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**Cu⁰-nanoparticles and its applications**

**Section 3.1 Activation of montmorillonite for nanoporous matrix formation and generation of Cu⁰-nanoparticles into the nanopores**

3.1.1 Introduction

Metal nanoparticles find wide range of applications in the field of catalysis, drug delivery, sensors, antimicrobial activities, abatement of pollution etc. due to their unique physico-chemical properties such as higher surface to volume ratio, quantum size effect etc. [1-4]. Recently, considerable afford has also been devoted to the application of Cu⁰/Cu-oxide-nanoparticles as substitutes of bulk Cu metal in different organic reaction such as oxidation [5], click reaction [6-8], Ullman coupling reaction [9,10], carbonylation of methanol [11] etc. The size and shape of nanoparticles as well as the nature of supporting materials on which the nanoparticles are stabilized are of utmost importance for providing highly active surface for catalysis. As the surface reactivity of nanosized metal particles is remarkably high, the metal nanoparticles immediately tend to aggregate once they are formed, which increases their particle size and make them inactive. For the stabilization of the metal nanoparticles against aggregation, various supports were used [12-21]. A good support and stabilizer is one that impedes aggregation of the nanoparticles during participation in any chemical activities like catalytic process but does not totally passivate the surfaces of the nanoparticles. In addition, the choice of a suitable stabilizer will also affect the core diameter, shape and size distribution of the nanoparticles. The most commonly used stabilizers are surfactants [13], polymers [14-16], alkylammonium salts [12, 17], organic ligands [18-20] etc. Now a days, porous substances with large internal surfaces e.g. zeolites,
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Charcoals containing nano size channels, clay minerals etc. are used for stabilization of metal nanoparticles [21-28].

In the last few years, attempts were made to stabilize metal nanoparticles into the interlamellar spaces of clay minerals of the smectite group like montmorillonite, hectorite and saponite [21-28]. Several methodologies were also reported in the literature for synthesizing metal nanoparticles into the interlayer space of modified montmorillonite [29-31]. The metal nanoparticles, supported on micro- and mesoporous materials, are expected to behave very differently from bulk metals and may exhibit unique catalytic activity, molecular selectivity and adsorption properties [12,22,32-33]. In this context, there has also been increasing interest in employing environmentally benign, cheap, easily available and robust support / stabilizer materials for the synthesis of metal nanoparticles. This chapter described the procedure for synthesizing Cu\textsuperscript{o}-nanoparticles using environmentally benign montmorillonite as a support, which is collected from the natural deposition of western part of India. The virgin montmorillonite was purified and activated with mineral acid under controlled conditions to generate a matrix having high surface area and contain micro- and mesopores on the surface [34]. The specific surface area and pore diameter as well as the pore size distribution of montmorillonite can be varied by controlling the acid activation conditions [35]. These nano range pores act as ‘host’ for \textit{in situ} generation of Cu\textsuperscript{o}-nanoparticles and also limit the growth of the particles upto desired range [36-41]. In this section, the nanopores of acid activated montmorillonite were utilized for stabilization of Cu\textsuperscript{o}-nanoparticles of narrow size distribution. The preparation consisted
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of impregnation of the acid activated montmorillonite with Cu(CH\textsubscript{3}COO)\textsubscript{2} solution followed by reduction with NaBH\textsubscript{4}.

3.1.2 Experimental

3.1.2.1 Support preparation

Purified Na-Mont. was activated with minerals acids in order to produce a matrix having high surface area and nano range pores on the surface. 10 g of Na-Mont. was dispersed in 200 ml 4 M sulphuric acid and refluxed for various time intervals (15 min, 1, 2 and 4 h). After cooling, the supernatant liquid was discarded and the acid activated Na-Mont. was repeatedly redispersed in deionized water until no SO\textsubscript{4}\textsuperscript{2-} ions could be detected by the BaCl\textsubscript{2} test. The acid activated Na-Mont. was recovered, dried in air at 50 ± 5 °C overnight to obtain the solid product. This acid activated montmorillonite were designated as AT-Mont.-I, AT-Mont.-II, AT-Mont.-III and AT-Mont.-IV indicating the activation time of 15 min, 1, 2 and 4 h respectively.

3.1.2.2 Cu\textsuperscript{0}-nanoparticles preparation

0.5 g of activated montmorillonite (AT-Mont.-I, -II, -III and -IV) were impregnated by 50 ml (2.54 mmol) aqueous solution of Cu(CH\textsubscript{3}COO)\textsubscript{2} under vigorous stirring condition. The stirring was continued for another 6 h before the mixture was evaporated to dryness in a rotavapour. 0.3 g of the clay-Cu(CH\textsubscript{3}COO)\textsubscript{2} composites was dispersed in 50 ml water in a 100 ml two necked round bottom flask and 10 ml aqueous solution of NaBH\textsubscript{4} (134 mg, 3.54 mmol) was then added slowly over 15 min in a nitrogen environment under constant stirring condition. The color changed immediately from blue to black due to conversion of Cu (II) into Cu\textsuperscript{0}-nanoparticles. The black solid
mass was recovered and washed with distilled water several times and then dried in a desiccator for 12 h. The samples thus prepared were designated as Cu\(^0\)-Mont.-I, -II, -III and -IV.

3.1.3 Results and discussion

3.1.3.1 Characterization of acid activated montmorillonite

3.1.3.1.1 Chemical analysis

The chemical compositions of different acid activated montmorillonite samples are given in the Table 3.1. It is clearly seen from the values that with increasing time of acid activation, amount of silica increases whereas aluminum content decreases. This is because acid activation modifies the layered structure of montmorillonite by leaching out aluminum from octahedral sites and thereby creates a porous matrix.

<table>
<thead>
<tr>
<th>Samples Name</th>
<th>Chemical analysis (%)</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO(_2)</td>
<td>Al(_2)O(_3)</td>
</tr>
<tr>
<td>Mont.</td>
<td>41.6</td>
<td>34.0</td>
</tr>
<tr>
<td>AT-Mont.-I</td>
<td>46.5</td>
<td>22.0</td>
</tr>
<tr>
<td>AT-Mont.-II</td>
<td>49.4</td>
<td>18.0</td>
</tr>
<tr>
<td>AT-Mont.-III</td>
<td>72.0</td>
<td>15.1</td>
</tr>
<tr>
<td>AT-Mont.-IV</td>
<td>73.0</td>
<td>14.0</td>
</tr>
</tbody>
</table>

3.1.3.1.2 Powder XRD analysis

The powder XRD patterns of four different modified micro- and mesoporous montmorillonite (AT-Mont.-I, -II, -III and -IV) along with parent clay (Mont.) were shown in Figure 3.1. The significant structural modification of montmorillonite was reflected in their relative intensity and location of basal reflection (d\(_{001}\)) peaks. The
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Parent montmorillonite exhibited an intense basal reflection at 7.06° 2θ corresponding to basal spacing of 12.5 Å. The peak intensity due to basal spacing (d₀₀₁) of the clay decreases gradually with increasing acid activation time and ultimately leading to no basal d₀₀₁ reflections in AT-Mont.-IV, which implies that the layered structure of clay disrupted [42]. A low intense broad reflection in the range 20 to 30° 2θ confirmed that the materials became amorphous silica [43].

![Figure 3.1 Powder XRD pattern of Mont. and AT-Mont.](image)

3.1.3.1.3 Specific surface area and pore size distribution

The surface area and pore size distribution of the AT-Mont. determined by N₂-adsorption study reveals that it contains both micro- (< 2 nm) and mesopores (2-50 nm). The N₂ adsorption-desorption isotherms [Figure 3.2] were of the type IV with a H3 hysteresis loop at P/P₀ ~ 0.4-0.9 clearly indicates mesoporous solids [44,45]. The specific surface area of parent montmorillonite was found 101 m²/g. Upon acid

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activation, the specific surface area value increased with activation time and showed a maximum of 417 m$^2$/g for AT-Mont.-II (1 h acid activation) with large specific pore volumes of 0.57 cm$^3$/g [Table 3.2] and thereafter on increase the acid activation time the surface area decreases remarkably but specific pore volume increases. The initial increase in surface area is may be due to the formation of micro- and mesopores by leaching out aluminum from octahedral sites. Further increase in the acid activation time with decrease of the surface area may be due to destruction of the pore walls, thereby forming bigger pores.

Figure 3.2 The stacking pattern of The N$_2$ adsorption-desorption isotherms of Mont. and AT-Mont.

The BJH pore size distribution plot [Figure 3.3] also indicates relatively a narrow pore size distribution in the initial activation time (upto 1 h) with a peak pore diameter centered within 4 to 6 nm, but, with increase in activation time gives wider range of pore size distribution and shifted towards higher value. Thus, the specific surface area as well as the pore size can be varied by applying controlled acid activation.
conditions and the desired nano range pores (pore diameter ~ 2-10 nm) can be advantageously utilized for the synthesis of metal nanoparticles with size less than about 10 nm.

**Table 3.2** Specific surface area, pore diameter and pore volume of different samples.

<table>
<thead>
<tr>
<th>Samples name</th>
<th>Specific Surface Area (m²/g)</th>
<th>Pore Diameter (nm)</th>
<th>Specific Pore Volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mont.</td>
<td>101</td>
<td>9.16</td>
<td>0.232</td>
</tr>
<tr>
<td>AT-Mont.-I</td>
<td>395</td>
<td>3.82</td>
<td>0.302</td>
</tr>
<tr>
<td>AT-Mont.-II</td>
<td>417</td>
<td>5.45</td>
<td>0.574</td>
</tr>
<tr>
<td>AT-Mont.-III</td>
<td>362</td>
<td>6.67</td>
<td>0.700</td>
</tr>
<tr>
<td>AT-Mont.-IV</td>
<td>327</td>
<td>8.35</td>
<td>0.762</td>
</tr>
</tbody>
</table>

**Figure 3.3** The stacking pattern of BJH pore distribution curves of Mont. and AT-Mont.

3.1.3.1.4 FT-IR analysis

The parent montmorillonite exhibited an intense absorption band at ~1034 cm⁻¹ for Si-O stretching vibrations of tetrahedral sheet. The bands at 522 and 460 cm⁻¹ were
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due to Si-O-Al and Si-O-Si bending vibrations [Figure 3.4]. Acid activation shifted the band from ~1034 cm⁻¹ to ~1083 cm⁻¹. The appearance of a pronounced band near 800 cm⁻¹ indicated amorphous silica [42]. Parent montmorillonite (Mont.) also showed absorption bands at 3633 cm⁻¹ due to stretching vibrations of OH groups of Al-OH. The bands at 917, 875 and 792 cm⁻¹ were related to AlAl-OH, AlFe-OH and AlMg-OH vibrations [42]. The gradual disappearance of these bands during acid activation indicated the removal of Al, Fe and Mg ions from the clay mineral structure.

![Image](image.png)  

**Figure 3.4** FT-IR spectra of Mont. and AT-Mont.

3.1.3.1.5 ²⁹Si and ²⁷Al MAS-NMR measurements

The parent montmorillonite showed an intense Si peak at about -93 ppm (Q³(OAl)), attributed to tetrahedral (3Si,Al) units of the octahedral sheet [Figure 3.5 (A)]. With increasing activation time, the intensity of the peak at -93 ppm gradually decreased and a new peak at -111 ppm due to Q⁴ Si appeared after 4 h acid activation.
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The $^{27}$Al MAS-NMR spectra of parent montmorillonite exhibited an intense peak at 3.92 ppm and a weak peak at 66.25 ppm for octahedral and tetrahedral Al respectively [Figure 3.5 (B)]. During acid activation, the intensity of the octahedral Al peak decreased and shifted to 1.6 ppm after 4 h acid activation (AT-Mont.-IV) while the tetrahedral Al peak remained unchanged.

Figure 3.5 (A) $^{29}$Si and (B) $^{27}$Al MAS NMR spectra of (a) Mont. (b) AT-Mont.-I, (c) AT-Mont.-II, (d) AT-Mont.-III and (e) AT-Mont.-IV.

3.1.3.1.6 SEM-EDX analysis

The typical SEM image of parent montmorillonite and AT-Mont. [Figure 36 (A) and (C)] indicate the formation of porous surface on montmorillonite upon acid activation which is not observed on untreated one. The EDX patterns of [Figure 3.6 (B)
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and (D)] show a decrease in Al content upon acid activation that clearly indicates the leaching of aluminum from the clay structure. Furthermore, EDX analysis at the pores of AT-Mont. [Figure 3.6 (E)] confirms the presence of silicon and oxygen in the pores.

**Figure 3.6** (A) SEM image of Mont., (B) EDX analysis of Mont., (C) SEM image of AT-Mont-III, (D) EDX analysis of AT-Mont-III at the surface and (E) EDX analysis of AT-Mont-III at pores.

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3.1.3.1.7 HRTEM investigation

The typical HRTEM image of AT-Mont.-II [Figure 3.7] showed the lattice fringe image of layered structure of clay minerals [46]. During controlled acid activation for 1 h, most of the layered structure of clay minerals is disrupted and only a fraction is retained [Figure 3.7 (A)]. Also upon supporting Cu⁰-nanoparticles (typical example Cu⁰-Mont.-II) on the acid activated clay [Figure 3.7 (B)] similar situation was observed. In Figure 3.7, both the layered and non-layered structures of clay mineral are seen.

![HRTEM images](image)

Figure 3.7 Typical HRTEM images of AT-Mont.-II. (A) before and (B) after supporting Cu⁰-nanoparticles (Cu⁰-Mont.-II)

3.1.3.2 Characterization of supported Cu⁰-nanoparticles

3.1.3.2.1 UV-Visible Spectra analysis

The preliminary investigation of the formation of Cu⁰-nanoparticles into the pores of modified montmorillonite nanoparticles (typical example Cu⁰-Mont.-II) was provided by UV-Visible spectroscopy [Figure 3.8]. The UV-Vis spectra of the prepared

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Cu⁰-nanoparticles show two extinction bands, which typically have two (in-plane and out-of-plane) plasmon modes [47]. In the spectra, the broad peak in the range 380-630 nm contain a contribution from the Cu interband transitions below 600 nm, while the broad and weak band at 450 nm may be attributed to the out-of-plane dipolar mode. Thus the appearances of this broad band confirm the formation of Cu⁰-nanoparticles.

![Absorbance vs Wavelength](image.png)

**Figure 3.8** UV-Visible spectra of Cu⁰-Mont.-II.

3.1.3.2 Powder XRD analysis

The crystalline natures of the Cu⁰-nanoparticles were confirmed by their corresponding powder XRD pattern [Figure 3.9]. The XRD shows three broad peaks of 2θ values 43.3, 50.3 and 74.1° which are assigned to the (111), (200) and (220) indices of fcc lattice of metallic Cu (JCPDS No. 85-1326) [32,33]. The XRD peaks for any other oxidation states of Cu atom were not observed, suggesting the presence of Cu only in zero oxidation state.
3.1.3.2.3 XPS analysis

To confirm the reduction of the impregnated copper salt on the pores of the activated montmorillonite, XPS analysis was carried out. Figure 3.10 shows the spectrum of the Cu 2p region. Two copper bands, Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ at 932.4 eV and 952.4 eV respectively was observed which are in good agreement with the metallic Cu [48,49]. However, the other peaks appearing at the higher binding energy may be due to the presence of oxidized Cu. The presence of oxidized Cu on the surface is presumably due to partial oxidation of the Cu$^0$-nanoparticles after deposition of the nanoparticles which is below the detection limit of XRD.
3.1.3.2.4 SEM-EDX analysis

SEM-EDX analysis also substantiated the formation of $\text{Cu}^0$-nanoparticles on the well-tuned pores of the AT-Mont. [Figure 3.11 (A)]. Furthermore, EDX analysis [Figure 3.11 (B)] indicates that Cu is present on the surface of modified montmorillonite along with other element of the clay.

![Figure 3.10 XPS pattern of $\text{Cu}^0$-Mont.-II.](image)

![Figure 3.11 (A) SEM image of $\text{Cu}^0$-Mont.-II and (B) EDX spot analysis of the pores.](image)
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3.1.3.2.5 TEM and HRTEM analysis

The TEM images of nanoparticles composites showed that dispersed Cu⁰-nanoparticles were formed in the micro- and mesopores of the acid activated montmorillonite [Figure 3.12]. The supported Cu⁰-nanoparticles were spherical in shape, well separated from each other and with sizes of 0-10 nm.

The distribution of the particles was dependent on the pore diameter of the support. Some of the Cu⁰-nanoparticles were found to be larger than the pore size of the support. HRTEM image of a single Cu⁰-nanoparticle [Figure 3.13 (A) and (C)] showed the reticular lattice planes inside the nanoparticles. The lattice planes continuously extended throughout the whole particles without stacking faults or twins, indicating the single crystalline nature. The measured inter-planar lattice fringe spacing is about 0.21 nm, which corresponds to the (111) plane of fcc copper crystals. The corresponding selected area electron diffraction (SAED) pattern of Cu⁰-nanoparticles was obtained by focusing the electron beam on the nanoparticle lying on the TEM grid [Figure 3.13 (B)]. The formation of hexagonal symmetrical diffraction spot patterns indicates that the generated Cu⁰-nanoparticles are single crystalline in nature.
3.1.3.2.6 Specific surface area and ICP-AES analysis

The surface properties of montmorillonite are found to be affected for loading the Cu⁰-nanoparticles into the micro- and mesopores of the matrix. The appreciable decrease in surface area and a smaller value of pore volume of the clay matrix were observed after supporting Cu⁰-nanoparticles [Table 3.3].
Figure 3.13 (A) HR-TEM images of Cu\textsuperscript{0}-Mont-II., (B) Selected area electron diffraction pattern (SEAD) of Cu\textsuperscript{0}-Mont-II. and (C) enlarge image of HRTEM with fringe spacing.

Table 3.3 Surface properties of montmorillonite after Cu\textsuperscript{0}-nanoparticles deposition.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Acid activated montmorillonite after deposition</th>
<th>Specific Surface Area (m\textsuperscript{2}/g)</th>
<th>Pore Diameter (nm)</th>
<th>Specific Pore Volume (cm\textsuperscript{3}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu\textsuperscript{0}-Mont.-I</td>
<td></td>
<td>201.5</td>
<td>3.50</td>
<td>0.2028</td>
</tr>
<tr>
<td>Cu\textsuperscript{0}-Mont.-II</td>
<td></td>
<td>299.0</td>
<td>5.18</td>
<td>0.3874</td>
</tr>
<tr>
<td>Cu\textsuperscript{0}-Mont.-III</td>
<td></td>
<td>245.8</td>
<td>6.96</td>
<td>0.4268</td>
</tr>
<tr>
<td>Cu\textsuperscript{0}-Mont.-IV</td>
<td></td>
<td>196.5</td>
<td>8.58</td>
<td>0.5039</td>
</tr>
</tbody>
</table>
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There could be several factors that might contribute to the observed trend of specific surface area and pore volume i.e. more Cu⁰-nanoparticles on the surface should result in smaller specific area and pore volume because of the physical occupancy of the internal space by the Cu⁰-nanoparticles. In addition, the introduction of Cu⁰-nanoparticles into the clay matrix may cause complexities in porosity measurement with nitrogen sorption, because the electrostatic forces between an adsorbate (i.e. nitrogen) and metallic surface may affect the measured values to some extent [50]. Furthermore, as discussed earlier, some of the Cu⁰-nanoparticles are slightly greater than the pore size, indicating that in some area, the Cu⁰-nanoparticles could have partially extruded into the pore walls. In such a case, the pores in the clay matrix would be blocked and become inaccessible to the pore volume and surface area measurement.

The Cu content in the Cu⁰-Mont.-II was estimated using ICP-AES, which show the presence of 1.04 wt % Cu in the nanocomposites.

3.1.4 Conclusion

The specific surface area and the pore diameter as well as the pore size distribution of montmorillonite were tuned by controlled acid activation. The pores provided the space for nanoparticle formation and limited the growth of the particles up to desired nano size range less than about 10 nm. Cu⁰-nanoparticles of size 0-10 nm are synthesized into the nanopores by impregnating Cu(CH₃COO)₂ into the pores of the acid activated montmorillonite followed by NaBH₄ reduction. Electron microscopy as well as other analytical techniques confirms the formation of Cu⁰-nanoparticles. The
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synthesized Cu⁰-nanoparticles are crystallized in fcc crystal lattice form and single crystalline in nature.
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Section 3.2  Application of Cu⁰-Mont. nanocomposite as heterogeneous catalyst

3.2.1 Introduction

The oxidation of alcohols to the corresponding carbonyl compounds is an important organic transformation, because of their applications in pharmaceuticals, dyestuffs, agrochemicals, plastic additives, photo initiator in UV-curing applications such as inks, imaging and clear coatings in the printing industries, precursor to useful resins and fragrances in perfumes industries [51-53]. Commonly, traditional alcohol oxidation employs the strongest stoichiometric oxidizing agents, such as pyridinium chlorochromate (PCC), pyridinium dichromate (PDC), KMnO₄, MnO₂, Na₂Cr₂O₇, (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO), CrO₃ etc. [54,55]. These oxidation operations are quite useful in laboratory, but these oxidants are expensive, hazardous or toxic. Moreover, toxic solvents are usually used to dissolve oxidizing agents and a large amount of inorganic wastes are produced after workup. So, catalytic oxidation over supported metal catalysts and use of environmentally friendly oxidant such as molecular oxygen without any other additive is the preferred method due to easy recovery of the heterogeneous catalyst from the products and its potential for recyclability [52,56-67]. A few processes have been reported for the liquid phase oxidation of aromatic alcohols to corresponding carbonyl compounds over Pd [63], Au [15-18], heteropoly acid [68], Ni-Al-hydrotalcite [69] etc. using molecular oxygen or aqueous H₂O₂ as oxidant. Although these methods often show good activity, many of these are associated with several shortcomings in terms of stability, economic viability,
low yield, selectivity etc. So, there is still a lot of scope to enhance the catalytic performance by improving the reaction time, catalyst quantity, selectivity etc. for the benign oxidation of aromatic alcohols.

In this section, the catalytic application of synthesized Cu\textsuperscript{o}-nanoparticles (considering the higher surface area of Cu\textsuperscript{o}-Mont.-II, thorough investigation have been carried out using Cu\textsuperscript{o}-Mont.-II) supported into the nanopores of acid activated montmorillonite (AT-Mont.), in the oxidation of aromatic alcohols to corresponding carbonyl compounds with high activity and selectivity is reported. The used catalysts were recycled several times to find out its catalytic efficiency.

3.2.2 Experimental

3.2.2.1 General procedure for oxidation reaction

1 mmol of the reactant was dissolved in 20 ml tetrahydrofuran (THF) followed by addition of 16 mg of Cu\textsuperscript{o}-Mont.-II into a two necked 100 ml round bottom flask and purged with oxygen. The reaction mixture was refluxed at 66 °C under oxygen atmosphere for a period of 4-9 h depending on upon the nature of the substrates used. To investigate the recyclability, the used catalyst was filtered after the reaction and washed with methanol followed by water and finally vacuum-dried at 40 °C before the next reaction run. The product mass along with the reactant were separated from the reaction mixture by evaporating the solvent in a rotavapor. The yields of the products were calculated by separating the individual components by column chromatography and the products were identified by using mass spectrometry and \textsuperscript{1}H NMR spectroscopy.
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3.2.3 Results and discussion

3.2.3.1 Catalytic application in oxidation of aromatic alcohols to the corresponding carbonyl compounds

The catalytic application of the synthesized Cu⁰-Mont.-II towards the oxidation of alcohol has been investigated [Scheme 3.1]. The results of the present study are presented in Table 3.4. A variety of aromatic alcohols are oxidized to their corresponding carbonyl compounds with very good yield and 100 % selectivity. However, a control reaction with AT-Mont.-II without the presence of Cu did not show any catalytic activity. Transition metals and metal oxides (particularly copper) often become nonstoichiometric and might accommodate a higher proportion of oxygen in their lattice position [70]. This helps the oxidation of alcohol to the corresponding carbonyl compounds under mild conditions presumably due to the nonstoichiometry, tenacious oxygen retention and oxygen-activating property of Cu⁰-nanoparticles. The presence of surface oxygen makes the oxidation entropically favorable and the most probable mechanism is via the abstraction of α-hydrogen by the surface oxygen [71-75].

![Scheme 3.1 Oxidation reaction of aromatic alcohols to the corresponding carbonyl compounds catalyzed by Cu⁰-Mont.-II.](image-url)
Table 3.4 Results of oxidation reaction of aromatic alcohols to the corresponding carbonyl compounds catalyzed by Cu⁰-Mont.-II

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Reaction time (h)</th>
<th>Yield (%</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C₆H₅CH₂OH</td>
<td>C₆H₅CHO</td>
<td>4.0</td>
<td>97.8 (1ˢᵗ run)ᵃ</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>93.6 (2ⁿᵈ run)ᵇ</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>92.1 (3ʳᵈ run)ᵇ</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>C₆H₅CH₃</td>
<td>C₆H₅COCH₃</td>
<td>5.0</td>
<td>82ᵇ</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>C₆H₅OH</td>
<td>C₆H₅COCH₃</td>
<td>5.0</td>
<td>78ᵇ</td>
<td>100</td>
</tr>
<tr>
<td>4</td>
<td>C₆H₅CH₂OH</td>
<td>C₆H₅CHOCH₃</td>
<td>6.5</td>
<td>69ᵇ</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>C₆H₅CH₂OH</td>
<td>C₆H₅CHOCH₃</td>
<td>9.0</td>
<td>54ᵇ</td>
<td>100</td>
</tr>
</tbody>
</table>

ᵃ GC yield, ᵇ Isolated yield

To investigate the effect of solvents on the oxidation reaction of benzyl alcohol in different solvent using Cu⁰-Mont.-II as catalyst was carried out [Table 3.5] and the most appropriate solvent in which the catalyst proceeds efficiently is tetrahydrofuran with 97.8 % conversion. The reaction was also investigated under solvent-free conditions and 55.2 % conversion was observed.

Table 3.5 Oxidation of benzylalcohol over Cu⁰-Mont.-II in different solvents

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Reaction Time (h)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DMF</td>
<td>4</td>
<td>5.0</td>
</tr>
<tr>
<td>2</td>
<td>THF</td>
<td>4</td>
<td>97.8</td>
</tr>
<tr>
<td>3</td>
<td>DCM</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>No Solvent</td>
<td>4</td>
<td>55.2</td>
</tr>
</tbody>
</table>
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3.2.3.1.1 Recyclability of recovered catalyst

Recyclability test of the catalyst were carried out on the oxidation reaction of benzyl alcohol using the recovered catalyst up to three times [Table 3.4]. The catalyst was recovered by simple filtration and vacuum dried at 40 °C before using in the next run. The reactions were carried out by maintaining the stoichiometry of reactant and recovered catalyst. Results show, that the catalyst remains active for several runs without significant lost of efficiency.

3.2.3.1.2 Characterization of recovered catalyst

To study the morphological changes occurred to the catalyst (Cu⁰-Mont.-II) after catalytic run, the recovered catalyst was investigated through TEM, powder XRD and N₂-adsorption analysis. The specific surface area of the recovered catalyst decrease to 218 (after 1ˢᵗ run), 193 (after 2ⁿᵈ run) and 122 (after 3ʳᵈ run) compared to 299 m²/g of freshly prepared catalyst [Figure 3.14]. The decrease of the surface area of the catalyst after reaction may be due to the partial destruction of the support in the reaction and blockage of pores by reactant molecules. The similar shapes of the isotherms reveal that the mesoporosity of the catalyst are retained even after successive catalytic reactions [Figure 3.14]. The BJH pore size distribution curve [Figure 3.15] of the recovered catalyst shows a slight broadening of the distribution pattern compared to fresh catalyst indicating breakdown of the pore walls forming larger pores.
Figure 3.14 The stacking pattern of N$_2$ adsorption-desorption curves of fresh and recovered catalyst (Cu$^0$-Mont.-II).

Figure 3.15 The stacking pattern of BJH pore distribution curves of fresh and recovered catalyst (Cu$^0$-Mont.-II).
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In the powder XRD of recovered catalyst [Figure 3.16], the appearance of low intensity broad peaks at around the 20 values 36 and 54⁰, along with other characteristic peaks of metallic Cu, indicates the formation of a small amount of CuO after the 1st run of the reaction [8]. However, the efficiency of the recycled catalyst was found to be almost unaffected although a fraction of Cu (0) is converted to CuO. Such efficiency of mixed Cu/CuO nanoparticles for the oxidation of alcohol is also documented in the literature [5].

![Figure 3.16 Powder XRD pattern of recovered catalyst (Cu⁰-Mont.-II).](image)

To investigate any morphological changes of Cu⁰-Mont.-II occurred after the reaction, TEM images of the recovered catalyst were recorded. TEM image [Figure 3.17] confirms that the Cu⁰-nanoparticles were still inside the clay matrix but small fractions of the particles agglomerated to form bigger size.
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![TEM image of the recovered catalyst after the 3rd run (Cu⁰-Mont.-II).](image)

**Figure 3.17** TEM image of the recovered catalyst after the 3rd run (Cu⁰-Mont.-II).

The Cu content in the recovered catalyst after third run was estimated using ICP-AES, which show the presence of 0.98 wt % Cu in the catalyst. This indicated that only very small amounts of Cu⁰-nanoparticles are leaching out and most of the Cu⁰-nanoparticles are into the clay matrix. Therefore, the catalyst remained active for several catalytic run without significant loss of its efficiency.

### 3.2.4 Conclusion

The synthesized Cu⁰-nanoparticles (Cu⁰-Mont.-II) were evaluated as a heterogeneous catalyst in oxidation of some potential aromatic alcohols to corresponding carbonyl compounds with 54-97.8 % conversion and 100 % selectivity. The used catalysts were recovered and found active for several runs without significant loss in activity. The characterization of the recovered catalyst by different analytical technique like XRD, HRTEM and N₂ adsorption-desorption have also been
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demonstrated and there is no significant change in size and shape of the Cu\textsuperscript{0}-
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