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Cu-incorporated mesoporous materials: Synthesis, characterization and catalytic activity in phenol hydroxylation

Huili Tang, Yu Ren, Bin Yue*, Shirun Yan, Heyong He*

Department of Chemistry and Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials,
Fudan University, Shanghai 200433, PR China

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Abstract

A series of novel Cu-incorporated mesoporous materials (CMMs) with molar ratios of Cu/Si ranging from 1/200 to 1/20 were synthesized by sol–gel method using glutaric acid as template. The materials were characterized by powder X-ray diffraction (XRD), N_2 adsorption, diffuse reflectance UV–vis spectroscopy and transmission electron microscopy (TEM). The results indicate that the CMMs have a three-dimensional (3D) worm-like mesoporous structure with a surface area between 600 and 800 $m^2\,g^{-1}$ and the copper ions are incorporated into the matrix with octahedral environment. The catalytic activity of these CMMs in the phenol hydroxylation using H_2O_2 as oxidant is comparable to that of TS-1. Effects of Cu/Si molar ratio in the catalyst and the influence of various reaction parameters on the catalytic activity were investigated in detail and the optimized reaction condition was acquired.

Keywords: Cu-incorporated mesoporous materials; Phenol; Hydroxylation; Glutaric acid; H_2O_2

1. Introduction

Diphenols (catechol and hydroquinone) are important chemicals which have been widely used in many aspects such as photographic developers, rubber and fat antioxidants, polymerization inhibitors, antiseptic and reducing agents, and pharmaceutical intermediates, etc. The production of diphenols from hydroxylation of phenol has attracted much attention since 1970s [1]. Up to now, many homogeneous and heterogeneous catalysts have been employed in this reaction. For the homogeneous systems, water soluble metal ions, metal complexes, and polyoxometalates were used to catalyze the phenol hydroxylation with aqueous H_2O_2 and other oxidants as oxygen donors [2–4]. However, the shortcomings of homogeneous catalysts, such as difficulties in recovery, relatively poor stability and low conversion, limited their industrial applications. Therefore, development of heterogeneous catalysts is particularly attractive. It was found that various bulk metal oxides or supported oxides, e.g., α-Fe_2O_3/SiO_2 [5], $Cu_2(OH)PO_4$ [6] and V–Zr mixed oxides [7], exhibited catalytic activity in the hydroxlation of phenol. Transition metal ion-exchanged layer clays, such as hydrotalcite [8,9] and montmorillonite [10], were also studied for this purpose.

The hydroxylation of phenol has become a promising environmental-friendly approach since TS-1 was used as the catalyst and aqueous H_2O_2 as the oxidant [11]. Several transition metal substituted microporous zeolites, such as TS-2, Ti-β, and Fe-Co/β, have also been studied [12–14]. However, the small pore size of microporous molecular sieves may arise the diffusion problem. The advent of mesoporous silica paved a new way for designing the catalysts with larger pore size where transition metal ions, metal oxides or metal complexes can be immobilized or supported on the channel surface or incorporated into the matrix of mesoporous silicas [15–22]. Some of these mesoporous materials showed catalytic activity of phenol hydroxylation [16,18–22]. But some problems, such as complicated preparation procedure and leaching of active species, are not well-resolved. Therefore, it is necessary to develop simple motheds for preparing environmental-friendly catalysts with high stability and high catalytic activity.

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* Corresponding authors. Tel.: +86 21 65643916; fax: +86 21 65642978.
E-mail addresses: yuebin@fudan.edu.cn (B. Yue), heyonghe@fudan.edu.cn (H. He).

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In our previous work, Ti^{4+}-containing mesoporous silicas which exhibited high catalytic activity in the cyclohexene epoxidation reaction were prepared by an "one-pot" method using short chain carboxylic acids as the templates [23]. Here we report synthesis and characterization of Cu-incorporated mesoporous materials CMM-*x* (*x* stands for Cu/Si molar ratio in starting materials) using glutaric acid as template and their catalytic activity in phenol hydroxylation reaction in details.

2. Experimental

2.1. Synthesis

Cu-incorporated mesoporous materials CMM-*x* with different Cu/Si molar ratios were synthesized by a sol–gel method using glutaric acid as template, copper(II) acetate as copper source, and tetraethylorthosilicate (TEOS) as silica source. Desired amounts of copper(II) acetate, glutaric acid, HCl ($2\,\mathrm{mol\,L^{-1}}$) and H_2O were stirred together. Then a desired amount of TEOS was added to form a clear solution with a molar ratio of 1.00 Si:*x* metal:0.50 glutaric acid:2 HCl:45 H_2O. After hydrolysis of TEOS for 1 h, the mixture was dried at 423 K for 2 h and a gel was obtained. Finally, the gel was calcined in air at 773 K for 5 h and the CMM-*x* catalysts were obtained. The final molar ratios of Cu/Si in the CMM samples determined by EDX are given in Table 1.

2.2. Characterization

The powder X-ray diffraction (XRD) patterns were obtained from a Rigaku D/MAX-II diffractometer with Cu Kα radiation. The BET surface areas, average pore sizes and pore volumes were determined by N_2 adsorption–desorption measurements at 77 K with a Micromeritics Tristar 3000 analyser. The pore size distributions were calculated from the desorption branch of the isotherms. The UV–vis diffuse reflectance spectra (DRS) were measured with a JASCO UV550 UV–vis absorption spectrometer. The transmission electron microscopy (TEM) images were obtained from a Jeol JEM 2011 electron microscope with a Link ISIS 300 EDX instrument. The leaching of Cu during the catalytic reaction was determined by ICP analysis on a Thermo Elemental IRIS Intrepid spectrometer. In the recycled runs, the catalyst was recovered by centrifugation and drying at 40 °C for 5 h.

Table 1
Physicochemical properties of the CMMs

Sample	Molar ratio of Cu/Si[a]	Average pore size (nm)	Pore volume ($cm^3\,g^{-1}$)	Surface area ($m^2\,g^{-1}$)
CMM-1/20	1/19.6	5.67	0.87	624
CMM-1/30	1/30.2	5.19	0.88	698
CMM-1/40	1/39.5	4.12	0.70	701
CMM-1/50	1/49.8	3.84	0.69	726
CMM-1/100	1/98.8	3.57	0.67	770
CMM-1/200	1/196.4	3.36	0.66	780

[a] Analyzed by EDX.

2.3. Catalytic activity test

Phenol hydroxylation was carried out at 343 K in a three-necked flask (50 mL) equipped with a magnetic stirrer and a reflux condenser. Phenol, distilled water and catalyst was added successively into the flask and heated to 343 K. A 30 wt.% H_2O_2 was then added dropwisely and the reaction was carried out for a certain period of time. The mixture was centrifugated to remove the catalyst and the liquid samples were further diluted to 100 mL with deionized water before analysis. The analysis of products was carried out on an Agilent 1100 HPLC equipped with a 150 mm reversed phase C18 column at ambient temperature [24,25] and a dual wavelength UV detector (245 and 280 nm). A methanol/water mixture (30/70 vol.%, $0.8\,\mathrm{mL\,min^{-1}}$) was used as the eluant. The conversion of phenol, the slectivity of diphenol and the product distribution are all based on molar pecentages.

3. Results and discussion

3.1. Characterization

3.1.1. X-ray diffraction

The XRD patterns of the CMMs are shown in Fig. 1. The XRD patterns of all the CMMs in the small angle region are similar to that of HMS mesoporous molecular sieve [26], showing only a broad peak in the region of 0.6–1.2°, which probably indicates the mesoporous feature. In large angle region of 10–60°, a hump at 15–30° is observed for all materials, which is from the amorphous silica. Besides the hump, CMM-1/50 and the samples with higher Cu content exhibit two weak diffractions at $2\theta = 35.3^\circ$ and 38.5° assignable to $(\bar{1}\,1\,1)$ and (1 1 1) diffractions due to the formation of minor tenorite phase of copper oxide. CMM-1/200 and CMM-1/100 exhibit no diffraction peaks of tenorite phase, indicating that the Cu species in the matrix are well dispersed.

3.1.2. N_2 adsorption analysis

The typical N_2 adsorption isotherm of CMM-1/50 shown in Fig. 2 is of type IV classification with a H2 hysteresis loop [27]. It has a sharp inflection at p/p_0 of 0.5–0.6 and an H2 hysteresis loop at p/p_0 between 0.4 and 0.8, indicating its mesopore system. The BET surface areas, pore volumes, and average pore diameters of all CMMs are listed in Table 1. The CMMs have average pore diameter in mesoporous range with large BET surface areas ($620–780\,m^2\,g^{-1}$) and large pore volume ($0.66–0.88\,cm^3\,g^{-1}$). BET surface area of the CMMs increases but pore size and pore volume roughly decrease with decreasing the molar ratio of Cu/Si.

3.1.3. TEM measurements

The TEM images of all CMMs show worm-like mesoporous structures, which is similar to that of HMS mesoporous materials [26]. A typical TEM image of CMM-1/50 is shown in Fig. 3(a). In order to check whether the pore structure of CMMs is three-dimensional (3D), an inverse carbonaceous mesoporous material was prepared using CMM-1/50 as hard template [28]. The TEM image of carbonaceous structure (Fig. 3(b)) reflects similar inter-