



Short Communication

Synthesis of copper-containing ordered mesoporous carbons for selective hydrogenation of cinnamaldehyde

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ABSTRACT

Copper-containing ordered mesoporous carbons (Cu-OMCs) for the selective hydrogenation of cinnamaldehyde were synthesized by an organic–organic self-assembly strategy. The as-prepared samples were characterized with nitrogen sorption, X-ray diffraction, and transmission electron microscopy. The exact Cu contents were determined by thermogravimetric analysis. The results showed that the Cu-OMCs possessed an ordered and uniform mesoporous structure, high surface areas and high pore volumes. Copper nanoparticles of size 4–15 nm were confined inside the mesopores or walls of the mesoporous carbon. By comparison with the traditional impregnated Cu/OMC and Cu/AC (activated carbon) catalysts, the Cu-OMC catalyst exhibited much higher activity and selectivity to cinnamyl alcohol.

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1. Introduction

Ordered mesoporous carbons (OMCs), with excellent structural ordering, well-defined pore size distribution and additional advantages on mass transfer and utility of internal surfaces, have attracted increasing interest due to their wide range of applications in separation, catalysis, biomedical engineering and energy storage/conversion systems [1]. There are two typical approaches for fabricating OMCs. One is nanocasting method with ordered mesoporous silica as the hard template [2,3], and the other is organic–organic self-assembly strategy (OSS) with surfactants as the soft template and phenolic resin as the carbon source [4,5]. Compared to the nanocasting method which is high-cost, low yielding and industrially unfeasible, the OSS has recently become a popular method to synthesize OMCs due to its simplified procedure, easy mass production and ability to produce various forms of OMCs like films, powders, monoliths, etc. More significantly, active metal species can be directly introduced into the carbon framework to prepare metal-containing ordered mesoporous carbons (M-OMCs) during the self-assembly process. To date, great success on the synthesis and application of M-OMCs has been achieved with the OSS [6–13].

Selective hydrogenation of cinnamaldehyde to the corresponding alcohols is of great importance in fine chemicals industry. Also, it is considered as a good model reaction in correlating the catalytic behaviors with microstructures of heterogeneous catalysts [14]. Generally, cinnamaldehyde (CMA) is hydrogenated to cinnamyl alcohol

(CMO) and hydrocinnamaldehyde (HCMA), depending on whether the C=C double bond is hydrogenated or the C=O bond. CMO and HCMA can both be further hydrogenated to hydrocinnamyl alcohol (HCMO) as the final product.

Copper-based catalysts are very efficient for many catalytic reactions, such as selective hydrogenation, oxidation and amination, etc. [15,16]. In this paper, to further broaden the variety of the M-OMCs materials synthesized with the OSS, we prepared copper-containing ordered mesoporous carbons (Cu-OMCs) via a one-pot aqueous self-assembly soft templating route followed by a direct carbonization process. The selective hydrogenation of CMA was used as a probe reaction to evaluate the catalytic performance of the Cu-OMCs. The results showed that Cu nanoparticles prepared with the OSS were highly dispersed in the mesoporous carbons, and the Cu-OMCs exhibited high activity and selectivity toward CMO in the hydrogenation of CMA.

2. Experiment

2.1. Synthesis of Cu-OMCs

For a typical synthesis of Cu-OMC, 0.015 mol of resorcinol (R) was dissolved in a solution composed of 2.5 g of F127 and 20 g of ethanol/water (1/1 vol%) under stirring. When a light brown solution was formed, a required amount of copper (II) nitrate together with 0.2 g of HCl (37 wt%) was added to act as both a copper source and a catalyst. After stirring for 2 h, 0.015 mol of formaldehyde (37 wt%) (F) was dropped into the solution. After an additional hour of stirring, the mixture was kept standing until it turned cloudy and began to separate into two layers. This two phase mixture was further kept

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Table 1
Textural properties of the blank OMC and the Cu-OMCs.

Sample number	Chemical compositions	S_{BET} (m^2/g)	V_{meso} (cm^3/g)	V_{p} (cm^3/g)	D_{p} (nm)
1	OMC	781	0.54	0.64	4.5
2	4.5Cu-OMC	745	0.51	0.62	5.1
3	7.2Cu-OMC	716	0.52	0.58	5.9
4	9.6Cu-OMC	695	0.50	0.57	6.2

aging for 4 days at room temperature. Subsequently, the upper layer was discarded while the lower polymer-rich phase was stirred overnight until a sticky monolith was formed. Finally, the monolith was cured at 85 °C for 2 days and carbonized under a N_2 atmosphere at 800 °C for 3 h at a ramping rate of 2 °C/min. The resulting composites are named *m*Cu-OMC, where *m* indicates Cu weight content (wt%) in the Cu-OMC. A blank OMC was also prepared under the same conditions as those for the Cu-OMCs, but without the adding of the copper (II) nitrate. The samples number and the corresponding chemical compositions of the resulting Cu-OMCs are shown in Table 1.

2.2. Characterization

Textural characterizations were carried out by adsorption of N_2 at –196 °C on a Micromeritics ASAP 2010 apparatus. The specific surface areas of samples were calculated by the BET equation. Powder X-ray diffraction (XRD) patterns were collected with D/Max- β b diffractometer using a Cu $K\alpha$ radiation source ($\lambda = 0.15432$ nm). Transmission electron microscopy (TEM) images were obtained on a JEOL 2000EX electron microscope operating at an accelerating voltage of 120 kV. The exact Cu contents of the samples were determined by burning a fraction of it at 650 °C under air flow up to constant weight.

2.3. Catalytic measurements

The hydrogenation of CMA was carried out in a Batch reactor at 100 °C, 3 MPa of H_2 , and a stirring speed of 400 rpm. After the addition of 0.2 g catalyst, 3 ml CMA, and 100 ml isopropanol was used. The reaction was monitored by taking around 1.0 ml samples from the reaction mixture periodically to determine the conversion and selectivity. The reaction products were analyzed by gas chromatography (Agilent 6890) equipped with a flame ionization detector and a 0.25 mm \times 30 m FFAP capillary column.

3. Results and discussion

3.1. Structural features

Fig. 1a exhibits the low angle XRD patterns of samples 1–4. For the four samples, there was a strong peak at $2\theta = 0.5\text{--}1^\circ$ which could be indexed as reflection of (100) a 2D $p6mm$ hexagonal mesostructure. Moreover, the (100) peaks seemed to have a shift toward the lower angles with an increase of the Cu content. In the wide angle range (Fig. 1b), the broad diffraction peaks at $2\theta = 24^\circ$ characteristic of amorphous carbon appeared. Three peaks, (111), (200) and (220) corresponding to $2\theta = 43.3^\circ$, 50.4° and 74.1° (JCPDs no.04-0836) assignable to Cu^0 were observed, which implied Cu^{2+} was completely reduced to Cu^0 with the face-centered cubic structure during the carbonization at 800 °C. The Cu particle sizes, calculated by the Scherrer equation, become larger from 4 nm to 15 nm as the copper loading increases.

Fig. 2 shows N_2 adsorption–desorption isotherms and pore size distributions of the samples 1–4. The four samples were typical type IV isotherms with well-defined H1 hysteresis loops, characteristic of mesoporous structure, which was in accordance with the

XRD results. The corresponding textural properties are summarized in Table 1. It was noted that with a rise of the Cu content, both the BET surface areas and the V_{p} decreased slightly. This result implied slight pore-blocking occurring upon the incorporation of Cu. The D_{p} of the samples 2–4 centered at 5.1 nm, 5.9 nm and 6.2 nm, respectively, showing a tendency that higher Cu loading could make the pore diameter become larger, suggesting that the presence of Cu could limit the shrinkage of the mesostructures of carbons during pyrolysis. This was likely due to the increasing consumption of carbon as copper (II) nitrate was reduced to Cu^0 by the surrounding carbon, which could accelerate the development of carbon structure and enlarge the pore size.

The TEM images in Fig. 3 clearly illustrate that the samples 1–4 have well ordered hexagonal mesostructures (Fig. 3a–d). The ordered structures of the Cu-OMCs with arrays of long 1-D channels were almost preserved even at the loadings of Cu as high as 9.6 wt%. By carefully examining the TEM images of the samples 2–4, it was clearly observed that the Cu particles with sizes of 4–14 nm are highly dispersed in the pores or on the walls of the OMC, which was similar to the calculations based on the Scherrer equation from the wide-angle XRD characterizations.

3.2. Catalytic hydrogenation of CMA

Over the past years, supported metal [17] catalysts have been extensively investigated for their selectivity to CMO in the hydrogenation of CMA. However, few reports deal with copper-based catalysts for this reaction although copper has been shown to preferentially hydrogenate the carbonyl group [18–20]. In the present work, we

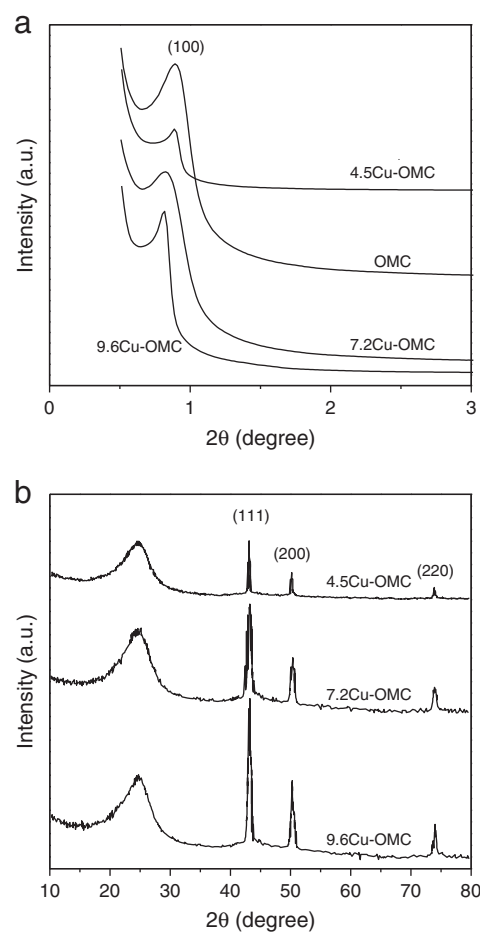


Fig. 1. Low (a) and wide (b) angle XRD patterns of the Cu-OMCs with different Cu contents.

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