AEROBIC OXIDATION OF ALCOHOLS CATALYZED BY A NEW ZnO-SUPPORTED COPPER OXIDE NANOCATALYST IN AQUEOUS MEDIA

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GRAPHICAL ABSTRACT

Abstract ZnO-supported copper oxide nanocatalyst is reported as an efficient recyclable catalyst for the aerobic oxidation of alcohols in the presence of oxygen as the oxidant. The catalyst was prepared by coprecipitation method and characterized by x-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and transmission electron microscopy (TEM) analysis. A variety of primary and secondary alcohols were oxidized into the corresponding carbonyl compounds in good to excellent yields. The catalyst can be recovered by simple filtration and recycled up to five consecutive runs without significant decrease in the catalytic activity.

Keywords Aerobic oxidation; alcohols; carbonyl compounds; CuO/ZnO nanocatalyst

INTRODUCTION

Oxidation reactions are among the most important transformations in organic chemistry and important methodologies have been proposed for the introduction

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and modification of functional groups. During the past three decades, there has been spectacular development in this field and a large number of practical oxidation reactions have been discovered. In particular, the development of efficient procedures for the selective aerobic oxidation of alcohols to produce carbonyl compounds with air or molecular oxygen as the oxidant is a grand challenge in organic synthesis and chemical industry. The main reasons for this approach can be attributed to the low cost and ready availability of oxygen and the fact that oxygen is a green oxidant, leading to water as the by-product. Metal-catalyzed reactions are some of the most widely used methodologies for the aerobic oxidation of alcohols. These reactions received significant attention from many organic chemists. Various catalysts, including Ru, Pd, Au, and Cu, have been shown to catalyze the oxidation of alcohols using oxygen as the primary oxidant. Recently, the practical applications of nanostucture metal oxides as catalysts in organic synthesis have increased because of their high catalytic activity resulting from their high surface area. These catalysts have proved to be useful to chemists in the laboratory and in industry because of the good activation of adsorbed compounds and reaction rate enhancement, selectivity, easier workup, recyclability of the catalyst, and the ecofriendly reaction conditions. In previous research, we have reported the preparation of CuO-CeO2 nanocomposite and its application in organic reactions. Owing to our research program on the preparation of such catalyst, and in continuation of our studies on aerobic oxidation of alcohols, herein we report the preparation of novel metal oxide of CuO/ZnO nanocatalyst and its catalytic application for the aerobic oxidation of alcohols (Scheme 1).

RESULTS AND DISCUSSION

The CuO/ZnO nanocatalyst was prepared in a one-step procedure by the coprecipitation method and characterized by x-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), surface area, scanning electron microscopy (SEM), and transmission electron microscopy (TEM) techniques.

Figure 1 shows the XRD analysis of pure ZnO and 20CuO/ZnO samples. There are several peaks attributed to ZnO at a wide range of 2θ = 31.7, 34.3, 36.3, 47.3, 56.4, 62.8, 66.2, 67.8, 69.0, 72.5, and 76.9 deg, which are characteristics of (100), (002), (101), (102), (110), (103), (200), (112), (201), and (004) and 38.7 and 38.92 deg are attributed to (002), (111), and (200) planes of cubic CuO, respectively (Code No. 05–0661). The peak intensities for ZnO crystals in
20CuO/ZnO have lower intensity and are broadened after addition of CuO to the ZnO support. That indicates lower crystallinity and smaller crystallite sizes of ZnO crystallites after addition of CuO, which may be due to the incorporation of CuO to the structure of ZnO. The ZnO crystallite sizes are about 23 and 12 nm for ZnO support and 20CuO/ZnO catalyst, respectively. Also, the average crystallite size of CuO in the catalyst, calculated by the Scherrer equation, is about 8 nm.

The BET surface area of ZnO support is 53 m²/g, and as 20 wt% CuO is loaded on the support, the surface area increases to 89 m²/g. The N₂ adsorption/desorption profiles for ZnO support and 20CuO/ZnO samples are shown in Fig. 2a. According to the IUPAC classification, the nitrogen adsorption isotherms can be categorized as a type IV at the borderline with type II, with a type H3 hysteresis loop. This isotherm adsorption indicates the presence of mesopores with a pore-size distribution continuing into the macropore domain[29] (Fig. 2b). In addition, the type H3 hysteresis is usually observed on solids containing aggregates or agglomerates of some particles, leading to slit-shaped pores with nonuniform size and shape.

Figure 3 displays the SEM analysis of ZnO support and 20CuO/ZnO catalyst. The ZnO micrograph (Fig. 3a) exhibits an aggregation of nano-slit-like particles. However, the morphology of the catalyst after Cu loading is changed drastically. As can be seen, incorporation of Cu into the ZnO support has a significant effect on the morphology of the catalyst. The 20CuO/ZnO sample exhibits an agglomerate of nanoparticles with a particle size of about 38 nm in diameter.

Figure 4 shows TEM image and the CuO particle-size distribution of 20CuO/ZnO nanocatalyst. More than 200 particles are measured to obtain particle-size distribution. CuO nanoparticles are highly dispersed on the catalyst surface. Figure 4 (inset) shows the CuO nanoparticle-size distribution, with an average CuO particle size of about 4.4 nm.

To optimize the reaction conditions, the oxidation of benzyl alcohol with O₂ in the presence of CuO/ZnO nanocatalyst was chosen as a model and its behavior was studied under a variety of conditions. The influence of various solvents on the yield
of the reaction was examined and water was chosen as the most efficient solvent. Among various bases, Cs$_2$CO$_3$ showed the best efficiency. Finally, the best result was achieved in the presence of 0.07 g of CuO/ZnO catalyst and 0.5 mmol of Cs$_2$CO$_3$ in water under reflux conditions (Table 1).

Using these optimized conditions, a wide range of various alcohols, including benzylic, primary, and secondary alcohols, were converted into the corresponding carbonyl derivatives (Table 2). All the reactions occurred with absolute selectivity for aldehydes or ketones and no other products were achieved in the reaction mixture. The products could be isolated by column chromatography with a proper mixture of ethyl acetate and n-hexane. It is noteworthy that all primary benzylic alcohols with both electron-donating or electron-withdrawing substituents could be oxidized.

Figure 2. (a) N$_2$ adsorption/desorption isotherms and (b) pore-size distributions of ZnO and 20CuO/ZnO samples.
efficiently to the corresponding aldehydes with excellent conversions (entries 1–10). Benzylic alcohols containing electron-donating substituents were found to be most reactive and were converted to the corresponding aldehydes in shorter reaction times. The rate of the reaction was slower when the ring contained an electron-withdrawing

Figure 3. SEM micrographs of (a,b) ZnO and (c,d) 20CuO-ZnO samples.

Figure 4. TEM image and particle-size distribution of 20CuO/ZnO nanocatalyst.
group. Satisfactory results were obtained with cyclic and linear alcohols. The oxidation of primary aliphatic alcohols under the same reaction conditions afforded the corresponding aldehydes in good to excellent yields (Table 2, entries 11–14). However, the oxidation of secondary aliphatic alcohols produced the corresponding

| Entry | Alcohol       | Time (min) | Yield (%)  |
|-------|---------------|------------|------------|
| 1     | C₆H₅CH₂OH     | 80         | 92         |
| 2     | 3-ClC₆H₄CH₂OH | 80         | 91         |
| 3     | 4-ClC₆H₄CH₂OH | 60         | 94         |
| 4     | 2-BrC₆H₄CH₂OH | 60         | 92         |
| 5     | 4-BrC₆H₄CH₂OH | 60         | 90         |
| 6     | 3-NO₂C₆H₄CH₂OH| 70         | 91         |
| 7     | 4-NO₂C₆H₄CH₂OH| 180        | 91         |
| 8     | 3,4,5-(MeO)₃C₆H₂CH₂OH| 30| 92 |
| 9     | 4-MeOC₆H₄CH₂OH | 45         | 93         |
| 10    | 4-MeC₆H₄CH₂OH  | 60         | 94         |
| 11    | C₆H₅CH₂CH₂OH  | 60         | 92         |
| 12    | C₆H₅CH₂CH₂CH₂OH| 60         | 90         |
| 13    | CH₃CH₂CH₂CH₂OH | 120        | 90         |
| 14    | CH₃CH₂CH₂CH₂OH | 100        | 91         |
| 15    | CH₃CH(OH)CH₃  | 120        | 89         |
| 16    |                | 220        | 87         |
| 17    |                | 180        | 88         |
| 18    |                | 220        | 86         |
| 19    |                | 120        | 90         |
| 20    |                | 120        | 88         |

*Isolated pure products. Reaction conditions: Benzyl alcohol (1 mmol), Cs₂CO₃ (0.5 mmol), O₂, reflux conditions.*
ketones in moderate yields (Table 2, entries 15–20). As shown in Table 2, lower yields were observed for the oxidation of some sterically hindered alcohols.

The experimental procedure with CuO/ZnO nanocatalyst is very simple, and the catalyst can be recovered easily by filtration. The recyclability of the CuO/ZnO nanocatalyst was also studied under the optimized conditions and the desired product was obtained in good yields after 1–5 runs (Table 3). To study this property, the oxidation of benzyl alcohol under the optimized conditions was selected as a model. After reaction completion, the catalyst was washed with hot acetone, dried, and stored for another reaction run. This process repeated for five runs, and no appreciable yield decrease was observed.

In conclusion, we have prepared and characterized the novel metal oxide of CuO/ZnO nanocatalyst and reported the catalytic activity of this catalyst for the oxidation of a variety of alcohols with O2 as the oxidant in water. CuO/ZnO nanocatalyst could also be recycled and reused for five runs without any significant loss of catalytic activity. Moreover, heterogeneous reaction conditions, good yields of products, simple workup, and relatively short reaction times will make this procedure a useful addition to the available methods. We are exploring further applications of CuO/ZnO nanocatalyst for the other types of organic reactions in our laboratory.

**EXPERIMENTAL**

Chemicals were purchased from Merck Chemical Company. All products were identified by comparison of their spectroscopic data (NMR, IR) and physical data with authentic samples. Yields refer to isolated pure products. The IR spectra were recorded on a Perkin Elmer 781 spectrophotometer. All the NMR spectra were recorded on a Bruker Advance 400-MHz instrument. A Bruker AXS D8 advanced diffractometer was used for the XRD analysis to determine structural properties of the catalyst. The sample was scanned over the range of 2θ = 10–80 deg at a rate of 0.05 deg/s using Cu Kα radiation (λ = 1.5406 Å). The specific surface area of samples was determined by nitrogen adsorption–desorption using BET method. BET tests were carried out using an automated gas adsorption analyzer (Tristar 3020, Micromeritics). Prior to BET tests the samples were degassed under vacuum at 150 °C for 2 h. The morphology of the catalyst was investigated comprehensively by field emission SEM and high-resolution TEM (HRTEM) techniques using a Hitachi S-4160 instrument and Jeol JEM-2100 (200 kV) microscope. Yields refer to isolated pure products.

### Catalyst Preparation

The 20 wt% CuO supported on ZnO catalyst was prepared via a coprecipitation method, by adding 0.5 M Na2CO3·H2O solution dropwise into a mixture of

| Run | 1 | 2 | 3 | 4 | 5 |
|-----|---|---|---|---|---|
| Time (min) | 80 | 90 | 90 | 100 | 120 |
| Yield (%)a | 92 | 91 | 90 | 89 | 87 |

aIsolated pure products.
0.03 M Cu(NO$_3$)$_2$ · 3H$_2$O and Zn(NO$_3$)$_3$ · 6H$_2$O solutions under continuous mixing. The obtained suspension was aged at pH 8.5 for 15 min at 65 °C, filtered, and washed with warm deionized water. The precipitates were dried for 12 h at 100 °C, followed by calcination at 300 °C for 3 h. In addition, a batch of ZnO support was prepared under this condition for the supplementary tests. The prepared catalyst is called as 20CuO/ZnO, where 20 is the amount of CuO wt% in the catalyst.

**General Procedure**

A mixture of alcohol (1 mmol), Cs$_2$CO$_3$ (0.5 mmol), and CuO/ZnO nanocatalyst (0.07 g) in water was stirred under an oxygen atmosphere in a slurry reactor with reflux conditions. After reaction completion, catalyst was recovered by filtration, washed with hot acetonitrile (2 × 5 mL), and dried. The filtrate was quenched with 2 M HCl aqueous solution, extracted with EtOAc three times, and dried over anhydrous MgSO$_4$. Evaporation of the solvent followed by column chromatography on silica gel afforded the pure products.

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**SUPPORTING INFORMATION**

Supplemental data for this article can be accessed on the publisher’s website.

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