2.1. ELECTRON DONOR-ACCEPTOR PROPERTIES

The formation of radical ions on the surface by electron transfer process is well established. The presence of electron donor sites on metal oxide surfaces are already reported [1-6]. The adsorption of electron acceptors/donors on the metal oxide will form corresponding radical ions, due to the electron transfer form adsorbent to the adsorbate. By measuring the radical forming activity of metal oxides, their electron donor or acceptor strength have been investigated [7-9] and this method has also been used for characterization of oxides [10-13].

The electron donor strength of metal oxide can be defined as the conversion power of an electron acceptor to its anion radical. If a strong electron acceptor is adsorbed on a metal oxide surface, the anion formation will take place at all donor sites. If a weak electron acceptor is adsorbed on the surface, the anion radical formation is expected only at the strong donor sites. If a very weak electron acceptor is adsorbed on the surface, the anion formation is not expected even at the strong donor sites. Thus the electron donocity
of an oxide surface can be expressed as the limiting electron affinity value of electron acceptor at which the anion radical formation is not observed on the metal oxide surface.

The formation of anion radicals on metal oxide surface by the adsorption of electron acceptors have been established by many workers [14-17]. Flockhart et. al obtained experimental evidence for the presence of electron donor sites on the surface of alumina by electron spin resonance spectroscopy technique [7,12,17]. They attempted the adsorption of TCNQ and chloranil for the estimation of electron donor properties of alumina surface of gibbsite, γ alumina and η alumina. In this respect they associated the electron donor sites with unsolvated hydroxyl ions and defect centers involving oxide ions [14]. The formation of anion radicals by the adsorption of nitrocompounds on the surface of MgO powder have been studied by ESR and reflectance spectrophotometry [9]. They found that negative radicals are formed on clean MgO surfaces in vacuum where as this no longer occurs if surface is contaminated with water and CO₂.

K. Kirota et. al were reported the formation of anion species when TCNE and benzophenone were adsorbed on ZnO and Al₂O₃ in vacuum[18]. Chemisorption of O₂ on MgO was observed under condition which involve different types of electron transfer process, either from electron donor centers formed by irradiation or by the addition of intrinsic impurity ions [19-20]. Carbon dioxide was adsorbed as CO₂⁻ ions by electron transfer from S center on irradiated MgO [21]. The electron donor properties of metal oxides (MgO, AlCl₃, SiO₂, TiO₂, ZnO & NiO) were investigated by means of TCNQ
adsorption by Hosaka et.al [12]. The order of radical forming activity determined by esr spectroscopy is as follows: MgO > ZnO > Al₂O₃ > TiO₂ > SiO₂ > NiO. The electron donor properties of metal oxide surfaces might be dependent on the nature of the semiconducting oxide and the surface hydroxyl ions. The reduction of I₂ to iodide ion occurs readily on the surface of partially dehydrated catalytic aluminas and silica aluminas [22]. An increase in alumina content results in an increase in reducing activity. These studies concur with those obtained with the study of reduction of TCNE on alumina surfaces.

The radical ion of nitrogen heterocycles and sulfur heterocycles have been generated and studied on a variety of oxide surfaces including SiO₂-Al₂O₃ and Mo₃O₇-Al₂O₃ by K.S. Seshdri and L. B. Petrakis [23-24]. The adsorption of a series of aromatic hydrocarbons from solution on hydroxylated and dehydroxylated surfaces have been investigated [25]. The dehydration of silica surfaces sharply diminishes the adsorption of aromatic hydrocarbons. Che et al [26] carried out systematic studies of adsorption of TCNE on the surface of TiO₂ and MgO. They found that electron donor centres are associated with OH groups present on the surfaces of the solid activated at low temperatures and coordinated O₂⁻ ions at higher temperatures. The electron donor properties of the several oxide powders activated in vacuum at temperatures up to 1200 K have been investigated using the esr spectroscopy of adsorbed azobenzene radical as a probe molecule [27]. The results show the correlation between electron donor activity
and the Lewis base strength indicating a direct connection between basic centers and electron donor sites.

Pigmentary samples of TiO$_2$ react with electron acceptors such as quinones, TCNE and TCNQ to give paramagnetic species [28] and it has been confirmed by visible absorption spectral measurements. A comparative study of variation of surface properties and catalytic activity of TiO$_2$ preheated in vacuum for the dehydration of formic acid has shown that the active sites in the reaction are the electron donor sites, the number of which have been determined by the adsorption of TCNE or trinitrobenzene and esr analysis of the paramagnetic anions formed [29].

The electron donor strength on a metal oxide is the conversion ratio of an electron acceptor adsorbed into its anion radical. The strength and distribution of electron donor sites of titania surface was evaluated by adsorption of four electron acceptors with electron affinities ranging from 1.26 to 2.84 eV from acetonitrile solution [30]. The concentration of anion radicals formed on the surface, as a result of electron transfer decreased with decreasing electron affinity of the acceptors. The decrease was very steeply between 1.26 and 1.77 eV. These results suggest that the limit of electron transfer from the titania surface to the electron acceptor ranged between 1.77 and 1.26 eV in terms of the electron affinity of the acceptor. The electron donor strength of alumina surface has also been studied by measuring the adsorption isotherms, ESR and electronic spectra [10].
The electron donor property of ZrO$_2$-TiO$_2$ systems were investigated by means of the adsorption of TCNQ [31] which has a much lower donocity than TiO$_2$.

The electron donor properties of metal oxides depend upon the pretreatment temperatures. The adsorptive characteristics of ZrO$_2$ have also been investigated by studying the adsorption of TCNQ [32], N$_2$, Ar and H$_2$O [33]. The radical concentrations decreased with increase in temperature, reached a minimum value at 700°C and then increased with rise in temperature. This behaviour has been explained by a change in the number of electron donor sites and their strength [32]. Surface properties were found to depend primarily upon the amount of irreversibly adsorbed water retained by the sample. Water was irreversibly adsorbed on ZrO$_2$ in amounts far in excess of that required for a classical chemisorbed monolayer [33].

Fowkes et al had studied the adsorption of acidic and basic molecules from neutral solvents on Fe$_2$O$_3$, SiO$_2$ and TiO$_2$ [34-36]. They found that the calorimetric heats of adsorption were actually the heats of acid-base interaction governed by the Drago equation [37] and that the Drago constants can be accurately determined for the surface sites of these inorganic solids. Adsorption of tetrachloro-p- benzoquinone (chloranil) from basic solvents on metal oxides, such as alumina and titania were carried out to understand the acid-base interaction at the interface [38]. The amount of chloranil adsorbed decreased with an increase of acid-base interaction between the basic solvents and chloranil and also decreased with an increase in acid-base interaction between the
acidic solvent and electron donor sites of the surface for both the metal oxides. The change in concentration of chloranil radicals formed was correlated with the acid-base interaction at the interfaces.

The electron donor properties of γ-alumina, silica and their supported palladium oxide have been studied [39]. It was observed that while γ alumina had both electron donor and acceptor sites, γ alumina supported palladium oxide showed better electron acceptor properties than donor properties. Silica supported palladium oxide showed only electron acceptor properties. For binary oxides the electron donor property of the surface depend upon the composition of the mixed oxides.

The electronic state of the adsorbed species was studied by UV-vis spectroscopy in addition to ESR spectroscopy to confirm the electron transfer process [10-12]. The bands appeared at 400 nm corresponds to the physically adsorbed neutral TCNQ molecule. The band extending to region of 600 nm was related to the dimeric TCNQ anion radical which absorbs light at 643 nm [40]. 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 radical are stable even at room temperature. Chloranil adsorbed samples gave absorption band at 745 nm [38]. ESR and electronic spectra provided evidence that TCNQ anion radicals are formed as a measure of electron transfer from metal oxide surface to adsorbed TCNQ.
Adsorption studies have also been studied for the characterisation and for the determination of the role of adsorbed species on the catalytic activity of perovskite type oxides [19,41-42]. These include mainly equilibrium and kinetics of adsorption successive or simultaneous adsorption of two gases, infra red spectroscopy and temperature programmed desorption.

It is also possible that cationic species will be formed on adsorbent of an electron acceptor if a strong electron donor is used as the adsorbate. Several examples of the observation of positive ions on electron acceptor sites in SiO₂-Al₂O₃ and zeolite systems have been reported [2,19-21, 45-46]. The presence of electron deficient centres on strongly dehydrated alumina surfaces sufficiently powerful to promote the formation of positive radical ions from aromatic hydrocarbons have also been demonstrated [5, 45, 47-48]. The formation of cationic species adsorbed on surfaces has been established by studies of the adsorption of hydrocarbons on SiO₂-Al₂O₃ catalysts [1-5].

Edlund et. al observed the ESR absorption spectra of singly charged monomeric and dimeric cation radicals at 77 K in a γ-irradiated C₆H₅-silica gel systems [49]. The formation of cation radical of triphenylamine on the surface of synthetic zeolite and anion radicals of naphthalene and biphenyl on silica gel have also been reported. Kinell et.al detected the cation radicals of naphthalene, anthracene, phenanthrene and biphenyl on SiO₂ gel by esr spectra [50].
Esumi et al. studied the solvent effect on the acid-base interaction of electron acceptors with metal oxides like \( \text{Al}_2\text{O}_3 \) and \( \text{TiO}_2 \) [51-52]. The saturated amounts 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 [38]. TCNQ radical concentration for both metal oxides decreased with increasing basicity of solvent. The adsorption on metal oxide was found to be strongly influenced by interaction between basic solvents and TCNQ or between basic solvent and donor sites of the metal oxides. Solvent effect of several aromatic solvents in charge transfer adsorption of TCNQ into metal oxide was also studied and it was found that TCNQ radical concentration depends on ionisation potential of the solvent [53].

Applying the relation between solubility and chemical potential expressed by Miller [54] it was found that adsorption of TCNE anion radical salts on alumina is not affected by solubility, but depend on the nature of cation. K. Esumi et al measured the zeta potential of \( \text{Al}_2\text{O}_3 \) and \( \text{TiO}_2 \) by adsorption of TCNQ from organic solvents [55]. They found that the zeta potential of oxide decreased with increasing concentration of TCNQ in acetonitrile and ethyl acetate indicating that TCNQ anion radical formed on oxide surface contribute to the decrease in zeta potential. Fomin et al have shown that electron transfer does occur in certain solvent systems provided a suitable acceptor is present [56].

Plasma treatment has become attractive [57] as a method for surface treatment, probably because it is a dry process at low temperature with a relatively low pressure gas.
Esumi et al [58] have studied surface modification of mesocarbon microbeads by various plasma treatment and found that it renders the surface more acidic owing to the formation of carbonyl group, whereas nitrogen or ammonia plasma treatment renders the surface more basic owing to the formation of amino group. Taking into consideration of these plasma treatments for carbon, there is a probability of modifying the electron donor properties of metal oxides by plasma treatment. The interaction of plasma treated metal oxides with TCNQ in acetonitrile solution was studied by measuring their adsorption intensity of TCNQ in acetonitrile solution [59]. The electron donocity is increased by the ammonia and nitrogen plasma treatments.

The electron donor properties of two component metal oxide systems like SiO$_2$, Al$_2$O$_3$, SiO$_2$-TiO$_2$, Al$_2$O$_3$-TiO$_2$ and ZrO$_2$-TiO$_2$ were studied by the adsorption of TCNQ [53,60]. Two component metal oxides showed lower radical forming activity than parent oxides and change in activity with composition was characteristic of metal oxide systems. These systems exhibited electron donor properties which would not be qualitatively predicted from consideration of the independent properties of the parent oxides [61-62]. The electron donor properties of some of the rare earth oxides and alumina supported rare earth oxides have also been studied [63-66] and the correlation with catalytic activity for certain organic reaction was also reported.
2.2. ACID-BASE PROPERTIES

It has been seen that surprisingly a large number of solids have surface acidity and basicity. The metal oxides and sulfides whose acid-base properties have already been reported are Al₂O₃, SiO₂, MgO, CaO, ZnO, SrO, BaO, TiO₂, V₂O₅, Sb₂O₅, Cr₂O₃, As₂O₃, CeO₂, ZnS and CdS. These solid acids and bases have found use as catalysts for many important reactions which find immense applications in heterogeneous catalysis [67,68]. Extensive investigations on solid acids and base catalysis in past few years discovered a number of new types of catalysts including single oxides, binary oxides and ternary systems having a wide variety of applications in different fields. Systematic studies on the correlation between catalytic activity and selectivity and acid-base properties of the catalyst surface has led to the determination of the optimum catalyst in terms of their surface properties.

The acid and basic properties of oxide catalysts are very important for the development of scientific criteria in the catalyst applications. The determination of the strength of acidic and basic sites exposed on the solid surface as well as their distribution is a necessary requirement to understand the catalytic properties of solid acids and bases. A complete description of acidic and basic properties of solid surface requires the determination of acidic and base strength, acid or base amount and nature of the such sites.
The acid strength of a solid surface is defined as its proton donating ability. Walling [69] defined acid strength of a solid as the ability of a surface to convert an adsorbed base into its conjugate acid. The strength of an acid can be characterised by its disassociation constant $K_a$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

which is usually reported in terms of the parameter $pK_a$. $pK_a$ values of the solid surfaces cannot be measured directly. Hammett and Deyrup [70] proposed an ordering of the acid strengths based on the Hammett acidity function $H_o$. $H_o$ scale permits the comparison of the strength of acids taking into account their capability to transfer a proton to neutral molecule of a basic indicator. Deyrup defined an indicator as a non-ionised or a neutral substance capable of adding a single hydrogen ion per molecule in such a way that a colour change indicates the extent of the reaction.

If the reaction proceeded by the proton transfer from surface to adsorbate, the acidity function $H_o$ can be expressed as

$$H_o = pK_a + \log \frac{[B]}{[B \cdot H^+]}$$
where \([B]\) and \([BH^+]\) are the concentrations of neutral base and its conjugate acid.

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

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

where \([AB]\) is the concentration of the neutral base which reacted with the Lewis acid or electron pair acceptor \(A\). Decreasing value of \(H_o\) indicates an increase in acid strength.

Basic strength of a solid surface is defined as the ability of the surface to convert an adsorbed neutral acid to its conjugate base. That is the ability of the surface to convert an electron pair to an adsorbed acid. When an acid indicator is adsorbed on a solid from a non polar solvent the colour of the acid indicator is changed to that of its conjugate base, provided that the surface has necessary base strength to impart electron pair to the acid. Base strength is quantitatively expressed by the Hammett and Deyrup \(H\)-functions, after the analogy of acid strength \(H_0\) function.

For the reaction of an acid indicator \(BH\) with a solid base \(B\),

\[
BH + B = B^- + BH^+
\]

the basic strength \(H\) is given by
$H_0 = pK_a + \log \frac{[B^*-]}{[BH]}$

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

For studies of solid acid-base catalysis, quantitative information on the acid base strength distribution of solid acid or base is essential. Quantitative determinations of acid base strength are known as acidity and basicity respectively. The acid or base amount usually expressed as the number or mmol of sites per unit weight or per unit surface area of the solid surface. A variety of methods have been suggested, which differ from each other in their chemical and physical principles and none of them can be regarded as universal in its use. Several reviews dealing with surface acidity and basicity of solid catalysts have been published [67-68,72-73]. The main methods for the quantitative acid base determination are the non aqueous titration method using Hammett indicators and gaseous acid or base adsorption.

The indicator method was originally reported by Walling [69] and is in extensive use. The colour of the suitable indicator adsorbed on a surface will give a measure of its acid strength. If colour is that of the acid form of the indicator, then the value of the $H_0$ function of the surface is equal to or lower than the $pK_a$ value of the conjugate acid of the indicator. That is the measure of the acid strength of the surface is the $pK_{BH}$ value of the
weakest basic indicator which after adsorption exhibits the colour of the conjugate acid. Lower values of the $H_0$ corresponds to the greater acid strength.

The titration method for the acidity determination was reported by Benesi [71] which is based on Johnsons experiment [74] and has been subsequently modified [75-76]. The amine titration method gives sum of the amounts of the both Bronsted and Lewis acid, since the surface will react with either electron pair (-N=) of the indicator or that of the amine (=N) to form a co-ordination bond [67]. Hirschler proposed the use of acidity function $H_r$ for the determination of protonic surface acidity by using any carbinol and phenyl methyl indicators [77]

Even though the titration method is limited to white coloured surface this method is rarely applied to coloured or dark samples where the usual colour change is difficult to observe. In such cases the titration method is carried out by mixing a white substance of known acidity with the sample or by employing spectroscopic method [67,68.85-86]. The end point is taken when the color change is observed on white solid and a correction is made for the amount of n-butylamine used for the added white material. Volts et. al [87] determined Hammett acidities of chromia catalysts using $F10 \ Al_2O_3$ and S-34 silica alumina as white solid (indicator catalyst). Trambouze and co workers found that the acid amount of coloured samples can be determined by calorimetric titration method using n-butylamine, ethyl acetate or dioxane as the titrating base [88].
The amount of gaseous bases which a solid acid can adsorb chemically from gaseous phase is a measure of the amount of acid on its surface. When gaseous bases are adsorbed on acid sites, a base adsorbed on a strong acid site is more stable than one adsorbed on a weak acid site which, is more difficult to desorbe. As elevated temperature stimulates the evacuation of the adsorbed bases from acid sites those at weaker sites will be preferentially evacuated. Thus the proportion of adsorbed base evacuated at various temperatures can give a measure of acid strength. When prolonged subsequent evacuation does not produce no further decrease in sample weight, then the base which is retained up on the sample is understood to be chemically adsorbed [67-68].

The bases used as adsorbate so far include quinoline, pyridine, piperidine trimethylamine, n-butylamine, pyrol and ammonia [67]. The various bases are adsorbed to different extent even by the same catalyst. Temperature programmed desorption of basic molecules was also used for the estimation of acid amount together with the acid strength of the solid [79].

The transformation of an indicator into its conjugate acid form can be detected spectrophotometrically and spectroscopic method was introduced by Leftin and Hobson and Terenin. [80-81]. Drussell and Sommers presented the use of a series of fluorescent indicators for use in spectrofluorometric titration [82]. UV spectrophotometry has been applied for measurement of acid strength of SiO$_2$-Al$_2$O$_3$ catalysts using 4-benzoazodiphenylamine, 4-nitroaniline and 2,4-dinitroquinoxaline[83]. The adsorption of
pyridine on V-Ti mixed oxide prepared by the gas phase method has been studied by IR spectroscopy [84]. V$_2$O$_5$-TiO$_2$ oxides exhibited both Bronsted and Lewis acid sites.

J. Take et al studied surface acidity by the titration of solid acid with indicator itself in a non polar solvent and it determines the number of acid sites from the amount of indicator adsorbed at saturation [89]. Yoshizumi et al determined acid strength distribution on SiO$_2$-Al$_2$O$_3$ catalyst calorimetrically by measuring the heat of adsorption of n-butylamine from benzene solution [90].

Previously reported methods for the determination of the acid amount measures either Lewis acid or Bronsted acid. It is necessary to distinguish between Bronsted acid and Lewis acid sites for the catalytic action of solid catalysts. Malinowski and Szczepanska measured the amount of Bronsted acid by potentiometric titration of a solid acid in anhydrous picoline with 0.1 N NaOH [91]. Leftin and Hall [92] reported that amount of Lewis acid can be determined from the amount of triphenyl carbonium ion formed when the solid acid abstracts a hydride ion from triphenyl methane as shown below.

\[
\text{Ph}_3\text{CH} \quad \text{Lac} \quad \rightarrow \quad \text{Ph}_3\text{C}^+ \quad \text{H}^- 
\]

In an IR study of pyridine chemisorbed on SiO$_2$-Al$_2$O$_3$ catalysts of varying Si content, Schwarz discovered a new method for the measurement of Lewis and Bronsted acid sites.
The spectrum of pyridine which is coordinatively bonded to the surface is very different from that of the pyridinium ion also permit differentiation between acid types on the surface of a solid acid [94].

The acid properties of single oxides TiO$_2$, SiO$_2$, Mo$_2$O$_3$, Al$_2$O$_3$ and binary oxides have also been studied [73]. Many combination of transition metal oxides have also found to show remarkable acidic properties [95-100]. C.G.R. Nair and coworkers reported the acid base properties of single oxides, binary oxides and ternary oxides prepared from SiO$_2$, Al$_2$O$_3$ and Mo$_2$O$_3$ by precipitation method at different pH [101]. They employed titration method of Benesi [71].

The amount of basic sites can be determined by titrating a suspension in benzene of a solid on which an indicator has been adsorbed in its conjugate basic form with benzoic acid dissolved in benzene. The benzoic acid titres are a measure of the amount of basic sites having basic strength corresponding to the pKa value of the indicator used [67]. Gaseous acid adsorption method can also be used for basicity determination. Acidic molecules like CO$_2$, NO and phenol are used as adsorbates [67,102]. Adsorption of phenol is not preferred because it is easily dissociated to adsorb on both acidic and basic sites. NO is used for the measurement of unusually strong basic sites [103].

A method of determining the basicity at various basic strength by titrating a solid suspended in benzene with trichloroacetic acid using a series of Hammett indicators was
proposed by K. Tanabe and T. Yamanaka [104]. J. Take developed a method for the
determination of basic strength of solid suspended in cyclohexane with benzoic acid using
a series of Hammett indicators [105]. They found that base strength of alkaline earth oxides increased remarkably upon heat treatment in vacuum. TPD measurements of desorbed CO₂ were also used for the measurement of basicity of alkaline earth oxides [106]. Ai have also reported the correlation between basicity measurements and oxidation activity [107].

Y. Namanaka and K. Tanabe determined the basicity of a series of oxides and found the order of basicity as follows, ZnO > γ Al₂O₃ > BaO > Act. Al₂O₃ > B₂O₃ > ZrO₂ > MgSO₄ > MoO₃ [104]. Basicity of Al₂O₃-MgO catalysts have also been studied. Fedorynska et al. studied the acidic and basic properties of alumina-silica catalysts. They found that the basicity of aluminosilicates is closely associated with decrease in amount of Al₂O₃ [108]. J.L. Zotin et al. prepared alumina from Al(OH)₃ prepared by different routes and characterised then in terms of their acidic and basic properties [109].

G.W. Wang et al. measured the acid base properties of ZrO₂-SnO₂ with different composition by indicator method [79]. A series of UV spectroscopic studies have been made for indicators adsorbed on alkaline earth oxides and adsorption maxima of the spectra was correlated with the basic strength of the solid [83, 110]. Basicity of Al₂O₃-MgO catalysts have been studied. In the series of Al₂O₃-MgO catalysts those containing about 75% Al₂O₃ showed highest basicity [111]. Microcalorimetric measurements of the
differential heat of adsorption were used to probe the distribution of acid strength on a series of silica supported catalysts [112].

The acid base nature and catalytic activity of rare earth oxides have been reviewed by Tanabe et al [73]. The rare earth oxides have been classified as the basic metal oxides on the basis of O_{18} binding energy study [113]. Nakashima et al measured the basicity of Sm_{2}O_{3} by benzoic acid titration method [114]. The basicity of rare earth oxides are responsible for the catalytic activity for many reactions [115]. V.R.Choudhary and V.H.Rane determined acid and base properties of metal oxides by stepwise thermal desorption of CO_{2} from 323 to 1173 K and TPD of ammonia [116]. Acid base properties of some rare earth oxides and binary oxides with Al_{2}O_{3}, ZrO_{2} have also been measured by titration method using Hammett indicators following Tanabe method [117-119]. Activity of the oxides were correlated with acid-base properties on a common Ho scale.

According to Tanabe [120] the acid base properties of mixed metal oxides can be varied by choosing different metal oxide compositions at different concentrations and changing the heat treatment of sample. Depositing oxides of following cations Ga^{2+}, Zn^{2+}, Al^{3+}, Fe^{2+}, Mg^{2+}, Si^{2+} on to SiO_{2} increased the acid strength of the catalyst. Gallium oxide is the most electronegative oxide and when it is added to SiO_{2} strong acid sites are generated. Both Lewis and Bronsted acid sites are present on the surface [121]. IR spectroscopic studies of benzene adsorbed on several K.H.β zeolites where the extent of
proton exchange (K/Al %) varied from 0 to 88.32 % have been undertaken at different conditions [122].

It was reported that acid/base property of metal oxides depend upon the pretreatment temperature. The acidity of alkaline earth oxide increased remarkably up on heat treatment in vacuum [93]. It has already been reported that the generation of strong acid sites depend on both pretreatment temperature and surface composition [123]. J.B Peri has demonstrated that site quality depends upon the evacuation temperature and at least five kinds of hydroxyl species were identified on the surface of the alumina [124].

The generation of acid sites on mixed oxides was first proposed by Thomas [125] and further modified by Tanabe and coworkers [126]. Connel and Dumesic have studied the generation of new and strong acid sites on SiO₂ surface by the addition of several kinds of dopant cations [127]. It has been widely accepted that the generation of acid sites on the mixed oxides was ascribed to charge imbalance localized on M₁-O-M₂ bondings formed on the mixed oxides, where M₁ is the host metal ion and M₂ is the dopant metal ion [126]. The charge imbalance might be expected even on the single component metal oxides consisting of small particles, since the electronic properties of small size metal or oxide particles are some what different from those of the bulk materials [127]. These differences are partially attributed to the surface imperfections of crystallographic structures.
in small sized particles. The relation between particle size and surface acidity of metal oxides have also been reported [128].

H.Nakabayashi [129] studied the mixed oxides of TiO$_2$-SiO$_2$ and TiO$_2$-Al$_2$O$_3$ by IR spectroscopy after pyridine adsorption. Both Lewis and Brosted acid site were found on the surface of SiO$_2$-TiO$_2$ mixed oxides though no Bronsted sites were found on the surface of pure SiO$_2$ and TiO$_2$, while on the surface of TiO$_2$-Al$_2$O$_3$ mixed oxide no Bronsted sites were generated. Recently he has developed an idea that new and strong acid sites will be generated on finely divided pure metal oxides and has demonstrated an increase in acid strength with decrease in particle size.

The existence of coordinately unsaturated cations were proposed to be responsible for Lewis acidity [130]. A coordinatively unsaturated center can chemisorb molecule of water resulting in the production of Bronsted acid sites [67]. At low activation temperature Bronsted acid sites are responsible for the acidity and at higher temperatures because of desorption of chemisorbed water molecules Lewis sites are probable. Two types of electron sources are reported for the basicity of the metal oxides. One of them is surface hydroxyl ion and the latter is trapped electron at intrinsic defect sites on the lattice. Since the concentration of the former decreases with increase in temperature, the trapped electron centers must be responsible for the increase in basicity of the oxide with
increasing in temperature. Surface lattice oxygen ions also considered to be involved in many basic sites.

2.3. CATALYTIC ACTIVITY

In heterogeneous catalysis by metal oxides many correlations between the catalytic activity, including its selectivity and acidity/basicity of the oxides have been indicated. Several studies have been reported to have systematic comparison of the acidic and catalytic properties of metal oxides and mixed metal oxides [67,73]. Solid acid catalysts are backbone of major process of petroleum chemistry such as cracking, hydrocracking reforming, isomerisation and disproportionation of aromatics [67]. There are many industrially important reactions catalysed by homogeneous bases such as oligomerisation, alkylation, addition, cyclisation, oxidation, dehydrogenation etc. [131].

Hydrogen transfer reactions have been studied and found its importance in organic chemistry by many workers. In these Meerwin Pondorf Verly reduction (MPV) is a well known reaction, the mechanism of which involves a hydride transfer from aluminium isopropoxide to the carbonyl carbon of the ketone. MPV reduction was discovered in 1925 and has been used successfully in a number of instances [132]. It is prominent in terms of its compatibility with many different types of functional groups, selectivity for reduction and low cost of isopropanol [133]. But this method calls for not only the addition of excess of catalyst (100-200 % amount) but also the neutralisation of alkoxide
salt with strong acids. Therefore it has disadvantages such as need for tedious work ups in purification process and the unreusability of the catalyst as the disadvantage.

Many heterogeneous catalysts for the reduction are known. The use of heterogeneous catalysts such as MgO [133], MgO-SiO₂ [134], CaO [135] and Al₂O₃ [136] have also been reported to be successful. Kibby and Keithhall [137] have reported a hydrogen transfer reaction between alcohols and aldehydes over hydroxy apatite catalysts and proposed a mechanism similar to that of original MPV reduction. The advantage of the heterogeneous catalysts over conventional catalysts are easy product separation, the lack of a need for maintaining water free conditions, reusability of the catalyst and durability of the activity.

Reduction of aldehydes and ketones and the amidation and esterification of carboxylic acids proceeded efficiently over hydrous Zr(IV) oxides [138-140]. The reduction of carboxylic acids and esters with 2-propanol over hydrous Zr(IV) oxide and several other heterogeneous catalysts in vapour phase have also been reported [141]. These methods have advantage in purification of process, but they need to be carried out in vapour phase and require a high reaction temperature. Shibagaki et. al [138] studied the liquid phase reduction of aldehydes and ketones with 2-propanol over hydrous Zr(IV ) oxides. Studies on the kinetic isotope effect have indicated that the reaction rate is of first order dependence in each of the concentrations of carbonyl compounds, 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.

The reduction with 2-propanol as a hydrogen source over hydrous tin (IV) oxide has been proved to be successful. The reduction of aliphatic carboxylic acids gives the corresponding alcohols. Aromatic carboxylic acids and their derivatives were further reduced and corresponding hydrocarbons were obtained. The reduction of aromatic ketones and derivatives of benzoyl alcohols also give hydrocarbons [142]. The reduction of methyl benzoate and benzoic acid on Y$_2$O$_3$ catalysts under H$_2$ gas has been examined by IR spectroscopic flow reaction at 250-450° C [143]. Some rare earth oxides and their mixed oxides with alumina and perovskite compound were also found to be effective catalyst for the reduction of ketones with 2-propanol as a hydrogen source [42-43, 65-66, 115-117].

The reverse reaction of MPV reduction is known as Oppenauer oxidation. In 1937 Oppenauer showed that unsolvated steroid alcohols could be oxidised to the corresponding ketones in excellent yields through the use of aluminium t-butoxide in the presence of a large amount of acetone, which can act as hydrogen acceptor, the large excess serving to shift the equilibrium in the desired direction [144]. In view of reversible nature of the reaction many statements as to the mechanism of MPV reduction are equally applicable to Oppenauer oxidation. Activation of the alcoholic hydrogen atom by the
aluminium resulting in the hydrogen bonding has also been proposed by Woodward et al [145].

Generally oxidation has been carried out by the use of metal alkoxide catalysts [140]. The most common catalysts used are aluminium t-butoxide, isopropoxides and phenoxides. Aluminium isopropoxides has been found to be best reagent for the oxidation [140,146]. In the modified reactions benzophenone was used as the oxidising agent since it cannot undergo condensation in the presence of a strongly basic catalysts. According to Oppenauer a solvent is necessary for oxidation of alcohols. Toluene is used occasionally [147]. Time and temperature can be varied over a wide range depending up on the alcohol to be oxidised, although the maximum temperature that can be attained was controlled by the choice of the solvent and hydrogen acceptor.

Heterogeneous catalysts for oxidation reaction have also been reported, which find advantages over the conventional reactions. SiO2, MgO, and Al2O3 have been proved to be successful [148]. Kuno et al have shown that liquid phase reduction of primary and secondary alcohols proceeded very efficiently using benzophenone as the hydrogen acceptor [149]. The influence of hydrogen acceptor on the oxidation rate has been investigated by the use of several ketones and the oxidation rate was influenced by the electron density and steric hindrance around the carbonyl group. The dependence of the reaction temperature was also investigated. The reaction of acids with alcohols was also developed to produce esters by catalysis with oxides.
2.3.1. Acid-base property and catalytic activity

Good correlation has been found in many cases between the total amount of acids and the catalytic activities of the solids. K. Tanabe has reported the correlation of activity of several reactions with acidity/basicity of oxide surface [67]. The nature and catalytic activity of the metal oxides, sulfates etc. were elucidated through the investigation of the structure of acid base centres and by the comparison with the kinetics of homogeneous acid base catalysis. The conversion and selectivity of a reaction depend upon the acid-base behaviour of the surface. The selectivity of solid catalysts is influenced by the acid-base properties and many other factors such as geometric structure (particularly pore structure) the distribution of sites and the polarity of the surface sites.

Catalytic activities of alumina in a range of reactions such as the isomerisation of hydrocarbons, the polymerisation of olefines etc. have been attributed to the acidic properties of surface [72,124], where the acidity remarkably changes with the degree of hydration. The influence of the acid strength of solid catalyst on their catalytic activity per unit surface amount of acid in the dimerisation of propylene, isobutylene and the dehydration of isopropyl alcohol have been studied by Dzisko [151]. The metal oxides show difference in the value of acidity depending upon the method of preparation. H.Pines and C.N. Pillai [152] reported that alumina catalysts prepared from sodium aluminate were only weakly acidic while alumina prepared from aluminium isopropoxide was slightly acidic, the former one did not cause extensive isomerisation of olefines during
dehydration of alcohol. H. Pines and H. Haag [153] proposed that \( \text{Al}_2\text{O}_3 \) had intrinsic acidity which was responsible for the typically acid catalysed reaction such as dehydration of alcohols and skeletal isomerisation of 3,3-dimethylbutene and cyclohexene.

Minachev et al. studied the hydrogenation of ethylene at low temperature as part of a study of the catalytic activity of rare earth oxides. \( \text{La}_2\text{O}_3 \) activated at high temperature was found to be highly active and activity has been correlated with basicity [154]. In the case \( \text{SiO}_2-\text{Al}_2\text{O}_3 \) and \( \text{NiO-SiO}_2 \) oxides, Ozaki and Kimura suggested that the Lewis acid sites could be effective for isomerisation, a proton being donated by the olefine molecule chemisorbed on the Lewis acid sites [155].

H. Hattori et al. studied the double bond migration of 2-propenyl ethers to 1-propenyl ether over solid base catalysts to develop a heterogeneous catalyst for reaction and to elucidate the reaction mechanism [156]. Among the catalysts, \( \text{CaO} \) exhibited the highest activity and \( \text{La}_2\text{O}_3, \text{SrO} \) and \( \text{MgO} \) also showed higher activities. \( \text{ThO}_2, \text{ZrO}_2 \), and \( \text{Y}_2\text{O}_3 \) were slightly active, but \( \text{ZnO}, \text{Al}_2\text{O}_3 \) and \( \text{SiO}_2-\text{Al}_2\text{O}_3 \) were completely inactive. The inactivity of oxides is probably because of the capacity of acidic sites on the surface to adsorb strongly the reactant by the lone pairs on the oxygen atoms. Double bond migration of alkylamines to enamine over basic oxide catalysts was also reported [157]. The double bond migration of n-butene over alumina was considered to be catalysed by Lewis acid sites [158].
The hydrogenation and isomerisation of n-butenes over basic La$_2$O$_3$ and ZnO were also reported [154,159-161]. Rosynek et.al [160] studied the catalytic activity of La$_2$O$_3$ and showed that basic sites were essential for the isomerisation of butenes. The isomerisation of butenes over several ThO$_2$ catalysts were also reported while investigating the nature of the active sites on the basis of observed surface properties and mechanistic study of reactions [162]. The number of basic sites of La$_2$O$_3$, Y$_2$O$_3$ and CeO$_2$ were determined and correlated with the catalytic activity for the decomposition of 4-hydroxy 4-methyl 2-pentanone and isomerisation of butene. The catalytic activity of these catalysts were attributed to basicity and good correlation of basicity with activity was found [163].

E.Rodenas et.al studied in detail the surface and catalytic properties of TiO$_2$-Al$_2$O$_3$ of various composition which were prepared from co-precipitation of Ti(SO$_4$)$_2$ and Al$_2$(SO$_4$)$_3$ with urea as well as with aqueous ammonia [164]. The effect of preparation method on the difference in composition between the surface layer and the bulk and on the acid-base and oxidising/reducing properties and catalytic activities for 1-butene isomerisation and 2-butanol dehydration have been examined. A good correlation was found between the acidity and activity for the dehydration. It has been reported that the results concerning the characterisation of acidity and basicity of a large series of metal oxides including supports, active phase and promoters have been reported by A.Gervasini et. al [165,166]. They studied the decomposition of isopropanol as test reaction for the determination of acid base character of catalyst.
The first order rate constant for the formation of benzyl benzoate from benzaldehyde over CaO calcined at various temperatures was found to change in parallel with the change in catalyst activity. There was good correlation between the activity and the amount of base per unit surface area [167]. The catalytic activity for oxidation and olefine isomerisation of the ternary system MoO$_3$-B$_{12}$O$_3$-P$_2$O$_5$ catalysts have been correlated with acid/base properties between the catalyst and the reactant [95]. The acidity and the basicity of a series of TiO$_2$-P$_2$O$_5$ and V$_2$O$_3$ system was measured by using static and pulse method and the catalytic behavior of the reactant was correlated with the acid base properties. Oxygen mobilities and acidity-basicity behaviour are responsible for their catalytic action [168]. Vapour phase conversion of cyclohexanol to cyclohexanon in the presence of different basic catalyst showed that some of them are able to activate dehydration and dehydrogenation simultaneously. The dehydrogenation activity was related to the existence of basic sites originating from the oxygen in the oxide lattice [169].

M. Waqif et. al studied acid properties of pure and sulfate promoted metal oxides and they used dehydration of methanol to dimethyl ether as the test reaction. It was found that this reaction is sensitive to sample acidity. J.L.Sotin [109] studied acid base properties and textural properties of aluminas prepared from aluminium hydroxides containing controlled amount of impurities. It was established that besides basicity the
pore size distribution of alumina strongly influence the catalytic activity in H₂S -SO₂ reaction due to the capillary condensation of sulfur in small pores.

Involvement of surface acid/base properties was tested by studying the benzonitrile formation from benzaldehyde and ammonia [171]. Investigations were carried out to have a systematic comparison of the acidic and catalytic properties of single oxides like SiO₂, TiO₂, Al₂O₃, MoO₃ and their binary oxides and ternary oxides. The acid base strength distributions were determined by titration methods and correlated with the catalytic activity for the alkylation of toluene and the dehydration of 2-propanol. Mosial catalysts (oxides of molybdenum) showed high activity towards the alkylation of toluene [101]. The acidic properties of a series of TiO₂-SiO₂ systems and their relations to the catalytic activities have been reported for the amination of phenol with ammonia to produce aniline eventhough both of single oxides SiO₂ and TiO₂ showed little acidity [171].

It was found that activity of the oxides depend upon the pretreatment temperature. For TiO₂-SiO₂ mixed oxides obtained by co-precipitation methods highest activity was found at 500°C [171]. The variation in catalytic activity of rare earth oxides and their analogous scandia and yttria in ethylene hydrogenation was studied as a function of pretreatment temperature between -12°C and 20°C [154]. Correlation between the surface properties and the catalytic activity of anhydrous ZrO₂ calcined at several temperatures was investigated, the best activity was obtained for the oxide calcined at 300°C [172].
Surface acidic priorities of Nb$_2$O$_5$ in H$_2$O and its catalytic activity for the isomerisation of 1-butene, polymerisation of propylene and the dehydration of 2-butanol were examined by Iizuka et al. The active sites on the catalyst preheated at moderate temperatures were ascribed mainly to Bronsted acid sites on the basis of IR study of adsorbed pyridine [173]. The catalytic activity for the decomposition of iso-butyl propionate in a homogeneous system was correlated with acid strength of Keggin type heteropoly acids [174]. The cis trans isomerisation of crotononitrile has been investigated using various catalyst including Al$_2$O$_3$-MgO, CaO, Na$_2$CO$_3$ and NaOH supported on SiO$_2$ gel and some organic compounds. It was found that the isomerisation is a base-acid bifunctional catalysis. The catalytic activity of butene over Sm$_2$O$_3$ has also been investigated in view of acid-base catalysis.

Concentration of Bronsted and Lewis acid sites on sulfated zirconia catalyst was determined by using $^{31}$P mass NMR spectroscopy [176]. The treatment at lower temperatures resulted in the generation of Bronsted acid sites and at higher temperatures three types of Lewis sites were generated. In a related study the catalytic activity of these oxides for alkylation of isobutene with 2-butanol was determined at different temperatures and the activity was found to depend upon the acidity.
2.4. ZIRCONIA AND RARE EARTH OXIDES AS CATALYSTS

ZrO₂ exhibit catalytic activity for a number of reactions. The interest in ZrO₂ as a catalytic material could be ascribed to its uniqueness in being the only single metal oxide which possess four chemical properties viz. acidity, basicity, oxidising and reducing properties [177]. It has been reported that zirconia shows specific catalytic activities for the cleavage of C–H bonds [178], the hydrogenation of 1-3-butadiene by molecular hydrogen and hydrogen donor molecules such as cyclohexadiene [179-181] and high selectivities for the formation of 1-olefine from secondary alcohols [182] and isobutane in the reaction of CO + H₂ [183]. All these characteristic behaviour of ZrO₂ were considered to be due to the acid base functional catalysis. Fugi et al found that ZrO₂ is an excellent support to La₀.₈ Sr₂ CoO₃ catalysts used for complete oxidation of propane [184].

Several ZrO₂ supported catalysts were prepared by metals like Pd, Cu and metal oxides like MgO SiO₂ and CrO₃ [185-187]. In an earlier report on Cu supported catalysts, it was found that Cu supported on ZrO₂ is superior to Cu supported on other oxides [188]. Cu supported ZrO₂ was found to be ideal catalyst for dehydrogenation of cyclohexanol, the selectivity to cyclohexanol was found to be 100 %, which is a typical property of the copper assisted by the predominant basic character of ZrO₂ [189]. The role of ZrO₂ as a support to the chromia catalyst in the aromatisation of isophoron to 3,5-xylenol which has importance as an industrially potential intermediate has also been studied [190].
Hydrodesulphurisation of sulfur containing aromatics has been major operation in the petroleum chemistry [191-192]. ZrO₂ as a support is receiving attention in recent years. It has been reported that Mo supported on ZrO₂ exhibit higher catalytic activity than Al₂O₃ supported systems [193]. Reddy et. al [194] reported hydrosulphurisation and hydrogenation activities of MoS₂/ZrO₂. Combining these values with that of Mo supported on Al₂O₃ it was found that MoS₂/Al₂O₃ is marginally more active than MoS₂/Al₂O₃. The activity for thiophene hydrodesulphurisation was also evaluated by Sedlack et. al [195]. It has been reported that activity per gram of metal is higher in the case of MoS₂/Al₂O₃. However Pratt et al [196] reported higher activity for MoS₂/ZrO₂ compared to Al₂O₃ supported on ZrO₂ for the same investigation. They have found that the morphology of the catalyst is different from that on Al₂O₃ supported ones.

Zirconium-Molybdate catalyst has been also found to be good catalyst for esterification reaction [197]. The presence of acid sites on the catalyst indicate good potential for application in Bronsted catalysis. It has also been observed that amorphous ZrO₂ possess greater number of acid sites as compared to crystalline material and the amorphous materials are more active [198]. The ion exchange property of α- zirconium phosphate has been examined in detail [199] and the hydrogen form has shown to be an acid catalyst.
Phenyl ethers and substituted phenyl ethers are important intermediates for the manufacture of different agrochemical and pharmaceutical based products. Heterogeneous esterification process using TiO$_2$, ZrO$_2$, ThO$_2$ etc., overcome the drawbacks over the conventional routs and provided a unique way for the large production of salt free ethers with high selectivity [200-201]. Depolymerisation of paraldehyde in non aqueous solvents catalysed by heterogeneous acids like ZrO$_2$, SnO$_2$-ZrO$_2$ have been studied and the activity was correlated with acid strength distribution of oxides calcined at various temperatures [202].

The conventional route for the synthesis of anthraquinone by Friedel Crafts reaction containing two steps involves the use of AlCl$_3$ and oleum leading to corrosion and environmental pollution. Continuous search was on for a suitable catalyst that can substitute for AlCl$_3$ and H$_2$SO$_4$ and also to make the process continuous in a single step. Several papers are reported describing the possibility of employing super acids such as SO$_4^{2-}$/ZrO$_2$ and rare earth exchanged Y zeolites for promoting the Fried Crafts acylation [203-206]. Acidic sites as well as basic sites are involved in the activity for the isomerization of 1-butene. Acid-base pair sites are probably exposed Zr ions with adjacent O$_{2-}$ ions which are generated by the removal of H$_2$O molecules from neighboring OH groups.

ZrO$_2$ aerogels are attracting much attention because of their promising potential as catalysts of use in combustion and hydrogenation, piezoelectric ceramics and thermal barriers [207]. However zirconia aerogels have been less investigated and used than those
of silica and alumina. It therefore appeared essential to obtain a deep and systematic insight into the synthetic chemistry of ZrO₂-based materials with optimum properties for selected areas of use. CeO₂-ZrO₂ aerogels have been characterized in order to elucidate the effect of the structural homogeneity as the stability of their total surface area at high temperature [208]. Fe₂O₃/ZrO₂ catalysts prepared by impregnation and co-precipitation methods were used for catalytic hydrogenation of CO and the role of zirconia in the catalyst was discussed by Chen et al. [209].

The stabilised cubic zirconia is widely studied and used as solid electrolytes for fuel cells, oxygen sensors and so on, because of its high ionic conductivity due to oxygen ion migration, its stability in wide temperature range and its negligible electronic conductivity. A systematic study of the structural and dynamical properties of oxygen conductor yttria stabilised zirconia for different dopant concentrations using a method of molecular dynamic simulation has been reported [210]. The reactivity of V₂O₅ with TiO₂-ZrO₂ mixed oxide support was investigated by the X-ray powder diffraction technique [211]. Catalytic activity of copper oxide catalyst for CO oxidation can be significantly enhanced by the oxygen ion conducting support, yttria stabilised zirconia [YSZ] which leads to supported copper oxide exhibiting a precious metal like catalytic behavior [212]. The activity enhancement of yttria stabilised supported copper oxide was attributed to the surface oxygen vacancy of YSZ support providing a second reaction pathway by means of the formation of interfacial active center, although the redox cycle mechanism is still operative on the CuO/YSZ catalyst. Catalytic property of ZrO₂-SiO₂ for cyclohexanone
conversion has been studied. Textural and morphological properties were correlated to explain catalytic behavior [213].

Although the investigations of the catalytic properties of rare earth sesquioxides have been multiplied, the primary modes of surface interaction on these materials remains largely undefined. Rare earth oxides are important in the fact that they find application in many catalytic reactions. It has been suggested that addition of CeO₂ and other earth oxides to alumina can stabilise the surface area and the spinel transition phases of the alumina support used in automotive catalysis [214].

Recent studies have demonstrated that several of the lanthanide sesquioxides (M₂O₃) are effective catalysts for the oxidative coupling of methane to ethane and ethylene [215]. The catalytic activity of rare earth oxides could be attributed to their basic property. Campbell et. al have indicated that the addition of rare earth oxides for the abstraction of H from the methane molecule to form methyl radicals can best be related to the basicity of the oxides [115,216]. Good correlation was found between the basicity and catalytic activity for the decomposition of 4-hydroxy 4-methyl-2-propanone on La₂O₃, similar to that of alkaline earth oxides [217]. The comparison of the catalytic activity and selectivity with the basicity of the catalyst shows that the higher conversion activity, C₂-selectivity and C₂ yield observed for La₂O₃ are consistent with higher basicity [116]. Otzuka [215,218] have shown that among the rare earth oxides Sm₂O₃ shows highest activity and C₂ selectivity for C₂-hydrocarbons in oxidative coupling of methane.
Empirical studies have demonstrated that, following appropriate pretreatment, rare earth sesquioxides are active catalysts for a variety of reactions including o/p hydrogen conversion [219], deuterium exchange reactions of hydrocarbons [220], H₂-D₂ equilibration [221], alcohol dehydration [222], olefine isomerisation [223], decomposition of N₂O and NO [224], and oxidation reaction of H₂ [225] and CO [224] and hydrocarbons [224]. In the last several years, it has been found in a series of the catalytic oxidations that the catalytic activity of the lanthanide oxides significantly differ from each other. Saznov and coworkers [226] measured the active cation energies of the isotopic exchange of oxygen and of the desorption of CO in the oxidation of CO and found that the dependence of activation energies on the atomic number was similar to that of the magnetic moment. Minachev et al [225] compared the catalytic activity in the oxidation of H₂ and propylene and found that catalytic activity depends on the binding energy of oxygen with the surface and on the valance of the lanthanide ions.

Bakumento and Chashenikov [227] found in the oxidation of hydrogen that activity of Er and Nd oxides were lower than Ce, Pr and Tb oxides with the tetravalent ions, which was explained on the basis of the heat formation of oxides. Lazukin and coworkers [228] found a good correlation between the activation energy of the oxidation of propylene and that of the electrical conductivity and concluded that the electron transfer from the reactant or intermediate to the catalyst surface is involved in the rate determining
step. Some of the authors [225-226] suggested from these that the catalytic activity of the lanthanide oxides depend on the electronic configuration of the inner 4f subshell.

The catalytic oxidation of butane was studied over a series of lanthanide oxides in order to investigate the effect of electronic configuration on the catalytic activity [229]. La$_2$O$_3$ was one of the least active catalyst. CeO$_2$ was the most active one and the activity decreased with an increase in the atomic number from Ce to Gd. The activity of Tb was the second highest and again the dependence of the activity on the atomic number was in good agreement with the heat of formation of oxide. The dependence of the electrical conductivity and the heat of formation could be related to the stability of M$^{4+}$ ion, to which the catalytic activity could be related by assuming that the rate determining step is the oxidation of M$^{3+}$ ion to the M$^{4+}$ ion. A good correlation was obtained between catalytic activity and fourth ionisation potential as a measure of the stability of M$^{4+}$ ion relative to the trivalent ion. The correlation of catalytic activity with the atomic number was interpreted in terms of two factors based on the electronic configuration of the 4f subshell and the exchange energy between the 4f electrons.

Rare earth oxides are stable to high temperatures with respect to its valance and crystallographic structures. They are also hardly reducible. The addition of some rare earth oxides to Rh-Al$_2$O$_3$ catalysts enhanced the activity of hydrogenation of CO to methane. There was linear correlation between the CO skeleton propagation of the hydrocarbons formed and the basicity of the rare earth oxides [230]. Surface parameters
and thermal dehydration/rehydration behaviour of La(OH)₃/La₂O₃ system have been examined with a view towards establishing suitable methods for preparing different catalytic forms of the rare earth oxides [222].

Temperature programmed desorption (TPD) and O₁₈⁻ tracer technique have been adopted to examine the contribution of the lattice oxygen (oxide ion) in rare earth oxide like Pr₂O₁₁ to the oxidation of CO [231]. The TPD measurements revealed that some of the lattice oxygen atom could be reduced by CO forming CO₂. However the oxygen vacancies formed by the reduction were completely filled with oxide ions, if oxygen existed in the gaseous phase. The multipath way (dehydration/dehydrogenation) conversion of ethanol has been used to investigate the nature of behaviour of catalytically active sites on La₂O₃ and Nd₂O₃ [232].

Minachev [225] has summarised many of the catalytic properties of Dy₂O₃ with particular reference to organic reactions. The activity of Dy₂O₃ is very similar to that of erbium oxide and it is especially active towards n-butane cracking and double bond migration of 1-butene. Many studies have been made in the case of reactions involving hydrogen or oxygen adsorption on Dy₂O₃ [233]. The hydrogen-deuterium exchange reactions occur with Dy₂O₃ above 250 K and shows a temperature dependence similar to the p-hydrogen conversion, leading to the conclusion that both these reaction involve equivalent dossociative mechanisms at these temperatures [234]. Selwood [235] studied the non dissociative mechanism in a magnetic field and observed an increase in activity

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towards p-hydrogen conversion in a strong field but no change in activity in a weak field. Oxygen exchange reactions indicate that activity increases with a rise in mobility of surface oxygen with Dy$_2$O$_3$ becoming active above 600°C.

The reduction of methyl benzoate and benzoic acid on Y$_2$O$_3$ under hydrogen has been examined by using an IR spectroscopic flow reactor at 250-450°C [236]. CO hydrogenation over mixed oxides of 3A and 5A groups (Y$_2$O$_3$, La$_2$O$_3$, CeO$_2$ and ZrO$_2$) with a 3B group (Al$_2$O$_3$, Ga$_2$O$_3$ and In$_2$O$_3$) was carried out and found good variation with rare earth concentrations [143]. Taylor and Diamond have reported that paramagnetic substances like Gd$_2$O$_3$, Dy$_2$O$_3$ are more active than non-paramagnetic substance. Selectivities of rare earth oxides for dehydration of butanols have also been reviewed and established the good correlation between product distribution and catalytic properties [228].
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