CHAPTER 8

OXIDATIVE DEHYDROGENATION OF ETHYLBENZENE

Abstract

The production of light olefins from alkanes separated from natural gas, today largely available and cheap, is a desirable option to limit the dependence from oil. This can be obtained through endothermic reactions such as steam cracking and thermal catalytic dehydrogenation or through an exothermic reaction such as oxidative dehydrogenation. However, several problems still remain, such as the formation of coke on the catalyst, thermodynamic constraints, and a large amount of wasted energy in the form of excess steam. Energy saving and more economical dehydrogenation processes are therefore desirable. For styrene synthesis, one of the ten most important industrial processes, the exothermic oxidative dehydrogenation of ethylbenzene is an elegant and promising reaction. Oxidative dehydrogenation has attracted much since it can be operated at low temperatures and it is free from equilibrium limitations. Oxidative dehydrogenation reactions also receive great attention in the synthesis of valuable alkenes but, the finding of efficient catalysts with good olefin production is still a critical point and these processes are still far from being widely used at industrial-scale.
8.1 INTRODUCTION

The utilization of relatively abundant and cheap alkanes in the chemical industry is always desirable. In the transformation of alkanes into valuable chemicals, selective oxidation is considered to be important. Styrene, one of the most important basic chemicals mainly used as the monomer for the production of different synthetic polymers, such as polystyrene, styrene-acrylonitrile and acrylonitrile-butadiene-styrene is produced commercially by dehydrogenation of ethylbenzene, using Fe-Cr-K as catalyst in the presence of a large amount of superheated steam as a diluent and heat carrier at high temperature of 550-650 °C. Small amounts of elements such as V, Mo, Ce, Co, and Ca were added to improve catalyst performance. The schematic representation of the ethylbenzene dehydrogenation is shown in scheme 8.1.

\[
\begin{align*}
\text{CH}_2\text{CH}_3 & \quad \text{ODH} \\
\text{Ethylbenzene} & \quad \text{CH}=\text{CH}_2 \\
+ & \quad \text{H}_2 \\
\text{Styrene} &
\end{align*}
\]

Scheme 8.1

This commercial process is equilibrium limited and has high energy consumption. Thus an alternative way is still being pursued. The advantage of an oxidative dehydrogenation process in the presence of oxygen is that, reaction is exothermic and it can be operated at lower temperatures\(^1\). Since the reaction would not be equilibrium limited and energy intensive, there is a strong incentive for the development of an oxidative dehydrogenation process\(^2\).

Oxidative dehydrogenation process (ODH) is promising due to its exothermic reaction, but such a process requires an active and selective
oxidation stable catalyst. Among the catalysts reported for the ODH of ethylbenzene includes metal oxides, supported oxides, phosphates and organic polymers\textsuperscript{3-6}. An extensive body of work has been published, aiming at the nature of the active phase and the role of promoters. Alumina is reported to be an active catalyst for the ODH of ethylbenzene and other alkylbenzenes. Moderate acid strength of silica-alumina, tin oxides and phosphates are reported to be the key factor for the ODH reaction.\textsuperscript{7} Among various metal oxide incorporated alumina, the introduction of Fe\textsubscript{2}O\textsubscript{3} and Cr\textsubscript{2}O\textsubscript{3} considerably enhanced the dehydrogenation activity.\textsuperscript{8} According to Sugunan et al.\textsuperscript{9} the ODH of ethylbenzene over rare earth promoted sulfated oxides exhibits better activity compared to non-sulfated and sulfated tin oxide systems. Nicolas et al.\textsuperscript{10} reported the catalytic use of onion-like carbon materials for styrene synthesis by oxidative dehydrogenation of ethylbenzene.

Oxidative dehydrogenation of alkanes has been studied with various vanadia based catalysts in presence of oxygen\textsuperscript{11,12}. VMgO was first reported to be active and selective in the ODH of ethylbenzene.\textsuperscript{13} For silica supported vanadia catalysts, the very high activity at low surface coverage is attributed to the highly dispersed species of (SiO)\textsubscript{3}V=O formed on the SiO\textsubscript{2} surface.\textsuperscript{14-16} This suggested that the redox properties are operative during ODH of lower alkanes since these surface species are more easily reducible than bulk phase. Kung and co-workers\textsuperscript{17-20} attributed magnesium orthovanadate (Mg\textsubscript{5}V\textsubscript{2}O\textsubscript{8}) as the active phase in the ODH of propane, n-butane, and cyclohexane over VMgO catalyst. Several metal orthovanadates have also been tested and found to be quite active and studies have also focused on vanadia supported alumina and titania.\textsuperscript{21} Three factors, viz. (a) the presence of tetrahedral VO\textsubscript{4}, (b) the
absence of V=O double bonds and (c) the difference in metallic vanadates, were pointed out to be responsible for the oxidative dehydrogenation properties of VMgO catalysts. According to Albonetti et al.\textsuperscript{22} vanadium is a key element for performing the oxidative dehydrogenation of propane to propene. N\textsubscript{2}O was used as an oxidizing agent by Lopez Nieto et al.\textsuperscript{23} for the oxidative dehydrogenation of n-butane and found higher selectivity for olefins compared with molecular oxygen. Unsupported and alumina supported NiO-V\textsubscript{2}O\textsubscript{5} are known as rather efficient catalysts for oxidative and non-oxidative dehydrogenation of various hydrocarbons\textsuperscript{24}. According to Petrov et al.\textsuperscript{25} the catalytic activity of binary NiO-V\textsubscript{2}O\textsubscript{5} catalysts for ethylbenzene dehydrogenation is due to predominantly V\textsubscript{2}O\textsubscript{5} phase while other phases catalyze mostly cracking and dealkylation reactions. The dehydrogenation activity of supported vanadia catalysts is dependent upon both the nature of the support and dispersion of the vanadium component on that support. Su et al.\textsuperscript{26} reported the first application of carbon nanotubes in the ODH of ethylbenzene. Report stated that the catalytic activity shows only a minor dependence on the oxygen concentration and activity and selectivity of the sp\textsuperscript{2} carbon is related to the optimized distribution of sites required for the oxygen activation and basic centers, where ethylbenzene adsorption takes place. Suzuki and coworkers\textsuperscript{27} reported that active carbon supported vanadium catalysts exhibit high catalytic activity in ODH of ethylbenzene to give styrene in the presence of carbon oxide. Oxidative dehydrogenation, ODH, of alkanes is a subject of an ever-growing interest as a source of cheap olefins for industrial applications and supported vanadium oxides are suitable catalysts for the ODH of alkanes\textsuperscript{28-30}. 

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8.2 INFLUENCE OF REACTION CONDITION

To get an idea about the influence of reaction conditions on the dehydrogenation activity and selectivity, the reaction was conducted by varying different properties. IOVCRS was taken as a representative catalyst to study the effect of properties viz. temperature, flow rate, air flow and time.

8.2.1 Effect of Temperature

The dependence of ethylbenzene dehydrogenation activity and selectivity on the reaction temperature for the catalysts is shown in Figure 8.1.

![Figure 8.1](image)

**Figure 8.1**

Reaction conditions: 10VCRS-500 mg, Flow rate- 4 ml/h, Airflow- 120 ml/min and Time -3 h.

The ODH of ethylbenzene was conducted with air at temperature range 523-723 K over 10VCRS catalyst. Ethylbenzene conversion and styrene selectivity increases with increase in temperature from 523 to 623 K. Further increases in reaction temperature slightly reduced ethylbenzene conversion and remain more or less constant throughout a period of 673-773 K. The decrease in conversion can be attributed to the blocking of active sites of catalyst by
Oxidative Dehydrogenation of Ethylbenzene

coke formation. The rate of coke deposition during ethylbenzene ODH depends on many factors among which reaction temperature is the crucial one. Indeed, an excessively high operation temperature enhances the cracking side reactions occurring on the acidic surface sites of the catalyst\textsuperscript{31,32}. The selectivity of styrene increases with rise in temperature up to 623 K and decreases thereafter. Since the formation of styrene by direct dehydrogenation of ethylbenzene is an endothermic reaction (\(\Delta H = 124.9 \text{ KJ/mol}\)), it is more favoured with high temperature\textsuperscript{33}. Cracking products formation and deep oxidation with increase in temperature could result in reduced styrene selectivity at high temperature. From the study, 623 K was chosen for further performance of the reaction.

8.2.2 Effect of Air flow

The variations of dehydrogenation activity and selectivity of catalyst with air flow is presented in Figure 8.2.

![Figure 8.2](image)

**Figure 8.2**

Reaction conditions:-10VCRS-500 mg, Temperature-623 K, Flow Rate- 4mlh\textsuperscript{-1} and Time-3 h.

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Dehydrogenation conducted in the absence of any air flow produced no styrene. The conversion rate and styrene selectivity was found increasing with increase in air flow rate reaches a maximum and then decreases. Supply of air helps the reaction by supply of oxygen needed for H abstraction by reoxidizing the catalyst. The surface adsorbed oxygen can improve the combustion of hydrocarbon. Increase in oxygen supply may result in complete oxidation products and thus yield of liquid products decreases along with styrene selectivity. In the supported vanadia catalysts, lattice oxygen is taking part in dehydrogenation. Activity and selectivity towards ODH decided by the average number of oxygen molecules that reacts with each hydrocarbon. Increase in air flow result in reduced oxygen molecules for reaction and decreases conversion rate and selectivity considerably.

8.2.3 Effect of Feed flow rate

The results of effect of flow rate on ODH are shown in Figure 8.3.

![Graph showing the effect of feed flow rate on conversion and selectivity of ethylbenzene and styrene.](image)

**Figure 8.3**
Reaction conditions:- 10VCRS-500 mg, Temperature-623 K, Air flow- 120mlmin⁻¹, and Time-3 h.
From Figure 8.3 it is shown that the conversion decreases with an increase in the flow rate of ethylbenzene from 2 to 5 ml/h since the contact time of the reactants with the catalyst surface reduces as the flow rate increases. At small flow rate the contact time of the reactant on the catalyst surface should be more. At higher flow rate of reactant, it will not get enough time to adsorb on the catalyst surface and which results in reduced conversion rate. High rate of ethylbenzene dehydrogenation at small flow rate (higher contact time) results due to the higher probability of reactive adsorption. Selectivity of styrene was increased with an increase in flow rate from 2 to 3 ml/h and maximum selectivity is observed for flow rate of 5 ml/h. At lower flow rate, the possibility of product readsorption and the production of more oxygenated products are probable which leads to less selectivity of styrene since more amounts of byproducts toluene and benzene are produced with increasing contact time\textsuperscript{37,38}. Small styrene selectivity at low flow rate could also be accounted for the thermal decomposition of ethylbenzene and styrene\textsuperscript{39}. Prevention of readsorption of styrene on catalyst surface can prevent the formation of oxygenated products at high flow rate giving rise to styrene selectively. The 3 ml/h was selected as the optimal flow rate for further reaction to obtain high conversion rate with styrene selectively.

8.2.4 Effect of Time

Effect of time on reaction is an important factor in vapour phase reactions. In figure 8.4 the conversion of ethylbenzene is plotted as a function of time-on-stream.
Reaction conditions: 10 VCRS - 500 mg, Temperature - 623 K, Air flow - 120 ml min⁻¹ and Flow rate - 3 ml h⁻¹.

Under the reaction conditions studied, the initial conversion rate and styrene selectivity was high. Conversion is almost constant after an initial period. However, with an increasing reaction period, the dehydrogenation rate and styrene selectivity decreased gradually. After 6 h run, the conversion rate and styrene selectivity was decreased considerably. The maximum styrene selectivity obtained is 89.6%. The yellow coloured catalysts turned black after the reaction period and could be regenerated after treatment at 773 K for 6 h. Reduction of metal ions on the catalysts surface can cause deactivation in reaction⁴⁰. The deposition of carbon on the catalyst surface also seems to be a major cause of deactivation of the catalyst. Deposited carbon can be burned off by high temperature treatment⁴¹.

8.3 OXIDATIVE DEHYDROGENATION OVER CATALYSTS

The catalytic performances of all the catalysts prepared were monitored in the oxidative dehydrogenation of ethylbenzene and the results are discussed...
Below. The selected conditions for the reaction to carry out are presented in Table 8.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Selected condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst/mg</td>
<td>500</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>623</td>
</tr>
<tr>
<td>Air flow/mlmin⁻¹</td>
<td>120</td>
</tr>
<tr>
<td>Flow rate/mlh⁻¹</td>
<td>3</td>
</tr>
<tr>
<td>Time/h</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 8.2 shows the results of the catalytic performance during the dehydrogenation of ethylbenzene over VC series of catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (wt.%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Styrene</td>
</tr>
<tr>
<td>C</td>
<td>19.9</td>
<td>49.1</td>
</tr>
<tr>
<td>2VC</td>
<td>7.4</td>
<td>85.9</td>
</tr>
<tr>
<td>4VC</td>
<td>9.6</td>
<td>82.8</td>
</tr>
<tr>
<td>6VC</td>
<td>10.0</td>
<td>72.4</td>
</tr>
<tr>
<td>8VC</td>
<td>8.8</td>
<td>77.6</td>
</tr>
<tr>
<td>10VC</td>
<td>8.4</td>
<td>79.2</td>
</tr>
</tbody>
</table>

The main product obtained by ethylbenzene dehydrogenation is styrene with small amounts of by-products such as benzene and toluene over all catalysts. Mass balance calculation showed that the formation of total oxidation products CO and CO₂ under the studied reaction conditions is negligible. This is attributed to the formation of stable dehydrogenated product.
styrene during the oxidation reaction of ethylbenzene. This phenomenon already reported by Centi et al.\textsuperscript{42}. The styrene preferentially adsorbed through its C=C bond and oxygen is chemisorbed over Lewis acid sites. The interaction of the olefinic double bond with the Lewis acid sites inhibits the oxygen adsorption and reduces the oxygen availability on the surface. As a consequence, the selectivity to carbon oxides is reduced.

Table 8.3 gives the catalytic performance during the dehydrogenation of ethylbenzene over VCRS series of catalysts.

Table 8.3

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (wt.%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RS</td>
<td>0.9</td>
<td>40.0</td>
</tr>
<tr>
<td>CRS</td>
<td>26.7</td>
<td>95.1</td>
</tr>
<tr>
<td>2VCRS</td>
<td>13.0</td>
<td>85.6</td>
</tr>
<tr>
<td>4VCRS</td>
<td>16.3</td>
<td>84.0</td>
</tr>
<tr>
<td>6VCRS</td>
<td>16.6</td>
<td>82.6</td>
</tr>
<tr>
<td>8VCRS</td>
<td>16.7</td>
<td>86.3</td>
</tr>
<tr>
<td>10VCRS</td>
<td>16.8</td>
<td>89.4</td>
</tr>
</tbody>
</table>

Compared to ceria, CRS support exhibited higher conversion rate and styrene selectivity. The supported vanadia catalysts exhibited higher styrene selectivity than ceria. Among supported catalysts, CRS supported vanadia exhibited higher conversion rate and styrene selectivity. As the vanadia loading is increased, the conversion of ethylbenzene on VC series catalysts first increases and then decreases. However, selectivity to styrene at the maximum
conversion of 6VC is 72.3 %, which is low compared to other loading. The activities of the CRS supported vanadia catalysts are higher than those of VC series with higher styrene selectivity. Among these, initially the ethylbenzene conversion increases slightly with the vanadia loading and remains the same thereafter.

Table 8.4 shows the results of the catalytic activity during the dehydrogenation of ethylbenzene with praseodymia containing catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (wt.%)</th>
<th>Selectivity (%)</th>
<th>Styrene</th>
<th>Benzene+Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>15.9</td>
<td>78.5</td>
<td>21.5</td>
<td></td>
</tr>
<tr>
<td>PRS</td>
<td>12.2</td>
<td>93.8</td>
<td>6.3</td>
<td></td>
</tr>
<tr>
<td>2VP</td>
<td>26.5</td>
<td>87.6</td>
<td>12.4</td>
<td></td>
</tr>
<tr>
<td>6VP</td>
<td>19.0</td>
<td>83.6</td>
<td>16.4</td>
<td></td>
</tr>
<tr>
<td>10VP</td>
<td>21.2</td>
<td>91.2</td>
<td>8.9</td>
<td></td>
</tr>
<tr>
<td>2VPTRS</td>
<td>10.9</td>
<td>94.8</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>6VPTRS</td>
<td>16.8</td>
<td>90.2</td>
<td>9.8</td>
<td></td>
</tr>
<tr>
<td>10VPTRS</td>
<td>9.2</td>
<td>96.8</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>37.4</td>
<td>21.8</td>
<td>78.2</td>
<td></td>
</tr>
<tr>
<td>6VRS</td>
<td>29.6</td>
<td>71</td>
<td>29.0</td>
<td></td>
</tr>
<tr>
<td>6VSG</td>
<td>19.7</td>
<td>71.4</td>
<td>28.6</td>
<td></td>
</tr>
</tbody>
</table>

The relation of the conversion of ethylbenzene on praseodymia containing catalysts shows a different pattern. PRS produced styrene selectively than praseodymia. When praseodymia was promoted with SiO₂, these catalysts exhibited higher conversion rate and styrene selectivity than
ceria containing catalysts. Further more, styrene selectivity reached nearly 90% with these supported vanadia catalysts. Among VP series catalysts, dehydrogenation rate decreases from 2VP to 6VP and then increases for 10VP. Styrene selectivity decreases up to 6VP and then enhanced for 10VP.

For comparison, the reaction was conducted also with V2O5 and various silica supported vanadia. V2O5 exhibits high conversion rate while styrene selectivity is very low. It produced more amounts of oxygenated products. Among 6VRS and 6VSG, VRS shows high conversion rate with similar styrene selectivity as that of 6VSG.

8.4 REGENERATION AND STABILITY

Regeneration and stability of the catalyst were tested over selected catalysts. Coke deposition must be the reason for the deactivation of catalysts under vapour phase reaction conditions. Other reasons include promoter’s loss or redistribution, ion reduction and physical degradation. Influence of time on dehydrogenation reaction show that after 6 h the catalytic activity along with styrene selectivity is reduced. Procedure for the stability study was chosen as follows. After dehydrogenation reaction for 6 h at 623 K, flow of reactant feed and air were stopped. Catalyst was allowed to stay in the reactor itself. Temperature was increased to 773 K, the calcination temperature of the catalyst. Under this condition, catalyst was allowed to stay within the reactor for 10 h in the presence of nitrogen flow. ODH of ethylbenzene conducted later show the same activity as that of fresh catalysts suggesting that catalysts can be regenerated without loss in activity.
8.5 DISCUSSION

There are two different kinds of oxidation reactions such as oxygen insertion reaction and oxidative dehydrogenation. In the case of oxides of vanadium, they possess catalytic activity for both oxidation reactions. However it is very difficult to control the selectivity between these two reactions since in some cases, they promote oxygen insertion and in other cases promote oxidative dehydrogenation. The selectivity varies according to the nature of reactants and products. Oxidation is performed by a redox cycle of metal oxide catalysts and, as a result, the oxidation activity is dependent on the redox action, that is, a pair of reducibility and reoxidizability of metal oxide. However, it is hard to understand satisfactorily the selectivity of catalysts in an oxidation reaction only by the redox properties. It has long been postulated that the catalytic activity and selectivity of an oxide in selective oxidation is related to the reduction rate of the oxide. Over an oxide, which is very difficult to reduce, the activity will be low for an oxide, which is very easy to reduce the activity is high but the selectivity low. An active and selective catalyst should have an intermediate ease of reduction.

It is known that surface acidity and basicity of a catalyst play an important role in partial oxidation and oxidative dehydrogenation. This was reviewed by Corma et al. It has been reported that the activation of olefins in partial oxidation and ODH occurs on acid sites of a catalyst surface. The strength of acid sites influences the strength of binding of a reagent to an active site. According to Tsybukh et al. the surface acidity of catalysts play an important role in the ODH of ethylbenzene over Fe-Bi-Mo-O catalysts. Supported vanadium oxides are among the most important heterogeneous
catalysts for the vapor-phase oxidation of alkylaromatics, alcohols, and alkenes. In this type of catalysts the nature of metal oxide support plays an important role modulating the nature of V species and the catalytic behavior for oxidation reactions. Vanadium dispersion (related to the loading and the nature of the support) and acidity of the catalyst are the main factors to be considered. A correlation between the isoelectric point (acid-base character) of the support and the photoluminescence of V=O groups has been recently found. Acidity determination evidenced that vanadia addition could impart more number of acid sites for ceria containing catalysts while number of acid sites was reduced for praseodymia catalysts. Thus a correlation between ODH activity and acid-base properties is very difficult. The physical and chemical characteristics are reflected in the catalytic performance of catalysts.

Characterization of the prepared catalysts by various complimentary techniques such as XRD, EDX, TG/DTG/DTA, FT-IR, FT-Raman, UV-vis DRS, solid state MAS NMR and TPR are presented in chapter 4. Studies show that structure of VOx species on the supports are different and depends on the nature of the support and amount of vanadia loading. The variation of ethylbenzene dehydrogenation activity with vanadia loading in the presence of air in tables 8.1 and 8.2 reveals that the impregnated vanadia phase on the support is positively affecting the reaction. The CRS supported catalysts gives better performance for the reaction than the ceria supported catalyst with the same vanadia content, since vanadia is more homogeneously distributed over the high surface area amorphous CRS support. High conversion in activity observed for VCRS series catalysts can be attributed to the high dispersion of
vanadia on the support. In these catalysts conversion rate remains more or less constant while styrene selectivity found decreasing initially and then increases.

For VC catalysts, the activity initially increases with vanadia loading and then decreases. The maximum activity appears at a vanadia loading of 6 wt.%, corresponding to monolayer surface coverage of vanadia on the ceria support, whereas the activity of the catalysts levels off at higher loading attributed to the formation of orthovanadate crystallites. This indicates that structure and dispersion of supported phase is related to the dehydrogenation reactivity. Initially styrene selectivity decreased up to 6 wt. % loading and then increased. Juarez Lopez et al.\(^{49}\) concluded that the presence of free vanadium and nickel oxides in the alumina supported MVSb catalysts negatively influenced the selectivity over the dehydrogenation of ethane. According to Daniell et al.\(^{50}\) in the study of catalytic activity of V\(_x\)-CeO\(_2\) catalysts for ODH of propane, 6 wt.% V\(_x\)-CeO\(_2\) displayed highest activity and selectivity towards propene. It is attributed to amorphous V\(_x\) surface species and higher loadings displayed deactivation due to CeVO\(_4\) phase formation with reduced surface area. Lopez Nieto et al.\(^{51}\) have summarized that the coordination number, the aggregation state of vanadium oxide surface species and the presence of acid-base sites are important factors in the selectivity of ODH reactions over vanadia catalysts. It was reported for V-Sb catalysts that reoxidation is the rate-limiting step and both metals in the bulk participate in the solid reoxidation mechanism\(^{52}\). It is also reported in the literature that limiting step in alkane oxidation or ODH is the H-abstraction\(^{53}\).

In the present case, X-ray diffraction pattern of VC series of catalysts show that the formation of orthovanadate starts with 6 wt.% loading and results
in high aggregated crystallites with further increase in vanadia loading. VCRS catalysts also exhibited the similar behaviour from NMR studies. BET surface area measurements displayed a lowering in surface area with increasing vanadia loading. UV-vis spectroscopy suggests that vanadia exists as monomeric vanadium (V) species with tetrahedral coordination at lower loading and indicates progressive condensation of vanadia species with increasing vanadia loading. Spectroscopic techniques evidenced the formation of orthovanadate structure for higher vanadia loading on the ceria support. The reducibility of the ceria containing catalysts show a shift in $T_{\text{max}}$ to lower temperature ($T_{\text{max2}}$) with an increase in vanadia loading from 2 to 6 wt. %. Various characterization results suggests that monomeric tetrahedral $\text{VO}_x$ species are predominant on the $\text{V}_2\text{O}_5/\text{CeO}_2$ catalysts at lower loading, while complete consumption of $\text{V}_2\text{O}_5$ occurs to form $\text{CeVO}_4$ as the loading increases to 10 wt. % $\text{V}_2\text{O}_5$.

The relationship observed between dehydrogenation rate and vanadia loading of VC catalysts can be explained on the basis of dispersion and aggregation of vanadia species. The activity for the catalysts with lower loading is the lowest since monomeric vanadia species predominant on this catalyst, are less active. Generally, an oxidation reaction involves the oxidation-reduction cycles of easily reducible centers. $\text{V}_2\text{O}_5/\text{CeO}_2$ catalysts consists of two redox centers viz. $\text{Ce}^{3+}/\text{Ce}^{4+}$ and $\text{V}^{4+}/\text{V}^{5+}$. The V-O-Support species appear to be more difficult to reduce than V-O-V or V=O sites in polymeric species. Thus reducibility of the catalysts increases with an increase in vanadia loading up to a limit of monolayer coverage. The activity decreases when a multilayer of polymerized $\text{V}^{5+}$ species is formed on the support surface.
at higher vanadia loading, which prevents the accessibility of the reactants to all of the active vanadium sites. Hence the maximum conversion rate is observed at intermediate surface densities corresponding to highly dispersed vanadia on the support. It was already reported that the activity for the ODH of ethane and propane over vanadia catalysts supported on MgO Al₂O₃, and ZrO₂ depend on the structure of the VOₓ overlayer. The observed selectivity also reveals that monomeric V⁵⁺ species are better suited for the dehydrogenation of ethylbenzene since the maximum styrene selectivity is observed at the lower vanadia loading. Styrene selectivity decreases with increase in vanadia loading. The more reducible the catalyst, less selective the supported system. For all the supported vanadium oxide catalysts, the vanadium loading is a parameter of paramount importance in the catalytic activity of the solid. As the vanadium loading increases, aggregation occurs, thus, varying the nature of the vanadium species and their catalytic properties. For instance, for the catalytic behavior of γ-alumina supported vanadium oxide for the oxidative dehydrogenation of ethane and n-butane, it has been observed that the activity for dehydrogenation increases as the vanadium loading, while the selectivity toward alkene formation reaches a maximum at 3-4 wt %. Apparently, the highest propene yields require of a solid containing redox sites of adequate potential combined with strong Lewis acid sites and mild basic sites. These findings seem to be in agreement with the operation of a Mars and van Krevelen mechanism, that requires the combination of these three types of sites. Vislovskiy et al. reported high activity and selectivity over various vanadia-alumina catalysts in dehydrogenation of EB to styrene with CO₂. Redox behavior of V₂O₅ played a key role in the dehydrogenation. Among several additives, antimony oxide has
been observed to improve catalyst stability as well as catalytic activity to produce styrene. Characterization revealed that the addition of the antimony oxide led to an easier redox cycle between fully oxidized and reduced vanadium species\textsuperscript{56}.

Praseodymia containing catalysts exhibited high conversion rate as well as styrene selectivity under the reaction conditions studied. According to Ruiqiang et al.\textsuperscript{57} high C\textsubscript{2} selectivity and yield were observed with SrF\textsubscript{2}/Pr\textsubscript{6}O\textsubscript{11} catalysts than Pr\textsubscript{6}O\textsubscript{11} in oxidative coupling of methane at high temperature. This is correlated to the decrease in secondary deep oxidation due to reduced mobility of lattice oxygen and the surface concentration of Pr\textsuperscript{+4} ion as well as the dispersion of F on the surface of the SrF\textsubscript{2} promoted Pr\textsubscript{6}O\textsubscript{11} catalysts. Influence of lanthana, ceria, praseodymia and neodymia incorporation into molybdena-alumina systems were studied towards ODH activity by Kim et al.\textsuperscript{58}. They concluded that praseodymia has the maximum effect among these lanthanide oxides. Among various rare earth orthovanadates (PrVO\textsubscript{4}, ErVO\textsubscript{4}, GdVO\textsubscript{4}, DyVO\textsubscript{4}, NdVO\textsubscript{4}, TbVO\textsubscript{4}, LuVO\textsubscript{4} and HoVO\textsubscript{4}) studied towards ODH of propane, PrVO\textsubscript{4}, ErVO\textsubscript{4}, GdVO\textsubscript{4}, DyVO\textsubscript{4}, NdVO\textsubscript{4} gave high propene selectivity. The difference in catalytic activities of the orthovanadates is related to its redox properties. Higher propene selectivity of the latter catalysts indicated easier reducibility by TPR analysis\textsuperscript{59}. In VP and VPRS series catalysts, the amount of V obtained from EDX measurements show high values compared to ceria containing catalysts. BET surface area values of the former were found to be lower. Thus formation of polymeric V-O-V species is predominant with these catalysts. According to Sakurai et al.\textsuperscript{60} at low loadings, only isolated VO\textsubscript{4} species were dispersed over the MgO support, whereas for higher loading,
polymeric species with bridging V-O-V oxide ions forming MgV$_2$O$_6$ and MgV$_2$O$_7$ are formed. The degree of polymerization of vanadate species increases with loading over praseodymia catalysts, which results in high styrene selectivity. The praseodymia catalysts produced styrene selectively than ceria containing ones. However, among catalysts, CRS supported vanadia exhibits comparatively higher activity than PRS supported vanadia catalysts. Solid state MAS NMR studies reveal that, only CeVO$_4$ formation is favourable with CRS support while compounds of SiO$_2$ and Pr$_x$O$_y$ is formed over PRS support. Thus Pr$_x$V$_2$O$_5$ can easily replace Si in place of Pr. Such species result in non reducible phases which in turn decrease the dehydrogenation activity.

8.6 CONCLUSION

The catalytic behaviour of rare earth oxides supported vanadia catalysts in the oxidative dehydrogenation ethylbenzene has been studied with air as the oxidant. Styrene was produced as the main product and styrene selectivity of all the supported catalysts found to be above 75%, but the activity of the catalysts differs from one another. The adsorption of styrene in the ODH of ethylbenzene inhibits the oxygen chemisorption at surface Lewis active sites, thus total oxidation of hydrocarbon molecule is controlled and the selectivity to total oxidation products decreases. The ethylbenzene dehydrogenation activity depends on the vanadia loading, nature of vanadia over the supports etc. The different catalytic activities of the rare earth supported catalysts can be related to their redox properties as well as to the surface properties of the catalysts. Presence of easily reducible polymeric vanadia species in praseodymia catalysts results in higher styrene selectivity than ceria supported catalysts.
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