CHAPTER 6

DIRECT HYDROXYLATION OF BENZENE TO PHENOL

6.1. Prologue

Many volatile organic compounds (VOCs) are toxic substances that can contaminate water and the air of enclosed atmospheres and even induce cancer. These compounds account for the potential production of photochemical oxidants such as ozone and peroxyacetyl nitrate. Major environmental problem associated with VOC is the destruction of the stratospheric ozone layer that may lead to global warming. Benzene, an important VOC, can cause diverse diseases. Nevertheless, it is widely applied in different fields of industry, such as petrochemical, motor fuels, solvent for fats, paints, plastics and manufacture of steel and detergents. Remarkable efforts are being made by researchers to explore methods that may allow the control of VOC and its effective treatment. Among them,
catalytic oxidation is one of the most promising ways. In addition, phenol is one of the valuable chemical intermediates for the synthesis of various industrial products such as phenol-formaldehyde resins, bisphenol A, caprolactam etc. The increasing demand towards this chemical motivated the research for synthetic phenol preparations, probably one of the most interesting pages in the history of organic chemistry. Phenol is traditionally produced by the three-step cumene process. It comprises: benzene alkylation to cumene, cumene oxidation to cumene hydroperoxide, and decomposition of the latter to phenol and acetone. But this reaction pathway is quite tedious and its disadvantages are (i) formation of explosive intermediate (cumene hydroperoxide) (ii) formation of undesired by-product acetone (iii) having a multistep character (iv) poor ecology. Hence the most suitable alternative method is the synthesis of phenol by direct hydroxylation of benzene which is attractive both economically and energetically. The direct oxygenation of the energetically stable benzene to produce phenol has been one of the most difficult oxidation reactions.

Numerous attempts have been made on this challenging reaction over catalysts using various oxidants, such as N₂O, oxygen and H₂O₂. The first direct oxidation of benzene to phenol has been previously reported using Fenton reagent (ferrous sulfate-hydrogen peroxide). Shiju et al. have reported a tetrahedrally coordinated iron in framework substituted microporous AlPO-5 catalysts for the hydroxylation of benzene to phenol, using nitrous oxide as the oxidant. Direct oxidation of benzene to phenol was also carried out using N₂O and FeZSM-5 as catalysts. Very recently, catalytic activities of octahedral molecular sieve (OMS-2), amorphous manganese oxide (AMO) and mixed copper manganese oxide (CuO/Mn₂O₃) have been investigated for gas-phase total oxidation of benzene under air atmosphere. At 250°C, the average conversion was
found to be 61%, 41% and 44% over OMS-2, AMO and CuO/Mn₂O₃ respectively. Vanadium catalysts can efficiently catalyze the oxidation of benzene to phenol with molecular oxygen.⁷ Pd(OAc)₂/phenanthroline catalyst system was reported for the phenol synthesis from benzene and O₂ via direct activation of a C-H aromatic bond.⁸ Tungsten(VI) oxide loaded with nanoparticulate platinum (Pt/WO₃) was demonstrated to exhibit photocatalytic activity for direct synthesis of phenol from benzene using water and molecular oxygen as reactants under ultraviolet or visible light irradiation.⁹ The selectivity obtained for phenol (74% at 69% of benzene conversion) on Pt/WO₃ photocatalysts was much high. Liquid phase hydroxylation of benzene to phenol using hydrogen peroxide studied over Ti-, V-, Mg-, Fe-, Co-, and Cu-containing catalysts. Only vanadium catalysts showed both high selectivity and sufficient activity. Recently, hydroxylation of benzene with hydrogen peroxide have been carried out using vanadium supported MCM-41 and SBA-15.¹⁰ Attempts have been made over Cu supported zeolites, Cu–MCM-41, Cu catalysts supported on various oxides and zeolites, Fe/MFI, Fe/ZSM-5.¹¹

Recently, direct oxidation of benzene to phenol in liquid phase by hydrogen peroxide (H₂O₂) was examined over titanium supported on high order nonporous silica catalyst in methanol and acetic acid as solvents.¹² The maximum yield and selectivity towards phenol was obtained in the presence of acetic acid. It can be attributed to the stabilization of H₂O₂ as peroxy acetic acid species in the radical mechanism for this reaction. Bahidsky et al. have studied the gas phase conversion of benzene to phenol over bimetallic hydroxyphosphates comprising calcium and copper.¹³ Nitrous oxide, produced in-situ from the catalytic oxidation of ammonia with air, enables selective hydroxylation of benzene. With H₂O₂, remarkable results (benzene conversion: 8.6%, phenol selectivity: 91% )
have been recently obtained by combining the use of a peculiar co-solvent (sulfolane) and a modified titanium silicalite (TS-1B) as the catalyst, at 100 °C.\(^{14}\) Tang et al. reported that the selectivity for phenol achieved was 93% and the yield of phenol was 10.1% when the reaction was investigated over a vanadium substituted hetero-polymolybdic acid catalyst with hydrogen peroxide.\(^{15}\)

Despite the fact that the direct oxidation of benzene is beneficial, it is associated with serious problems like rapid deactivation of the catalyst that results in lower yield and shorter lifespan of the catalyst. In many studies concerning the oxidation of benzene to phenol over zeolite catalysts, it has been found that the activity of the catalyst gradually reduces with time on stream due to formation of carbonaceous deposits (coke), which is a serious obstacle for commercialization of this elegant synthesis route.

Normally, the direct hydroxylation of benzene to phenol is performed both in the liquid and in the gas phase. To avoid deep oxidation of benzene, an oxygen species of mild reactivity seems to be necessary.\(^{15}\) Nowadays, a great emphasis is associated to the use of environmentally friendly oxidants (“green” oxidants) that lead to a minimum amount of wastes. One of the attractive oxidant is hydrogen peroxide since i) it can provide the high percentage of active oxygen of around 47% (active oxygen content is the ratio between the weight of the oxygen atoms to be transferred to the substrate and the weight of the oxidant itself.) ii) it can avoid the formation of toxic by-products iii)it is relatively cheap and available.

In this chapter, we explored the catalytic activity of the prepared ceria-zirconia catalysts for the hydroxylation of benzene with H\(_2\)O\(_2\) as oxidant in the liquid phase reaction.
6.2. Influence of Reaction Parameters

The reaction was carried out by the procedure given in chapter 2 (section 2.4.3). Generally in any reaction, the yield and selectivity to a desired product depend on various reaction parameters. Reaction scheme for the hydroxylation of benzene is given below.

![Reaction scheme for the hydroxylation of benzene](image)

Scheme 6.1. Reaction scheme for the hydroxylation of benzene

6.2.1. Effect of Temperature

Temperature variation studies were done over 8CrCZ catalyst. The results are given in Fig. 6.1.

![Effect of temperature on hydroxylation of benzene](image)

Fig.6.1. Effect of temperature on hydroxylation of benzene. (Reaction Conditions: 8CrCZ-0.1g, Acetonitrile-5ml, Benzene: H₂O₂-1:2, Time-6hrs)
The conversion of benzene is increased up to 60°C while a further increase in temperature decreased the conversion. This may be due to the thermal decomposition of H₂O₂ and the volatilization of substrate at higher temperatures. Previously it was reported that the reduction in the conversion of benzene was attributed to reduced solubility of oxygen at higher temperature. Notably, in our studies phenol is a major product whose selectivity is increased with increasing temperature. At 70°C, phenol selectivity decreases. At high temperatures, phenol is further oxidized to dihydroxybenzenes such as hydroquinone and catechol.

6.2.2. Effect of Benzene to H₂O₂ ratio

In a set of experiments the catalytic activity for 8CrCZ was scanned by taking different volume ratios of benzene to H₂O₂ with optimized conditions.

Fig. 6.2. Effect of benzene to H₂O₂ ratio on hydroxylation of benzene. (Reaction Conditions: 8CrCZ-0.1g, Acetonitrile-5ml, Temperature-60°C, Time-6hrs)

Fig. 6.2 reveals the effect of vol. ratio of benzene to H₂O₂ on the oxidation reaction. It is clear that substrate:oxidant ratio has a profound
influence on the catalytic activity. No oxidation products are observed without the use of H$_2$O$_2$. The percentage conversion increases with increase in H$_2$O$_2$ concentration up to 1:2 ratios. Ying Tang et al. have noted that the catalyzed benzene oxidation is accompanied by self-decomposition of the hydrogen peroxide.$^{15}$ Therefore H$_2$O$_2$ present in the mixture is consumed not only for the hydroxylation reaction but also for its self decomposition. Therefore good conversion of benzene can be achieved by increasing the oxidant amount. However, further increase in vol. ratio causes a decrease in conversion. Amit Dubey et al. reported that at higher concentration of H$_2$O$_2$, due to the high exothermic nature of the reaction the reaction temperature shoots up leading to decomposition and undesired consumption of H$_2$O$_2$.\textsuperscript{11} It is clear from the graph that selectivity towards phenol is found to decrease with amount of H$_2$O$_2$. Other products include hydroquinone and catechol. Farook Adam et al. have reported that decrease in phenol selectivity at higher H$_2$O$_2$ concentrations can be due to the increased formation of water in the reaction mixture, resulting in lowering of solubility, and/or to over-oxidation reactions of phenol to form byproducts.\textsuperscript{2}

### 6.2.3. Effect of Catalyst Amount

Fig. 6.3 illustrates the influence of catalyst weight on the oxidation reaction. Benzene conversion increases with increasing catalyst amount. No reaction is observed in the absence of catalyst implying that reaction proceeds through pure heterogeneous manner. As the amount of catalyst increase from 0.05 to 0.1g, the percentage conversion increases from 30 to 51%. Further increase of catalyst amount to 0.2g results only a slight increase in conversion (3%). Therefore catalyst amount of 0.1g was selected for further studies.
6.3. Catalytic Activity of Prepared Catalyst Systems

A comparative evaluation of the catalytic activity of the prepared catalysts on the hydroxylation of benzene is presented in Table 6.1. Pure CZ gives negligible conversion of benzene. The addition of metal on to ceria-zirconia improved the conversion of benzene. For vanadium modified catalysts, oxidation activity increases and reaches maximum activity (25.4%) and then decreases. Radhika et al. have studied benzene oxidation over vanadia catalysts supported on ceria promoted with rice husk silica.\(^\text{17}\) Maximum activity was observed for 8 wt.% V loaded catalysts which decreases with increase in V loading. They elucidated that surface species in low vanadia loading is an isolated VO\(_x\) monomer whereas at higher loading, CeVO\(_4\) phase formed decreases the number of available surface VO\(_x\) sites thereby decreasing the catalytic activity. Therefore, decreased activity for 12VCZ may be due to the presence of cerium vanadate. Chromium modified catalysts show the maximum benzene conversion. For a series of chromium modified catalysts, activity increases with increase in loading.
percentage and maximum conversion is found for 12CrCZ (71.4%). Phenol selectivity also increases with Cr content. According to Viswanathan et al., mesoporous Cr-AlPO₄ exhibits both acidic and redox properties by promoting de-alkylation and oxidation in a concerted manner, whereas, under identical conditions, Cr-MCM-48 promotes only oxidation. Farook et al. have reported that presence of CuO together with lattice oxygen rich CeO₂ can make the redox mechanism easier and lead to effective activation of the oxygen to oxidize the highly stable benzene molecule. The highest catalytic activity observed for Cr modified catalyst may be because of their ability to undergo redox reactions. For Mn modified catalysts also, the activity increases with Mn content. Pr modified catalysts show low conversion of benzene. 12PrCZ gives a maximum conversion of 13%.

**Table 6.1.** Effect of catalysts on hydroxylation of benzene. (Reaction Conditions: Temperature-60°C, Acetonitrile-5ml, Benzene: H₂O₂-1:2, Time-6hrs)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
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<tbody>
<tr>
<td>CZ</td>
<td>5</td>
<td>68</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td>4VCZ</td>
<td>23</td>
<td>90</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>8VCZ</td>
<td>25</td>
<td>72</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>12VCZ</td>
<td>21</td>
<td>64</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>4CrCZ</td>
<td>29</td>
<td>61</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>8CrCZ</td>
<td>51</td>
<td>87</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>12CrCZ</td>
<td>71</td>
<td>88</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>4MnCZ</td>
<td>20</td>
<td>68</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td>8MnCZ</td>
<td>26</td>
<td>63</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>12MnCZ</td>
<td>27</td>
<td>58</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>4PrCZ</td>
<td>8</td>
<td>46</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>8PrCZ</td>
<td>9</td>
<td>51</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>12PrCZ</td>
<td>13</td>
<td>60</td>
<td>40</td>
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</table>
The selective oxidation of hydrocarbons is speculated to proceed by the activation of oxygen to generate active oxidizing species. For the oxidation of aromatics with hydrogen peroxide over modified metal oxides, it has been proposed that the hydroxylation of the aromatic ring occurs through heterolytic mechanism which involves the formation of a metalloperoxide species.\textsuperscript{20} We have not attempted any detailed mechanism studies in the present work.

6.4. Concluding Remarks

- The prepared ceria-zirconia catalysts were used in order to perform and study the direct hydroxylation reaction of benzene to phenol in the liquid phase condition, with eco-friendly hydrogen peroxide oxidant, which is a reaction of high industrial interest.

- Metal modified ceria-zirconia catalysts have improved the catalytic activity for the reaction.

- Chromium modified catalysts exhibited more catalytic activity than other prepared catalysts. Moreover, the metal loading has pronounced influence on % conversion and selectivity.

- The present method proved to be applicable as a convenient eco-friendly substitute, thus offering an adaptable method for one step reaction of benzene to phenol which is a challenge in catalytic chemistry.
References


