CHAPTER IV

CATALYTIC ACTIVITY
Introduction

It is concluded from the characterisation methods that the physical and chemical properties of the rare earth oxides are significantly influenced by vanadia incorporation. Amorphous and crystalline tetrahedral vanadium species are present in the system. Since the acid base properties of the systems are modified due to impregnation of vanadia, it is plain that the catalytic activity of the supported system would be greatly affected. The different catalytic properties of bulk and supported vanadia are usually related to the modification in the coordination and environment of the vanadium species, which can modify its redox properties. V$_2$O$_3$ based systems are renowned for their catalytic activity towards oxidation reactions. Vanadium ions in different oxidation states, the presence of which is characteristic of vanadia catalysts facilitate the electron transfer between the reactants and the catalyst.

It was reported that systems active and selective in the formation of acidic products contain usually the elements forming oxides of more acidic character than vanadium (Mo, P etc.) whereas ODH reactions, which produce basic substances proceed well on systems of basic oxides [1]. For investigating the catalytic activity of rare earth oxide supported vanadia system, we have selected oxidative dehydrogenation of ethyl benzene and ethanol. Phenol methylation reactions using methanol is also carried out which is found to depend on the acid base property of the system. Behaviour of the supported system towards the aforementioned reactions is discussed in the following sections.

4.1 Oxidative dehydrogenation of Ethyl benzene

Oxidative dehydrogenation of ethyl benzene yields styrene (Fig. 4.1). It is a highly significant reaction from the industrial point of view due to the commercial importance of styrene. Industrially, styrene is prepared by alkylation of benzene
using ethylene. Generally used catalyst systems for the preparation of styrene from ethyl benzene include SiO$_2$ Al$_2$O$_3$ [2,3] V-Mg-O [4], SnO$_2$-P$_2$O$_5$ system [5] etc.

![Fig. 4.1.1 Oxidative dehydrogenation of ethyl benzene to styrene](image)

The reaction was performed in a vapour phase down flow silica reactor. The products were analysed using a Shimadzu GC-15 A gas chromatograph fitted with a xylene master capillary column and FID. Influence of rare earth oxide supports, role of oxygen, influence of reaction temperature and flow rate etc. are analysed in detail.

Data on ODH of ethyl benzene for the three rare earth oxide supported vanadia systems are given in Tables 4.1.1 to 4.1.3. Pure vanadia and rare earth oxide support are also used as catalysts to study the effect of supporting vanadia on the catalytic properties. Along with styrene, small amount of benzene and toluene are also detected among the products. Carbon oxides are the other products, which are formed by the complete oxidation of the organics.

Calculations are done in the following manner.

- **EB conversion** = $\frac{\text{mol EB converted}}{\text{mol EB fed}}$
- **Selectivity to ST, B or T** = $\frac{\text{mol product formed}}{\text{mol EB converted}}$
- **Selectivity to CO or CO$_2$** = $\frac{\text{mol product formed}}{(8 \times \text{mol EB converted})}$

where, EB = Ethyl benzene; ST = Styrene; B = Benzene; T = Toluene
Table 4.1.1 Oxidative dehydrogenation of ethyl benzene over La / V system

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Styrene</td>
<td>Toluene</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>35.8</td>
<td>0.0</td>
</tr>
<tr>
<td>La₂O₃</td>
<td>18.5</td>
<td>42.1</td>
</tr>
<tr>
<td>L3</td>
<td>16.5</td>
<td>65.1</td>
</tr>
<tr>
<td>L7</td>
<td>15.6</td>
<td>71.8</td>
</tr>
<tr>
<td>L11</td>
<td>16.0</td>
<td>70.3</td>
</tr>
<tr>
<td>L15</td>
<td>17.4</td>
<td>71.9</td>
</tr>
</tbody>
</table>

Reaction conditions: Reaction temperature: 475 °C; Feed rate: 6 ml/h; Catalyst: 2 g; Time on stream: 1 h.; Air flow rate: 20 ml/min.

Selective oxidation activity of pure vanadia was too poor, which catalysed almost complete oxidation of ethyl benzene, leading to more oxygenated products as evidenced by the higher percentage of carbon oxides formed. Carbon oxide selectivity of pure La₂O₃ was also high. From the ODH data, it is obvious that, selective oxidation activity of ethyl benzene to styrene is greatly influenced by V₂O₅.

Table 4.1.2. Oxidative dehydrogenation of ethyl benzene over Sm / V system

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Styrene</td>
<td>Benzene</td>
</tr>
<tr>
<td>S3</td>
<td>8.1</td>
<td>77.0</td>
</tr>
<tr>
<td>S7</td>
<td>13.8</td>
<td>84.7</td>
</tr>
<tr>
<td>S11</td>
<td>14.9</td>
<td>87.3</td>
</tr>
<tr>
<td>S15</td>
<td>16.6</td>
<td>86.6</td>
</tr>
</tbody>
</table>

Reaction conditions: Reaction temperature: 475°C; Feed rate: 6 ml/h; Catalyst: 2 g; Time on stream: 1 h.; Air flow rate: 20 ml/min.
Table 4.1.3. Oxidative dehydrogenation of ethyl benzene over Dy / V system

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Styrene (%)</th>
<th>Benzene (%)</th>
<th>C-oxides (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D3</td>
<td>15.5</td>
<td>2.3</td>
<td>85.0</td>
<td>1.7</td>
<td>11.0</td>
</tr>
<tr>
<td>D7</td>
<td>22.1</td>
<td>2.0</td>
<td>90.2</td>
<td>1.5</td>
<td>6.3</td>
</tr>
<tr>
<td>D11</td>
<td>23.2</td>
<td>1.4</td>
<td>91.2</td>
<td>0.9</td>
<td>6.5</td>
</tr>
<tr>
<td>D15</td>
<td>25.2</td>
<td>1.2</td>
<td>91.2</td>
<td>0.5</td>
<td>7.2</td>
</tr>
</tbody>
</table>

Reaction conditions: Reaction temperature: 475°C; Feed rate: 6 ml/h; Catalyst: 2 g; Time on stream: 1 h; Air flow rate: 20 ml/min.

incorporation. Addition of vanadia to La₂O₃ induces remarkable selective oxidation activity. Selectivity of styrene was almost doubled. Styrene selectivity was found to be independent of percentage conversion of ethyl benzene. Styrene selectivity was found to be maximum for Dy / V systems. Almost constant selectivity was detected for the three systems at higher vanadia loadings.

4.1.1 Selective oxidation activity of the supported system

The selectivity enhancement observed in the supported systems is explained as follows. V₂O₅ is having layer structure and all the layers take part in the oxidation reaction because diffusion of oxygen from other layers of the lattice is much faster in V₂O₅ [6]. This will lead to complete oxidation preferentially. According to Sachtler et al. [7,8], the selectivity in oxidation reaction is determined by two factors; 1) by the intrinsic activity of lattice oxygen 2) by their availability. If only a limited number of lattice oxygen is available, oxidation stops at a particular level to result partial oxidation products. Abstraction of too many hydrogen will lead to breaking of C – C bond resulting total oxidation products. In the supported systems, there is no large reservoir of bulk oxygen that is available to abstract so many oxygen. Thus the locally limited amount of reactive lattice oxygen might be the explanation for
selective oxidation activity. Pure rare earth oxides also catalyse complete oxidation of the organics. Lanthanide oxides possess low binding energy that in turn makes the lattice oxygen highly mobile [9]. So oxygen insertion takes place in the partial oxidation products resulting carbon oxides.

Of the transition metal oxides, V-Mg-O system was found to be the most active and selective catalyst in the ODH of ethyl benzene to styrene [4]. Almost constant styrene selectivity independent of reaction temperature and ethyl benzene conversion was reported for V-Mg-O systems, especially for magnesium orthovanadate (Mg₃V₂O₈). The selectivity of styrene reported by us using Ln/V systems is comparable to that obtained for magnesium orthovanadates. Maximum selectivity of styrene was achieved when vanadia was supported on Dy₂O₃. The styrene selectivity order was Dy/V > Sm/V > La/V.

According to Tagawa et al., the acid sites of Hammett Hₐ values between 1.5 and -5.6 are found to be the active site for ethyl benzene conversion which adsorb ethyl benzene reversibly. Oxidation of the same occurs on the basic sites of pKa lying between 17.2 and 26.5 [3]. The tendency to have maximum activity suggests the cooperative effect of the acid base properties of the catalyst. However, in the rare earth oxide supported vanadia systems, no such sites were detected by Hammett indicator method. So the influence of acid base properties on the selective oxidation activity will be negligible here. According to Blasco et al., the catalytic behaviour of vanadium based systems in selective oxidation strongly depend on the redox property of the vanadium species as well as on the acid base character of support and catalyst [10,11]. So apart from the acidic basic properties, the redox property plays an important role in ODH reaction of ethyl benzene.

The role of vanadia in developing selective oxidation activity to styrene on rare earth supports is apparent from the data in Tables 4.1.1 to 4.1.3. The activity for partial oxidation of the supported system is due to the coordination environment of
vanadium ion in the catalysts. Two types of vanadia species were detected in Ln / V systems. Surface vanadia species and lanthanide orthovanadates. The absence of polyvanadates and the existence of vanadia as vanadia tetrahedra are concluded from the IR data. The IR band observed in the region ~ 1060 cm\(^{-1}\) indicates the presence of monooxo species on the surface. It is generally accepted that at very low vanadia loadings, tetrahedral isolated vanadium species are present on the surface of the support [12]. Monomeric tetrahedral systems of the type (M-O)\(_3\) -V =O are reported on the surface of the catalyst systems at low loadings for a number of supported systems [13,14]. Corma et al [15] and Patel et al. [16] also confirmed the existence of vanadium species as isolated tetrahedra on the surface of the support.

Grzybowska et al. have shown that V\(^{5+}\) exists in isolated VO\(_4\) tetrahedra and orthovanadates [1]. Isolated tetrahedral V\(^{5+}\) species are proven to be active and selective centers for oxidative dehydrogenation reactions. It is accepted that vanadia in a tetrahedral coordination is most active in oxidative dehydrogenation [17,18,19]. This is in agreement with the report that in the case of alkanes, orthovanadates were observed to be selective in ODH reactions [16]. Further evidence is provided by Corma et al. who reported high selectivity for orthovanadates including LaVO\(_4\) and SmVO\(_4\) in which vanadium is in tetrahedral coordination [15]. For the present system, both the species being in tetrahedral geometry, this condition is satisfied, which indicate the active species to be vanadia in tetrahedral coordination both in amorphous and crystalline form.

Both the species have a common feature that they have isolated vanadate units, where every oxygen ion links one vanadium and one lanthanide ion. The environment of vanadyl units, ie., the existence of bond V – O – M in the catalyst affect the distribution of electron cloud around vanadium and oxygen atoms which will reflect in the degree of ionicity of V – O bond; ie., nucleophilicity of vanadium ions and electrophilicity of vanadium ions. In oxidation reactions, surface oxygen is proposed as a site capable of abstracting H atoms as H ions to form an OH group.
So the activity depends on the nucleophilicity of the oxygen of the catalyst. Oxygen attached to a $V^{2+}$ in tetrahedral coordination is found to be highly nucleophilic [1].

Among the three systems, Dy / V series showed higher activity. The lowest activity was found for La / V systems. Conversion of ethyl benzene increased with vanadia loading in the case of Sm/V and Dy/V systems. In the case of La/V series, conversion decreases with vanadia loading and then increased (This will be explained later, while discussing the reaction path). The difference in activity among the three supported systems can be correlated with their redox properties of the ion in Ln – O – V bond. Deo et al. have showed that the strength of the V – O – M (M = metal ion of the support) bond primarily determines the catalytic activity in the case of supported vanadia systems [21]. Reducibility plays an important role in deciding the activity of the supported system [6]. Higher the reducibility of the metal ion in the support metal oxide, higher the activity towards oxidation reactions. Among the three lanthanide ions, Dy is most reducible and it exhibits higher activity.

Above 3 % vanadia, styrene selectivity was almost constant. Here this behaviour is supposed to be due to the formation of lanthanide orthovanadate, which may be forming predominantly after 3 % vanadia. Up to 3 %, V$_2$O$_5$ surface species may be contributing to styrene selectivity. At higher vanadia concentration, vanadates have a prominent role, which exhibits a constant selectivity towards styrene. This is a characteristic behaviour of magnesium orthovanadate, which exhibits constant styrene selectivity even when the reaction parameters are changed [4].

Enhancement of selectivity by tetrahedral vanadium is connected with the availability of the lattice oxygen at the reaction site apart from the nucleophilicity of lattice oxygen. This oxygen availability is expressed as the average number of oxygen molecule that reacts with each hydrocarbon molecule, otherwise known as
average oxygen stoichiometry (AOS) [17]. The number of vanadyl units that can effectively interact with the adsorbed hydrocarbon unit determines the AOS in the case of a particular system. The effective size of such a unit is governed both by the size of the reactant and the rate of reoxidation of the active center. In the case of rare earth supported vanadia, VO₄ units are isolated (sufficiently apart), which supplies only a limited number of oxygen atoms to react with hydrocarbon molecule, improving selectivity. Higher AOS will lead to low selectivity. Apart from this, the rate of creation of oxygen vacancies, and the rate of replenishing of oxygen by migration of lattice oxygen decide the activity.

Superiority of supported catalyst over crystalline vanadia is established as follows. In crystalline vanadia V-O-V bonding is present. In supported system, V-O-Ln bond is present. The oxygen of the V-O-Ln bond is richer in electron density than in V-O-V, since lanthanide ion has lower electronegativity than vanadium ion. This renders the oxygen in Ln-O-V bond comparatively nucleophilic than the one in V₂O₅. For selective oxidation to occur, the oxygen should attack the hydrogen of the side chain, which is more probable by nucleophilic oxygen. So comparatively nucleophilic oxygen in orthovanadate prefer to attack high electrophilic hydrogen in the side chain of ethyl benzene. For complete oxidation to occur, bonding between carbon and oxygen has to occur. The carbon atom is sandwiched between π electrons. So the ‘H’ in this carbon would be attacked preferentially by an electrophilic oxygen over a nucleophilic one. In the case of V-O-V, the oxygen is more electrophilic and interacts with the ring hydrogen. This leads to rupture of C-C bond offering complete oxidation products [4].

In retrospect, the bonding in M-O-V was suggested to be the primary factor that determines the selectivity in ODH reaction [22,23]. Reducibility of the lanthanide ion affect the ease of removal of oxygen ions, i.e., the oxidizing ability of the system. The reducibility of an oxide is thought to be an important property affecting its catalytic performance and selectivity. A catalyst that is too difficult to
be reduced is too inactive with high selectivity, while that is too easily reduced is active but non selective. So if the vanadate unit is composed of a more reducible ion, the selectivity of ODH product will be low with high activity [16]. Here, the reducibility of the rare earth ions is in the order, La < Sm < Dy. La is least reducible. In other words, oxygen in La-O-V is more nucleophilic to attack the H of the ethyl benzene. So maximum selectivity is anticipated for L series of catalysts. In this study, results obtained are contradictory. Styrene selectivity was found to be high for Dy / V system. La / V system has the lowest styrene selectivity among the series. This is highlighted in Fig. 4.1.2.

The unexpected behaviour of La/V systems can be explained as follows. After ‘H’ abstraction, the partial oxidation product can desorb to gas phase or undergo further reaction with insertion of oxygen to form carbon oxides. The fate of the adsorbed product depends on a) the number of available lattice oxygen in the vicinity and the mobility of oxygen. i.e., mobility of oxygen which help to replenish the oxygen vacancies formed on oxidation. It leads to products with higher number of oxygen and eventually result in more percentage of carbon oxides; b) desorption rate of styrene. i.e., rate of diffusion of the oxygen in the lattice relative to the residence time of organic species on the catalyst surface. It affects the selectivity. Residence time of the product on the surface before desorption is an important factor which controls the selectivity of the products. The residence time will depend on the ease of desorption of styrene from the catalyst surface, which in turn depends on the acido-basic properties of the catalyst. This is dependent on the nature of adsorbate, an acidic product formed will be easily desorbed from an acidic catalyst, and a basic one get easily detached from a basic surface. Styrene being basic is less strongly bound and thus more easily desorbed from a catalyst, which shows higher basicity. As far as this factor is considered, the selectivity of styrene is expected to be high for the La/V series. Higher basicity of La/V series is confirmed though acid base property studies. But here, the first factor, that is the replenishment of lattice oxygen or the mobility may be the significant contributing factor. Rare earths possess low
binding energy for lattice oxygen and among La, Sm and Dy, O\textsuperscript{18} binding energy is low for La [9]. More mobile lattice oxygen leads to higher degree of oxidation leading to complete combustion products on La / V samples. So the selectivity follows the order Dy / V > Sm/V > La / V.

![Graph showing selectivity of styrene for the different supported systems](image)

**Fig. 4.1.2. Selectivity of styrene for the different supported systems**

The formation of toluene and benzene is caused by the interaction of ethyl benzene with acidic and basic centres of the catalyst surface. Wang et al. suggested that strong acidic sites could abstract alpha hydrogen of ethyl benzene facilitating the formation of benzene [24]. From ammonia desorption studies it was concluded that Lewis acid sites are decreasing with vanadia addition. Lewis acid sites are the strong acid sites on the catalysts surface. The decrease of benzene selectivity as vanadia content increases is explained by the reduction of Lewis sites. Similar observation was made with La/V systems also. An increased Lewis acidity was observed by vanadia addition at higher vanadia loadings, which leads to an increased
selectivity for benzene for L11 and L15. Strong basic sites on the catalyst preferably abstract beta hydrogen leading to cleavage of C-C bond of side chain resulting high yield of toluene. Krause proposed the role of strong basic sites for toluene formation [25]. Thus the decrease of toluene formation observed at higher vanadia percentage is explained since basic sites are reduced at higher vanadia loadings. From adsorption measurements using electron acceptors, strong basic sites are found to be consumed as the vanadia composition increases. The toluene selectivity order for La / V series also follows the order of basicity of the oxides.

4.1.2 Reaction in absence of air

To understand the reaction mechanism, the dehydrogenation of ethyl benzene is carried out in the absence of air. Data on dehydrogenation reaction of ethyl benzene is given are Tables 4.1.4 - 4.1.6.

The reaction proceeds considerably in the absence of air. In the absence of external oxygen, ethyl benzene conversion was almost halved. Reason for the reduced conversion may be the reduction of the catalyst. The formation of styrene reduces the catalyst system and the possibility of reoxidation is limited. In ODH, conversion is higher because external supply of air maintains the conversion by supplying $O_2$ needed for hydrogen abstraction by reoxidising the catalyst. Besides, deposition of carbonaceous materials is also another factor, which leads to poisoning of active sites.

The selectivity towards styrene formation is increased under nonoxidative reaction conditions. High styrene selectivity in absence of air must be due to absence of gaseous oxygen. A reduction of styrene selectivity in presence of gaseous oxygen is reported by Chang et al. [4]. This is in agreement with the conclusion of a kinetic
Table 4.1.4. Dehydrogenation of ethyl benzene over La / V system

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Styrene</td>
<td>Toluene</td>
</tr>
<tr>
<td>La2O3</td>
<td>6.2</td>
<td>78.3</td>
</tr>
<tr>
<td>L3</td>
<td>6.5</td>
<td>82.3</td>
</tr>
<tr>
<td>L7</td>
<td>7.3</td>
<td>86.6</td>
</tr>
<tr>
<td>L11</td>
<td>7.2</td>
<td>85.3</td>
</tr>
<tr>
<td>L15</td>
<td>7.8</td>
<td>87.2</td>
</tr>
</tbody>
</table>

Reaction conditions: Reaction temperature: 475 °C; Feed rate: 6 ml/h; Catalyst: 2 g; Time on stream: 1 h.

Table 4.1.5 Dehydrogenation of ethyl benzene over Sm / V system

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Styrene</td>
<td>Toluene</td>
</tr>
<tr>
<td>S3</td>
<td>6.4</td>
<td>82.9</td>
</tr>
<tr>
<td>S7</td>
<td>6.8</td>
<td>90.8</td>
</tr>
<tr>
<td>S11</td>
<td>7.2</td>
<td>90.0</td>
</tr>
<tr>
<td>S15</td>
<td>7.5</td>
<td>87.9</td>
</tr>
</tbody>
</table>

Reaction conditions: Reaction temperature: 475 °C; Feed rate: 6 ml/h; Catalyst: 2 g; Time on stream: 1 h.

study on ethyl benzene conversion over a V-Mg-O catalyst that surface adsorbed oxygen is active in the combustion of hydrocarbon [26]. A similar degradation by gaseous oxygen of the dehydrogenation product of butene has been reported on iron oxide [27].
Table 4.1.6. Dehydrogenation of ethyl benzene over Dy / V system

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion</th>
<th>Selectivity (%)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Styrene</td>
<td>Toluene</td>
<td>Benzene</td>
<td>C-oxides</td>
</tr>
<tr>
<td>D3</td>
<td>6.5</td>
<td>85.0</td>
<td>5.0</td>
<td>4.0</td>
<td>6.0</td>
</tr>
<tr>
<td>D7</td>
<td>5.5</td>
<td>90.9</td>
<td>4.5</td>
<td>2.7</td>
<td>1.9</td>
</tr>
<tr>
<td>D11</td>
<td>5.7</td>
<td>91.2</td>
<td>4.3</td>
<td>2.2</td>
<td>2.1</td>
</tr>
<tr>
<td>D15</td>
<td>6.8</td>
<td>91.7</td>
<td>2.2</td>
<td>2.6</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Reaction conditions: Reaction temperature: 475 °C; Feed rate: 6 ml/h; Catalyst: 2 g; Time on stream: 1 h.

The comparatively low activity observed for vanadia based systems for the oxidative dehydrogenation can be explained by the structure of vanadia species in the system. The activity depends on the availability of the active sites. Since the lattice oxygen is taking part in dehydrogenation, the reactivity and selectivity towards ODH product is decided by the AOS (average number of oxygen molecules that react with each hydrocarbon). The number of vanadia species, which constitutes the surface active sites that can effectively interact with adsorbed alkyl species determines the availability of AOS. Orthovanadates and surface vanadia species constitute the active phase, where the VO$_4$ units are isolated from each other. So hydrocarbon interacts with a limited number of VO$_4$ units leading to low conversion with high selectivity [17].

Effect of reaction temperature, contact time and time on stream for the reaction were studied over the supported vanadia systems. Since all the three series exhibited more or less the same behaviour, S7 is taken as a representative of the supported systems.
4.1.3 Effect of reaction temperature

ODH of Ethyl benzene was performed at different temperatures (475, 500 and 525°C) to understand the effect of reaction temperature on the system. Activity and selectivity of the system at different temperatures are given in Table 4.1.7. The conversion was increased with temperature, while the selectivity exhibited no considerable variation, as depicted in Fig. 4.1.3. Among various catalysts employed for ODH of ethyl benzene, Mg₃V₂O₈ exhibited a similar behaviour [4]. Styrene selectivity was constant independent of reaction temperature and ethyl benzene conversion. This is a unique property of magnesium orthovanadate. Other magnesium vanadates do not exhibit such an activity.

Table 4.1.7. Influence of reaction temperature on conversion and selectivity

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Styrene</th>
<th>Toluene</th>
<th>Benzene</th>
<th>C-oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>475</td>
<td>13.1</td>
<td>84.6</td>
<td>2.7</td>
<td>3.0</td>
<td>9.7</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>18.0</td>
<td>85.0</td>
<td>2.0</td>
<td>3.0</td>
<td>10.0</td>
<td></td>
</tr>
<tr>
<td>525</td>
<td>24.0</td>
<td>83.3</td>
<td>1.2</td>
<td>3.5</td>
<td>12.0</td>
<td></td>
</tr>
</tbody>
</table>

Reaction conditions: Catalyst : 2 g; Flow rate : 6 ml/h; TOS : 1h.; Air flow rate : 20 ml/min.

4.1.4 Effect of flow rate

The reaction was performed under different flow rates, 2, 6 and 8 ml/h. Higher feed rate decreases the contact time of the reactants with the catalyst surface. The results are shown in Figure 4.1.4. It is plain that a small feed rate will increase the residence time of the reactant on the catalyst surface. The higher the residence time, higher is the probability of reactive adsorption leading to higher conversion. So the increase of activity is expected. The possibility of product readsorption and the
production of more oxygenated products is probable at low flow rates, which leads to less selectivity. This is of prime importance while explaining the lower selectivity of styrene at low flow rates, because the mobile lattice oxygen produces more carbon oxides at higher contact times.

4.1.5 Deactivation study

Time on stream studies conducted on S7 revealed that these systems showed little change in activity and selectivity Fig.4.1.5. The conversion was more or less the same, although a slight deactivation was observed after 6 hours. Hence the stability of the catalyst system upon reduction was elucidated. Selectivity also remained a constant. The catalyst turned dark grey after continuous use, probably due to carbon deposits and reduction of the catalyst. The original colour could be regained by treating the catalyst in flowing air at 400°C for 2 h.

![Graph showing conversion and selectivity vs temperature](image.png)

Fig. 4.1.3 Effect of temperature on ethyl benzene conversion and styrene selectivity
Mechanism

The fact that the catalytic activity and percentage conversion were significantly reduced when the experiment was conducted in absence of air, pointed out to the role of gaseous oxygen in the reaction. In ODH of ethyl benzene, one of
the most probable mechanism consists of the abstraction of H from ethyl benzene by the lattice oxygen to form styrene and the reoxidation of the catalyst by gas phase oxygen [28]. This mechanism is known as Mars and van Krevelen mechanism. On rare earth supported systems, oxidative dehydrogenation is supposed to occur through the above mechanism, where reoxidation of the reduced vanadia based catalyst comprise chemisorption of an oxygen molecule from gas phase. In non-oxidative dehydrogenation, the absence of gaseous O\(_2\) may be reducing the activity. This type of mechanism is shown by Tagawa et al. on Si-Al system [3].

This can be represented as,
\[
\text{EB} + [\text{O}] \rightarrow \text{ST} + \text{[ ]}
\]
\[
\text{[ ]} + \frac{1}{2} \text{O}_2 \rightarrow [\text{O}]
\]

where [O] is the lattice oxygen and [ ] is the vacancy site in the lattice.

In the ODH of ethyl benzene, the activation of a C-H bond should be considered first, which is often regarded as the rate determining step [3]. The dissociative adsorption is not taking place on the catalyst surface. In the activation of hydrocarbons containing \(\pi\) electrons, abstraction of H atom on an oxide centre is facilitated by the donation of \(\pi\) electrons to a Lewis site, which leads to the weakening of the C-H bond (allylic type oxidation). The oxygen in the catalyst abstracts the H in ethyl benzene. Hydrocarbon activation centre is then considered to be a couple of M\(^{\pi^*}\)-O which is regarded as an acid base pair. In the stationary state of all oxidation products, catalysts contain both oxidised and reduced vanadium ions, the ratio depending on the reaction conditions and the nature of hydrocarbon being oxidised. Reduced vanadium ions chemisorb gaseous oxygen reversibly and are converted to lattice O\(^2-\). Stoichiometric vanadium never chemisorb oxygen. Dissociation of molecular oxygen with electron transfer according to overall reaction is shown below [29, 30].

\[
\text{O}_2\text{gas} \rightleftharpoons \text{O}_2\text{ads} \rightleftharpoons \text{O}_2^-\text{ads} \rightarrow 2\text{O}^-
\]
The electrons will be supplied by the reduced vanadium ions \((V^{5+} \text{ or } V^{4+})\) in the lattice. The oxygen supplying entity in the case of ODH reaction of ethyl benzene is a matter of dispute even now. The role of \(V=O\) of the terminal group in hydrogen abstraction was suggested. But studies on molybdina supported vanadia revealed that such an active species is not necessary to create the active site [1]. It was shown by quantum chemical calculations that stronger OH bonds are formed for bridging oxygen. The oxygen of \(M - O - V\) bond was proposed as the 'H' abstracting unit, since it was found to form strong H bonding by abstracting 'H' from the hydrocarbon [1]. In some other cases, the Bronsted acid sites were also suggested to be the active 'H' abstracting site [1]. But according to the reports, higher nucleophilic character of bridging oxygen leads to selectivity in orthovanadate systems. Thus a tentative suggestion can be given that the bridging oxygen may be active species that abstract the hydrogen from ethyl benzene. But the probability of Bronsted sites as the active site cannot be ruled out here since it was observed that vanadia addition enhances Bronsted acidity from TPD studies by ammonia.

Oxidation reactions on vanadia based systems follow the process mechanism involving parallel and consecutive reactions. The oxygenated products are formed in a series of successive steps (with or without the desorption of intermediate products to gas phase.) Carbon oxides are formed both in parallel route directly from a substrate and through consecutive route by the oxidation of final oxygenated products.

The role of vanadia species in creating active sites for selective oxidation clearly explains the improved conversion as the addition of \(V_2O_5\) is increased for Sm/V and Dy/V series. Styrene selectivity was almost independent of conversion indicating that acid base property has no significant influence and the redox property governs the activity and selectivity. So the activity increase is entirely attributed to increase in percentage of vanadia in tetrahedral coordination. In the case of Sm/V and Dy/V systems this is true. But in La/V series activity for ODH was not proportional to vanadia content pointing to the fact that some other factor decides the
activity. Effect of vanadia loading on the activity in terms of conversion for the three systems is revealed in Fig 4.1.6.

![Graph showing effect of V2O5 % on activity](image)

**Fig. 4.1.6** Effect of V2O5 % on activity

The activity of La/V systems first decreases and then increases at higher vanadia percentages, the order being L3 > L7 < L11 < L15. So the deciding factor for activity may not be the vanadate units exclusively. Acid base properties also may be involved [10,11]. The role of basic surface OH groups and Lewis acid sites are also suggested as sources of activity for some systems [3]. But such active acid and base sites were found to be absent in the rare earth supported vanadia systems. However, a tentative mechanism according to the above reference can be cited. The various steps are 1) coordination of ethyl benzene to the Lewis acid sites of the support, enhancing the acidic nature of alpha hydrogen. 2) basic group adjacent to the acid group abstract α H from the ethyl benzene to give a relatively stable adsorbed species. 3) elimination of water after the abstraction of α H creating anion vacancy. 4) reversibly adsorbed surface oxygen is converted to O' species. 5) the abstraction of β H of ethyl benzene by this oxygen to regenerate the catalyst. The reaction pathway according to the above reference is shown in figure (Fig.4.1.7).
This mechanism suits well with the data on acidity and basicity measurements. The temperature programmed desorption studies using ammonia revealed that after 7 wt % vanadia, there was an increase of Lewis sites, which was peculiar for the La/V catalysts. Again, from the adsorption studies using electron acceptors and indicator method, basic OH groups are increasing for 11 and 15 wt % vanadia. The basic OH may be either from La or V. Taking these two aspects into consideration, the trend in activity exhibited by La / V catalysts can be justified. But the type of active sites observed on Si-Al system is not seen in La / V systems. Participation of acid base properties for the reaction is obvious from the results. But this type of influence is not prominent in Sm/V and Dy/V systems, where the redox property of the Ln-O-V bond decides the activity.

Fig. 4.1.7. Reaction mechanism for ODH of ethyl benzene
4. 2 Oxidative dehydrogenation of ethanol

Introduction

Decomposition of ethanol is an important reaction in connection with the utilization of biomass as a chemical source. The reaction was performed in a vapour phase down flow silica reactor. An infusion pump on the top of the reactor introduced ethanol. The products were collected and analysed by gas chromatograph using a Porapak N column fitted with TCD.

Table 4.2.1. Data of ethanol decomposition on La2O3/V2O5 system

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>CH3CHO</th>
<th>CH3COOH</th>
<th>Ethylene</th>
<th>C-oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>La2O3</td>
<td>80.0</td>
<td>14.5</td>
<td>-</td>
<td>60.0</td>
<td>25.5</td>
</tr>
<tr>
<td>L3</td>
<td>77.9</td>
<td>28.0</td>
<td>12.8</td>
<td>49.2</td>
<td>10.0</td>
</tr>
<tr>
<td>L7</td>
<td>80.2</td>
<td>34.4</td>
<td>14.3</td>
<td>41.0</td>
<td>10.1</td>
</tr>
<tr>
<td>L11</td>
<td>81.4</td>
<td>41.5</td>
<td>16.4</td>
<td>32.0</td>
<td>9.5</td>
</tr>
<tr>
<td>L15</td>
<td>90.1</td>
<td>45.6</td>
<td>15.6</td>
<td>31.8</td>
<td>7.0</td>
</tr>
<tr>
<td>V2O5</td>
<td>95.0</td>
<td>5.0</td>
<td>-</td>
<td>2.0</td>
<td>93.0</td>
</tr>
</tbody>
</table>

Reaction conditions: Reaction temperature: 300°C; Flow rate: 8 ml/h; air flow rate: 30 ml/min; TOS: 1h; Catalyst: 2.5 g

\[
\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{ODH}} \text{CH}_3\text{CHO} + \text{CH}_3\text{COOH} + \text{CH}_2=\text{CH}_2
\]
4.2.1 Effect of vanadia

Oxidative dehydrogenation of ethanol yield acetaldehyde and ethylene as the major products (Table 4.2.1). Further oxidation of acetaldehyde formed acetic acid on the rare earth oxide. Complete oxidation of the organics gave carbon oxides. Pure vanadia gave more than 80 % carbon oxides. Acetaldehyde selectivity was about 5 %. This is not surprising while we consider the higher mobility of oxygen in vanadia system [6]. Oxygen from other layers of the lattice also migrates to the reaction site. Hence the activity is very high. The consecutive oxidation leads to almost complete oxidation of ethanol on the active sites. Lanthanide oxide also catalysed complete oxidation due to mobility of oxygen in the lattice along with dehydration [9]. Supported oxides exhibited high selectivity indicating the participation of vanadia in the active species. Partial oxidation activity in terms of the total amount of acetaldehyde and acetic acid formation increased with vanadia content.

While comparing the ODH activity of the system for ethyl benzene and ethanol it is noticed that the activity is comparatively high in the case of ethanol. Though the activity was less, the selectivity of partial oxidation products was high for ethyl benzene oxidation. It was reported that alcohols get dissociatively adsorbed on vanadia catalysts as alkoxy groups [21]. These alkoxy groups can undergo various reaction pathways to yield different products. The types of reaction pathways adopted depend on the nature of active sites present on the catalyst surface (redox and acid base sites). Redox sites favour selective oxidation of alcohol while acid/base sites catalyse dehydration. Strong basic sites interact with the reactants so as to produce C-oxides ultimately. Comparison of the activity and selectivity of La$_2$O$_3$ and supported analogues shows that the amount of partial oxidation products (acetaldehyde and acetic acid) increases as the vanadium oxide is deposited on La$_2$O$_3$. It is clear from the results that the selectivity of partial oxidation products doesn’t follow any particular trend with acid base properties. So it is confirmed that redox properties are predominating in determining the selectivity. The formation of higher
amount of partial oxidation products on the catalysts indicates that surface vanadia forms redox sites.

Fig. 4.2.1. Activity and selectivity of La/V system for the oxidative dehydrogenation of ethanol.

Table 4.2.2. Ethanol decomposition data on La/V catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH₃CHO</td>
<td>CH₃COOH</td>
</tr>
<tr>
<td>L15</td>
<td>90.1</td>
<td>45.6</td>
</tr>
<tr>
<td>S15</td>
<td>80.1</td>
<td>40.3</td>
</tr>
<tr>
<td>D15</td>
<td>78.2</td>
<td>38.6</td>
</tr>
</tbody>
</table>

Reaction conditions: Reaction temperature: 300°C; Flow rate: 8 ml/h; air flow rate: 30 ml/min; TOS 1 h.; Catalyst: 2.5 g
Three types of sites on the surface were proposed to be active in the case of supported systems for the ODH of ethanol [31]. i.e., M-O −V, V-O-V and V=O bonds, where ‘M’ is the metal ion in the support. The V-O-V bridges are found to be active in certain catalysts [32]. But the characterisation techniques have revealed that there are no such bonds in rare earth oxide supported vanadia, since crystalline vanadia is absent in the supported catalysts. Only terminal V=O and M-O-V bonds are present, which originate either from the surface vanadia or from lanthanide othovanadate. Hence only the other two factors are important.

The knowledge of V-O-M bond strength and hence the number of active sites is one of the fundamental criteria that determines the oxidation activity of supported metal oxides. According to Deo et al., the activity of the catalyst is related to the number of participating surface vanadia groups and depends on the reducibility of M-O-V bond (M is the metal ion in the support), where bridging oxygen controls the activity [21]. The reducibility of the metal ion in the V-O-M bond becomes the deciding factor. Accordingly, if the metal ion is more reducible, the activity of oxygen for hydrogen abstraction will be high, which leads to high conversion. In the present case, Dy ion is more reducible and is expected to show maximum activity while La/V, which is least reducible should exhibit low activity. The data on catalytic activity shown in Table 4.2.2. is contradictory. Activity (in terms of conversion) is high for the La/V system. So the possibility of V-O-S bond as the active site is ruled out.

The participation of V=O in determining the activity of ODH of ethanol has been emphasised by several authors [33,34]. This is in accordance with the result of methanol oxidation reported by Trifiro et al. [35]. According to them, the activity is directly connected to M=O terminal bonds, which opens with the addition of a hydrogen atom from alcohol which in turn leaves a free valence for the metal used for bonding with the dehydrogenated molecule (oxy reduction mechanism). Hence the active sites are concluded to be V=O species in the catalyst. This may be
originating from both surface species and orthovanadates. Studies on ethanol oxidation in which amorphous vanadia i.e., the extra lattice vanadia, act as the active sites are reported in literature [33]. V=O in orthovanadates may also be participating in catalysing the oxidative dehydrogenation. This is supported by the views of Ramis et al. that magnesium orthovandates are active and selective for the decomposition of alcohols that get adsorbed in a dissociative manner [36]. Extension of this observation can be applied to rare earth supported systems also, where orthovanadates occur as isolated tetrahedra similar to magnesium orthovanadates. Here a striking similarity is noticed between magnesium orthovandate and LnVO₄ that they are more active in ethanol ODH when compared to alkanes. Active two dimensional vanadates for ethanol oxidative dehydrogenation are reported by Nakagawa et al. [34]. It was presumed that oxygen in the V=O act as strong basic sites which abstract hydrogen from alcohols. The selectivity towards partial oxidation products can be explained on the basis of basicity of the supported vanadia systems. Basic catalyst could activate oxygen but it may not be sufficient to activate a basic product like acetaldehyde or ethylene that is essential for total oxidation activity. So the complete oxidation activity is found to be low for the supported analogues.

It was found that as vanadium content is increased ethylene selectivity also exhibited a corresponding reduction. Pure La₂O₃ was found to be very active for dehydration. This may be due to decrease of Lewis acid sites on the surface. It is accepted that Lewis acid sites on the supports play an important role in the dehydration of ethanol on supported catalysts [32]. As vanadia was deposited the number of active sites was diminished. It is not surprising since surface vanadium oxide is known to titrate surface lewis acid sites as evident from acid base properties studies. Vanadia species was getting anchored through the Lewis acid sites on the surface. This was confirmed earlier by the ammonia desorption studies. Through TPD studies it was observed that Lewis acidity is decreasing as the vanadia concentration in the catalyst increased. Involvement of acid base properties apart from the redox properties was evident from these results. In this context, it is relevant.
to consider the selectivity of the supported system towards dehydration in cyclohexanol decomposition. Decomposition of cyclohexanol carried out on the supported vanadia yielded a higher percentage of cyclohexene as vanadia content was increased indicating that dehydration was prominent. This is because, cyclohexanol dehydration is known to take place on weakly acidic sites [37]. The generation of weak acid sites (Bronsted) by vanadia addition explains the higher selectivity of cyclohexene formation. But dehydration of ethanol was not so prominent because ethylene formation needs much stronger sites. It is also confirmed that vanadia incorporation reduces the number of strong acid sites.

4.2.2 Effect of support

Oxidative dehydrogenation of ethanol was carried out using different supported systems to study the effect of support on the activity of the active species. In the case of methanol oxidation, it was observed that the reactivity depends on the nature of the oxide support [21]. Comparison of the three supported vanadia analogues shows that La/V catalyst is more active and selective among the three systems under study (Table 4.2.2.). The higher activity of La/V is explained on the basis of strength of terminal V=O species.

Fig. 4.2.2 Activity and selectivity of different supported systems
The strength of V=O bond was related with the position of Raman band in the case of alcohol decomposition by Deo et al. on various supported vanadia systems [21]. In the present study, IR band position was correlated to the V=O strength. The position of IR band of terminal V=O bond was directly related to the V=O bond strength and a stronger V=O bond gave a higher IR band position. As explained in the previous chapter, among the three supported systems, La/V showed lowest terminal V=O bond strength (both for surface species and orthovanadates) indicating weak terminal bonds while comparing among the systems. The V=O band position was related to the electronegativity of the metal ion in the oxide support. La being less electronegative, showed lowest value for V=O frequency in the IR spectrum. So the oxygen in V=O will be more basic to enable the easy abstraction of hydrogen from alcohol species. This results in higher activity towards ethanol ODH (Fig. 4.2.2.).

**Mechanism**

![Reaction mechanism for selective oxidation of ethanol over supported vanadia system.](image)

Fig. 4.2.3 Reaction mechanism for selective oxidation of ethanol over supported vanadia system.
The selective oxidation of ethanol over supported metal oxides was studied extensively and a general pathway for the reaction was established. Different steps in the reaction are a) adsorption and activation of ethanol on active metal site b) decomposition and desorption of the ethoxide species and c) reoxidation of the catalyst [32,33]. Following this route, Kannan et al. suggested a mechanism for the reaction on vanadia species [Fig. 4.2.3]. A dissociative adsorption of ethanol was proposed and the V=O groups are found to be responsible for the aldehyde formation [33]. As per this mechanism, the selectivity depends on the V=O bond strength.
4.3 Methylation of Phenol

Introduction

Influence of vanadia addition on the acid base property of the supported system is well established through different analytical procedures in the previous chapter. These catalysts should be screened for various acid and base catalysed reactions. Vapour phase methylation of phenol was selected as the test reaction. Reaction of methanol with phenol is an acid base reaction, catalysed by both acid and basic sites. Both O- and C- alkylated products are derived from the reaction, which include anisole, methyl anisole, o-cresol, different isomers of xylenol, trimethyl phenols etc.

Alkyl phenols are industrially important intermediates in the manufacture of plastics, pesticides, pharmaceuticals etc [38,39]. Most important ones among this category are o-cresol and 2,6-xylenol. They are used widely in the production of resins, insecticides and antioxidants. Ortho cresol is used in the manufacture of epoxy cresol novalak resins. 2,6-xylenol is a monomer of a good heat resisting poly-(2,6-dimethyl) phenylene oxide resin, which is a component in the alloys used in electronic industry [40].

The reaction was carried out in vapour phase with 3 g catalysts in a silica reactor. Prior to reaction, the catalysts were activated at 500 °C for 2 h in flowing air. The products were analysed by a GC 15 A gas chromatograph fitted with FID and a FAP – S- 10 % on 60/80 Chromosorb W (AW) column. Phenol conversion and selectivities are expressed in wt %. The selectivity of products are obtained in the following manner.

\[
Selectivity(\%) = \frac{Yield}{Total\ conversion\ of\ phenol} \times 100
\]
Both O- and C- alkylated products are obtained for the catalyst systems. Anisole, ortho cresol, 2,6-xylenol and trimethyl trimethyl phenol (TMP) were the main products. Traces of methyl anisole were also detected in some systems. The reaction can be expressed as shown in Figure 4.3.1.

![Diagram of chemical structures](image)

**Fig. 4.3.1 Products of methylation of phenol.**

The catalytic activity and selectivity of the supported systems towards methylation of phenol is given in Tables 4.3.1 to 4.3.3.
Table 4.3.1 Conversion and selectivity of products in the methylation of phenol on Dy/V system

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Anisole</td>
</tr>
<tr>
<td>D3</td>
<td>29.5</td>
<td>4.1</td>
</tr>
<tr>
<td>D7</td>
<td>47.1</td>
<td>2.1</td>
</tr>
<tr>
<td>D11</td>
<td>68.1</td>
<td>2.6</td>
</tr>
<tr>
<td>D15</td>
<td>73.5</td>
<td>5.1</td>
</tr>
</tbody>
</table>

Reaction conditions: Reaction temperature: 350 °C; Phenol: methanol ratio: 1:7; Flow rate: 4 ml/h; TOS: 1.5 h.

Table 4.3.2 Conversion and selectivity of products in the methylation of phenol on Sm/V system

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Anisole</td>
</tr>
<tr>
<td>S</td>
<td>20.0</td>
<td>5.6</td>
</tr>
<tr>
<td>S3</td>
<td>21.8</td>
<td>3.5</td>
</tr>
<tr>
<td>S7</td>
<td>43.3</td>
<td>3.2</td>
</tr>
<tr>
<td>S11</td>
<td>74.5</td>
<td>5.5</td>
</tr>
<tr>
<td>S15</td>
<td>78.3</td>
<td>4.4</td>
</tr>
</tbody>
</table>

Reaction conditions: Reaction temperature: 350 °C; Phenol: methanol ratio: 1:7; Flow rate: 4 ml/h; TOS: 1.5 h.
Table 4.3.3 Conversion and selectivity of products in the methylation of phenol on La/V system

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Anisole</th>
<th>Me anisole</th>
<th>o-cresol</th>
<th>2,6-xylenol</th>
<th>TMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>L3</td>
<td>13.7</td>
<td>26.7</td>
<td>-</td>
<td>69.3</td>
<td>4.0</td>
<td>-</td>
</tr>
<tr>
<td>L7</td>
<td>26.3</td>
<td>29.2</td>
<td>-</td>
<td>57.2</td>
<td>12.1</td>
<td>1.5</td>
</tr>
<tr>
<td>L11</td>
<td>23.3</td>
<td>24.8</td>
<td>-</td>
<td>67.1</td>
<td>6.7</td>
<td>1.4</td>
</tr>
<tr>
<td>L15</td>
<td>22.4</td>
<td>22.7</td>
<td>-</td>
<td>68.7</td>
<td>7.2</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Reaction conditions: Reaction temperature: 350 °C; Phenol: methanol ratio: 1:7; Flow rate: 4 ml/h; TOS: 1.5 h.

Major fraction of the products includes ring-alkylated phenols, which indicate catalysis of C- alkylation by rare earth oxide supported vanadia. Ring alkylated products include o-cresol, 2,6-xylenol and trimethyl phenol (TMP). O-alkylated products include anisole derivatives. C-alkylated product selectivity was more than 70% for all the systems. La/V series showed lowest conversion of phenol among the three supported system. Order of catalytic activity in terms of phenol conversion was Dy/V > Sm/V > La/V. Anisole formation was high for the La/V series of catalysts. Sm/V and Dy/V series exhibited poor selectivity towards O-alkylation. Anisole (O-methylation) first formed undergoes further methylation on Sm/V and Dy/V catalysts. No methyl anisole is detected in the case of vanadia supported on La2O3. It was found that as the vanadia percentage increased, concentration of higher alkylated phenol also increased with a corresponding decrease of o-cresol.
4.3.1 Influence of acid base properties on selectivity

In general, basicity was found to have an adverse effect on the catalytic activity towards phenol alkylation. Higher concentration of ring-alkylated products indicates that weak acidic/strong basic sites are present in the supported system. Earlier workers have reported that weak acid/strong basic sites favour C-alkylation [41,42]. In the present case, it was confirmed through adsorption of electron acceptors that supported vanadia system possesses strong basic sites. Moreover, for all the three systems there was an enhancement in weak acidic sites as evident from the ammonia adsorption studies. Enhancement of C-alkylation by weak acidic sites was confirmed through further studies [43,44].

Anisole formation was comparatively higher for La / V systems. Only traces of anisole were observed for S and D series. Anisole formation over systems of L series can be explained by the higher acidity of the samples. This is in accordance with the studies by Benzouhanava et al. [42] that strong acidic sites favour O-alkylation. Amount of ammonia desorbed at higher temperature was large for vanadia supported on La2O3 indicating the presence of strong acid sites.

Several mechanisms were suggested for the alkylation of phenol [45]. Alkylation over acidic catalysts was supposed to proceed through anisole formation, which rearranges intramolecularly to give o-cresol. Stronger acidic sites favour meta and para cresols. Xylenol formation occurs via consecutive methylation of cresol. Basic and bifunctional catalysts adopt direct ring alkylation route. Ortho product selectivity is found to be high on basic systems by direct ring alkylation. Conversion of phenol decreases with decrease in basicity if the reaction proceeds through the rearrangement of an anisole intermediate. In contrast increase in basicity decreases the activity if direct C-alkylation takes place to give o-cresol selectively. Here it is found that conversion of phenol is increasing with decrease in basicity of the catalyst. Hence direct ring alkylation is expected to take place on the supported system without the formation of anisole intermediate. From the data in Tables 4.3.1 to 4.3.3, it is
clear that ortho cresol selectivity decreases with vanadia addition. 2, 6-Xylenol selectivity first increases followed by a decrease as the vanadia content increased, whereas TMP selectivity goes on increasing. Hence it can be inferred that ortho cresol formed undergoes consecutive methylation to give higher alkylated phenols. So the reaction pathway can be considered as shown in the figure.

![Reaction pathway of methylation of phenol on rare earth oxide supported vanadia.](image)

**Fig. 4.3.2** Reaction pathway of methylation of phenol on rare earth oxide supported vanadia.

### 4.3.2 Ortho selectivity

Ortho selectivity of the supported systems are shown in Fig. 4.3.3. For Sm/V and Dy/V systems, ortho selectivity (o-cresol, 2,6-xylenol and methyl anisole) decreased with vanadia addition. It can be understood in terms of decrease of basicity as confirmed by Hammett indicator and adsorption studies. Selectivity for the formation of ortho products is in the order of basicity. For Sm/V and Dy/V series basicity order was $3 > 7 > 11 > 15 \%$ vanadia. For La/V systems, the order is $3 > 7 < 11 < 15$. These orders were maintained in the ortho product selectivity. This agrees well with Tanabe [46] that basic catalysts alkylate selectively at ortho position. Accordingly, the o-selectivity should be proportional to basic strength. This is in agreement with our data (Tables 4.3.1-4.3.3). However, there are reports that acidic catalysts predominantly alkylate at ortho position [47].
According to Tanabe et al. [48] Bronsted sites interact with the electron cloud of benzene ring. So ring will be parallel to the surface giving access to positions other than ortho for attack by alkylation group. So strong Bronsted acid sites reduces the ortho product selectivity. The interaction can be shown as follows.

\[
\text{\textbf{Fig. 4.3.3 Interaction of phenol with Bronsted sites}}
\]

It was found that ortho selectivity is decreasing by vanadia addition, which is achieved through adsorption of phenol on Lewis acid sites as reported by Klemm et al. (shown in Fig. 4.3.5) [49]. Such an orientation prevents the interaction of the catalyst with the \( \pi \) electron cloud of the benzene ring. Phenol interacts with Lewis
acid base centers giving phenolate ion (on Lewis acid site) and H⁺ (on basic site). This proton induces formation of carbonium ion from methanol, which interact with the adsorbed phenolate ion at ortho positions

\[
\text{A} \quad \text{B} \quad + \quad \text{H}^+ 
\]

\[
\text{A} \quad \text{B} \quad \text{ortho products}
\]

\[
\begin{align*}
\text{A} & \quad \text{B} \\
\text{A} & \quad \text{B} \\
\end{align*}
\]

\[ \text{A} = \text{Lewis acid site}, \quad \text{B} = \text{Lewis base site} \]

Fig. 4.3.5 Adsorption of phenol on Lewis site

Lewis acid base sites are necessary for adsorption of phenol to yield ortho methylated products. It was confirmed through acid base studies that both Lewis acidity and Lewis basicity are decreasing with increase of vanadia loading since vanadia species get adsorbed by the titration of basic OH groups and Lewis acid sites on the surface of the support. From the TPD of ammonia, it is confirmed that Bronsted acid sites are increasing with a concomitant decrease of Lewis sites. The ortho selectivity at low vanadia loadings can be understood from these observations. At higher vanadia loadings, Bronsted acid sites increase yielding higher methylated phenols. For La/V systems, number of strong Bronsted sites is decreasing and Lewis acidity is increasing at higher vanadia percentage, favouring the formation of ortho products for L11 and L15.
As a generalization, Tanabe et al. proposed a model for adsorption of phenolate ion on acidic and basic systems. The selectivity of the products during alkylation can be explained by the adsorption mode of phenolate ion on the surface of the catalyst. IR study of phenol adsorbed on Si-Al and MgO revealed that o-selectivity is strongly controlled by the adsorbed states of phenol [50]. The different modes of adsorption of phenolate ion on basic and acidic catalyst are shown in figure 4.3.6.

Fig. 4.3.6 Different adsorption modes of phenolate ion on basic and acidic catalysts

On basic catalyst, the electron cloud of the benzene ring will be repelled by the catalyst surface, rendering the adsorbed phenolate ion in an almost vertical position. So the ortho position will be easily susceptible for attack by an adsorbed methyl group. This type of repulsion will be comparatively low in case of an acidic catalyst. So the alkyl group will have access to other positions as well, yielding higher alkyl phenols.
References


