorption sites of titania act as electron donor to the adsorbed
molecule with electron affinity larger than 1.77 eV but not to those smaller than 1.26 eV. Accordingly the limit of electron transfer from electron donor sites of titania to electron acceptor molecule is located between 1.77 and 1.26 eV in the electron affinity of the electron acceptor.

On comparing the model of Lewis acidity or basicity of a surface with surface state model Morrison suggested that basic centers can in many cases be coincident with sites providing surface state [34]. D.Cordishi and V.Indovina investigated the electron donor properties of CaO, MgO, ZnO, Al₂O₃ and SiO₂-Al₂O₃ activated in vacuo at temperatures upto 1200 K using ESR of adsorbed nitro radicals as a probe [35]. The results indicated the existence of a correlation between electron donor activity of oxides and their Lewis base strength.

Ishikawa et al have shown that there are two kinds of irreversible adsorption site for CO₂ on non-stoichiometric strontium-calcium hydroxy apatites (SrCa HAP) [36]. Irreversible adsorption of CO₂ on these samples depends on the nonstoichiometry.
The study of the adsorption of anion radical salts on metal oxides can provide useful information concerning the interaction between anion radical salts and metal oxide surfaces [37]. Esumi and Meguro reported the adsorption of TCNQ anion radical salts such as Li\(^+\) TCNQ, Na\(^+\) TCNQ\(^-\) and K\(^+\) TCNQ\(^-\) on alumina from a solution in acetonitrile by measuring the adsorption isotherms and the ESR and electronic spectra of these adsorbed TCNQ anion radical salts. They found that TCNQ anion radicals were adsorbed at electron deficient sites on the alumina surface.

Recently plasma treatment has become attractive as a method for surface treatment, probably because it is a dry process at low temperatures with a relatively low pressure gas [38]. Esumi et al have studied the surface modification of meso carbon microbeads [39-41] by various plasma treatments and found that oxygen plasma treatment renders the surface more acidic owing to the formation of carbonyl groups, whereas nitrogen or ammonia plasma treatment renders the surface more basic owing to the formation of amino groups. The interaction of plasma treated metal oxide with TCNQ in acetonitrile solution was
studied by measuring their adsorption intensity of TCNQ in acetonitrile solution [42]. The electron donicity is increased by the ammonia and nitrogen plasma treatments.

Fowkes et al [2,4] have studied the interaction between inorganic solids and basic adsorbates by using the Drago correlations of the heats of acid-base interactions, and have determined the Drago parameters for several solids such as silica, rutile and magnetite. Esumi et al when studied the adsorption of tetrachloro-p-benzoquinone from various solvents on metal oxides, interpreted their adsorption results in terms of acid-base theory [43]. For this they employed the Drago equation [44],

\[- \Delta H_{ab}^{\text{ab}} = C_A C_B + E_A E_B\]

where \( E \) and \( C \) are the Drago constants for the acidic compound (A) and the basic compound (B). They suggested that a useful approach for relating interfacial interactions quantitatively has been the Drago equation of enthalpy in acid-base complexation.

K.Esumi, K.Miyata and K.Meguro examined the electron donor-acceptor interactions on metal oxides by
means of 7,7,8,8-tetracyanoquinodimethane (TCNQ) adsorption from various solvents [45]. They found that amount of TCNQ adsorbed on metal oxides decreased with an increase in acid-base interaction between TCNQ and basic solvents.

Skourtis et al have shown that electron transfer (ET) reactions play a significant role in biology [46]. They constitute important steps in processes such as photosynthesis and oxidative phosphorylation. Biological ET reactions are also important from a physico-chemical point of view, because they involve the tunnelling of an electron over a long distance.

2.2 SOLID ACIDS AND BASES

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 [47] by H.A. Benesi and B.H.C. Winquist. Surface acidic and basic sites of oxides are involved in the catalytic activity for various reactions such as cracking, isomerization and polymerization [48].
The microcalorimetric measurements of the heats of adsorption of ammonia and carbon dioxide have been used to elucidate the acidic and basic properties of a number of oxides [49]. The results showed that greater the degree of covalency of the oxide expressed by higher value of charge/radius ratio, the more likely is the acidity to be observed. An oxide with a low value of charge/radius ratio is more ionic in nature and present more basic sites.

The aqueous methods for the determination of acidity consists of direct titration of an aqueous suspension of the sample of powdered solid with a dilute base to a neutral end point. Webb et al gave a method of measuring the amount of acid sites by the extent to which they neutralise a solution of KOH as revealed by subsequent titration with HCl using phenolphthalien as indicator [50]. This method is least suitable because the state of the surface of the solid catalyst in a water suspension is radically different from its state during use as an acidic catalyst.

Non-aqueous methods for the determination of surface acidity represent a considerable improvement over aqueous methods, because the solvents used (eg., benzene,
iso-octane) do not react with catalyst surface. Of the available non-aqueous methods [48,51,52] simplest is that employing adsorbed indicators.

Following Walling [53] the acid-strength of a solid surface can be defined as its proton donating ability, quantitatively expressed by Hammett and Deyrup's $H_O$ function [54,55].

$$H_O = -\log a_{H^+} f_B / f_{BH^+}$$

$$H_O = pK_a + \log [B]/[BH^+]$$

where $a_{H^+}$ is the proton activity, $[B]$ and $[BH^+]$ are the concentration of the neutral base and its conjugate acid, $f_B$ and $f_{BH^+}$ are the corresponding activity coefficients. If the reaction takes place by electron pair transfer from adsorbate to the surface, $H_O$ is expressed by

$$H_O = -\log a_A f_B / f_{AB}$$

$$H_O = pK_a + \log [B]/[AB].$$

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 indicator to its conjugate base, 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 solvent, the base strength is determined from the colour changes of the indicator over a range of pKa values. For the reaction of an indicator AH with a solid base B

\[ \text{AH} + \text{B} = \text{A}^- + \text{BH}^+ \]

\[ H_o = \text{pK}_a + \log([\text{A}^-])/[\text{AH}] \]

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

The initial colour change and the subsequent change in the intensity are observed at values of pK_a±1. If we assume that the intermediate colour appears when the basic form reaches 50% ie., when [A^-]/[AH] = 1, we have \( H_o = \text{pK}_a \).
Solid acids and bases are characterized by amount, strength and nature of acid and base centers. 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 (or mmol) of basic sites per unit weight or unit surface area of the solid.

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 [56]. Walling [53] suggested that such colour tests could be used to measure acid strength of solid surfaces in terms of Hammett acidity function. This approach was extended by Benesi [57].

The indicator method is by far the 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.

Amine titration method, one of the several methods used to determine acidity was reported first by Benesi [57] and is based on O.Johnson's experiment [58], and has been subsequently modified [59,60]. The acid amount measured is the sum of Bronsted and Lewis acid sites.

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 [61]. 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 measurements of acid strength like visual colour change method [62], spectrophotometric method using fluorescent indicators [63], and gaseous adsorption method [50]. For basic strength, method using indicators [64], phenol vapour adsorption method [65] and temperature programmed desorption technique [66] are generally employed.

The very significant work of Hirschler has shed some light on acid strength distribution of cracking catalysts [62]. The use of a series of substituted aryl cerbinols gave an acid strength distribution curve which is in keeping with the heterogenous distribution of energy sites determined by other physical studies. The formation of coloured carbonium ion led to the conclusion that acid sites on the surface of the catalyst is protonic (Bronsted) [67].
Parry showed that adsorption of pyridine on silica involved association through surface hydrogen bonds [68]. Basila et al have gone one step further and have proposed that primary sites on silica-alumina are of the Lewis type (centered 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 group [69].

To evaluate the catalytic activity of zeolite it is necessary to determine the nature, strength and distribution of acid sites. Zeolite acidity can be determined by n-butyl amine titration [70]. UV spectrophotometry has been applied for measurement of acid strength of silica-alumina catalysts using 4-benzene azodiphenylamine, 4-nitroaniline and 2,4-dinitroquinoline [71].

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 [72].
T. Yamanaka and K. Tanabe determined the basicity of a series of oxides and found that basicity at basic strength ($H_o \gg 1.5$) has the order, \( \text{ZnO} > \text{TiO}_2 > \gamma \text{Al}_2\text{O}_3 > \text{BaO} > \text{activated Al}_2\text{O}_3 > \text{B}_2\text{O}_3 > \text{ZrO}_2 > \text{MgSO}_4 > \text{MoO}_3 \) [73].

The amount of basic sites can be determined by titrating a suspension of a solid in benzene on which an indicator has been adsorbed on its conjugate base form with benzoic acid dissolved in benzene [48]. The benzoic acid titres are a measure of the amount of basic sites having basic strength corresponding to the $pK_a$ value of the indicator. Malinowski and Sczepanska have devised titration methods for use with aqueous solution and with anhydrous acetic acid [64].

J. Take, N. Kikuchi and Y. Yoneda 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 [74]. They found that base strength of alkaline earth oxides increased remarkably upon heat treatment in vacuuo and basicity decreased in the order \( \text{SrO} = \text{CaO} > \text{MgO} \).
T. Itzuka, K. Ogasawara and K. Tanabe examined the acid strength of \( \text{Nb}_2\text{O}_5.\text{nH}_2\text{O} \) by indicator adsorption method [75]. The surface of \( \text{Nb}_2\text{O}_5.\text{nH}_2\text{O} \) showed strong acidic character which disappears on heat treatment at higher temperature. P. A. Burke and E. I. Ko also observed that acidity of niobia diminishes with increase in calcination temperature [76].

A method of determining the basicity at various base strength by titrating a solid suspended in benzene with trichloroacetic acid using a series of Hammett indicators was proposed by K. Tanabe and Y. Yamanaka [73]. The method makes it possible to determine the basic strength expressed by a Hammett acidity function and hence the acid base strength distribution of solid surface on a common scale. This method permits the determination of basicity at relatively weak basic strength which was not previously proposed.

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 0.1N solution of sodium methoxide [64]. 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 [77].

\[
\text{Ph}_3\text{CH} + \text{Lewis acid} \rightarrow \text{Ph}_3\text{C}^+ + \text{H}^- 
\]

In an infra red study of pyridine chemisorbed on silica-alumina catalysts of varying silica content, Schwarz described a new method for the measurement of Lewis and Bronsted acid sites [78]. Gay and Liang have investigated the surface acidities of silica, alumina and silica-alumina by \(^{13}\)C NMR spectra of a variety of aliphatic and aromatic amines adsorbed on these solids [79]. 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 [80].
Silica-magnesia is an important binary oxide because of the potential utility as a matrix in zeolite containing cracking catalysts [81]. An infra red study by Kermarec et al shows that the surface acidity of silica-magnesia appears to be more complex than that of silica-alumina [82]. From infra red spectra of pyridine and 2,6-dimethyl pyridine chemisorbed on silica-magnesia, they deduce that Bronsted and Lewis acid sites are present.

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 [$H_0 \leq 5.6$] was obtained at a composition of 50% m (mole %) ZrO$_2$ [83].

Surface acidities of Al$_2$O$_3$-TiO$_2$, SiO$_2$-TiO$_2$ and TiO$_2$-ZrO$_2$ preparations heated at various temperatures have been reported by Walvekar and Halgeri [84]. Butylamine titers of each binary oxide increase as calcination temperature is increased, go through maximum value and finally decrease.

Tanabe et al found that silica-titania is highly acidic and has high catalytic activity for phenol amination
with ammonia and for double bond isomerization in butenes [85,86]. The highest acidity per unit weight of catalyst was obtained when TiO$_2$-SiO$_2$ (1:1 molar ratio) was heated at 500°C.

Silica is an ideal host oxide with high electronegativity and the oxygen coordination is two which leads to the existence of coordinatively unsaturated dopant cations on the surface [87]. For two-cations in similar coordination and bonding sites the cation with higher electronegativity to be a stronger Lewis acid site [87]. 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 [88]. Depositing oxides of the following cations i.e., Ga$^{2+}$, Zn$^{2+}$, Al$^{3+}$, Fe$^{3+}$, Fe$^{2+}$, Mg$^{2+}$ and Sc$^{2+}$ on to 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 [89,90].
According to Tanabe 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 [91].

Infra red spectroscopic studies of benzene adsorbed on several KH $\beta$ zeolites where the extent of potassium exchange K/Al (%) varied from 0 to 88.32% have been undertaken under different conditions. The bands of adsorbed benzene on KH $\beta$ zeolites is in the range 2050-1700 cm$^{-1}$ [92]. KH $\beta$ zeolite exhibits basicity when K/Al ≤ 88.32% where its basicity is stronger and acidity is weaker. The order of stability of various adsorbed benzene species on the samples is as follows:

$\text{O}^-\text{(benzene)} > \text{H}^+\text{(benzene)} > \text{K}^+\text{benzene} > \text{benzene}.$

V.R.Choudhary and V.H.Rane have showed that rare earth oxide catalysts differ widely in their acidity and basicity and in the site energy distribution of both the acid and basic sites [65]. The acid and basic sites on the catalysts are the accessible $M_{Lc}^{n+}$ cations and $O_{Lc}^{2-}$ anions on the oxide surface and the site energy distributions of acid and base sites is mostly attributed to the $M_{Lc}^{n+}$ and $O_{Lc}^{2-}$ ions.
in different coordination, the lower coordinated ion site being responsible for the stronger acid-base sites.

2.3 CATALYTIC ACTIVITY

Although the fundamental catalytic and surface properties of alkali, alkaline earth and other basic oxides have been extensively studied [48], equivalent information about the series of basic rare earth oxides is much less. Empirical studies have demonstrated that following appropriate pretreatment, rare earth oxides are active catalysts for a number of reactions.

Taylor and Diamond have shown that paramagnetic oxides \( \text{Gd}_2\text{O}_3 \) and \( \text{Nd}_2\text{O}_3 \) are more active in catalysing ortho-para hydrogen conversion [93]. Minachev compared the catalytic activity in oxidation of hydrogen and propylene with that in the isotopic exchange of oxygen and suggested that the catalytic activity depends on the binding energy of oxygen with the surface and on the valence of lanthanide ions [94].

Hopkins and Taebel have measured the catalytic activity of rare earths for oxidation, hydrogenation,
decomposition and synthesis of organic compounds [95]. Oxidation-reduction reactions are important in organic chemistry. Rare earth oxides like $\text{La}_2\text{O}_3$ and $\text{Dy}_2\text{O}_3$ are effective in Meerwein-Ponndorf-Verley type reduction of ketones [96,97].

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 reaction [98]. Reduction of carbonyl groups is one of the most fundamental operations in organic chemistry. This is called Meerwein Ponndorf-Verley reduction. It was discovered in 1925 and has been used successfully in a number of instances [99].

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 neutralisation of alkoxide salt with strong acid. Heterogenous catalysts for the reduction reaction are known [100]. 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 [101].
M. Shibagaki et al. studied the liquid phase reduction of aldehydes and ketones with 2-propanol over hydrous zirconium oxide [102]. 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 isotope 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 [103]. 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 oxidised to the corresponding ketone in excellent yields through the use of aluminium t-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.
In view of the reversible nature of the reaction, many statements as to the mechanism of the Meerwein-Ponndorf-Verley reduction [99] are equally applicable to the Oppenauer oxidation. Activation of the alcoholic hydrogen atom by the aluminium resulting in hydrogen bonding has also been proposed [105] by Woodward et al.

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 [106].

The three most common catalysts in the Oppenauer oxidation are aluminium t-butoxide, isopropoxide and phenoxyde. Aluminium isopropoxide and in particular phenoxyde is easier to prepare. Aluminium isopropoxide is the most powerful oxidising agent [107]. In the modified Oppenauer oxidation benzophenone was found to be satisfactory oxidising agent [108] since it cannot undergo condensation in the presence of a strongly basic catalyst.
According to Oppenauer a solvent is necessary for the oxidation of alcohols [105]. Toluene is employed occasionally [109]. Time and temperature can be varied over a wide range, depending upon the alcohol to be oxidised, although the choice of solvent and hydrogen acceptor naturally controls the maximum temperature that can be reached. This method has several disadvantages such as need for tedious purification and unreusability of the catalyst.

Heterogenous catalysts for the oxidation are known. Silica, MgO and Al₂O₃ have been reported to be successful catalysts [110,111]. This process has several advantages in the isolation of products and require a high reaction temperature.

Kuno et al have shown that liquid phase oxidation of primary and secondary alcohols proceeds efficiently using benzophenone as the hydrogen acceptor [112,113].

Correlation between acid-base properties and catalytic activity

Rare earth oxides have been recognized as solid base catalysts. The solid acids and bases have been
usefully employed as catalysts in various acid-base catalysed reactions. A parallel has been found between the base strength of various solids as measured by the phenol vapour adsorption method and that the catalytic activity for the dehydrogenation of isopropyl alcohol [114].

The dehydrogenation of isopropyl alcohol to propylene is a measure of the acidity of the catalyst [115,116], and the (dehydrogenation rate/dehydration rate) ratio is a measure of the basicity [117]. The dehydration is catalysed at acidic sites and the dehydrogenation is catalysed at both acidic and basic sites.

It has been reported by several workers [118-120] that a large part of the basic sites determined by the adsorption of acidic substances consist of surface lattice oxygen, $O^{2-}$ ions. Keulks and Wragg et al have reported that the active oxygen species available for oxidation is lattice oxygen $O^{2-}$ ions. The acidic sites contribute to the activation of electron donor type reactants such as olefins and are connected with the oxidising sites [121-122].
Fukuda et al. studied the decomposition of 4-hydroxy-4-methyl 2-pentanone over La$_2$O$_3$, Y$_2$O$_3$ and CeO$_2$ [123]. It was found that maximum activity was obtained by pretreatment at 500°C for La$_2$O$_3$ and at 700°C for Y$_2$O$_3$. In the case of La$_2$O$_3$, variation on the activity with the pretreatment temperature was similar to that of the basicity. The activities of three oxides for the decomposition reaction are in the following order, La$_2$O$_3$ > Y$_2$O$_3$ > CeO$_2$.

Good correlation have been found in many cases between the total amount of acid (Bronsted plus Lewis type usually measured by the amine titration method) and the catalytic activities of solid acids. The rates of both the catalytic decomposition of cumene and the polymerization of propylene over SiO$_2$-Al$_2$O$_3$ catalysts were found to increase with increasing acid amount at strength $H_0 \leq +3.3$ [125,126].

Catalytic activity of alumina in a range of reactions such as isomerization of hydrocarbons, polymerization of olefins have all been attributed to the acidic properties of the surface [127].

Minachev et al. studied the hydrogenation of ethylene at low temperature as part of a study of catalytic
activity of rare earth oxides [128]. They found that La_2O_3 is highly active for hydrogenation when pretreated at high temperatures. They also correlated basicity with catalytic activity.

The catalytic activity of lanthanide sesquioxides for the double bond isomerization of n-butenes has been studied in the temperature range 0-50°C [129]. Activity increases with increasing pretreatment temperature due to removal of surface hydroxyls and then decreases with increase in pretreatment temperature due to decrease of surface anion disorder. Rosynek et al reported that basic sites in La_2O_3 were essential for the isomerization of butenes [130].

As a measure of the base strength of metal oxide catalysts Davis suggested the alcohol conversion selectivity [131]. The amount of alkene produced by the water elimination depends on the base strength. It was found that ZnO is a stronger base than CaO and MgO, and the oxides of Zr, In, Th and Y are stronger base than ZnO [132]. Vapour phase conversion of cyclohexanol to cyclohexanone in the presence of different basic catalysts showed that some of them are able to activate dehydration
and dehydrogenation simultaneously. The dehydrogenation activity is related to the existence of basic sites originating from the oxygen in the oxide lattice.

The catalytic isomerization of butenes over samarium oxide has been investigated in view of acid-base catalysis [133]. The ratio cis/trans 2-butenes formed from 1-butene isomerization was 22.2. The reaction profile of the butene isomerization obtained from the relative rate constant was of the cis-convex type. The basic sites on the oxide surface have been revealed by the benzoic acid titration method.

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 temperatures with the formation of new sites of Lewis acidity from exposed metal cations [134]. Upon calcination dehydration activity of ceria increases. According to the mechanism proposed for this reaction it is suggested that exposed couples of Ce\(^{4+}\) and O\(^{2-}\) ions are active sites.
Zhang et al have investigated the aldol addition of butyraldehyde on alkaline earth oxides, zirconium oxide and lanthanum oxide, to compare the active site and mechanism with those for aldol addition of acetone [135]. It is found that active site is the surface $O^{2-}$ and the rate determining step is the $\alpha$-H abstraction.

Catalytic properties of chromium oxide are very sensitive to its method of preparation. Dyne et al have found an increase in activation energy and specific activity for hydrogenolysis and polymerization of cyclopropane after recrystallization of an amorphous sample [136]. L. Nondek and M. Kraus have found that catalytic properties of chromium oxide depends mainly on its temperature of calcination which governs the surface concentration of hydroxyl groups and the state of coordination of surface $Cr^{3+}$ ions [137].

The surface of $Nb_2O_5.nH_2O$ showed considerably strong acidic character and rather weak basic property. The acidic sites on these catalyst surface are thought to be the isolated OH groups as Bronsted acid sites and exposed metal ions as heavier acid sites; both of which appear after vigorous heat treatment [75].
Selectivity of butenes produced from 2-butanol is very sensitive to the surface acidic and basic property [138]. The oxide catalysts which have both acidic and basic sites such as ThO$_2$ and ZrO$_2$ produces 1-butene dominantly [139]. Polymerization of propylene proceeds on Bronsted acid sites on Nb$_2$O$_5$.nH$_2$O pretreated at low temperatures; but Lewis acid sites become main active sites after treatment at lower temperatures [75].

Usually the reactions which are catalysed by solid bases are polymerization, isomerization, alkylation, condensation, addition and dehydrohalogenation. The oxides, carbonates and hydroxides of alkali metals and alkaline earth metals (MgO, CaO, SrO, Na$_2$CO$_3$, CaCO$_3$, SrCO$_3$, NaOH, Ca(OH)$_2$) have been found active in the high polymerization of formaldehyde, ethylene oxide, propylene oxide and propiolactone [140-143].

A first order rate constant for the formation of benzyl benzoate from benzaldehyde over calcium oxide calcined at various temperatures is found to change in parallel with the change in catalyst basicity. There is a good correlation between catalytic activity and amount of base per unit surface area [144].
Hydrous zirconium oxide is an amorphous solid and has several catalytic activity [145]. The oxide was changed to crystalline zirconium by calcination at high temperature and the catalytic activities were lowered. The correlation between surface property and catalytic activity was investigated on hydrous zirconium oxide calcined at several temperatures, the best activity was obtained on the oxide calcined at 300°C. The quantity of surface acid or basic sites was measured by the butylamine or trichloroacetic acid titration method respectively using various Hammett indicators.

Investigations are carried out to have a systematic comparison of the acidic properties and catalytic activities of single oxides \( \text{SiO}_2, \text{TiO}_2, \text{Al}_2\text{O}_3 \) etc., their binary oxides and the ternary oxide \( \text{TiO}_2-\text{SiO}_2-\text{Al}_2\text{O}_3 \) [146]. The acidity distribution is measured by using butylamine titration technique and the reaction selected for the catalytic activity measurements are alkylation of toluene with 2-propanol and dehydration of 2-propanol. On comparing acid properties with catalytic activity it appears that the isopropylation of toluene requires acid sites of strength \( \text{H}_{\text{O}}\leq +1.5 \).
Mizuno et al carried out olefin polymerization over silica-alumina and found that strong Lewis acid sites are active in this reaction [147]. Binary metal oxides such as SiO$_2$-Al$_2$O$_3$, SiO$_2$-MgO, SiO$_2$-ZrO$_2$ and Al$_2$O$_3$-B$_2$O$_3$ have been used as solid acid catalysts, since their surface acidic properties are well known [148]. Many other combinations such as TiO$_2$-Al$_2$O$_3$ [149], TiO$_2$-ZnO [150], SiO$_2$-ZnO [151], SiO$_2$-TiO$_2$ [151] and Al$_2$O$_3$-MgO [152] have been found to show remarkable acid properties and catalytic activities in various acid catalysed reactions.

The acidity and basicity of the ternary system MoO$_3$-Bi$_2$O$_3$-P$_2$O$_5$ catalysts have been studied by adsorption of acidic and basic compounds in the gas phase. Catalytic activity for oxidation and olefin isomerization have also been studied and established the concept that the catalytic activity and selectivity in mild oxidation can be well interpreted in terms of the acid and base properties between the catalyst and the reactant [153].

M.Ai used static and pulse methods to study acidity and basicity of a series of TiO$_2$-V$_2$O$_5$-P$_2$O$_5$ system by the adsorption of acidic and basic molecules in the gas phase [154]. The vapour phase oxidation of electron donor
type reactants such as butadiene, 1-butene and that of acetic acid as an acidic reactant was carried out and the relationship between the catalytic behaviour and the acid-base properties was investigated. The acid-base properties of the catalyst and oxygen mobilities are responsible for the catalytic action. The acidic sites (probably consisting of metal ions with a high electron affinity) play a role in electron transfer from the reactant sites resulting in the formation of a cationic intermediates and a reduced metal ion [155] ie., the acidic sites contribute to the activation of the reactant.

The basic sites owing to their ability to donate electrons to oxygen contribute to adsorb and activate the gaseous oxygen and also reoxidise the reduced metal ions, ie., basic sites are connected with the oxidising site, probably consisting of lattice oxygen $O^{2-}$ [156]. The combination of the metal oxides contribute to the modification of both the acidic and basic properties of the catalyst.
REFERENCES


