5

OXIDATIVE DEHYDROGENATION OF ETHYLBENZENE

5.1 INTRODUCTION

Styrene is an important monomer used for industrial production of many synthetic polymers. It is commercially manufactured by the catalytic dehydrogenation of ethylbenzene (1,2). This classical thermal dehydrogenation of paraffins to give the corresponding olefins and H₂ is a strongly endothermic process, which has to be carried out at temperatures above 600°C and its conversion is limited by thermodynamic equilibrium (3). Such high reaction temperatures lead to unwanted side reactions producing coke and smaller hydrocarbons. Hence, a continuous catalyst mediated oxidative dehydrogenation appears to be more promising compared to simple dehydrogenation (4-7). Oxidative dehydrogenation involves the removal of hydrogen from the reactant molecules by oxygen from the feed to form the corresponding olefins without parallel or consecutive oxidation reactions giving carbon monoxide or dioxide as non-selective products. Air is the most economically preferred oxidant as it can maintain high selectivity. The formation of H₂O as by product for the ODH reaction makes the process endothermic and the conversion becomes significant at much lower temperature. Generally the oxidative dehydrogenation of alkanes produces a considerable amount of carbon oxides reducing the selectivity of catalyst employed. Thus the key aspect of technology is development of catalysts capable of activating only the C-H bonds of the alkane molecule in a flow of oxygen.

Dehydrogenation of ethylbenzene was carried out over a variety of catalysts and reaction conditions of temperature, diluents, and catalyst promoter. Many catalysts such as cobalt, copper, iron and zinc oxide have been studied, with and without promoters (8) When promoted with potassium, all these catalysts exhibited enhanced activity, but
maximum activity was shown by the iron system. Further studies showed that the active phase in potassium promoted iron oxide catalyst is potassium ferrite KFeO_2 (9,10).

Most works on the oxydehydrogenation of ethylbenzene (Scheme 5.1) has been devoted to the selection of suitable catalyst and appropriate reaction conditions for improved styrene yield and selectivity. The general catalysts reported for the ODH of ethylbenzene includes metal oxide (11-16), phosphates (7,17-19) and organic polymers (20,21).

\[
\text{(Ethylbenzene)} \xrightarrow{\text{ODH}} \text{(Styrene)}
\]

Scheme 5.1 Oxidative dehydrogenation of ethylbenzene to styrene

The oxydehydrogenation activity of various acidic catalysts has received increasing attention in recent years. Tagawa et al. (4,6,17,22,23) after examining the catalytic activity of tin oxides and phosphates concluded that moderate acid strength is the key factor in deciding the reactivity. Removal of strong acid sites by addition of sodium acetate improved the selectivity, but excessive sodium deactivated the catalyst. Fiedorow et al. (24) also obtained similar results with alumina where small amounts of sodium did not affect activity even though strong acid sites would have been removed. Echigoya et al. (25) found that introducing acidity into silica by addition of either magnesium or zirconium correlated well with oxydehydrogenation activity. Alumina is reported to be an active catalyst for oxidative dehydrogenation of ethylbenzene and other alkylbenzenes (26-28). Alumina when treated with mineral acids showed an enhancement in activity (29,30). Kania et al. (31) investigated the effect of incorporation of Fe_2O_3, Cr_2O_3, NiO, MoO_3 and MgO on the oxydehydrogenation activity of γ- alumina and observed that introduction of Fe_2O_3 and Cr_2O_3 leads to a considerable increase in the catalytic activity.
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Catalysts based on phosphates of nickel-zirconium, aluminium, cerium and calcium have also been reported to be active for the oxidative dehydrogenation reactions (32,33). In the pulse reaction of ethylbenzene over SnO$_2$ catalyst, non-selective oxidation proceeded. But the addition of phosphorus to SnO$_2$ suppressed the total oxidation reaction and enhanced the formation of styrene. This suggests the cooperative effect of acid base properties of the catalyst in influencing the reaction. It was also shown that mixed metal phosphates such as Zr-Sn and Sn-Ge systems display improved catalytic performances with respect to the single phosphates (34,35). High selectivity of about 97% to styrene was reported on Sn-Ge mixed phosphate (35). Among different condensed phosphates, the pyrophosphate group showed superior activity than the orthophosphates or oxides towards the oxydehydrogenation of ethylbenzene (18).

Jyothi et al. investigated the catalytic activity of rare earth promoted sulphated tin oxide for the oxidative dehydrogenation of ethylbenzene and found that these systems exhibit better oxidation activity when compared to the non-sulphated analogues and sulphated tin oxide (36). Kim et al. (37) studied the influence of incorporation of lanthana, ceria, praseodymia and neodymia on the activity of molybdena-alumina systems and among the four lanthanides used, praseodymia showed the maximum promoting effect.

5.2 PROCESS OPTIMISATION

For any reaction, conversion and product selectivity is influenced not only by the catalyst composition, but also by the reaction conditions like temperature, time on stream, feed rate, etc. So before carrying out the reaction over all the catalyst systems for comparing the catalytic activity of these prepared systems, it becomes highly essential to fix the optimum parameters for the reaction.

i) Influence of reaction temperature

In order to study the temperature influence on the ODH of ethylbenzene to styrene, the reaction was performed over a selected catalyst system at various temperatures such as 400, 450, 500 and 550°C. The reactant feed rate and air flow rate were maintained at 4 mL/h and 15 mL/h respectively. The results depicted in Figure 5.1 points to the fact that as temperature increases the conversion of ethylbenzene increases, but this hike in
conversion is at the cost of decrease in the selectivity of styrene. As the temperature was raised in steps from 450 to 550°C, selectivity for styrene falls from 86% to 64% and the amount of benzene, toluene and C-oxides formed showed an enhancement. The overall conversion of ethylbenzene showed a leap after 500°C. This may be due to the excessive cracking of ethylbenzene to toluene and benzene at high temperatures.

![Graph showing influence of temperature on activity and selectivity for oxidative dehydrogenation of ethylbenzene](image)

Figure 5.1 Influence of temperature on the activity and selectivity for oxidative dehydrogenation of ethylbenzene

Reaction conditions: 0.5 g M24 activated at 700°C, Flow rate- 4 mL/h, Duration- 2 h

**ii) Influence of flow rate**

Flow rate is another important parameter that influences the reactivity in the case of gas phase reactions. The feed rates examined for this reaction were 4, 5, 6 and 7 mL/h. The reaction was carried out over M24 system at 450°C and at an air flow rate of 15 mL/h. The reaction mixture was analysed after 2h. The conversion was found to be higher at lower flow rates and it was adversely affected by the increase in flow rate (Figure 5.2). This may be due to the fact that with an increase in flow rate, the reactants will spend less time on the catalyst surface, leading to the decrease in the contact time between the reactants and catalyst. At higher feed rates reactants will not get enough time to get adsorbed on the catalyst surface for the reaction to take place. Thus the increase in flow
rate has a negative effect on the conversion. However, high selectivity for styrene was observed at a feed rate of 7 mL/h, which might be due to the prevention of re-adsorption of styrene on catalyst surface to get converted into unwanted products.

![Graph showing conversion vs flow rate](image)

**Figure 5.2 Variation of catalytic activity with flow rate for the oxidative dehydrogenation of ethylbenzene**

**Reaction conditions:** 0.5 g Mфан activated at 700°C, Duration − 2 h

**Reaction temperature** − 450°C

**iii) Influence of time on stream – Deactivation studies**

An excellent catalyst is one that retains its catalytic activity and selectivity even after repeated runs. In order to test the deactivation of the prepared systems, the reaction was carried out continuously for 5 hours and the reaction mixture was analysed after every one hour. The results depicted in Table 5.1 shows that the reactivity of the catalyst system decreases to some extent in the first three hours and after that the conversion remains more or less constant. Another important observation was that the selectivity towards styrene remained almost the same even after 5 h.
Table 5.1 Deactivation studies in the oxidative dehydrogenation of ethylbenzene to styrene

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Conversion (wt%)</th>
<th>Benzene</th>
<th>Toluene</th>
<th>Styrene</th>
<th>Carbon oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40.83</td>
<td>4.68</td>
<td>4.73</td>
<td>86.92</td>
<td>3.67</td>
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<tr>
<td>2</td>
<td>37.53</td>
<td>6.29</td>
<td>5.43</td>
<td>85.63</td>
<td>3.65</td>
</tr>
<tr>
<td>3</td>
<td>35.89</td>
<td>6.32</td>
<td>5.37</td>
<td>84.78</td>
<td>3.53</td>
</tr>
<tr>
<td>4</td>
<td>33.75</td>
<td>5.08</td>
<td>6.52</td>
<td>85.63</td>
<td>2.97</td>
</tr>
<tr>
<td>5</td>
<td>32.18</td>
<td>4.78</td>
<td>7.58</td>
<td>84.57</td>
<td>3.27</td>
</tr>
</tbody>
</table>

Reaction conditions: 0.5 g M24 activated at 700°C, Reaction temperature-450°C, Flow rate- 4 mL/h

5.3 CATALYST COMPARISON

In order to determine the effect of catalyst composition on the catalytic activity for the ODH of ethylbenzene, we carried out the reaction under optimised conditions over the prepared systems. All the catalysts gave styrene as the selective product and toluene, benzene and carbon oxides as non-selective products. Sulphate modification and incorporation of three different transition metal oxides had a positive influence on the catalytic activity of tin oxide towards the reaction.

In the case of all three systems studied catalytic activity and selectivity for styrene increased to a maximum until a certain percentage loading, and further addition of metal oxides decreased the activity and selectivity. Molybdenum oxide systems showed the least activity (Table 5.2) in spite of the fact that these systems were the most acidic among the three series. Acidity determination using different independent methods showed that addition of molybdenum oxide enhances the acidity of the catalyst systems, concomitantly reducing the basicity as evident from the cyclohexanol decomposition reaction. Tagawa et al. has showed that both acidic and basic sites are required for the oxidative
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dehydrogenation reactions (5). Thus lack of enough number of surface basic sites may be the cause for the low activity of the molybdenum oxide systems.

Table 5.2 Effect of molybdenum oxide loading on the oxidative dehydrogenation of ethylbenzene to styrene

<table>
<thead>
<tr>
<th>Systems</th>
<th>Conversion (wt%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Benzene</td>
<td>Toluene</td>
</tr>
<tr>
<td>S</td>
<td>15.55</td>
<td>7.97</td>
</tr>
<tr>
<td>SS</td>
<td>21.65</td>
<td>3.18</td>
</tr>
<tr>
<td>M4</td>
<td>34.07</td>
<td>5.36</td>
</tr>
<tr>
<td>M8</td>
<td>35.94</td>
<td>4.15</td>
</tr>
<tr>
<td>M12</td>
<td>37.36</td>
<td>3.66</td>
</tr>
<tr>
<td>M16</td>
<td>39.73</td>
<td>2.88</td>
</tr>
<tr>
<td>M20</td>
<td>33.59</td>
<td>4.25</td>
</tr>
<tr>
<td>M24</td>
<td>29.83</td>
<td>5.33</td>
</tr>
</tbody>
</table>

Reaction conditions: 0.5 g catalyst activated at 700°C, Reaction temperature-450°C, Flow rate- 4 mL/h, Duration – 2 h.

Among the molybdenum, tungsten and iron systems studied, iron oxide loaded systems showed the maximum catalytic activity and selectivity (Table 5.3) compared to tungsten and molybdenum oxide modified systems. Iron loaded systems showed only a slight enhancement in acidity than the pure and sulphated tin oxide when compared to the other two metal oxide loaded systems. Cyclohexanol decomposition studies showed that iron systems have both dehydration (acidic sites) and dehydrogenation (basic sites) activity indicating the presence of both acidic and basic sites in iron oxide modified sulphated tin oxide systems. There are many reports suggesting that both acidic and basic sites are required for the oxidative dehydrogenation. So maximum activity for this reaction will be obtained over those catalysts, which have a perfect balance between the acidic and basic sites.
Table 5.3 Catalytic activity and selectivity for the iron oxide systems in the oxidative dehydrogenation of ethylbenzene to styrene

<table>
<thead>
<tr>
<th>Systems</th>
<th>Conversion (wt %)</th>
<th>Benzene</th>
<th>Toluene</th>
<th>Styrene</th>
<th>Carbon oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>15.55</td>
<td>7.97</td>
<td>3.62</td>
<td>70.50</td>
<td>17.91</td>
</tr>
<tr>
<td>SS</td>
<td>21.65</td>
<td>3.18</td>
<td>5.86</td>
<td>79.91</td>
<td>11.05</td>
</tr>
<tr>
<td>F₄</td>
<td>33.59</td>
<td>4.71</td>
<td>3.78</td>
<td>89.41</td>
<td>2.11</td>
</tr>
<tr>
<td>F₈</td>
<td>41.09</td>
<td>2.67</td>
<td>4.18</td>
<td>92.15</td>
<td>1.00</td>
</tr>
<tr>
<td>F₁₂</td>
<td>52.83</td>
<td>0.99</td>
<td>1.23</td>
<td>95.87</td>
<td>1.91</td>
</tr>
<tr>
<td>F₁₆</td>
<td>40.10</td>
<td>3.36</td>
<td>6.31</td>
<td>87.85</td>
<td>2.24</td>
</tr>
<tr>
<td>F₂₀</td>
<td>43.12</td>
<td>2.92</td>
<td>3.56</td>
<td>91.16</td>
<td>2.36</td>
</tr>
<tr>
<td>F₂₄</td>
<td>35.23</td>
<td>3.16</td>
<td>4.59</td>
<td>90.35</td>
<td>1.92</td>
</tr>
</tbody>
</table>

Reaction conditions: 0.5 g catalyst activated at 550°C, Reaction temperature- 450°C, Flow rate- 4 mL/h, Duration - 2 h.

In the case of tungsten modified systems ethylbenzene conversion and styrene selectivity improved with increase in the tungsten oxide loading, up to W₁₆ system and then it showed a decline (Table 5.4). The catalytic activity enhancement for tungsten oxide systems is higher when compared with the molybdenum systems. From the acidity values determined by TPD measurement and thermodesorption of pyridine, it can be observed that these systems are less acidic than the molybdenum systems. That may be the reason for the better activity of these systems.
### Table 5.4 Variation of catalytic activity with tungsten oxide loading in the oxidative dehydrogenation of ethylbenzene to styrene

<table>
<thead>
<tr>
<th>Systems</th>
<th>Conversion (wt%)</th>
<th>Benzene</th>
<th>Toluene</th>
<th>Styrene</th>
<th>Carbon oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>15.55</td>
<td>7.97</td>
<td>3.62</td>
<td>70.50</td>
<td>17.91</td>
</tr>
<tr>
<td>SS</td>
<td>21.65</td>
<td>3.18</td>
<td>5.86</td>
<td>79.91</td>
<td>11.05</td>
</tr>
<tr>
<td>W₄</td>
<td>35.22</td>
<td>4.97</td>
<td>4.52</td>
<td>85.60</td>
<td>4.99</td>
</tr>
<tr>
<td>W₅</td>
<td>38.35</td>
<td>6.55</td>
<td>4.49</td>
<td>87.87</td>
<td>1.58</td>
</tr>
<tr>
<td>W₁₂</td>
<td>40.83</td>
<td>4.24</td>
<td>5.68</td>
<td>88.03</td>
<td>2.06</td>
</tr>
<tr>
<td>W₁₆</td>
<td>43.83</td>
<td>3.12</td>
<td>3.04</td>
<td>91.86</td>
<td>1.98</td>
</tr>
<tr>
<td>W₂₀</td>
<td>32.24</td>
<td>6.44</td>
<td>4.43</td>
<td>87.06</td>
<td>2.07</td>
</tr>
<tr>
<td>W₂₄</td>
<td>36.53</td>
<td>4.29</td>
<td>5.43</td>
<td>85.63</td>
<td>1.92</td>
</tr>
</tbody>
</table>

Reaction conditions: 0.5 g catalyst activated at 700°C, Reaction temperature-450°C, Flow rate-4 mL/h, Duration – 2 h

### 5.4 MECHANISM OF OXYDEHYDROGENATION REACTION

A redox reaction was proposed as a possible mechanism for oxydehydrogenation in many literatures (4,17,38). In the oxidative dehydrogenation of ethylbenzene the most probable mechanism is the one, which involves the abstraction of hydrogen from ethylbenzene by lattice oxygen on the surface to form styrene though a 1-allyl intermediate, and the reoxidation of the catalyst by gas phase oxygen. A 1-allyl mechanism is generally accepted in the oxidation of olefins. The following sequences involve the redox cycle of adsorbed ethylbenzene on the catalyst surface, as suggested by Hanuza and co-workers (39).

\[
\text{EB} + [\text{O}] \rightarrow \text{ST} + [ \ ] \\
[ \ ] + \frac{1}{2} \text{O}_2 \rightarrow [\text{O}]
\]
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where [ ] is the anion vacancy and [O] is the lattice oxygen. Schalter and DeBoer have reported that the rate-determining step of propylene oxidation is the dissociative adsorption of propylene by the cleavage of the C-H bond in the methyl group of propylene in $^{14}$C tracer studies. Moreover, the competitive reaction of ethylbenzene with other aromatic hydrocarbons over SnO$_2$-P$_2$O$_5$ catalysts suggests that ethylbenzene is adsorbed by the abstraction of $\alpha$-hydrogen on the catalyst (4). Tagawa et al. showed that the $\beta$-hydrogen of the terminal CH$_3$- group of ethylbenzene molecule is unexchangeable; but the $\alpha$-hydrogen and the hydrogen in the benzene ring are exchangeable. However, the exchange on the $\alpha$-hydrogen is predominant to that on the aromatic ring. Thus, the adsorbed species can be regarded as being dissociated reversibly at the $\alpha$-position of ethylbenzene. The basic site i.e., -OH group adjacent to the acidic site will abstract $\alpha$-hydrogen and acts as the adsorption site for ethylbenzene (22). It was also concluded from the quantum calculations that the acid sites withdraw the electrons to reduce the electron density of the aromatic ring and enhances the acidic property of the $\alpha$-hydrogen and it then interact with the -OH group near the acidic site (40). Grunewald et al. showed that catalysts based on pyrolysed systems also function via a hydrogen abstraction mechanism. It is difficult to conclusively decide whether this was hydrogen atom or hydride abstraction. Most likely it is a concerted process, as proposed by both the Emig and Cadus groups (7,41). In this process the hydrogenated catalyst was then returned to its original state by reaction with air to produce H$_2$O.

Several literatures give strong evidence that surface acidity of the catalyst plays a direct (24,22) or an indirect (18,34) role in the oxydehydrogenation. It has been proposed that the selectivity of a catalyst during the oxidative dehydrogenation can be related to the oxidation degree of the surface (42). This implies that the acid base character of the catalyst surface oxygens must play an important role for the oxidative dehydrogenation of alkanes (43-46). Various studies on oxidation reactions suggest the participation of acidic sites (47,48) and basic sites (49) in the partial oxidation reactions. Tagawa et al. (22) investigated the oxidative dehydrogenation ethylbenzene over SnO$_2$-P$_2$O$_5$ and other solid acid catalysts and concluded that acid-base sites with suitable strength ranges are essential sites for oxidative dehydrogenation. Alkhasov et al. assumed that in the oxidative dehydrogenation, ethylbenzene is first adsorbed on acid sites of the catalyst surface. They
claimed that the reaction pathway depends on the strength of the adsorption; the stronger the adsorption the greater is the conversion of ethylbenzene (including the formation of carbon oxides). In this process, base centres of the catalyst surface also play an important role as they activate the oxygen from the gas phase which take part in this reaction. Oxygen activated on strong base centers at high temperature was found to be responsible for the total oxidation of hydrocarbons. Therefore, a catalyst which has acid and base centres of moderate or weak strength, is most suitable for the oxidative dehydrogenation of ethylbenzene. Base sites of higher strength activate the adsorbed molecular oxygen to the form O$_2^-$ and O', which at higher temperatures oxidise the hydrocarbons to carbon dioxides. SnO$_2$-P$_2$O$_5$ and SnO$_2$-SiO$_2$ catalysts exhibited high selectivity to styrene, which may be due to the remarkable suppression of complete oxidation. Tagawa et al., suggested that acid site of H$_0$ between 1.5 and -5.6 are proven to be the active sites, which could adsorb ethylbenzene reversibly, whose oxidation on the other hand occurs by the intervention of strong basic sites.

For nickel phosphate systems, a decrease in styrene yield was observed with the increase in surface Brønsted site concentration. A probable explanation of this fact is that a very high concentration of protons on the catalyst surface can diminish the rates of adsorption or the styrene formation steps either by screening the ethylbenzene molecule from coordination to hydrogen abstraction centres on the catalyst surface or by lowering the concentration of the ethylbenzene available. (50). In the case of Fe$_2$O$_3$-Al$_2$O$_3$ and Cr$_2$O$_3$-Al$_2$O$_3$ systems the amount of acid and base centres of moderate and weaker strength increases, which can be assumed to be the reason for the increase in the activity of these catalysts in the oxidative dehydrogenation of ethylbenzene (31). The improvement in the partial oxidation activity of rare earth modified systems can be attributed to the fact that the highly mobile oxygen species generated by the rare earth species can migrate to the surface of SnO$_2$ and regenerate the active sites by the reoxidation (remote control mechanism) (36).

A plausible mechanism for the oxidative dehydrogenation of ethylbenzene over the metal oxide modified sulphate tin oxide systems involving the adjacent acidic and basic sites are depicted in Figure 5.3.
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Figure 5.3 A plausible mechanism for the oxidative dehydrogenation of ethylbenzene over transition metal oxide modified sulphated tin oxide catalyst.
REFERENCES

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