

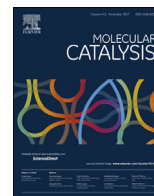


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# Nanoporous montmorillonite clay stabilized copper nanoparticles: Efficient and reusable catalyst for oxidation of alcohols

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### ABSTRACT

Stable and spherical copper nanoparticles of size less than 10 nm were generated into nanopores of activated montmorillonite clay and evaluated their catalytic activity for liquid phase alcohol oxidation to corresponding carbonyl compounds. Synthesis of copper nanoparticles was accomplished by incipient wetness impregnation of  $\text{Cu}(\text{CH}_3\text{COO})_2$  into the nanopores of the acid activated montmorillonite followed by reduction with  $\text{NaBH}_4$ . The activation of montmorillonite was carried out by treating with mineral acid such as  $\text{H}_2\text{SO}_4$  under controlled conditions at  $80^\circ\text{C}$  to generate nanopores and high surface area. Powder-XRD, SEM-EDX, HRTEM,  $\text{N}_2$  adsorption, XPS etc. analysis were carried out to characterize the stabilized copper nanoparticles as well as the support. The synthesized copper nanoparticles may serve as a new alternative to ligand and additive free green catalyst for broad range of oxidation of alcohols with molecular  $\text{O}_2$  to corresponding carbonyl compounds with excellent yields (up to 97%) and selectivity (100%) under mild reaction conditions. The metal nanocatalysts exhibit good reusability, simple workup procedure and straightforward approach to carbonyl compound formation.

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## 1. Introduction

Currently, nanomaterials have attracted great attention due to their wide range of applications in different fields such as catalysis, water purification, biodiesel production, fuel cell application, drug delivery, thin film solar cell production, nanotoxicology etc [1–4]. Considerable effort has been devoted to nano composite materials containing metal nanoparticles, particularly copper/copper-oxide nanoparticles for its potential as a high-critical-temperature superconductor, heterogeneous catalyst, complex magnetic phase, p-type semiconductor and its use in electrochemical cells [5–8]. Recently, copper/copper-oxide nanoparticles has been extensively studied as substituent of bulk copper metal in different organic reaction such as oxidation [7], click reaction [9–11], Ullman coupling reaction [12,13], carbonylation of methanol [14] etc. The size and shape of nanoparticles as well as the nature of supporting materials on which the nanoparticles are stabilized are utmost important for providing highly active surface for catalysis. In this context, there has also been increasing interest in employing environmentally benign, cheap, easily available and robust support/stabilizing materials for the synthesis

of copper nanoparticles. Earlier, we reported the environmentally benign montmorillonite support collected from western depot of Gujarat, India, and its purification and activation with mineral acid under controlled conditions to generate a high surface area matrix containing micro- and mesopores on the surface [15–20], in order to stabilize copper nanoparticles.

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 [21–23]. General approach of alcohol oxidation employs the strong stoichiometric oxidizing agents such as pyridinium chlorochromate (PCC), pyridinium dichromate (PDC),  $\text{KMnO}_4$ ,  $\text{MnO}_2$ ,  $\text{Na}_2\text{Cr}_2\text{O}_7$ , (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO),  $\text{CrO}_3$  etc [24,25]. These oxidative 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 which makes these reagents less convenient for both environmental and economical point of view. Recently, catalytic aerobic oxidations over supported metal catalysts get much attraction because oxygen is the cheapest oxidizing agent and produces only water as by-product [26–30].

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There are several reports for catalytic oxidation of alcohols to corresponding carbonyl compounds using primarily precious metal or metal based compounds as catalysts, such as Au [30,31], Ag [32], Pd [33,34], Ru [35,36], Os [37,38], Pt [39,40] etc. Numerous studies have also been devoted to other transition metal based catalysts, such as Ni [28,41], V [42], Co [43], Cr [44], Zn [45], Mo [46], Fe [47], Re [48] and Cu [28,29], for oxidation of alcohols with molecular oxygen. Although, many studies have been reported using transition metal catalysts, but the disadvantages of the above mentioned catalysts are the use of complex ligands or expensive metal supports or difficulty in preparation. Therefore, adaption of facile preparation method using more abundant and cheap transition metals like copper with high selective and environmental friendly system for the catalytic oxidation of alcohols to carbonyl compounds are of great importance. So far copper nanoparticles supported montmorillonite is not explored for the oxidation of alcohols to prepare corresponding carbonyl compounds. Here, we report the catalytic performance of the copper nanoparticles supported into the nanopores of modified montmorillonite on the oxidation of different primary and secondary alcohols to corresponding carbonyl compounds. Moreover, systematic characterization of copper nanoparticles, reduced catalyst loading, use of cheap oxidizing agent and no over oxidized product made the present work more significant compared to our previously published articles [17,18].

## 2. Experimental

### 2.1. Materials and methods

Bentonite clay (collected from Gujarat, India) was purified to collect the  $< 2 \mu\text{m}$  fraction by dispersion cum sedimentation technique as they contain various impurities like silica sand, iron oxide, quartz etc. Air dried samples were then converted to the homoionic  $\text{Na}^+$ -exchanged form by stirring in 2 M NaCl solution for about 72 h, washed and dialysed against distilled water until the conductivity of the water approached that of distilled water. Na-exchanged montmorillonite was characterized by XRD and basal spacing ( $d_{001}$ ) value was found to be 12.5 Å. Specific surface area determined by  $\text{N}_2$  adsorption was 105  $\text{m}^2/\text{g}$ . The cation exchange capacity (CEC) was 126 meq per 100 g of clay (sample dried at 120 °C). Most of the reagents were purchased from Sigma Aldrich, USA and used as without further purification.

Solid state UV–vis spectra were recorded at room temperature by the UV–vis spectrophotometer model Lambda 35, Perkin Elmer. Powder X-ray Diffractions were acquired on a Rigaku Ultima IV X-ray diffractometer from 2 to 80° 2 $\theta$  using  $\text{CuK}\alpha$  source ( $\lambda = 1.54 \text{ \AA}$ ). Specific surface area, pore volume and average pore diameter were measured by using Autosorb-1 (Quantachrome, USA). Field Emission Scanning Electron Microscope (FESEM), (made Carl Zeiss, Sigma VP) was utilized for determining the FESEM images and energy dispersive X-ray spectroscopy (EDX) patterns. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were recorded on a JEOL JEM-2011 electron microscope and specimens were prepared by dispersing powder samples in isopropanol and placing them on a carbon coated copper grid and allowing them to dry. XPS experiments were performed on a Kratos ESCA model Axis 165 spectrophotometer with a position sensitive detector and hemispherical energy analyzer in an ion pumped chamber. The amount of Cu content was determined by atomic absorption spectrophotometer (Model: A Analyst, –700, Perkin Elmer).

The preparation of the activated montmorillonite support as well as the stabilized copper nanoparticles prepared by adapting our earlier reported methods [17] are described below:

### 2.2. Preparation of support

8 g of Na-montmorillonite was dispersed in 200 ml of 4 M sulphuric acid in a three necked round bottom flask and the resulting dispersion was kept at 80 °C for 1 h. After 1 h, the solution is allowed to cool and the supernatant liquid was discarded. The acid activated Na-montmorillonite was washed repeatedly in deionized water until no  $\text{SO}_4^{2-}$  ions could be detected by the  $\text{BaCl}_2$  test. The acid activated Na-montmorillonite was recovered, dried in air at  $40 \pm 5 \text{ }^\circ\text{C}$  overnight to obtain the solid product. This acid activated montmorillonite is designated as AT-Mont.

### 2.3. Preparation of copper nanoparticles

5 g of AT-Mont. was taken into 250 ml round bottom flask at room temperature and 100 ml of water was added to it under stirring condition. 0.2 g of  $\text{Cu}(\text{CH}_3\text{COO})_2$  metal precursor was dissolve in minimum amount of distilled water and then added drop wise into the clay dispersion with vigorous stirring condition for 7–8 h. The resultant slurry was aged for an additional day under ambient condition followed by evaporation to dryness in a rotary evaporator. The dry clay- $\text{Cu}(\text{CH}_3\text{COO})_2$  composite was dispersed in 50 ml water and 10 ml of aqueous solution of  $\text{NaBH}_4$  (3 mmol) was then added slowly over a 15 min in a nitrogen environment under constant stirring condition. The reaction started immediately and colour changed from blue to black due to conversion of Cu(II) into Cu(0) and the stirring was continued for another 2 h. The black solid mass was filtered and washed with distilled water several times and then dried in a desiccator for 12 h.

### 2.4. General procedure for oxidation reaction

1 mmol of the reactant was dissolved in 20 ml tetrahydrofuran (THF) followed by addition of 16 mg of copper nanoparticles 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 upon the nature of the substrates used. Upon completion of the reaction (monitored by thin layer chromatography), the catalyst was separated by simple filtration and the filtrate was poured into water. The organic product was extracted with ethyl acetate. The combined organic fractions were dried over  $\text{Na}_2\text{SO}_4$  and concentrated. The residue was purified by column chromatography using silica gel (60–120 mesh) with ethyl acetate/hexane as eluent to obtain the desired product. To investigate the recyclability, after separation, the used catalyst was washed with methanol followed by water and finally vacuum-dried at 40 °C before the next reaction run. The products were characterized by standard analytical techniques such as  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, FTIR, melting point determination and GC. All the products are known compounds and compared with data of those commercially available.

## 3. Results and discussion

### 3.1. Characterization of support

The oxide compositions of the clay before and after acid activation were determined by wet chemical and flame photometric methods and presented in Table 1. Upon acid activation for 1 h, the surface area and the pore volume of AT-Mont. increase to 417  $\text{m}^2/\text{g}$  and 0.574  $\text{cm}^3/\text{g}$  from 105  $\text{m}^2/\text{g}$  and 0.232  $\text{cm}^3/\text{g}$  of the parent Na-montmorillonite respectively. Acid activation facilitate surface texture modification of layered structure of montmorillonite through partial leaching of Al from their tetrahedral and octahedral sites introducing porosity on the clay surface along with the partial retention of layered structure. The SEM images of parent

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