Chapter-6

Selectivity Tailoring in Liquid Phase Oxidation of p-cresol over MWNT-Mn$_3$O$_4$ Nanocomposite Catalysts

Highly selective multiwall carbon nanotube (MWNT)-Mn$_3$O$_4$ nanocomposite catalyst was designed for liquid phase oxidation of p-cresol, which gave highest selectivity of 90% to the first step oxidation product, namely, p-hydroxy benzyl alcohol. Mn$_3$O$_4$ nanoparticles and MWNT-Mn$_3$O$_4$ nanocomposites were synthesized by co-precipitation route using mixed precursors under controlled conditions. High-resolution transmission electron microscopy revealed the selective exposure of (101) and (001) planes of Mn$_3$O$_4$ nanoparticles in the MWNT-Mn$_3$O$_4$ composite. From the cyclic voltammetry study, lowering in oxidizing capacity of MWNT-Mn$_3$O$_4$ nanocomposite was confirmed which was due to incorporation of electron rich MWNT. Thus, selectivity tuning of the new material (MWNT-Mn$_3$O$_4$ nanocomposite) was found to be due to alteration in both the geometric as well as electronic properties. A plausible reaction pathway is proposed involving the predominant role of nucleophilic lattice oxygen (O$^{2-}$) species due to exposure of particular crystal planes giving highest selectivity to p-hydroxy benzyl alcohol.
6.1 Introduction

Catalytic liquid phase oxidation of alkyl groups in substituted phenols is a core technology in fine chemicals and pharmaceutical industries.\textsuperscript{1-4} Therefore developing new materials by modifying their intrinsic properties has been a continuing effort for the last two decades.\textsuperscript{5-8} The major challenges in developing new catalysts are (i) stability of the metal function without leaching under oxidation conditions, (ii) maintaining activity in the presence of antioxidizing substrates like cresols, (iii) tailoring selectivity to the desired oxidation products, particularly to the first step oxidation product, and (iv) minimizing reaction time as well as the catalyst concentration. \textit{p}-Cresol oxidation is an example of industrial oxidation process which involves stepwise oxidation to give a mixture of \textit{p}-hydroxy benzyl alcohol, \textit{p}-hydroxy benzaldehyde, and \textit{p}-hydroxy benzoic acid depending upon the catalyst used and reaction conditions.\textsuperscript{5-7,9,10} Among these, both alcohol and aldehyde derivatives are important intermediates for the manufacture of vanillin (a widely used flavoring agent), trimethoxy benzaldehyde, various agrochemicals, and pharmaceuticals such as semisynthetic penicillin, amoxicillin, and the antiemetic drug trimethobenzamide.\textsuperscript{4,11,12} Efficient catalysts for oxidation reactions mainly involve oxides of transition metals having capability to form redox couples. In particular, Co-based catalyst systems and metals such as Cu, Mn supported on molecular sieves, carbon, resins and $\gamma$-Fe$_2$O$_3$ have been extensively studied for this oxidation reaction.\textsuperscript{13-15,16}

Among different types of catalysts, nanostructured catalysts have shown higher activity than their bulk counterparts which is observed in case of nanostructured Co$_3$O$_4$ catalysts,\textsuperscript{17} which could not only be due to the size reduction (high surface/volume ratio) alone but also due to the modified adsorption characteristics caused by geometric and electronic effects. Hence the present work was undertaken to further explore and understand the fundamental aspects of the nanostructured catalysts that govern their performance, especially their role in directing the selectivity pattern in a consecutive oxidation reaction. For this purpose, we synthesized nanostructured Mn$_3$O$_4$ and its composites with multiwalled carbon nanotube (MWNT) with different degrees of loading and investigated the correlation between its constitution, structural aspects, and the activity for oxidation of \textit{p}-
cresol.\textsuperscript{[18]} Mn$_3$O$_4$ alone has been reported in the context of catalytic oxidation of methane, carbon monoxide,\textsuperscript{[19]} decomposition of NO and N$_2$O,\textsuperscript{[20-22]} deoxygenation of nitrobenzene,\textsuperscript{[23]} while MWNT-Mn$_3$O$_4$ nanocomposite has been studied only in the context of supercapacitor and magnetism applications.\textsuperscript{[24,25]} To the best our knowledge, ours is a first report of highly selective MWNT-Mn$_3$O$_4$ nanocomposite developed for selective liquid phase oxidation of $p$-cresol to intermediate $p$-hydroxy benzyl alcohol under mild conditions. The selective formation of intermediate $p$-hydroxy benzyl alcohol in a sequential oxidation of $p$-cresol could be attributed to the alterations in geometric as well as electronic characteristics of Mn$_3$O$_4$ by introducing electron rich rigid material like MWNT. The role of both these aspects has been studied in detail by high-resolution transmission electron microscopy (HR-TEM), X-ray Diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and cyclic voltametry (CV).

6.2 Experimental

6.2.1 Materials

Manganese acetate tetrahydrate, ethanol and xylene were obtained from Merck. Oleylamine was taken from Fluka. MWNT was purchased from Aldrich Chemicals. $p$-cresol was supplied by Loba Chemie, while sodium hydroxide was obtained from Merck. MWNT was purchased from Aldrich Chemicals. Analytical grade and HPLC grade methanol and n-propanol were obtained from Rankem.

6.2.2 Synthesis of Mn$_3$O$_4$ and MWNT-Mn$_3$O$_4$ nanocomposites

Nanostructured Mn$_3$O$_4$ was prepared using Manganese acetate, oleylamine, xylene and ethanol by co-precipitation method.\textsuperscript{[26]} In order to prepare 3% MWNT-Mn$_3$O$_4$ nanocomposite, commercially available MWNT was first functionalized with HNO$_3$ and H$_2$SO$_4$ in 1:3 ratios. In a typical procedure, 0.24 g of Manganese acetate and 0.0075 g of functionalized MWNT were properly dispersed in xylene at room temperature for 30 mins. To this, 4 ml of oleylamine was added and this mixture was then transferred to a round bottom flask, which was heated, from room temperature to 363 K under stirring. After the temperature reached 363 K, 1 ml H$_2$O was added and the stirring was continued at this temperature for 3 h. Then the mixture was cooled to room temperature, and highly dispersed 3% MWNT-Mn$_3$O$_4$ nanocomposites was
made to settle down by the addition of sufficient amount of ethanol. Then the solid material was isolated by centrifugation. The nanocomposite powder thus obtained was dried at 333 K for 3 h. The same procedure was followed for the synthesis of other MWNT-Mn$_3$O$_4$ composites with different degrees of loadings (Ratio of Mn$_3$O$_4$ to MWNT).

6.2.3 Characterization

The synthesized catalyst samples were characterized by X-ray powder diffraction using Philips X’Pert PRO diffractometer with nickel-filtered Cu K$_a$ radiation, Raman spectroscopy using LabRAM HR800 from JY Horiba, high resolution transmission electron microscopy (HR-TEM) using IFEI, Tecnai F30, with 300 KV FEG and field-emission scanning electron microscopy (FESEM; Hitachi S-4200). The surfaces of the catalysts were examined by X-ray photoelectron spectroscopy (XPS) on a VG scientific ESCA-3000 spectrometer using non-monochromatized Mg K$_\alpha$ radiation (1253.6eV) at a pressure of about 1 x 10$^{-9}$ Torr. The surface area values of all the samples were determined by BET adsorption method (Quadrasorb automatic volumetric instrument). The percentage metal oxide loading was obtained by the ICP (Inductive coupled plasma) analysis with Spectro 165 High Resolution ICP-OES Spectrometer (model no-ARCOSFHS12).

6.2.4 Catalytic activity

All the catalytic oxidation reactions were carried out in a 300 cm$^3$ capacity high-pressure Hastelloy reactor supplied by Parr Instruments Co. U.S.A. The reactor was connected to an air reservoir held at a pressure higher than that of the reactor. A Hewlett-Packard model 1050 liquid chromatograph equipped with an ultraviolet detector was used for the analysis. HPLC analysis was performed on a 25 cm RP-18 column supplied by Hewlett-Packard. The products and reactants were detected using a UV detector at $\lambda_{\text{max}} = 223$ nm. 35% aqueous methanol was used as mobile phase at a column temperature of 308 K and a flow rate of 1 ml/min. Samples of 10 $\mu$L were injected into the column using an auto sampler HP 1100.

In a typical experiment, 3g of p-cresol, 4.5 g of NaOH and 70 cm$^3$ of n-propanol were heated in a flask with a reflux condenser until the NaOH dissolved completely. This reaction mixture was charged to a 300 cm$^3$ par autoclave. Then
0.02g catalyst was added, and the reaction mixture was heated to 373 K. After the desired temperature was attained, the reactor was pressurized with 6.5 bar nitrogen and 2.4 bar oxygen. Then the reaction was started by agitating at 900 rpm. When the pressure was absorbed, the reactor was again filled by oxygen. This was continued up to 2 h. The progress of the reaction was monitored by observing the pressure drop in the reservoir vessel as a function of time. After 2 h the reactor was cooled to room temperature and the unabsorbed nitrogen gas was vented out. Then the content of the reactor was discharged and the final volume was noted down. The final samples were analyzed in HPLC.

6.3 Results and Discussions

![Figure 6.1](image.png)

**Figure 6.1:** (a) XRD spectra of Mn$_3$O$_4$ and 3%MWNT-Mn$_3$O$_4$; inset shows shift of (211) peak towards lower 2θ due to addition of MWNT; (b) Raman spectra of Mn$_3$O$_4$, acid treated MWNT, 3%MWNT-Mn$_3$O$_4$; inset shows broadening of D band.

As shown in **Figure 6.1a**, the XRD patterns of both Mn$_3$O$_4$ and 3% MWNT-Mn$_3$O$_4$ nanocomposites are identical with an intense peak at 2θ =36° corresponding to (211) plane. The other peaks of lower intensity are also identical for both the samples and matches with those of tetragonal hausmannite phase (JCPDS card no. 24-0734). In both samples, no other peaks corresponding to any impurity phase(s) are seen, confirming that the product was tetragonal Mn$_3$O$_4$. In order to distinguish Mn$_3$O$_4$ from γ-Mn$_2$O$_3$ which has similar structure and unit cell parameter as that of Mn$_3$O$_4$, our samples were also characterized by other techniques, which are discussed below. No signature of MWNT is observed in the XRD spectra of MWNT-Mn$_3$O$_4$ nanocomposite due to low concentration (only a few percent) of MWNT in the
composite. Also there is a considerable shift in the peaks of MWNT-Mn$_3$O$_4$ composites towards lower 2θ value as shown in the inset of Figure 6.1a. This shift in the peak is due to the strain involved during the formation of nano-composites. The Raman spectra for Mn$_3$O$_4$, MWNT, and MWNT-Mn$_3$O$_4$ nano-composite are shown in Figure 6.1b. A single intense peak at 659 cm$^{-1}$ confirms the highly pure phase of the synthesized Mn$_3$O$_4$.\[^{28}\] In the case of the MWNT sample, the two peaks are observed at 1328 cm$^{-1}$ and 1579 cm$^{-1}$ corresponding to D and G bands respectively, which match well with those reported in the literature.\[^{29}\] In the case of 3% MWNT-Mn$_3$O$_4$ nanocomposite sample, distinct peaks corresponding to MWNTs as well as Mn$_3$O$_4$ are observed. The interesting feature of the Raman spectra of MWNT-Mn$_3$O$_4$ nanocomposite is the broadening of the Mn$_3$O$_4$ and MWNT peaks as compared to the bare Mn$_3$O$_4$ nanoparticles and MWNT case. The broadening of D band of MWNT is shown in the inset of Figure 6.1b. Such a broadening can occur because of two possibilities viz. (i) strain gradient originating from interface integration during the formation of MWNT-Mn$_3$O$_4$ composite, which involves anchoring of Mn$_3$O$_4$ on the molecular moiety like –COOH due to functionalization of MWNT and/or (ii) slightly broader particle size distribution which in the present case was in the range of 12-15 nm. This increase in particle size can also be correlated with the inset figure in XRD spectra which is shown in Figure 6.1a, where the peak is slightly broader in case of Mn$_3$O$_4$ than 3% MWNT-Mn$_3$O$_4$ nanocomposite. In addition, the nanosized nature of the material leads to a higher concentration of surface atoms and attendant phonon softening which can contribute to peak broadening. Such broadening is also reported in case of TiO$_2$-MWNT nanocomposite.\[^{30}\]

X-ray photoelectron spectroscopy is used to determine the surface oxidation states of all the species present in the bare Mn$_3$O$_4$ nanoparticles and various percentages of nanocomposites (Figures 6.2a-f). Figure 6.2a and b show the C1s XPS spectra of pristine MWNT and acid functionalized MWNT, respectively. Please note the different energy (x-axis) scales on the two figures. In the case of pristine MWNT the C1s peak can be resolved into two peaks which represent presence of two distinct chemical states of carbon on the surface of MWNT. The peak at the binding energy 284.6 eV corresponds to C-C carbon,\[^{31}\] and the peak at 286.1 is due to C-O carbon. Upon acid functionalization of MWNT, the C1s peak structure is seen to be
modified significantly. After deconvolution it exhibits four contributions for the best fit. The most resolved peak located at 284.6 eV is once again assigned to the C-C bonds, while the other three peaks having binding energies 285.4 eV, 286.9 eV and 290.1 eV correspond to carbon in the C-O, carbonyl (C=O) and carboxyl (-COOH) bonds, respectively.\cite{24, 32-33} Emergence of the new contributions clearly signifies introduction of polar oxygen groups into the surface of MWNT.

Figure 6.2 : XPS spectra of (a) C1s spectra of pristine MWNT, (b) C1s spectra of acid treated MWNT, (c) Comparison of C1s XPS spectra of MWNT, 3% MWNT-Mn$_3$O$_4$, (d) Comparison of Mn2p spectra for Mn$_3$O$_4$, 3% MWNT-Mn$_3$O$_4$, (e) Comparison of O1s XPS spectra Mn$_3$O$_4$, 3% MWNT-Mn$_3$O$_4$, MWNT, (f) O1s spectra of 3% MWNT-Mn$_3$O$_4$.

The C1s spectra of MWNT-Mn$_3$O$_4$ nanocomposite (3% case shown, others at low concentrations being nominally similar) and MWNT nanoparticles are compared in Figure 6.2 c, which reveal a significant shift towards the higher binding energy in the case of the nanocomposites. This shift can be attributed to the considerable strain imparted to the C-C bond configuration of MWNT and the related modification of the
electronic environment due to the anchoring of Mn$_3$O$_4$ nanoparticles on the surface of MWNT. The inset to Figure 6.2c is the enlarged view of the same spectra in the region of the binding energy from 285 eV to 295 eV. A distinct hump is clearly seen around 290 eV in the spectrum of MWNT which is due to the carboxylic group on the surface of MWNT. But this hump is absent in the case of the nanocomposite. This signifies the attachment of Mn$_3$O$_4$ to the carboxylic oxygen present on the surface of MWNT.

Figure 6.2d shows the comparison of the Mn2p XPS spectra for 3% MWNT-Mn$_3$O$_4$ nanocomposite and bare Mn$_3$O$_4$ nanoparticles. These two spectra are nearly similar having almost equal binding energy. The peak at a binding energy of 641.7 eV is due to Mn2p3/2 and the peak at 653.3 eV is assigned to Mn2p1/2. These binding energy values match with the reported values for Mn$_3$O$_4$.\[24,34-36\]

The comparison of O1s spectra for MWNT, bare Mn$_3$O$_4$, and 3%MWNT-Mn$_3$O$_4$ are shown in Figure 6.2e. Comparing all the O1s spectra, it can be seen that there is a shift in the case of the nanocomposites toward lower binding energy, which is again due to the strain involved during the formation of composites. The O1s peaks for the nanocomposites are more similar to the O1s peak of bare Mn$_3$O$_4$, which is due to the uniform dispersion of Mn$_3$O$_4$ nanoparticles on the surface of MWNT with good surface coverage. The binding energy for O1s is shown in Figure 6.2f for the case of 3% MWNT-Mn$_3$O$_4$. After deconvolution, the peak shows two contributions. The peak at a binding energy of 529.8 eV is due to the lattice oxygen and the peak present at 531.8 eV can be attributed to either surface OH groups or other oxygen containing groups.\[34\]

Figure 6.3a shows HRTEM image of Mn$_3$O$_4$, revealing highly faceted morphology with a nanoparticle size in the range of 8-10 nm (Figure 6.3a inset). As shown in Figure 6.3b-f, MWNT-Mn$_3$O$_4$ nanocomposite is again faceted type but with some degree of elongation along the MWNT length. This could be attributed to the anisotropic surface diffusion of adsorbed species and the differential role of axis vs curvature. These nanoparticles are seen to be uniformly dispersed on the MWNT surface with a size distribution of ~12-15 nm (Figure 6.3c, d). Figure 6.3e is a
Figure 6.3: (a) HR-TEM image of Mn₃O₄; inset is a high magnification image showing 8-12 nm particles (b-f) HR-TEM image of 3% MWNT-Mn₃O₄.

section of a Mn₃O₄ nanoparticle showing the axial growth in the direction of (101) with a lattice spacing of 0.48 nm and the other exposed side along the (001) plane. This was inferred from the inter-plane angle measured directly from the HR-TEM image. All these HRTEM images of MWNT-Mn₃O₄ composites indicate that most of the exposed sides of Mn₃O₄ nanoparticles are along two specific planes (101) and (001).

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Materials</th>
<th>BET Surface Area (m² g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mn₃O₄</td>
<td>65.89</td>
</tr>
<tr>
<td>2</td>
<td>3% MWNT-Mn₃O₄</td>
<td>20.14</td>
</tr>
<tr>
<td>3</td>
<td>MWNT</td>
<td>15</td>
</tr>
</tbody>
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Table 6.1: BET surface area measurements of Mn₃O₄, MWNT, 3% MWNT-Mn₃O₄.

Table 6.1 shows the surface area values for bare Mn₃O₄ and the MWNT-Mn₃O₄ nanocomposites. The surface area of the bare Mn₃O₄ nanoparticles was found to be 65.8 m² g⁻¹, which is seen to decrease substantially (to about 20 m² g⁻¹) in the case of the 3% MWNT-Mn₃O₄ nanocomposite. This decrease in the surface area of
nanocomposites could be due to the dispersion of Mn$_3$O$_4$ on a confined area of the MWNT matrix. This is also in accordance with the increase in particle size from 8-10 nm to 12-15 nm of bare Mn$_3$O$_4$ and MWNT-Mn$_3$O$_4$ nanocomposites, respectively. The surface area of only MWNT was found to be 15 m$^2$g$^{-1}$. In the nanocomposite, the Mn$_3$O$_4$ nanoparticles are anchored uniformly on the surface of MWNT, shielding some portion of the MWNT surface and dominating the m$^2$g$^{-1}$ area estimate, albeit with somewhat enhanced size (12-15 nm).

The percent loading of metal oxide in the composites was studied by ICP analysis. The highest metal loading of 88% was observed for the case of 1% MWNT-Mn$_3$O$_4$ catalyst (Figure 6.4). The percent loading slightly decreased from 88 to 86 and 85% for 2 and 3% MWNT cases, respectively. Beyond 3% MWNT case, the metal oxide loading decreased continuously and significantly to 11% in the case of 10% MWNT, the maximum MWNT concentration examined in this work. The percent conversion and the selectivity patterns roughly follow similar trend as a function of nanocomposite composition, except for the 10% case. Also they bear an interesting nonmonotonic correlation, vis a vis, the metal oxide loading.

![Figure 6.4: Percentage loading of Mn$_3$O$_4$ from ICP analysis in comparison with selectivity and conversion.](image)

The percentage selectivity is seen to increase up to 90% in the case of 3% MWNT-Mn$_3$O$_4$ and then decreases. This could be explained by the relative degree of
heterogeneous and homogeneous nucleation of Mn$_3$O$_4$ nanoparticles. At low MWNT concentration (e.g., the 1% MWNT-Mn$_3$O$_4$ case), due to less concentration of MWNT it is possible that a fraction of Mn$_3$O$_4$ nanoparticles is formed by homogeneous nucleation and the same is not anchored on MWNT leading to higher performance. With increasing percent of MWNT to 2 and 3%, more Mn$_3$O$_4$ nanoparticles would form on the surface of MWNT and homogeneous nucleation contribution should decrease (Figure 6.5) leading to increasing conversion and selectivity. For further increase in MWNT percent (e.g., 4-10%), although all the nanoparticles would form on the MWNT surface, the exposed MWNT surface containing acid groups would get exposed more and more, leading to the formation of nonoxidation products. This would then decrease the selectivity considerably, as observed.

![Possible homogeneous and heterogeneous nucleation of Mn$_3$O$_4$ nanoparticles in 1% to 4% MWNT-Mn$_3$O$_4$ nanocomposites.](image)

**Figure 6.5**: Possible homogeneous and heterogeneous nucleation of Mn$_3$O$_4$ nanoparticles in 1% to 4% MWNT-Mn$_3$O$_4$ nanocomposites.

The activity results of bare Mn$_3$O$_4$ and MWNT-Mn$_3$O$_4$ nanocomposites for the oxidation of $p$-cresol are discussed on the basis of conversion of $p$-cresol and selectivity to various products. The % conversion and selectivity were calculated by using equations (1) and (2) respectively as follows
% Conversion = \( \frac{C_i - C_f}{C_i} \times 100 \)

6.1

% Selectivity = \( \frac{C_p}{C_x} \times 100 \)

6.2

Where \( C_i \) = initial concentration of \( p \)-cresol

\( C_f \) = final concentration of \( p \)-cresol

\( C_p \) = concentration of product formed

\( C_x \) = concentration of \( p \)-cresol consumed

In order to study the product distribution, a few preliminary experiments of \( p \)-cresol oxidation were carried out using \( \text{Mn}_3\text{O}_4 \) and MWNT-\( \text{Mn}_3\text{O}_4 \) nanocomposites in \( n \)-propanol solvent under high-pressure conditions. The progress of the reaction was monitored by liquid phase analysis as a function of time. It was observed that the initial oxidation product was \( p \)-hydroxy benzyl alcohol that undergoes further oxidation to give \( p \)-hydroxy benzaldehyde and \( p \)-hydroxy benzoic acid. Based on this the reaction pathway of \( p \)-cresol oxidation is shown in Scheme 6.1.

\[
\begin{align*}
\text{OH} & \quad \text{Catalyst} & \quad \text{OH} \\
\text{CH}_3 & \quad \text{O}_2 & \quad \text{CH}_2\text{OH} & \quad \text{CHO} & \quad \text{COOH} \\
\text{p-cresol} & \quad \text{p-hydroxy benzyl alcohol} & \quad \text{p-hydroxy benzaldehyde} & \quad \text{p-hydroxy benzoic acid}
\end{align*}
\]

Scheme 6.1: \( p \)-cresol oxidation reaction

Results on catalyst screening for \( p \)-cresol oxidation are shown in Figure 6.6. Bare \( \text{Mn}_3\text{O}_4 \) shows 46% conversion of \( p \)-cresol and a selectivity of 43% toward \( p \)-hydroxy benzyl alcohol, the remaining constituents being \( p \)-hydroxy benzaldehyde and \( p \)-hydroxy benzoic acid. \( p \)-cresol conversion decreased to 26 and 35% in the case of 1 and 2\%MWNT-\( \text{Mn}_3\text{O}_4 \) nanocomposites. In the case of 3\%MWNT-\( \text{Mn}_3\text{O}_4 \), the conversion remains almost same, that is, 36%. But conversion decreases in the case of
4 and 5%, which was 32 and 23%, respectively. This decrease in $p$-cresol conversion for MWNT-Mn$_3$O$_4$ composite was not in the proportion to the decrease in surface area from 65 to 20 m$^2$g$^{-1}$ for the change in material from bare Mn$_3$O$_4$ to MWNT-Mn$_3$O$_4$ composite respectively. Nevertheless, the decrease in surface area was attributed to the dispersion of Mn$_3$O$_4$ on a confined area of MWNT that also might restrict the access of substrate molecules to the active sites on the surface of catalyst. This explanation is supported by a separate oxidation experiment carried out using a physical mixture of 3% MWNT and Mn$_3$O$_4$ in which 42% conversion of $p$-cresol was obtained which was very close to that obtained for bare Mn$_3$O$_4$. This experiment also showed that the selectivity of $p$-hydroxy benzyl alcohol is due to the composite formation only.

It is interesting to note a steep increase in the selectivity to an intermediate product, $p$-hydroxy benzyl alcohol up to 90% for both 2 and 3% MWNT-Mn$_3$O$_4$ composite catalysts as compared to 43% in the case of bare Mn$_3$O$_4$. $p$-Cresol oxidation over a variety of heterogeneous catalysts reported so far has shown mainly the formation of $p$-hydroxy benaldehyde. Thus, the challenging task of obtaining the highest selectivity up to 90% toward first step oxidation product ($p$-hydroxy benzyl
alcohol) was achieved by 3% MWNT-Mn$_3$O$_4$ nanocomposites. The critical role of addition of MWNT on the selectivity pattern is discussed in detail below.

![Crystal structure of Mn$_3$O$_4$ spinel](image)

**Figure 6.7:** Crystal structure of (a) Normal spinel Mn$_3$O$_4$, (b) (001) plane of Mn$_3$O$_4$ spinel showing only Mn$^{3+}$, (c) (101) plane of Mn$_3$O$_4$ showing both Mn$^{2+}$ and Mn$^{3+}$

In the case of the MWNT-Mn$_3$O$_4$ nanocomposites, selective exposure of two planes (101) and (001) of Mn$_3$O$_4$ was observed due to the structured support unlike
the case of bare Mn$_3$O$_4$ where several planes can be exposed to the substrate molecules. Such correlations between the exposure of selective planes and catalytic activity have been reported.$^{[37-38]}$

**Figure 6.7a** represents the crystal structure of Mn$_3$O$_4$, which corresponds to a normal spinel structure with Mn$^{2+}$ and Mn$^{3+}$ in tetrahedral and octahedral sites, respectively. The selectively exposed planes (001) and (101) appear as shown in **Figure 6.7b,c,** respectively, which clearly indicate that the (001) plane contains only Mn$^{3+}$ species and the (101) is composed of a mixture of Mn$^{3+}$ and Mn$^{2+}$ species. Between Mn$^{3+}$ and Mn$^{2+}$ species, Mn$^{3+}$ is active for oxidation of $p$-cresol, because of its ability to be reduced to Mn$^{2+}$ thus forming a redox couple (Mn$^{3+}$ to Mn$^{2+}$). A plausible mechanistic pathway for $p$-cresol oxidation over MWNT-Mn$_3$O$_4$ composite is shown in **Figure 6.8.** This oxidation pathway is proposed considering the role of lattice oxygen as a primary oxidant in the oxidation process. $^{[23,39-41]}$ As shown in **Figure 6.8,** the first step involves the adsorption of $p$-cresol molecule on the Mn$^{3+}$ sites followed by C-H bond polarization.$^{[42]}$ Formation of C-O bond takes place by the abstraction of one of the lattice oxygen associated with Mn$^{3+}$, which in turn gets reduced to Mn$^{2+}$ as shown in the second step. The lattice oxygen vacancy created on the Mn$^{3+}$ site is compensated by the neighboring Mn$^{2+}$ atom. Concurrently, the electron produced at the Mn$^{3+}$ center is transferred to the neighboring Mn$^{2+}$ site. The molecular oxygen is adsorbed on the vacant Mn$^{2+}$ site and it gets converted to lattice oxygen to replenish the oxygen loss.$^{[43]}$ The last step involves desorption of $p$-hydroxy benzyl alcohol leading to the regeneration of catalyst, and another $p$-cresol molecule gets adsorbed and the cycle is repeated. Thus, Mn$^{2+}$ and Mn$^{3+}$ maintain a catalytic redox cycle for the conversion of molecular oxygen to lattice oxygen (O$^2^-$) and hence the reoxidation of active centers (Mn$^{3+}$) takes place. Apart from the nucleophilic lattice oxygen species O$^2^-$, some other reactive electrophilic oxygen species such as O$^-$ and O$^{2^-}$ are also formed from the molecular oxygen.$^{[43]}$ However, it is considered that the formation of nucleophilic lattice oxygen species on the surface are responsible for selective oxidation, while the electrophilic oxygen species are considered as strong oxidants leading to deep oxidation products. In the case of the MWNT-Mn$_3$O$_4$ nanocomposite, the formation of lattice oxygen species may be more favored than the formation of electrophilic oxygen species due to the selective
exposure of planes. This would lead to the oxidation of $p$-cresol primarily to $p$-hydroxy benzyl alcohol preventing the formation of subsequent oxidation products such as $p$-hydroxy benaldehyde and $p$-hydroxy benzoic acid.

*Figure 6.8: Possible mechanism pathway of oxidation of $p$-cresol to $p$-hydroxy benzyl alcohol.*
The selective formation of intermediate $p$-hydroxy benzyl alcohol can be also explained by comparing redox potential profiles of various catalysts obtained by CV measurements. For this purpose, CV measurements were performed at a scan rate of 50 mV s$^{-1}$ for the acid-treated MWNT, Mn$_3$O$_4$ nanoparticles, and 3% MWNT-Mn$_3$O$_4$ nanocomposite samples over the potential range of 1.6 to -0.2 V with standard hydrogen electrode (SHE) and 2M aqueous KCl solution. Figure 6.9 shows the plots of current density versus potential for all the above cases. Since MWNT did not show any oxidation activity (Figure 6.6) as expected, no oxidation or reduction peaks were observed. However, Mn$_3$O$_4$ nanoparticles and 3% MWNT-Mn$_3$O$_4$ nanocomposite showed clearly the presence of oxidation and reduction peaks (blue and green respectively, Figure 6.9). In both cases, the first anodic peak in the low potential region could be assigned to the oxidation of Mn$^{2+}$ to Mn$^{3+}$, while the second one to the oxidation of Mn$^{3+}$ to Mn$^{4+}$. Similarly, the cathodic peak present at higher potential could be assigned to the reduction of Mn$^{4+}$ to Mn$^{3+}$ and the second one to the reduction of Mn$^{3+}$ to Mn$^{2+}$. Comparison of the reduction peaks of Mn$_3$O$_4$ nanoparticles and 3% MWNT-Mn$_3$O$_4$ nanocomposite, showed a clear and substantial shift (~200 mV) toward higher potential values for 3% MWNT-Mn$_3$O$_4$ nanocomposite. Reduction peak indicates the oxygen reduction ability hence; higher
the potential value higher is the oxygen reduction ability, that is, lesser oxidizing ability. Thus lesser oxidizing ability of 3% MWNT-Mn$_3$O$_4$ composite than that of Mn$_3$O$_4$ is quiet evident from their CV profiles. Similar study has been reported in the case of iron nitride-doped carbon nanofibers.[44] From this discussion, it can be inferred that Mn$_3$O$_4$ nanoparticles show higher oxidizing ability than that of MWNT-Mn$_3$O$_4$ nanocomposite, which results into deep oxidation giving a mixture of all the sequential oxidation products. Therefore, an electron rich system such as MWNT was deliberately introduced in the present composite to increase the electron density on Mn$_3$O$_4$ that restricts the oxidizing ability of the MWNT-Mn$_3$O$_4$ nanocomposite to achieve highest selectivity to $p$-hydroxy benzyl alcohol.

The selective formation of $p$-hydroxy benzyl alcohol (90%) could also be well correlated with the experimental observation that the moles of oxygen consumed for the $p$-cresol oxidation over MWNT-Mn$_3$O$_4$ nanocomposites are lower (0.026 mols) than those consumed over bare Mn$_3$O$_4$ (0.034 mols for 43% selectivity to alcohol and remaining aldehyde and acid) under identical conditions. With an increase in MWNT concentration from 4 to 10%, not only the selectivity to $p$-hydroxy benzyl alcohol is seen to decrease but also no other sequential oxidation product formation such as aldehyde and acid is noted. Instead other byproduct formation is observed. Similar product distribution was also observed for the case of only acid-treated MWNT where mainly other byproduct formation was observed without any significant conversion to well-defined sequential oxidation products. The decrease in selectivity in the case of 4, 5, and 10% MWNT nanocomposites can thus be attributed to the decrease in the percentage of Mn$_3$O$_4$ loading.

In order to study the stability of our catalysts, the recycling experiments were carried out in the following way: after the first oxidation run with the fresh 3% MWNT-Mn$_3$O$_4$ nanocomposite catalyst, it was filtered out and dried in an oven at 373 K for 3 h and was recharged to the reactor for the subsequent run. The procedure was followed for two subsequent oxidation experiments, and the results are shown in Figure 6.10. The catalyst was found to retain its activity even after second recycle.
Also no leached component of the catalyst was found in the solution under the reaction conditions which is confirmed by its characterization.

![Figure 5.5: Catalyst recycling results of 3% MWNT-Mn$_3$O$_4$.](image)

6.4 Conclusion

The nanocomposites of Mn$_3$O$_4$ -MWNT (% MWNT between 0-10%) synthesized by co-precipitation route, show an excellent activity for liquid phase oxidation of $p$-cresol. It is clear from CV analysis that introduction of an electron rich system such as MWNT increases the electron density over Mn$_3$O$_4$ that could control the deep oxidation ability resulting in highest selectivity toward the first step oxidation product, namely $p$-hydroxy benzyl alcohol. Also HRTEM results reveal the exposure of particular crystal planes (101, 001) of Mn$_3$O$_4$ in the case of the nanocomposite that favor the formation of nucleophilic lattice oxygen (O$^2$) species responsible for the highest selectivity of 90% to $p$-hydroxy benzyl alcohol. This is dramatically higher than that observed for the bare Mn$_3$O$_4$ nanoparticles (43%). The catalyst was recycled twice with retention of its activity. No leached components of the catalyst were found in solution under the reaction conditions of the present work.
6.5 References


