Short Communication

Solvent-free oxidation of cyclohexene over catalysts Au/OMS-2 and Au/La-OMS-2 with molecular oxygen

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ABSTRACT

Supported gold catalysts Au/OMS-2 and Au/La-OMS-2 were prepared and used for liquid phase oxidation of cyclohexene with oxygen as an oxidant. These catalysts were characterized by XRD, SEM, TEM and EDX. The reactions were carried out in an autoclave at 80 °C without any solvent. Effects of Au content and La content on catalytic performance were studied. Au/La-OMS-2 (0.24) was found to be an efficient catalyst for the oxidation of cyclohexene with a high conversion (48.0%). More than 86% selectivity for $\sum C_6$ (including cyclohexene oxide, 2-cyclohexene-1-ol, 2-cyclohexene-1-one) was obtained.

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1. Introduction

The catalytic aerobic transformation of alkenes into value-added oxygenated derivatives is still a challenge in the modern chemistry and industry world [1]. Traditionally, these catalytic procedures produced a great deal of environmentally undesirable wastes [2–4]. It is highly desirable to replace the traditional process by a green procedure [5,6]. There are many easily available oxidants including molecular oxygen and H_2O_2. Although the use of H_2O_2 is atom efficient and the only by-product is water, compared with molecular oxygen, the relatively high cost of H_2O_2 severely hinders its wide application in catalytic oxidation [7,8]. Therefore, many effective and recyclable heterogeneous catalytic systems for olefin oxidation using oxygen in the liquid phase have been studied. Unfortunately, most of these catalysts are prepared by immobilization of biomimetic catalysts [9–11], preparation processes of which are troublesome and expensive. Some of these catalytic systems are generally performed in volatile and toxic organic solvents [12,13], which involve a difficult process for product separation. In view of above, oxidation of alkenes with oxygen under a solvent-free condition would be valuable.

Nowadays, the research of gold has made great development [14–16]. It was discovered that gold has remarkable catalytic properties for selective oxidation of cyclohexene [8]. Extensive studies on oxidation of cyclohexene have been carried out due to the potential uses of the products, including 2-cyclohexene-1-ol, 2-cyclohexene-1-one and many other chemical intermediates [17]. Cyclohexene oxidation over the Au/C catalyst with oxygen gave a good conversion (approximately

50.2%) along with many notable products [8]. The properties of molecular sieves have made them highly desirable as support materials for gold [18,19]. Some manganese compounds are good catalysts for cyclohexene oxidation [20]. Manganese oxide octahedral molecular sieve (K-OMS-2 or OMS-2) has been reported as an effective catalyst in many oxidation reactions [21,22]. Ce-incorporated OMS-2 material displays a good combination of high activity, stability patterns and capacity for reactive phenol adsorption [23]. Therefore, we chose La (III), which lies in the same group with Ce (III), to modify K-OMS-2. In this work we report the application of Au/OMS-2 and Au/La-OMS-2 to improve efficiency of the catalyst for cyclohexene oxidation using oxygen as oxidant, and explore the effect of composition of catalysts on oxidation of cyclohexene.

2. Experimental

2.1. Catalyst preparation

K-OMS-2 was prepared according to procedures described in the literature [24]. Potassium permanganate solution in deionized water (0.4 mol L^{-1}, 225 mL) was added to a mixture of manganese sulfate hydrate solution (1.75 mol L^{-1}, 67.5 mL) and concentrated nitric acid (6.8 mL) in a 500 mL flask fitted with a reflux condenser. The slurry was refluxed for 24 h, then filtered and washed with deionized water several times. The catalyst was dried at 120 °C overnight before use.

K^+ ions were then exchanged with La^{3+} ions by ion-exchanging K-OMS-2 with La$(NO_3)_3 \cdot 6H_2O$ to obtain La-OMS-2. 2.0 g K-OMS-2 was added to 15 mL La$(NO_3)_3 \cdot 6H_2O$ methanol solution. The slurry was stirred vigorously at room temperature for 8 h. After filtration, the solid was washed with deionized water several times. The product

was dried at 120 °C overnight and then calcined in air at 300 °C for 3 h. The final material was named La-OMS-2 (0.12) with the number in brackets indicating the molar concentration (mol L^{-1}) of La (NO$_3$)$_3$·6H$_2$O methanol solution.

Au/OMS-2 and Au/La-OMS-2 catalysts with varied gold loadings were prepared by the DP procedure. 2.0 g K-OMS-2 or La-OMS-2 was stirred in 0.5 mmol L^{-1} HAuCl$_4$ aqueous solution for 1 h at 60 °C. The pH of the slurry was kept at 10 adjusted with 1.0 mol L^{-1} NaOH solution. After filtration, the resulting solid was first washed with 15 mL ammonia liquor (4.0 mol L^{-1}) and then washed twice using 20 mL deionized water to remove Cl$^-$ ions. Finally, the resulting solid was dried at 120 °C overnight and calcined at 300 °C for 3 h, Au/OMS-2 or Au/La-OMS-2 was obtained.

2.2. Catalyst characterization

Scanning electron micrographs were taken on a Zeiss ULTRA 55 Gemini field emission scanning microscope with a Schottky Emitter at an accelerating voltage of 3 kV. Transmission electron microscopy (TEM) images were obtained on a JEM-200CX at 80 kV. The structure of these materials was studied by X-ray diffraction experiments. A D/max-RA instrument with CuKα radiation with a beam voltage of 40 kV and a beam current of 40 mA was used to collect the X-ray data. The chemical compositions of the synthesized catalysts were determined by an energy dispersive X-ray analysis (EDX) on a Philips Oxford 7426 EDX spectrometer. This analysis provides a measure of the amount of La^{3+} in the tunnel of K-OMS-2 which was exchanged with K$^+$ cations.

2.3. Catalytic testing

The catalytic experiments for cyclohexene oxidation were carried out in a PTFE-lined autoclave (Capacity = 30 mL, pressure maximum 6 MPa). In a typical oxidation reaction, 20 mL cyclohexene and 0.20 g catalyst were placed into the autoclave. The reactor was then heated to the desired reaction temperature in oil bath under oxygen pressure with a magnetic stirrer. After reaction, the reactor was cooled to room temperature and the liquid phase was separated from the reaction slurry. The solid catalyst was washed by acetone and dried at 120 °C for 5 h. The liquid samples were analyzed by gas chromatography (GC) with an SE-54 capillary column (30 m × 0.32 mm × 0.5 μm) and a flame ionization detector (FID). N-heptane was used as the internal standard for product analysis.

3. Results and discussion

3.1. Catalyst properties

The scanning electron micrographs show a fibrous needle-like morphology of K-OMS-2 and La-OMS-2 in Fig. 1. The morphology of K-OMS-2 is similar to that of La-OMS-2. The result shows that the tunnel cation substitution has no effect on the morphology. TEM images in Fig. 2 show that the gold particle sizes of Au/OMS-2 and Au/La-OMS-2 are around 10–20 nm.

The X-ray diffraction patterns (Fig. 3) of K-OMS-2, Au/La-OMS-2 and regenerated Au/La-OMS-2 show that the catalysts are pure phases and comparable to standard OMS-2 materials (JCPDS file #29-1020). No typical signal of gold at 38.19° and 44.42° is observed in Au/La-OMS-2 in Fig. 3. This is due to the low loadings (0.75 %) and high dispersions of gold, which are out of detection limit for the diffractioner. The XRD patterns show that the catalyst retains its structure after ion-exchange with La^{3+}, loading with Au, and regeneration of Au/La-OMS-2.

From the EDX analysis data the amount of K$^+$ cation in OMS-2 and Au/La-OMS-2 materials was obtained as shown in Table 1. The
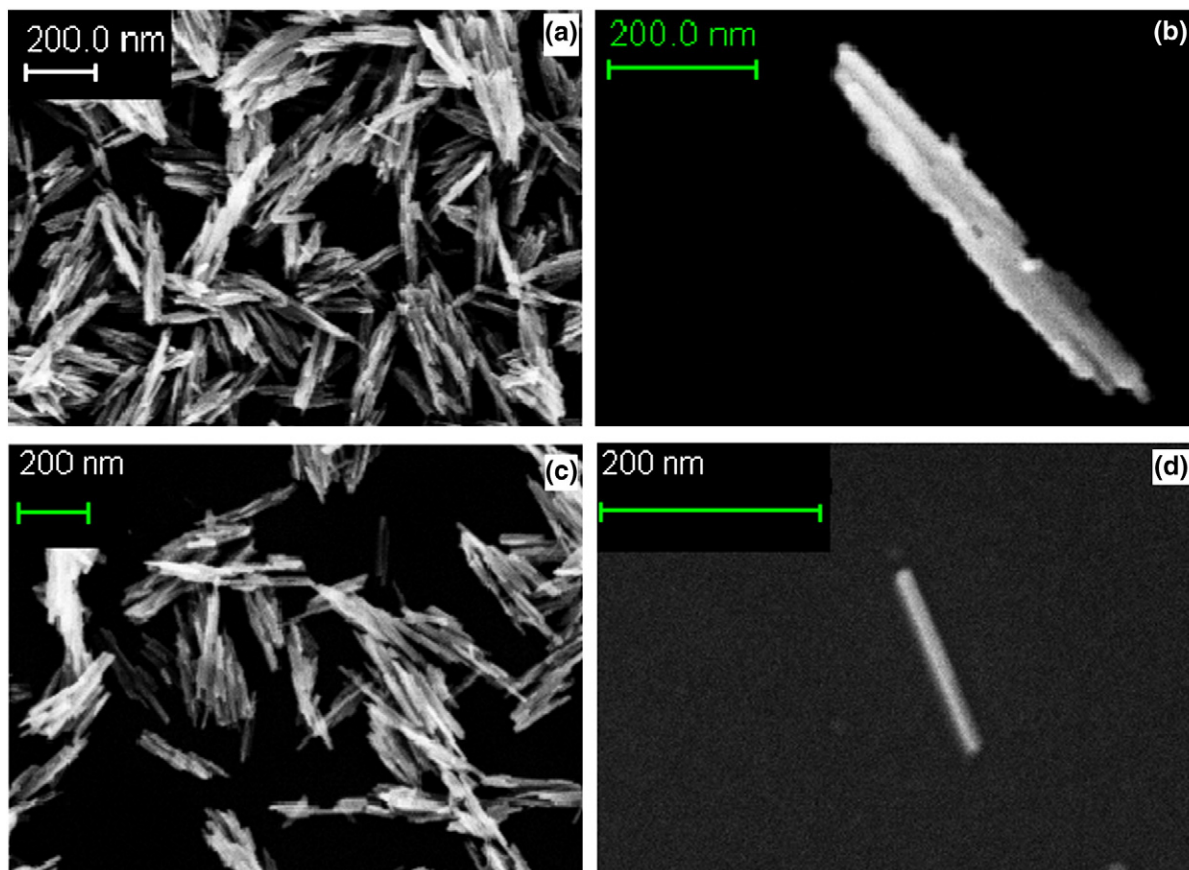

Fig. 1. SEM micrograph of K-OMS-2 (a), (b) and La-OMS-2 (c), (d).