Chapter 3

Selective oxidation of cyclohexane to adipic acid using Co substituted K-OMS-2 catalysts
3.1. Introduction

Selective oxidation of hydrocarbons is an important process in the chemical industry, as it helps to manufacture of many useful chemicals like alcohols, aldehydes and carboxylic acids [1]. Though there were many publications/patents that deal with this area, it still remains a very significant research challenge as many processes need green chemical routes and cost effective manufacturing. As a result, there is a vigorous drive to develop green and efficient processes for the oxyfunctionalization of hydrocarbons [2]. Usually; efficient activation of a hydrocarbon requires precious metal catalyst and strong oxidizing agents (H$_2$O$_2$, TBHP and HNO$_3$). The impact on the environment would have been much greater, had it not been for continuous improvement of various green technologies applied for production of various chemicals [3].

Currently, partial oxidation processes are conducted either in the gas or liquid phase using homogeneous/ heterogeneous catalysts. Since molecular oxygen is cheap and omnipresent, it is the most practicable oxidant for partial oxidation processes. But, most of the heterogeneous catalyst based processes offer poor selectivity for the desired product when molecular oxygen is used as an oxidant. Large quantities of energy are needed to separate the desired product from unwanted side products. In addition, it leads to waste generation and inefficient use of starting materials [4]. Hence, achieving desired product selectivity remains an important task in the case of selective oxidation of hydrocarbons using heterogeneous catalyst processes.

Adipic acid (AA) is an important selective oxidation product, which is obtained starting from cyclohexane. The projected consumption of AA is expected to be around 6 billion pounds by 2017 at a projected growth rate of 5-7 % [5]. Major part of AA produced is used as a precursor for the synthesis of nylon-6,6. In addition, AA is widely used for the production of polyesters, polyurethane resins, plasticizers in the production of polyvinyl chloride (PVC) and polyvinyl butyral (PVB) [6]. Current industrial production of AA involves multi steps as well as highly corrosive environmentally hazardous acids. Thus, developing novel, clean and green routes for AA production is an important research theme.
3.2. Current industrial processes for the production of AA

Adipic acid is produced in a two step selective oxidation process. The first one is (as in practice today) oxidation of cyclohexane with air to get a mixture of cyclohexanone/cyclohexanol (called KA oil); the second one is the oxidation of KA oil or cyclohexanol with nitric acid [7].

3.2.1. First step: Oxidation of cyclohexane with air

Cyclohexane (CyH) is produced either by the hydrogenation of benzene or separated from the naphtha fraction in small amounts. Selective oxidation of CyH was first demonstrated by Dupont in mid 20th century. The process was successfully conducted at 10-20 atm pressure, 423-453 K with Co and Mn organic salts as catalysts. The process constitutes two steps. The first step is a partial oxidation to get peroxide, which is carried out without catalyst. The second step is deperoxidation which must be done always in the presence of a catalyst. The rate limiting step of the process is the production of hydroperoxides, which is carried out in the absence of transition metal complexes in the passivated reactors in order to avoid the decomposition of hydroperoxides. The selectivity to KA oil is about 75-80%, the by-products are carboxylic acids. The unconverted cyclohexane is recycled [8].

\[
2 \text{CyH} + \frac{3}{2} \text{O}_2 \rightarrow \text{CyH}_2\text{O} + \text{CyH}_2\text{O}_2
\]

Scheme 3.1. Cyclohexane oxidation to cyclohexanol and cyclohexanone.

\[
\text{Cyclohexane} + \frac{1}{2} \text{O}_2 \rightarrow \text{Cyclohexanol} \quad \Delta H_R = -47.4 \text{Kcal/mol}
\]

\[
\text{Cyclohexane} + \text{O}_2 \rightarrow \text{Cyclohexanone} + \text{H}_2\text{O} \quad \Delta H_R = -98 \text{Kcal/mol}
\]

The chemistry of the reaction is a homolytic auto oxidation. Alcohol is formed from RO• radical (R = C₆H₁₁).

\[
\text{RH (CyH) + Co (III) (or In•) \rightarrow R• (cyclohexyl radical) + Co (II) + H⁺ (or InH)}
\]

\[
\text{R• + O}_2 \rightarrow \text{ROO•}
\]
Chapter 3: Co-K-OMS-2 catalysts for cyclohexane oxidation

\[ \text{ROO} \cdot + \text{RH} \rightarrow \text{ROOH (cyclohexylhydroperoxide)} + \text{R} \cdot \]

The vital role of Co is to accelerate the reaction by decomposition of the intermediate hydroperoxides, ROOH, leading to the formation of alkoxy or peroxyl radicals (Haber-Weiss mechanism) [9].

\[
\begin{align*}
\text{ROOH} + \text{Co (II)} & \rightarrow \text{RO} \cdot + \text{Co (III)} + \text{OH}^- \quad \text{(in non-polar solvents)} \\
\text{ROOH} + \text{Co (III)} & \rightarrow \text{ROO} \cdot + \text{Co (II)} + \text{H}^+ \quad \text{(in polar solvents)}
\end{align*}
\]

Which corresponds to:

\[2 \text{ROOH} \rightarrow \text{RO} \cdot + \text{ROO} \cdot + \text{H}_2\text{O}\]

At high concentration of Co (II) it competes with cyclohexane for the alkylperoxy radical:

\[\text{ROO} \cdot + \text{Co (II)} \rightarrow \text{ROOCo(III)}\]

And therefore termination step would occur instead of propagation step. In that case, catalyst would act as an inhibitor of the reaction.

Russell mechanism of decomposition of secondary cyclohexylperoxy radicals is a prevailing reaction for the formation of alcohol and ketone. It consists in coupling of alkylperoxy radical, which then reacts by a non-radical, six-center 1,5H atom shift, which is also a terminating step of the radical chain reaction.

\[
\begin{align*}
2\text{ROO} \cdot & \leftrightarrow \text{ROOOOR} \\
\text{ROOOOR} & \rightarrow \text{C}_6\text{H}_{11}\text{OH} + \text{C}_6\text{H}_{11}\text{O} + \text{O}_2.
\end{align*}
\]

3.2.2. Second step: Oxidation of KA oil with nitric acid

\[
\begin{align*}
\text{Cyclohexane} + 1.5 \text{HNO}_3 & \rightarrow \text{Cyclohexanediol} + \frac{3}{4} \text{N}_2\text{O} + \text{H}_2\text{O} \\
\text{Cyclohexane} + 2 \text{HNO}_3 & \rightarrow \text{Cyclohexanedicarboxylic acid} + \text{N}_2\text{O} + 2\text{H}_2\text{O}
\end{align*}
\]
The second step in the production of adipic acid is oxidation of KA oil in presence of large excess of 65% nitric acid (molar ratio of HNO₃/KA oil is at least 7/1), in the presence of Cu (II) ammonium metavanadate catalyst [10].

\[
\begin{align*}
\text{Cyclohexanone} & \rightarrow \text{AA} \quad \Delta H_R = -172 \text{ Kcal/mol} \\
\text{Cyclohexanol} & \rightarrow \text{AA} \quad \Delta H_R = -215 \text{ Kcal/mol}
\end{align*}
\]

**Scheme 3.2.** Oxidation of cyclohexanol & cyclohexaone to adipic acid.

The reaction is carried out in two in-series reactors, first one operating at 333-353 K, the second one at 363-373 K at a pressure of 1-4 atm. The molar yield for total KA oil conversion is 95%, the by products are glutaric acid (selectivity 3%) and succinic acid (selectivity 2%).

### 3.2.3. Environmental impact of the second step

The intermediate of the nitric acid oxidation is HNO₂, which ultimately decomposes to NO and NO₂. These two gases can be simply recovered in water by absorption in a multistage column, yielding nitric acid solution, which can be reused in the oxidation process.

\[
\begin{align*}
2\text{NO} + \text{O}_2 & \rightarrow 2\text{NO}_2 \\
3\text{NO}_2 + \text{H}_2\text{O} & \rightarrow 2\text{HNO}_3 + \text{NO}
\end{align*}
\]  

(3.1) \hspace{1cm} (3.2)

Because of the poor solubility of NOₓ in water, the key factors for this process are the temperature and the pressure. However, it is possible to have a complete recovery of NOₓ. Meanwhile the co-products of the nitric oxidation of KA oil, NO and NO₂ are easily recoverable, as shown above (eq. 3.1, 3.2), co-production of N₂O represents a big drawback of the second step of the synthesis of AA.

Nitrous oxide belongs to so called long lived greenhouse gases LLGHGS (other being CH₄, CO₂ and radioactively active constituents such as ozone and different types of aerosol), which contribute to the climatic changes [11]. The estimated atmospheric lifetime of N₂O is 150 years and the estimated impact of N₂O is a 6% increase in the ozone depletion layer. Although the absolute concentration of

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N₂O is relatively low, 300 ppbv, it influences climatic changes as a result of one of its stratospheric removal reaction:

\[ \text{N}_2\text{O} + \text{O} (1\text{D}) \rightarrow \text{NO} + \text{NO} \ (61.7\%) \quad (3.3) \]

\[ \rightarrow \text{N}_2 + \text{O}_2 \ (38.3\%) \quad (3.4) \]

The equations show that the major part of N₂O is converted to NO, which is unambiguously implicated in catalytic ozone destruction [12].

The emission factor of adipic acid is estimated to be about 300 kg of N₂O per ton of adipic acid, depending on the amount of catalyst used and KA oil composition. In 1990, adipic acid production was the largest source of industrial N₂O emissions. By 1999 all major adipic acid producers have implemented N₂O abatement technologies and, as a result, this source has been decreased substantially [13]. Consequently, currently the production of nitric acid is the largest industrial source of N₂O.

3.3. Alternate Pathways for AA production

In addition to the above discussed commercial process, there are alternative routes for the production of AA.

3.3.1. Oxidation of cyclohexene

There were a plethora of reports in the literature for AA production from cyclohexene. The best result was reported by Noyori [14] with 30% hydrogen peroxide as oxidant and in the presence of small amounts of NaW₀₄ and phase transfer catalyst (PTC) (in this case CH₃(n-C₈H₁₇)NHSO₄) in the absence of solvent.

![Scheme 3.3. Single step oxidation of cyclohexene to adipic acid with aqueous H₂O₂](image)
3.3.2. Butadiene as a starting material

BASF has proposed a very innovative process, methoxycarbonylation of butadiene in the presence of the Co-based catalyst [15]. Although a good amount of AA yield (~ 72%) was obtained using this system, the process didn’t lead to the implementation, possibly because of the extreme reaction conditions used. First step under 300 atm and the second step under the pressure of 150–200 atm) [16].

\[
\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 + \text{CO} + \text{CH}_3\text{OH} \rightarrow \text{CH}_2=\text{CH}-\text{CH}(_2\text{O})\text{Me} + \text{CO} + \text{CH}_3\text{OH}
\]

Scheme 3.4. Methoxycarbonylation of butadiene to adipic acid.

3.3.3. n-Hexane as a starting material

It is very well known that alkanes are difficult to oxidize. Performing oxyfunctionalization selectively at terminal positions is almost impossible. This reaction is catalyzed by enzymes with non-heme iron active center.

Robert Raja et al. reported production of AA from n-hexane using Co framework substituted aluminophosphate catalyst (Co-AlPO-18, Co-AlPO-5) in air. After 24 hours of reaction at 373 K under air pressure of 1.5 MPa, 9.5% of n-hexane was converted with 33.6% selectivity to AA. Among the other detected products were 2-hexanone and 2-hexanol [17].

3.3.4. D-Glucose as a starting material

Preparation of AA from renewable source like glucose has been proposed by Frost [18]. It consist of enzymatic transformation of D-glucose to cis,cis-muconic via 3-dehydroshikimic acid, protocatechuic acid and catechol. The key parameter of these steps is the presence of three enzymes not typically found in ESTERICHIA Coli. The
final step of the reaction is hydrogenation of the cis,cis-muconic, using supported Ru, Pt catalyst. Under the pressure of 3400 kPa of H\textsubscript{2} 97% of cis,cis-muconic acid into AA can be converted after 2.5 hours of the reaction at the ambient temperature, see scheme 3.5. Still the problems concerning scaling-up and process implementation have to be solved and these problems could make this process economically viable.

![Scheme 3.5](image)

**Scheme 3.5.** Enzymatic transformation of D-glucose to adipic acid.

### 3.4. Literature overview of one step oxidation of cyclohexane

Single step production of AA from cyclohexane with air as an oxidant is a highly tempting idea, because of the abundance and cost of the green oxidant. Replacing the corrosive oxidizing agent with air also makes the investment cost low.

#### 3.4.1. Homogeneous catalysts

Cyclohexane oxidation was carried out using Co and Mn containing catalyst. By changing reaction conditions, it is possible to synthesize AA using the same catalyst. In fact Asahi almost 70 years ago industrialized this process, using Co acetate as catalyst and acetic acid as solvent, under 30 atm of O\textsubscript{2} pressure and at temperature 363–373 K. Conversion of CyH 50-75% and 70% selectivity to AA was achieved (the main byproduct was glutaric acid) [19].

In order to attain maximum AA yield, many industries experimented with different catalyst compositions and reaction conditions. For example in the Gulf process the reaction is carried out at the same temperature as the original Asahi process, using the same solvent but with higher concentration of catalyst, the AA selectivity obtained was 70-75% with 80-85% conversion of CyH [20]. Amoco process achieved 98% conversion of CyH with 88% yield of AA under 70 atm of air.
pressure at 368 K [21]. However, all these were homogeneous catalyst based processes.

### 3.4.2. Heterogeneous catalysts

Schuchardt et al. thoroughly reviewed both homogeneous and heterogeneous catalytic systems, reported in the literature up to the year 2000 including those that use oxidants other than oxygen (e.g., H₂O₂ or TBHP) [22]. Recent review by Van de Vyver et al. discussed emerging catalytic processes for the production of AA [23]. Sankar et al. obtained a very high selectivity to cyclohexanol/cyclohexanone, at 9.6% cyclohexane conversion (T=423 K) using Co-AlPO-36 as catalyst [24]. Good AA yield was achieved by J.M.Thomas group by using Fe-AlPO-31 [25]. Still improved yield was observed when they used a solid source of active oxygen (acetylperoxy borate) and H₂O₂ [26]. On CeO₂ supported on alumina, the oxidation of CyH was performed under 15 atm pressure of O₂ in the presence of cyclohexanone as a co-oxidant at 383 K. The conversion of cyclohexane was 36% with AA selectivity of 42%. The by-products of the reaction were lower dicarboxylic acid (glutaric, succinic), COx and caprolactone [27]. Using Ti-containing beta zeolite and hydrogen peroxide as oxidant and 2-butanone as a solvent, 47% conversion of cyclohexane with 54% selectivity to AA was obtained after 1 hour of reaction at 369 K [28].

Nano structured gold catalysts were also reported for the oxidation of CyH which include catalysts like Au/graphite, Au/Al₂O₃, Au/TiO₂, Au nano particles on Ti-doped SiO₂, Au/MCM-41, Au/SBA-15 and Au/C [29]. Recently, Alshammari et al. reported that by fine tuning Au particle size on TiO₂ supported catalysts, AA can be obtained to some extent with acetonitrile as solvent and TBHP as an initiator [30]. Low yield of AA was the major issue in addition to the recovery of catalysts for the scale up of above reported processes.

Ishii group had conducted the reaction using N-hydroxyphthalimide (NHPI, 10-20 mol %) as radical initiator and Mn and Co acetates as homogeneous catalysts and got maximum selectivity of 73 mol% along with CyH conversion of 73%, which was scaled up by Daicel chemical industry [31]. The major limitation in the Ishii process was that metal salts contaminate the products which require one more step for
purification. So, instead of metal salts a heterogeneous catalyst containing Co & Mn should be used which can be easily separated from the product. Therefore there is a need to get maximum selectivity and conversion with a heterogeneous catalysts using molecular O$_2$ as oxygen source.

Scheme 3.6. Oxidation of cyclohexane and their products.

3.5. Experimental procedures

3.5.1. Materials

Potassium permanganate, manganese (II) sulphate and cobalt nitrate were used (Loba chemical Ltd.) for the preparation of K-OMS-2. acetic acid, methanol, NHPI (N-hydroxyphthalimide) and sodium hydroxide were purchased from Thomas Baker Pvt. Ltd. N-acetoxyphthalimide (NAPI) was prepared in laboratory. All the chemicals were used without any further purification.

3.5.2. Initiator Preparation

N-Acetoxyphthalimide (NAPI)

N-Hydroxyphthalimide (0.7 g, 4.35 mmol), acetic acid (HOAc, 258μL, 4.35 mmol), and dicyclohexylcarbodiimide (DCC 0.85 g, 4.35 mmol) were added to dry ethyl acetate (EtOAc, 125mL) and the mixture was stirred for 3h at room temperature and then filtered. The filtrate was dried (Na$_2$SO$_4$), and the residue was crystallized from ethanol to give a white solid [32].
3.5.3. Experimental setup

Selective oxidation of CyH was performed in a 50 ml titanium lined Parr Reactor (4842) which was connected to an O₂ cylinder. In a typical run, reactor was charged with 8 mmol of CyH, 20 mol % of NAPI and 20 mL of acetic acid and 150 mg of catalyst. The whole mixture was stirred at 373 K at 500 rpm. After reaching to desired temperature, O₂ was filled into the reactor to reach the desired pressure. After completion of reaction, solid part was separated by simple filtration and liquid portion was analyzed by GC (Agilent 7890) equipped with HP-5 capillary column to arrive at conversion of cyclohexane, selectivity's of cyclohexanol and cyclohexanone. The product mixture with solvent (acetic acid) was subjected to rotavaporator so that the solvent can be evaporated; the remaining solid was dissolved in 10ml of millipore water and filtered to obtain soluble diacids in water, with initiator being insoluble. The soluble part was made up to 10 mL.

3.6. Analytical procedure

3.6.1. Esterification procedure of diacids

Part (2 mL) of the above solution was esterified using (4 mL) 4% BF₃ methanol solution for 12h at 353 K. To this mixture, 4 mL of millipore water and 4 mL dichloromethane was added, since the required esters dissolves in DCM. Aqueous and organic layers were separated by using separating funnel. The final DCM mixture was analyzed by GC for finding the selectivity of diacids.

3.7. Textural Characterization of Catalysts

3.7.1. Powder X-ray diffraction (PXRD)
The XRD patterns of K-OMS-2 and Co-K-OMS-2 are given in Fig. 3.1. XRD peaks of all catalysts match with the reported data of cryptomelane OMS-2 (JCPDS 05-0681). Peaks in Co-OMS catalysts are sharp and similar to the OMS-2, showing that the substituted cobalt OMS-2 materials also crystallized with cryptomelane structure. It also confirms that cryptomelane structure of OMS-2 material is retained even after substitution of cobalt. No additional peaks corresponding to cobalt oxides were observed, indicating the absence of any other cobalt containing oxides, which confirms the substitution of Co into OMS-2.

Fig 3.1. XRD pattern of (a) K-OMS-2, (b) Co-OMS-I (0.58 wt %), (c) Co-OMS-II (1.03 wt %), (d) Co-OMS-III (2.26 wt %) (e) Co-OMS-IV (2.98 wt %).

3.7.2. N2 Physisorption

The N2 adsorption/desorption isotherms of parent and Co doped samples are given in Fig. 3.2. (A). All the samples showed a characteristic Type II sorption and H3-type hysteresis loop for P/P₀ > 0.6 that can be attributed to inter crystalline mesopores between particles with non uniform size or shapes. With increasing Co content in the sample, surface area, pore volume of the material dropped. This decrease may be attributed to partial blockage of pores by extra lattice cobalt oxide which is not detected by XRD due to its very low content. Micropore and total pore volume of the sample also decreased with Co doping but the H-K pore size of the
material is increased which was tabulated in Table 3.1. The H-K plot of parent and Co doped OMS-2 materials are illustrated in Fig. 3.2. (B).

Table 3.1. N$_2$ physisorption data of the prepared materials

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Co content</th>
<th>BET Surface Area (m$^2$/g)</th>
<th>Pore Volume (cc/g) @p/p$_0$ = 0.95</th>
<th>Micropore volume (cc/g) DR Method</th>
<th>Pore Size (Å) H-K Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-OMS-2</td>
<td>--</td>
<td>97.6</td>
<td>0.27</td>
<td>0.031</td>
<td>5.025</td>
</tr>
<tr>
<td>Co-OMS-I</td>
<td>0.58</td>
<td>81.5</td>
<td>0.17</td>
<td>0.026</td>
<td>5.075</td>
</tr>
<tr>
<td>Co-OMS-II</td>
<td>1.03</td>
<td>79.0</td>
<td>0.16</td>
<td>0.024</td>
<td>5.174</td>
</tr>
<tr>
<td>Co-OMS-III</td>
<td>2.26</td>
<td>74.8</td>
<td>0.14</td>
<td>0.023</td>
<td>5.175</td>
</tr>
<tr>
<td>Co-OMS-IV</td>
<td>2.98</td>
<td>60.4</td>
<td>0.11</td>
<td>0.021</td>
<td>5.525</td>
</tr>
</tbody>
</table>

Fig. 3.2. (A) N$_2$ adsorption/desorption isotherms; (B) H-K plots of (a) K-OMS-2, (b) Co-OMS-I (0.58 wt %), (c) Co-OMS-II (1.03 wt %), (d) Co-OMS-III (2.26 wt %) (e) Co-OMS-IV (2.98 wt %).

3.7.3. Raman spectroscopy

Raman spectroscopy was used to probe the effect of Co substitution and also look for the presence of segregated metal oxides. The regular OMS-2 (cryptomelane) belongs to the I4/m space group [33]. Using Factor group analysis, [34] the following irreducible representations (without tunnel cations contribution) can be attributed to the Mn-O lattice vibrations within the MnO$_6$ octahedral double chain:

$$\Gamma = 6A_g + 6B_g + 3E_g + 2A_u + 3B_u + 5E_u$$
Where the $A_g$, $B_g$ and $E_g$ (double-degenerated) modes are Raman active, the $A_u$ and $E_u$ (double-degenerated) modes are IR active and the $B_u$ mode is silent. The Raman spectrum obtained for the regular OMS-2 material only shows six Raman peaks at around 750, 647, 582, 480, 392 and 187 cm$^{-1}$ as opposed to fifteen peaks predicted from Factor group analysis (Fig. 3.3). This could be because of low polarizabilities of some of these modes and low resolution of other modes [34].

The two strong, sharp peaks at 647 and 582 cm$^{-1}$ correspond to $A_{1g}$ spectroscopic modes whereas the peaks at 480 cm$^{-1}$ correspond to the $F_{2g}$ spectroscopic species [35]. The two sharp peaks at 647 cm$^{-1}$ and 582 cm$^{-1}$ are associated with Mn-O vibrations that are orthogonal and along the direction of the MnO$_6$ octahedral double chains, respectively, which are indicative of a well-developed tetragonal structure with 2×2 tunnels [36].

There was no segregated undoped cobalt oxide peaks expected at 455 and 675 cm$^{-1}$ [37]. The Raman spectra, with respect to the crystallinity are in good agreement with the structural data obtained by XRD for these materials.

Fig. 3.3. Raman spectra of (a) K-OMS-2, (b) Co-OMS-I (0.58 wt %), (c) Co-OMS-II (1.03 wt %), (d) Co-OMS-III (2.26 wt %) and (e) Co-OMS-IV (2.98 wt %).
3.7.4. Fourier-Transform infrared spectroscopy

On substitution of Mn in the octahedral OMS-2 framework by other isomorphous metal ions, the local environment of oxygen coordination around the octahedral site changes along with the masses of the lattice vibrators hence, the bond length and force constant. Consequently, the lattice vibrations and spectral features of the bulk OMS-2 material changes. As a result, the peak positions will shift and/or the peak intensities will vary [38]. Because of the sensitivity of IR spectroscopy towards lattice vibrational changes, this technique was used to probe the effect of multiple substitution(s) on the spectral features of cryptomelane.

The results of the IR spectrum of the as-synthesized regular OMS-2 material shows features similar to those previously reported; namely, absorption bands at around 720, 590, 530, and 470 cm\(^{-1}\) [36]. These bands are ascribed to the regular Mn-O lattice vibrations of the MnO\(_6\) octahedra framework (Fig. 3.4). Upon doping of Co into the OMS-2 structure, a dramatic fall in peak intensities was observed. This attenuation of peak intensity needs to be investigated further. The IR data depicted the absence of segregated metal oxide impurities and therefore corroborates the Raman and the XRD data, that showed no extra peaks attributed to segregated metal oxide.

Fig. 3.4. FT-IR spectra of (a) K-OMS-2, (b) Co-OMS-I (0.58 wt %), (c) Co-OMS-II (1.03 wt %), (d) Co-OMS-III (2.26 wt %) and (e) Co-OMS-IV (2.98 wt %).
3.7.5. Thermo gravimetric analysis

Thermal stability of Co-OMS-2 materials was studied through thermo gravimetric analysis (TGA) in air flow in the temperature range 293-1273 K at a ramping rate of 10 K/min, which are depicted in Fig. 3.5.

Fig. 3.5. TGA in air of (a) K-OMS-2, (b) Co-OMS-I (0.58 wt %), (c) Co-OMS-II (1.03 wt %), (d) Co-OMS-III (2.26 wt %) and (e) Co-OMS-IV (2.98 wt %).
Parent K-OMS-2 material synthesized by reflux method shows weight loss in the temperature range between 293-1273 K. The initial weight loss (2.5%) in the temperature range of 323-543 K is attributed to the loss of water in the sample. The second weight loss of about 6.4% in the 543-973 K temperature zone is due to loss of lattice oxygen, as the manganese cations reduce to lower oxidation state forming manganese oxide such as bixbyite (Mn$_2$O$_3$) [41].

The third weight loss of about 2.7%, observed in the temperature zone of 973-1173 K is attributed to a further loss of oxygen from bixbyite leading to the formation of more stable spinel hausmanite (Mn$_3$O$_4$) [42]. The general trend remained similar for each temperature zone but the weight loss differed based on cobalt content in the OMS-2 structures. The weight losses attributed to water loss in the samples was 2.7% for Co-OMS-I, 3.3% for Co-OMS-II, 3.9% for Co-OMS-III, and 4.2% for Co-OMS-IV. The first weight loss increases with Co loading which suggest that water in the lattice increases with Co loading.

The 2$^{nd}$ weight loss is due to change in phase of manganese from KMn$_8$O$_{16}$ to Mn$_2$O$_3$ in the mid temperature zone of 543-973 K. The weight loss slightly increases with Co loading. The weight losses were 5.9, 6.4, 6.5 and 7.2 wt % for Co-OMS-I, Co-OMS-II, Co-OMS-III and Co-OMS-IV respectively. The 3$^{rd}$ weight loss, for phase transition from Mn$_2$O$_3$ to Mn$_3$O$_4$, was almost similar as that of K-OMS-2 without any trend. The weight losses were 3.0, 3.1, 2.8, and 2.8 wt% for Co-OMS-I, Co-OMS-II, Co-OMS-III and Co-OMS-IV respectively. The DTG of materials found that the major weight loss occurred at 870 K and 1135K. Substituted OMS-2 materials show slightly lower thermal stability, which in turn may be attributed to the substitution of Co into OMS-2 lattice.

3.7.6. Scanning Electron Microscopy

The scanning electron micrographs show fibrous needle-like morphology of K-OMS-2 and Co-K-OMS-2 (Fig. 3.6). The morphology of K-OMS-2 is similar to that of Co-K-OMS-2 with 20 to 200 nm size fiber length. The length and breadth of the rods increased with Co doping. The result shows that the Co substitution affects
the rod dimensions and morphology. The fibrous morphology of the produced materials is indicative of an anisotropic growth behavior of OMS-2 [43].

During the crystallization process of the undoped synthetic OMS-2 material the crystal growth in the c-direction [44] leads to the formation of fibrous/nanorods with 1×1 and 2×2 tunnels running along the length of the nanofibers/nanorods. The increase in width and length of our Co doped materials was probably due to a slight distortion of the tetragonal crystal structure of cryptomelane to the monoclinic geometry. No particles as secondary phases were observed in the products, an indication of highly pure nanofibers as synthesized products.

![Fig. 3.6. SEM of (a) K-OMS-2 and (b) Co-OMS-IV (2.98 wt %).](image)

3.7.7. Transmission electron microscopy (TEM)

High resolution TEM images of materials K-OMS-2 and Co-K-OMS-2 are given in Fig. 3.7. They show the nanoscale size of the fibers self-assembled into the complex hollow structures. The well-defined lattice planes observed in the high-resolution TEM (HRTEM) images of undoped, Co doped K-OMS-2 confirmed the excellent crystallinity of these nano materials. The lattice fringe spacing of 0.47 & 0.69 nm in the undoped K-OMS-2 can be attributed to the (2 0 0) and (1 1 0) planes respectively which corresponds to the planes of the cryptomelane structure [45]. In Co-OMS-I & Co-OMS-IV, the (2 0 0) plane was identified which is in agreement with parent K-OMS-2 structure.
Fig. 3.7. TEM of (a) K-OMS-2, (b) Co-OMS-I (0.58 wt %), (c) Co-OMS-III (2.26 wt %), (d) Co-OMS-IV (2.98 wt %).

In case of Co-OMS-III, the 0.23 nm and 0.33 nm spacing's can be assigned to (2 1 1) and (3 1 0) planes of its crystal structure. Perfect surface structures were observed; hence, no obvious surface defect sites were formed in the typical structures of undoped, Co doped K-OMS-2 material.

3.7.8. H₂-Temperature programmed reduction

The H₂-TPR profiles of the synthesized materials are shown in Fig. 3.8. Four prominent peaks were observed in the TPR analysis. The assignment of each peaks is as follows: Peak I, relates to the consumption of structural oxygen close to the
surface, without decomposition of the material; Peak II, Peak III and Peak IV are related to the following reduction processes: \( \text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 \) (Peak II), \( \text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4 \) (Peak III) and \( \text{Mn}_3\text{O}_4 \rightarrow \text{MnO} \) (Peak IV) [39]. It is evident that with increasing Co loading, there is a slight reduction in the temperature of I, II, and III reduction peaks. The data suggests that the oxygen available for reduction is strongly influenced by the presence of Co in the samples, which is related to oxygen mobility. The doping cation (Co in this case) substantially effects the change in reactivity and availability of oxygen due to heat of formation of corresponding oxides and their electro negativity properties [40]. Accordingly, the presence of Co in the material influences the reactivity of the oxygen in the Mn–O–Co bridges. Since Co (1.88) has higher electro negativity compared to Mn (1.55), there will be electron delocalization and consequently weaker Mn-O bond. The reduction temperature of the \( \text{Mn}_3\text{O}_4 \rightarrow \text{MnO} \) (Peak IV) hardly changed, on modifying with doping cation, suggesting an important role of the structural and morphological properties of the material in the reactivity of lattice oxygen.

![H2-TPR of (a) K-OMS-2, (b) Co-OMS-I (0.58 wt %), (c) Co-OMS-II (1.03 wt %), (d) Co-OMS-III (2.26 wt %) and (e) Co-OMS-IV (2.98 wt %).](image)

**Fig. 3.8.** H2-TPR of (a) K-OMS-2, (b) Co-OMS-I (0.58 wt %), (c) Co-OMS-II (1.03 wt %), (d) Co-OMS-III (2.26 wt %) and (e) Co-OMS-IV (2.98 wt %).

3.7.9. X-ray Photoelectron Spectroscopy

XPS measurements were carried out to investigate the oxidation state, surface composition and atomic environment of Mn, O and Co Species.
3.7.9.1. Mn 2p spectra

The Mn 2p\(_{3/2}\) spectra of the OMS-2 nanorod samples are given in Fig. 3.9.

![Mn 2p spectra of (a) K-OMS-2, (b) Co-OMS-I (0.58 wt %), (c) Co-OMS-II (1.03 wt %), (d) Co-OMS-III (2.26 wt %) and e) Co-OMS-IV (2.98 wt %).]

These spectra were deconvoluted into two peaks around 642.1 and 643.4 eV (Fig. 3.9), which are attributed to the Mn\(^{2+}\) and Mn\(^{4+}\) species [46]. Considerable change in Mn\(^{4+}/\text{Mn}^{2+}\) intensity ratios with Co loading was observed, which is tabulated in Table 3.2 (a). This change in the ratio is attributed to replacement of Mn\(^{2+}\) by Co\(^{3+}\) (0.685 Å) which has similar crystal radius like Mn\(^{4+}\) (0.67 Å). Hence, with increase in Co doping, Mn\(^{4+}/\text{Mn}^{2+}\) ratios were found to decrease.

**Table 3.2 (a) Variation of Mn\(^{4+}/\text{Mn}^{2+}\) ratio with Co loading.**

<table>
<thead>
<tr>
<th>CATA</th>
<th>Mn(^{4+}/\text{Mn}^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-OMS-2</td>
<td>1.30</td>
</tr>
<tr>
<td>Co-OMS-I</td>
<td>1.19</td>
</tr>
<tr>
<td>Co-OMS-II</td>
<td>1.15</td>
</tr>
<tr>
<td>Co-OMS-III</td>
<td>1.04</td>
</tr>
<tr>
<td>Co-OMS-IV</td>
<td>0.97</td>
</tr>
</tbody>
</table>

**Table 3.2 (b) Binding energies of Mn 2p in K-OMS-2**

<table>
<thead>
<tr>
<th>Mn 2p 3/2 (eV)</th>
<th>Mn 2p 1/2 (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(^{2+})</td>
<td>Mn(^{4+})</td>
</tr>
<tr>
<td>642.18</td>
<td>643.46</td>
</tr>
<tr>
<td>653.77</td>
<td>654.9</td>
</tr>
</tbody>
</table>
3.7.9.2. Oxygen 1s spectra

Fig. 3.10. shows the Oxygen 1s spectra of the K-OMS-2 and Co substituted materials. Based on the peak positions, three types of oxygen species can be identified: the lower binding energy peak (O_l ~ 529.7 ev), which is attributed to lattice oxygen or oxygen ions bonded to metal cations in coordinatively saturated environment (O^{2-}), the medium value binding energy peak (O_n ~ 531.3 ev) assigned to surface adsorbed oxygen or oxygen ions bonded to metal ions in coordinatively unsaturated environment (O^{2-} or O^-, -OH groups and oxygen vacancies) and finally the high binding energy peak (O_{III} ~ 533.1 ev), likely associated with adsorbed molecular water [47]. The peak positions and relative abundance of O_l, O_n and O_{III} species are listed in Table 3.3. The principal component corresponds to the lattice oxygen, followed by the peak O_n of adsorbed oxygen and O_{III} of adsorbed water. The relative abundances of O_l and O_n species are listed in the table below. The ratio of O_{II}/O_l increases with the increasing of cobalt content (from 20.1% to 27%), implies that more cobalt is incorporated into the framework of the OMS-2 results in higher surface metal cations in a low coordination environment, implying that there was gradual increase in oxygen vacancies with Co doping. The interaction of these point defects with molecular oxygen and/or water leads to generation of peroxides, superoxides and hydroxyl species [48]. Thus, insertion of Co in the oxide structure enhances the oxygen lability and reducibility of the material which is in agreement with earlier discussed TPR results.

Table 3.3 Variation of oxygen species with Co loading

<table>
<thead>
<tr>
<th>CATA</th>
<th>O_l (%)</th>
<th>O_n (%)</th>
<th>O_{III} (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Lattice)</td>
<td>(Surface)</td>
<td>(H_2O)</td>
</tr>
<tr>
<td>K-OMS-2</td>
<td>71.3</td>
<td>23.5</td>
<td>5.0</td>
</tr>
<tr>
<td>Co-OMS-I</td>
<td>66.6</td>
<td>27.2</td>
<td>6.0</td>
</tr>
<tr>
<td>Co-OMS-II</td>
<td>63.9</td>
<td>31.5</td>
<td>4.4</td>
</tr>
<tr>
<td>Co-OMS-III</td>
<td>59.7</td>
<td>34.5</td>
<td>5.5</td>
</tr>
<tr>
<td>Co-OMS-IV</td>
<td>54.5</td>
<td>40.4</td>
<td>5.0</td>
</tr>
</tbody>
</table>
3.7.9.3. Co 2p spectra

The Co 2p spectrum of cobalt doped OMS-2 is given in Fig. 3.11. All Co-containing samples consisted of two main peaks at about 777 and 795 eV, corresponding to Co 2p$_{3/2}$ and Co 2p$_{1/2}$, respectively. A spectral feature that distinguishes between Co$^{2+}$ and Co$^{3+}$ is that the main Co$^{2+}$ peaks present a satellite, arising from interaction of photoemitted electrons with core vacancy and valence electrons, whereas Co$^{3+}$ peaks do not [49]. All Co doped samples exhibited a satellite (788.9 ev) at higher BE by about 6 eV compared to Co 2p$_{3/2}$, indicating the presence of Co$^{4+}$. With increasing in Co loading, the intensity ratio of the 2p$_{3/2}$ satellite to the relevant main peak decreased from $I_{sat}/I_{main} = 0.39$, close to the value reported for CoO [50], to $I_{sat}/I_{main} = 0.32$, indicating the presence of an increasing amount of Co$^{3+}$. The spin-orbit separation between Co 2p$_{3/2}$ and Co 2p$_{1/2}$ is around 16.2 eV, thus confirming a parallel increase in Co$^{3+}$.
Chapter 3: Co-K-OMS-2 catalysts for cyclohexane oxidation

Table 3.4 XPS parameters of Co-OMS-IV

<table>
<thead>
<tr>
<th>CATA</th>
<th>$\text{Co}^{2+}/\text{Co}^{2-}$</th>
<th>$I_{\text{sat}}/I_{\text{main}}$</th>
<th>Spinorbit Separation $(\Delta_{1/2-3/2})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-OMS-IV</td>
<td>2.57</td>
<td>0.39</td>
<td>16.2 eV</td>
</tr>
</tbody>
</table>

Fig. 3.11. Co 2p spectra (a) Co-OMS-IV (2.98 wt %).

3.8. Catalytic Activity-Single step selective oxidation of cyclohexane to adipic Acid

For the preparation of adipic acid from cyclohexane in a single step, a heterogeneous catalyst was chosen in such a way that it contains both Co & Mn, since both metals work synergistically in oxidation reactions. The heterogeneous catalyst should have metal (Mn or Co) with different oxidation states, as it is important for partial oxidation reactions that metal should have variable oxidation states. The catalyst should be non toxic and cheap for commercial use of the process. The above oxidation reaction should be possible to carry out with molecular oxygen. Following
these criteria, cobalt substituted manganese containing octahedral molecular sieves were chosen. Instead of NHPI (N-Hydroxyphthalimide) as radical initiator, which was used in the Ishii process, we have tested NAPI (N-Acetoxyphthalimide) which is a acetylated derivative of NHPI [21].

3.8.1. Effect of temperature on Adipic acid yield

The effect of the reaction temperature on the catalytic activity of Co-OMS-2 in the oxidation of CyH is given in Table 3.5. As one would expect, with increasing reaction temperature, the conversion of CyH increased significantly. At 353 K, CyH conversion was 52.8 % with 90.6 % selectivity for AA. By increasing the temperature further, the selectivity's of by-products succinic and glutaric acids increased. Tinker et al. have also observed similar effect. Increasing reaction temperature leads to enhanced decarboxylation rate of adipic acid [51]. Hence, in order to have high yield of AA, reaction was optimized at 363 K. With K-OMS as catalyst, the yield of AA was low due to the low conversion of CyH (entry 5). This shows that by substituting Mn with cobalt in OMS-2, the reaction rate is accelerated as a result of synergistic effect.

Table 3.5. Influence of reaction temperature on selective oxidation of cyclohexane

<table>
<thead>
<tr>
<th>S. No</th>
<th>Temp (K)</th>
<th>Conversion of CyH (mol %)</th>
<th>Product Selectivity (mol %)</th>
<th>AA (Yield %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cyclohexanol</td>
<td>Cyclohexanon</td>
</tr>
<tr>
<td>1</td>
<td>353</td>
<td>52.8</td>
<td>2.9</td>
<td>0.2</td>
</tr>
<tr>
<td>2</td>
<td>363</td>
<td>96.9</td>
<td>0.0</td>
<td>0.9</td>
</tr>
<tr>
<td>3</td>
<td>373</td>
<td>95.6</td>
<td>0.4</td>
<td>0.7</td>
</tr>
<tr>
<td>4</td>
<td>383</td>
<td>98.7</td>
<td>0.0</td>
<td>1.2</td>
</tr>
<tr>
<td>5*</td>
<td>363</td>
<td>54.9</td>
<td>2.2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Conditions: Cyclohexane = 8 mmol, NAPI = 20 mol%, Acetic acid = 20 mL, Time = 3h, Co-OMS-I = 150 mg, 20 bar O₂,* Catalyst K-OMS-2 (150mg)

3.8.2. Effect of reaction time on AA yield

The effect of the reaction time on the catalytic activity and selectivity of different products in oxidation of CyH is given in Fig. 3.12. After one hour of
reaction, CyH conversion was 56.6% with AA selectivity at 89.8%. With increase in reaction time to 2h, conversion has increased to 76.3 mol% with AA selectivity nearly same at 89.6%. After 3 hours, conversion further increased to 95.8%, but AA selectivity decreased to 84.1%. After 4 hours of reaction, conversion almost remained unchanged (96.2%), but AA selectivity decreased to 80.3%. With increasing reaction time, the yield of adipic acid increased as a result of increase in CyH conversion. However, on further increasing time, the rate of side reactions (degradation) gradually increased to form GA followed by SA.

![Figure 3.12. Effect of reaction time on cyclohexane oxidation.](image)

**Fig. 3.12.** Effect of reaction time on cyclohexane oxidation.

**Conditions:** Cyclohexane = 8 mmol, NAP1 = 20 mol%, Acetic acid = 20 mL, Co-OMS-I = 150 mg, Temp = 363 K, 20 bar O2.

Kollar et al. have also made similar observations in the selective oxidation of cyclohexane to AA [52]. Even though the AA selectivity decreased after 3h, we have optimized the reaction time to 3h, to get higher conversion of CyH that lead to higher AA yield.

### 3.8.3. Effect of Catalyst content on AA yield

The effect of the catalyst content on catalytic activity in the selective oxidation of CyH is illustrated in Fig. 3.13. With a catalyst content of 50mg, CyH conversion was 69.9% with AA selectivity at 90.2%. With increasing the amount of catalyst the CyH conversion also increased, which shows the promotional effect of increasing
catalytic sites on the reaction. With 100 mg of catalyst, 80.8% CyH conversion and 90.7% AA selectivity were obtained, whereas the selectivity for by products GA, SA increased slightly. However, when the amount of catalyst is further increased to 150 mg, the conversion reached to a maximum of 97%, while selectivity of AA decreased to 84.2% and there was two fold increase in GA and SA selectivity's. The overall yield of AA was maximum after 3h due to the increase in conversion. With time on stream, the selectivity's of the decarboxylated by products increased due to Co$^{2+}$ catalyzed degradation of dicarboxylic acid. The rate of degradation of acid increased with temperature and cobalt catalyst concentration [51].

![Graph showing conversion and selectivity of various compounds with catalyst weight](image)

**Fig. 3.13. Influence of catalyst content on cyclohexane oxidation.**

*Conditions: Cyclohexane = 8 mmol, NAPI = 20 mol%, Acetic acid = 20 mL, Temp = 363 K, Time = 3 h, Co-OMS-1, 20 bar O$_2$.**

### 3.8.4. Effect of initiator amount on the yield of AA

Figure 3.14 shows the effect of the initiator content on the catalytic activity in the selective oxidation of CyH. Initiator content plays a vital role in hydrocarbon oxidation. CyH conversion increased with increasing initiator content. Conversion of 64.2, 73.8, 84.6 and 95.8% were obtained for initiator contents a 5, 10, 15 and 20 mol%, respectively after 3h of reaction. Kerry *et al.* also reported similar effect of increase in conversion with initiator content [53]. The AA selectivity is independent of initiator content, which implies that the role of initiator is just to initiates the reaction by forming the radical producing species of substrate and has nothing to do
with the product selectivity’s. At 20 mol% of the initiator, the rate of reaction was fast and yield of AA was high after 3h of reaction itself.

![Graph showing the effect of initiator content on selective cyclohexane oxidation.](image)

**Fig. 3.14.** Effect of initiator content on selective cyclohexane oxidation.

*Conditions:* Cyclohexane = 8 mmol, Acetic acid = 20 mL, Co-OMS-I = 150 mg, Temp = 363 K, Time = 3 h, 20 bar O₂.

### 3.8.5. Effect of Co content in the catalyst on the yield of AA

The influence of Co content in the catalyst on CyH selective oxidation was examined and the results are shown in Fig. 3.15. With increasing Co content, conversion of CyH increased, while the AA selectivity decreased. Selectivity of AA was found to be 82.2, 79.8, 77.5 and 73.1% for the catalyst Co-OMS-I, Co-OMS-II, Co-OMS-III and Co-OMS-IV respectively. The decrease in AA selectivity and simultaneous increase in by-product (SA and GA) selectivity’s indicate degradation of AA in subsequent steps. With Co-OMS-IV catalyst, high amount of by-products were found. Hence, at higher temperatures and high Co concentrations, the rate of degradation of AA is higher. Belkhir *et al.* reported almost similar observations of Co concentration effect in AA selectivity in their investigations using Co molecular sieves [54]. These results substantiate our observations on catalyst content study.
Fig. 3.15. Influence of Co content on cyclohexane oxidation

Conditions: Cyclohexane = 8 mmol, Acetic acid = 20 mL, NAPI = 20 mol%
Catalyst = 150 mg, Temp = 363 K, Time = 3 h, 20 bar O₂.

3.8.6. Recycle study of the catalyst

To study the recyclability of Co-K-OMS-2 catalyst in selective oxidation of CyH, catalyst was recovered after the completion of reaction by centrifugation, washed with methanol till it is free from organic substrate and dried at 373 K for 4h.

Fig. 3.16. Catalyst reusability study in cyclohexane oxidation

Conditions: Cyclohexane = 8 mmol, Acetic acid = 20 mL, NAPI = 20 mol%, Co-OMS-I = 150 mg, Temp = 363 K, Time = 3h, 20 bar O₂.
This catalyst was re-used for the reaction with fresh reactant. The catalyst was found to be quite stable even after the 5 recycles. After the 1st recycle, there was some loss in conversion; however, no further loss in conversion was observed in subsequent runs. The AA selectivity was almost stable, though slight reduction in GA selectivity was observed. The spent catalyst (after the 5th recycle) was characterized by ICP-OES. No loss in Co or Mn content was detected in the used catalyst. The results are given in Fig. 3.16., which shows that catalyst was recycled at least five times with not much loss in activity.

3.9. Proposed reaction mechanism

From the experimental data and literature reports a tentative reaction scheme was proposed for the oxidation of CyH to adipic acid as follows:

Cyclohexane $\rightarrow$ Cyclohexyl radical $\rightarrow$ Cyclohexylhydroperoxide $\rightarrow$ Cyclohexanol & -one $\rightarrow$ $\alpha$-keto radical $\rightarrow$ Adipic Acid $\rightarrow$ Succinic & Glutaric acids.

The conversion of CyH in the presence of Co & Mn catalysts with NAPI involves series of steps including inert C-H bond activation, enolization of ketone, electron transfer oxidation, redox decomposition of hydroperoxides.

The possible mechanism of Co-K-OMS-2 & NAPI catalyzed oxidation of cyclohexane is presented in Scheme 3.8. It proceeds in three steps. The first step involves the generation of phthalimido-N-oxyl radical (PINO) from NAPI. The generated radical abstracts hydrogen from the inert C-H bond of hydrocarbon to form cyclohexyl radical [55] (eq. 3.5). The produced highly reactive radical rapidly reacts with O$_2$ to form cyclohexyl hydroperoxide (CHHP) which in turn generates cyclohexanol and cyclohexanone by the decomposition assisted by Co (III) (eq. 3.6).

The second step involves the generation of $\alpha$-keto radicals from cyclohexanone in the presence of bifunctional Mn (IV) ion (Lewis acid & redox). Mn-(III), which forms Mn (IV) by oxidation with peroxyradicals via oxidation of the enol form of the ketone, is essential for the cleavage of the cyclohexanone, formed at first
instance in the autoxidation [56]. This cleavage proceeds through the formation of the α-keto radicals via oxidation of the enol form of the ketone (eq 3.7). Once formed, the α-keto radicals are quickly trapped by oxygen, leading to the formation of adipic acid (eq. 3.8, 3.9 & 3.10) [57].

**Step 1 (Oxidation of cyclohexane to ol and one)**

\[
\text{Cyclohexane} + \text{O}_{2} \rightarrow \text{O}_{2} \cdot + \text{Co(III)} + \text{OH}^{-} + \text{Co(III)} \tag{3.6}
\]

**Step 2: (Oxidation of cyclohexanone to Adipic acid)**

\[
\text{Cyclohexanone} + \text{Mn(IV)} + \text{H}^{+} \rightarrow \text{Adipic Acid} + \text{Mn(IV)} \tag{3.8}
\]

\[
\text{Cyclohexanone} + \text{Mn(III)} + \text{OH}^{-} + \text{Co(III)} \tag{3.9}
\]
Step – 3 (Decarboxylation of AA to GA and SA)

\[
\begin{align*}
&\text{COOH-(CH}_2\text{)}_4\text{-COOH} + \text{Co(III)} \rightarrow \text{COOH-(CH}_2\text{)}_4\text{-COOH} + \text{CO}_2 + \text{Co}^{2+} + \text{H}^+ \\
&\text{COOH-(CH}_2\text{)}_2\text{-COOH} \rightarrow \text{COOH-(CH}_2\text{)}_3\text{-COOH} - \text{CO}_2 - \text{H}^+
\end{align*}
\]

(3.11)

Scheme 3.8. Plausible mechanism for the oxidation of cyclohexane.

The third step proceeds via the decarboxylation of product adipic acid into glutaric and succinic acids. The decarboxylation of AA proceeds via the generation of alkyl radical R\(^\ast\) (COOH-(CH\(_2\))\(_4\)) with CO\(_2\) as byproduct in the presence of Co (III). The originated radical undergoes terminal oxidation to form glutaric acid which is the decarboxylated product of AA. The GA undergoes further decarboxylation to generate succinic acid [56] (eq 3.11).

The availability of Mn (IV) and Mn (III) in the catalyst play key role in electron transfer oxidation (eq 3.7), while the Co (III, II) is more effective in the redox decomposition of the hydroperoxides (eq 3.10).

3.10. Conclusions

In the present investigation, Co substituted octahedral molecular sieves (Co-K-OMS-2) were synthesized, characterized and used as selective oxidation catalysts for CyH conversion. Catalysts with different Co content were prepared through a simple reflux method. They were characterized by different physico-chemical techniques to understand their structural and textural characteristics. No perceptible changes were observed in the cryptomelane phase of KOMS-2 on substitution of cobalt. Similarly, no additional phases belonging to cobalt or cobalt oxide were observed through powder XRD investigations. The Co-OMS-2 catalysts show well resolved sharp XRD peaks. Compared to the KOMS-2, cobalt substituted Co-OMS-2 catalysts have relatively lower surface area and pore volume. Scanning electron microscopy confirmed formation of pure phases of cryptomelane with fibrous morphology for parent K-OMS-2, but the width and length of the rod
increased with Co loading. TEM images of both parent and doped samples were used for calculating lattice planes and d-spacings. Profiles of H$_2$-TPR confirm that Mn-O bond strength weakens on Co doping. Raman and IR spectroscopy demonstrated the absence of peaks that corresponds to the segregated cobalt oxide. Thermo gravimetric analysis of Co-OMS-2 materials indicate similarity in weight losses in different temperature regimes when compared to K-OMS-2 materials, but slightly lower thermal stabilities were seen as compared to the K-OMS-2. From XPS data it was found that, with increase in Co doping the Mn$^{4+}$/Mn$^{3+}$ ratio was found to decrease, surface oxygen content increased and Co$^{3+}$ is present in higher content.

The Co-K-OMS-2 catalysts were investigated for selective oxidation of CyH to adipic acid. The catalysts showed their utility and versatility for the oxidation reaction. The catalysts were highly active for the above oxidation giving good conversion, AA selectivity at short reaction times. High conversion (95.6%) of CyH was obtained with 83.2% adipic acid selectivity. Temperature, time, catalyst content, initiator amount, Co content plays vital role and on AA yield depends on them. Further, the catalysts are stable under the reaction conditions and retain good activity and selectivity for at least upto five successive runs. The catalysts reported here are easy to prepare, the initiator and the process are a step forward in the direction for potential commercial exploitation of these materials for selective heterogeneously catalyzed oxidations.
3.11. References


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52 J. Kollar *US patent* US 5321157 A