Chinese Chemical Letters xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Original article

Preparation of nano-CuO-loaded halloysite nanotubes with high catalytic activity for selective oxidation of cyclohexene

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ARTICLE INFO

Article history:
Received 10 June 2015
Received in revised form 2 July 2015
Accepted 8 July 2015
Available online xxx

Keywords:
Cyclohexene
CuO
Selective oxidation
HNTs

ABSTRACT

A facile preparation method of nano-CuO catalysts, assembled in the hollow nanotube of halloysite nanotubes (HNTs), was developed. The characterizations of XRD, TEM, SEM, BET, XRF and FT-IR were used to analyze the structure and properties of the nano-CuO/HNT loaded catalyst. The XRD patterns indicated that the CuO nanoparticles on HNTs were monoclinic phase. The TEM-EDX and SEM images confirmed that most of nano-CuO catalysts with the crystal size of *ca.* 20 nm were assembled into the hollow nanotube of HNTs. The catalytic performance of the nano-CuO/HNT catalysts was evaluated by using selective oxidation of cyclohexene. The reaction temperature and recycling times were investigated. The results reveal that the nano-CuO/HNT catalysts exhibit an excellent catalytic oxidation performance for selective oxidation of cyclohexene to 2-cyclohexene-1-one.

1. Introduction

In the past, the α,β-unsaturated ketones found broad applications in many fields, for example, as chemosensors for metal ions [1], intermediates of many natural products and bioactive compounds [2] and building blocks and products of pharmaceutical interest [3].

Cyclohexene is a promising starting material in the one-step production of adipic acid with H_2O_2 as oxidant [4,5]. Cyclohexene can be epoxidized to form epoxycyclohexane using hydroperoxide as oxidant [6,7]. The allylic oxidation of cyclohexene is also industrially relevant because it produces α,β-unsaturated alcohols and ketones, which are important intermediates in the fragrance industry and organic synthesis [8]. Numerous studies have revealed that the epoxidation of cyclohexene is catalyzed by homogeneous Fe, Mn, Cu, Cr catalysts, or their immobilized versions [9,10]. Titanosilicate molecular sieves and metal–organic frameworks are promising solid catalysts for the epoxidation [11]. Mesoporous silica-supported Fe, Co, and Au catalysts have been reported as active for the aerobic oxidation of cyclohexene [12]. Metal–organic frameworks containing transition metals (*e.g.*, Fe, Cr, Cu, V, *etc.*) are regarded as active catalysts for the aerobic allylic oxidation of cyclohexene [13–18]. The VO_2-supported SiO_2 catalysts offer excellent activity, which exhibited 21% cyclohexene conversion and 84% selectivity toward epoxide [19]. The effect of the size of gold nanoparticle-supported SiO_2 catalyst on their catalytic activity in the aerobic oxidation of cyclohexene revealed that Au particles with a larger size than 2 nm were active in cyclohexene oxidation [20]. CuO nanorods efficiently catalyzed selective oxidation of cyclohexene to 2-cyclohexene-1-one (99% conversion and 95% selectivity) using TBHP as oxidant [21]. A trimetallic, hybrid, nano-mixed oxide ($RuO_2/Co_3O_4/CeO_2$) catalyst was used to catalyze selective oxidation of cyclohexene to 2-cyclohexene-1-one (97.7% conversion and 95% selectivity) [22]. More recently, the active nitrogen-doped CNTs (NCNTs), as metal-free catalysts, have exhibited an excellent activity in the allylic oxidation of cyclohexene in the liquid phase using oxygen as oxidant [23]. Since the active metal, or metal oxide particles, are prone to aggregate, resulting in difficultly being separated and recovered from the solution after the reaction, therefore, the supported technology was developed for the sake of blocking the aggregation of the active metal or metal oxide particles. Based on these reasons, the support of the loaded catalysts was mainly focused on catalysts, such as TS-1 [11], MCM-41 [12], metal–organic frameworks [11–18], SiO_2 [19], CNTs [23] and so on.

Halloysite nanotubes (HNTs) 0.2–2 μm in length, 40–70 nm in outer diameter and 10–30 nm in inner diameter, as two-layered aluminosilicate clay, have exhibited promising results as a catalyst support due to their inherent hollow nanotube structure and different outside and inside chemistry [24,25]. A number of studies

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http://dx.doi.org/10.1016/j.cclet.2015.08.002
1001-8417/

Please cite this article in press as: Z.-L. Cheng, W. Sun, Preparation of nano-CuO-loaded halloysite nanotubes with high catalytic activity for selective oxidation of cyclohexene, Chin. Chem. Lett. (2015), http://dx.doi.org/10.1016/j.cclet.2015.08.002

have demonstrated that HNTs have been of great interest in applications as nanomaterials over different fields, particularly on catalysis. As proved, nano-CuO catalysts were highly active for selective oxidation of cyclohexene to 2-cyclohexene-1-one [21]. The study of HNTs supported nano-CuO catalysts for selective oxidation of cyclohexene has yet to been found.

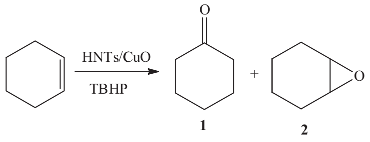
Herein, this work presents the facile preparation method and a series of characterizations of the nano-CuO-loaded HNT catalysts using the impregnation method. The catalytic performance of the nano-CuO/HNT catalysts was evaluated by the catalytic oxidation of cyclohexene to 2-cyclohexene-1-one.

2. Experimental

Catalyst preparation: The HNT mineral powder, as clay mineral, was purchased from Tianjin Linruide Co., Ltd. in China. The original HNT nanomaterials are approximately 0.5 μm in length and 27 nm in inner diameter. Firstly, the HNT powder was dried in an oven at 120 °C before use. Next, the saturated solution of $Cu(NO_3)_2$ was prepared at room temperature, and then an amount of urea was added to prepare the transparently mixed solution. Then, the mixed solution was added dropwise to the hot HNT powder taken from oven until the surface of HNT powder was moist. The moist powder was transferred to an oven and treated at 120 °C for 6 h. Finally, the sample was calcined at 500 °C for 3 h. The obtained sample was denoted as nano-CuO/HNTs. The nano-CuO particles were prepared by using sol-gel method in previous work [26].

Catalyst characterization: The morphology and element composition of samples was observed by a transmission electron microscope (TEM) and energy-dispersive X-ray spectrometry analysis (EDX) (Tecnai 12, Philips Co.). The surface morphology was examined by a scanning electron microscopy (SEM) (S4800II, Hitachi) at an acceleration voltage of 15 kV. The FT-IR spectrum was analyzed by a Varian IFS66/S spectrometer. The BET properties of the HNTs and catalysts were characterized by using a Quantachrome Autosorp 2000. The composition of HNTs and catalysts was analyzed by LAB CENTER XRF-1800 X ray fluorescence spectrometer (Shimadzu Corp.).

Cyclohexene oxidation: The catalytic oxidation of cyclohexene with tertiobutylhydroperoxyde TBHP (AR grade), as an oxidant, was carried out in a two neck glass round-bottom flask equipped with a magnetic stirrer and a reflux condenser. Typically, 10 mmol of cyclohexene, 100 mL of acetonitrile, and 50 mg of the nano-CuO/HNT catalysts were placed in the above flask and then stirred at a stirring speed of 1000 rpm for several minutes. Then, a certain amount of TBHP was rapidly added with stirring at the reaction temperature for 6 h. The reaction products were identified by comparison with authentic products and the course of reactions was followed by gas chromatography–mass spectroscopy (GC–MS: Trace DSQ II, Thermo Co. USA). After reaction completion, the catalysts were calcined for regeneration at 500 °C for 3 h. The oxidation reaction of cyclohexene employed CuO/HNTs catalyst is presented in Scheme 1.



Scheme 1. Oxidation of cyclohexene by TBHP in the presence of CuO/HNTs catalyst.

3. Results and discussion

Fig. 1 shows the XRD patterns of HNTs, nano-CuO and nano-CuO/HNTs. For the HNTs sample, all of the observed peaks mainly can be indexed to the characteristic peaks of the halloysite, as shown in Fig. 1-HNTs [26]. But for nano-CuO/HNTs sample, there appears five fresh peaks in the XRD pattern of nano-CuO/HNTs besides the significantly reduced feature peaks of HNTs. Compared to nano-CuO, these fresh peaks can be indexed to the main characteristic peaks of the monoclinic phase of CuO, which is in good accordance with JCPDS card No. 48-1548. The crystal size of CuO particles on HNTs as evaluated by the Scherrer formula is 19.2 nm. Compared to HNTs, the characteristic peaks of HNTs in the nano-CuO/HNT pattern are obviously reduced, which is ascribed to the transformation of crystal-phase structure of the tube wall of HNTs to the amorphous phase during calcining at 500 °C. Table 1 gives the compositions of HNTs and nano-CuO/HNTs. The loaded amount of nano-CuO is about 8.4%.

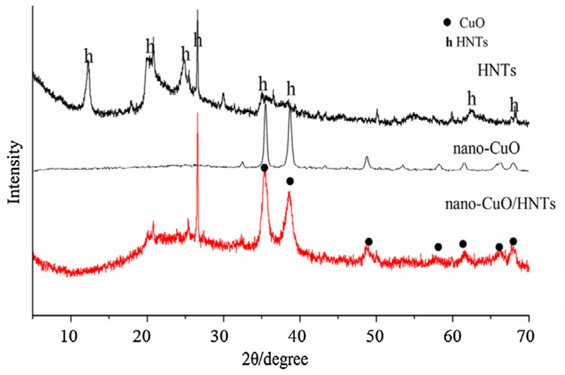


Fig. 1. XRD patterns of HNTs, nano-CuO and nano-CuO/HNTs.

The TEM-EDX and SEM photos of nano-CuO/HNTs are displayed in Fig. 2. The EDX spectrum (inset) indicates that the nanoparticles in hollow nanotube of HNTs contain a large concentration of the Cu element, thereby confirming the existence of CuO. The CuO particles are of the size of 20 nm, which is closer to the calculated value achieved by XRD. As shown in the SEM photo, no independent particles are found in outer area of HNTs. These results indicate that the impregnation method developed in this work is highly efficient on assembling nanoparticles in the hollow nanotubes of HNTs. The BET data of HNTs and nano-CuO/HNTs are listed in Table 2. Owing to nanoparticles occupying in nanotube of HNTs, the specific surface area, pore volume and average pore diameter of all nano-CuO/HNTs are decreased.

Fig. 3 shows the FT-IR spectra of HNTs, nano-CuO and nano-CuO/HNTs catalysts. The nano-CuO/HNTs possess some typical signals of HNTs, such as the deformations of Al–O–Si at 538 cm^{-1}, Si–O–Si at 462 cm^{-1}, and Si–O broad stretching band at about 1010 cm^{-1}. However, the O–H groups of the inner hydroxyl groups in HNTs at 909 cm^{-1} have disappeared, which may be assumed to be due to the transformation of the crystal-phase structure of the tube wall. This verifies the concluded results of XRD above. As to the feature peaks of CuO at the stretching band of 584 cm^{-1} and the lattice vibration of 530 cm^{-1}, respectively, and the nano-CuO/HNTs are only detected at the characteristic signal of 586 cm^{-1}.

The catalytic activities of HNTs, nano-CuO and nano-CuO/HNT catalysts as a function of reaction temperature are shown in Fig. 4. As to the HNT catalysts for selective oxidation of cyclohexene to 2-cyclohexene-1-one, almost no catalytic activity is found.

Table 1
XRF analysis of chemical composition of HNTs and nano-CuO/HNTs.

Composition (m/%)	SiO_2	Al_2O_3	CuO	Other oxide
HNTs	50.95	40.76	0	8.29
Nano-CuO/HNTs	46.35	38.35	8.40	6.90

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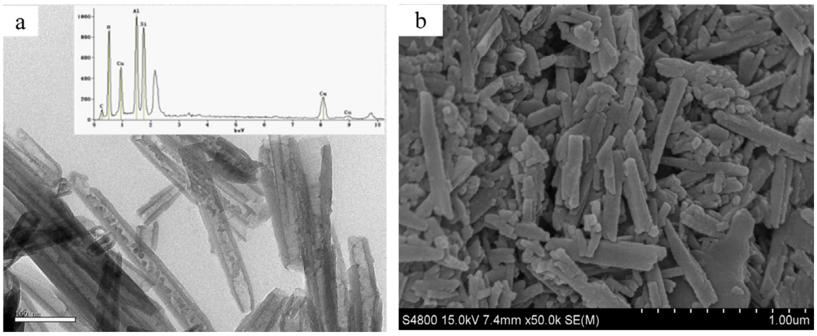

Fig. 2. TEM-EDX (inset) and SEM photos of nano-CuO/HNT catalysts (a) TEM, (b) SEM.

However, the nano-CuO catalysts exhibit a higher selective oxidation performance, achieving an 84% maximum conversion and 82% maximum selectivity for 2-cyclohexene-1-one at 70 °C. But for the nano-CuO/HNT catalysts, as the reaction temperature elevated to 70 °C, the conversion of cyclohexene and selectivity of the target product of 2-cyclohexene-1-one both are remarkably increased up to the maximum values of 99% and 98%, respectively, exhibiting 15% higher than those of the nano-CuO catalysts. This result can be further confirmed through GC diagram, as shown in Fig. 4b. With the further increasing of reaction temperature, the selectivity of the target product of 2-cyclohexene-1-one descends to 65% at 80 °C, whereas the conversion of cyclohexene exhibits little change. This is attributed to the increases of the by-products at that reaction temperature. In addition, the nano-CuO/HNT catalysts have a higher selectivity of the target product of 2-cyclohexene-1-one than that of CuO nano-rods reported by Zhu *et al.* [21].

Fig. 5 shows the recyclability of the nano-CuO/HNT catalysts. It can be interestingly found that the nano-CuO/HNT catalysts *via* the three-times-recycling still maintain the stabilizing conversion and excellent selectivity. This suggests the nano-CuO/HNT catalysts are desirable and promising catalysts applied in the selective oxidation of cyclohexene to 2-cyclohexene-1-one.

The reason the nano-CuO/HNT catalysts possess good catalytic performance is that the nanotube structure of HNTs, in the forming of nano-CuO catalysts, provides a native nano-space, thus improving the dispersion of nano-CuO particles and preventing their aggregation in the reaction. Furthermore, the structure and composition properties of HNTs also produce an influence for catalytic activity.

Table 2
BET data of HNTs and nano-CuO/HNTs.

Sample name	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
HNTs	45	0.26	27
Nano-CuO/HNTs	28	0.13	15

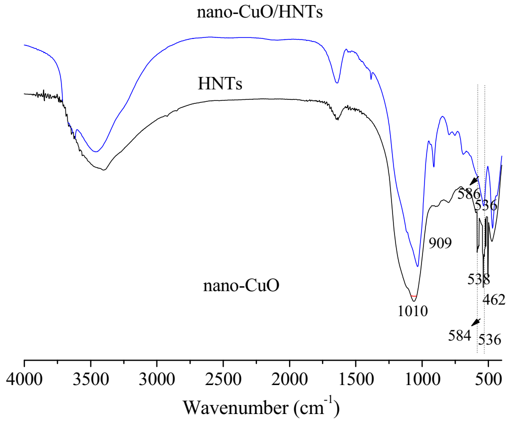

Fig. 3. FT-IR spectra of HNTs, nano-CuO and nano-CuO/HNT catalysts.

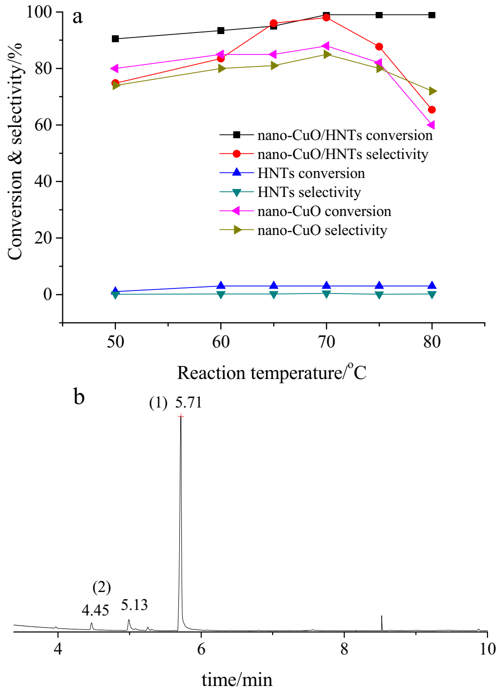

Fig. 4. Catalytic activities of HNTs, nano-CuO and nano-CuO/HNT catalysts as a function of reaction temperature (a) and GC diagram of the oxidation system of cyclohexene after reaction at 70 °C (b).

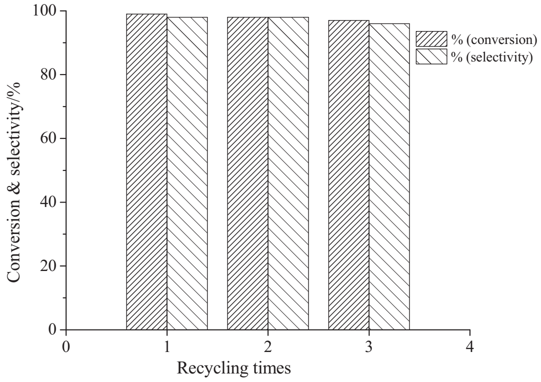

Fig. 5. The recyclability of nano-CuO/HNT catalysts.

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4. Conclusion

In this work, we successfully prepared the nano-CuO-loaded HNT catalysts with excellent catalytic activity for the selective oxidation of cyclohexene to 2-cyclohexene-1-one. The nano-CuO/HNT catalysts exhibit a 99% conversion of cyclohexene and 98% selectivity of the target product of 2-cyclohexene-1-one using TBHP as the oxidant in CH_3CN.

Acknowledgments

This work was supported by the Talent Introduction Fund of Yangzhou University, Jiangsu Social Development Project (No. BE2014613) and Six Talent Peaks of Jiangsu Province (No. 2014-XCL-013). The authors also acknowledge the Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions. The data of this paper originated from the Test Center of Yangzhou University.

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