CHAPTER 5

OXIDATIVE DEHYDROGENATION OF ETHYLBENZENE

Abstract

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. 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. The oxidative dehydrogenation of ethylbenzene, based on an introduction of oxidant to the ethylbenzene feed, seems to be one of the promising methods.
5.1. Introduction

The catalytic dehydrogenation of ethylbenzene is now a days the main method of styrene production, which is one of the most important basic chemicals as a monomer of synthetic polymers. The process is performed at elevated temperatures (550-650°C) in the presence of potassium doped hematite catalysts\(^1\). Additional promoters (e.g. Cr\(_2\)O\(_3\), Ce\(_2\)O\(_3\), MgO and MoO\(_3\)) are used in order to enhance the activity and selectivity, as well as stability of the catalytic system. Ethylbenzene dehydrogenation is endothermic and limited by thermodynamic equilibrium. An excess of superheated steam is therefore used to supply the heat of reaction and shift the equilibrium to higher styrene yields by a decrease in the partial pressures of reactants\(^2,3\). Oxidative dehydrogenation of ethylbenzene was proposed as an alternative route in styrene production\(^4,6\). Due to the exothermic effect of oxydehydrogenation, a higher conversion of ethylbenzene at significantly lower temperatures can be obtained compared to that in a classical dehydrogenation process. The schematic representation of the ethylbenzene dehydrogenation is shown in scheme 5.1.

\[ \text{CH}_2\text{-CH}_3 \xrightarrow{\text{ODH}} \text{CH} = \text{CH}_2 + \text{CH}_3 \xrightarrow{\text{C-Oxides}} \text{C-Oxides} \]

Scheme: 5.1: Reaction scheme of oxidative dehydrogenation of ethylbenzene

For this reaction, the economically preferred oxidant is air if high selectivity can be maintained. Various promoters like primary halides and sulphur compounds were tried\(^7,8\). Though these provided high conversions and selectivity, the severe problems arise in terms of corrosion, recovery, recycle of the catalyst and removal of
the impurities from the reaction product. So these have not been extended into commercial processes. In oxydehydrogenation, the formation of carbon oxides is often a side reaction. The process economy rapidly deteriorates when ethylbenzene is extensively oxidized to carbon oxides. The formation of carbon oxides requires large quantities of oxygen, which limits the conversion to styrene. Moreover, formation of carbon oxides is extremely exothermic. Therefore the catalyst should be very selective in the minimum production of carbon oxides and reasonably active in order to limit the reactor size. Too much activity can cause problems with heat transfer and runaway reaction. Thus most of the work on ethylbenzene has been devoted to the selection of suitable catalysts and appropriate reaction conditions for improved styrene yield and selectivity.

Figueiredo et al. investigated in detail the oxidative dehydrogenation of ethylbenzene over activated carbon catalysts and studied the catalytic deactivation\textsuperscript{10-12}. They suggested a redox mechanism of the Mars-van-Krevelen type, where the quinone surface groups are reduced to hydroquinone by the adsorbed ethylbenzene, and reoxidised back to quinone by oxygen. The ODH of ethylbenzene was studied over Mg\textsubscript{3} (VO\textsubscript{4})\textsubscript{2}-MgO systems by Oganowski et al.\textsuperscript{13} and their findings showed that magnesium orthovanadate forms with magnesium oxide an active biphasic system very efficient in the ODH of ethylbenzene to styrene.

Recently, CO\textsubscript{2} has been extensively utilized by several authors\textsuperscript{14-23} for the last two decades in the oxidative dehydrogenation of ethylbenzene to styrene as oxidant as well as diluent for the replacement of superheated steam that is used in commercial plants for maintaining the high temperatures at 600-700°C over potassium promoted iron based catalysts\textsuperscript{1}. Burri et al.\textsuperscript{14} studied the influence of SBA-15 support on CeO\textsubscript{2}-ZrO\textsubscript{2} catalyst for the oxidative dehydrogenation of ethylbenzene to styrene with CO\textsubscript{2}. All their catalysts were effective in oxidative dehydrogenation and there was a sequential enhancement in the catalytic activity from individual oxides to mixed
oxides followed by supported mixed oxide catalysts. The higher activity of the catalyst in the presence of CO₂ is due to the dissociation of CO₂ on the catalyst surface to produce active oxygen species. This active species oxidizes H₂ that is produced in the simple ethylbenzene dehydrogenation process into H₂O by reverse water-gas shift reaction and thereby releases the limitation of thermodynamic equilibrium. Cr-MCM-41 catalyst was found to be an effective catalyst with CO₂ for dehydrogenation of ethylbenzene. It was suggested that the rate of CO formation during the dehydrogenation of ethylbenzene with CO₂ over Cr-MCM-41 was well accounted for by assuming parallel occurrence of two reactions, i.e., direct oxidative dehydrogenation of ethylbenzene with CO₂ and simple dehydrogenation of ethylbenzene thermodynamically assisted by reverse water-gas shift reaction. However, carbon dioxide introduced to the ethylbenzene stream acts both as an oxidizing agent and as a diluent similar to water vapour. The effectiveness of CO₂ as the oxidant is limited. On the other hand, it was found that the presence of CO₂ could favor the fast deactivation of a catalyst by the formation of catalytically inactive coke.

Nitrous oxide (N₂O) seems to be a more promising oxidizing agent than carbon dioxide. The utilization of N₂O is of additional interest as nitrous oxide has been recognized to be one of green house gases causing global warming. Coupling the N₂O decomposition with the ethylbenzene dehydrogenation over γ-Al₂O₃ supported transition metal (Fe, Cr and Cu) oxide catalysts led to high conversions of ethylbenzene and N₂O. Furthermore, a replacement of the alumina support by mesoporous silicas (SBA-15, MCF, MCM-48 and MSU) characterized by high surface area gave the Fe-, Cr- and Cu- containing catalysts which were active in the oxidative dehydrogenation of ethylbenzene with N₂O. Kustrowski and co-workers studied the ODH of ethylbenzene with N₂O over vanadia supported on SBA-15. They observed an increase in the catalytic activity with raising the vanadium content. They
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proved that monomeric $V^{5+}$ species were considerably more active and selective in styrene formation than oligomeric ones.

Spinel oxides were reported to be an active catalyst in the oxidative dehydrogenation of ethylbenzene. Krishnasamy et al.\textsuperscript{28} studied the oxidative and nonoxidative dehydrogenation of ethylbenzene over Zn-Fe-Cr ternary spinel systems. They revealed that a redox cycle involving $Fe^{3+} \leftrightarrow Fe^{2+}$ is the active site for this reaction. Mathew et al.\textsuperscript{29} prepared ferrites of copper and cobalt and studied the ODH of ethylbenzene. They have the same conclusion as proposed by Krishnasamy and explained the results with the mechanism of dehydrogenation of ethylbenzene proposed by Wang\textsuperscript{30} and Krouse\textsuperscript{31}. Strong basic sites facilitate the formation of toluene whereas strong acid centers result in high yield of benzene. The active site balanced with acidic and basic sites is important for an efficient ethylbenzene dehydrogenation.

This section presents the exhaustive investigation on vapour-phase oxidative dehydrogenation of ethylbenzene over different series of chromite spinels. It was observed that the catalytic performance of spinels for the oxidative dehydrogenation of ethylbenzene to styrene was fairly good. In all cases, some amount of benzene, toluene and carbon oxides was detected as by-products. A detailed discussion of process optimization by studying the effect of reaction temperature, flow rate and air flow rate are also included in this section.

5.2. Influence of Reaction Conditions

Various reaction parameters such as temperature, flow rate and airflow rate were optimized in order to maximize the product yield and selectivity. Effect of reaction conditions for oxidative dehydrogenation of ethylbenzene with air was initially assayed in non-optimized conditions with CCoCr-2 as the catalyst.
5.2.1. Effect of air flow rate

The dehydrogenation of ethylbenzene to styrene over oxide catalysts may take place in the presence or absence of oxygen. In the absence of oxygen, lattice oxygen directly participates in the reaction resulting in the bulk reduction of the catalyst. The variation of ethylbenzene conversion and styrene selectivity with air flow is presented in figure 5.1.

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

Reaction conditions: Catalyst-CCoCr-2, Catalyst weight-0.5 g, Temperature-450°C, Flow rate- 4 ml/h, Time-2 h

Figure 5.1: Effect of air flow on ODH of ethylbenzene

It was observed that ethylbenzene conversion increased from 15.4% to 26% on increasing the air flow from 40 to 70 ml/min. Meanwhile, styrene selectivity decreased correspondingly. The percentage selectivity of the side products such as benzene and carbon oxides increased with more air. At higher air flow, styrene selectivity remained almost same. Therefore, 70 ml/min was selected as the optimized air flow for further studies.

5.2.2. Effect of Temperature
To study the effect of temperature on the oxidative dehydrogenation of ethylbenzene, reaction was carried out at various temperatures keeping other parameters constant. The results obtained are presented in figure 5.2.

![Graph showing the effect of temperature on oxidative dehydrogenation of ethylbenzene](image)

Reaction conditions: Catalyst - CCoCr-2, Catalyst weight - 0.5g, Air flow rate - 70 ml/min, Flow rate - 4 ml/h, Time - 2 h.

Figure 5.2: Effect of temperature on ODH of ethylbenzene

Ethylbenzene conversion was 20% at 400°C, which increased remarkably to 46% at a temperature of 550°C. The results indicated that there was a direct relation between temperature and activity of the catalyst. Styrene selectivity decreased marginally when the temperature was increased from 400 to 550°C. The noticeable decrease in styrene selectivity at 550°C was due to cracking of ethylbenzene into benzene, toluene and carbon oxides. An optimum temperature of 500°C was selected for further studies.

5.2.3. Effect of flow rate

The effect of flow rate on ethylbenzene conversion and styrene selectivity is presented in figure 5.3. The reaction was carried out at different flow rates of 3-6ml/h.
The conversion depends on the residing time of the reactant on the catalyst surface. Increase in flow rate decreased the residing time and hence lowered the conversion. Moderate conversion and styrene selectivity was obtained at a flow rate of 4ml/h and is selected for further studies.

![Reaction conditions: Catalyst-CCoCr-2, Catalyst weight-0.5g, Temperature-500°C, Air flow rate-70 ml/min, Time-2 h](image)

**Figure 5.3: Effect of flow rate on ODH of ethylbenzene**

The reaction was carried out over all the catalysts with the reaction conditions given in table 5.1.

**Table 5.1: Optimized conditions for oxidative dehydrogenation of ethylbenzene**

<table>
<thead>
<tr>
<th>Reaction Parameters</th>
<th>Selected conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>500°C</td>
</tr>
<tr>
<td>Air flow rate</td>
<td>70 ml/min</td>
</tr>
<tr>
<td>Flow rate</td>
<td>4 ml/h</td>
</tr>
<tr>
<td>Time</td>
<td>2 h</td>
</tr>
<tr>
<td>Catalyst weight</td>
<td>0.5 g</td>
</tr>
</tbody>
</table>
5.2.4. Effect of time on stream

In order to check the catalytic stability, a set of reactions were carried out at 500°C for 8 h over five catalyst samples. The results obtained are presented in figure 5.4.

![Conversion vs Time Graph](image)

**Figure 5.4:** Effect of time on stream on ODH of ethylbenzene

Reaction conditions: Temperature-500°C, Flow rate-4 ml/h, Air flow rate-70 ml/min, Catalyst weight-0.5g

Deactivation was observed in all the catalysts with increase in time. Coke deposition may be the reason for the deactivation of catalysts under vapour phase reaction conditions. CZCr-3 showed a better stability upto 8 h.

5.3 Oxidative Dehydrogenation of Ethylbenzene over Prepared Catalysts

The reaction was carried out over all the catalysts prepared and the results obtained are presented in table 5.2.
Table 5.2: Oxidative dehydrogenation of ethylbenzene over the prepared catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Ethylbenzene conversion (wt %)</th>
<th>Styrene</th>
<th>Benzene</th>
<th>Toluene</th>
<th>C-Oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCr</td>
<td>29.0</td>
<td>88.7</td>
<td>3.2</td>
<td>2.7</td>
<td>5.3</td>
</tr>
<tr>
<td>CFCr-1</td>
<td>24.8</td>
<td>90.8</td>
<td>4.1</td>
<td>1.5</td>
<td>6.8</td>
</tr>
<tr>
<td>CFCr-2</td>
<td>30.9</td>
<td>87.9</td>
<td>5.1</td>
<td>2.3</td>
<td>4.5</td>
</tr>
<tr>
<td>CFCr-3</td>
<td>34.3</td>
<td>89.8</td>
<td>2.9</td>
<td>1.7</td>
<td>5.6</td>
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<tr>
<td>CF</td>
<td>25.9</td>
<td>90.4</td>
<td>1.0</td>
<td>1.0</td>
<td>7.6</td>
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<td>CMCr-1</td>
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<td>88.4</td>
<td>4.1</td>
<td>2.8</td>
<td>4.7</td>
</tr>
<tr>
<td>CMCr-2</td>
<td>28.7</td>
<td>87.3</td>
<td>4.2</td>
<td>2.1</td>
<td>6.4</td>
</tr>
<tr>
<td>CMCr-3</td>
<td>23.2</td>
<td>86.9</td>
<td>3.5</td>
<td>1.8</td>
<td>7.8</td>
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<tr>
<td>MCr</td>
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<td>CCoCr-1</td>
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<td>1.9</td>
<td>5.9</td>
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<td>CoCr</td>
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<td>87.3</td>
<td>4.7</td>
<td>2.6</td>
<td>5.4</td>
</tr>
<tr>
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<td>91.2</td>
<td>2.3</td>
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<td>5.5</td>
</tr>
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<td>1.7</td>
<td>1.0</td>
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<td>3.2</td>
<td>1.6</td>
<td>7.5</td>
</tr>
<tr>
<td>NCr</td>
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<td>3.4</td>
<td>1.2</td>
<td>6.0</td>
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<td>87.9</td>
<td>3.0</td>
<td>1.3</td>
<td>7.7</td>
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<td>3.9</td>
<td>2.1</td>
<td>6.1</td>
</tr>
<tr>
<td>CZCr-3</td>
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<td>86.0</td>
<td>5.1</td>
<td>2.7</td>
<td>6.3</td>
</tr>
<tr>
<td>ZCr</td>
<td>36.2</td>
<td>85.1</td>
<td>4.1</td>
<td>3.3</td>
<td>7.5</td>
</tr>
</tbody>
</table>
5.4. Discussions

The oxidative dehydrogenation of ethylbenzene to styrene in the presence of air was carried out at 500°C over all the spinel catalysts prepared. Moderate ethylbenzene conversion and more than 80% selectivity to styrene was achieved over all the catalytic systems studied. Toluene, benzene and carbon oxides were also formed as side products during this reaction.

According to Wang\textsuperscript{30} and Krouse\textsuperscript{31}, the formation of toluene and benzene during the oxidative dehydrogenation reaction is caused by the interaction of acid-base centres on the catalyst surface. Strong basic sites can abstract the β-H of the adsorbed ethylbenzene, which facilitates the cleavage of side chain C-C bond resulting in the formation of toluene, whereas, strong acid centres can abstract α-hydrogen of ethylbenzene and facilitates the cleavage of phenyl-C bond resulting in the high yield of benzene. However, the formation of benzene and toluene require relatively high temperature. A balance of acid-base property is very important for an efficient ethylbenzene dehydrogenation.

In all the catalytic systems, the products benzene and toluene were formed in small quantities. From the ammonia TPD results, the amount of ammonia desorbed at higher temperatures (strong acid sites) is very low, which is in agreement with the benzene selectivity obtained during the oxidative dehydrogenation of ethylbenzene. Cyclohexanol decomposition reaction over the prepared catalysts produced the dehydrated product in major scale than the base catalyzed dehydrogenated product, cyclohexanone. In the ODH of ethylbenzene, toluene was produced in very small amount, which was in agreement with the results of cyclohexanol decomposition reaction.
5.5. Mechanism of the reaction

Several mechanisms have been proposed for the oxidative dehydrogenation of ethylbenzene. The most probable one is known as Mars-van Krevelen mechanism\textsuperscript{34,35} which consists of abstraction of hydrogen from ethylbenzene by the lattice oxygen on the surface to form styrene through a $\pi$ allyl intermediate and reoxidation of the catalyst\textsuperscript{36,37}. A condition for the operation of this mechanism is that the catalyst must contain metal ion with variable valancies, notably transition metal ion able to cope with the varying degree of surface oxidation\textsuperscript{38}.

In non-oxidative dehydrogenation, the absence of gaseous oxygen may lower the activity. The following sequence was suggested by Tagawa et al.\textsuperscript{39} on Si-Al systems. Hanuza and co-workers\textsuperscript{37} also suggest the same sequence.

\begin{align*}
\text{EB} + [\text{O}] & \quad \rightarrow \text{ST} + [\ ] \\
[ ] + \frac{1}{2} \text{O}_2 & \quad \rightarrow [\text{O}]
\end{align*}

Where, EB is ethylbenzene, ST is styrene, [O] is the lattice oxygen and [ ] is anion vacancy.

According to Bautista\textsuperscript{40}, oxidation of ethylbenzene is a concerted process over the Lewis acid sites. According to this mechanism, direct transfer of two oxygen atoms to a triplet oxygen molecule is considered. Activation of the triplet state is achieved by the action of Lewis acid sites. The gas phase dehydrogenation mechanism is non-oxidative as well in oxidative conditions and can be explained within the framework of a concerted process. Alkhazov et al. assumed that in the ODH of ethylbenzene over modified alumina, ethylbenzene is adsorbed first on the acid centers of the catalyst surface\textsuperscript{41}. They claimed that the reaction pathway depends on the strength of adsorption; stronger the adsorption, the greater is the ethylbenzene conversion. In this process, base centers on the catalyst surface also play an important
role, as they activate the oxygen from the gas phase, which takes part in this reaction. Oxygen activated on strong base centers at higher temperature has been found to be responsible for the total oxidation of hydrocarbons. Therefore, such a catalyst, which has acid and base centers of moderate or weaker strength on its surface, is the most suitable for the ODH of ethylbenzene.

Bagnasco et al.\(^4^2\) suggested that surface acid site of medium- high strength play significant role in the ODH of ethylbenzene. Hagemeyer et al.\(^4^3\) claimed a redox process involving the dehydrogenation of ethylbenzene by contact with a catalyst containing a reducible metal oxide (Bi\(_2\)O\(_3\), CeO\(_2\) and Cr\(_2\)O\(_3\)) in the absence of oxygen and simultaneous reduction of the catalyst, followed by oxidation of reduced catalyst with an oxidizing agent. From the investigations over rare earth promoted sulphated tin oxide, Sugunan et al.\(^4^4\) suggested that the strong acid sites generated by the sulphated treatment is accountable in the activation of ethylbenzene and enhance the catalytic activity. The strong basic site enhances the formation of the non-selective product, toluene.

A plausible mechanism for the oxidative dehydrogenation of ethylbenzene is described below. At first, ethylbenzene is coordinated to the acid site of the catalyst and the basic group adjacent to the acid site abstracts the \(\alpha\)- hydrogen from the coordinated ethylbenzene to give a stable adsorbed species. The OH group thus formed over the catalyst surface then abstracts the \(\beta\)- hydrogen and the subsequent desorption of water activates the molecular oxygen. The reversibly adsorbed oxygen is converted to \(O\) species over the catalyst surface, which regenerates the active site.

5.6. Conclusions

The conclusions from the present results can be summarized as given below.
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✓ Oxidative dehydrogenation of ethylbenzene over transition metal substituted copper chromite spinel catalysts showed good catalytic activity.

✓ Reaction variables such as air flow, temperature and flow rate had strong influence on ethylbenzene conversion and product selectivity.

✓ Reaction always gave styrene as the major product with trace amount of benzene, toluene and carbon oxides.

✓ A plausible reaction mechanism was proposed for the formation of styrene.

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