CHAPTER I

GENERAL INTRODUCTION
1.1 Catalysis

The history of catalysis began from 1796 with the studies by von Marum on the dehydrogenation of alcohols using metals. However, the term catalysis was first formulated by John Jacob Berzelius in 1836. Ostwald defined catalyst as a substance, which increases the rate of a chemical reaction. Today, in one form or another, catalytic science reaches across the entire field of reaction chemistry and catalytic technology is a keystone of much of modern industry which is used for the manufacture of value added fine chemicals. The field of catalysis is now so wide and detailed and its applications are numerous. The development of novel catalysts, making efficient use of energy and raw materials with minimal impact on the environment is an extremely challenging task.

The replacement of homogeneous catalysts by heterogeneous systems in chemical industry has brought about efficient catalytic processes that eliminate or minimise the use and possible release of environmentally hazardous materials. Heterogeneous catalysis facilitates the separation of catalyst from the products and offer new reaction pathways for higher product selectivity with costless disposal of the used catalyst in comparison with the homogeneous catalysts. Low energy synthesis, prevention of reactor corrosion etc. are other attractive features of heterogeneous catalysis.

Catalyst design, which is most crucial for the development of new catalytic processes, is an exclusively interdisciplinary endeavor, which is located at the interface of chemistry, chemical engineering and material science. It requires some understanding of the mechanism of the catalytic reaction, and the knowledge of vital structural parameters that determine the activity, selectivity and lifetime of the catalyst and their interdependence. Studies on the interrelation between structure and chemical properties of the solid materials and catalytic properties (structure - activity
relationships) are at the origin of catalyst design. Various concepts and techniques of solid state and surface chemistry are applied for synthesizing and modifying catalyst materials with the required structural and chemical properties. Another important aspect of catalyst design is the tailoring of textural properties, i.e. geometrical shape, surface area and pore structure, which is essential for optimizing the mass transfer of the reactants and products in the process network of the catalyst.

Based on the physico chemical nature catalysts are generally classified as,
- metal oxides / mixed metal oxides
- zeolites
- natural clay minerals
- metal complexes
- enzyme catalyst
- cation exchanged resins

Apart from this, they can also be classified on the basis of their functions as,
- shape selective catalysts
- phase transfer catalysts
- redox catalysts
- acid base catalysts

Another mode of classification is based on their behaviour in a particular reaction; as structure sensitive and structure insensitive. Rates of structure sensitive catalytic reactions alter markedly when the crystallite size of the system is changed, whereas rate is independent of crystallite size for structure insensitive reactions.

1.2 Metal oxide catalysts

The developments in surface science techniques have provided important information about the surface structures, chemical compositions and electronic properties of the metal oxide surfaces. In metal oxides, coordinative unsaturation is principally responsible for the ability towards adsorption and catalysis of various reactions. Metal oxides are made of cations and anions. The ionicity of the lattice,
which is often less than that predicted by the formal oxidation states results in the presence of charged adsorbate species and the common heterolytic dissociation of the molecules. Exposed cations and anions form acidic and basic sites as well as acid base pairs. Besides this, the variable valency of the cation results in the ability of the oxides to undergo oxidation and reduction. These properties have determining effects on the interaction of molecules with oxide surface. In addition to being used as catalysts, metal oxides are also precursors for other important catalysts. For eg, in hydrodesulfurisation catalysts, cobalt molybdenum sulfide is the active phase in which Co-Mo mixed metal oxide is used as precursors.

The foremost use of metal oxides in catalysis is towards oxidation reactions, on which a large number of industrial processes are based. Generally these metal oxides are divided into four main categories; simple, mixed, modified and supported. The major advantage of multi component systems is that it is possible to tune oxygen sorption properties by meticulously choosing the required metal components so as to crystallize in a particular structural pattern. The reactivity of oxygen in this case is strongly dependent on the kind of neighbouring metal ions as well as M-O bonding distance and bond strength.

The present investigation is based on supported vanadia catalysts. This category of catalyst has innumerable applications in fine chemical industry, especially in the area of oxidation reactions of industrial importance. Vanadia has an age-old history in the vast area of heterogeneous catalysis as the catalyst used for contact process. It has an unusually large number of stoichiometries. Their structures are very similar and can be constructed from the same building blocks. This contributes to the easy conversion of one oxide to another of adjacent stoichiometry by oxidation or reduction. The easy oxidation and reduction and the existence of cations of different oxidation states in the intermediate oxides have been proved to be important factors for these oxides to possess a prominent role in redox catalysis. But for pure V$_2$O$_5$, the selectivity to a desired product is too low, which often exhibits complete
oxidation activity. It is accepted that addition of other elements improves the selectivity. This is achieved by supporting vanadia on suitable supports. The fine dispersion of the active species on the support makes supported vanadia dominate over bulk vanadia. Supported vanadia catalysts are renowned for their activity towards various types of partial or selective oxidation reactions. A large number of research work have been devoted to provide insight into the nature and reactivity of supported vanadia catalysts.

1.3 Methods of preparation of supported vanadia catalysts

Crystallographic form of the supported oxide depends on the preparation method. The principal technique of supported catalyst preparation involves two stages. First stage is dispersion and is achieved by impregnation, adsorption from solution, co precipitation or deposition etc. while the second stage involves calcination. The loading as well as the details of drying and calcination conditions affects the dispersion of the final oxide on the support.

1.3.1 Impregnation method

In impregnation, a solution containing the desired cation is added to the support. If the volume of the solution is just enough to fill the pore volume of the support, the method is called impregnation by incipient method. Excess of the solution may be used and solvent is evaporated and the oxide is formed after calcination; the method is known as wet impregnation. The loading can be varied over a wide range by changing the concentration and the amount of solution used. The pH of the solution decides the final dispersion of the active oxide species. Different species will be generated in the solution with variation of the pH. For eg., at pH < 1, vanadyl cation, pH < 4 three dimensional decavanadate [HV_{10}O_{28}]^{5-}, pH < 7 two dimensional tetra and trivanadate, 9 - divanadate, 12 - monovanadate are the different species formed [1].
1.3.2 Ion exchange method

This process can be applied for oxides that have precursor compounds that dissolve in water and form ionic complexes that contain the desired metal ion. It involves ionization of the surface hydroxyl group of the support in aqueous medium. The desired ion is then attached to the surface by electrostatic force. Subsequent calcinations of the ion exchanged material produces the oxide. High dispersion can be attained through this method, since the electrostatic repulsion keeps the complexes apart.

Spraying in vacuo a solution of the precursor on the oxide is another method reported in the case of Fe₂O₃-MoO₃ [2]. Precursors can also be introduced in gas phase. This method is adopted for the preparation of V₂O₅/Al₂O₃ by treating Al₂O₃ with a stream of nitrogen containing VOCl₃. VOCl₃ is then hydrolysed with steam diluted with nitrogen. The process can be repeated to increase the vanadium loading.

1.3.3 Chemical vapour deposition

Active component is deposited from a volatile inorganic or organometallic compound on the surface of the support by reaction with the OH groups. For eg, TiO₂ supported on alumina can be prepared using a heptane solution of TiCl₄ or Ti(OC₃H₇)₄ [3].

1.3.4 Co-precipitation Method

In this method, the active and supporting oxides or their precursors may be co precipitated from a solution containing compounds of each element. Here the active component is dispersed throughout the bulk as well as on the surface. This method was adopted by Cavani et al. in the preparation of V/Ti systems by adding NH₄OH to a mixed V(IV) and Ti (IV) solution [4].
Another method is heating a mixture of the oxides. This leads to the spreading of the active oxide over the support. Repeated impregnation or a combination of ion exchange and impregnation can increase the final loading.

1.4 Structure of supported catalysts; metal-support interaction

Vanadia species get stabilised on the surface of the metal oxide support. The interaction, which results in the stabilisation can be viewed either in terms of minimization of surface free energy or in terms of formation of new chemical compounds. The actual structure present will depend amongst other things on the chemical nature and crystal structure of the support, the vanadium loading, and on the presence of adventitious impurities. Metal - support interaction leads to several physical and morphological changes of the support as well as the active oxide species. Often oxides are prepared by calcinations at relatively high temperature that reduces the surface area. A support effectively reduces sintering and thereby enhances the effective surface area. Support also serves as a heat conduction medium. This is particularly applicable for oxidation reactions, which have large heat of reaction. A support of high thermal conductivity helps to remove heat from the reaction site and reduces hot spots, which usually degrade selectivity. Apart from this, supports are used to improve mechanical strength, thermal stability and lifetime of the active metal species. In some other cases, support provides a certain desirable morphology for the oxides, like exposure of a particular plane, which will be active for specific reactions.

Results reported in bibliography indicate that the dispersion of vanadium oxide as well as the structure can be understood on the basis of the acid base character of the supports used; the basic and amphoteric oxides favour the bidimensional dispersion (often with the formation of compounds), whereas acidic supports favour three-dimensional micro units of \( V_2O_5 \). The formation of new compounds is thermodynamically favourable, but kinetically limited. High temperature calcination enhances the formation of compounds. The tendency of the vanadia species to get dispersed is related to its basicity and decreases as basicity decreases. The
agglomeration of vanadia species to form crystalline vanadia is favoured with the acid character of the support. Accordingly, V$_2$O$_5$ crystals supported on SiO$_2$ is reported by Lopez Nieto et al [5]. Metal vanadates are observed on basic metal oxide supports [6].

The formation of these different types of vanadia species can be accounted as follows; since vanadia is comparatively acidic, it reacts easily with basic oxides with preferential formation of vanadates, whereas a weaker interaction with the acidic supports favor the aggregation of VO$_x$ leading to the formation of crystalline V$_2$O$_5$. Earlier works in this regard are briefly discussed below.

Dispersion of vanadia on ZrO$_2$ system is reported by Schart et al [7] and Sohn et al [8]. A rapid formation of a multilayered structure has also been observed on ZrO$_2$/V$_2$O$_5$, as a consequence of weak interaction between the support and the dispersed vanadium oxide. If vanadium loading exceeds theoretical monolayer, Zr$_2$V$_2$O$_7$ is formed [9]. Dependence of surface species formation on the acid base behaviour of the support has been further proved by various studies [7, 10].

On the most basic support, MgO, isolated VO$_4$ tetrahedra without bridging V-O-V oxygen ions forming Mg$_3$V$_2$O$_8$ like structure appeared within a larger range of vanadium loading. Dimeric VO$_4$ tetrahedra of the type Mg$_3$V$_2$O$_7$ and the mixed ortho and pyro magnesium vanadates have also been observed depending on the catalyst preparation procedure or vanadium loading [11-14]. Formation of the dispersed species at lower coverages and formation of crystalline vanadates at higher vanadia loadings are observed in the case of basic metal oxides like La$_2$O$_3$, Sm$_2$O$_3$ and Bi$_2$O$_3$ [6].

Vanadium oxide formation intermediate between those on MgO and Al$_2$O$_3$ or SiO$_2$ has been observed on catalysts supported on hydrotalcites. The results obtained for vanadia supported on mixed oxides suggest that it is possible to control the
structure and reactivity of vanadia monolayers by modifying the local structure of the support. Martralis et al. observed an important influence of Ti/Al ratio on the type of vanadium species in vanadia supported on TiO$_2$/Al$_2$O$_3$ supports [15]. Thus for a given vanadium loading, the higher the alumina content, (within the range of 10-82 wt. %) the higher is the surface area and the dispersion of vanadia. Modification of support TiO$_2$ lead to the formation of surface species on V/Ti-Al while crystalline V$_2$O$_5$ was seen on V/Ti catalyst.

Characterisation studies on V-SiO$_2$ systems have shown the existence of isolated VO$_4$ tetrahedra of the type (SiO)$_3$-V=O in dehydrated catalysts [16]. Isolated tetrahedral species are also observed on catalysts supported on Al$_2$O$_3$, TiO$_2$ and ZrO$_2$ at very low vanadium loadings. At higher vanadia percentage, VO$_4$ tetrahedral units form aggregates leading to chains or bidimensional arrays. At higher surface coverages the $V^{5+}$ become six coordinated similar to that of metavanadate or decavanates. On metals oxides like Al$_2$O$_3$ and TiO$_2$, tetrahedral species are favoured together with other species upon dehydration. V$_2$O$_5$ crystallites appeared only above 60 % of monolayer coverage by vanadia for Al$_2$O$_3$. For TiO$_2$, crystalline vanadia appeared above 100% of the theoretical monolayer coverage [5].

In addition to acid base properties, the final vanadium content depends on the possible modification of the support during impregnation / or calcination steps. The structure of TiO$_2$ [17] and ZrO$_2$ [18] can be transformed during calcination and these modifications are enhanced in the presence of vanadia. Modification of the support during calcination step is also observed in natural sepiolite [19, 20] or Mg-Al hydrotalcite like materials [21] used as supports. In the former case, the initial Mg$_8$Si$_{12}$O$_{30}$(OH)$_{4}$ crystalline phase is transformed into MgSiO$_3$ in a degree which depend on vanadia loading and calcination temperature. In the latter case, Al$_2$O$_3$ is greatly dispersed on amorphous MgO material. In the case of zirconia – vanadia system, transition from amorphous to tetragonal phase is delayed in proportion to vanadia content [8].
In the case of MgO, it is transformed to Mg(OH)$_2$ when the impregnation is carried out in the presence of water. In this circumstance, vanadia is partially occluded in the bulk of the catalyst and results in a lower surface vanadium concentration after calcinations. This has been concluded from the difference in values of the bulk and surface V/Mg atomic ratios [22]. Phase transformation of the support may be enhanced by the adding vanadium oxide as seen in the case of TiO$_2$ (anatase to rutile).

1.5 Structural models for surface vanadia species

Various structural models proposed for the surface vanadia are given in Figure. 1.

1.6 Selective oxidation activity and acidity generation by vanadia loading

The most important aspect of supported vanadia systems is the selective oxidation activity towards partial oxidation products. The complete oxidation of the organics is minimised in the case of supported vanadia systems and thereby enhances selective oxidation products, which are industrially important. The selective oxidation activity is attributed to the lattice oxygen mobility. Isotopic oxygen exchange reaction conducted on supported vanadia call attention to the significance of lattice oxygen mobility of the systems in oxidation reactions [23]. Two vacancies are required for the exchange and it is available on the catalyst surface of pure V$_2$O$_5$ indicating high oxygen mobility. All layers in the crystals can participate because diffusion of oxygen is much faster. This will result in over oxidation. In the case of supported system, either one or two exchange may take place due to low diffusion rate since no bulk oxygen is available in supported V$_2$O$_5$, where the vanadia species are bound to support.
Figure 1.1. Structural models of surface vanadia species

This inference can be applied to the activity of the catalysts for partial oxidation reactions. Deo et al. determined the reactivity of several supported systems in the partial oxidation of methanol [24]. The selectivity towards acetaldehyde followed the same trend in oxygen exchange reaction. The above-mentioned order
for supported system was also observed for the partial oxidation of butane to maleic anhydride [25].

Oxidation reactions over supported vanadia catalysts are known to take place through Mars and van Krevelen mechanism. In this mechanism, the reactant is first oxidized by lattice oxygen. The catalyst in turn is oxidized by gaseous oxygen to regenerate the system. On supported metal oxides, there is no large reservoir of bulk oxygen, which is able to abstract large number of hydrogen atoms. According to Sachtler et al., the selectivity in the Mars and Van Krevlen oxidation reactions is determined by the intrinsic activity of oxygen species and their availability, i.e. the first one or two oxygen atoms must be active, but the other lattice oxygen must be inactive. Only then the oxidation stops at the desired level of a partially oxidized product [26, 27]. Abstraction of many hydrogen atoms from the hydrocarbon will lead to a breaking of C-C bonds and consequently to complete oxidation. Thus, the locally limited amount of reactive oxygen atoms might be responsible for the high selectivity of the supported metal oxides.

Vanadia addition increases both Lewis and Bronsted type acidity. It has been proposed that surface Bronsted acid sites are also there in supported catalysts, which are located at bridging V-O-support bond. At lower percentage of vanadia, Bronsted acidity was found to increase. At higher vanadia composition, number of both Lewis and Bronsted acid sites sites are enhanced [28]. Studies by Hatayama et al. are also in agreement with this result. Bronsted acid sites were found to increase with vanadia composition [29]. Vanadium ion acts as the center for Lewis acidity. This view is in agreement with the work reported by Miyata et al. [30]. Both the types of acidities are remarkably increased by vanadia loading in the case of ZrO2/V2O5.
1.7 Reactions of supported vanadia catalysts

1.7.1 Oxidative dehydrogenation

Oxidative dehydrogenation (ODH) reactions constitute a major portion among the reactions catalysed by supported vanadia catalysts. In the case of ODH reactions, it is the selective oxidation activity that makes the system superior to pure vanadia. Bulk vanadia is known to possess a vast reservoir of oxygen, which becomes highly mobile when the oxide is in a partially reduced state, leading to over oxidation [31]. When incorporated on suitable supports, the selective oxidation activity is increased to a large extent. The different catalytic behaviour of bulk and supported vanadia catalysts are usually related to the modifications and environment of V-species, which can modify its redox properties. Some of the selective oxidative dehydrogenation reactions catalysed by supported vanadia catalysts are discussed below.

Active and selective catalysts for the oxidation of alkanes are obtained by mixing vanadium and magnesium oxides. Magnesium vanadates, ie. $\text{Mg}_2\text{V}_2\text{O}_8$, and/or $\text{Mg}_3\text{V}_2\text{O}_7$, are observed in the most effective catalysts suggesting that these constitute the active phases in the ODH of butane [31]. However, while V-Mg-O catalysts seem to be the most active and selective catalysts in the ODH of propane and n-butane, they show a low selectivity to ethane during the ODH of ethane [32, 33]. In an opposite trend, V/Al catalysts are found to be very much active for ethane [34] and propane oxidative dehydrogenation [35]. But selectivity to $\text{C}_4$ olefins is low in the case of n-butane ODH [36]. The role of 'Mo' in molybdenum doped V-Mg-O catalysed butane ODH has been reported by Dejoz et al. [37]. The incorporation of Mo modifies the number of $\text{V}^{5+}$ species on the catalyst surface, reducibility of selective sites and catalytic performance. Here the selectivity and yield of ODH products were very low.
Different activity of these vanadates can be explained by their redox properties. If the vanadate is composed of a more reducible cation, it would be able to form oxygen anion vacancies more easily and migration of oxygen in the lattice is also more rapid. These will replenish the oxygen more easily and so, selectivity towards dehydrogenation will be lower. When ODH of butane was investigated over vanadates of Mg, Sm, Nd, Zn, Cr, Eu, Ni, Cu and Fe, there was a general correlation between selectivity for dehydrogenation with the reduction potential of the cation; the more easily reducible the cations are, the less selective the catalysts is. The only notable exception was Cr, which may be due to the presence of Cr$^{5+}$ on the surface [38].

Corma et al. studied the catalytic properties of the supported vanadium oxide catalysts in the ODH of propane [6]. The most selective catalysts were obtained when vanadia was supported on basic metal oxide supports, ie., MgO, Bi$_2$O$_3$, La$_2$O$_3$ and Sm$_2$O$_3$, while acidic oxide supports exhibited very low activity suggesting a parallelism between the appearance of metal vanadates (and absence of V$_2$O$_5$) and selectivity to ODH products. Efforts aimed at relating the structure of the dispersed vanadia to its activity and selectivity suggested that both isolated and oligomeric tetrahedral species can provide active and selective sites for ODH.

Comparison of the most effective supported vanadium oxide catalysts in the ODH of propane shows that except in the case of V/ Ti catalysts, a higher selectivity is obtained at vanadium loading below that of the theoretical monolayer [31]. In addition, for most of these catalysts, tetrahedral V$^{5+}$ species are proposed to be the selective site in ODH reaction, as they are the main species present at sub monolayer coverages.

Propane ODH over V-Zr catalysts indicates high C-oxide selectivity on bulk ZrV$_2$O$_7$ and at low surface densities and appear to be associated with exposed unselective V-O-Zr and Zr-O-Zr sites. At low surface coverages, rate increases due
to the increase of polyvanadate species and decreases further with vanadia addition. This is due to the formation of V$_2$O$_5$, which decreases the concentration of VO$_x$ species exposed at cluster surface. At a given surface vanadia density, rate increases with increase in calcination temperature. This was explained by the formation of polyvanadate species at higher temperature. So the oxygen in the poly vanadate species is more active than in isolated surface vanadyl species [39].

An attempt to relate the catalytic performance and redox properties of the catalysts was done by Lopez Nieto et al. [40]. They pointed out that, the reducibility of vanadium atom will influence the selectivity to oxidative dehydrogenation products. This dependence is explained by its effect on the rate of selective redox processes involving vanadium species on the catalyst surface.

More recently, V- containing molecular sieves have been found to be highly active for the formation of oxyhydrogenation products during oxidation of ethane [41, 42] and propane [43-45]. Other studies include selective oxidation of $n$-butane to maleic anhydride on V-P-O catalysts, selective oxidation of paraffins [46-49], ODH of ethane on V-Mo-Nb-O catalysts [50, 51].

Blasco et al. studied and summarized the general factors, which affect the ODH activity of supported systems [31]. He pointed out that apart from vanadia loading there are some other factors which control the activity and selectivity in ODH reactions. The selectivity was found to depend on the nature of alkane fed. Depending on the size of the reactant, the distance between the active sites also has a deciding role. Aggregate forms of vanadium and its coordination number are the other factors, which influence the activity and selectivity of supported vanadia catalysts. Both isolated and dimeric tetrahedral V$^{5+}$ species were found to be active and selective towards partial oxidation products. The reducibility plays a major role in selectivity in the sense that the more reducible the catalyst, the less selective the
supported system. A good correlation was obtained for the catalytic activity and selectivity with the reducibility for ODH reactions on supported vanadia systems.

### 1.7.2 Ammoxidation

Ammoxidation is the reaction in which the CH$_3$ group in a side chain of an aromatic system or heterocyclic ring is converted into –CN (nitriles) in presence of ammonia and oxygen. Vanadium oxide based catalysts are frequently used for catalyzing this reaction [52-54]. Propane ammoxidation was investigated by J. Nilsson et al. using Al-Sb-V catalysts [55]. The active phase identified for the system was Al$_{1-x}$SbV$_x$O$_4$. Acrylonitrile selectivity was determined by the presence of isolated vanadium centers which are surrounded by Al and/or Sb.

In the ammoxidation of 3-picoline over V$_2$O$_5$ [56], the nitrile formation was reported at (010) plane. The plane exposes equal number of V=O groups and naked V$^{5+}$ ions [57]. The amount of toluene adsorbed was correlated to V=O frequency and each molecule adsorbed covers eight V=O groups having eight neighbouring naked vanadium ions [58]. The active site used in the description of the mechanism is chosen to be an ensemble of four V=O groups having neighbouring V ions exposed.

### 1.7.3 Oxidation of methanol

The selective oxidation of methanol to formaldehyde is extensively studied on vanadia-based catalysts. Pure V$_2$O$_5$ and a number of supported VO$_x$ monolayer catalysts at low temperature dehydrates methanol to dimethyl ether. Selectivity to formaldehyde is usually increased, while activity is decreased with decreasing reducibility of the catalysts. High selectivity to formaldehyde (< 90 %) has been found with VO$_x$/SiO$_2$ [59] and VO$_x$/SnO$_2$ catalysts [60]. Recently it has been reported methyl formate could be directly produced with high selectivity and yield by catalytic methanol oxidation on V-Ti oxide [61, 62].
Structure sensitivity of methanol oxidation reaction on single crystals of V$_2$O$_5$ and MoO$_3$ was reported by Tatibouet [63]. Product selectivity is found to change with the crystal planes of the single crystals of V$_2$O$_5$ and the percentage of vanadia. Formaldehyde selectivity increased with increase in area of (001) crystal face of vanadia. Improved selectivity are obtained in the catalytic oxidation of methanol to formaldehyde using hexagonal orthovanadates of the type Sr$_{3-x}$La$_{2x}$O$_4$ in comparison with those using the strontium and lanthanum orthovanadates reported separately by P. Salagre and J. E. Sueiras [64].

Selective catalytic reduction of nitrogen oxides is an important reaction in connection with the abatement atmospheric pollution. Selective catalytic reduction using ammonia is an effective method for treating flue gases from stationary combustion sources. Vanadia based systems were found to be very effective for the reduction of nitrogen oxides [65-67]. Highest activity reported for V$_2$O$_5$/ TiO$_2$ system was found to be associated with two-dimensional VO$_x$ clusters at intermediate loadings as reported by Nickll et al. [68].

Partial oxidation of methane is another reaction catalysed by supported vanadia systems efficiently [69-72]. Oxidation of toluene to benzaldehyde over V$_2$O$_5$/ TiO$_2$ samples was reported by H. Miyata et al. A π complex formation of toluene was reported with the vanadium ion and CH$_3$ groups of the π complex are in turn dehydrogenated by V=O species to form benzyl species. The formation of an aldehyde type intermediate before the oxidation of the benzyl species to benzoate on the system was also confirmed. Aniline alkylation was also attempted with supported vanadia catalysts [73].

Only a limited number of reports are seen in literature on rare earth oxide supported vanadia systems. They include oxidative dehydrogenation of propane reported by Corma and co workers and [6] and oxidative dehydrogenation of butane over LnVO$_4$ [74]. They proposed that redox properties of the cation ‘M’ in the
support having $M - O - V$ bridging unit would affect the reactivity and selectivity of the catalyst.

### 1.8 Rare earth oxides as catalysts

Rare earth oxides are widely accepted basic catalysts. The activity is very much independent of electronic and magnetic properties of the oxides and is believed to depend on the relative basicity or surface structure. Paramagnetic nature, lattice oxygen mobility and/or variable valency of lanthanide ions have deciding role in the activity towards various reactions.

Oxygen exchange reactions conducted on these catalysts with the aim to establish correlation between the rate of exchange of oxygen ions in the various oxides and their behaviour as heterogeneous catalysts point to the high mobility of lattice oxygen. The slow step was the dissociative adsorption of molecular oxygen, the rate being dependent on the 4f electronic configuration of the metal cation. Winter has proposed that the kinetic features of lattice oxygen exchange in the rare earth oxides are dependent primarily on the unit cell volume of the Ln$^{3+}$ ion and ascribes the rate-limiting step to desorption of molecular oxygen.

Activities of rare earth oxides have been explored for a wide variety of oxidation reactions, which depend on the lattice oxygen mobility and potential cation variable valency. Oxidation of molecular hydrogen is an important reaction in this category. Activation energy determined for the reaction was the same as that corresponding to $^{18}\text{O}_2$ exchange reaction indicating lattice oxygen participation for oxidation. As expected, nonstoichiometric oxides of Pr and Tb are found to possess maximum activity in which Ln$^{3+} \rightarrow$ Ln$^{4+}$ inter conversion occurs more rapidly. CO oxidation carried out over rare earth oxides confirms this conclusion. The rate of CO oxidation increased with mobility of lattice oxygen [75]. But the acidic CO$_2$ gets adsorbed on comparatively basic rare earth oxides forming carbonate species, causing self inhibition [75, 76]. So the overall reaction was expected to depend on the rate
of CO\textsubscript{2} desorption. Studies conducted on CeO\textsubscript{2} also agreed well with the participation of lattice oxygen in oxidation process [77, 78].

Other rare earth catalysed reactions include hydrogenation and dehydrogenation reactions. Hydrogenation studies of ethylene reported over these systems indicate that neither lattice oxygen mobility nor cation variable valency are important factors in governing the activity. Activity of these systems towards dehydrogenation of a variety of hydrocarbons is reported [79, 80]. Overall dehydrogenation activity for most reactions increased regularly with increase in atomic number of rare earth metal in the oxide.

Double bond migration causing isomerisation of cyclic olefins, 1-hexene and 1,5-hexadiene are reported over rare earth oxides, which were pre-calcined in air. Catalysts that were vacuum calcined showed much higher activity for the above reaction, revealing that anion vacancies and other surface defects are the leading factors [81].

Winter has done a detailed study of the decomposition of nitrogen oxides (N\textsubscript{2}O) over rare earth oxides and a mechanism was also put forward by him [82-85]. Lattice oxygen participation was obvious from the activation energy of the reaction. A close inverse correspondence exists between decomposition activity and oxide lattice parameters, such as molecular volume and nearest Ln-O or O-O bond distance. But no correlation was seen between catalytic activity and magnetic properties of Ln\textsuperscript{3+} ions which do not vary regularly with lattice parameters. The general features of NO decomposition also closely parallel to those observed for the conversion of N\textsubscript{2}O [82].

Catalytic cracking of butane was reported by Minachev et al. [86]. Activities were quite low compared to conventional cracking agents like Al\textsubscript{2}O\textsubscript{3}. Another set of reaction studied over earth oxides include ketonization of acids and alcohol. Oxide
basicity was found to be an important factor contributing to catalytic activity since ketone yield from a given reactant has generally been observed to decrease with decrease in the radius of rare earth cation.

Exchange type reactions constitute another interesting category that utilized the activity of rare earth oxides. These catalysts are found to be efficient for the interconversion of ortho and para hydrogen. The reaction proceeds by a physical paramagnetic mechanism where the 4f electronic configuration of the cation was found to be the deciding factor at low temperature, whereas 5s and 5p electrons control the activity by a chemical mechanism at higher reaction temperature [87, 88]. Minachev et al. studied the deuterium exchange on cyclohexane over CeO$_2$, Nd$_2$O$_3$, and Gd$_2$O$_3$ and found more or less equal activity with Al$_2$O$_3$ under similar reaction conditions.

1.9 Acid base properties

Surface acidity and basicity investigation have received considerable attention in recent years, since they provide significant information in determining the behaviour of the catalyst surface. A systematic investigation of the activity and selectivity of a catalyst and acid base property (strength, amount and type) enabled the identification of an optimum catalyst with desired acid base properties for a specific reaction. Development in this area has given rise to numerous methods for exploring these properties. They include visual colour change method using indicators, spectrophotometric method, gaseous adsorption studies etc. Discrimination between Lewis and Bronsted type acidities is also feasible by the above-mentioned techniques.

1.9.1 Hammett indicator method

Hammett indicator method proposed by Walling using adsorption of electrically neutral indicators is a simple method to determine and compare the acid base property of solid catalysts [89]. The solid is titrated against an organic base /
acid using Hammett indicators in nonaqueous solvents such as benzene. Nonaqueous condition ensures practically no interaction with the catalyst surface. Here the acid/base strength is expressed by the Hammett acidity function, $H_0$. If the colour of the indicator adsorbed on the solid is acidic, the $H_0$ of the solid surface will be lower than the $pK_a$ of the indicator. If colour is basic, $H_0$ value will be greater than the $pK_a$ of the indicator applied.

Acid strength of a solid catalyst is described as the ability of the solid to convert an adsorbed neutral base into its conjugate acid. The amount of acid or acidity is the number in mmols of the acid sites per unit weight of the oxide. This is measured as the amount of base, which reacts with the solid acid. If the reaction proceeds by proton transfer from surface to indicator [a neutral base, B] acid strength is expressed by Hammett acidity function,

$$H_0 = pK_a + \log [B / BH^+]$$

where $BH^+$ is the concentration of the conjugate acid.

In the case of a Lewis acid site,

$$H_0 = pK_a + \log [B / AB]$$

where A is a Lewis acid or electron pair acceptor.

The lower the $pK_a$ of the colour changing indicator, the greater the acid strength of the system.

Similarly, it is possible to determine the base strength, which is defined as the ability of the solid surface to donate electron pair to an adsorbed acid indicator by observing colour change of an acid indicator. At the end point, the colour due to the conjugate acid form of the indicator appears.
For the reaction of indicator AH with solid base B,

\[ AH + B \rightarrow A^- + BH^+ \]

\[ H_0 = pK_a + \log [A^-/AH] \]

Approximate value of the basic strength on the surface is the pK\(_a\) value of the indicator at which the intermediate colour appears.

Indicators with different pK\(_a\) values enable the determination of the amount of acid of various strengths. According to Tanabe, the total amount, i.e. both Lewis and Bronsted type of acidity/basicity can be measured by Hammett indicator method [90]. But some contradictory reports are there that only Bronsted acidity can be evaluated through this procedure since this method is limited to solids where exchange of protons occurs [91]. Hammett indicator is mainly useful to determine the acid-base property of white samples. In the case of coloured samples, a standard white sample is added during the experiment [90]. However, it should be emphasised that the reference used should exhibit a wider range of acidity than the sample.

Yamanaka and Tanabe have described a common scale for the determination of the distribution of surface acid/base strength taking into account the bifunctional character of the surface [92, 93]. The curves for acidic and basic strength distribution intersects at the point were both acidity and basicity is equal to zero. This point is defined as the \( H_{0,\text{max}} \) parameter by the authors. This value was found to be better than the zero point charge determined for water solutions since it expresses actual acid/base property taking into account all parameters like structure of the surface, moisture content and the intrinsic nature of the solid [94].

1.9.2 Electron donating property studies

Metal oxides are well known for their basicity due to the presence of electron transfer sites, which make them suitable for catalyzing a wide variety of reactions. The adsorption of electron acceptors has been investigated to study and characterize
the electron donating property of the metal oxides [95, 96]. Flockhart and coworkers associated the donor sites on the metal oxide with unsolvated hydroxyl ions and defect centers involving oxide ions [97]. As a result of electron transfer, radical anion formation occurs on the surface of the solid. The surface shows remarkable colouration by the adsorption of the electron acceptor. The generation of radical anions is further confirmed by ESR spectral studies. The spectra obtained was unresolved indicating that the anisotropy of the hyperfine structure arises from the hindered rotational freedom of the adsorbed species. This has been confirmed from literature [95, 98]. A g value of 2.003 was obtained for ESR spectra of TCNQ adsorbed oxides, which was identified to be that of TCNQ anion radical.

Electron donor strength of a metal oxide surface is defined as the conversion power of an adsorbed electron acceptor to its anion radical. If the electron acceptor used is a strong one, ie., with high electron affinity value, anion radical formation takes place both at strong and weak donor sites, whereas a weak acceptor get adsorbed only on strong donor sites. The electron donating capacity can be expressed as the limiting electron affinity value at which free radical anion formation is not observed at the metal surface.

Studies carried out on TiO$_2$ by Che et al. inferred that surface hydroxyl ions are the sources of basicity at low activation temperature; weakly coordinated oxide ions having major contribution at higher activation temperature [99]. A detailed investigation of electron donating sites on oxide surfaces has been carried out by D. Cordischi and co workers [100]. A correlation between electron donating capacity and Lewis basicity was suggested and the donor sites were proposed to be a coordinatively unsaturated oxygen ion, $(O^{2-}_{\text{uns}})$ associated with a nearby OH$^\cdot$ group, whose proton interacts with the radical anion formed giving stability. Adsorbed radical interact with the protons. So Bronsted acidity stabilizes the radical ion formed. The active site can be considered as acid base pair as shown in figure.
Meguro et al. reported adsorption of electron acceptors on alumina and they proposed that surface hydroxyl groups are responsible for electron donating property of the oxides [98]. A plausible mechanism was suggested by them for the adsorption of electron acceptors on alumina surface activated at 500°C, due to surface hydroxyl ions. The ionization potential of hydroxyl ion being small (~ 2.6 eV in gas phase), [101], an oxidation reduction process was put forward.

\[
\text{OH}^- + \text{A} \rightarrow \text{OH} + \text{A}^-
\]

Electron donating property of ZrO₂ studied by Esumi et al. revealed the effect of calcination temperature on adsorption of electron acceptors [102]. An increase of calcination temperature reduces the amount of adsorbed electron acceptor indicating reduction of OH on the surface. Above 900°C, amount adsorbed again increased due to the formation of surface oxide ions.

Solvent effects on the acid base interaction of the electron acceptor with the metal oxide was studied on alumina and TiO₂ [103]. The amount of TCNQ adsorbed and the concentration of anion radicals formed decreased with an increase in acid base interaction between TCNQ and basic solvent for both the oxides. The effect of solvent on adsorption of chloranil was further reported by Esumi and co-workers [104]. The amount of chloranil adsorbed decreased with an increase of acid base interaction between the basic solvent and chloranil and also decreased with an increase of acid base interaction between the acidic solvent and electron donor sites. Drago equation was applied to understand the nature of interaction of different solvents with TCNQ. Acid base enthalpy is high for acetonitrile and the order was acetonitrile > ethyl acetate > 1,4-dioxane. So adsorption is depressed by the interaction between TCNQ and acetonitrile. The concentration of radical anions
formed decreased with increase of acid base interaction between electron acceptor and organic solvent.

Sugunan et al. carried out a detailed study of electron donating capacity of rare earth oxides and their mixed analogues as a function of temperature and composition [105-107]. Electron donating capacity of lanthanum oxide and the influence of addition of strontium oxide was studied and found that electron donating capacity was improved by doping strontium [108]. Magnetic and electron donating properties of samaria at different activation temperatures were also reported by the same authors [109]. It was found that the number of both strong and weak donor sites are increased with increase in activation temperature. During adsorption, magnetic moment decreased and reached a limiting value at the same concentration at which limiting amount of EA was adsorbed. Reports on electron donating capacity of mixed oxides of La and Al showed the limit of electron transfer to be between 1.77 and 2.40. La₂O₃ promoted surface properties of alumina without altering the limit of electron transfer [110]. The increase of electron donating capacity was attributed to increase of Al-O-La bonds. The same group also reported investigation of electron donating property of manganese ferrospinels and the limit of electron transfer was found between 1.77 and 2.40 in terms of electron affinity of the electron acceptor [111].

1.9.3 Temperature Programmed Desorption Studies

Chemisorption of molecules such as ammonia, pyridine, CO₂ etc. is often used as a probe for the surface properties of metal oxides. By probing the interaction of the molecules with the surface, information can be obtained on the oxidation state of the metal ion, coordination symmetry, degree of coordinative unsaturation of the surface OH and presence and nature of Lewis and Bronsted acid sites. Among these categories, TPD of ammonia is one of the most promising technique, facilitating the direct determination of the strength and distribution of acid sites. Interaction with the surface will be quite strong since ammonia is a fairly hard base. Ammonia being a strong Lewis base and smaller than pyridine, can detect most of the acid sites and
the distribution of sites according to the acid strength can be obtained. However, a quantitative distinction between the Lewis and Bronsted acid sites cannot be achieved by this method. This can be attained by in situ IR measurement of adsorption of pyridine on the solid surface.

When chemisorbed on a surface possessing acid properties, NH₃ can interact with acidic protons, electron acceptor sites and hydrogen from neutral or weakly acidic hydroxyls [112]. NH₃ when adsorbed on a surface can be retained in different modes, [113]. a) hydrogen bonding via one of its hydrogen atoms to a surface oxygen atom or oxygen of the hydroxyl group (weakest interaction) b) transfer of protons from surface OH to ammonia (Bronsted acidity). These two interactions will involve neighbouring anions or OH groups. Another mode of interaction, which is the strongest interaction, is the coordination to an electron deficient atom (Lewis acidity). The fourth one involves dissociative adsorption in the form of surface NH₂ or NH and OH. A complete transfer of H⁺ to ammonia from Bronsted sites to produce NH₄⁺ ions also occurs.

The advantage of the TPD method over other techniques is that it allows the study of the catalyst under conditions more or less similar to that of reaction. A minimum temperature of about 100°C is necessary to eliminate physical adsorption. Both Lewis and Bronsted type of activities are obtained by temperature programmed desorption studies using ammonia.

1.9.4 Cyclohexanol decomposition – a test reaction for acidity

The utility of alcohol decomposition as a test reaction for acid base property studies of metal oxides is well established. Since alcohols are amphoteric, they interact easily with both acid and base sites. It was observed that metal oxides are catalysing both dehydration and dehydrogenation of alcohols. Alkene formation associated with dehydration was proposed to be due to the participation of Bronsted acid sites. Acidic OH groups catalyses dehydration reaction.
Davis suggested alcohol conversion selectivity as a measure of basicity of metal oxides [114]. 1-alkene formation accompanied by water elimination was observed to depend on the base strength of the oxide. Alcohol decomposition was carried out over various systems by Mamoru Ai while studying acid base properties of various metal oxides. Dehydration rate was found to be proportional to acidity whereas dehydrogenation, which proceeds by a concerted mechanism was found to be proportional to both acidity and basicity [115].

Bezouhanava et al. have proposed cyclohexanol decomposition as a simple and fast method to determine the functionality of metal oxide catalysts [116]. They interpreted the dehydrogenation activity as related to the existence of basic sites originating from the lattice oxygen. Dehydrogenation of the ring was observed in this case and was related to the influence of transition metal. Stronger acid sites are needed for dehydration to take place compared to other secondary and tertiary alcohols, like isopropyl alcohol or tertiary butyl alcohol.

Catalytic decomposition of cyclohexanol over Mg_{1-x}Zn_xAl_2O_4 reported by Joshi and co workers gave idea about the surface properties, structure and catalytic activity correlation. Correlation was established between transport properties, surface acidity and catalytic behaviour [117]. Results on alumina published by Pines et al. point out to the formation of methyl cyclopentene on stronger acidic sites which is formed by the isomerisation of cyclohexene [118].

1. 10 Reactions selected for the present study

Oxidative dehydrogenation reactions are an attractive alternative to classical dehydrogenations. Dehydrogenation of the alkanes to corresponding alkenes is a highly endothermic process that has to be carried out at temperature above 600°C. At this high temperature, other unwanted reactions leading to coke formation also occur, and catalyst needs frequent regeneration. Since this process is equilibrium limited and energy intensive, there is strong incentive for the development of ODH process.
In ODH reactions, abstracted hydrogen is oxidized, releasing heat of reaction and the conversion becomes significant at a much lower reaction temperature which is not equilibrium limited. For the present investigation, oxidative dehydrogenation of ethyl benzene and ethanol are selected.

1.10. 1 Oxidative dehydrogenation of ethyl benzene

Vanadium based catalysts are extensively used for oxidative dehydrogenation of ethyl benzene. The main product of commercial importance is styrene along with ethylene, traces of benzene, toluene etc. Commercial processes use high reaction temperatures and low ethyl benzene pressures in the feed to achieve favourable ethyl benzene conversions. Super heated steam is used to provide the energy needed by the reaction, to dilute the reactant and to reduce catalyst coking.

The catalysts reported in the literature for the ODH of ethyl benzene to styrene include metal oxides [119-126], and phosphates [127-129] and organic polymers [130, 131]. Two possible types of catalysis have been proposed for the ODH of ethyl benzene. First one involves redox operation of transition metal oxide and the other involves catalytically active coke.

Of the transition metal oxides, V-Mg-O system is the most active and selective for ethyl benzene to styrene conversion. Chang et al. reported the reaction over V(V) and V(IV) magnesium vanadates [132]. It was observed that the activity and selectivity of ODH of ethyl benzene do not correlate with the oxidation state of vanadium and show a constant styrene selectivity with little dependence on reaction temperature and ethyl benzene conversion. The active species responsible for the formation of styrene was concluded to be Mg₃V₂O₈. Explanation for this behaviour was achieved by quoting studies done by Kung et al. [133,33]. The V-O-V bond in MgV₂O₆ and Mg₂V₂O₇ permits easy oxygen removal from the lattice and thereby preferring complete oxidation of hydrocarbon. But in case of magnesium orthovanadate, all the oxygen atoms are bonded on V-O-Mg. Thus oxygen removal
will be difficult and the activity for total oxidation will be low yielding selective oxidation product.

Murakami and co workers studied this reaction over SnO2-P2O5 system [134]. \( \alpha \) -'H' abstraction leading to \( \pi \) allyl mechanism was suggested for the reaction pathway. The active component was recognized to be a type of Sn-P compound. A reduction - oxidation mechanism was suggested by them for the reaction, where tin, the basic component activates oxygen and 'P' the acidic component activates ethyl benzene.

Deuterium exchange studies carried out on Si- Al catalysts have shown that the adsorbed intermediate of ethyl benzene are dissociated in the \( \alpha \)-position [135]. The active oxygen on the surface was found to be the O' species. The lattice oxygen in turn supplies O'. The acid site of Ho between 1.5 and -5.6 is proposed to adsorb ethyl benzene reversibly abstracting the \( \alpha \) H at the basic OH site adjacent to the acid site, and the base sites of pKa between 17.2 and 26.2 activates gaseous oxygen to form O' which abstract the \( \beta \) hydrogen.

A number of studies have been devoted to the active oxygen species that is responsible for ODH reactions. An improved activity for lattice oxygen was observed on 'Mo' containing oxides [136]. In some other cases, active species were also supposed to be M = O groups [124,137,138]. In the case of spinel ferrites, adsorbed oxygen species (O') were the active species [137-139]. Their studies concluded that acid sites withdraw electron of the aromatic ring to enhance the acidic property of the \( \alpha \) hydrogen and is interacting with OH near to surface.

An investigation about the mechanism of the reaction suggested active participation of lattice oxygen. Lattice oxygen abstracts H and oxidation of the catalyst occurs by gas phase oxygen [122]. Lattice oxygen appears from the surface
layer, whereas bulk oxygen was reported to be inactive [140]. The participation of the lattice oxygen is further supported by the work done by Haber et al. [136].

Kim et al. studied and reported oxidation of ethyl benzene over lanthanide promoted catalysts [141]. They found that pure lanthanide oxide catalyses almost complete oxidation of the organics. Praseodymia was found to be the best promoter among the various oxides used (La, Ce, Pr and Nd). They attributed this enhanced activity to the low activation energy for electronic conduction compared to other three systems.

1.10.2 Oxidative dehydrogenation of Ethanol

Recently, oxidative dehydrogenation of ethanol to value added fine chemicals have reserved an interesting technological importance in connection with the utilization of biomass as a chemical source [142]. Commercially used catalysts are silver based ones. Nowadays metal oxides are explored for their substitution. Among the oxides screened, molybdenum and vanadium based catalysts are the promising candidates for the above reaction [143]. Oyama et al. reported structure insensitivity of ethanol decomposition over SiO$_2$-V$_2$O$_5$ system [144]. At low temperature, acetaldehyde was the main product while at high temperature it was ethylene. Acetic acid formation was also observed at intermediate temperatures. At low conversion, vanadia species was found to be responsible for the activity. Quaranta and co workers extended this work by using TiO$_2$ coated SiO$_2$ as support. An enhancement in activity towards acetaldehyde was observed due to the interaction of TiO$_2$ and molecular dispersion. An improved selectivity for acetaldehyde, on the basis of greater heat dissipation and isothermicity was observed on $\alpha$-Al$_2$O$_3$/ V$_2$O$_5$ as reported by Quaranta et al. [145].

MgO–V$_2$O$_5$ system was selected as catalyst for the above-mentioned reaction and the selectivity towards acetaldehyde was found to depend on the nature of compound formation between MgO and V$_2$O$_5$. The Mg$_3$V$_2$O$_8$ was found to be the
most active and selective catalyst than MgV₂O₆ that exhibited very low selectivity and activity. The high activity of Mg₃V₂O₈ was correlated with creation of holes and the position of the Fermi potential [146].

Decomposition of ethanol over vanadium silicate molecular sieves have been reported [147]. It was presumed that acetaldehyde formation was facilitated by the V=O species while simultaneous interaction of both V=O and V-O-Si linkages is responsible for ethylene formation. Nakagawa et al. studied the promoting effect of V₂O₅ on V/Ti system in the oxidation of ethanol and the promoting effect is attributed to the formation of amorphous or two dimensional vanadium oxide [148]. Oxygen in the V=O species act as strong basic site, playing significant role in hydrogen abstraction from alcohol. Generally the total oxidation activity of V₂O₅ based catalysts is attributed to the high activity of oxygen sites. Samples with higher V⁴⁺ species were found to favour partial oxidation products and the reactivity was influenced by the acidity of the systems.

1.10. 3 Methylation of phenol

In recent years, alkyl phenol synthesis has become interesting, since the products are of high commercial value. Both O- and C- alkylated compounds are formed and the selectivity of the products was found to depend upon the acid base property of the catalysts employed [149, 150]. The demand for these chemicals has increased in recent years owing to the growing use of their derivatives. Products include o-cresol, 2,6-xylenol, anisole etc. Generally attempted catalysts include γ-Al₂O₃, silica alumina, SAPOs, zeolites, ALPOs, metallic sulfates, phosphates etc. It has been found that strong acidic sites favour O-alkylation, while strong basic sites favour C-alkylation [151]. A contradictory claim was put forward that it is the acidic sites that favour C-alkylation [152, 153]. This was in agreement with Balsama et al. who confirmed the enhancement of C-alkylated products by strong acidic sites [154].
Methylation of phenol was studied by S. Velu and co-workers on Mg-Al hydroxides[155]. Activity of the reaction was compared with pure MgO and Al₂O₃ and physically mixed MgO-Al₂O₃. Of these, calcined hydroxides with Mg-Al ratio of 4:1 was the most active. They suggested a participation of combined acidic and basic sites for the reaction.

An IR study of phenol adsorbed on SiO₂-Al₂O₃ and MgO revealed that ortho selectivity is strongly controlled by the adsorbed states of phenol [156]. Since in the case of SiO₂/Al₂O₃, the plane of benzene ring of phenolate ion is close to the catalyst surface, any of ortho, meta and para position can be attacked by a methyl cation formed from methanol. On the other hand, only the ortho position can be methylated in the case of MgO, because ortho position is near to the surface. The difference in adsorption depends on the acid strength of the catalyst. Since the acid strength if Si/Al is very high, the acid sites interact with the π electron of the benzene ring of the phenolate ion bending the molecule slightly towards the surface.

1.11 Present work

The need for novel oxidation catalysts prompted us to use La₂O₃, Sm₂O₃ and Dy₂O₃ as the supports for the present investigation. Rare earth oxides are excellent supports for oxidation reactions since they are highly non-reducible. Besides, their binding energy is very low which makes the replenishment of consumed oxygen very easy. Reports on catalysis by vanadia supported on these oxides are very rare. Different vanadia loadings are attempted to modify the properties of rare earth oxides and to get an understanding of the active species of vanadia on the support. Since the supports are basic in nature, impregnation of vanadia is expected to bring about vanadates, which are excellent catalysts for oxidative dehydrogenation reactions. Vanadia impregnation also leads to acidity generation so that acid catalysed reactions would be feasible over these systems.
1. Objectives of the work

Main objectives of the present work are

- To prepare rare earth oxide supported vanadia with different vanadium loadings and to examine the surface properties employing different instrumental techniques like EDX, XRD, FTIR, BET surface area, pore volume measurements etc.

- To understand surface species of vanadia on basic lanthanide oxides.

- A thorough understanding of the acid base properties of V-Ln catalysts using techniques like TPD, adsorption studies, cyclohexanol decomposition and conventional Hammett indicator method.

- To test the activity of supported systems in the oxidative dehydrogenation of ethyl benzene and to understand the active vanadia species.

- To evaluate the catalytic activity of these systems in the oxidative dehydrogenation of ethanol.

- To test the catalytic activity of these systems in the alkylation of phenol with methanol and to attempt the correlation of acid base properties of the catalysts and the product selectivity.
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