Research is going on in full swing to develop new efficient oxygenation catalysts for functionalizing feedstock alkanes to raw oxygen-containing chemicals. New environment friendly catalytic processes using clean oxidants like molecular oxygen or hydrogen peroxide are being explored exhaustively recently. In this direction, $\text{H}_2\text{O}_2$ in presence of active metal oxide catalysts is extensively explored towards low temperature oxidation reactions. However, in presence of transition metal ions, applications of hydrogen peroxide as an oxidant has been limited due to the self-decomposition of the oxidant. But fine dispersion of transition metal ions on suitable supports overcomes this demerit by site isolation of redox metal ions, and has been proven as an excellent catalyst for a variety of oxidation reactions.

Phenol, one of the most important intermediate for organic synthesis is commercially prepared by multistep cumene process which has several serious disadvantages. The direct hydroxylation of benzene with hydrogen peroxide as oxidant is widely attempted green process at the mild conditions which would be one of the most useful processes in the future. Here in we report liquid phase hydroxylation of benzene with $\text{H}_2\text{O}_2$ over transition metal impregnated PILCs and PCHs under mild reaction conditions.
6.1 Introduction

Phenol is an important intermediate in the chemical industry used for the manufacturing of resins, caprolactam, adipic acid, fibers, antioxidants, agrochemicals and many other chemicals. Phenol is commercially produced via the multy step Hock process [1], where benzene is converted into cumene by the alkylation of benzene with propene in presence of silica supported phosphoric acid and then cumene is non catalytically oxidized to cumene hydroperoxide in aqueous emulsion and it is followed by its subsequent cleavage in acidic media yield equimolar amounts of phenol and acetone (Scheme 6.1). The process has several disadvantages like low yield of phenol, high energy cost, an explosive intermediate (cumene hydroperoxide) and requirement to treat the by-product of acetone. Moreover, the economy of this process is strongly dependent on the market price of the side product acetone. Thus, the direct hydroxylation of benzene to phenol with high atom efficiency and high selectivity becomes one of the most challenging task and has attracted much attention.

Scheme 6.1 Cumene Precess
To achieve direct hydroxylation of aromatic compounds, a neutral oxygen species or radical oxygen species might work as the active species. A variety of oxygen sources such as O$_2$ [2-3], H$_2$O$_2$ [4-7], N$_2$O [8-9] and a mixture of oxygen and hydrogen [10] have been utilized for the direct hydroxylation of benzene. When molecular oxygen is used as the oxidant for hydroxylation of benzene, sacrificial reductant such as hydrogen [10–14], carbon monoxide [15], ammonia [16-17], ascorbic acid etc. are usually required. High selectivity to phenol could be obtained with nitrous oxide as the oxidant at higher reaction temperature, but the source of raw material is limited. Benzene hydroxylation using oxygen requires the activation of C–H bonds in the aromatic ring and the subsequent insertion of oxygen. Most heterogeneous catalysts that contain transition metals, supply an oxygen species that has a negative charge, such as O$^-$, O$_2^-$ and O$_2^{2-}$, all of which cause oxidation of benzene via the electrophilic reaction mechanism [18]. Air or oxygen is easily available. However, the efficiency of the catalysts is far from the level of industrial application. Amongst the oxidants, hydrogen peroxide has some obvious advantage due to the fact that water is the only byproduct and the process is simple, green, and economic. Hence direct hydroxylation of benzene in liquid phase with H$_2$O$_2$ in milder conditions is regarded as beneficial.

Hydroxylation of benzene to phenol was studied initially in the view of understanding the biological processes which showed the formation of biphenyl through cyclo hexadienyl radical and for understanding of Fenton’s mechanism [19-22]. Friedel and Crafts studied the conversion of benzene to phenol using oxygen in gas phase in presence of aluminium chloride [23]. Later molybdenum, tungsten, copper, and vanadium oxides were explored for
hydroxylation of benzene using oxygen as oxidant [24-26]. However the practical application was limited as selectivity of phenol was very low. There were numerous investigations on liquid phase hydroxylation of benzene using homogeneous heteropolyacid catalysts such as iron and chromium containing phosphotungstic salts, vanadium substituted phosphotungstic acids and phosphomolybdates with hydrogen peroxide as an oxidant [27-32]. However, benzene conversion was very low over those catalysts.

Perego et al. evaluated the catalytic activity of titanium silicates for hydroxylation of benzene soon after its synthesis [33]. Bengoa et al. investigated the influence of structural properties of TS-1 on catalytic hydroxylation of benzene and indicated that synthesis conditions must be controlled carefully to get pure TS-1, as the presence of extra-framework titanium will inhibit benzene hydroxylation [34]. Balducci et al. observed a dramatic improvement of selectivity by using sulfolane as a cosolvent in a NH₄HF₂ modified TS-1 catalyst (TS-1B) due to the formation of complexes with phenolic compounds limiting the formation of over oxidation products [35].

Transition metal incorporated microporous or mesoporous materials were reported as active catalysts for direct hydroxylation of benzene to phenol. Ion-exchanged NaY zeolite with various cations (Cu²⁺, Ni²⁺, Zn²⁺, Fe³⁺, Cr³⁺, Bi³⁺ and V⁴⁺) were evaluated for hydroxylation of benzene with hydrogen peroxide [36]. The highest conversion of benzene (33.2%) was achieved using Cu-NaY with 100% selectivity to phenol. When 1:1 molar ratio of benzene/H₂O₂ was used, no over oxidation products were observed for all ion exchanged NaY zeolites. There were several reports about the hydroxylation of benzene over vanadium containing catalysts, such as VO₃ species anchored
Hydroxylation of benzene on amorphous siliceous material of MCM type catalysts such as MCM-41 [37-38], MCM-48) [39], VO<sub>x</sub> species supported on SBA-15 [40], SBA-16 [41] and clay [42]. Vanadium containing microporous material VS-1 with different vanadium contents were evaluated for benzene hydroxylation and the leaching behavior were examined under different conditions. The results indicated that the mononuclear octahedral V<sup>V</sup>, tetrahedral V<sup>V</sup> and V<sup>IV</sup> species in the framework showed good stability under the hydroxylation conditions [43]. V-HMS catalysts with isolated tetrahedral VO<sub>4</sub> species in the frame work were also studied for the title reaction in aqueous acetic acid as solvent [44]. Zhu et al. found in VO<sub>x</sub>/SBA-16 that not only the highly dispersed isolated VO<sub>4</sub> species, but also the polymerized VO<sub>4</sub> units and the microcrystal of V<sub>2</sub>O<sub>5</sub> on the surface of catalyst played key roles in the hydroxylation of benzene to phenol [41]. Vanadyl acetylacetonate complex grafted periodic mesoporous material prepared by the anchoring of vanadyl acetyl acetate group in to the amino functionalized MCM-41 showed better catalytic activities with higher stability than the framework substituted V-MCM-41 materials and the vanadium peroxo complex of V<sup>5+</sup>-O-O<sup>•</sup> radicals played an important role in the hydroxylation of benzene to phenol [45]. Tanarungsun et al. studied the hydroxylation of benzene with H<sub>2</sub>O<sub>2</sub> using various transition metal catalysts (Cu, V, Fe) supported on TiO<sub>2</sub> support [46-47]. The addition of vanadium in the Fe/TiO<sub>2</sub> improved the activity of catalysts. A ternary metal catalyst composed of Cu, V and Fe showed good activity and ratio of Cu, V and Fe have tremendous effect on phenol yield and phenol selectivity [48]. Sugunan et al. studied the hydroxylation of benzene over chromium loaded mesoporous zirconium cerium mixed oxide and found to be promising.
Cu (II) substituted molecular sieves were found to be is active centre and efficient catalysts in liquid phase oxidation of aromatic compounds. Wang and coworkers studied the hydroxylation of benzene over Cu-MCM-41 prepared by sol-gel method with varying copper content [49]. The catalytic activity revealed that benzene conversion could reach 52.9%, but the phenol selectivity was greatly reduced due to the over oxidation. The selectivity to phenol was improved by the addition of acidic promoters such as B, Al to Cu-MCM-41 material [50]. X.Y. Qi et al. compared the activity of copper substituted aluminophosphate molecular sieves CuAPO-11 having AEL topology with its redox analog CuAPO-5 having AFI topology [51]. The product distributions were governed by the nature of structure types of the copper-substituted materials. The peculiar porous structure related to AEL or AFI topology governed the product distributions in which phenol as a sole product was yielded over the AEL structure, whereas the formation of catechol and hydroquinone were favored over the AFI structure, particularly at higher benzene conversions. CuO supported hexagonal SBA-15 [52], cubic KIT-6 [53], aluminium pillared clays [54] and Cu containing LDHs [55] were also reported for the title reaction.

Hydroxylation of benzene was also investigated over mesoporous Fe-MCM-41, Co-MCM-41 and Ni-MCM-41 catalysts with hexagonal and well-ordered structure [56]. The catalytic activity and selectivity of these catalysts were influenced by the quantity of the metal incorporated in the framework, adsorption capacity and stability of the catalyst against leaching. High benzene conversion (80.4%) was obtained with Co-MCM-41 (9.2% Co) in acetonitrile at 50°C. It was revealed in Ti grafted MCM-41 that the surface hydrophobicity/hydrophilicity of the catalysts significantly affects the affinity
of the catalyst surface for reactant molecules with different polarity, thereby influencing the selectivity in the hydroxylation of benzene [57]. Iron oxide supported catalyst such as Fe/MgO [58], Fe$^{3+}$/Al$_2$O$_3$ [59] were also proved to be effective for direct hydroxylation of benzene to phenol.

From the above discussion it was clear that amount, dispersion and nature of active metal oxide species in the metal supported catalysts have tremendous influence on benzene conversion and selectivity of phenol. Here in we report liquid phase hydroxylation of benzene with 30% H$_2$O$_2$ over transition metal impregnated PILCs and PCHs under mild reaction conditions. The reactions were done as the procedure described in section 2.4.2. The effect of various parameters were studied and optimized to get maximum conversion.

![Scheme 6.2 Direct hydroxylation of benzene](image)

### 6.2 Effect of Reaction Parameters

#### 6.2.1 Effect of solvents

Solvents play a crucial role in benzene hydroxylation as keeping both benzene and hydrogen peroxide in one phase and facilitate an intimate contact between the reactants and the catalysts. Reactions were carried out in different solvents such as acetonitrile, dioxane and methanol and results are given in Figure 6.1. It was found that the benzene conversion was the highest for the acetonitrile solvent. This may be due to high dielectric constant of acetonitrile and low hydroxyl ion scavenging ability of acetonitrile. Probably the reaction
may be taking place through an ionic intermediate, which is most stabilized in a solvent of highest polarity. Some researchers have the opinion that acetonitrile does not behave as an inert solvent, but most likely forms a reactive intermediate with hydrogen peroxide, which by itself seems to be the active oxidant responsible for the phenol formation and thus leads to the highest benzene conversion [60].

![Figure 6.1 Effect of solvents, Catalyst- Cu(5)ZrPC, Temperature -60°C, Time -3h, Benzene-10 mmol, Benzene to H2O2 ratio- 1:3, Solvent -5 mL, Catalyst -100mg](image)

**Figure 6.1** Effect of solvents, Catalyst- Cu(5)ZrPC, Temperature -60°C, Time -3h, Benzene-10 mmol, Benzene to H2O2 ratio- 1:3, Solvent -5 mL, Catalyst -100mg

### 6.2.2 Effect of solvent amount

The effect of volume of acetonitrile was studied by varying the volume of acetonitrile from 5mL to 10mL. The volume of solvent is crucial as it may influence the polarity of reaction mixture and stabilize the reaction intermediates and keep benzene and H2O2 in one phase. The conversion increases with solvent amount and after an optimum amount conversion falls due to the competitive adsorption of solvent molecules over the active sites. The optimum acetonitrile amount is found to be 7.5 mL.
6.2.3 Effect of time

The Figure 6.3 depicts the progress of reaction with respect to time. A gradual increase in conversion was noted with increase in reaction time and maximum conversion was observed at 3\textsuperscript{rd} hour and thereafter conversion remains the same. The selectivity of phenol decrease with time as the phenol formed is further hydroxylated and converted in to other byproducts. Hence 3\textsuperscript{rd} hour is taken as optimum time for further studies.

Figure 6.3 Effect of reaction time, Catalyst- Cu(5)ZrPC, Temperature -60\degree C, Benzene-10 mmol, Benzene to H\textsubscript{2}O\textsubscript{2} ratio- 1:3, Catalyst -100mg, Acetonitrile -7.5 mL
6.2.4 Effect of catalyst amount

The effect of catalyst amount was studied by varying catalyst amount from 80 mg to 140 mg. The conversion increases with increase in catalyst amount due to the proportional increase in active sites. Initially selectivity of phenol increases with catalyst amount and then selectivity of phenol decreases due to over oxidation of phenol to other byproducts.

![Graph showing conversion and selectivity of phenol vs catalyst weight.]

Figure 6.4 Effect of catalyst amount on hydroxylation benzene
Catalyst- Cu(5)ZrPC, Temperature -60°C, Time -3h, Benzene-10 mmol, Benzene to H₂O₂ ratio- 1:3, Acetonitrile -7.5 mL

6.2.5 Effect of temperature

Hydroxylation reaction was performed in the temperature range of 30–70°C and the results are given in Figure 6.5. Conversion of benzene increases with increase in temperature and maximum conversion is obtained at 60°C. It can be seen that phenol selectivity gradually increases from 30 to 70°C. At low temperature, the lower phenol selectivity can be due to the fact that phenol is more active than benzene and phenol is further hydroxylated to diphenols and other by products. Above 60°C the conversion drops due to the competitive self decomposition of H₂O₂ without being involved in desired reaction. This
behavior is similar to other Cu-based materials like Cu-HMS [55] and Cu AIPC [54] catalysts reported in literature.

![Graph showing conversion and selectivity of phenol as a function of temperature.]

**Figure 6.5** Effect of temperature, Catalyst - Cu(5)ZrPC, Time -3h, Benzene-10 mmol, Benzene to H₂O₂ ratio- 1:3, Catalyst -120mg, Acetonitrile -7.5 mL

### 6.2.6 Effect of oxidant ratio

The effect of benzene to oxidant (30% H₂O₂) ratio was studied from molar ratio 1 to 4 and the results are given in Figure 6.6.

![Graph showing selectivity and conversion as a function of benzene to oxidant ratio.]

**Figure 6.6** Effect of oxidant ratio, Catalyst- Cu(5)ZrPC, Temperature -60°C, Time -3h, Benzene-10 mmol, Acetonitrile -7.5 mL, Catalyst -120mg
The conversion and selectivity of phenol increases with oxidant amount and maximum conversion is obtained at benzene to H₂O₂ ratio of 1:3 and then conversion and selectivity falls. This may be ascribed to the self-catalytic decomposition of H₂O₂ and formation of deep oxidation products at higher oxidant amount.

### 6.2.7 Effect of different catalysts

The hydroxylation of benzene was performed over prepared catalysts with the optimized conditions and the results are summarized in the Table 6.1.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Optimized conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>60°C</td>
</tr>
<tr>
<td>Time</td>
<td>3 hour</td>
</tr>
<tr>
<td>Solvent</td>
<td>Acetonitrile (7.5 mL)</td>
</tr>
<tr>
<td>Benzene</td>
<td>10 mmol</td>
</tr>
<tr>
<td>Benzene to H₂O₂ Ratio</td>
<td>1:3</td>
</tr>
<tr>
<td>Catalyst Amount</td>
<td>120 mg</td>
</tr>
</tbody>
</table>

It is clear from the Table 6.2 that Cu and V incorporated catalysts showed better activity compared to other metal incorporated catalysts. Cu incorporated catalysts showed the highest conversion which may prove that Cu is a highly active center of catalysts for the benzene hydroxylation. The bare zirconium pillared clay show low activity which substantiates the necessity of active redox metal species for benzene hydroxylation.
Hydroxylation of benzene

Table 6.2 Effect of catalyst on hydroxylation of benzene

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Conversion of benzene (%)</th>
<th>TON</th>
<th>Selectivity (%)</th>
<th>Phenol</th>
<th>Catechol</th>
<th>Hydroquinone</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrPC</td>
<td>2</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(1)ZrPC</td>
<td>37</td>
<td>47370</td>
<td>97</td>
<td>2</td>
<td>-</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Cu(3)ZrPC</td>
<td>51</td>
<td>20939</td>
<td>93</td>
<td>4</td>
<td>2</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Cu(5)ZrPC</td>
<td>59</td>
<td>10264</td>
<td>89</td>
<td>7</td>
<td>3</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>V(1)ZrPC</td>
<td>11</td>
<td>8632</td>
<td>98</td>
<td>1</td>
<td>1</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>V(3)ZrPC</td>
<td>23</td>
<td>6087</td>
<td>92</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>V(5)ZrPC</td>
<td>38</td>
<td>4918</td>
<td>86</td>
<td>8</td>
<td>4</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Ni(5)ZrPC</td>
<td>8</td>
<td>1181</td>
<td>95</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Co(3)ZrPC</td>
<td>15</td>
<td>4159</td>
<td>89</td>
<td>7</td>
<td>4</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Co(5)ZrPC</td>
<td>26</td>
<td>4038</td>
<td>79</td>
<td>13</td>
<td>6</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>FeAlPC</td>
<td>23</td>
<td>832</td>
<td>96</td>
<td>3</td>
<td>1</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Ce(3)FeAlPC</td>
<td>25</td>
<td>646</td>
<td>94</td>
<td>4</td>
<td>2</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>CuZrSiPCH</td>
<td>32</td>
<td>8968</td>
<td>95</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>VZrSiPCH</td>
<td>28</td>
<td>6896</td>
<td>92</td>
<td>4</td>
<td>3</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>CoZrSiPCH</td>
<td>13</td>
<td>2746</td>
<td>90</td>
<td>5</td>
<td>3</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

$TON = \frac{\text{mmoles of reactant reacted}}{\text{mmoles of active metal}} \times 100$

The catalytic activity in terms of Turn Over Number (TON) was also calculated and is given in Table 6.2. The TON is maximum for Cu(1)ZrPC catalysts where the active Cu species is well dispersed as isolated copper oxide species. For the same metal species the conversion of benzene in zirconium pillared clay is higher than that of porous clay heterostructures probably due to the fact that benzene is more strongly adsorbed on the strong Lewis sites than on Bronsted sites. This is in accordance with earlier reports [50].

6.2.8 Effect of metal amount

Figure 6.7 depicts the influence of copper and vanadium content on the reaction. In copper and vanadium incorporated zirconium pillared clays, the
conversion of benzene increases with increase in metal content up to 5% and then the conversion decreases. In the case of copper incorporated zirconium pillared clays, this may be due to the nonproductive self decomposition H$_2$O$_2$ over copper aggregates. From XRD and TPR data it was confirmed that copper was dispersed as isolated copper oxides species up to 5% Cu loading then clusters or aggregates of copper oxides are formed in zirconium pillared clays. Bahranowski et al. [61] have proved that isolated copper act as an active center for the oxidation of aromatic hydrocarbon and copper particularly in cluster form can catalyze the self decomposition of H$_2$O$_2$. It is also reported that isolated VO$_x$ species of tetrahedral coordination in lower loading is more effective for the oxidation of aromatics than polymerized VOx species in higher vanadium loading [62]. In vanadium impregnated zirconium pillared clays conversion increases up to 5% due to the fact that vanadium exists as isolated VO$_x$ species as evident from XRD and TPR analysis. The selectivity of phenol decreases with increase in metal content due to the over oxidation of phenol in to other by products over active sites.

![Figure 6.7 Effect of metal content](image)
6.3 Mechanism of reaction

In oxidation reactions using hydrogen peroxide, the cleavage of the oxygen–oxygen bond in peroxides takes either of two distinct pathways: homolitic cleavage leading to a radical pathway or heterolitic cleavage leading to an ionic mechanism. For the oxidation of aromatics with hydrogen peroxide over transition metal oxide supported catalysts, it has been proposed that the hydroxylation of the aromatic ring occurs via the heterolytic mechanism, involving the formation of a metalloperoxide species [63-64]. The metalloxo hydroperoxide species may be stabilized by hydrogen bonding between the hydroperoxide ion and the oxygen atom of support [66] or polar solvent like acetonitrile. Even though no detailed mechanistic studies have been carried out in the present case hydroxylation of the ring indicates the possibility of heterolytic cleavage involving an ionic mechanism as depicted in the Scheme 6.3.

Scheme 6.3 Mechanism of reaction

6.4 Conclusions

- Copper and vanadium incorporated zirconium pillared clays were found to be effective catalyst for direct hydroxylation of benzene to phenol under milder reaction conditions.
Nature and dispersion of metal species have tremendous effect on conversion and selectivity. Isolated Cu and vanadium oxide species were found to be active centres for hydroxylation of benzene. Selectivity of phenol decreases with metal content.

Acetonitrile was found to be best solvent for the reaction as it may stabilize the reaction intermediate.

Conversion increases with temperature and maximum conversion is obtained at 60°C. The phenol selectivity decreases with temperature.

A mechanism involving ionic intermediate and metaloxo hydroperoxide species was proposed.

References

Hydroxylation of benzene


Hydroxylation of benzene


