

## Original article

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

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## 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.

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## 1. Introduction

In the past, the  $\alpha,\beta$ -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  $\text{H}_2\text{O}_2$  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  $\alpha,\beta$ -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  $\text{VO}_2$ -supported  $\text{SiO}_2$

catalysts offer excellent activity, which exhibited 21% cyclohexene conversion and 84% selectivity toward epoxide [19]. The effect of the size of gold nanoparticle-supported  $\text{SiO}_2$  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 ( $\text{RuO}_2/\text{Co}_3\text{O}_4/\text{CeO}_2$ ) 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 difficulty 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],  $\text{SiO}_2$  [19], CNTs [23] and so on.

Halloysite nanotubes (HNTs) 0.2–2  $\mu\text{m}$  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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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 be 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  $\mu\text{m}$  in length and 27 nm in inner diameter. Firstly, the HNT powder was dried in an oven at 120  $^{\circ}\text{C}$  before use. Next, the saturated solution of  $\text{Cu}(\text{NO}_3)_2$  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  $^{\circ}\text{C}$  for 6 h. Finally, the sample was calcined at 500  $^{\circ}\text{C}$  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 tertibutylhydroperoxyde 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  $^{\circ}\text{C}$  for 3 h. The oxidation reaction of cyclohexene employed CuO/HNTs catalyst is presented in Scheme 1.

## 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

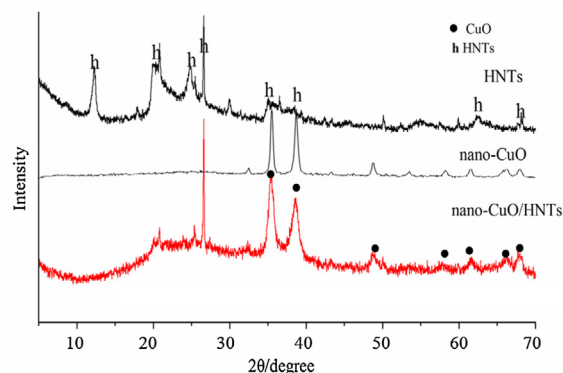


Fig. 1. XRD patterns of HNTs, nano-CuO and nano-CuO/HNTs.

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  $^{\circ}\text{C}$ . Table 1 gives the compositions of HNTs and nano-CuO/HNTs. The loaded amount of nano-CuO is about 8.4%.

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.

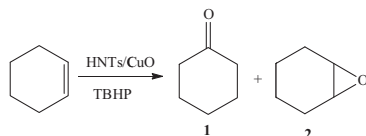
Fig. 3 shows the FT-IR spectra of HNTs, nano-CuO and nano-CuO/HNTs catalysts. The nano-CuO/HNTs possess some typical signals of HNTs, such as the deformations of Al–O–Si at 538  $\text{cm}^{-1}$ , Si–O–Si at 462  $\text{cm}^{-1}$ , and Si–O broad stretching band at about 1010  $\text{cm}^{-1}$ . However, the O–H groups of the inner hydroxyl groups in HNTs at 909  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  and the lattice vibration of 530  $\text{cm}^{-1}$ , respectively, and the nano-CuO/HNTs are only detected at the characteristic signal of 586  $\text{cm}^{-1}$ .

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%)	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	CuO	Other oxide
HNTs	50.95	40.76	0	8.29
Nano-CuO/HNTs	46.35	38.35	8.40	6.90



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

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