Chapter II

SURFACE ELECTRON PROPERTIES
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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 gibbsite, $\gamma$-Al$_2$O$_3$ and $\eta$-Al$_2$O$_3$, 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, spectrosopically 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 C₆H₆-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 O₂ 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, Al₂O₃, SiO₂-Al₂O₃) 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 TiO₂ 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 TiO₂ and MgO at higher temperature, weakly coordinated O₂⁻ 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 H₂O [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 TiO₂ 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 Ti³⁺ 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 m² formed on the metal oxides was found to be as follows:
MgO > ZnO > Al₂O₃ > TiO₂ > SiO₂ > 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, SiO₂-Al₂O₃, SiO₂, TiO₂, Al₂O₃-TiO₂ and ZrO₂-TiO₂ 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 acceptors with metal oxides, $\text{Al}_2\text{O}_3$ and $\text{TiO}_2$. 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 $\text{Li}^+ \text{TCNQ}^- > \text{Na}^+ \text{TCNQ}^- > \text{K}^+ \text{TCNQ}^-$. 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 Al₂O₃, TiO₂ and ZrO₂-TiO₂ 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 Al₂O₃ and TiO₂ 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 Al₂O₃ which had been dedehydrated 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$_2$O$_3$ 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$_3$, LnNiO$_3$, 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 alumina 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$_2$O$_3$ with alumina and Dy$_2$O$_3$, mixed oxides of Y$_2$O$_3$ with γ-alumina. The extent of electron transfer is understood from magnetic measurement [82].

The electron donor properties of Pr$_6$O$_{11}$ 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 character. 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],

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

or

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

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,
$$H_o = -\log \frac{a_{AB}}{f_{AB}}$$

or

$$H_o = pK_a + \log \frac{[B]}{[AB]}$$

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 $pK_a$ 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,

$$H_o = pK_a + \log \frac{[A^-]}{[AH]}$$

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 $pK_a \pm 1$. If we assume that the intermediate colour appears when the basic form reaches 50% i.e., when $[A^-]/[AH] = 1$, we have $H_o = pK_a$.

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

$$pK_{BH^+} < H_0 < pK_{BH^+}$$

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$_A$ 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 $H_0$ value of the acidic sites is equal to the strongest $H_0$ of the basic sites. Yamanaka et al. [110] defined $H_{0,\text{max}}$ as the $H_0$ value at the point of intersection. This value may not be the exact value of the maximal $H_0$ parameters. The acidic and basic sites of the same $H_0$ do not coexist that, $H_{0,\text{max}}$ is lower than $H_0$ for the case where the measured acidity is minimal, and higher than $H_0$ when the measured basicity is minimal.
Yamanaka and Tanabe [110] have shown that the $H_{o, \text{max}}$ 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$_2$O$_3$ > BaO > activated alumina > B$_2$O$_3$ > 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 szepanska 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].

\[
\begin{align*}
\text{Ph}_3\text{CH}^+ & \quad \text{Lewis acid} \\
\quad & \quad \rightarrow \quad \text{Ph}_3\text{C}^+ \quad + \quad \text{H}^- 
\end{align*}
\]

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 TiO₂-ZrO₂ system as a function of composition and method of preparation. Highest titer of strong acid sites \( [H_+ \leq 5.6] \) was obtained at a composition of 50% M (mole %) ZrO₂ [118]. Surface acidities of Al₂O₃—TiO₂, SiO₂—TiO₂ and TiO₂—ZrO₂ 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 TiO₂—SiO₂ (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 i.e., Ga²⁺, Zn²⁺, Al³⁺, Fe³⁺, Fe²⁺, Mg²⁺ and Sc²⁺ 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 ≤ 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 O₁₈ 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 CO₂ 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, europium 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 Fe₂O₃ were caused by treatment with sulfate ion. The sulfate treated catalyst showed possibility for bearing the surface acidity higher than that of SiO₂—Al₂O₃ 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, CO₂ 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, ZrO₂—SiO₂ 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 H₂SO₄ enhanced the activities of the catalysts remarkably, being responsible for the superacidic properties of the modified catalysts [145].

The Lewis acidity of ZrO₂ and sulfated zirconia has been investigated by using the probe molecules CO, CO₂, CH₃SH and pyridine [146]. It was found that pure ZrO₂ 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, SnO2, TiO2, V2O5, NiO, MoO3 and Cu2O. Recent work has also been reported on ZrO2 [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\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, catalysts were found to increase with increasing acid amounts at strength $H_a \leq +3.3$.

Approximately linear relationship have however been demonstrated between the acid amount for SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{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\textsubscript{2}–Al\textsubscript{2}O\textsubscript{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\textsubscript{2}–Al\textsubscript{2}O\textsubscript{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$_c$ $\leq$ +3.3 of zeolite 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$_2$O$_3$.B$_2$O$_3$ in the transalkylation of aromatic compounds is found to be higher than that of SiO$_2$.Al$_2$O$_3$. The higher activity seems to be essentially due to the higher concentrations of acid sites on Al$_2$O$_3$.B$_2$O$_3$. It is also found that Al$_2$O$_3$.B$_2$O$_3$ 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 straightforward 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 SiO2–ZrO2 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 MoO3–Fe2(MoO4)3 catalysts at H0 ≤ +4.0 and their activity in the oxidation of methanol to formaldehyde.
Tani and Ogino, found that the activity of ZnO-Cr₂O₃-SiO₂-Al₂O₃ 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 \( H_{\circ} \leq +3.3 \) 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 \( H_{\circ} \leq +3.3 \).

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 $H_0 > +3.3$ 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$_2$O$_3$ 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$_2$SO$_4$, CCl$_3$COOH 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 $4\text{MgCO}_3\cdot\text{Mg(OH)}_2\cdot4\text{H}_2\text{O}$ [217], $\text{Ce}_2\text{O}_3\cdot\text{MnO}\cdot\text{MgO}$ [92] and $\text{Fe}_2\text{O}_3\cdot\text{ZnO}$ [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 ($\text{MgO, CaO, SrO, Na}_2\text{CO}_3, \text{K}_2\text{CO}_3, \text{SrCO}_3, \text{NaOH, Ca(OH)}_2$ etc.) have been found active in the high polymerization of formaldehyde [218], ethylene oxide [219] propylene oxide [220], lactam [221] and $\beta$-propiolactone [222].

A solid base like $\text{Na/Al}_2\text{O}_3$ 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 $^{14}\text{C}$ 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 $\text{Na/Al}_2\text{O}_3$, $\text{NaH}$, $\text{K/graphite}$ etc. The activities for aldol type
formaldehyde and acetaldehyde condensation over NaOH/SiO₂, 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°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 alcolholate 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 SO₄²⁻ and SO₃²⁻ considerably less than PO₄³⁻, CO₃²⁻ and BO₂⁻ [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/SO₄²⁻–SiO₂ or Pt/SO₄²⁻–ZrO₂ catalysts, the sulfated mixed oxides show an enhancement of the catalytic activity that increases with the content of ZrO₂ reaching its maximum at values between 10 and 15 wt % zirconia. The characterization of the samples reveals that at this stoichiometry, the highest H₂-consumption of the samples as well as
the top value of strong Bronsted acid sites occurs according to the TPD–H₂ 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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