

A facile direct route to synthesize large-pore mesoporous silica incorporating high CuO loading with special catalytic property

AiGuo Kong, HaiWen Wang, Xin Yang, YaWei Hou, YongKui Shan *

Department of Chemistry, East China Normal University, North Zhongshan Road 3663, Shanghai 200062, China

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ABSTRACT

CuO-loaded large-pore mesoporous SBA-15 silica was synthesized by a simple and efficient direct route in an acid media. Owing to a mesophase transformation behavior induced by inorganic salts, cubic meso-structured silica was also obtained in this system. Characterization of these mesostructured materials by the XRD, TEM, BET, FT-IR, UV-VIS, XPS, CV and ICP-AES showed that ~37 wt.% or ~45 wt.% copper oxide was directly introduced into hexagonal or cubic large-pore mesoporous silica, respectively. The mechanism study revealed that in-situ formation of a large amount of copper oxalate was the key step in this synthesis. The catalytic hydroxylation of benzene to phenol reveals that the direct-synthesized mesoporous CuO/silica showed the special catalytic property in comparison to the post-impregnated samples.

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1. Introduction

Copper oxide supported on mesoporous silica materials, i.e. MCM-41 and SBA-15, can prepare the novel redox catalysts, which has shown the excellent catalytic activity in many heterogeneous oxidation reactions such as the oxidation of phenol, benzene, trimethylphenol, and alcohol [1–3]. Generally, two preparative routes can be developed to introduce copper oxide into mesoporous molecular sieve: (i) the direct synthetic method; (ii) the post-synthesis modification using the grafting or the wet impregnation technique [4]. Comparatively, the direct synthetic route is industrially more feasible method because of its simple and controllable synthetic procedure. What is more, the direct-synthesized mesoporous CuO/silica materials often show more excellent catalytic activity probably because of the well-dispersed CuO and more catalytic active sites [5].

Much successful work has been done to directly prepare the small-pore mesoporous silica with the different CuO loading, i.e. MCM-41 and MCM-48 [6–10]. However, owing to the special sol-gel chemistry of copper ions and the easily leaching of copper inorganic salts in acid solution, it is difficult that a large amount of copper oxide was directly introduced into large-pore mesoporous SBA-15 or KIT-6 silica [11–14]. But in many catalytic reactions, high content of well-dispersed CuO is desirable for high catalytic performance. Very recently, Wu et al. [11] reported a special strategy, and cubic Ia3d large-pore mesoporous silica with ~30 wt.%

CuO can be directly obtained. Unfortunately, this synthesis was sensitive to the pH value of the synthetic system, and a small amount of zinc oxide was inevitably remained in the final CuO/SiO₂ products. As we known, hexagonal mesoporous CuO/SBA-15 with over 10 wt.% Cu content have not been prepared by the direct route. It is still attractive to develop a simple direct method in the preparation of large-pore mesoporous silica with high CuO loading.

Basing on the oxidation of triblock-polymer template, we herein developed a novel and direct method to obtain large-pore mesoporous silica with high CuO loading. In this method, a large amount of copper oxalate was in-situ produced and deposited on the surface of block polymer templated mesoporous silica. It can suffer from the erosion in this acid media. As a result, mesoporous hexagonal SBA-15 or cubic KIT-6 with high CuO loading can be easily prepared by this direct approach. In comparison to the corresponding post-impregnated samples, the hydroxylation of benzene to phenol reveals their special catalytic properties.

2. Experimental section

2.1. Synthesis of mesoporous CuO/SBA-15 and CuO/KIT-6

A typical preparation procedure of CuO-loaded mesoporous SBA-15 is as follows: 1.0 g CuSO₄ · 5H₂O, 7.5 g Al(NO₃)₃ · 9H₂O, 6.2 g H₃PO₄ (85%) and 30.0 g de-ionized water were mixed and heated to 328 K in water bath, and then an ethanolic solution containing 1.0 g of Pluronic P123 (EO₂₀PO₇₀EO₂₀, M_w = 5800, Aldrich) and 10 g ethanol was added and stirred for 12 h. After that, 2.1 g of tetraethyl orthosilicate (TEOS) was added and further stirred for

* Corresponding author. Tel./fax: +86 21 6223 3503.

E-mail address: ykshan@chem.ecnu.edu.cn (Y. Shan).

20 h at this temperature. The resulting mixtures were transferred to a sealed autoclave and heated at 373 K for two days. The resultant samples were subsequently filtered off, washed with a large amount of de-ionized water and dried at 373 K. Finally, ordered mesoporous SBA-15 silica with high CuO loading was obtained by calcination at 823 K for 4 h, with a heating rate of 1 K/min. The synthetic procedure of CuO-loaded cubic mesoporous silica was similar to that of CuO/SBA-15 samples above, except that the amount of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was increased to 4.0 g. The direct-synthesized products are referred to as CuO/SBA-15-D and CuO/KIT-6-D, respectively.

For comparison, CuO-loaded mesoporous SBA-15 or KIT-6 materials also were prepared by the typical one-step impregnation with 1 M ethanol solution of Cu(II) nitrate, and finally the dried mixtures containing Cu(II) nitrate and mesoporous silica were calcined at 823 K for 4 h [15–16]. The post-impregnated samples are referred to as CuO/SBA-15-P and CuO/KIT-6-P. The corresponding CuO content in two samples was 34.3 wt.% and 41.2 wt.%, respectively.

2.2. Characterizations

The X-ray diffraction patterns of all samples were collected in θ - 2θ mode using a Rigaku Corporation D/MAX 2200PC diffractometer (Cu $K\alpha$ radiation; $\lambda = 0.154$ nm). The electric current and voltage of X-Ray is 32kV/20 mA or 40kV/40 mA for the low-angle or wide-angle patterns, respectively. The porous textures of mesoporous materials were analyzed from nitrogen adsorption–desorption isotherms at 77 K by using a Micromeritics ASAP 2000 system. Surface areas were determined according to the BET method, while the pore size distributions were calculated from the desorption isotherm using the BJH model. Transmission electron microscopy (TEM) images were measured with JEM-2010 electron microscope operated at 200 kV. Infrared spectra (FT-IR) were recorded on a Nexus-870 Fourier-transform spectrophotometer from KBr pellets with a measuring range 400–4000 cm^{-1} . The amount of Cu, Si, Al and P in the synthesized samples was determined by ICP–AES analysis on a Thermo Elemental PERKIN ELMER PASMA-2000 spectrometer. The UV–VIS diffuse reflectance spectra were measured with a JASCO UV550 UV–VIS absorption spectrometer. The X-ray photoelectron spectra measurements were performed on the instrument of Thermo ESCALAB 250 using Al $K\alpha$ radiation (1486.6 eV), and C1 s (284.6 eV) was utilized as a reference to correct the binding energy. The cyclic voltammograms (CV) were recorded at room temperature using a CHI 760 C potentiostat/galvanostat with three-electrode cell configuration. The working electrode was prepared as follows: about 25 mg of samples and 125 mg of carbon black were mixed through several drops of liquid paraffin, and then the viscous mixtures were filled into a clean polypropylene tube (1 mm inner diameter) to closely encapsulate a copper metal wire core. After that, the electrode was dried at room temperature for two days. Sodium sulfate (0.05 M) was used as the electrolyte solution. The counter and reference electrodes are Pt foil and saturated calomel electrode, respectively. The electrodes were cycled from +0.4 to -0.45 V at a scan rate of 50 mVs^{-1} .

2.3. Catalytic testing

The liquid-phase oxidation of benzene was carried out in a 100 ml flask. In a typical reaction, 0.05 g of mesoporous CuO/silica samples, 7.5 mL of 70 vol.% acetic acid and 1 ml of benzene (11.2 mmol) were added, and then the resultant mixtures were heated to the reaction temperature in a water bath. After that, 2 ml (21.2 mmol) of H_2O_2 (25 wt.%) was added, and the reaction mixtures were further stirred for 2 h with a magnetic stirrer. Finally, the catalyst materials were collected by the centrifugation,

and the resulting solution was analyzed by GC. The amount of phenol was determined by using the toluene as interior label.

3. Results and discussion

3.1. The mesostructure of materials

Fig. 1 shows the low-angle XRD patterns of mesoporous CuO/silica synthesized by the direct strategy. It can be seen that CuO/SBA-15 material (Fig. 1a) exhibits a very sharp (100) diffraction peak together with well-resolved higher order (110) and (200) reflections, indicating that it has a long-range ordered 2D hexagonal (P6mm) structure. With the increase of copper sulfate to 4 g in this system, the cubic mesostructured CuO/silica can be obtained. Two diffraction peaks of typically cubic Ia3d mesostructure, assigned to the (211) and (220) reflections [16], are observed in the corresponding low-angle XRD patterns. When further examination in the light of the corresponding TEM (Fig. 2c and d), a cubic Ia3d mesostructure can be confirmed. This mesophase transform phenomenon may result from the salt effect in this system, similar to the results reported by Wu et al [11]. The high-angle XRD patterns (Fig. 1 inset) of both mesoporous CuO/silica composites show the well-resolved diffraction peaks in agreement with the monoclinic phase of CuO, indicating that the copper oxide has been successfully loaded on the large-pore mesoporous silica in acid media. The particle size of CuO calculated from the Scherrer formula are about 9 nm for the CuO/SBA-15 samples, in agreement with the TEM result, indicating that most of copper oxide can be introduced into the channels of SBA-15. In the case of CuO/KIT-6, the CuO particle size is about 15 nm, above the pore size of KIT-6 silica, which may result from the formation of CuO nanowires in the pore channels or the existence of some bulk CuO on the external surface of mesoporous silica.

TEM images of CuO/SBA-15 samples (Fig. 2a) are recorded along the different directions, which confirm their ordered hexagonal mesostructure over a large area. Corresponding to the XRD results above, TEM images of mesoporous CuO/silica obtained with 4.0 g $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ precursors reveal a cubic Ia3d structure [16]. The filling phenomenon of CuO can be observed in all these images because of their more dark contrast grade, similar to the reported literature [11,17]. In addition, a few of the bulk copper oxide particles on the external surface of mesoporous SBA-15 can be found

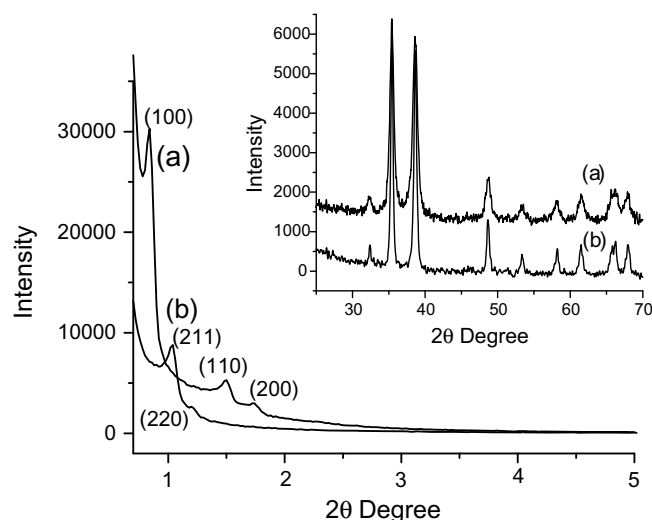


Fig. 1. The low-angle XRD patterns of (a) hexagonal CuO-loaded mesoporous SBA-15 silica and (b) cubic mesoporous CuO/silica materials synthesized by the direct method. Inset is the corresponding high-angle XRD patterns, respectively.

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