Abstract

Direct oxidation of benzene with $H_2O_2$ to form phenol is a very promising tool for the chemical industry, since the commonly employed 'cumene' process being of uncertain profitability and technologically complex. Due to the high stability of benzene, the direct oxygenation of benzene has been thought to be one of the most difficult oxidation reactions but also to be one of the most challenging oxidation from the point of view of synthetic organic chemistry. Phenol has been known to be a versatile intermediate for the manufacture of various petrochemicals such as phenolic resins, adipic acid, caprolactum, bisphenol, nitro and chlorophenols, phenol sulfonic acid, and is mainly produced by 'cumene' process. However, this process consists of three steps, and has many disadvantages. Hence, finding a one-step process for the production of phenol by direct oxidation of benzene, which is one of the most challenging tasks in oxidation catalysis, attracts much attention in recent years.
5.1. INTRODUCTION

At the present time, phenol an important intermediate for the manufacture of petrochemicals, agrochemicals and plastics is commercially produced via the so-called “Cumene Process” which accounts for more than 90% of the world output with only 5% of phenol yield. The advantage of “Cumene Process” (Hock Process) is that it take two inexpensive starting materials, benzene and propylene, and converts them into two expensive useful products, phenol and acetone, just using air¹. However, the marketability of acetone by-product and the need of a high capital investment due to its characteristic multi-step process are disadvantages. For these reasons, a process is desired whereby phenol can be formed in one step². The reaction pathways involved in one step production of phenol from benzene is shown in Scheme 5.1.

![Scheme 5.1](image)

It is not easy to get the relatively higher conversion of benzene oxidation due to the difficulty of overcoming its resonance energy. Nowadays,
the selective insertion of the hydroxyl group onto the aromatic ring, to manufacture phenols and naphthols is a very promising tool for the chemical industry. A one-step production of phenol through the direct oxygenation of benzene has so far been attempted using various catalytic systems by many researchers. The practical development of one step production of phenol will have advantages in cost reduction and energy saving.

The direct oxygenation of benzene formally includes insertion of an oxygen atom between the C-H bonds to form phenol. The oxygen insertion for benzene oxidation is shown in Scheme 5.2.

Many approaches have been reported in the literature for the oxidation of benzene to produce phenol. Classical system such as Fenton’s reagent (Fe\(^{2+}\)-H\(_2\)O\(_2\)), Udenfriend’s reagent (Fe\(^{2+}\)-EDTA-O\(^2-\)-ascorbic acid), and Hamilton’s reagent (Fe\(^{2+}\)-catechol-H\(_2\)O\(_2\)) has been known to yield phenol from benzene. Recently, iron- and chromium-containing phosphotungstate salts were reported as efficient catalysts for benzene hydroxylation.

Direct benzene to phenol oxidation over iron modified zeolites of MFI structures using N\(_2\)O as an oxidant has been developed for the last 10 years, which resulted in commercialization of new technology for phenol production.
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at Solutia\textsuperscript{11}. In recent years, a new class of commercial oxidation catalysts, Fe-ZSM5 has emerged for phenol production from benzene using nitrous oxide as oxidizing agent\textsuperscript{12-14}. Influence of acidity, both the Bronsted acid sites and the Lewis ones on benzene to phenol hydroxylation over iron modified zeolite ZSM-5, was discussed extensively in the literature\textsuperscript{15}. At the beginning, the acidic centers were believed to be responsible for this reaction. However, Panov and co-workers\textsuperscript{16} have shown that benzene to phenol oxidation does not occur according to acidic mechanism and they proved the exceptional role of iron complexes for this reaction. After the finding that benzene can be selectively oxidized to phenol over ZSM-5 type zeolites using N\textsubscript{2}O as an oxidant, several research groups have investigated the mechanism of such a reaction, reaching different conclusions\textsuperscript{17,18}. The presence of Bronsted acid sites on the catalyst surface was demonstrated to be necessary but, according to Burch and Howitt, not sufficient for assuring high activity and selectivity, while Lewis acid sites should be inactive\textsuperscript{19}. Liang et al.\textsuperscript{20} reported that heterogeneous modified mesoporous SBA-15 catalyst by the covalent grafting of ferrocene complex show high catalytic activity for benzene oxidation with hydrogen peroxide as the oxygen source and the excellent stability of these catalysts is attributed to the covalent grafting between the organic ligand and the inorganic mesoporous material.

Molecular oxygen is an ideal oxidant, but aerobic oxidation is often difficult to control and only one oxygen atom has been used in most reactions (50 % atom efficiency) thus oxidation requires reducing agents\textsuperscript{21,22}. H\textsubscript{2}O\textsubscript{2} is considered as an ideal oxidant due to its high oxidizing ability and lack of toxic by-products since it produces water as the only by-product\textsuperscript{23}. The catalytic
hydroxylation of aromatics with aqueous $\text{H}_2\text{O}_2$ has been widely investigated with catalysts such as iron complexes, silica-supported iron salts, titanosilicates and V-substituted polyoxometalates. In recent years, many efforts have also been published in the field of cheaper $\text{H}_2\text{O}_2$ production since it is too expensive compared to the frequently applied air and/or oxygen. Several researchers reported very cheap and clean $\text{H}_2\text{O}_2$ technology, in which $\text{H}_2\text{O}_2$ is produced in situ and reacts in one pot with an organic substrate. In 'Niwa concept' with the oxidation of benzene to phenol as the model reaction consists of a $\text{H}_2$-permeable Pd based membrane through which $\text{H}_2$ is transported as an active hydrogen atom towards the reaction side of the membrane reactor containing oxygen and benzene. Takahiro et al. reported the liquid-phase oxidation of benzene by various supported Cu catalysts using molecular oxygen as an oxidant and ascorbic acid as a reductant. A Fenton-type reaction scheme was suggested by the accumulation of $\text{H}_2\text{O}_2$ during the benzene oxidation. According to Feng-Shou Xiao et al., benzene oxidation with $\text{H}_2\text{O}_2$ on Cu catalysts produced phenol selectively with high conversion rate in comparison with TS-1 catalyst. The high catalytic activity is related to the intensity of hydroxyl radicals resulting from the interaction of Cu-OH with $\text{H}_2\text{O}_2$ from EPR analysis.

Noble metal-vanadium (V) oxide catalysts supported on SiO$_2$ have been reported to be active for benzene oxidation to phenol in the presence of both gaseous oxygen and hydrogen under a pressurized atmosphere. Vanadium catalysts supported on SiO$_2$ and Al$_2$O$_3$, have also been utilized for the benzene oxidation using gaseous oxygen as an oxidant and ascorbic acid as a reducing agent. Kenji Nomiya et al. studied the catalytic hydroxylation of...
benzene using mono-vanadium (V) substituted heteropolymolybdate as single species in presence of H₂O₂. They have summarized the requirement of one vanadium center acting in cooperation with the Mo(VI) atom constructed on the A-site of the α-Keggin polyoxoanion structure in contrast to the bimetallic vanadium species with the corner-shared octahedra. John et al.\textsuperscript{37} reported that V₂O₅/TiO₂ can be used to achieve the oxidation of monochlorobenzene at moderate temperatures and the higher catalytic activity is due to the crystalline vanadia species on the surface of the catalyst. Vanadium containing mesoporous materials such as V-MCM-41 showed good catalytic activity for the oxidation of benzene over biocatalytic system with Pd-metal catalysts\textsuperscript{38,39}. In complete benzene oxidation, the promoting effect of Pd and Ag over supported vanadium oxide has been related to the activation of oxygen on the metal particles, which enables the reverse oxidation of V⁴⁺ and leads to an equilibrium in the redox process\textsuperscript{40,41}. The complete benzene oxidation over titania, zirconia and ceria supported gold-vanadia catalysts have shown that the highest activity and stability was established for the ceria supported catalysts, which can be connected with high oxygen storage capacity of ceria\textsuperscript{42-45}.

5.2 INFLUENCE OF REACTION CONDITION

Influence of reaction conditions is essential for a chemical reaction to occur with high percentage conversion and selectivity for products. The influence of different reaction parameters was analyzed in order to maximize the product yield and selectivity. Effect of reaction conditions for benzene oxidation with H₂O₂ was initially assayed in non-optimized conditions with
6VC as the catalyst. No phenol was produced when the reaction is carried out without catalyst and in the absence of either oxidant or solvent.

### 5.2.1 Effect of Temperature

The dependence of phenol production on the reaction temperature was studied by varying the temperature between 298 and 373 K while other parameters were kept constant. Results are presented in Figure 5.1.

![Figure 5.1](image.png)

**Figure 5.1**

Reaction conditions: 6VC-100 mg, Benzene-34 mmol, Acetonitrile-191 mmol, H₂O₂-88 mmol and Time-5 h.

No reaction occurs at room temperature. However, when temperature was increased from 313 to 333 K, conversion rate increased drastically with phenol as the only product. Further increase in reaction temperature increased the conversion rate with decreased phenol selectivity. At higher temperature, the self-decomposition of H₂O₂ to molecular oxygen proceeds faster and it could not participate efficiently for the oxidation process⁴⁶. Temperature above 353 K produced small quantities of catechol and hydroquinone as secondary
oxidation products of phenol. Evaporation of the solvent at higher temperature may also result in reduced conversion. The decreased conversion with increasing temperature suggests that the activation energy for $\text{H}_2\text{O}_2$ decomposition is lower than that for the oxidation reaction\(^\text{47}\). For the present reaction the temperature selected was 333 K in order to get phenol selectively.

### 5.2.2 Effect of Solvent

In order to investigate the role of solvent, the oxidation of benzene was carried out in water, acetone, acetic acid and acetonitrile. The influence of these solvents on phenol production is shown in Figure 5.2.

![Figure 5.2](image)

**Figure 5.2**

Reaction conditions: Temperature-333 K, 6VC-100 mg, Benzene-34 mmol, Solvent-191 mmol, $\text{H}_2\text{O}_2$-88 mmol and Time-4 h.

The choice of solvent is crucial in the case of liquid phase oxidation reactions and it is known that solvent had a great influence on the catalytic activity and selectivity since they can affect the mass transfer and diffusional problems with heterogeneous solid catalysts. It is clear that water does not act
as a good solvent for the system. Acetic acid and acetone gave profound conversion but phenol selectivity was low. The presence of acidic component strongly affected the catalytic activity of hydroxylation with H₂O₂ as oxidant⁴⁸. Acetonitrile is found to be best solvent for the reaction system with high phenol selectivity and it could be due to its polarity. It has a comparatively good solubility power for both the organic substrate as well as the aqueous H₂O₂. In this aprotic solvent, activity of the catalyst increased since the phase separation between the aromatic substrate and the aqueous oxidant is greatly reduced which enables easy transport of the active oxygen species for the oxidation⁴⁹. It was reported that the double phase system composed by water-acetonitrile-benzene is an efficient solvent system for the hydroxylation of benzene⁵⁰. In this biphasic reaction medium, the resulting phenol was extracted into the organic phase and the catalyst was soluble in the aqueous phase. It could enhance the selectivity of the benzene hydroxylation by reducing the contact between phenol and the catalyst. While acetone and methanol can be used as solvents, it has been found that the hydroxylation of benzene without any organic solvent, i.e., in a triphase system, is 20 times faster than when using acetone or acetonitrile as solvents. It is evident that for this reaction the hydrophobic/hydrophilic properties of the catalyst should be of paramount importance. Thus a more hydrophobic catalyst should favor the adsorption of organophilic reagents (benzene) toward other more polar ones (H₂O₂, acetone)⁵¹.

5.2.3 Effect of Catalyst weight

The dependence of the amount of the catalyst on the production of phenol is presented in Figure 5.3.
The influence of catalyst amount is studied by taking different weight of catalyst while keeping other parameters constant. No oxidation occurs in the absence of catalyst. The oxidation rate sharply increased from 2.3 to 10.9 % as the amount of the catalyst increased from 50 to 100 mg. Further increase of catalyst amount caused a decline in the selectivity and production rate of phenol. Lowering of selectivity with more catalyst can be attributed to further oxidation of phenol. Amount of catalyst is crucial in heterogeneous reactions. The dependence of product formation on the amount of catalyst suggests that the reaction proceeds purely in a heterogenic fashion. The catalyst amount selected for the present reaction is 100 mg for the selective production of phenol.

5.2.4 Effect of Acetonitrile volume
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The effect of the volume of acetonitrile on the production of phenol is illustrated in Figure 5.4.

![Figure 5.4](image)

Reaction conditions:- 6VC-100 mg, Temperature-333 K, Benzene-34 mmol, H₂O₂-88 mmol and Time -5 h.

In order to study the effect of amount of solvent present in the reaction, the oxidation was conducted as a function of acetonitrile concentration. The conversion increased with increase in acetonitrile volume and passed through a maximum value at a volume corresponding to 191 mmol with maximum phenol selectivity. Further increase in acetonitrile volume causes a reduction to both conversion and phenol selectivity. The acetonitrile with the concentration of 191 mmol was thus found to be an optimum solvent to yield phenol selectively with high conversion rate. This can be attributed to different concentrations of benzene or catalyst between the organic and aqueous phase, which is dependent upon the added solvent and H₂O₂. When the solvent was excess, the benzene or catalyst concentration at the interface may be lower, thus resulting in a decreased conversion rate.
5.2.5 Effect of Benzene volume

The effect of the benzene concentration for the oxidation was investigated and the results are shown in Figure 5.5.

![Figure 5.5](image)

**Figure 5.5**

Reaction conditions:- 6VC-100 mg, Temperature-333 K, Acetonitrile-191 mmol, H₂O₂-88 mmol and Time-5 h.

It is seen that the oxidation rate increases with an increase in benzene concentration reaches a maximum and then decreases. Phenol selectivity remains the same. When the substrate concentration is high, an enhanced poisoning effect may arise from the strong adsorption of the products formed on the catalyst surface. This restricts further adsorption of the reactant molecules on the active sites and thus reduces the total conversion rate.\(^{53}\)

5.2.6 Effect of H₂O₂ volume

The effect of the amount of H₂O₂ on the oxidation reaction was investigated and the results are presented in Figure 5.6.
With small amount of $\text{H}_2\text{O}_2$, the solution becomes completely miscible and conversion and selectivity was low. An increase in the amount of $\text{H}_2\text{O}_2$ resulted in a decrease of conversion initially while conversion rate increases gradually with high phenol selectivity and reaches a maximum at 88 mmol. A decrease in both conversion and selectivity was observed with further increase of the amount of $\text{H}_2\text{O}_2$. This can result from either the oxidation of phenol formed or can be explained by the negative effect due to the production of $\text{H}_2\text{O}$ as a byproduct\textsuperscript{54}. The water and oxidant compete for complexation to the vanadium center, therefore excess water relative to $\text{H}_2\text{O}_2$ inhibits the reaction. Small amounts of hydroquinone and catechol are produced besides the main product. The stoichiometric ratio of $\text{H}_2\text{O}_2$ to benzene for the oxidation reaction is 1:1. However the results show that the $\text{H}_2\text{O}_2$ needed for the favourable oxidation is about double its stoichiometry. Generally, the benzene oxidation
catalysis is accompanied by the self-decomposition of $\text{H}_2\text{O}_2$. The amount of $\text{H}_2\text{O}_2$ consumed in self-decomposition was much more than that consumed in the oxidation reaction. This may be why more than stoichiometric amount of $\text{H}_2\text{O}_2$ is needed$^{55}$.

5.2.7 Effect of Time

The formation and selectivity of products always depends upon the reaction time in heterogeneous catalysis. Effect of time on benzene oxidation is shown in Figure 5.7.

![Figure 5.7](image)

**Figure 5.7**

Reaction conditions: 6VC-100 mg, Temperature-333 K, Acetonitrile-191 mmol, Benzene-34 mmol and $\text{H}_2\text{O}_2$-88 mmol.

The conversion rate increased with the reaction time up to around 5-6 h, but the extent of the increase in the oxidation rate and phenol selectivity declined beyond reaction times of around 7 h. Literature reports support the present information that much longer reaction times would cause less phenol
yield\textsuperscript{56}. This is attributed to the poisoning of the surface sites by the reaction products, which in turn block the active sites\textsuperscript{57}. Lowering of phenol selectivity after 7 h indicates the further conversion of phenol to other products with long time of reaction. The optimized reaction time was 6 h.

5.3 BENZENE OXIDATION OVER PREPARED CATALYSTS

The above observations reveal that in the liquid-phase oxidation of benzene using hydrogen peroxide as oxidant on supported vanadia catalysts, the reaction parameters play a decisive role in determining the oxidation rate and phenol selectivity. The oxidation of benzene reaction was carried out over all the prepared catalysts under the selected reaction conditions (Table 5.1) in order to produce phenol more selectively.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Selected condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature/K</td>
<td>333</td>
</tr>
<tr>
<td>Acetonitrile/mmol,</td>
<td>191</td>
</tr>
<tr>
<td>Benzene/mmol</td>
<td>34</td>
</tr>
<tr>
<td>H\textsubscript{2}O\textsubscript{2}/mmol</td>
<td>88</td>
</tr>
<tr>
<td>Time/h</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 5.2 shows the activity for benzene oxidation over VC series of catalysts along with silica supported V\textsubscript{2}O\textsubscript{5}.
**Oxidation of Benzene**

Table 5.2

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (wt.%)</th>
<th>Phenol</th>
<th>Hydroquinone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2VC</td>
<td>2.0</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>4VC</td>
<td>6.5</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>6VC</td>
<td>14.0</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>8VC</td>
<td>15.6</td>
<td>98.5</td>
<td>1.5</td>
</tr>
<tr>
<td>10VC</td>
<td>8.3</td>
<td>92.4</td>
<td>7.6</td>
</tr>
<tr>
<td>V</td>
<td>22.0</td>
<td>88.9</td>
<td>11.1</td>
</tr>
<tr>
<td>6VRS</td>
<td>20.4</td>
<td>96.1</td>
<td>3.9</td>
</tr>
<tr>
<td>6VSG</td>
<td>42.0</td>
<td>45.6</td>
<td>54.4</td>
</tr>
</tbody>
</table>

No oxidation reaction occurs with ceria. The oxidation products formed over VC catalysts suggest the presence of vanadium in the reaction. Phenol is produced as the main product over VC series of catalysts. Small amount of hydroquinone is detected as secondary oxidation products with high vanadia loading. The production of phenol increases rapidly with increasing vanadia loading until 8 wt.% V₂O₅. An increase in vanadium content beyond this results in reduced conversion rate and phenol selectivity. V₂O₅ show conversion of 22 % with phenol selectivity of 88.9 %. Among silica supported vanadia 6VRS gave 20.4 % benzene conversion with 98.2 % phenol. Even though, 6VSG could convert 42 % benzene, the phenol selectivity is found to be only 45.6 %.

Table 5.3 shows result of benzene oxidation over VCRS series of catalysts.
Only phenol was detected as the oxidation product for all VCRS catalysts. These catalysts exhibit higher activity in comparison to the VC series of catalysts. Amount of phenol generated increases rapidly with increasing vanadia loading until a plateau is reached. An increase in vanadia content beyond this point, results in decreased phenol production. Catalytic activity increases up to 8 wt. % V₂O₅ while further increase to 10 wt.% reduces the conversion.

Table 5.4 shows result of benzene oxidation over praseodymia catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (wt.%)</th>
<th>Phenol (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>PRS</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2VP</td>
<td>1.0</td>
<td>100</td>
</tr>
<tr>
<td>6VP</td>
<td>3.5</td>
<td>100</td>
</tr>
<tr>
<td>10VP</td>
<td>1.6</td>
<td>100</td>
</tr>
<tr>
<td>2VPRS</td>
<td>1.2</td>
<td>100</td>
</tr>
<tr>
<td>6VPRS</td>
<td>5.2</td>
<td>100</td>
</tr>
<tr>
<td>10VPRS</td>
<td>1.7</td>
<td>100</td>
</tr>
</tbody>
</table>
Benzene oxidation over praseodymia containing catalysts show that the activity was very low compared to that of ceria containing catalysts. Only phenol was produced on supported vanadia catalysts while no product formed with Pr and PRS supports. Catalysts with 6 wt. % vanadia exhibit higher activity than the 10 wt.% vanadia loading.

5.4 EFFECT OF LEACHING

Leaching of the supported metal ion into the reaction solution during the catalytic reaction is a concomitant concern whenever a supported metal catalyst is utilized in a liquid-phase reaction with organic hydroperoxides or \( \text{H}_2\text{O}_2 \). The influence of leaching of V species from the catalyst into the reaction solution during the production of phenol was investigated using the filtrate and the used catalyst, respectively, separated by filtration while hot after the first benzene oxidation. According to Sheldon et al. the heterogeneity of a catalyst can be better understood only if the catalyst applied under reaction conditions will be removed after half an hour of the run and carrying out the reaction with filtrate under similar reaction conditions. The benzene oxidation with the catalyst in acetonitrile/hydrogen peroxide mixture was stirred at 333 K. The catalyst was removed from the reaction mixture after \( \frac{1}{2} \) h by filtration while hot. The filtrate was refluxed under same reaction conditions for 2 h. Filtered catalyst was again used for the reaction after washing, drying and calcination process.

Table 5.5 shows the effect of V leaching into the reaction solution during oxidation.
Accordingly, resubmission of the filtrate under the reaction conditions (for 4VC, 6VC and 4VCRS, 6VCRS) shows an enhancement in conversion rate, pointing out that some of the vanadium atoms on the surface are leached out during the run and thus the observed enhanced activity of the filtrate may result from the leached vanadia species. When the filtrate was further studied for reaction without catalyst after half an hour reaction the amount of phenol was decreased due to further oxidation. Water is a best known solvent for phenol oxidation and the leached V species can oxidize phenol easily under the reaction conditions. However, VCRS catalysts showed high stability against leaching of the active species into the liquid phase under the set reaction conditions than VC catalysts. This is achieved by the presence of silica on the support, which makes highly dispersed species over the surface. \( \text{H}_2\text{O}_2 \) is an aggressive oxidant and can leach metal cation from framework of mesoporous silicas. This was observed in V-, Co-, Fe-, and Ti-containing mesoporous catalysts. Acetonitrile is sufficiently coordinating and the V-O-Si bonds are...
sufficiently labile for the formation of soluble vanadium oxides in acetonitrile\textsuperscript{64}. In the present case the leaching observed correlates with these factors.

5.5 REGENERATION AND STABILITY

After 2 h reaction, the catalysts was recovered by hot filtration, washed several times with acetone, dried at 383 K overnight and calcined for 5 h at 773 K. The recovered catalysts were reused for benzene oxidation under the same reaction conditions.

The catalytic behaviour in the reuse of the catalysts during oxidation is reported in Table 5.6.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cycle</th>
<th>Conversion (wt%)</th>
<th>Phenol (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4VC</td>
<td>1</td>
<td>4.9</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>3.4</td>
<td>97.6</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.8</td>
<td>96.5</td>
</tr>
<tr>
<td>6VC</td>
<td>1</td>
<td>9.2</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>7.9</td>
<td>98.7</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3.2</td>
<td>95.3</td>
</tr>
<tr>
<td>4VCRS</td>
<td>1</td>
<td>6.0</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>4.7</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2.1</td>
<td>98.5</td>
</tr>
<tr>
<td>6VCRS</td>
<td>1</td>
<td>13.0</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>11.6</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>10.4</td>
<td>98.2</td>
</tr>
</tbody>
</table>
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The production of phenol over the recovered catalysts was obviously lower than that over the corresponding fresh catalysts. Results indicated a decrease in conversion rate from 4.9 to 1.8 (wt %) for 4VC and 9.2 to 3.2 (wt %) for 6VC after third cycle of use. After second recycling itself phenol selectivity of these catalysts was found decreasing. Activity drop-off is less for 4 and 6VCRS catalysts and phenol selectivity decreased only during the third cycle of use.

The recovered catalysts were characterized by UV-vis DRS. Spectra are depicted in Figure 5.7.
The UV-vis spectra of 6VC and 6VCRS are characterized by charge transfer (CT) transitions between central vanadium atoms and oxygen ligands. The absorption band at ~350 nm can be assigned to V$^{5+}$ species in a tetrahedral environment characterized by a V=O bond. The absorption bands around ~600 nm is assigned to the d-d transitions of V$^{4+}$ which are not observed for catalysts after reaction. The absence of absorption in the 600-800 nm suggests that catalysts contain only V$^{5+}$. The UV-vis spectra obtained for 6VC and 6VCRS after reaction time of 6 h were similar to the fresh one suggesting no change of coordination site for vanadium during oxidation reaction.

5.6 DISCUSSION

The catalytic activity observed in the present study and structural analysis studies in previous section allow a better understanding of the influence of catalyst characteristics on the catalytic activity. It seems that the parameters, which influences the catalytic activities are the dispersion of
supported vanadia species and the characteristic of the active species over the support surface.

Selective oxidation reactions of aromatics are known to follow a Mars-van Krevelen mechanism\textsuperscript{67}. As lattice oxygen is inserted into the molecule, the reaction can occur in the absence of gas-phase \( \text{O}_2 \). The capability of oxygen insertion is associated with the presence of reducibility and reoxidizability of the supported catalysts. Active centers convert sufficiently fast between two boundary oxidation states to keep their population constant in a steady state of the catalytic reaction. Sachter et al.\textsuperscript{68,69} reported that the activity and selectivity in oxidation reactions are determined by the intrinsic activity of lattice oxygen and their availability.

In the case of \( \text{V}_2\text{O}_5/\text{CeO}_2 \) catalysts, we have observed that the catalysts with a lower vanadia loading up to 6 wt. \% \( \text{V}_2\text{O}_5 \) exhibit higher catalytic activity and phenol selectivity in comparison to the series loading up to 10 wt.\% \( \text{V}_2\text{O}_5 \). Phenol selectivity decreased with 8 wt. \% while conversion rate reduced only for 10 wt. \% \( \text{V}_2\text{O}_5 \) loading. VCRS series of catalysts selectively produced phenol with high conversion rate. Conversion decreased after 8 wt. \% \( \text{V}_2\text{O}_5 \) loading. Praseodymia containing catalysts show very low catalytic activity than ceria catalysts.

The XRD analysis of VC catalysts evidenced that supported vanadia seems highly dispersed over the surface of the support for low loading and crystallization or compound formation occurs as the loading increases. Predominantly \( \text{CeVO}_4 \) formation observed at calcination temperature of 773 K in the \( \text{V}_2\text{O}_5/\text{CeO}_2 \) catalysts above 6 wt. \% \( \text{V}_2\text{O}_5 \) loading. UV-vis spectral
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analysis indicates tetrahedral $V^{5+}$ species for highly dispersed VC series of catalysts at lower loading. As the loading increases to 10 wt. % $V_2O_5$, agglomeration of vanadia particles envisaged from SEM pictures could reduce the number of active surface monolayer species, which results in polyvanadate species formation. A gradual reduction of surface area was observed after vanadia incorporation over ceria. This observation is parallel to the increased crystallite size observed from XRD data. $^{51}V$ MAS NMR and FT-Raman of the prepared catalysts exhibit features corresponding to CeVO$_4$. This trend becomes more evident as vanadium loading increases. These catalysts exhibit a change in the structure and catalytic performance during benzene oxidation, which is related to the deactivation of the catalysts with fall in phenol selectivity. During alkane oxidation reactions, the conversion decreases due to deactivation, due to the formation of CeVO$_4$, which is already reported$^{70,71}$.

Various studies have been attempted to understand the mechanism of aromatic oxidation over vanadium containing molecular sieves. Tetrahedral vanadium species ($V^{5+}$) with redox properties are the only active phase$^{72}$. The presence of vanadium must play a critical role in the oxidation reactions. However, the formation of bridged vanadia groups most likely represents the inactive catalyst form and these species, which are presumably responsible for the decrease in activity under high catalyst loading$^{73}$.

In ceria containing catalysts, a redox mechanism can be fairly operative at low loading since vanadia is highly dispersed over the support. Increasing vanadia content to submonolayer coverage causes the formation of CeVO$_4$ in which Ce is 3+ and V is 5+. It can possess oxygen insertion capacity through the redox pairs Ce$^{3+/4+}$ and V$^{5+/4+}$. However, high concentration at higher
loading, results in the formation of crystallites of CeVO₄, which makes availability of the active sites for redox mechanism difficult which in turn reduces the total activity. It has been related to the surface modification of vanadia/ceria catalysts through the facile oxygen vacancies creation since no indication of V⁴⁺ could be obtained from the characterization of catalysts. Mohamed et al.⁷⁴ studied the CO oxidation over MoO₃/CeO₂ catalysts and inferred that surface molybdate that permits the formation of Mo⁶⁺ in highly dispersed state beside the Ce³⁺/Ce⁴⁺ redox couples were responsible for the revealed catalytic activity. Higher conversion rate at low loaded catalysts can arise from the presence of monovanadate species as Ce-V-O however, the decrease in activity and phenol selectivity can be attributed to the presence of V-O-V species formed at higher loading. Phenol formed can be quickly oxidized to dihydroxyl benzene at the set conditions.⁷⁵ According to Ayusman et al.⁷⁶ over vanadia containing catalysts the drop-off in activity was attributed to equilibrium between the catalytically active monomeric vanadium species and an inactive dimer. The oxidation states in CeVO₄ are V⁶⁺ and Ce³⁺ and UV-vis analysis after reaction show no reduction of V⁵⁺ during oxidation reaction. It is assumed that the catalytic redox cycle on ceria-supported vanadia may be due to the redox cycle of cerium near vanadium; unlike the most supported vanadia catalysts, which work on the redox cycle of vanadium sites. A similar observation was reported for ceria supported chromia catalysts.⁷⁶ The EPR data also favour this interpretation. The interaction of ceria with vanadia stabilizes surface Ce³⁺ sites, which in turn moderates the valence change ability of the Ce³⁺/Ce⁴⁺ pair, as well as block the corresponding V redox pairs. Vanadium would moderate the liability of ceria oxygen sites.
In VCRS series of catalysts, conversion is found higher compared to VC series of catalysts. BET surface area and pore volume analysis shows high values for VCRS catalysts. Silica helps to form highly dispersed vanadia species by providing high surface area. Powder XRD suggested more dispersion of vanadia over CRS support than ceria alone. As evidenced from $^{29}$Si MAS NMR, no compound formation occurs between SiO$_2$ and supported V$_2$O$_5$. TPD-NH$_3$ analysis results a higher number of acid sites for VCRS catalysts than VC series of catalysts. Highly selective formation of phenol over VCRS catalysts is attributed to highly dispersed tetrahedral V$^{5+}$ surface species. Silica promotion of ceria makes the supported vanadia to be in amorphous state with the help of large number of silanol groups present in silica. According to Park et al. mesoporous molecular sieves make benzene molecule favourable to move easily towards active sites due to its large pore size and could provide more active sites because of very high surface area. Lower activity of microporous molecular sieves was attributed to lower number of silanol defect sites on the surface, where the vanadium ions can be anchored, in comparison with the mesoporous materials. The more surface vanadium species of V-MCM-41 resulted in higher catalytic activity. An important condition for the achievement of catalyst capable of activating H$_2$O$_2$ is site isolation to avoid extensive H$_2$O$_2$ radical decomposition. It was reported that titania based amorphous solids fail to promote oxidations with H$_2$O$_2$ because of its hydrophilic properties compared to the hydrophobic silicalites. According to Klein et al. hydrophilic sol-gel TiO$_2$-SiO$_2$ amorphous solids with more number of surface silica could enhance surface polarity which in turn could achieve good oxidation rates with H$_2$O$_2$. They also documented
that surface polarity can affect not only the reaction rate and selectivity but also the overall conversion and catalyst lifetime. According to Chiara et al.\textsuperscript{80} in oxidation of olefins the activity and selectivity of the catalyst and the extent of \( \text{H}_2\text{O}_2 \) decomposition seem to be controlled by an appropriate polarity of the medium, by the polarity/acidity of the surface, and by the possibility to carry out the reaction at lower temperatures where the acidity effects of \( \text{H}_2\text{O}_2 \) and the silica matrix could be minimized.

A good catalyst for partial oxidation must have two redox couples, one of which should have a reduction potential higher than the other one, in order to facilitate an efficient electron transfer and promoting the reoxidation of oxygen-inserting sites\textsuperscript{81}. The separation of the reduction temperatures observed in the TPR-\( \text{H}_2 \) experiments, which is related to the difference in the reduction potentials present in the supported catalyst, could correlate to the higher activity of VCRS catalysts than VC catalysts.

The X-ray diffraction pattern of praseodymia supported vanadia catalysts correspond to Pr\(_x\)V\(_2\)O\(_7\) type pyrovanadate structure formation as the vanadia loading increases. Pyrovanadates contain two tetrahedrally coordinated vanadium atoms connected by bridging oxygen in a V\(_2\)O\(_7^4\) unit, which consists mainly V-O-V bonds. BET measurements resulted low surface area compared to ceria containing catalysts. Supported VP and VPRS catalysts presents endotherm corresponding to pyrovanadate type formation, Pr\(_6\)V\(_2\)O\(_7\) depending upon the vanadia loading. The formation of silicate like Si-O-Pr configuration was evidenced from \( ^{29}\text{Si} \) MAS NMR studies for VPRS catalysts. The observed low activity of VP and VPRS catalysts can be attributed to the low oxygen storage property of praseodymia. Under reaction conditions the
redox behaviour of praseodymia is different from that of ceria. Ceria is relatively easy to reoxidise while with praseodymia the reoxidation is too slow to provide the necessary oxygen storage properties under reaction conditions. The oxidation of CO over Pd/praseodymia catalysts exhibited a similar behaviour. If Pr$_6$O$_{11}$ once reduced to Pr$_2$O$_3$ the reoxidation by exposure to O$_2$ is difficult.

5.7 CONCLUSION

Investigation of the one step liquid-phase oxidation of benzene to phenol by hydrogen peroxide on various rare earth oxide supported vanadia is described. Ceria containing catalysts are found to catalyze the oxidation with higher conversion rate than praseodymia catalysts. Among ceria catalysts VCRS series of catalysts exhibits higher conversion rate and phenol selectivity in comparison to VC catalysts. Praseodymia supported vanadia catalysts show negligible oxidation activity. Studies on influence of reaction parameters such as temperature, solvent, time and volume of oxidant, substrate and solvent suggests that these are crucial in determining catalytic efficiency in heterogeneous catalytic systems. The catalytic activity of the ceria containing catalysts was presumably related to the strong interaction between the support and vanadia as emphasized by means of FT-IR (V=O and V-O-Support linkages), UV-vis DRS (dispersed tetrahedral V$^{5+}$), XRD (crystallite size), EPR (Ce$^{3+}$/Ce$^{4+}$) and MAS NMR (V$^{5+}$) techniques. Comparatively very low activity of VP and VPRS catalysts can be attributed to the formation of poly vanadate species of the type V-O-V and Si-O-Pr species.
REFERENCES

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Chapter 5

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