Chapter 5

Metal aluminosilicate catalysts for oxidation of veratryl alcohol
5.1. INTRODUCTION

Mesoporous aluminosilicates have attracted much attention in recent years because of their prospective applications in heterogeneous catalysis [1-5], separation processes [6], biology [7], pharmaceuticals [8] and environmental monitoring [9]. Industrial applications of pure silica are hardly possible hence, special attention has been devoted for developing meso structured aluminosilicates with high aluminum content to impart stability to them due to tetrahedral aluminum [1]. There are a number of successful approaches to introduce an heteroatom (such as Co, Mn, Fe, Na, Cu, etc.) into mesoporous aluminosilicates materials [10-16]. Some of these involves, (i) direct-synthesis under microwave-hydrothermal conditions [17], (ii) use of strong acidic media [18, 19], (iii) template-assisted method [19, 20], (iv) hydrothermal method [21] and (v) co-precipitation method [22]. However, major challenge is still the synthesis of mesoporous aluminosilicates with the lowest possible Si:Al (1:10) ratio that is with the highest aluminium content. Herein, using an inexpensive and simple in-situ co-precipitation method [2, 22-25], metal containing (cobalt, iron, copper and manganese) mesoporous aluminosilicate catalysts is reported.

Recently, we have reported cobalt containing aluminosilicate (cobalt-saponite having Si:Al ratio ~8:1) as solid catalysts for side chain oxidation of phenol derivative such as p-cresol [22]. This catalyst (15% cobalt aluminosilicate) when tested for liquid phase oxidation of veratryl alcohol (non-planar bulkier molecule), did not show any activity. The poor activity of this catalyst was due to limited pore size (micropores with pore diameter ~1.17 nm) and restricted mobility of substrate in a two dimensional (2D) layered saponite clay. Considering this limitation, silica alumina (Si:Al) ratio was changed from 10:1 to 1:10 to obtain mesoporous aluminosilicate with a
pore diameter of \( \sim 4.04 \) nm which showed an excellent activity for oxidation of veratryl alcohol to veratryl aldehyde. Veratryl alcohol oxidation is an industrially important reaction as the end product veratryl aldehyde finds wide range commercial applications in food and pharmaceutical industries [26].

Cobalt aluminosilicate catalysts with varied Si:Al ratio and cobalt compositions were prepared by a simple protocol, these were then characterized by various techniques such as N\(_2\) adsorption-desorption isotherm, BET surface area, XRD, XPS, FTIR, TG-DTA, SEM-EDX, TEM, DRUV-vis, TPR, TPO, CV and EXAFS. Among various compositions, 15% cobalt aluminosilicate (Si:Al 1:10) calcined at 573 K (CSA-4) showed an excellent activity and selectivity (86% conversion and 94% selectivity to veratryl aldehyde) for the liquid phase oxidation of veratryl alcohol. Effects of various reaction parameters such as catalyst loading, temperature, oxygen partial pressure on the conversion and selectivity pattern were also investigated. The stability of the catalyst was confirmed by the catalyst recycle experiments.

5.2. RESULTS AND DISCUSSION

5.2.1. N\(_2\) adsorption isotherm

The textural properties of the 15% cobalt aluminosilicate having various silica alumina (Si:Al) ratios as 10:1 (CSA-1), 1:1 (CSA-2), 1:5 (CSA-3), 1:10 (CSA-4) and of the calcined sample of CSA-4 at two different temperatures, 573 K and 773 K (CSA-4-3C, CSA-4-5C respectively) determined by nitrogen adsorption-desorption measurements, are shown in Figure 5.1(a-f). All the samples showed type IV isotherm (Figure 5.1, a-f) [27-30]. The hysteresis feature of the as synthesized cobalt aluminosilicates (CSA-1, CSA-2 and CSA-3) at the relative pressure \((p/p_0)\) of 0.4-0.9 were classified as the type H3 loop, while in case of CSA-4 sample, the hysteresis at the
relative pressure of 0.1-0.9 was classified as the type H4 loop [28, 31]. The type H3 loop, was observed with aggregates of plate-like particles giving rise to narrow slit shaped pores (diameter \~1.17 and \~3.40 nm). Similarly, the type H4 loop is often associated with uniform two parallel plates. In case of CSA-4 sample, the type IV isotherm was indicative of both meso and microporous nature with pore diameters of 4.04 and 2.0 nm (Figures 5.1 and 5.2). The gradual increase in pore diameter from 1.17 to 2.0 nm and 3.40 to 4.04 nm was observed with increase in aluminium content (Si:Al from 10:1 to 1:10) [32]. On the other hand, (CSA-4) calcined at temperatures 573 K and 773 K (CSA-4-3C and CSA-4-5C) showed hysteresis at the relative pressures of 0.1-0.9 and 0.4-0.9 respectively and were classified as the H2 type loop (Figure 5.3). The type H2 loop is a mixture of pores with micro and meso dimensions [28]. The calcination at higher temperature (773 K) caused shift in hysteresis feature from relative pressure 0.1-0.9 to 0.4-0.9. This might be due to dehydroxylation resulting in either disruption or collapse of mesopores and resulting into the formation of microporous (pore size from 4.10 to \~2.0) materials. A sharp decrease in surface area from 232.8 to 6.1 m$^2$/g and increase in pore diameter from 1.17 nm to 4.04 nm was observed on changing the composition from 10:1 to 1:10 (Table 5.1) (Figure 5.2). Similar results was reported in the literature for Si-MMS, Si-MCM-41, Al-MCM and Al-MMS materials [33]. The significant decrease in surface area was due to increase in aluminium composition which caused hydrophilicity (weight loss increased from 26.1% to 77.5%) as observed in TG-DTA analysis. However, in case of CSA-4 sample calcined at 573 K, increase in surface area from 6.1 to 113.4 m$^2$/g was observed as a result of dehydration or decomposition of water (weight loss 77.5%) present in the mesopores (pore diameter 4.04 nm) as observed in TG-DTA and FTIR analysis (Table 5.1) (Figure 5.3). Further increase in calcination temperature (773 K) caused decrease in surface area from 113.4 to 96.3 m$^2$/g due to restructuring.
which induces disappearance of spaces between cobalt aluminosilicate as observed in TEM studies discussed later (sections 5.2.5 and 5.2.8). From the pore size distribution curve, it was found that all the samples showed a bimodal pore distribution as determined by using the Barrett-Joyner-Halenda (BJH) method with smaller pores in the region of ~1.5-2.0 nm and larger pores ranging from ~3.8-4.1 nm (Table 5.1).

Thus, above observations established that the textural properties of the material can be varied from microporous (~2.0 nm) to mesoporous (~4.1 nm) by changing the Si:Al ratio (from 10:1 to 1:10) and calcination at 573 K.
Figure 5.1. Adsorption isotherm of (A) CSA-1, (B) CSA-2, (C) CSA-3, (D) CSA-4, (E) CSA-4-3C and (F) CSA-4-5C samples

Figure 5.2. Pore size distribution of (A) CSA-1, (B) CSA-2, (C) CSA-3 and (D) CSA-4 samples
Figure 5.3. Pore size distribution of (A) CSA-4, (B) CSA-4-3C and (C) CSA-4-5C samples

Table 5.1. Textural properties of cobalt catalysts prepared with at different silica alumina (Si:Al) ratios and calcination temperatures

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Si:Al ratio</th>
<th>Calcination temperature (K)</th>
<th>Surface area (m²/g)</th>
<th>Pore size, BJH (nm)</th>
<th>Pore volume, BJH (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSA-1</td>
<td>10:1</td>
<td>423</td>
<td>232.8</td>
<td>1.17</td>
<td>0.17</td>
</tr>
<tr>
<td>CSA-2</td>
<td>1:1</td>
<td>423</td>
<td>134.3</td>
<td>2.81</td>
<td>0.29</td>
</tr>
<tr>
<td>CSA-3</td>
<td>1:5</td>
<td>423</td>
<td>13.3</td>
<td>3.40</td>
<td>0.48</td>
</tr>
<tr>
<td>CSA-4</td>
<td>1:10</td>
<td>423</td>
<td>6.1</td>
<td>4.04</td>
<td>0.50</td>
</tr>
<tr>
<td>CSA-4-3C</td>
<td>1:10</td>
<td>573</td>
<td>113.4</td>
<td>4.10</td>
<td>0.79</td>
</tr>
<tr>
<td>CSA-4-5C</td>
<td>1:10</td>
<td>773</td>
<td>96.3</td>
<td>3.98</td>
<td>0.58</td>
</tr>
</tbody>
</table>

5.2.2. X-ray diffraction (XRD)

Powder X-ray diffraction patterns of 15% cobalt aluminosilicate samples with different Si:Al ratios, calcined at 573 K and 773 K at different calcination times are shown in Figures 5.4 (a), (b) and (c) respectively. Intense peaks in case of CSA-1, CSA-2 and CSA-3 samples observed at
$\theta = 12.2^\circ (110), 19^\circ (101), 23.5^\circ (300), 32.1^\circ, 37.3^\circ, 48.3^\circ \text{ and } 60.2^\circ (060)$ could be assigned to smectite phase. These peaks became broader and less intense with change in silica alumina ratio from 10:1 to 1:5 (Figure 5.4, a). This might be due to increase in aluminium content causing slight change in layered morphology to amorphous nature [34]. This indicates the formation of saponite clay especially smectite type with a tri-octahedral structure and divalent cobalt being inserted in tetrahedral positions within the layer; replacing sodium to some extent. The peaks at $\theta = 31.1^\circ, 37.3^\circ, 48.3^\circ \text{ and } 62.2^\circ (060)$ confirmed that material with mixed phases was formed [2]. However, further change in silica: alumina ratio to 1:10 (CSA-4) caused disappearance of the peaks at $\theta = 12.2^\circ (110), 19^\circ (101), 23.5^\circ (300), 32.1^\circ, 37.3^\circ, 48.3^\circ \text{ and } 60.2^\circ (060)$ and formation of new peaks at $\theta = 29.6^\circ (321), 31.2^\circ (321), 38.2^\circ (216) \text{ and } 48.7^\circ (611)$, which correspond to the garnet (spinel) phase of aluminosilicate (JCPDS = 86-0657). The higher proportion of aluminum insertion in case of CSA-4 (Si:Al 1:10) sample indicated the formation of either pillaring or disruption of layer morphology as observed in nitrogen adsorption-desorption isotherm discussed in the Section 5.2.2. Also, there was little or no ordered stacking of the layers, as evidenced by the absence of a reflection at $\theta = 60.2^\circ (060)$.

Increase in calcination temperature from 573 to 773 K (CSA-4) caused gradual increase in intensities and the slight decrease in widths of the peaks at $\theta = 29.6^\circ (321), 31.2^\circ (321), 38.2^\circ (216) \text{ and } 48.7^\circ (611)$ (Figure 5.4(b)). These samples did not show any shift in peak position or additional peaks after calcination indicating that there was no delamination and the sample (CAS-4) was highly stable having amorphous nature, even after calcination (Figure 5.4(b)). Further, CSA-4 sample was calcined at 573 K with increase in calcination time from 1 to 6 h (Figure 5.4(c)). With increase in calcination time from 1 to 6 h, increase in intensity of peaks at
$2\theta = 29.6^\circ$ (321), $31.2^\circ$ (321), $38.2^\circ$ (216) and $48.7^\circ$ (611) was observed. Above observations established the fact that increase in aluminium content, calcination temperature and time facilitated the increase in garnet phase of spinel cobalt aluminosilicate.

![XRD patterns of (A) CSA-1, (B) CSA-2, (C) CSA-3 and (D) CSA-4 samples](image1.jpg)

**Figure 5.4(a).** XRD patterns of (A) CSA-1, (B) CSA-2, (C) CSA-3 and (D) CSA-4 samples

![XRD patterns of (A) CSA-4, (B) CSA-4-3C, (C) CSA-4-4C and (D) CSA-4-5C samples](image2.jpg)

**Figure 5.4(b).** XRD patterns of (A) CSA-4, (B) CSA-4-3C, (C) CSA-4-4C and (D) CSA-4-5C samples
5.2.3. X-ray photoelectron spectroscopy (XPS)

The Co 2p XPS spectra of 15% cobalt aluminosilicates as a function of silica alumina ratio (10:1, 1:1, 1:5 and 1:10) are shown in Figure 5.5. CSA-2, CSA-3 and CSA-4 samples show contain the Co 2p$_{3/2}$ and Co 2p$_{1/2}$ core level peaks at binding energies of 780.1 and 795.4 eV having difference of 15.3 eV which is almost equivalent in all samples except CSA-1 (13.9 eV). The increase in aluminium content caused gradual increase of peak intensities at binding energies of 780.1, 795.4 and 801.6 eV, which might be due to the change in layered morphology of clay to disordered layer morphology of aluminosilicate which is in accordance with XRD as discussed in Section 5.2.2 [35, 36]. Co 2p$_{3/2}$ peaks observed at binding energies of 780 eV was very close to those reported for Co$^{2+}$ as well as Co$^{2+}$ exchanged NaY and for highly dispersed cobalt species.
in Co-ZSM-5 indicating that cobalt was coordinated to lattice oxygen probably associated with aluminum and silanol groups [35, 36]. In addition to these spin-orbital peaks, the satellite peak for Co 2p$_{3/2}$ was also observed at 786.2 eV, confirming that maximum species were in cobalt (II) state [37, 38].

![Figure 5.5. XPS of (A) CSA-1, (B) CSA-2, (C) CSA-3 and (D) CSA-4 samples](image)

**5.2.4. Diffuse reflectance UV-visible spectroscopy**

DRUV-Visible spectra recorded for samples with varying Si:Al ratios, calcined at 573 and 773 K and with different cobalt loadings (5%, 15% and 30%) are shown in Figures 5.6(a), (b) and (c). The samples with Si:Al-10:1 (CSA-1) and Si:Al-1:2 (CSA-2) ratios showed a band at 242 nm. With further increase in aluminium content (Si:Al-1:1), CSA-3 sample showed a shift of 242 nm band to 263 nm and finally for Si:Al-1:10, CSA-4 showed two bands at 263 nm and 305 nm associated with oxygen to cobalt charge transfer (CT) transition assigned to tetrahedral Co$^{2+}$. 
species (Figure 5.6, a) [39]. Among all the samples, CSA-4 sample showed relatively stronger bands at 522 and 625 nm. A band at 522 nm suggests the presence of an extra lattice Co(II) in octahedral symmetry [40], whereas band at 625 nm was assigned for charge transfer (CT) transition band between oxygen to cobalt assigned to octahedral Co\(^{3+}\) species [41]. The intensities of all bands in case of CSA-1, CSA-2 and CSA-3 samples were relatively lower than those for the CSA-4 sample. This might be due to the incorporation of most of the cobalt into aluminosilicate (clay) lattice and not present on the surface as also observed in XPS studies discussed in Section 5.2.4.

The CSA-4 sample calcined at 573 K showed a slight increase in band intensities at 263, 305, 522 and 625 nm (Figure 5.6, b). This might be due to \(~70\%\) weight loss below 573 K (observed in TG-DTA) which caused opening of the mesopores (4.04 nm) of cobalt aluminosilicates and calcination in air causing oxidation of some of Co\(^{2+}\) species to Co\(^{3+}\) [40], as evidenced by FTIR, XPS, TPR and TPO studies. However, further increase in calcination temperature from 573 to 673 and 773 K, caused increase in intensities of bands at 263, 305, 522, 625 nm and an additional band appeared at 380 nm (Figure 5.6, b). Thus, the interaction of cobalt either with aluminium or with silica due to dehydroxylation of surface hydroxyl group at higher temperature, caused disruption/collapse of cobalt aluminosilicate structure which was also evidenced by nitrogen adsorption-desorption isotherm, surface area, pore size distribution and pore volume studies. In case of CSA-4 sample calcined at 573 K, slight increase in intensity of a peak at 625 nm indicated that tetrahedral Co\(^{2+}\) in the framework of the aluminosilicates was interconverted to Co\(^{3+}\) upon oxidation.

The cobalt loading in aluminosilicates (Si:Al; 1:10) was varied in the range of 5\% to 30\% (Figure 5.6, c). The intensities of bands at 263, 305, 522 and 625 nm increased with increase in
cobalt loading from 5% to 30%. As a result of increase in cobalt loading, distribution of both cobalt Co\(^{2+}\) and Co\(^{3+}\) species also increased [42-44].

**Figure 5.6(a).** DRUV-vis spectra of (A) CSA-1, (B) CSA-2, (C) CSA-3 and (D) CSA-4 samples

**Figure 5.6(b).** DRUV-vis spectra of (A) CSA-4, (B) CSA-4-3C, (C) CSA-4-4C and (D) CSA-4-5C samples
Figure 5.6(c). DRUV-vis spectra of (A) 5%, (B) 15% and (C) 30% cobalt loading on SA-4 (Si:Al-1:10) samples

5.2.5. Thermo gravimetric analysis (TGA)

TG-DTA of 15% cobalt aluminosilicates with different Si:Al ratios (from 10:1 to 1:10) is shown in Figure 5.7. With change in Si:Al ratio from 10:1 to 1:10, the total increase in weight loss was observed from 26.19% to 77.5% (Table 5.2). An appreciable weight loss of 20%, 15%, 27% and 57% was observed below 453 K, in case of CSA-1, CSA-2, CSA-3 and CSA-4 samples respectively, due to the loss of water absorbed and coordinated to and/or present in the meso-/micro pores [45]. The gradual increase in percentage weight loss due to increase in aluminium content, resulted into change in cobalt aluminosilicate property from hydrophobic to hydrophilic [45]. The second weight loss of 2.1%, 9.1%, 12% and 27% in case of all samples below 573 K was due to decomposition and dehydroxylation of carbonate (reaction product of urea), trace of acetate from cobalt acetate, undissolved nitrate and hydroxyl group which were confirmed from FTIR examination. The continuous percentage weight loss of 4.1%, 7.1%, 7.6% and 7.5% above
573 K was due to the dehydroxylation of surface Si-OH or cobalt acetate present/trapped in meso pores of the sample. Among all the samples, CSA-1 showed weight loss in a single step, while remaining all showed the weight loss in three steps. This might be due to the disorder in layered morphology as well as increase in pore diameter from 1.17 nm to 4.04 nm as observed in nitrogen adsorption-desorption isotherm and XRD analysis. The increase in disorder in morphology leads to difficulty in the removal/escape of water molecules trapped in layer or meso-/micro pores which require higher temperature [46, 47]. However, the presence of interlayer water and swelling properties of the clay clearly demonstrate that the material is not talc [48, 49].

![Graph](image)

**Figure 5.7.** TG-DTA of (A) CSA-1, (B) CSA-2, (C) CSA-3 and (D) CSA-4 samples
Table 5.2. Summary of thermogravimetric analysis

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Temperature range (K)</th>
<th>Percentage weight loss</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300-370</td>
<td>15.0 5.0 18.0 16.0</td>
<td>Loss of physically adsorbed water molecules.</td>
</tr>
<tr>
<td></td>
<td>373-473</td>
<td>5.0 10.0 9.0 41.0</td>
<td>Loss of physically adsorbed/trapped water molecules.</td>
</tr>
<tr>
<td></td>
<td>473-573</td>
<td>2.1 9.1 12.0 13.0</td>
<td>Decomposition of carbonate anions, acetate and nitrate.</td>
</tr>
<tr>
<td></td>
<td>573-873</td>
<td>4.1 7.1 7.6 7.5</td>
<td>Dehydroxylation of surface hydroxyl group.</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>26.2 31.2 46.6 77.5</td>
<td></td>
</tr>
</tbody>
</table>

5.2.6. Fourier-transform infrared spectroscopy (FTIR)

The FTIR spectrum of 15% cobalt aluminosilicate samples having different Si:Al ratios and CSA-4 sample calcined at 573 and 773 K are shown in Figure 5.8. The very strong and relatively sharp peaks at 1005, 1386 and 1648 cm\(^{-1}\), were due to carbonate (product of urea), trace of acetate from cobalt acetate, undissolved nitrate and hydroxyl group present in CSA-1, CSA-2, CSA-3 and CSA-4 samples (Figure 5.8, A-D). Three small and broad peaks at 468, 620 and 780 cm\(^{-1}\) observed in all the samples were due to Si-O/Al-O and Co-O vibrations [50]. The two broad and intense bands at 3345 cm\(^{-1}\) were attributable to structural \(\nu(\text{OH})\) and a broader band at 3605 cm\(^{-1}\) to the \(\nu(\text{OH})\) of interlayer water. The intensities of these bands gradually increased with increase in aluminium content (from 10:1 to 1:10), confirming the shift in nature of samples from hydrophobic to hydrophilic which was also evidenced in TG-DTA analysis. However due to calcination at 573 K and 773 K, the peaks at 3605, 3345, 1648, 1386 and 1005 cm\(^{-1}\) disappeared.
(Figure 5.8, E-F). This was mainly due to the decomposition and dehydroxylation of water, carbonate, acetate, nitrate and hydroxyl molecules present before calcination in the CSA-4 sample. Also, two low intensity peaks appeared at 676 and 546 cm\(^{-1}\) assigned to Co\(^{2+}\) in a tetrahedral and Co\(^{3+}\) in octahedral positions observed in CSA-4-3C and CSA-4-5C samples [51, 52]. This might be due to calcination at 573 and 773 K converting some of the Co\(^{2+}\) into Co\(^{3+}\), which was also confirmed from DR-UV, XPS, CV, TPR and TPO studies.

![Figure 5.8. FTIR spectra of (A) CSA-1, (B) CSA-2, (C) CSA-3, (D) CSA-4, (E) CSA-4-3C and (F) CSA-4-5C samples](image)

5.2.7. Scanning electron microscope (SEM) and Energy dispersive X-ray (EDX)

SEM spectra of 15% cobalt aluminosilicate samples having different Si:Al ratios are shown in Figure 5.9. The average size of particles was found to be ~10-25, 10-28, 20-40 and 30-60 μm in
case of CSA-1, CSA-2, CSA-3 and CSA-4 samples respectively. The gradual increase in the particle size was in order with the increase in aluminium content due to the hydrophilicity which caused the particles to come closer and remain intact. The particles showed the aggregates formed by packing of sheets thus demonstrating that the synthesis method can lead to the formation of materials with layered morphology.

**Figure 5.9.** SEM spectra of (A) CSA-1, (B) CSA-2, (C) CSA-3 and (D) CSA-4 samples
The elemental composition of cobalt aluminosilicates samples having different Si:Al ratios and cobalt loadings (5% to 30%) Si:Al were determined by EDX, as shown in Figure 5.10. CSA-1, CSA-2, CSA-3 and CSA-4 samples showed the presence of cobalt, aluminium, silicon, sodium, oxygen, nitrogen and traces of carbon. The calculated (especially silicon and aluminium) elemental ratio of Si:Al in weight percentages were found to be about ~1:10, 1:1, 1:5 and 1:10 which were in excellent agreement with the theoretical percentages (Table 5.3). The percentage of cobalt loading in case of CSA-1, CSA-2, CSA-3 and CSA-4 samples found to be in the range of 14.2 to 15.2% closely matching with the theoretical cobalt loading of ~15%, (Table 5.3). The cobalt loadings in case of 5%, 15% and 30% samples were found to be 3.1%, 15.2% and 18.5% of cobalt respectively (Table 5.3). The lower percentage found in case of both 5% and 30% samples might be because some of the cobalt was incorporated within aluminosilicates layer and/or leached out.
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**Figure 5.10.** EDAX of (A) 15% CSA-1, (B) 15% CSA-2, (C) 15% CSA-3, (D) 15% CSA-4, (E) 5% CSA-4 and (F) 30% CSA-4 samples

**Table 5.3.** Elemental compositions of cobalt aluminosilicate catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Co</th>
<th>O</th>
<th>Si</th>
<th>Al</th>
<th>Na</th>
<th>N</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>15% CSA-1</td>
<td>14.9</td>
<td>40.0</td>
<td>32.0</td>
<td>3.5</td>
<td>4.5</td>
<td>1.2</td>
<td>5.8</td>
</tr>
<tr>
<td>15% CSA-2</td>
<td>14.3</td>
<td>62.0</td>
<td>9.0</td>
<td>10.0</td>
<td>3.0</td>
<td>2.0</td>
<td>4.0</td>
</tr>
<tr>
<td>15% CSA-3</td>
<td>14.2</td>
<td>62.0</td>
<td>3.0</td>
<td>15.0</td>
<td>1.0</td>
<td>3.0</td>
<td>2.0</td>
</tr>
<tr>
<td>15% CSA-4</td>
<td>15.2</td>
<td>26.8</td>
<td>3.2</td>
<td>32.9</td>
<td>2.0</td>
<td>14.0</td>
<td>7.0</td>
</tr>
<tr>
<td>5% CSA-4</td>
<td>3.1</td>
<td>33.9</td>
<td>3.8</td>
<td>45.2</td>
<td>1.1</td>
<td>2.1</td>
<td>9.8</td>
</tr>
<tr>
<td>30% CSA-4</td>
<td>18.5</td>
<td>29.0</td>
<td>3.2</td>
<td>37.0</td>
<td>1.5</td>
<td>4.6</td>
<td>6.2</td>
</tr>
</tbody>
</table>
5.2.8. Transmission electron microscopy

In order to know the effect of calcination temperature (573 and 773 K) on layered morphology of CSA-4 sample, characterization by TEM was studied (Figure 5.11). The sample calcined at 573 K (CSA-4-3C) showed the opening of mesopores (pore diameter 4.10 nm) while sample calcined at higher temperature of 773 K (CSA-4-5C) showed that the sheet morphology was significantly hampered due to the disappearance of interparticle spaces and decrease in pore size from 4.10 nm to ~2.0 nm (peak intensity at 2.0 nm is higher than the of 3.98 nm peak) as observed in the pore size distributions (Section 5.2.1). The significant increase in surface area in case of CSA-4-3C (calcination at 573 K) sample by seventeen times (from 6.1 to 113.5 m²/g). This might be due to a weight loss of ~70% (dehydration and decomposition) below 573 K resulting into the opening of the pores. However, in case of CSA-4-5C sample calcined at 773 K caused dehydroxylation which significantly resulted into disruption of layered structure and pores opening which is observed in TG-DTA, surface area, pore size distribution and DRUV examinations.
5.2.9. Temperature programmed reduction / Temperature programmed oxidation (TPR/TPO)

TPR experiments were carried out in order to study the change in redox behavior of cobalt aluminosilicate having different Si/Al ratios and effect of calcination temperatures (573 and 773 K) on CSA-4 samples (Figure 5.12). Broad and less intense peaks appeared in the range of 373-873 K, while intensity of characteristics Co\(^{2+}/Co^{3+}\) reduction peak was too low in case of CSA-1, CSA-2, CSA-3 and CSA-4 samples. The broad and less intense reduction peaks might be due to the ~26.2%, 31.2%, 46.6% and 77.5% weight loss as a result of loss of water, acetate, carbonate of urea which were present in interlayer/mesopores. CSA-4 sample calcined at 573 and 773 K showed an intense single peak in the range of 470-673 K assigned to the sequential reduction of (Co\(^{3+}\)) trivalent cobalt oxide to (Co\(^{2+}\)) divalent cobalt oxide (CoO) and further reduction to metallic cobalt (Co\(^{0}\)) [53-55]. The calcination caused dehydration and decomposition of molecules (water, acetate, carbonate of urea) resulting in to opening of interlayer and meso pores.
causing significant increase in cobalt active species as evidenced by nitrogen adsorption-desorption isotherm, surface area, XPS, TEM, FTIR and DRUV studies.

The change in Si:Al composition from 10:1 to 1:10 showed slight increase in H$_2$ up take (2.1, 2.3, 2.7 and 3.3 mmol) (Table 5.4), which was found to be very less (435.0 mmol) than that observed for pure spinel Co$_3$O$_4$ (Co-3C-a) catalyst. However, CSA-4 sample calcined at 573 and 773 K showed 1.5 and 1.2 times higher H$_2$ up take (681.4 and 527 mmol) respectively, than spinel Co$_3$O$_4$ catalyst. This remarkable enhancement in H$_2$ up take was due to distribution of 15% cobalt (Co$^{2+}$/Co$^{3+}$) species over aluminosilicate surface and within the meso pores.

![Figure 5.12. TPR of (A) CSA-1, (B) CSA-2, (C) CSA-3, (D) CSA-4, (E) CSA-4-3C and (F) CSA-4-5C samples](image)

The ability of oxidation of pre-reduced cobalt aluminosilicate catalysts having different Si:Al ratio (10:1 to 1:10) and CSA-4 samples calcined at 573 and 773 K, was calculated by using TPO analysis as shown in Figure 5.13. The broad and less intense peak in the range of 450-550 K in
all the samples was attributed to sequential oxidation of metallic cobalt oxide (Co°) to divalent cobalt oxide (CoO) and finally to trivalent cobalt oxide (Co₃O₄) [52, 56]. With change in Si:Al ratio (from 10:1 to 1:10) and calcination temperature (CSA-4-3C and CSA-4-5C), slight increase in peak intensity was observed.

As much as about twice increase in O₂ up take (from 7.8 to 14.6 mmol) was observed with change in Si:Al from 10:1 to 1:10, while both these values were lower than that for the spinel Co₃O₄ (20.6 mmol) sample (Table 5.4). However, with increase in calcination temperature to 573 and 773 K, there was a significant increase in O₂ up take by 2 times and 1.5 times respectively, compared to spinel Co₃O₄ catalyst.

**Figure 5.13.** TPO of (A) CSA-1, (B) CSA-2, (C) CSA-3, (D) CSA-4, (E) CSA-4-3C and (F) CSA-4-5C samples
### Table 5.4. TPR/TPO-H₂/O₂ uptake profile of cobalt aluminosilicate catalysts with different Si:Al ratio and calcined samples of CSA-4 at 573 and 773 K

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Si:Al ratio</th>
<th>Calcination temperature (K)</th>
<th>H₂ (mmol)</th>
<th>O₂ (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSA-1</td>
<td>10:1</td>
<td>423</td>
<td>2.1</td>
<td>7.8</td>
</tr>
<tr>
<td>CSA-2</td>
<td>1:1</td>
<td>423</td>
<td>2.3</td>
<td>8.2</td>
</tr>
<tr>
<td>CSA-3</td>
<td>1:5</td>
<td>423</td>
<td>2.7</td>
<td>10.8</td>
</tr>
<tr>
<td>CSA-4</td>
<td>1:10</td>
<td>423</td>
<td>3.3</td>
<td>14.6</td>
</tr>
<tr>
<td>CSA-4-3C</td>
<td>1:10</td>
<td>573</td>
<td>1781.4</td>
<td>43.5</td>
</tr>
<tr>
<td>CSA-4-5C</td>
<td>1:10</td>
<td>773</td>
<td>1027.3</td>
<td>31.9</td>
</tr>
<tr>
<td>Co-3C-a</td>
<td>NA</td>
<td>573</td>
<td>435.0</td>
<td>20.6</td>
</tr>
</tbody>
</table>

Where; NA is not applicable

#### 5.2.10. Cyclic voltammogram (CV)

The redox potential profiles of the cobalt aluminosilicate catalysts with various Si:Al ratios were obtained by cyclic voltammogram (Figure 5.14). All the samples showed broad oxidation and reduction peaks. The cathodic peak in the lower potential region (0.41 V) could be assigned to the oxidation of Co²⁺ to Co³⁺. Similarly, the anodic peak present at higher potential (0.5 V) could be assigned to the reduction of Co³⁺ to Co²⁺. The anodic and cathodic peak intensities gradually increased from CSA-1 to CSA-4 samples. This was due to the gradual increase in number of surface active tetrahedral (Co³⁺) and octahedral (Co³⁺) species as a result of enhancement in the redox potential, indicating that among the prepared catalysts, higher oxidizing ability of CSA-4 catalyst was due to its enhanced redox potential.
5.2.11. Fourier Transform Extended X-ray Absorption Fine Structure (EXAFS)

FT-EXAFS was studied to understand the cobalt interaction with aluminosilicate (CSA-4) and the effect of calcination temperature (573 and 773 K) on the bond distance and environment around Co (Figure 5.15). The peaks appearing at 1.46, 2.45 and 3.04 Å were assigned to Co-O, Co-Co and Co-O bond distances respectively (Figure 5.15, A) [57, 58]. These observed bond distances were almost identical to those observed for the spinel Co$_3$O$_4$ however, the peak showed lower intensities (Figure 5.15, D). This might be due to incorporation of cobalt in the aluminosilicate environment. The CSA-4 sample calcined at higher 573 and 773 K caused increase in bond distances by 0.6, 0.26 and 0.27 Å assigned to Co-O, Co-Co and Co-O bonds respectively, while new additional peak at 1.1 Å for the Co-O bond was observed in CSA-4-3C.
and CSA-4-5C samples (Figure 5.15, B and C). The calcination at higher temperature resulted in dehydration, decomposition and most importantly, dehydroxylation of silanol and cobalt hydroxyl groups, due to which recombination of all bonds resulted in to shift in peaks from 1.46, 2.45, 3.04 Å to 1.52, 2.71, 3.31 Å respectively. The new Co-O bond at 1.1 Å confirmed that Co-O bond was affected due to interaction of Co-O in the interlayer more with tetrahedral than the octahedral layer (Figure 5.15, B and C) [59]. The slight decrease in peak intensity and change in bond distance for Co-O in case of calcined catalyst suggested that the peaks at 1.1 and 1.6 Å were due to the tetrahedral Co-O binding with octahedral layers of the silanol and aluminium respectively. The slight change in inter atomic M-O bond distance was due to the release of water molecules from inter layers of clay resulted in an increase in pillaring by 0.2 Å of cobalt cation. The decrease in intensity of Co-O at 2.71 Å suggested the formation of Al$_2$O$_3$CoO as well as spinel SiO$_4$Co (garnet phase). There was also a possibility of the formation of slight spinel Co$_3$O$_4$ which can coordinate with either the octahedral or the tetrahedral layer via oxygen which is in accordance with XRD, DRUV, FTIR, XPS, TPR, TPO and CV results [60, 61].
5.3. ACTIVITY MEASUREMENT

In our previous studies, it was found that cobalt aluminosilicate (especially saponite clay) was highly active for catalytic oxidation of \( p \)-cresol under mild reaction conditions [22]. Therefore as a continuation of this work, CSA-1 (cobalt aluminosilicate with Si:Al ratio 10:1) was evaluated for the liquid phase oxidation of veratryl alcohol (Scheme 5.1). However, CSA-1 did not show any activity for this reaction (Table 5.5, next section) due to its layered morphology (with restricted space mobility to two dimension) with small pore diameter (1.17 nm) and most of the surface active sites were trapped inside the layers. Veratryl alcohol having non-planar geometry with a larger size (9.2151 Å) than \( p \)-cresol (7.5454 Å) [Figure 5.16, A and B] [62-64] was rather difficult to diffuse through the pores (with 11.7 Å diameter) to access the cobalt active species.

Figure 5.15. FT-EXAFS of (A) CSA-4, (B) CSA-4-3C, (C) CSA-4-5C, (D) Co-3C-a (Co\(_3\)O\(_4\)) and (E) CA-6C (CoAl\(_2\)O\(_4\)) samples.
present inside. Considering this, cobalt aluminosilicates with different silica alumina ratios were prepared in order to get aluminosilicates with large pores so as to enable the substrate having non-planer geometry like veratryl alcohol can easily diffuse to interact with the active species. Vienna \textit{ab-initio} Simulation Package (VASP) was used for the optimization of the structures [Figure 5.16, A and B] [62-64].

**Scheme 5.1.** Pictorial representation of oxidation reaction over the cobalt aluminosilicate Catalysts
Figure 5.16. Three dimensional (3D) representations of (A) veratryl alcohol and (B) $p$-cresol molecules
5.3.1. Catalyst screening

The liquid phase oxidation of veratryl alcohol was carried out by using cobalt aluminosilicate catalysts with various Si:Al ratios (from 10:1 to 1:10). Based on the highest activity of the CSA-4 (having Si:Al ratio 1:10), other transition elements such as Cu, Mn and Fe were also used to prepare the corresponding metal aluminosilicate keeping Si:Al ratio constant at 1:10. The catalytic performance of these prepared catalysts is discussed in the following sections.

5.3.1.1. Effect of different transition elements

Various transition metal (such as Co, Cu, Fe and Mn) incorporated aluminosilicate with a constant Si:Al ratio of 1:10 were screened for the liquid phase oxidation of veratryl alcohol and results are shown in Table 5.5. Cobalt [43, 65], copper [66], iron [67] and manganese [68] were of particular interest since, these have long been known to reversibly bind and activate dioxygen forming mononuclear superoxo species responsible for catalytic oxidation of phenolic substrates [69]. Inspite of having almost equivalent surface areas (CSA-4, CuSA-4, FeSA-4 and MnSA-4); CSA-4 catalyst showed the highest activity among all the catalysts. The higher activity of the cobalt aluminosilicate than that of copper, iron and manganese catalysts was because of highly efficient redox system of cobalt (Co$^{2+} \leftrightarrow$ Co$^{3+}$) responsible for the oxidation. The catalytic oxidation of veratryl alcohol to veratryl aldehyde over different catalysts was found to be in the following order: cobalt > iron > manganese > copper.
Table 5.5. Comparative catalytic activity and stability results of various metals aluminosilicate with Si:Al ratio 1:10

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Elements</th>
<th>Surface area (m²/g)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>Leaching of metal (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Veratryl aldehyde</td>
<td>Veratric acid</td>
</tr>
<tr>
<td>CSA-4</td>
<td>Cobalt</td>
<td>6.1</td>
<td>24.4</td>
<td>&lt; 99.9</td>
<td>&gt;0.1</td>
</tr>
<tr>
<td>CuSA-4</td>
<td>Copper</td>
<td>5.4</td>
<td>15.7</td>
<td>&lt; 99.9</td>
<td>&gt;0.1</td>
</tr>
<tr>
<td>FeSA-4</td>
<td>Iron</td>
<td>6.0</td>
<td>23.7</td>
<td>&lt; 99.9</td>
<td>&gt;0.1</td>
</tr>
<tr>
<td>MnSA-4</td>
<td>Manganese</td>
<td>5.8</td>
<td>19.8</td>
<td>&lt; 99.9</td>
<td>&gt;0.1</td>
</tr>
</tbody>
</table>

Reaction conditions: temperature, 413 K; oxygen pressure, 2.01 MPa; veratryl alcohol, 0.5 g (3 mmol); catalyst, 0.3 g; solvent toluene, 70 mL; NaOH, 1.0 g (24 mmol); agitation speed, 900 rpm; reaction time, 5 h. *ND: not detected

5.3.1.2. Effect of cobalt loading

The effect of cobalt loading (5-30%) in aluminosilicate (CSA-4) for the liquid phase oxidation of veratryl alcohol was studied and the results are shown in Figure 5.17. For this purpose, cobalt aluminosilicate catalysts were prepared with varying cobalt percentage from 5 to 30% and were evaluated for the oxidation of veratryl alcohol at 413 K and 2.01 MPa O₂ pressure conditions. It was observed that the conversion of veratryl alcohol increased with increase in Co loading from 5 to 15% and then remained constant up to 30% of Co loading. Hence, further work on the effects of various reaction parameters on conversion of veratryl alcohol and product selectivities was carried out over 15% cobalt aluminosilicate (CSA-4) catalyst. In each experiment, the final sample was analyzed by HPLC to calculate the conversion and product selectivities.
Figure 5.17. Effect of cobalt loading in aluminosilicate on catalytic oxidation of veratryl alcohol
Reaction conditions: temperature, 413 K; oxygen pressure, 2.01 MPa; veratryl alcohol, 0.5 g (3 mmol); catalyst, 0.3 g; solvent toluene, 70 mL; NaOH, 1.0 g (24 mmol); a gitation speed, 900 rpm; reaction time, 5 h.

5.3.1.3. Effect of Si:Al ratio on activity

The results of Si:Al ratio on activity of alumina silicate for the liquid phase oxidation of veratryl alcohol to veratryl aldehyde are shown in the Table 5.6. For this purpose, cobalt (15%) aluminosilicate samples were prepared with varying Si:Al ratios in the range of 10:1 to 1:10. Among the prepared catalysts, highest catalytic activity was shown by CSA-4 sample (24.4% conversion and complete selectivity to veratryl aldehyde). The increase in conversion by six times (from 4.0% to 24.4%) due to gradual increase in pore diameter from 1.17 nm to 4.04 nm and increase in surface active cobalt Co^{2+}/Co^{3+} species resulted in enhancement of the formation of a redox couple on the surface as was observed in XPS, FTIR, TPR, TPO and CV analysis. Thus highest activity for the bulkier non-planar veratryl aldehyde molecule over CSA-4 catalyst
(inspite of having lower surface area 6.1 m²/g) was due to mesopores with diameter 41 Å (4.10 nm) which allowed easy diffusion and adsorption via pore resulting into highest activity.

**Table 5.6.** Catalytic activity of 15% cobalt loading in aluminosilicate having different Si:Al ratio

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Si:Al ratio</th>
<th>Surface area (m²/g)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Veratryl aldehyde</td>
</tr>
<tr>
<td>CSA-1</td>
<td>10:1</td>
<td>232.8</td>
<td>4.0</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>CSA-2</td>
<td>1:1</td>
<td>120.0</td>
<td>7.6</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>CSA-3</td>
<td>1:5</td>
<td>13.3</td>
<td>15.8</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>CSA-4</td>
<td>1:10</td>
<td>6.1</td>
<td>24.4</td>
<td>&gt;99.9</td>
</tr>
</tbody>
</table>

Reaction conditions: temperature, 413 K; oxygen pressure, 2.01 MPa; veratryl alcohol, 0.5 g (3 mmol); catalyst, 0.3 g; solvent toluene, 70 mL; NaOH, 1.0 g (24 mmol); agitation speed, 900 rpm; reaction time, 5 h.

### 5.3.2. Effect of catalyst pretreatment conditions

#### 5.3.2.1 Effect of calcination temperature

Various samples of CSA-4 catalyst were prepared and calcined in a temperature range of 573-773 K. As can be seen from the Table 5.7, it was observed that the conversion increased more than three times (from 24.4 to 86%) with increase in calcination temperature from 423 to 573 K. However, the selectivity to veratryl aldehyde decreased from 99.9% to 94%, due to further oxidation of veratryl aldehyde to veratric acid. The increase in conversion by more than three times was due to increase in surface area by 18 times from 6.1 to 113.5 m²/g which eventually caused a significant increase in cobalt (Co²⁺ and Co³⁺) active species. The significant increase in active species in case of a sample calcined at 573 K was due to dehydration and decomposition.
of water molecules and other starting precursors present in the mesopores (diameter 4.04 nm) and on the surface, as evidenced by various characterization results discussed in previous sections. However, with increase in calcination temperature from 573 to 673 and 773 K, marginal decrease in activity was observed (from 86% to 80.7% and 78.9% respectively). The increase in calcination temperature from 573 K to 673 K caused dehydroxylation of surface hydroxyl group causing disruption of surface morphology, slight decrease in pore diameter from 4.10 nm to 3.98 and slight decrease in surface area from 113.5 to 102.2 and 96.2 m²/g resulted in decrease in number of active sites as well as it retarded diffusion of the substrate through the micropores.

**Table 5.7. Effect of calcination temperature on catalytic activity**

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Calcination temperature (K)</th>
<th>Surface area (m²/g)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Veratryl aldehyde</td>
</tr>
<tr>
<td>CSA-4</td>
<td>423</td>
<td>6.1</td>
<td>24.4</td>
<td>&lt; 99.9</td>
</tr>
<tr>
<td>CSA-4-3C</td>
<td>573</td>
<td>113.5</td>
<td>86.0</td>
<td>94.0</td>
</tr>
<tr>
<td>CSA-4-4C</td>
<td>673</td>
<td>102.2</td>
<td>80.7</td>
<td>93.0</td>
</tr>
<tr>
<td>CSA-4-5C</td>
<td>773</td>
<td>96.2</td>
<td>78.9</td>
<td>94.0</td>
</tr>
</tbody>
</table>

Reaction conditions: temperature, 413 K; oxygen pressure, 2.01 MPa; veratryl alcohol, 0.5 g (3 mmol); catalyst, 0.3 g; solvent toluene, 70 mL; NaOH, 1.0 g (24 mmol); agitation speed, 900 rpm; reaction time, 5 h.
5.3.2.2. Effect of calcination time

The calcination times was varied from 1 to 6 h for the CSA-4 sample at constant calcination temperature (573 K). The catalytic activity of these catalysts prepared with different calcination time was evaluated in toluene and the activity was found to be increase by about three times, with increase in calcination time from 1 to 6 h (Table 5.8). Enhancement in the catalytic activity was due to increase in active sites resulted from increase in surface area by nine times (from 12.6 to 114.2 m²/g) for the increase in calcination time from 1 to 6 h. The increase in calcination time facilitates the removal of water and other starting precursors trapped in the inter layers and mesopores of the catalyst, leading to significant increase in cobalt active species (Co²⁺ and Co³⁺). The optimum calcination time was found to be 5 h required to remove these molecules from CSA-4 catalyst, beyond which (6 h) both surface area and catalytic activity were found to be constant.

Table 5.8. Effect of calcination time on catalytic performance

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Calcination Time, (h)</th>
<th>Surface area, (m²/g)</th>
<th>Conversion, (%)</th>
<th>Selectivity, (%)</th>
<th>Veratryl aldehyde</th>
<th>Veratric acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSA-4-3C</td>
<td>1</td>
<td>12.6</td>
<td>31.3</td>
<td>98.0</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>CSA-4-3C</td>
<td>2</td>
<td>26.5</td>
<td>45.4</td>
<td>97.5</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>CSA-4-3C</td>
<td>3</td>
<td>57.3</td>
<td>48.9</td>
<td>97.0</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>CSA-4-3C</td>
<td>4</td>
<td>99.3</td>
<td>61.7</td>
<td>93.0</td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td>CSA-4-3C</td>
<td>5</td>
<td>113.5</td>
<td>86.0</td>
<td>94.0</td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td>CSA-4-3C</td>
<td>6</td>
<td>114.2</td>
<td>86.6</td>
<td>94.0</td>
<td>6.0</td>
<td></td>
</tr>
</tbody>
</table>

Reaction conditions: temperature, 413 K; oxygen pressure, 2.01 MPa; veratryl alcohol, 0.5 g (3 mmol); catalyst, 0.3 g; solvent toluene, 70 mL; NaOH, 1.0 g (24 mmol); agitation speed, 900 rpm; reaction time, 5 h.
5.3.3. Optimization of reaction conditions

Among the prepared catalysts, CSA-4-3C (cobalt aluminosilicate with Si:Al 1:10 and calcined at 573 K) was found to exhibit the highest activity for liquid phase oxidation of veratryl alcohol. Further catalyst development as well as optimization of reaction conditions using active CSA-4-3C catalyst is discussed in the following sections.

5.3.3.1. Effect of NaOH concentration

Although, veratryl alcohol is a dimethoxy aryl alcohol, we expected that NaOH would play a role similar to that in case of phenolic –OH. Hence effect of NaOH concentration on the veratryl alcohol conversion and oxidation product selectivities was studied and the results are shown in Figure 5.18. It is known that oxidation of phenolic (such as p-cresol) compounds proceeds only after the conversion of –OH group into its sodium salt [3]. The conversion of veratryl alcohol increased from 35 to 90% with increase in NaOH concentration from 3 to 30 mmol while the selectivity to veratryl aldehyde decreased from 100 to 93% and that for veratric acid increased from 0 to 7%. Beyond 24 mmol of NaOH concentration, conversion of veratryl alcohol marginally increased from 86 to 90%. With further increase in NaOH concentration to 30 mmol, conversion of veratryl alcohol was almost constant. A blank run (without NaOH) showed 20% conversion with complete selectivity to veratryl aldehyde. Only with increase in NaOH concentration conversion of veratryl alcohol increased while veratryl aldehyde to veratric acid remained almost same. However, more detailed investigation is necessary to study the exact role of NaOH in enhancing the catalytic activity especially, when non phenolic compound was used.
5.3.3.2. Effect of temperature

The effect of temperature on veratryl alcohol conversion and selectivity was studied in the temperature range of 393 to 433 K and the results are presented in Figure 5.19. The conversion of veratryl alcohol increased from 44 to 96% with increase in temperature from 393 to 433 K. The selectivity to veratryl aldehyde decreased gradually (100 to 80%) giving veratric acid with increase in temperature. This clearly indicated that veratryl aldehyde was the first intermediate formed in veratryl alcohol oxidation, while the reaction pathway was found to be similar with the reaction with nano Co-3C-a (Co$_3$O$_4$) spinel catalyst (Scheme 3.1, Chapter 3). The rate of oxidation increased with increase in temperature, and the activation energy evaluated from the Arrhenius plot was 26.76 KJmole$^{-1}$K$^{-1}$ (Figure 5.20).

**Figure 5.18.** Effect of NaOH concentration on oxidation of veratryl alcohol on CSA-4-3C catalyst

Reaction conditions: temperature, 413 K; oxygen pressure, 2.01 MPa; veratryl alcohol, 0.5 g (3 mmol); catalyst, 0.3 g; solvent toluene, 70 mL; agitation speed, 900 rpm; reaction time, 5 h.
Figure 5.19. Effect of reaction temperature on conversion and selectivity

Reaction conditions: oxygen pressure, 2.01 MPa; veratryl alcohol, 0.5 g (3 mmol); catalyst, 0.3 g; solvent toluene, 70 mL; NaOH, 1.0 g (24 mmol); agitation speed, 900 rpm; reaction time, 5 h.

Figure 5.20. Arrhenius plot
5.3.3.3. Effect of pressure

In order to study the effect of partial oxygen pressure on conversion of veratry 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 5.21. It was found that the conversion of veratryl alcohol increased from 46 to 95% as the oxygen pressure increased from 0.68 to 4.13 MPa. However, the selectivity to veratryl aldehyde decreased from 98 to 86% due to its further conversion to veratric acid at higher concentration of oxygen. The substantial increase in conversion was due to the higher oxygen solubility at higher pressures [70].

![Conversion and Selectivity vs Pressure](image)

**Figure 5.21.** Effect of pressure on catalytic activity

Reaction conditions: temperature, 413 K; veratryl alcohol, 0.5 g (3 mmol); catalyst, 0.3 g; solvent toluene, 70 mL; NaOH, 1.0 g (24 mmol); agitation speed, 900 rpm; reaction time, 5 h.
5.3.3.4. Effect of catalyst loading

Effect of catalyst loading in the range of 0.1 to 0.3 g on veratryl alcohol conversion and product selectivity was also studied and the results are presented in Figure 5.22. The veratryl alcohol conversion increased from 27 to 86% with increase in catalyst loading from 0.1 to 0.3 g. This is obvious since with increase in catalyst concentration; the number of active cobalt sites also increased which facilitated the conversion of veratryl alcohol to veratryl aldehyde. However, the selectivity for veratryl aldehyde decreased from 100 to 94% as the catalyst concentration increased from 0.1 to 0.3 g due to its further conversion to veratric acid.

![Figure 5.22](image)

**Figure 5.22.** Result of catalyst loading on liquid phase oxidation of the veratryl alcohol

Reaction conditions: temperature, 413 K; oxygen pressure, 2.01 MPa; veratryl alcohol, 0.5 g (3 mmol); solvent toluene, 70 mL; NaOH, 1.0 g (24 mmol); agitation speed, 900 rpm; reaction time, 5 h.
5.3.3.5. Solvent screening

The oxidation of veratryl alcohol was also investigated in various solvents and the results are shown in Table 5.9. The CSA-4-3C catalyst was found to be active only in non polar toluene solvent while it was inactive in all polar solvents. This order of activity was not consistent with the order of polarity of the solvents [71], and it was rather dependent on the hydrophilic property of the catalyst which in polar solvents cause the blockage of active species significantly as evidenced by TG-DTA, SEM, TEM, TPR and TPO characterizations discussed in earlier sections. Thus, the choice of solvent was critical in order to achieve the optimum activity.

Table 5.9. Solvent effect on catalytic performance of CSA-4-3C sample

<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>Water</td>
<td>&lt;0.1</td>
<td>99</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Methanol</td>
<td>&lt;0.1</td>
<td>99</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>&lt;0.1</td>
<td>99</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>n-propanol</td>
<td>&lt;0.1</td>
<td>99</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>86.0</td>
<td>94.0</td>
<td>6.0</td>
<td></td>
</tr>
</tbody>
</table>

Reaction conditions: temperature, 413 K; oxygen pressure, 2.01 MPa; veratryl alcohol, 0.5 g (3 mmol); catalyst, 0.3 g; solvent, 70 mL; NaOH, 1.0 g (24 mmol); agitation speed, 900 rpm; reaction time, 5 h.

5.3.3.6. Reusability and stability experiment

In order to ensure that the activity of CSA-4-3C catalyst was constant during the run, catalyst recycle experiments were carried out, in which the catalyst was found to retain its original activity and selectivity even after the fifth recycle (Figure 5.23). The stability of the CSA-4-3C
catalyst under the reaction conditions was also confirmed by conducting leaching test. For this purpose, the oxidation experiment was interrupted after (3 h) a partial conversion of ~ 57% and the catalyst was removed by filtration and the reaction was further continued without the catalyst. As can be seen from Figure 5.24, the conversion of veratryl alcohol remained constant at ~ 57% after continuing the reaction without the catalyst. Thus above results indicated true heterogeneous nature of our catalyst.

**Figure 5.23.** Catalyst recycle study

Reaction conditions: temperature, 413 K; oxygen pressure, 2.01 MPa; catalyst, CSA-4-3C; veratryl alcohol, 0.5 g (3 mmol); catalyst, 0.3 g; solvent toluene, 70 mL; NaOH, 1.0 g (24 mmol); agitation speed, 900 rpm; reaction time, 5 h.
Figure 5.24. Leaching test for the CSA-4-3C catalyst during oxidation of veratryl alcohol

Reaction conditions: temperature, 413 K; oxygen pressure, 2.01 MPa; veratryl alcohol, 0.5 g (3 mmol); catalyst, 0.3 g; solvent toluene, 70 mL; NaOH, 1.0 g (24 mmol); agitation speed, 900 rpm; reaction time, 5 h.

5.4. CONCLUSIONS

- The cobalt aluminosilicates catalysts with various Si:Al ratios were prepared by simple co-precipitation method.

- The change in Si:Al ratio from 10:1 to 1:10 caused change in the physico-chemical properties as well as change from hydrophobic to hydrophilic nature which was confirmed by various characterization techniques. The pore diameter changed from 1.17 nm to 4.04 nm with increase in pore diameter from 1.17 to 4.04 nm and enhancement in the redox ability due to increase in distribution of surface active $\text{Co}^{2+}/\text{Co}^{3+}$ species. The catalytic
oxidation of veratryl alcohol to veratryl aldehyde over different catalysts (aluminosilicates with Si:Al 1:10 ratios) was found to be in the following order: cobalt > iron > manganese > copper.

- Among the prepared catalysts, aluminosilicates with Si:Al 1:10 ratio having 15% cobalt loading showed the highest conversion of 86% for the oxidation of veratryl alcohol with a selectivity 94% to veratryl aldehyde and 6% veratric acid.

- Increase in Si:Al ratio from 10:1 to 1:10 caused increase in pore diameter from 1.17 to 4.04 nm leading to activity enhancement by six times (from 4% to 24%) for veratryl alcohol oxidation.

- Activation energy for oxidation of veratryl alcohol over CSA-4-3C catalyst found to be 26.7 KJmole⁻¹K⁻¹.
5.5. REFERENCES


