Selective oxidation of natural resource is a task of key importance for producing oxygenates to be employed as building blocks in chemical processes that range from kilogram scale application in pharmaceuticals to thousand tonne scale in industries. Both the gas phase oxidation of volatile substrates and liquid phase high boiling compound benefit from using catalysts able to lower the activation energy. The oxidation of alcohols and polyols is of interest owing to large array of biological hydroxyl derivatives obtained from natural and renewable sources in large amounts. In particular selective oxidation can transform alcohols and polyols into corresponding carbonylic or carboxylic derivatives which both generally represent attractive chemicals for organic synthesis. This chapter deals with the selective oxidation of benzyl alcohol to benzaldehyde over transition metal modified pillared clays and porous clay heterostructures in liquid phase under mild reaction conditions using hydrogen peroxide as oxidant.
Chapter 7

7.1 Introduction

The oxidation of alcohols to aldehydes or ketones is one of the fundamental and important functional group transformation in organic synthesis [1-3]. The desired aldehyde, ketone, ester and acid products are valuable intermediates for the fine chemical, agrochemical, and pharmaceutical sectors, with allylic aldehydes in particular high value components used in the perfume and flavourings industries [4]. For example, crotonaldehyde is an important agrochemical and valuable precursor to the food preservative sorbic acid, while citronellyl acetate and cinnamaldehyde confer fruity and cinnamon flavors respectively. The commercial synthesis of such compounds usually utilizes toxic or hazardous stoichiometric oxidants such as chromates, permanganates etc [5]. In addition to safety considerations, such current technologies are also atom inefficient due to poor selectivity and additional separation and treatment steps to isolate the product. Hence the development of effective heterogeneous catalytic routes using environmentally benign and inexpensive oxidants such as oxygen, hydrogen peroxide is an important challenge as water is the only main side product of these reactions.

Benzaldehyde is a very important organic intermediate in the industry of perfumery, pharmaceutical, dyestuff, flavoring and agrochemicals [6]. It is traditionally produced by hydrolysis of benzyl chloride and by oxidation of toluene [7,8]. However, benzaldehyde produced from hydrolysis of benzyl chloride often contains traces of chlorine impurities and is associated with copious evolution of waste products and the oxidation of toluene is usually carried out in organic solvents which are environmentally undesirable. Catalytic vapor phase oxidation of benzyl alcohol to benzaldehyde is a widely investigated alternative process as it provides chlorine-free benzaldehyde
required in perfumery and pharmaceutical industries. Selective aerobic oxidations of benzyl alcohol were reported over platinum group metals (Pt, Pd) and their nanoparticles supported materials [9-12]. Particle size dependent catalytic selective oxidation of benzyl alcohol to benzaldehyde has been reported for Pd cluster SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}[13] and NaX zeolite supports [14]. Palladium nanoparticles anchored on multi-walled (MWCNT) and single walled carbon nanotubes (SWCNT) show better selectivity and activity for aerobic selective oxidation of benzyl alcohol and cinnamyl alcohol compared with activated carbon [15-16]. Gold nanoparticles confined within SBA-15 [17] and GMS [18] mesoporous silicates are very selective for the aerobic oxidation of benzyl alcohol to benzaldehyde. Gold on amino-modified fumed silica can efficiently catalyze primary alcohol oxidation selectively to their esters in a single step [19]. While the use of molecular oxygen or air as an oxidant is particularly attractive, it raises a number of challenges in terms of activating the oxygen bond at low temperature (typically $< 160 \degree$C) in a three-phase system with the suppression of the decomposition and the combustion of reactant molecules [20]. Because of the formation of carbon-oxides which leads to appreciable carbon loss in the vapor phase reaction, it is preferable to produce benzaldehyde more selectively by catalytic liquid phase oxidation of benzyl alcohol.

Both homogeneous and heterogeneous catalysts have been successfully applied in liquid phase oxidation of alcohols. Efficient homogeneous catalysts based on cobalt [21-22] copper [23] palladium [24-25] and ruthenium [26-27] have been reported. Recently, monometallic and bimetallic gold based materials in the liquid phase alcohol oxidation are successfully explored [28]. The beneficial role of gold is related to an enhanced rate and selectivity of the
oxidation more over to an improved resistance to catalyst deactivation. Because of obvious advantage of heterogeneous catalysts in product isolation and catalyst recycling and facility for continuous processing via packed bed flow reactors with additional safety, economic and environmental benefits, liquid phase oxidation of alcohols using solid catalysts has attracted much attention in recent years.

In the past decade, many heterogeneous catalytic systems had been explored for selective-oxidation of benzyl alcohol with \( \text{H}_2\text{O}_2 \) such as Au/U\(_3\)O\(_8\) [28], Cu, Ni and Co complexes encapsulated in zeolites [29], Fe-containing coordination polymers [30], hydrotalcites [31,32], layered-double hydroxides [33], Sn-MCM-48 [34] alkali treated ZSM-5 [35], Cu-SBA-15[36], transition metal incorporated SBA-15 [37], spinels and inverse spinels [38], V doped TiO\(_2\) [46]. Wang et al. reported a MCM-41 immobilized Cr (salen) catalyst for the oxidation of benzyl alcohol and the catalytic performance was improved by surface-modification with hydrophobic methyl group [39]. Recently metalloporphyrin complex, [tetrakis(\(o\)-chlorophenyl)porphyrinato] Ni(II) in functionalized rice husk silica [40], phosphotungstic acid immobilized on graphene oxide [41] were employed for the title reaction. Chen et al. developed a mesoporous polyoxometalate based ionic hybrid [TMGHA]\(_{2.4}\) H\(_{0.6}\)PW for catalyzing water-mediated triphase oxidations of alcohols with \( \text{H}_2\text{O}_2 \) [42]. Zhan et al. proposed a Langmuir Hinshelwood model for the oxidation of benzyl alcohol over bio reduced Au/TS-1 catalysts [43].

Most of the catalysts reported in literature for the alcohol oxidation is based on noble metal supported catalysts and air oxidation under high pressure which is very expensive. Here in we report liquid phase oxidation of benzyl alcohol over transition metal incorporated pillared clays and porous clay
heterostructures under ambient conditions as the procedure described in section 2.4.2. Effect of different parameters such as effect of solvent, temperature, oxidants and catalyst amount were studied. Reaction mainly yielded benzaldehyde which further undergoes oxidation to form benzoic acid.

7.2 Effect of Reaction Parameters

7.2.1 Effect of solvents

It has been reported that the solvents and their polarity have profound influence on liquid phase oxidation of benzyl alcohol. Oxidation of benzyl alcohol was done in various solvents and results are given in Figure 7.1.

Figure 7.1 Effect of solvents, Reaction temperature- 70°C, Catalyst amount- 100 mg, Benzyl alcohol-10 mmol, Benzyl alcohol to \( \text{H}_2\text{O}_2 \) ratio-1: 3, Time- 4 hour, Catalyst - V(5)ZrPC
The conversion of benzyl alcohol is very low when the reactions were done without solvents. Conversion is high in polar aprotic solvents such as acetonitrile and dioxane compared to nonpolar solvent hexane. In acetonitrile, the phase separation between benzyl alcohol and the aqueous oxidant was greatly decreased there by the easy transport of the active oxygen species for oxidation is permitted.

### 7.2.2 Effect of catalyst amount

The influence of catalyst amount on the oxidation of benzyl alcohol is depicted in Figure 7.2. The Conversion of benzyl alcohol increases with increase in catalyst amount due to the proportional increase of active sites with catalyst amount. The selectivity of benzoic acid increases with catalyst amount. Maximum conversion is obtained for 100 mg of catalyst but considering the selectivity factor, 80 mg was selected as optimum catalyst amount for further studies.

![Figure 7.2 Effect of catalyst weight, Reaction temperature- 70°C, Benzyl alcohol-10 mmol, Benzyl alcohol to H₂O₂ ratio - 1: 3, Time- 4 hour, Solvent-acetonitrile, Catalyst-V(5)ZrPC](image)

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**Chapter 7**

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Department of Applied Chemistry, CUSAT
7.2.3 Effect of temperature

It has been reported that the temperature has strong influence on the progress of benzyl alcohol oxidation, which is believed as a very slow, kinetically controlled reaction with the catalyst and oxidant H₂O₂. The effect of reaction temperature on the reaction was studied in the temperature range 40°C to 70°C keeping all other parameters constant and the results are presented in the Figure 7.3. The results suggest that conversion of benzyl alcohol increases with increase in temperature and reaches maximum at 70°C. This result is in accordance with earlier literature [44]. Further increase in temperature decreases the conversion. At higher temperature the self decomposition of H₂O₂ is prominent and it could not participate in the oxidation reaction. At higher temperature the evaporation of solvent is also high which may also result in the reduced conversion and hence 70°C was taken as optimum temperature. A slight increase in benzoic acid selectivity is observed with increase in temperature.

![Figure 7.3](image)

**Figure 7.3** Effect of temperature, Benzyl alcohol-10 mmol, Benzyl alcohol to H₂O₂ ratio -1: 3, Time- 4 hour, Solvent-acetonitrile, Catalyst amount-80 mg, Catalyst-V(5)ZrPC
7.2.4 Effect of oxidants

Liquid phase oxidation of benzylalcohol was done with two oxidants 30% H$_2$O$_2$ and TBHP keeping all other constraints constant. Comparable results were obtained for both oxidants with a small increment for TBHP. But the selectivity of benzaldehyde was less for oxidant TBHP than that of H$_2$O$_2$. Hence H$_2$O$_2$ is taken as the oxidant for further studies.

![Figure 7.4 Effect of oxidants, Benzyl alcohol-10 mmol, Benzyl alcohol to oxidant ratio- 1:3, Time- 4 hour, Solvent-acetonitrile, Catalyst amount-80 mg, Temperature -70°C, Catalyst-V(5)ZrPC](image)

7.2.5 Effect of oxidant ratio

The dosage of hydrogen peroxide is another important parameter that influence rate of the oxidation reaction. Effect of mole ratio of benzyl alcohol to hydrogen peroxide was investigated in the range of 1:1 to 1:5 and the results are given in Figure 7.5. A lower conversion is observed with 1:1 stoichiometric ratio. Conversion increases with increase in oxidant ratio and conversion is maximum at benzyl alcohol to hydrogen peroxide ratio 1:3. Further increase in oxidant ratio results in decrease in conversion which may be due to the auto
decomposition of H₂O₂ at higher concentration. The presence of excess oxidant favors the further oxidation of initially formed product benzaldehyde to benzoic acid. This observation was also in accordance with earlier reports [41].

![Figure 7.5](image)

**Figure 7.5** Effect of oxidant ratio, Temperature -70°C, Time- 4 hour, Solvent-acetonitrile, catalyst amount-80 mg, Benzyl alcohol-10 mmol, Oxidant-H₂O₂, Catalyst-V(5)ZrPC

### 7.2.6 Effect of time

The effect of time on the progress of benzyl alcohol oxidation and the selectivity to benzaldehyde at different reaction time is shown in Figure 7.6. Initial conversion of benzyl alcohol increase as reaction proceeds and maximum conversion is reached at fifth hour and then remained stable, which is due to the exhaustion of H₂O₂ by oxidation of benzyl alcohol and self-decomposition of H₂O₂. Not much increase in conversion was noted from fourth hour to fifth hour. However a prominent decrease in selectivity of benzaldehyde was noted. So the fourth hour is taken as optimum time for further studies. The selectivity of benzaldehyde decreases with time as benzaldehyde is further oxidized to benzoic acid.
7.2.7 Performance of different catalyst systems for the oxidation of benzyl alcohol

From the above observations it is clear that reaction conditions play a crucial role for the liquid phase oxidation of benzyl alcohol and its product distribution. Oxidation of benzyl alcohol was done over the prepared catalysts under optimized conditions described in the Table 7.1 as to obtain maximum conversion and selectivity.

Table 7.1 Optimised reaction conditions

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Optimized conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>70°C</td>
</tr>
<tr>
<td>Catalyst amount</td>
<td>80 mg</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>10 mmol</td>
</tr>
<tr>
<td>Oxidant (30% H₂O₂) ratio</td>
<td>1:3</td>
</tr>
<tr>
<td>Time</td>
<td>4 hour</td>
</tr>
<tr>
<td>Solvent</td>
<td>Acetonitrile</td>
</tr>
</tbody>
</table>
Oxidation of benzyl alcohol

Table 7.2 Effect of different catalysts on benzyl alcohol oxidation

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Conversion of benzyl alcohol (%)</th>
<th>Product distribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Benzaldehyde</td>
</tr>
<tr>
<td>ZrPC</td>
<td>21</td>
<td>95</td>
</tr>
<tr>
<td>Cu(1)ZrPC</td>
<td>33</td>
<td>92</td>
</tr>
<tr>
<td>Cu(3)ZrPC</td>
<td>48</td>
<td>90</td>
</tr>
<tr>
<td>Cu(5)ZrPC</td>
<td>58</td>
<td>92</td>
</tr>
<tr>
<td>Ni(1)ZrPC</td>
<td>29</td>
<td>93</td>
</tr>
<tr>
<td>Ni(3)ZrPC</td>
<td>32</td>
<td>91</td>
</tr>
<tr>
<td>Ni(5)ZrPC</td>
<td>45</td>
<td>88</td>
</tr>
<tr>
<td>V(1)ZrPC</td>
<td>33</td>
<td>97</td>
</tr>
<tr>
<td>V(3)ZrPC</td>
<td>49</td>
<td>93</td>
</tr>
<tr>
<td>V(5)ZrPC</td>
<td>66</td>
<td>91</td>
</tr>
<tr>
<td>Co(3)ZrPC</td>
<td>35</td>
<td>95</td>
</tr>
<tr>
<td>Co(5)ZrPC</td>
<td>47</td>
<td>92</td>
</tr>
<tr>
<td>FeAlPC</td>
<td>35</td>
<td>93</td>
</tr>
<tr>
<td>Ce(3)FeAlPC</td>
<td>43</td>
<td>95</td>
</tr>
<tr>
<td>CuZrSiPCH</td>
<td>49</td>
<td>96</td>
</tr>
<tr>
<td>NiZrSiPCH</td>
<td>47</td>
<td>97</td>
</tr>
<tr>
<td>CoZrSiPCH</td>
<td>56</td>
<td>93</td>
</tr>
<tr>
<td>VZrSiPCH</td>
<td>72</td>
<td>91</td>
</tr>
<tr>
<td>Nil</td>
<td>2</td>
<td>100</td>
</tr>
</tbody>
</table>

In all cases benzaldehyde was the major product and a small amount of benzoic acid was also detected. The long time paradox that why benzaldehyde readily undergoes autoxidation to form benzoic acid on exposure to air at room temperature and yet it can be formed in high yield from the oxidation of benzyl alcohol using a variety of procedures and catalysts have recently been resolved [45]. It is confirmed that benzyl alcohol (and a number of other
alcohols), even at low concentrations in benzaldehyde, inhibits the autoxidation of benzaldehyde to benzoic acid.

The bare ZrPC and ZrSiPCH have very low activity. Incorporation of transition metals improves the catalytic activity in both pillared clays and porous clay heterostructures. Among various metal loaded catalysts vanadium loaded pillared clays and porous clay heterostructures showed maximum activity. Vanadia and vanadium oxide supported catalysts have a prominent role in redox catalysis owing to easy oxidation, reduction and the existence of cation of different oxidation states as intermediates. The most important aspect of vanadia supported system is the selective oxidation activity towards partial oxidation products due to lattice oxygen mobility [47]. Very recently vanadium doped titania [46] and vanadium phosphorous oxides promoted by cobalt [48] were reported for benzyl alcohol oxidation with excellent activity and benzaldehyde selectivity. Copper loaded catalysts also showed remarkable activity owing to high redox and oxidation capabilities.

Figure 7.7 Correlation between activity and metal content
The conversion of benzyl alcohol increases with increase in metal content and the selectivity of benzaldehyde decrease with metal content. This may be due to further oxidation of benzaldehyde over the active metal species to benzoic acid. So attempt was made to correlate the activity of catalyst with metal content in metal loaded zirconium pillared clays (Figure 7.7) and a good correlation was obtained.

Porous clay heterostructures got higher conversion than pillared clays. For the same metal, the conversion of benzyl alcohol is higher in porous clay heterostructures than in pillared clays. This may be due to higher surface area and pore diameter of porous clay heterostructures which facilitate the easy diffusion of the products (benzaldehyde and benzoic acid). Lewis acid sites were believed as the active sites in catalytic oxidation of benzyl alcohol with H₂O₂ in polar solvents. In porous clay heterostructures the conversion of benzyl alcohol can be correlated with α-methyl styrene selectivity in cumene cracking reaction which corresponds to Lewis sites. Such correlation is not seen in metal loaded pillared clays.

![Figure 7.8 Correlation between activity and acidity](image-url)
Chapter 7

7.2.8 Leaching studies

A very important subject to be considered for the solid catalyst is the leaching phenomenon. Leaching can take place during a catalyzed reaction without an induction period and the nature of the reaction may gradually change from heterogeneous to homogeneous without any indication in the reaction profile. To prove the heterogeneous nature of the catalyst, the leaching studies of the two effective catalysts V(5)ZrPC, VZrSiPCH catalyst were carried out. The catalyst was removed by filtration after second hour from the reaction mixture and the mother liquor was again subjected for further reaction at the same conditions for an hour. The conversion remains more or less constant after the removal of the catalyst showing that metal ions were not leached from the catalyst surface during the oxidation process. The quantitative analysis of filtrate was also done which confirmed the absence of metal ions in the filtrate.

Table 7.3 Leaching studies

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Time (h)</th>
<th>Conversion of benzyl alcohol (%)</th>
<th>Product distribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Benzaldehyde</td>
</tr>
<tr>
<td>V(5)ZrPC</td>
<td>2</td>
<td>32</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>33</td>
<td>94</td>
</tr>
<tr>
<td>VZrSiPCH</td>
<td>2</td>
<td>36</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>36</td>
<td>93</td>
</tr>
</tbody>
</table>

7.2.9 Reusability studies

The advantages of heterogeneous catalysis include the easy separation of catalysts from the final reaction mixture and subsequent reusage of the catalysts. The recycling of the catalyst for the same reaction is also a measure of catalyst structural stability. To study the reusability, the catalysts were removed
from the reaction mixture after the reaction by filtration. It was thoroughly washed with acetone and dried in an air oven and activated for 3 hours at 400°C. The same catalyst was used again for carrying out another reaction under the same reaction conditions. The catalyst retained its activity even after fourth cycle. A slight decrease in selectivity of benzoic acid is observed after each cycle.

![conversion graph](image)

Figure 7.9 Reusability studies of VZrSiPCH for oxidation of benzyl alcohol.

7.3 Conclusions

- Various metal incorporated PILCs and PCHs were effectively utilised for the oxidation of benzyl alcohol under milder reaction conditions with green oxidant hydrogen peroxide.

- The imperative roles played by the various reaction conditions were established and various reaction conditions are optimized to get maximum conversion.

- In metal Incorporated PILCs conversion increases with increase in metal content and good correlation is obtained with conversion and metal content.
In metal incorporated PCHs a good correlation is obtained with conversion and methyl styrene selectivity in cumene cracking reaction.

Vanadium incorporated PILCs and PCHs were found to be the effective catalyst for the oxidation of benzyl alcohol.

Metal leaching studies revealed the true heterogeneous nature of the catalysts. The catalysts were found to be reusable and are resistant to rapid deactivation.

References


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