Chapter 3

Effect of preparation methods on physico-chemical properties and activity of Co$_3$O$_4$ catalyst for oxidation of lignin sub-structured compounds
3.1. INTRODUCTION

Selective catalytic transformations for obtaining valuable products from biomass are becoming increasingly important for the evolution of green processes [1-3]. Liquid phase catalytic oxidation of various lignin derived sub-structured compounds such as veratryl alcohol, vanillin alcohol, sinapyl alcohol, coniferyl alcohol, \( p \)-coumaryl alcohol, etc, give respective aldehydes (Figure 3.1) and acids. These are used as flavoring agents and also as important pharmaceutical intermediates e.g. veratryl aldehyde for the manufacture of angiocardiopathy drugs such as donepezil [4].

![Chemical structures of lignin derived sub-structured compounds](image)

**Figure 3.1.** Oxidation products of lignin derived sub-structured compounds

These lignin derived sub-structured compounds come from the processes such as alkaline pulping of lignin [5, 6], pyrolysis of dimeric lignin [5], hydrolysis of the alcell lignin (Scheme
3.1), etc. Ultimately, lignin depolymerization results into the breaking of the \( \beta-O-4 \) linkages to form monomeric and dimeric nonphenolic and phenolic sub-structured compounds as side products [2].

\[ \text{Lignin pretreatment, Pyrolysis, Hydrolysis} \]

\[ R = -\text{CH}_2, -\text{CHCH}_2, -\text{CHCH}_3 \]
\[ X = -\text{OCH}_3, -\text{H} \]
\[ Y = -\text{OCH}_3, -\text{OH}, -\text{H} \]
\[ Z = -\text{OCH}_3, -\text{H} \]

**Scheme 3.1.** Lignin bleaching/deggradation

Oxidation of lignin derived sub-structured compounds was conventionally carried out using homogeneous complexes of non-noble and noble metals like Co, Fe, V, Mn, V, Au and Re in
alkaline medium (Scheme 3.2), which pose serious environmental and operational problems as discussed in chapter 1 (Section 1.9) [7-9].

\[
\begin{align*}
&\text{ ROH } \\
&\text{ Z } \quad \text{ X } \\
\rightarrow \quad \text{ Catalyst} \\
&\text{ Base } \\
&\text{ RCHO } \\
&\text{ Z } \quad \text{ X } \\
&\text{ + } \\
&\text{ RCOOH } \\
&\text{ Z } \quad \text{ X }
\end{align*}
\]

\[
\begin{align*}
\text{ R} &= \text{-CH}_2, \text{-CHCH}_2, \text{-CH-CH}_3 \\
\text{ X} &= \text{-OCH}_3, \text{-H} \\
\text{ Y} &= \text{-OCH}_3, \text{-OH, H} \\
\text{ Z} &= \text{-OCH}_3, \text{-H}
\end{align*}
\]

Scheme 3.2. Catalytic oxidation of lignin derived sub-structured compounds

In this work, I prepared heterogeneous oxidation catalysts involving metal oxides such as Co$_3$O$_4$, ZnCo$_2$O$_4$, CoAl$_2$O$_4$ and cobalt aluminosilicates with different silica/alumina ratios (Chapter 2). In recent years, interest in nano-scale metal oxides has been growing because of their relatively enhanced redox ability and electrochemical properties as compared to those of their bulk forms [10]. For this reason, various morphologies of Co$_3$O$_4$ such as nano rods and nano spheres with meso and/or microporous characteristics are reported by using different synthesis methods [10-15]. These are (i) hydrothermal [16, 17], (ii) combustion [18], (iii) micro emulsion [19], (iv) chemical spray pyrolysis [20], (v) chemical vapor deposition [21], (vi) ionic liquid assisted synthesis [22], (vii) an ultrasonic assisted route [23], (viii) ball milling [24], (ix) microwave-assisted route [25] and (x) mechanochemical [26]. However, most of these methods require
toxic, costly reagents, high temperatures, expensive sophisticated instruments and long reaction times. Thus, a simple, inexpensive and nontoxic route for the preparation Co₃O₄ nano particles at relatively low temperature is desirable. We have therefore preferred the preparation methods such as co-precipitation [10, 11], sol-gel [27, 28], and thermal decomposition [29, 30].

Among the preparation methods studied in this work, Co₃O₄ prepared via co-precipitation gave rod-like morphology in nano regime (10-20 nm) which was not observed either by sol-gel or by thermal decomposition. We report here for the first time, the use of molecular oxygen without using any alkali for oxidation of veratryl alcohol to veratryl aldehyde over non noble metal Co₃O₄ catalysts [10]. The nano-structured Co₃O₄ (Co-3C-a) catalyst showed 75% and 38% conversion of veratryl alcohol in toluene and water respectively, with complete selectivity to veratryl aldehyde. We also investigated the change in catalyst activity due to change in catalyst morphology which in turn was found to be a function of pH, calcination temperature and time. Co-3C-a catalyst was also tested for the liquid phase oxidation of other lignin sub structure compounds under optimized reaction conditions that showed the conversion >50%. The catalysts were characterized by various techniques like N₂-adsorption-desorption isotherm, XRD, XPS, TG-DTA, FT-IR, HRTEM, temperature programmed reduction and oxidation (H₂/O₂ TPR/TPO) measurement, cyclic voltammogram (CV), FT-EXAFS and EPR. The stability of the catalyst was studied by the catalyst recycle experiments.

3.2. EXPERIMENTAL

Details of preparation of nano Co₃O₄ via simultaneous co-precipitation and digestion, sol-gel and thermal decomposition methods are described in section 2.2. The prepared catalysts were evaluated for the liquid phase oxidation of veratryl alcohol and lignin derived phenolic and non
phenolic sub structured compounds. For this purpose, the experimental set up used and experimental procedure are described in section 2.4 while the catalyst characterization and analytical methods are given in sections 2.3 and 2.5 respectively.

3.3. RESULTS AND DISCUSSION

The results in this section discussed are on the characterization of Co\textsubscript{3}O\textsubscript{4} catalysts prepared by various methods. At the same time, results on effect of preparation parameters on the physico-chemical characteristics are also presented. Finally, activity comparison of Co\textsubscript{3}O\textsubscript{4} samples prepared by various methods is presented to understand the structure-activity relationship.

3.3.1. Co\textsubscript{3}O\textsubscript{4} prepared by simultaneous co-precipitation and digestion method

3.3.1.1. Surface area

The influence of pH on the porous structure and particle size of spinel Co\textsubscript{3}O\textsubscript{4} samples prepared by co-precipitation method was studied in a pH range of 7-8 (Co-3C-a), 9-10 (Co-3C-b), 11-12 (Co-3C-c) and 13-14 (Co-3C-d). The effect of calcination temperature on the physico-chemical properties of Co\textsubscript{3}O\textsubscript{4} was also studied at 573 K and 873 K. The textural properties of these samples examined by the nitrogen adsorption-desorption measurements and the results are shown in Table 3.1 and Figures 3.2(a-d). All the samples showed type IV isotherm [31], showing the similar nature of mesoporous material being formed in the pH range of 8 to 10 (Co-3C-b) while at pH =12, the sample (Co-3C-c) showed the decrease in pore diameter from 16.7 to 2.5 nm indicating a change of nature of material from mesoporous to microporous (Figures 3.2(a-c)). The hysteresis feature of the Co\textsubscript{3}O\textsubscript{4} sample at the relative pressure of 0.6-0.9 was classified as the H\textsubscript{3} loop, suggesting the presence of aggregates of nano tube particles with slit-shaped pores.
A sharp decrease in surface area (110 to 58.4 m$^2$/g) and pore diameter (16.7 to 2.5 nm) was observed for increase in pH from 8 to 12 while further increase in pH to 14 showed higher surface area 121.6 m$^2$/g and pore diameter of 2.5 nm. Initial decrease in surface area and pore diameter with increase in pH from 8 to 12 might be the result of aggregation of Co$_3$O$_4$ nano particles which induces disappearance of spaces between Co$_3$O$_4$ nano particles that was also observed in HRTEM and discussed later in Section 3.3.1.7 [32]. Interestingly, increase in pH to 14 resulted in increase in surface area also upto 121.6 m$^2$/g for the sample (Co-3C-d), due to increase in concentration of (OH)$_2$ which might restrict the aggregation of primary Co(OH)$_2$ particles.

**Table 3.1.** Textural properties of catalysts prepared at different pH and calcination temperatures

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>pH</th>
<th>Calcination temperature (K)</th>
<th>Surface area (m$^2$/g)</th>
<th>Pore size, BJH$_{DEP}$ (nm)</th>
<th>Pore volume, BJH$_{DEP}$ (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-3C-a</td>
<td>8</td>
<td>573</td>
<td>110.0</td>
<td>16.7</td>
<td>1.30</td>
</tr>
<tr>
<td>Co-3C-b</td>
<td>10</td>
<td>573</td>
<td>74.5</td>
<td>15.1</td>
<td>0.71</td>
</tr>
<tr>
<td>Co-3C-c</td>
<td>12</td>
<td>573</td>
<td>58.4</td>
<td>2.5</td>
<td>0.33</td>
</tr>
<tr>
<td>Co-3C-d</td>
<td>14</td>
<td>573</td>
<td>121.6</td>
<td>2.5</td>
<td>0.34</td>
</tr>
<tr>
<td>Co-6C-a</td>
<td>8</td>
<td>873</td>
<td>24.5</td>
<td>1.8</td>
<td>0.11</td>
</tr>
</tbody>
</table>

From the pore size distribution curve (Figure 3.3), it was found that all the samples showed a bimodal pore distribution determined by using the Barrett-Joyner-Halenda (BJH) method, that is smaller pores in the region of 2-5 nm and larger pores ranging from 5 to 30 nm. Sample (Co-3C-a) calcined at 573 K (pH= 7-8, calcination time =5 h) showed type IV isotherm whereas sample
(Co-6C-a) calcined at 873 K (pH= 7-8, calcination time =5 h) showed a mixed behavior of type I and type IV isotherms (Figure 3.2(e)) [31], showing the shifting of mesoporous to microporous nature with rise in calcination temperature from 573 to 873 K. A sharp decrease in surface area (110 to 24.5 m²/g) and pore diameter (16.7 to 1.8 nm) were also observed at higher calcination temperature of 873 K (Table 3.1, Entries 1 and 5, Figure 3.4). Decrease in surface area and pore diameter at higher calcination temperature might be the result of restructuring of Co₃O₄ nano particles which induces disappearance of spaces between Co₃O₄ nano particles [33]. The above observations establish that the textural properties of catalyst could be tuned by changing the pH during catalyst preparation and pretreatment conditions such as calcination temperature after the preparation. These variations in textural properties are expected to affect the catalytic performance of the same catalyst as discussed in Section 3.3.4.

![Graph](a)
Chapter 3

Effect of preparation methods...

(b)

Volume adsorbed [cc/g]

Partial Pressure, [P/Po]

(c)

Volume adsorbed [cc/g]

Partial Pressure, [P/Po]
Figure 3.2. Adsorption isotherm of (a) Co-3C-a, (b) Co-3C-b, (c) Co-3C-c, (d) Co-3C-d and (e) Co-6C-a samples
Figure 3.3. Pore size distribution of (a) Co-3C-a, (b) Co-3C-b, (c) Co-3C-c and (d) Co-3C-d samples

Figure 3.4. Pore size distribution of (a) Co-3C-a and (b) Co-6C-a samples
3.3.1.2. X-ray diffraction (XRD)

The powder X-ray diffraction patterns of spinel Co₃O₄ samples prepared at different pH values, calcination temperatures and time are shown in Figure 3.5(a-d). The calculated lattice parameter for all the samples, \( a = 8.087 \, \text{Å} \) corresponds to the cubic type which was in good agreement with the reported value for Co₃O₄ powder \( (a = 8.084 \, \text{Å}; \text{JCPDS } \# \, 9-418) \), except as-dried Co-a and Co-d samples (Figure 3.5(c-d)) [11, 34]. For all the samples except as-dried samples (Co-a and Co-d), the peaks at \( 2\theta = 19.2^\circ \) (111), 31.2° (220), 36.84° (311), 44.84° (400), 55.65° (422), 59.42° (511) and 65.21° (422) reveal the reflections of a spinel Co₃O₄ (Figure 3.5b). For the change in pH from 8 to 12, intensity of the peaks at \( 2\theta = 19.2^\circ \) (111), 31.2° (220), 36.84° (311), 44.84° (400), 55.65° (422), 59.42° (511) and 65.21° (422) increased while at pH=14, broad and less intense peaks appeared at \( 2\theta = 19.2^\circ \) (111), 31.2° (220), 36.84° (311), 44.84° (400), 55.65° (422), 59.42° (511) and 65.21° (422). Initially at pH=8, concentration of (OH) is less however with increase in pH from 8 to 12, concentration of (OH) increased, as a result of which the primary particles of Co(OH) orientated in such way that crystallite size increased from 12 to 85 nm in case of Co-3C-a, Co-3C-b and Co-3C-c samples. However, further increase in concentration of (OH) might control the orientation of primary particles of cobalt hydroxyl carbonate (Co(OH) CO₃) (20-40 nm) that showed less intense peaks as in case of Co-3C-d (pH=14) sample (Table 3.2). The crystallite size determined by Scherrer equation (2.4) was found to be 12-38, 20-60, 30-85 and 20-40 nm, observed in case of the Co-3C-a, Co-3C-b, Co-3C-c and Co-3C-d samples and matched very well with the HRTEM results.

The XRD patterns of as-dried samples of Co-a (pH = 8) calcined at different temperatures from 573 K to 873 K at constant calcination time of 5 h is shown in Figure 3.5b. The increase in
calcination temperature (573-873 K) caused gradual increase in intensity and the slight decrease in the width of peaks at $2\theta = 19.2^\circ$ (111), $31.2^\circ$ (220), $36.84^\circ$ (311), $44.84^\circ$ (400), $55.65^\circ$ (422), $59.42^\circ$ (511) and $65.21^\circ$ (422). Crystallite sizes of Co-3C-a, Co-4C-a, Co-5C-a and Co-6C-a calculated using the Scherrer equation were found to be in the range of 12-38, 15-40, 15-52 and 20-70 nm respectively (Table 3.2). Thus, increase in crystallite size for Co-6C-a was mainly due to restructuring of the material at 873 K [35].

The XRD pattern of as-dried samples of Co-a (pH=8) and Co-d (pH=14) calcined at constant 573 K temperature with varying calcination times from 1 to 6 h are shown in Figures 3.5c-d. The intensity of the peaks at $2\theta = 19.2^\circ$ (111), $31.2^\circ$ (220), $36.84^\circ$ (311), $44.84^\circ$ (400), $55.65^\circ$ (422), $59.42^\circ$ (511) and $65.21^\circ$ (422) increased with increase in calcination time from 1 to 6 h in both Co-a and Co-d samples. With increase in calcination time from 2 to 6 h (Co-a), crystallite size of Co$_3$O$_4$ increased from 5-25 nm to 15-52 nm. Similarly, in case of Co-d (2 to 6 h) samples also crystallite size increased from 5-20 nm to 18-34 nm (Table 3.2). This increase of crystallite size is related with the increase in peak intensity and corresponds to the transformation of as-dried cobalt hydroxy carbonate to spinel Co$_3$O$_4$[36].
Figure 3.5a. XRD of spinels (A) Co-3C-a, (B) Co-3C-b, (C) Co-3C-c and (D) Co-3C-d catalysts

Figure 3.5b. XRD of spinels (A) Co-3C-a, (B) Co-4C-a, (C) Co-5C-a and (D) Co-6C-a catalysts
Figure 3.5c. XRD of spinels (A) Co-a as-dried, (B) Co-3C-a-1, (C) Co-3C-a-2, (D) Co-3C-a-3, (E) Co-3C-a-4, (F) Co-3C-a-5 and (G) Co-3C-a-6 catalysts.

Figure 3.5d. XRD of spinels (A) Co-d as-dried, (B) Co-3C-d-1, (C) Co-3C-d-2, (D) Co-3C-d-3, (E) Co-3C-d-4, (F) Co-3C-d-5 and (G) Co-3C-d-6 catalysts.
Table 3.2. Crystallite sizes of the prepared samples as determined by the Scherrer equation

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Crystallite Size (nm)</th>
<th>Catalysts</th>
<th>Crystallite Size (nm)</th>
<th>Catalysts</th>
<th>Crystallite Size (nm)</th>
<th>Catalysts</th>
<th>Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-3C-a</td>
<td>12-38</td>
<td>Co-3C-a</td>
<td>12-38</td>
<td>as-dried</td>
<td>ND</td>
<td>as-dried</td>
<td>ND</td>
</tr>
<tr>
<td>Co-3C-b</td>
<td>20-60</td>
<td>Co-4C-a</td>
<td>15-40</td>
<td>Co-3C-a-1</td>
<td>ND</td>
<td>Co-3C-d-1</td>
<td>ND</td>
</tr>
<tr>
<td>Co-3C-c</td>
<td>30-85</td>
<td>Co-5C-a</td>
<td>15-52</td>
<td>Co-3C-a-2</td>
<td>5-25</td>
<td>Co-3C-d-2</td>
<td>5-20</td>
</tr>
<tr>
<td>Co-3C-d</td>
<td>20-40</td>
<td>Co-6C-a</td>
<td>20-70</td>
<td>Co-3C-a-3</td>
<td>6-30</td>
<td>Co-3C-d-3</td>
<td>8-22</td>
</tr>
</tbody>
</table>

- - - - - Co-3C-a-4 9-32 Co-3C-d-4 12-25
- - - - - Co-3C-a-5 12-38 Co-3C-d-5 15-28
- - - - - Co-3C-a-6 15-52 Co-3C-d-6 18-34

3.3.1.3. X-ray photoelectron spectroscopy (XPS)

In order to study the oxidation states of various Co species formed under various preparation conditions of co-precipitation method, the Co 2p XPS spectra of Co-3C-a, Co-3C-b, Co-3C-c and Co-3C-d samples were observed. As can be seen from Figure 3.6a, the Co 2p XPS contains the Co 2p\textsubscript{3/2} and Co 2p\textsubscript{1/2} core level peaks at binding energies of 779.3 and 794.4 eV having a difference of 15.1 eV respectively, in all the samples [11]. The Co 2p\textsubscript{3/2} peak on deconvolution gives two peaks at binding energies of 779.4 and 781.9 eV which correspond to Co\textsuperscript{3+} and Co\textsuperscript{2+} species (Figure 3.6b). This evidences the formation of spinel Co\textsubscript{3}O\textsubscript{4} in all the samples [37, 38].

The surface compositions of fresh and used samples of active Co-3C-a catalyst in different solvents were investigated by deconvolution of Co2p\textsubscript{3/2} and O1s peaks (Figure 3.7(a-b)). The oxygen peak at 529.3 eV was attributed to the lattice oxygen (LO) of oxides of both tetrahedral
Co\(^{2+}\) and octahedral Co\(^{3+}\), while peak at 531.3 eV was assigned to the adsorptive oxygen (AO) due to formation of Co(OH)\(_2\) (Figure 3.7(b)) [39-41]. The surface composition calculated in terms of atomic percentage was quantified by atomic sensitivity factor and area under the curve after deconvolution of Co2p\(_{3/2}\) and O1s spectra (Figure 3.8) [42-45]. The atomic sensitivity factors (ASF) for cobalt and oxygen were 3.88 and 0.66 ASF respectively [46-48]. The fresh Co3C-a catalyst showed 40% cobalt surface composition (CSC) consisting of the Co\(^{2+}\) (13%) and Co\(^{3+}\) (27%) together while, remaining 60% included AO and LO with 44% and 16% (Figure 3.8). This evidenced the formation of stoichiometric AB\(_2\)O\(_4\) type spinel (CoOCo\(_2\)O\(_3\)). The polar and non polar solvents were used to identify the species participating during the reaction. The used catalyst in toluene solvent showed decreased CSC from 40% to 25% (Co\(^{2+}\) (5%), Co\(^{3+}\) (20%)) consequently AO/LO composition increased to 75%, when catalytic activity was 75% as shown in section 3.3.4.3.5, indicating utilization of both CSC and AO/LO species during the reaction. However, in water as a solvent, CSC and AO/LO remained almost the same as that for the fresh catalyst 43% (Co\(^{2+}\) (15%), Co\(^{3+}\) (28%)) and 57% of AO/LO when catalytic activity was only 38%. In order to know CSC and AO/LO composition at intermediate stage in toluene solvent, timely withdrawn samples (from the reaction) containing reactant and the catalyst were taken and the catalyst was filtered, washed by toluene and the surface composition was determined by XPS (when catalytic activity was 40% equivalent to that in water) (Figure 3.8). CSC was found to be 50% (Co\(^{2+}\) 17%, (Co\(^{3+}\) 33%) and AO/LO oxides composition was 50% (24 and 26%). These compositions were almost equivalent to the compositions found in fresh sample separated from the reaction crude in water medium. The CSC ratios in methanol and ethanol solvents were found to be 57% [(Co\(^{2+}\) 17%, (Co\(^{3+}\) 40%) and 31% [(Co\(^{2+}\) 11%, (Co\(^{3+}\) 20%)] respectively (Figure 3.8). Thus, contribution of CSC and AO/LO species towards oxidative
dehydrogenation reaction was found to depend on the reaction medium [49]. The above observations established that similar types of surface species of the catalyst may be active during the reaction in polar as well as in non polar solvent however, the change in the concentration of these active species varied as per the reaction medium.

Figure 3.6a. XPS of (A) Co-3C-a, (B) Co-3C-b, (C) Co-3C-c and (D) Co-3C-d samples

Figure 3.6b. Deconvolution spectra of Co2p$_{3/2}$
Figure 3.7. XPS deconvoluted (a) Co2p$_{3/2}$ and (b) O1s peaks of Co-3C-a-Fresh, Co-3C-a-Toluene, Co-3C-a-%Toluene, Co-3C-a-Water, Co-3C-a-Ethanol and Co-3C-a-Methanol samples.

Figure 3.8. Quantification of surface active species in Fresh (Co-3C-a) and used Toluene (Co-3C-a), %Toluene (Co-3C-a), Water (Co-3C-a), Ethanol (Co-3C-a), Methanol (Co-3C-a) samples.
### 3.3.1.4. Fourier transform Extended X-ray absorption fine structure (FT-EXAFS)

FT-EXAFS was studied to understand the extent of the structural disorder in fresh Co-3C-a, Co-6C-a and used samples of Co-3C-a in toluene, water, methanol and ethanol solvents and the results are shown in Figure 3.9. All the samples showed first FT peak at 1.52 Å corresponding to Co-O bond and second peak at ~2.4 Å (split in to 2.45 Å and 3.04 Å) assigned to Co-Co and Co-O bonds. While, third peak at 4.6 Å was assigned to the metallic Co-Co bond [34, 50]. The main inter atomic distances between Co and oxygen in case of used Co-3C-a and that for Co-6C-a sample calcined at high temperature (873 K) were almost identical to the fresh Co-3C-a sample (Figure 3.9).

**Figure 3.9.** EXAFS of (A) Fresh Co-3C-a, (B) Fresh Co-6C-a, (C) Used Co-3C-a toluene, (D) Used Co-3C-a water, (E) Used Co-3C-a methanol and (F) Used Co-3C-a ethanol samples

### 3.3.1.5. Thermo gravimetric analysis (TGA)

TG-DTA curves of the as-dried Co-a (pH =8), Co-b (pH =10), Co-c (pH =12) and Co-d (pH =14) samples are shown in Figure 3.10. These catalysts showed weight losses in two-steps. The first continuous weight loss of 37%, 30%, 8% and 5% was observed from room temperature to 373 K
due to the loss of physically adsorbed/trapped water molecules in meso and micro pores of all the samples [34, 36]. The gradual decrease in weight loss might be due to the gradual decrease in pore diameter (16.7-2.5 nm) and pore volume (1.3-0.33 cm$^3$/g) with change in pH from 7 to 14. This resulted in decrease in the extent of physically adsorbed water. While, in the second step, weight losses of 11.4%, 17%, 18.5% and 17.6% for the respective catalysts below 540 K temperature were due to the decomposition of carbonate anions and dehydroxylation [34, 36]. Based on these observations, calcination temperature for the formation of spinel was chosen as 573 K in all the samples.

![Figure 3.10. TG-DTA profile of (A) Co-a, (B) Co-b, (C) Co-c and (D) Co-d as-dried samples](image-url)
3.3.1.6. Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra of Co-3C-a, Co-3C-b, Co-3C-c and Co-3C-d samples showed two distinct bands at 568 and 660 cm\(^{-1}\) assigned to stretching vibrations of the metal-oxygen bonds (Figure 3.11). The peak at 568 cm\(^{-1}\) corresponds to Co\(^{3+}\) in an octahedral position while the other peak at 660 cm\(^{-1}\) corresponds to the Co\(^{2+}\) in a tetrahedral position confirming the formation of Co\(_3\)O\(_4\) spinel in all the samples [51, 52]. The broad peaks at 3460 and 1619 cm\(^{-1}\) were attributed to metal hydroxyl stretching vibrations in all the samples, however in case of Co-3C-a and Co-3C-d samples, additional low intensity weak peak at 3734 cm\(^{-1}\) was observed which is assigned to metal hydroxyl stretching vibrations [53, 54], whereas this peak (3734 cm\(^{-1}\)) was not observed in case of Co-3C-b and Co-3C-c samples. The presence of additional surface hydroxyl (3734 cm\(^{-1}\)) species at pH 8 and 14 may be probably due to better control of pH and in-situ generated hydroxyl species which might help to control the orientation of particles in the nano regime as observed in HRTEM. While hydroxyl bending vibration at 1061 cm\(^{-1}\) was observed only in Co-3C-a sample [53, 54]. The corresponding peaks in all used catalysts after the first recycle also remained intact indicating that the catalyst was stable under the reaction conditions (Figure 3.12).
Figure 3.11. FTIR profile of (A) Co-3C-a, (B) Co-3C-b, (C) Co-3C-c and (D) Co-3C-d samples

Figure 3.12. FTIR profile of (A) Co-3C-a fresh, (B) Co-3C-a used, (C) Co-3C-b fresh, (D) Co3C-b used, (E) Co-3C-c fresh, (F) Co-3C-c used, (G) Co-3C-d fresh and (H) Co-3C-d used samples
3.3.1.7. **High resolution transmission electron microscopy (HR-TEM)**

The morphologies along with the particle sizes of the catalysts prepared at various pH values ranging from 8 to 14 were examined by HR-TEM (Figure 3.13 (A-D)). Co-3C-a (pH=8) sample showed nano rod morphology having length in the range of 10-20 nm (Figure 3.13, A). Increase in pH from 8 to 10 (Co-3C-b) resulted in increase in the particle length upto 20-60 nm (Figure 3.13, B). Whereas Co-3C-c sample (pH=12) showed rod shape as well as agglomerated elongated spherical particles in the range of 20-80 nm (Figure 3.13, C). The sample prepared at pH=14 (Co-3C-d) showed distinctly separated rod shape as well as elongated spherical particles having diameters in the range of 25-30 nm (Figure 3.13, D). However with increase in calcination temperature from 573 to 873 K, increase in length in the range of 55-65 nm was observed for Co-6C-a sample, which is in good agreement with the XRD results (Figure 3.13, E) [36]. The sample calcined at 573 K for 1 h (Co-3C-a-1) showed rod length in the range of 5-10 nm (Figure 3.13, F). The increase in calcination time from 1 to 5 h caused increase in rod length in the range of 10-20 nm. The characteristic planes obtained from the SAED image and ‘d’ spacings of the pattern of fringes (Figure. 3.13 (A-F)) were found to be due to the planes (111), (220), (311), (400), (422), (511) and (422), which matched with the XRD data confirming the perfect orientation of the particles in spinel Co$_3$O$_4$ for all the samples.
Chapter 3

Effect of preparation methods …..
Figure 3.13. HRTEM of (A) Co-3C-a, (B) Co-3C-b, (C) Co-3C-c, (D) Co-3C-d, (E) Co-6C-a and (F) Co-3C-a-1 samples

3.3.1.8. Energy dispersive X-ray (EDX)

Figure 3.14 shows EDX of Co-a, Co-b, Co-c and Co-d samples confirming the presence of cobalt, oxygen, carbon elements and absence of any residual potassium.
3.3.1.9. Temperature programmed reduction / Temperature programmed oxidation (TPR/TPO)

The reducibility of the catalysts prepared at various pH (7-14) and calcined at 573 K and 873 K was studied by H₂-TPR (Figures 3.15 and 3.16). The peaks observed in the range of 450-600 K were attributed to the reduction of trivalent cobalt oxide (Co₃O₄) to divalent cobalt oxide (CoO). Another broad peak in a higher temperature range of 600-850 K in all the samples was attributed to the reduction of divalent cobalt oxide (CoO) to metallic cobalt (Co⁰) [51, 55]. The slight shift in the first peak from temperature 533 to 538 and 546 K for the samples Co-3C-a, Co-3C-b and Co-3C-c, were observed with a change in pH from 8 to 12, while for the sample prepared at pH=14, the peak appeared at the same temperature of 533 K as that for the sample prepared at pH= 8. This slight increase in temperature for reduction for the samples Co-3C-b and Co-3C-c might be due to the increase in crystallite sizes from ~12-40 to ~30-85 nm as observed in XRD and HRTEM, which might require higher temperature for reduction of the bigger particles [56].

Figure 3.14. EDX of (A) Co-a, (B) Co-b, (C) Co-c and (D) Co-d samples
Co-3C-a sample showed 435 mmol of H\textsubscript{2} up take (Table 3.3) while, with change in pH from 8 to 12 for the preparation of Co-3C-b and Co-3C-c samples, lower H\textsubscript{2} up take of 251 mmol and 176 mmol was observed as compared to Co-3C-a sample (Table 3.3). This was due to the aggregation of primary particles (cobalt hydroxyl carbonate) which also exhibited decrease in surface area (74.5 and 58.4 m\textsuperscript{2}/g for Co-3C-b and Co-3C-c samples respectively). Co-3C-d (prepared at pH=14) sample showed 347 mmol of H\textsubscript{2} up take which was also lower than that for Co-3C-a sample (Table 3.3). The Co-6C-a and Co-6C-d (calcined at 873 K) samples showed shift in reduction peaks to the higher temperatures of 567 and 570 K respectively than that for Co-3C-a and Co-3C-d samples (calcined at 573 K) (Figure 3.16, B). The slight shift in reduction peak to the higher temperature might be due to the increase in crystallite size from 12-32 to 20-70 nm and from 20-40 to 30-70 nm as confirmed by XRD and HRTEM. Calcination at high temperature (873 K) caused decrease in H\textsubscript{2} up take from 435 to 304 mmol and from 347 to 243 mmol for the samples Co-6C-a and Co-6C-d respectively (Table 3.3). ~30\% lower reducibility of 873 K calcined samples (Co-6C-a and Co-6C-d) than those calcined at 573 K (Co-3C-a and Co-3C-d) was due to the re-structuring of primary particles at higher temperature (873 K) and decrease in surface area (from 110 to 24.5 m\textsuperscript{2}/g and 121 to 23.5 m\textsuperscript{2}/g for Co-6C-a and Co-6C-d samples respectively) resulting into incomplete reduction of bulk particles. The above observation shows that the extent of reducibility depends mainly on the calcination temperature and pH.
Figure 3.15. TPR profiles of (A) Co-3C-a, (B) Co-3C-b, (C) Co-3C-c and (D) Co-3C-d samples

Figure 3.16. TPR profiles of (A) Co-3C-a, (B) Co-6C-a, (C) Co-3C-d and (D) Co-6C-d samples

The ability of oxidation of pre-reduced catalysts prepared at various pH (7-14) and calcined at 573 K and 873 K, was also studied using TPO technique and the results are shown in Figures 3.17 and 3.18. The peak in a range of 373-430 K in all the samples was attributed to the oxidation of metallic cobalt (Co°) to divalent cobalt oxide (CoO). Another broad peak appearing
in the range 470-690 K in all the samples indicates the oxidation of divalent cobalt oxide (CoO) to trivalent cobalt oxide (Co$_3$O$_4$) [52, 53]. The slight shift in the first oxidation peak (curve A) from temperature 410 to 423, 439 and 420 K (curves B, C and D respectively) were observed with change in pH from 8 to 14 used in the preparation protocol. This slight increase in oxidation temperature might be due to the increase in crystallite size and change in morphology of the particles, which requires higher temperature for oxidation [56]. Co-3C-a sample showed 20.6 mmol of O$_2$ up take (Table 3.3), while Co-3C-b and Co-3C-c samples showed 16.1 and 9.9 mmol O$_2$ up take respectively. This could be due to decrease in surface area of the samples by changing the pH from 8 to 12. While, Co-3C-d sample showed 17.8 mmol of O$_2$ up take which was less than that required for Co-3C-a and higher than Co-3C-b and Co-3C-c samples (Table 3.3). The O$_2$ consumption of these samples was much less than H$_2$ consumption observed in TPR. This might be due to the fact that oxygen having the co-ordinative nature hence forming a multi-metal nucleated species and also due to distortion of the surface during chemical absorption [41]. Calcination at higher temperature of 873 K caused decrease in O$_2$ up take from 20.6 to 18.6 and from 17.8 to 14.5 mmol in case of Co-6C-a and Co-6C-d samples respectively (Table 3.3). The lower O$_2$ up take by sample calcined at higher temperatures was also due to the decrease in surface area values indicating that higher oxidizing ability of Co-3C-a catalyst was due to its rod-like morphology, appropriate surface area and higher redox ability.
Figure 3.17. TPO profiles of (A) Co-3C-a, (B) Co-3C-b, (C) Co-3C-c and (D) Co-3C-d samples

Figure 3.18. TPO profiles of (A) Co-3C-a, (B) Co-6C-a, (C) Co-3C-d and (D) Co-6C-d samples
Table 3.3. \( \text{H}_2/\text{O}_2 \) uptake profile of catalysts prepared at various pH

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalysts</th>
<th>pH</th>
<th>Surface area (m(^2)/g)</th>
<th>TPR</th>
<th>TPO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Temperature (K)</td>
<td>( \text{H}_2 ) (mmol)</td>
</tr>
<tr>
<td>1</td>
<td>Co-3C-a</td>
<td>8</td>
<td>110.0</td>
<td>440-750</td>
<td>435</td>
</tr>
<tr>
<td>2</td>
<td>Co-3C-b</td>
<td>10</td>
<td>74.5</td>
<td>440-820</td>
<td>251</td>
</tr>
<tr>
<td>3</td>
<td>Co-3C-c</td>
<td>12</td>
<td>58.4</td>
<td>450-820</td>
<td>176</td>
</tr>
<tr>
<td>4</td>
<td>Co-3C-d</td>
<td>14</td>
<td>121.6</td>
<td>450-850</td>
<td>348</td>
</tr>
<tr>
<td>5</td>
<td>Co-6C-a</td>
<td>8</td>
<td>24.5</td>
<td>490-820</td>
<td>304</td>
</tr>
<tr>
<td>6</td>
<td>Co-6C-d</td>
<td>14</td>
<td>23.5</td>
<td>530-850</td>
<td>243</td>
</tr>
</tbody>
</table>

3.3.1.10. Cyclic voltammogram (CV)

The redox potential profiles of the catalysts prepared at pH value ranging from 8 to 14 were examined by cyclic voltammogram (Figure 3.19). All the samples showed broad oxidation and reduction peaks. The cathodic peak in the lower potential region (1.21 V) could be assigned to the oxidation of Co\(^{2+}\) to Co\(^{3+}\). Similarly, the anodic peak present at higher potential (1.28 V) could be assigned to the reduction of Co\(^{3+}\) to Co\(^{2+}\). The peak intensity gradually decreased from samples Co-3C-a to Co-3C-c. Interestingly, Co-3C-d sample showed higher peak intensity than that for Co-3C-b and Co-3C-c samples. The decrease of peak intensity in case of Co-3C-b and Co-3C-c samples might be due to the decrease in surface area from 110 to 74.5 and 58.4 m\(^2\)/g respectively, which might in turn reduce the number of surface active species. In spite of having higher surface area (121 m\(^2\)/g) Co-3C-d sample showed lower peak intensity than the Co-3C-a
sample. This might be due to the lower redox ability of Co-3C-d, confirmed by TPR/TPO or mixed morphology of rod and elongated spherical particles. The Co-6C-a and Co-6C-d samples calcined at higher temperature of 873 K (Figures 3.20 and 3.21), showed the peaks of lower intensity and shift in anodic peaks from 1.28 to 1.20 and 1.25 V and cathodic peaks from 1.21 to 1.15 to 1.18 V respectively. The shift in electrochemical potential and lowering of peak intensity in case of high temperature calcined catalyst (873 K) might be due to lowering of surface area (from 110 to 24.5 m²/g and 121 to 23.5 m²/g). As a result of lowered electrochemical/redox potential, shifts in reduction peak to higher temperatures from 533 to 567 K and from 533 to 570 K in TPR profiles and oxidation peak from 410 to 415 K and from 420 to 440 K in TPO profile were observed (Figures 3.16 and 3.18). The lower electrochemical potential which could be due to decrease in surface active species at higher temperature as indicated by TPR and TPO profiles indicates lower oxidation ability which affects the CV behavior of samples calcined at higher temperature. Amongst the prepared catalysts, higher redox potential was observed for Co-3C-a catalyst leading to its higher oxidation activity as discussed later.
Figure 3.19. CV profiles of (A) Co-3C-a, (B) Co-3C-b, (C) Co-3C-c and (D) Co-3C-d samples

Figure 3.20. CV profiles of (A) Co-3C-a and (B) Co-6C-a samples
3.3.1.11. Electron paramagnetic resonance (EPR)

The EPR spectra of Co-3C-a catalyst recorded at temperature 50 K is shown in Figure 3.22. In case of spinel Co$_3$O$_4$ (Co-3C-a), magnetic moment arises due to Co$^{2+}$ ions largely because of spins, with a small contribution from spin–orbit coupling [57, 58]. The stronger peak intensity and larger peak area of Co$^{2+}$ prove the higher concentration of Co$^{2+}$ ions, required for the higher availability for oxygen vacancies [59]. However, among all the catalysts prepared, the XPS, TPR/TPO and CV results showed that Co-3C-a had higher concentration of Co$^{3+}$ species existing on the surface, which seemed to be contradictory to the EPR results. This was probably due to increased Co$^{3+}$ concentration on the surface had promoting effect on the formation of Co$^{2+}$ in the bulk phase [58, 59]. The higher concentration of surface Co$^{3+}$ could promote the adsorption and
activation of substrate (such as veratryl alcohol), while increased Co\(^{2+}\) in the bulk benefited the formation of oxygen vacancy required for catalyzing the oxidation reaction.

![Graph](image)

**Figure 3.22.** EPR of Co-3C-a sample

3.3.2. **Co\(_3\)O\(_4\) preparation by sol-gel method**

Sol-gel is another efficient method for preparation of nano materials at moderate conditions. It is believed that sol-gel derived nano particles generally possess good chemical homogeneity (unlike in co-precipitation method which generally gives inhomogeneity) and high purity. Co\(_3\)O\(_4\) prepared by sol-gel method was also evaluated for the liquid phase oxidation of veratryl alcohol.

3.3.2.1. **Surface area measurement by BET method**

Table 3.4 presents BET surface areas of catalysts prepared via sol-gel (Co-e) method and calcined at two different temperatures, 573 and 873 K. The Co-3C-e catalyst showed 21.2 m\(^2\)/g surface area which decreased to 13.2 m\(^2\)/g for Co-6C-e sample with increase in calcination temperature from 573 to 873 K. The decrease in surface area was due to the increased crystallite
size as observed in the XRD and HRTEM discussed later. However, the surface area of these catalysts was found to be much lower (5-8 times) than the catalyst prepared by co-precipitation method and calcined at 573 K (Co-3C-a, 110 m²/g). From the above observations, it is confirmed that one can prepare a catalyst with higher surface area via controlled co-precipitated method rather than by the sol-gel method.

**Table 3.4. BET surface area of Co₃O₄ samples prepared via sol-gel method**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalysts</th>
<th>Calcination temperature, (K)</th>
<th>Specific Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Co-3C-e</td>
<td>573</td>
<td>21.2</td>
</tr>
<tr>
<td>2</td>
<td>Co-6C-e</td>
<td>873</td>
<td>13.2</td>
</tr>
<tr>
<td>3</td>
<td>Co-3C-a</td>
<td>573</td>
<td>110</td>
</tr>
</tbody>
</table>

### 3.3.2.2. X-ray diffraction (XRD)

XRD patterns of Co-3C-e and Co-6C-e samples are presented in Figure 3.23. All the samples exhibited the diffraction peaks at 2θ = 19.2° (111), 31.2° (220), 36.84° (311), 44.84° (400), 55.65° (422), 59.42° (511) and 65.21° (422), which were attributed to the spinel phase of Co₃O₄. The calculated lattice parameter for all the samples was found to be ~8.085 Å matching with the reported value of 8.084 Å (JCPDS # 9-418) of the cubic Co₃O₄. Crystallite sizes of Co-3C-e and Co-6C-e samples calculated using the Scherrer equation were found to be in the range of 75-100 and 90-160 nm respectively. Thus, increase in crystallite size for Co-6C-e was mainly due to restructuring of the sample at 873 K. However, sample prepared by co-precipitation method under the same calcination temperature showed crystallite size of 12-38 nm which is very much
lower than that prepared by sol-gel method (Section 3.3.1.2). The crystallite sizes of these samples matched very well with the HRTEM results.

![XRD graph](image)

**Figure 3.23.** XRD of (A) Co-3C-e and (B) Co-6C-e samples

### 3.3.2.3. X-ray photoelectron spectroscopy (XPS)

Figure 3.24a shows the Co 2p XPS spectrum for the Co-3C-e sample. The Co 2p spectrum contains Co 2p<sub>3/2</sub> and Co 2p<sub>1/2</sub> core level peaks at binding energies of 779.1 and 794.4 eV having difference of 15.3 eV [11]. The Co 2p<sub>3/2</sub> peak on deconvolution gives two peaks at binding energies of 779.1 and 781.9 eV which correspond to Co<sup>3+</sup> and Co<sup>2+</sup> species respectively (Figure 3.24b). This evidenced the formation of spinel Co<sub>3</sub>O<sub>4</sub> [37, 38].
Figure 3.24a. XPS of Co-3C-e sample

Figure 3.24b. Deconvolution spectra of Co 2p\textsubscript{3/2}
3.3.2.4. Thermo gravimetric analysis (TG-DTA)

Figure 3.25 exhibits the TG-DTA for the as-prepared Co-e (sol-gel) sample. The catalyst showed weight losses in four steps. The first weight loss of 9% was observed from room temperature to 413 K due to the loss of physically adsorbed water molecules. The second weight loss (28%) near to 443 K could be assigned for dehydration of chemically bonded water in the CoC$_2$O$_4$.4H$_2$O [39] that was trapped in the gel after the gelation point. Third weight loss (25%) observed near to 650 K, which might be due to decomposition of ethylene glycol and acetate in to CO and CO$_2$. The fourth weight loss (10%) appeared near to 700 K, which could be assigned for dehydroxylation of surface hydroxy groups. Based on the above observations, temperature in the range of 773-823 K was required to calcine the Co-e catalyst (acetate/ethylene glycol) completely (Figure 3.43). This was much higher than the calcination temperature (573 K) required in case of co-precipitation catalyst (Figure 3.10).

![Figure 3.25. TG-DTA of Co-e sample](image-url)
### Table 3.5. Summary of thermogravimetric analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (K)</th>
<th>Weight loss (w/w. %)</th>
<th>Peak maximum (K)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-e (solv-gel)</td>
<td>413</td>
<td>9</td>
<td>333</td>
<td>Loss of physically adsorbed water</td>
</tr>
<tr>
<td></td>
<td>443</td>
<td>28</td>
<td>443</td>
<td>Dehydration of chemically bonded water in the CoC$_2$O$_4$·4H$_2$O</td>
</tr>
<tr>
<td></td>
<td>650</td>
<td>25</td>
<td>673</td>
<td>Decomposition of physically adsorbed/excess ethylene glycol.</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>10</td>
<td>723</td>
<td>Dehydroxylation of surface hydroxy groups</td>
</tr>
</tbody>
</table>

#### 3.3.2.5. Fourier-Transform infrared spectroscopy (FT-IR)

FT-IR spectra of Co-3C-e and Co-6C-e samples showed two distinct bands at 567 and 666 cm$^{-1}$ assigned to stretching vibrations of metal-oxygen bonds (Figure 3.26). The peak at 567 cm$^{-1}$ corresponds to Co$^{3+}$ in an octahedral position while the other peak at 666 cm$^{-1}$ corresponds to the Co$^{2+}$ in a tetrahedral position confirming the formation of Co$_3$O$_4$ spinel in the Co-3C-e and Co-6C-e samples [51, 52]. The broad peaks observed at 1407 and 1428 cm$^{-1}$ in case of as prepared (Co-e) and 573 K calcined samples, were assigned to asymmetric bending and stretching vibrations of (-CH$_3$) and (COO$^-$) in ethylene glycol and acetate respectively [57-58, 60]. These results were in accordance with the TG-DTA results. The broad peaks at 3420 and 1627 cm$^{-1}$ were attributed to metal hydroxyl stretching vibrations observed in both as prepared (Co-e) and Co-3C-e samples [54, 55], indicating that the catalyst calcined at 573 K had Co$_3$O$_4$ phase and
also contained some sort of organic impurities, while these impurities were not present in case of 873 K calcined sample.

![Figure 3.26. FTIR of (A) Co-3C-e, (B) Co-6C-e and (C) Co-e samples](image)

### 3.3.2.6. High resolution transmission electron microscopy

The morphologies of the samples calcined at 573 K (Co-3C-e) and at 873K (Co-6C-e) were examined by HR-TEM (Figure 3.27). The Co-3C-e sample showed the aggregation of non uniform elongated spherical particles having diameter in the range of 80-100 nm. However with increase in calcination temperature from 573 to 873 K, increase in particle diameter in the range from 80-110 to 110-160 nm was observed for Co-6C-e sample, which was in good agreement with the XRD results.
Figure 3.27. HRTEM of (A) Co-3C-e and (B) Co-6C-e samples
3.3.2.7. Temperature programmed reduction / Temperature programmed oxidation (TPR/TPO)

The reducibility of the Co-3C-e and Co-6C-e catalysts, was studied by H2-TPR (Figure 3.28). The peak observed in the range of 500-680 K was attributed to the reduction of trivalent cobalt oxide (Co3O4) to divalent cobalt oxide (CoO). Another broad peak at higher temperature in the range of 700-950 K in both the samples was attributed to the reduction of divalent cobalt oxide (CoO) to metallic cobalt (Co0) [54, 59]. The significant enhancement in the reduction temperature from 450-600 K to 500-680 K and 600-850 K to 700-950 K was observed for Co-3C-e of the catalyst prepared via sol-gel method as compared to co-precipitated catalysts (Section 3.3.1.9). This might be due to substantial increase in crystallite size from 12-32 nm to 75-100 nm as well as organic (trace of acetate) impurities present in the Co-3C-e catalyst as observed in TG-DTA and FTIR analysis. The Co-6C-e (calcined at 873 K) sample showed shift in reduction peaks to higher temperature from 590 to 610 K and from 640 to 650 K respectively. The slight shift towards higher reduction temperature might be due to increase in crystallite size from 75-100 to 90-160 nm which was confirmed by XRD and HRTEM. Co-3C-e sample showed 27 mmol of H2 up take (Table 3.6). However, sample calcined at high temperature (873 K) showed three times increase in H2 up take from 27 to 89 mmol in spite of having higher crystallite size (90-160 nm). The calcination at higher temperature of 873 K might have caused decomposition of organic impurities, which significantly cleaned the surface of active sites resulted in higher reducibility compared to 573 K calcined sample, as confirmed from the FTIR and TG-DTA analysis, indicating that catalysts prepared via sol-gel method required higher temperature for reduction and showed lower reducibility compared to co-precipitated catalysts due to bigger crystallite size.
The oxidizability of pre-reduced Co-3C-e and Co-6C-e catalysts was studied by TPO and the results are presented in Figure 3.29. The first peak in a range of 400-450 K in both the samples was attributed to the oxidation of metallic cobalt oxide (Co) to divalent cobalt oxide (CoO). Second broad peak appearing in the range 450-650 K in both the samples indicated the oxidation of divalent cobalt oxide (CoO) to the trivalent cobalt oxide (Co$_3$O$_4$) [55, 56]. The slight shift in both oxidation peaks from temperature 373-430 K to 400-450 K and second peak from 470-690 K to 450-650 K compared to co-precipitated catalysts (Section 3.3.1.9), was due to increase in reduction temperature of these catalysts as established by TPR. Co-6C-e sample showed three times (3.8 mmol) higher O$_2$ up take than the Co-3C-e (1.2 mmol) sample (Table 3.6). From these results it can be inferred that the catalysts prepared by sol-gel method showed higher oxidizing ability than Co-6C-e catalyst hence, the former would have the maximum number of active sites available on the surface.

**Figure 3.28.** TPR of (A) Co-3C-e and (B) Co-6C-e samples
Figure 3.29. TPO of (A) Co-3C-e and (B) Co-6C-e samples

Table 3.6. H₂/O₂ uptake by TPR/TPO peak for Co₃O₄ catalysts prepared via sol-gel method

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalysts</th>
<th>TPR</th>
<th>TPO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Temperature (K)</td>
<td>H₂ (mmol)</td>
</tr>
<tr>
<td>1</td>
<td>Co-3C-e</td>
<td>500-700</td>
<td>27</td>
</tr>
<tr>
<td>2</td>
<td>Co-6C-e</td>
<td>500-700</td>
<td>89</td>
</tr>
<tr>
<td>3</td>
<td>Co-3C-a</td>
<td>440-750</td>
<td>435</td>
</tr>
</tbody>
</table>
3.3.3. Co$_3$O$_4$ preparation by thermal decomposition

Thermal decomposition technique is a versatile process leading to synthesis of single phase, solid solutions, composites as well as complex oxide phases with uniform composition. For the production of a variety of advanced materials, the thermal decomposition method proves to be an efficient and simple process. This process is preferred for its additional characteristic features such as (i) rapid heating rates, (ii) use of relatively simple equipment (iii) formation of products of virtually any size and shape. Thus, this process leads to the formation of final products with higher order of purity and better mechanical properties. However, controlling the heating and cooling rates enables to obtain metastable materials with new and unique properties \[61\]. Deshpande et al. \[62\] reported that proper choice of starting precursor and its concentration could invariably produce materials with improvement in composition and properties. Therefore, I have selected cobalt nitrate (Co-f) and cobalt acetate (Co-g) samples for the preparation of Co$_3$O$_4$. Finally, the structure-activity correlation of the prepared samples was also studied and compared with the samples prepared by co-precipitation, sol-gel and commercial Co$_3$O$_4$.

3.3.3.1. Surface area measurement by BET method

BET surface areas of Co$_3$O$_4$ samples prepared via thermal decomposition (TD) of cobalt nitrate (Co-f) and cobalt acetate (Co-g) followed by calcination at 573 and 873 K and of commercial Co$_3$O$_4$ are presented in Table 3.7. The BET surface area decreased from 51.7 to 31 m$^2$/g with change in the cobalt precursor from nitrate (Co-3C-f) to acetate (Co-3C-g) due to the decomposition of nitrate at lower temperature (<523 K) compared to acetate (>543 K) precursor.

The effect of decomposition temperature on the crystallite/particle size is discussed in more detail in XRD, HR-TEM and TG-DTA studies in the later sections. The commercial Co$_3$O$_4$
sample showed the lowest surface area of 21 m²/g. Increase in calcination temperature from 573 to 873 K, resulted in three times decrease in surface area from 51.7 to 16.5 m²/g and 31 to 11.8 m²/g observed in case of Co-6C-f and Co-6C-g samples prepared by using nitrate and acetate precursors respectively. Nevertheless, the surface area of these (573 K) catalysts was found to be lower than that for Co-3C-a (110 m²/g) catalyst. Thus, Co₃O₄ with higher surface area could be obtained by co-precipitation method rather than sol-gel and thermal decomposition methods.

Table 3.7. BET surface area of Co₃O₄ samples prepared via thermal decomposition method

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalysts</th>
<th>Calcination temperature (K)</th>
<th>Specific Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Co-3C-f</td>
<td>573</td>
<td>51.7</td>
</tr>
<tr>
<td>2</td>
<td>Co-6C-f</td>
<td>873</td>
<td>16.5</td>
</tr>
<tr>
<td>3</td>
<td>Co-3C-g</td>
<td>573</td>
<td>31.0</td>
</tr>
<tr>
<td>4</td>
<td>Co-6C-g</td>
<td>873</td>
<td>11.8</td>
</tr>
<tr>
<td>5</td>
<td>commercial Co₃O₄</td>
<td>_</td>
<td>21.0</td>
</tr>
</tbody>
</table>

3.3.3.2. X-ray diffraction (XRD)

XRD patterns of samples prepared by thermal decomposition of cobalt nitrate (Co-f) and cobalt acetate (Co-g) samples and calcined at 573 and 873 K and of commercial Co₃O₄ are presented in Figure 3.30. All the samples exhibit the diffraction peaks at 2θ =19.2° (111), 31.2° (220), 36.84° (311), 44.84° (400), 55.65° (422), 59.42° (511) and 65.21° (422), which could be attributed to the spinel phase of Co₃O₄. The calculated lattice parameter for all the samples was found to be
~8.086 Å, which matched very well with the reported value of 8.084 Å (JCPDS # 9-418) of the cubic Co$_3$O$_4$. The crystallite sizes of Co-3C-f, Co-3C-g and commercial Co$_3$O$_4$ samples calculated using the Scherrer equation were found to be in the range of 25-40, 25-48 and 80-110 nm respectively. The increase in calcination temperature from 573 to 873 K caused gradual increase of peak intensity and the slight decrease in the peak width for the peaks at 2$\theta$ = 19.2° (111), 31.2° (220), 36.84° (311), 44.84° (400), 55.65° (422), 59.42° (511) and 65.21° (422). Thus, increase in crystallite size of Co-6C-f (50-70 nm) and Co-6C-g (65-90 nm) was mainly due to their restructuring at 873 K. The crystallite sizes of these samples matched very well with the HRTEM results.

**Figure 3.30.** XRD of (A) Co-3C-f, (B) Co-6C-f, (C) Co-3C-g, (D) Co-6C-g and (E) commercial Co$_3$O$_4$ samples
3.3.3.3. X-ray photoelectron spectroscopy (XPS)

The XPS spectra of Co-3C-f, Co-3C-g and commercial Co$_3$O$_4$ samples are shown in Figure 3.31a. The Co 2p spectrum contains the Co 2p$_{3/2}$ and Co 2p$_{1/2}$ core level peaks at binding energies of ($\pm$0.4) 779.5 and 794.4 eV having a difference of 15.1 eV respectively, in all the samples [11]. The Co 2p$_{3/2}$ peak deconvoluted into two peaks, at binding energies of ($\pm$0.4) 779.4 and 781.9 eV which correspond to Co$^{3+}$ and Co$^{2+}$ species (Figure 3.31b). This evidenced the formation of spinel Co$_3$O$_4$ in all the samples [37, 38].

![Figure 3.31a. XPS of (A) Co-3C-f, (B) Co-3C-g and (C) commercial Co$_3$O$_4$ samples](image-url)
3.3.3.4. Thermo gravimetric analysis (TG-DTA)

The decomposition of cobalt nitrate hexahydrate (Co-f) and cobalt acetate tetrahydrate (Co-g) samples was examined by TG-DTA (Figure 3.32, A and B). The Co-f sample showed 77.5% weight loss in four steps (Table 3.8). First two small endothermic peaks showed a total 32% weight loss (12% and 20% weight loss) below 423 K, third endothermic peak at temperature 453 K showed 15% weight loss, that was due to the loss of physically adsorbed water and dehydration of chemically bonded water in the Co(NO$_3$)$_3$·6H$_2$O (Figure 3.32, A). While, in the forth step, 28% weight loss was observed below 518 K due to the decomposition of Co(NO$_3$)$_3$ into NO, N$_2$ and O$_2$ molecules [63]. However, Co-g sample showed 71.9% weight loss in three steps (Figure 32, B). In the first step, 20% weight loss was observed due to dehydration of chemically bonded water in the CoC$_2$O$_4$·(4H$_2$O) below temperature at 403 K (Table 3.8). At 543 K, another small endothermic peak was observed, due to partial weight loss of chemically bonded acetate with cobalt. In the second step, 13% weight loss was observed below 553 K.

![Figure 3.31b. Deconvolution spectra of Co 2p$_{3/2}$](image)
temperature. In the third step, 36% weight loss observed below 673 K might be due to decomposition of acetate into CO and CO₂ [64]. Based on the above results, an optimum calcination temperature required for Co-f and Co-g samples were 523 K and 633 K respectively. Among the preparation methods (co-precipitation method, thermal decomposition and sol-gel) studied in this work, co-precipitation required lowest calcination temperature to obtain spinel Co₃O₄.

**Table 3.8. Summary of thermogravimetric analysis**

<table>
<thead>
<tr>
<th>Samples</th>
<th>TG</th>
<th>DTA</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature range (K)</td>
<td>Weight loss (w/w. %)</td>
<td>Peak maximum (K)</td>
</tr>
<tr>
<td>Co-f (cobalt nitrate)</td>
<td>378-403</td>
<td>12</td>
<td>363</td>
</tr>
<tr>
<td></td>
<td>403-438</td>
<td>20</td>
<td>423</td>
</tr>
<tr>
<td></td>
<td>438-473</td>
<td>15</td>
<td>453</td>
</tr>
<tr>
<td></td>
<td>473-563</td>
<td>28</td>
<td>518</td>
</tr>
<tr>
<td>Co-g (cobalt acetate)</td>
<td>333-413</td>
<td>20</td>
<td>393</td>
</tr>
<tr>
<td></td>
<td>413-563</td>
<td>13</td>
<td>543</td>
</tr>
<tr>
<td></td>
<td>563-673</td>
<td>36</td>
<td>628</td>
</tr>
</tbody>
</table>
Figure 3.32. TG-DTA profile of (A) Co-f and (B) Co-g samples
3.3.3.5. Fourier-Transform infrared spectroscopy (FT-IR)

FT-IR spectra of Co$_3$O$_4$ (using nitrate and acetate precursors) samples and calcined at 573 K and commercial Co$_3$O$_4$ samples are shown in Figure 3.33. The peak at 567 cm$^{-1}$ corresponds to Co$^{3+}$ in an octahedral position while the other peak at 666 cm$^{-1}$ corresponds to the Co$^{2+}$ in a tetrahedral position confirming the formation of spinel Co$_3$O$_4$ in Co-3C-f, Co-3C-g and commercial Co$_3$O$_4$ samples [48, 55]. The broad peaks at 3420 cm$^{-1}$ and 1630 cm$^{-1}$ were attributed to metal hydroxyl stretching vibrations observed in all the samples [53, 54]. However, the Co-f sample showed a peak corresponding to the stretching vibration at 1331 cm$^{-1}$ which was not observed in case of a sample calcined at 573 K temperature (Co-3C-f) (Figure 3.33, A and B) [65], indicating complete decomposition of cobalt nitrate to form pure Co$_3$O$_4$ spinel. While, the Co-g sample (cobalt acetate) showed the peaks at 1319, 1388 and 1548 cm$^{-1}$ assigned to stretching vibrations of COO$^-$ (acetate) group which were also present in Co-3C-g sample even though calcined at 573 K (Figure 3.33, C and D) [60, 61]. This indicated that Co-3C-g is a spinel Co$_3$O$_4$ however, contained an impurity of acetate which is due to the incomplete combustion of acetate. Similar observation was seen in case of TG-DTA examination (elaborated in Section 3.3.3.4).
3.3.3.6. High resolution transmission electron microscopy

The morphologies of Co-3C-f, Co-6C-g and commercial Co$_3$O$_4$ samples were examined by HR-TEM (Figure 3.34). The Co-3C-f sample showed aggregate of rod-like morphology having a length in the range of 30-40 nm (Figure 3.34, A). The change of cobalt precursor from nitrate to acetate was associated with the aggregation of elongated rods in the range of 40-55 nm (Figure 3.34, B). The increase in rod length from 30-40 to 40-55 nm might be due to the presence of some acetate groups which might hold neighbouring particles [66]. This was also supported by TG-DTA and FTIR results as discussed above. The commercial sample of Co$_3$O$_4$ showed the aggregation of non-uniform rod shape particles having the length in the range of 80-110 nm (Figure 3.34, C). The particle size of these samples were in good agreement with the results of ...
XRD studies. From the above observations, it was established that in spinel type $\text{Co}_3\text{O}_4$ having a nano range particle size with controlled morphology can be best prepared by co-precipitation method.
Figure 3.34. HRTEM of (A) Co-3C-f, (B) Co-3C-g and (C) commercial Co$_3$O$_4$ samples
3.3.3.7. **Temperature programmed reduction / Temperature programmed oxidation (TPR/TPO)**

H$_2$-TPR results of the Co-3C-f, Co-3C-g and commercial Co$_3$O$_4$ samples are presented in Figure 3.35. The peak observed in the range of 500-630 K was attributed to the reduction of trivalent cobalt oxide (Co$_3$O$_4$) to the divalent cobalt oxide (CoO) in case of Co-3C-f and Co-3C-g samples. Whereas, this peak was observed at higher temperature (550-820 K) in case of commercial Co$_3$O$_4$ sample. In case of Co-3C-f and Co-3C-g samples, second broad peak appeared in the range of 630-930 K, while in commercial Co$_3$O$_4$ sample the same peak appeared at higher range of 800-900 K that was assigned to the reduction of divalent cobalt oxide (CoO) to metallic cobalt (Co$^0$) [51, 55]. The change in cobalt precursor from nitrate to acetate showed a slight shift in the first reduction peak from 590 to 600 K and in case of commercial Co$_3$O$_4$ it was observed at still higher temperature of 720 K. This increase in reduction temperature might be due to the increase in crystallite size from ~30-40 to ~40-55 and 80-110 nm as observed in XRD and HRTEM, which requires higher temperature for reduction of bulk particles compared to the small particles [56]. Co-3C-f and Co-3C-g samples showed 145 and 68 mmol of H$_2$ up take respectively (Table 3.9). ~50% lower reducibility of Co-3C-g as compared to Co-3C-f sample was due to its higher crystallite size (40-55 nm) and the of trace of acetate groups might block the active sites resulted in lower reducibility, which were also in accordance with FTIR and TG-DTA results. Despite of having the higher crystallite size of 40-55 nm of commercial Co$_3$O$_4$ sample it showed ~35% higher reducibility than that for the Co-3C-f sample due to its crystallinity and exposure of specific planes as observed in HRTEM.
The oxidizability of pre-reduced Co-3C-f, Co-6C-g and commercial Co$_3$O$_4$ catalysts was calculated by using TPO technique as shown in Figure 3.36. The first peak in a range of 380-480 K in both the samples was attributed to the oxidation of metallic cobalt oxide (Co$^0$) to divalent cobalt oxide (CoO) in case of Co-3C-f and Co-3C-g samples. Whereas, this peak in case of a commercial Co$_3$O$_4$ was observed at significantly higher temperature (500-650 K). In case of the Co-3C-f and Co-3C-g samples, second broad peak appeared in the range of 480-620 K, while in commercial Co$_3$O$_4$ sample, it was observed in the range of 650-850 K which was assigned to the oxidation of divalent cobalt oxide (CoO) to trivalent cobalt oxide (Co$_3$O$_4$) [52, 53]. Co-3C-f sample showed ~45% (6.2 mmol) higher O$_2$ up take than that of the Co-6C-g (3.5 mmol) sample.
(Table 3.9). The reason for lower O$_2$ consumption in case of Co3C-g sample could be its higher crystallite size (40-55 nm) and the trace of acetate groups, which might block the active sites. However, commercial Co$_3$O$_4$ sample showed higher O$_2$ consumption (7.2 mmol) than the Co-6C-f and Co3C-g sample, in spite of its higher crystallite size. This might be because of higher extent of exposure of active sites arising from the difference of precursor used and method of its preparation.

**Figure 3.36.** TPO of (A) Co-3C-f, (B) Co-3C-g and (C) commercial Co$_3$O$_4$ samples
Table 3.9. H₂/O₂ uptake of Co₃O₄ catalysts prepared via thermal decomposition method and commercial Co₃O₄ samples

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Calcination temperature (K)</th>
<th>H₂ (mmol)</th>
<th>O₂ (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-3C-f</td>
<td>573</td>
<td>145</td>
<td>6.2</td>
</tr>
<tr>
<td>Co-3C-g</td>
<td>573</td>
<td>68</td>
<td>3.5</td>
</tr>
<tr>
<td>commercial Co₃O₄</td>
<td>Not Known</td>
<td>221</td>
<td>7.2</td>
</tr>
<tr>
<td>Co-3C-a</td>
<td>573</td>
<td>435</td>
<td>20.6</td>
</tr>
</tbody>
</table>

3.3.4. ACTIVITY MEASUREMENT

3.3.4.1. Screening of catalysts

The comparative catalytic activity results of spinel Co₃O₄ prepared by different preparation methods (co-precipitation, sol-gel and thermal decomposition) and calcined at 573 and 873 K temperatures and of commercial Co₃O₄ sample for the oxidation of veratryl alcohol are presented in Table 3.10. Among these, Co-3C-a sample prepared via co-precipitation method showed the highest conversion of 38% with complete selectivity to veratryl aldehyde (Table 3.10, Entry 1).

The decrease in catalytic activity with change in pH (from 8 to 12) and preparation parameters/methods was due to decrease in active sites as a result of decrease in surface area, increase in crystallite/particle size and decrease in redox ability as evidenced by BET surface area, XRD, TPR, TPO and CV characterization [10, 67]. Inspite of having higher surface area (121.6 m²/g) Co-3C-d catalyst showed decrease in conversion by 15% as compared to the Co-
3C-a catalyst (Table 3.10, Entry 7), due to change from mesoporous to microporous nature and lower oxidizability (~17%) of elongated rod-like particles which was also in accordance with the TPR/TPO results. However, Co-3C-e (prepared by sol-gel method) and Co-3C-g (prepared by thermal decomposition method using cobalt acetate) catalysts showed the lowest catalytic activity with only 2.5 and 6.5% conversion respectively. This was due to the blockage of active sites by organic impurities as was observed in FTIR, TG-DTA, TPR and TPO studies (Table 3.10, Entry 7). The calcination at higher temperature of 873 K caused decrease in conversion to the extent of 25 to 40%, due to the sintering of nanoparticles as evidenced by lower surface area and larger crystallite size (Table 3.10) [10, 67]. Inspite of having lower surface area of Co-6C-e and Co-6C-g samples, both showed almost two times higher activity than those samples calcined at 573 K. This might be due blockage of active sites by organic impurities present in the sample calcined at 573 K as evidenced from TG-DTA and FTIR studies. Under similar reaction conditions, commercial Co₃O₄ catalyst showed lower activity, that could be attributed to its lower surface area (21 m²/g) and lower oxidizing ability than that of Co-3C-a catalyst.

Above observations established that catalyst prepared by a co-precipitation method and controlled pH (7-8) and calcined at 573 K showed the highest activity among all the samples prepared by other methods (sol-gel, thermal decomposition) and the commercial Co₃O₄.
Table 3.10. Catalytic activity of prepared (Co$_3$O$_4$) catalysts via various methods and commercial Co$_3$O$_4$ samples for liquid phase oxidation of veratryl alcohol to veratryl aldehyde

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalysts</th>
<th>Preparation method</th>
<th>Calcination temperature (K)</th>
<th>Surface area (m$^2$/g)</th>
<th>Conversion (%)</th>
<th>Selectivity (%) Veratryl aldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Co-3C-a</td>
<td>CP</td>
<td>573</td>
<td>110.0</td>
<td>38.0</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>2</td>
<td>Co-6C-a</td>
<td>CP</td>
<td>873</td>
<td>24.5</td>
<td>14.1</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>3</td>
<td>Co-3C-b</td>
<td>CP</td>
<td>573</td>
<td>74.5</td>
<td>28.3</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>4</td>
<td>Co-6C-b</td>
<td>CP</td>
<td>873</td>
<td>19.2</td>
<td>11.2</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>5</td>
<td>Co-3C-c</td>
<td>CP</td>
<td>573</td>
<td>58.4</td>
<td>19.2</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>6</td>
<td>Co-6C-c</td>
<td>CP</td>
<td>873</td>
<td>13.7</td>
<td>5.0</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>7</td>
<td>Co-3C-d</td>
<td>CP</td>
<td>573</td>
<td>121.6</td>
<td>32.5</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>8</td>
<td>Co-6C-d</td>
<td>CP</td>
<td>873</td>
<td>23.5</td>
<td>13.5</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>9</td>
<td>Co-3C-e</td>
<td>SG</td>
<td>573</td>
<td>21.2</td>
<td>2.5</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>10</td>
<td>Co-6C-e</td>
<td>SG</td>
<td>873</td>
<td>13.2</td>
<td>6.0</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>11</td>
<td>Co-3C-f</td>
<td>TD</td>
<td>573</td>
<td>51.7</td>
<td>14.5</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>12</td>
<td>Co-6C-f</td>
<td>TD</td>
<td>873</td>
<td>16.5</td>
<td>5.3</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>13</td>
<td>Co-3C-g</td>
<td>TD</td>
<td>573</td>
<td>31.0</td>
<td>4.5</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>14</td>
<td>Co-6C-g</td>
<td>TD</td>
<td>873</td>
<td>11.8</td>
<td>10.0</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>15</td>
<td>Commercial Co$_3$O$_4$</td>
<td>NK</td>
<td>NK</td>
<td>21.0</td>
<td>22.0</td>
<td>&gt;99.9</td>
</tr>
</tbody>
</table>

Reaction conditions: temperature, 413 K; oxygen pressure, 0.689 MPa; veratryl alcohol, 0.5 g (3 mmol); catalyst, 0.1 g (0.42 mmol); solvent water, 70 mL; reaction total volume, 70.6 mL; agitation speed, 900 rpm; reaction time, 7 h.

Where, CP: co-precipitation; SG: sol-gel; TD: thermal decomposition and NK: not known
3.3.4.2. Effect of catalyst preparation parameters

Since Co$_3$O$_4$ prepared by co-precipitation method showed the highest activity for liquid phase oxidation of veratryl alcohol to veratryl aldehyde, the effect of various parameters varied during its preparation on the activity performance was also studied.

3.3.4.2.1. Effect of calcination temperature

The calcination of co-precipitated Co$_3$O$_4$ sample was carried out at two different temperatures of 573 to 873 K and the results are shown in Table 3.11. The significant decrease in catalytic conversion from 38 to 14.1% was observed with increase in calcination temperature from 573 to 873 K (Table 3.11). Such a dramatic decrease in catalytic activity was due to the following reasons: i) change in mesoporous (pore size 16.7 nm and pore volume 1.3 cm$^3$/g) to microporous nature (pore size 1.8 nm and pore volume 0.11 cm$^3$/g), ii) substantial decrease in surface area from 110 to 24.5 m$^2$/g and iii) increase in crystallite/particle size from 12-38 to 20-70 nm as observed in XRD and HRTEM studies. The microporous nature would cause difficulties for the substrate to diffuse onto the active sites inside the pores. The number of active sites formed might be also less at high calcination temperature as has been evidenced from TPR, TPO and CV characterization. Thus the above observations established that optimum calcination temperature was 573 K for co-precipitated catalyst in order to achieve the highest catalytic activity.
Table 3.11. Effect of calcination temperature on catalytic activity

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Calcination temperature (K)</th>
<th>Specific Surface area (m²/g)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Veratryl aldehyde</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-3C-a</td>
<td>573</td>
<td>110.0</td>
<td>38.0</td>
<td>&gt;99.9</td>
<td></td>
</tr>
<tr>
<td>Co-4C-a</td>
<td>673</td>
<td>67.3</td>
<td>31.9</td>
<td>&gt;99.9</td>
<td></td>
</tr>
<tr>
<td>Co-5C-a</td>
<td>773</td>
<td>28.5</td>
<td>16.5</td>
<td>&gt;99.9</td>
<td></td>
</tr>
<tr>
<td>Co-6C-a</td>
<td>873</td>
<td>24.5</td>
<td>14.1</td>
<td>&gt;99.9</td>
<td></td>
</tr>
</tbody>
</table>

Reaction conditions: temperature, 413 K; oxygen pressure, 0.689 MPa; veratryl alcohol, 0.5 g (3 mol); catalyst, 0.1 g (0.42 mmol); solvent water, 70 mL; agitation speed, 900 rpm; reaction time, 7 h.

3.3.4.2.2. Effect of calcination time

In order to study the influence of calcination time on catalytic activity, the Co-a and Co-d samples were calcined at constant temperature of 573 K for different time periods of 1 to 6 h (Tables 3.12, 3.13, 3.14 and 3.15). From the studies of effects of solvents as discussed in 3.2.4.1.2, toluene and water were selected for further studies on optimization of reaction parameters for the oxidation of veratryl alcohol. The catalytic activities of Co-a (1 to 6 h) catalysts in water and toluene as solvents were found to decrease by 1/4th and 1/5th respectively, with increase in calcination time from 1 to 6 h (Tables 3.12 and 3.13). The decrease in catalytic activity was due to the decrease in surface area by half (from 194.4 to 95.9 m²/g) and increase in crystallite size from 5-25 nm to 15-52 nm (XRD and HRTEM) with increase in calcination time from 1 to 6 h. While in both the solvents, leaching of catalysts was observed for calcination period upto 3 h which then decreased with increase in calcination time from 4 to 6 h (Tables 3.12 and 3.13). The metal leaching for the sample calcined for 3 h, could be due to the fact that the
catalysts had lower crystallite size and unconverted cobalt hydroxy carbonate was present on the catalyst surface (XRD). Similarly, the activity of Co-d (1 to 6 h) catalyst in water and toluene was found to decrease by ~40% with increase in calcination time from 1 to 6 h (Tables 3.14 and 3.15). The decrease in catalytic activity might be due to the decrease in surface area by half (from 206.1 to 107.2 m²/g) and increase in crystallite size from 5-20 nm to 18-34 nm (XRD). The metal leaching pattern observed was similar to that for Co-d, as discussed above. However, Co-3C-a (1 h calcined) showed lower leaching as compared to that for Co-3C-d (1 h calcined) in both the solvents due to better crystallinity and high crystallite size. The highest activity of the catalyst could be achieved for catalyst that was calcined at 573 K for 5 h.

Table 3.12. Effect of calcination time on the activity of Co-a in water

<table>
<thead>
<tr>
<th>Calcination time (h)</th>
<th>Specific Surface area (m²/g)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Leaching of cobalt (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>194.4</td>
<td>53.5</td>
<td>&gt;99.9</td>
<td>18.52</td>
</tr>
<tr>
<td>2</td>
<td>148.0</td>
<td>31.2</td>
<td>&gt;99.9</td>
<td>6.81</td>
</tr>
<tr>
<td>3</td>
<td>131.5</td>
<td>33.2</td>
<td>&gt;99.9</td>
<td>3.15</td>
</tr>
<tr>
<td>4</td>
<td>119.4</td>
<td>35.6</td>
<td>&gt;99.9</td>
<td>0.98</td>
</tr>
<tr>
<td>5</td>
<td>110.0</td>
<td>38.0</td>
<td>&gt;99.9</td>
<td>0.11</td>
</tr>
<tr>
<td>6</td>
<td>95.9</td>
<td>34.9</td>
<td>&gt;99.9</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Reaction conditions: temperature, 413 K; oxygen pressure, 0.689 MPa; veratryl alcohol, 0.5 g (3 mmol); catalyst, 0.1 g (0.42 mmol); water, 70 mL; agitation speed, 900 rpm; reaction time, 7 h.
### Table 3.13. Effect of calcination time on the activity of Co-a in toluene

<table>
<thead>
<tr>
<th>Calcination time (h)</th>
<th>Specific Surface area (m²/g)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Leaching of cobalt (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Veratryl aldehyde</td>
<td>Veratric acid</td>
</tr>
<tr>
<td>1</td>
<td>194.4</td>
<td>98.0</td>
<td>80.0</td>
<td>20.0</td>
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<tr>
<td>2</td>
<td>148.0</td>
<td>85.5</td>
<td>90.0</td>
<td>10.0</td>
</tr>
<tr>
<td>3</td>
<td>131.5</td>
<td>79.4</td>
<td>95.5</td>
<td>4.5</td>
</tr>
<tr>
<td>4</td>
<td>119.4</td>
<td>78.3</td>
<td>97.5</td>
<td>2.5</td>
</tr>
<tr>
<td>5</td>
<td>110.0</td>
<td>75.0</td>
<td>99.0</td>
<td>1.0</td>
</tr>
<tr>
<td>6</td>
<td>95.9</td>
<td>53.0</td>
<td>&gt;99.9</td>
<td>&lt;0.1</td>
</tr>
</tbody>
</table>

Reaction conditions: temperature, 413 K; oxygen pressure, 0.689 MPa; veratryl alcohol, 0.5 g (3 mmol); catalyst, 0.1 g (0.42 mmol); toluene, 70 mL; agitation speed, 900 rpm; reaction time, 7 h.

### Table 3.14. Effect of calcination time on the activity of Co-d in water

<table>
<thead>
<tr>
<th>Calcination time (h)</th>
<th>Specific Surface area (m²/g)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Leaching of cobalt (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Veratryl aldehyde</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>206.1</td>
<td>48.0</td>
<td>&gt;99.9</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>162.7</td>
<td>41.8</td>
<td>&gt;99.9</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>144.0</td>
<td>37.1</td>
<td>&gt;99.9</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>132.6</td>
<td>34.6</td>
<td>&gt;99.9</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>121.6</td>
<td>32.5</td>
<td>&gt;99.9</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>107.2</td>
<td>29.0</td>
<td>&gt;99.9</td>
<td></td>
</tr>
</tbody>
</table>

Reaction conditions: temperature, 413 K; oxygen pressure, 0.689 MPa; veratryl alcohol, 0.5 g (3 mmol); catalyst, 0.1 g (0.42 mmol); water, 70 mL; agitation speed, 900 rpm; reaction time, 7 h.
Table 3.15. Effect of calcination time on the activity of Co-d in toluene

<table>
<thead>
<tr>
<th>Calcination time (h)</th>
<th>Specific Surface area (m²/g)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Leaching of cobalt (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Veratryl aldehyde</td>
<td>Veratric acid</td>
</tr>
<tr>
<td>1</td>
<td>206.1</td>
<td>89.0</td>
<td>91.0</td>
<td>9.0</td>
</tr>
<tr>
<td>2</td>
<td>162.7</td>
<td>85.5</td>
<td>95.0</td>
<td>5.0</td>
</tr>
<tr>
<td>3</td>
<td>144.0</td>
<td>79.4</td>
<td>95.5</td>
<td>4.5</td>
</tr>
<tr>
<td>4</td>
<td>132.6</td>
<td>78.3</td>
<td>97.3</td>
<td>2.7</td>
</tr>
<tr>
<td>5</td>
<td>121.6</td>
<td>75.0</td>
<td>99.0</td>
<td>1.0</td>
</tr>
<tr>
<td>6</td>
<td>107.2</td>
<td>53.0</td>
<td>99.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Reaction conditions: temperature, 413 K; oxygen pressure, 0.689 MPa; veratryl alcohol, 0.5 g (3 mmol); catalyst, 0.1 g (0.42 mmol); toluene, 70 mL; agitation speed, 900 rpm; reaction time, 7 h.

3.3.4.3. Effect of reaction variables

The nano Co-3C-a catalyst was found to be stable and reusable in water as a solvent, while large activity drop (1/3rd) was observed in toluene after the first recycle (Section 3.3.4.3.6). Hence work on optimization of further reaction conditions was carried out in water as a solvent.

3.3.4.3.1. Effect of temperature

The effect of temperature on conversion of veratryl alcohol and selectivity to veratryl aldehyde was studied using the most active nano Co-3C-a catalyst in the range of 393-433 K (Figure 3.37). The conversion of veratryl alcohol increased from 67 to 90% while the selectivity to veratryl aldehyde decreased from 99.9% to 90% with an increase in temperature from 393 to 433 K (pressure 4 MPa) [10]. The decrease in selectivity to veratryl aldehyde was due to its further
oxidation to veratric acid at higher temperature. Hence the optimum temperature was found to be 413 K. Activation energy as calculated from the Arrhenius plot in water was found to be 42.46 kJ mole\(^{-1}\)K\(^{-1}\) (Figure 3.38).

**Figure 3.37.** Influence of temperature on oxidation of veratryl alcohol using Co-3C-a catalyst

Reaction conditions: oxygen pressure, 4 MPa; veratryl alcohol, 3 mmol; solvent water, 70 mL; catalyst loading, 0.84 mmol; reaction time, 7 h.

**Figure 3.38.** Arrhenius plot
3.3.4.3.2. Conversion and product distribution with time

Figure 3.39 shows the conversion and product selectivities vs. time profile for veratryl alcohol oxidation using nano Co-3C-a catalyst at an optimum temperature of 413 K. The initial oxidation product formed was veratryl aldehyde that underwent further oxidation to give veratric acid with the highest conversion of 85% of veratryl alcohol.

![Conversion and product distribution with time for oxidation of veratryl alcohol over Co-3C-a catalyst](image)

**Figure 3.39.** Conversion and product distribution with time for oxidation of veratryl alcohol over Co-3C-a catalyst

Reaction conditions: temperature, 413 K; oxygen pressure, 4 MPa; veratryl alcohol, 0.5 g (3 mmol); catalyst, 0.84 mmol; solvent water, 70 mL; agitation speed, 900 rpm; reaction time, 7 h.

3.3.4.3.3. Effect of pressure

In order to study the effect of partial oxygen pressure on conversion of veratryl alcohol and selectivity to veratryl aldehyde, oxidation experiments were carried out by varying the oxygen
pressure in the range of 0.68-4 MPa at 413 K and the results are shown in Figure 3.40. It was found that the conversion of veratryl alcohol increased from 37 to 85% with an increase in partial pressure of oxygen from 0.68 to 4 MPa, while selectivity to veratryl aldehyde remained almost constant (97%) [10]. The substantial increase in conversion was due to the higher oxygen solubility at higher pressure [68].

![Figure 3.40](image_url)

**Figure 3.40.** Influence of pressure on oxidation of veratryl alcohol using Co-3C-a catalyst

Reaction conditions: temperature, 413 K; veratryl alcohol, 0.5 g (3 mmol); catalyst, 0.2 g (0.84 mmol); solvent water, 70 mL; agitation speed, 900 rpm; reaction time, 7 h.
3.3.4.3.4. Effect of catalyst loading

Veratryl alcohol conversion increased from 22 to 85% (Table 3.17) with increase in amount of catalyst from 0.05 g to 0.2 g. However, the selectivity to veratryl aldehyde decreased by 4%. At higher catalyst loading, enhanced availability of active sites would facilitate the further oxidation of aldehyde to acid.

Table 3.16. Catalyst loading effect by using Co-3C-a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst loading (g)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Veratryl aldehyde</th>
<th>Veratric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.05</td>
<td>22</td>
<td>&gt;99.9</td>
<td>&lt;0.1</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.1</td>
<td>36</td>
<td>&gt;99.9</td>
<td>&lt;0.1</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.2</td>
<td>85</td>
<td>96</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

Reaction conditions: temperature, 413 K; oxygen pressure, 4 MPa; veratryl alcohol, 0.5 g (3 mmol); solvent water, 70 mL; agitation speed, 900 rpm; reaction time, 7 h.

3.3.4.3.5. Effect of solvent

Since the catalyst calcined at 573 K (Co-3C-a) showed the highest activity, the effect of various solvents on its performance was investigated and the results are shown in Table 3.12. The catalytic activity in different solvents was found to be in the following order: toluene > water > ethanol > methanol. The highest conversion of 75% was observed with 99% selectivity to veratryl aldehyde when non polar solvent such as toluene was used (Table 3.12, Entry 1). Among the polar solvents, highest conversion of 38% was observed in water (Table 3.12, Entry 2), however in case of methanol and ethanol, 21% and 29% conversions were observed respectively with complete selectivity to veratryl aldehyde in all the solvents (Table 3.12, Entries 3 and 4).
The highest catalytic activity in toluene solvent than that in polar solvents was due to the solubility of oxygen and non interaction of polar solvent with the intermediate state which is discussed in detailed in Section 3.3.4.3.5 [40, 60]. Thus, the preference of solvent allowed to achieve the desired catalytic activity.

Table 3.17. Activity of Co-3C-a catalyst in different solvents

<table>
<thead>
<tr>
<th>Solvents</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Veratryl Aldehyde</th>
<th>Veratric Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>75</td>
<td>97.5</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>38</td>
<td>&gt;99.9</td>
<td>&lt;0.1</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>21</td>
<td>&gt;99.9</td>
<td>&lt;0.1</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>29</td>
<td>&gt;99.9</td>
<td>&lt;0.1</td>
<td></td>
</tr>
</tbody>
</table>

Reaction conditions: temperature, 413 K; oxygen pressure, 0.689 MPa; veratryl alcohol, 0.5 g (3 mmol); catalyst, 0.1 g (0.42 mmol); water, 70 mL; agitation speed, 900 rpm; reaction time, 7 h.

3.3.4.3.6. Catalyst recycles studies

In order to ensure that the catalytic activity of nano Co-3C-a spinel catalyst in water and toluene as solvents was constant during the run, we carried out catalyst recycle experiments. For this purpose, the catalyst after the first run was recovered by centrifugation. It was then washed with either by water or toluene and dried at 373 K for 2 h and reused for the subsequent run. It was found that in water as solvent, the catalyst showed almost the same selectivity with marginal decrease in conversion of veratryl alcohol even after the third recycle but in toluene after the first recycle, its activity decreased from 75 to 56% as shown in Figure 3.41. The marginal decrease in
conversion from 38 to 34% in water was due to the handling losses of the catalyst. However, these results were found to be in agreement with the CSC (cobalt surface composition) ratio found after first recycle in water ~1:2 which was the same as fresh catalyst (1:2) while in toluene it changed to ~1:4 confirmed by XPS examination. In order to know the stability during reaction, catalyst leaching test was also done after first recycle by ICP-OES and the results confirmed no leaching of the active metal function was observed in both the solvents (water and toluene) (Tables 3.13 and 3.14). These results established that catalytic activity in water solvent was lower but catalyst was able to form redox couple in water while this was not possible in toluene. This clearly demonstrated that spinel type nano-structured Co-3C-a was truly a heterogeneous, highly efficient catalyst for aqueous phase oxidation.

![Figure 3.41. Recycle study of Co-3C-a catalyst in water and toluene solvents](image)

**Figure 3.41.** Recycle study of Co-3C-a catalyst in water and toluene solvents

Reaction conditions: temperature, 413 K; oxygen pressure, 0.689 MPa; veratryl alcohol, 0.5 g (3 mmol); catalyst, 0.1 g (0.42 mmol); solvent, 70 mL; agitation speed, 900 rpm; reaction time, 7 h.
3.3.4.4. Substrate screening

The oxidation of various phenolic and non phenolic substrates representing sub structure of lignin compounds were tested over active nano $\text{Co}_3\text{O}_4$ (Co-3C-a) catalyst (Table 3.18). Among phenolic compounds, di-substituted vanillin alcohol showed a maximum conversion of 86% with 81% and 11% selectivities to vanillin and vanillic acid respectively. With an increase in unsaturation, conversion dropped down to 61% for the coniferyl alcohol with 82% selectivity to coniferyl aldehyde. The substituents on the phenolic compounds showed a significant influence on the oxidation activity depending on their ability of electron donation. The planar benzyl alcohol showed only 17.4% conversion while for the mono-substituted phenolic compounds, 51.8% conversion of the $p$-hydroxy benzyl alcohol was obtained with 84% selectivity to $p$-hydroxy benzaldehyde. Similarly, 28% conversion of $p$-coumaryl alcohol was observed with 100% selectivity to $p$-coumaryl aldehyde. The tri-substituted phenolic compounds showed much higher activity, e.g. 77% conversion of the $p$-sinapyl alcohol was obtained with 78% selectivity to sinapyl aldehyde. Among the non-phenolic substrates, the veratryl alcohol showed highest conversion of 85% with 96% selectivity to veratryl aldehyde. On the other hand, mono-substituted methoxy groups such as $p$-anisic alcohol showed 55% conversion with 100% selectivity to $p$-anisaldehyde, while 3,4,5-tri methoxy benzyl alcohol showed higher conversion of 76.8% with 79% aldehyde selectivity. Highest conversion and selectivity of 90% to 4-hydroxy 3-methoxy alpha methyl benzylalcohol (4H3MAMBA) was obtained for the aromatic secondary alcohol viz. 1-(4-hydroxy-3-methoxyphenyl) ethanone. The activity of various substructures of lignin compounds studied in this work was found in the following order of: secondary alcohol > di-substituted > tri-substituted > mono-substituted > non-substitution.
Table 3.18. Oxidation of non-phenolic and phenolic sub structure of lignin compounds catalysed by nano Co-3C-a spinel

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrates</th>
<th>Conv. (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Aldehyde</td>
</tr>
<tr>
<td>1</td>
<td>vanillin alcohol</td>
<td>86.0</td>
<td>81</td>
</tr>
<tr>
<td>2</td>
<td>veratryl alcohol</td>
<td>85.0</td>
<td>96</td>
</tr>
<tr>
<td>3</td>
<td>(p)-sinapyl alcohol</td>
<td>77.0</td>
<td>78</td>
</tr>
<tr>
<td>4</td>
<td>3,4,5-tri-methoxy benzyl alcohol</td>
<td>76.8</td>
<td>79</td>
</tr>
<tr>
<td>5</td>
<td>(p)-anisic alcohol</td>
<td>55.0</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>6</td>
<td>coniferyl alcohol</td>
<td>61.0</td>
<td>82</td>
</tr>
<tr>
<td>7</td>
<td>(p)-hydroxy benzyl alcohol</td>
<td>51.8</td>
<td>84</td>
</tr>
<tr>
<td>8</td>
<td>(p)-coumaryl alcohol</td>
<td>28.0</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>9</td>
<td>4H3MAMBA</td>
<td>90.0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>benzyl alcohol</td>
<td>17.4</td>
<td>78</td>
</tr>
</tbody>
</table>

Reaction conditions: temperature, 413 K; oxygen pressure, 4 MPa; substrate, 3 mmol (0.5 g); water, 70 mL; catalyst loading, 0.84 mmol; reaction time, 7 h. Where; \(^a\) = 1-(4-hydroxy-3-methoxyphenyl) ethanone.

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3.3.4.5. Reaction mechanism

It is well known that the two oxidation states of Co\(^{2+}\) and Co\(^{3+}\) coexist in the spinel Co\(_3\)O\(_4\) and a dynamic equilibrium is set up involving Co\(^{2+}\), Co\(^{3+}\), and the lattice oxygen (O\(_2^-\)) species under liquid phase oxidation conditions [14]. Oxidative dehydrogenation proceeds via approach of substrate (veratryl alcohol) towards the cobalt octahedral species having lattice oxide ion as shown in Scheme 3.3 [41, 69-71]. The adsorbed veratryl alcohol formed intermolecular bonding between cobalt(III) and oxygen while surface oxide ion formed intermolecular bonding with hydrogen of alcoholic group. Subsequently Co\(^{III}\)OH species were formed due to abstraction of hydrogen by oxide ion [72]. Activated Co\(^{III}\)OH species were capable of forming another intermolecular hydrogen bond and abstraction of an electron forms the major product veratryl aldehyde, Co(II) and water molecule [72]. The reduced Co(II) species get reoxidized using molecular oxygen to form again active Co\(^{III}\)O species. The formation of veratric acid by further oxidation of veratryl aldehyde using molecular oxygen is also systematically shown in Scheme 3.3. However, the catalytic activity over nano Co-3C-a catalyst was found to depend on the reaction medium (Table 3.12). The lower catalytic activity in polar solvents might be due to an interaction of the solvent via intermolecular bonding with hydrogen and cobalt oxide ion either at the initial step or after the activation of reactant as shown in Scheme 3.3. Thus, active sites were blocked in presence of polar solvents resulting in lower catalytic activity. However, in case of the non polar (toluene) solvent, absence of any proton (hydrogen) does not form an intermolecular bond with cobalt oxide. As a result of this, maximum active sites were available leading to the higher conversion (75%). Similarly, the oxidative dehydrogenation of the other sub-structure lignin compounds also might proceed via similar reaction mechanism. In order to
investigate the role of organic and inorganic polar solvents in this oxidation reaction further studies are in progress.

**Scheme 3.3.** Plausible catalytic path way for oxidation of veratryl alcohol

### 3.4. CONCLUSIONS

- Nano spinel Co$_3$O$_4$ catalyst (Co-3C-a) prepared by co-precipitation in a pH range of 7-8 and calcined at 573 K for 5 h time, showed the highest catalytic activity (38%), among the catalysts prepared by sol-gel, thermal decomposition and commercial Co$_3$O$_4$ samples. The highest activity of Co-3C-a catalyst was due to its rod-like morphology having particle size of 10-20 nm with mesoporous nature (pore size of 16.7 nm, pore volume of 1.3 cm$^3$/g) and surface area (110 m$^2$/g).
The increase in calcination temperature from 573 to 873 K led to decrease in catalytic activity from 38% to 14.1%, mainly due to decrease in surface area from 110 to 24.5 m$^2$/g, change in morphology from mesoporous to microporous nature and increase in crystallite size from 12-38 to 20-70 nm.

XRD patterns of samples prepared by various preparation methods and that of commercial Co$_3$O$_4$ exhibited the diffraction peaks at $2\theta = 19.2^\circ$ (111), 31.2$^\circ$ (220), 36.84$^\circ$ (311), 44.84$^\circ$ (400), 55.65$^\circ$ (422), 59.42$^\circ$ (511) and 65.21$^\circ$ (422), which were attributed to the cubic spinel phase of Co$_3$O$_4$.

The Co 2p XPS spectra of Co 2p$_{3/2}$ peak at binding energies 779.4 and 781.9 eV which corresponded to Co$^{2+}$ and Co$^{3+}$ species. This evidenced the formation of spinel Co$_3$O$_4$ in all the samples.

The surface composition from XPS examination established that there was participation of similar type of catalyst surface active species during reaction in polar and also in non polar solvents.

Inter atomic bond distances between Co-O and Co-Co remained the same in case of fresh and used (Co-3C-a) catalyst in different solvents as observed from FT-EXAFS examination.

FTIR of the prepared catalysts and commercial Co$_3$O$_4$ samples showed peaks at 568 and 660 cm$^{-1}$ corresponding to Co$^{3+}$ in octahedral and Co$^{2+}$ in tetrahedral positions of Co$_3$O$_4$ spinel. The samples calcined at 573 K viz. Co-3C-e (sol-gel) and Co-3C-g (thermal decomposition, cobalt acetate) showed the presence of organic impurities, while this was not observed in case of co-precipitated and Co-3C-f (thermal decomposition, cobalt nitrate) catalysts. However,
used samples of (co-precipitated) catalysts showed the peaks same as those in the fresh samples indicating the stability of the catalyst under reaction conditions.

- Among various co-precipitated catalysts, only Co-3C-a (pH=8) and Co-3C-d (pH=14) showed uniform nano rod-like (10-20 nm) as well as elongated spherical (25-30 nm) morphology respectively.

- The highest redox ability of Co-3C-a was due to the presence of higher number of octahedral Co$^{3+}$ and tetrahedral Co$^{2+}$ species evident from XPS, FTIR, TPR, TPO and CV studies.

- The catalytic oxidation of veratryl alcohol to veratryl aldehyde in different solvents was found to be in the following order: toluene > water > ethanol > methanol.

- The optimum calcination time was 5 h, at 573 K for achieving the highest activity without active metal leaching.

- Activation energy calculated from the Arrhenius plot in water was found to be 42.46 kJ mole$^{-1}$K$^{-1}$.

- Catalyst reusability studies showed that nano Co-3C-a was truly a heterogeneous, highly efficient catalyst for aqueous phase oxidation of the C-OH at 413 K in water as a solvent.

- The activity of various sub-structure of lignin compounds studied in this work was found to be in the following order: secondary alcohol > di-substituted > tri-substituted > mono-substituted > non-substitution.
3.5. REFERENCES


