

Preparation of amorphous copper - chromium oxides catalysts for selective oxidation of cyclohexane

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ABSTRACT

In this work, amorphous copper-chromium catalysts with different Cu/Cr molar ratios have been prepared by a sol-gel method and were used in the oxidation of cyclohexane to KA-oil. The catalysts have been characterized by a variety of analytical techniques including XRD, XPS, Raman, FT-IR, BET, TEM and SEM. XRD results confirmed that the formation of amorphous structure. The XPS and Raman results indicated that most of Cu species existed in well-dispersed tetrahedral coordination before calcination. After calcination, the tetrahedrally coordinated Cu ions are transformed into octahedral coordination and the activity of catalyst is significantly reduced. The results show that the tetrahedrally coordinated Cu ions play the synergistic catalytic role with Cr ions. Interestingly, oxidation of cyclohexane is more inclined to produce cyclohexanol with uncalcined catalyst due to the presence of the tetrahedrally coordinated Cu ions; however, the appearance of surface lattice oxygen makes the reaction more conducive to cyclohexanone after calcination. After optimizing conditions, Cu-Cr oxide catalyst with the molar ratio 1:1 shows the highest activity, which obtains 62.2% yield and 92.4% selectivity for KA-oil using H₂O₂ as oxygen source.

1. Introduction

It is commonly known that direct functionalization of saturated sp³ C–H bond is a major challenging in chemical reaction engineering [1,2]. Cyclohexane is a vital saturated hydrocarbon, whose oxidation products are mainly cyclohexanol and cyclohexanone (a mixture called KA-oil). They are important chemical raw materials for the synthesis of caprolactam, adipic acid and other fine chemicals such as pharmaceutical coating dyes. Caprolactam and adipic acids are the raw materials for synthetic fibers nylon 6 and nylon 66 [3,4]. In industry, oxidation of cyclohexane mainly uses cobalt salt and boric acid as the homogeneous catalysts under 413–453 K and 0.81–1.22 MPa and produces KA-oil with 75–80% selectivity, limiting the conversion to 3–4% [5]. Obviously, severe pollution, low conversion and higher energy consumption are becoming increasingly serious. It is necessary to raise the KA-oil yield under mild conditions.

Heterogeneous catalysts are widely applied in chemical industry because of simple separate features [6]. Lots of researchers have been devoted to heterogeneous catalysts instead of conventional homogeneous catalysts, including precious metals such as Au [7,8], transition

metal oxides [9,10], molecular sieves [11], phosphates [12,13] and heterogeneous metal complexes [14,15]. Various sources of oxidants have been explored such as oxygen [16], hydrogen peroxide [12,15] and alkylhydroperoxide [17,18]. However, in view of its unstable chemical nature, TBHP is inconvenient to transport and has potential safety hazards [19]. Meanwhile, compared with hydrogen peroxide, the activity of molecular oxygen is not high, which hardly forms highly reactive oxygen radicals [20]. Therefore, as an efficient, clean and green oxidant, hydrogen peroxide has become a hot research topic in recent years, especially in the field of C–H bond oxidation [21].

Compared with crystalline catalysts, amorphous catalysts have their own unique superiority, for example, highly surface area and dispersed active ingredients [22,23]. They are very interesting and worth exploring for catalysis. In fact, some catalytic reactions, such as aldol condensation [24], hydrogen generation [25], oxidation [26,27] and alkylation [28] have been reported. For example, Gedanken reported amorphous transition metal iron oxide loaded TiO₂ catalyzed cyclohexane oxidation at 70 °C, which gave 21.3% cyclohexane conversion [23]. Herein, we have synthesized high specific surface amorphous copper-chromium mixed oxides by propylene oxide aided sol-gel

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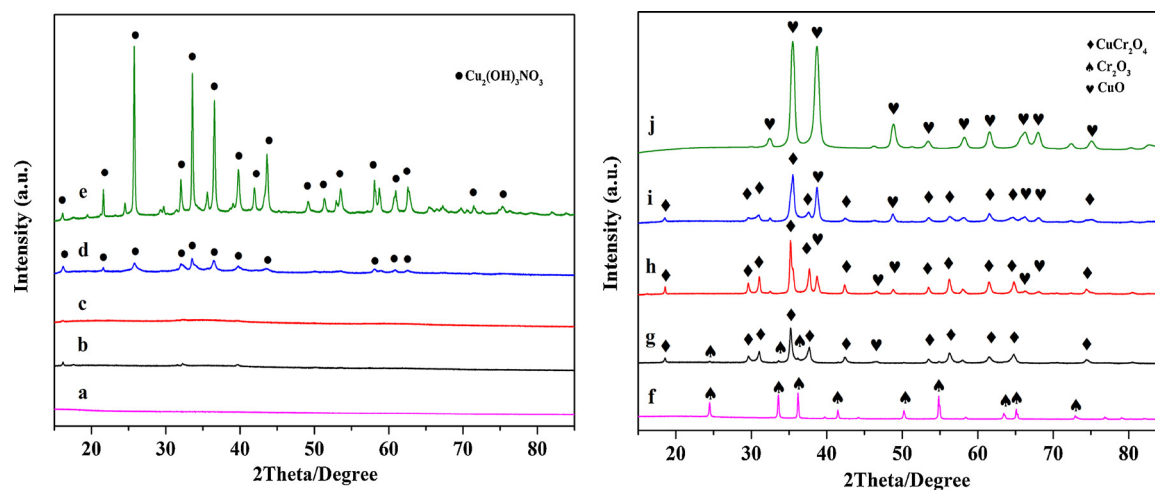


Fig. 1. XRD patterns of the (a) CrO_3 , (b) CuCr_2O_5 , (c) CuCrO_5 , (d) Cu_2CrO_5 , (e) CuO_5 , (f) CrO_5 (cal), (g) CuCr_2O_5 (cal), (h) CuCrO_5 (cal), (i) Cu_2CrO_5 (cal) and (j) CuO_5 (cal).

method, whose catalytic activity was explored in selective oxidation of cyclohexane. The cyclohexane conversion and KA-oil selectivity were obtained as 67.3% and 92.4% respectively, using H_2O_2 as the oxygen source at 65 °C. The characterization and experimental results show that the tetrahedrally coordinated Cu ions are associated with the activity of the catalyst. Moreover, oxidation of cyclohexane is more inclined to produce cyclohexanol with uncalcined catalyst due to the presence of the tetrahedrally coordinated Cu ions; however, the appearance of surface lattice oxygen makes the reaction more conducive to cyclohexanone after calcination.

2. Experimental

2.1. Catalyst preparation

All chemicals were analytic grade without any purification. Copper-chromium amorphous catalysts have been prepared by a sol-gel method using propylene oxide [28]. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ were used as the reaction precursor. The reagents were added maintaining the mole ratio of Cu : Cr = 1:2, 1:1 and 2:1, respectively. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ were added into 25 ml of absolute ethanol. The solution was sonicated at room temperature for 0.5 h. To this solution, 10.5 ml propylene oxide was added dropwise with stirring. A dark green xerogel was formed after 20 min of ultrasound exposure. Then the xerogel was washed five times by ethanol, dried at 80 °C in vacuum and calcinated at 650 °C for 6 h. The catalysts were labeled as $\text{Cu}_x\text{Cr}_{1-x}\text{O}_5$ before calcination (where x represents the Cu/(Cr + Cu) atomic mole ratio), and $\text{Cu}_x\text{Cr}_{1-x}\text{O}_5(\text{cal})$ after calcination. CrO_5 and CuO_5 were synthesized by the same procedure.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded by a Rigaku/Max-3A X-ray diffractometer with Cu K α radiation ($\lambda = 0.15418$ nm). Diffraction patterns in the 5°–90° 2 θ range were collected at a rate of 0.5 degrees per minute. X-ray photoelectron spectra (XPS) were collected on a Thermo Fisher ESCALAB250XI X-Ray photoelectron spectrometer and the binding energies (± 0.1 eV) were determined with respect to the position of C 1s peak at 284.56 eV. The FT-IR spectra were recorded using Bruker Tensor 27 Fourier-transform infrared spectrometer employing KBr disks. Scanning electron microscopy (SEM) images were taken on a FEI Quanta 200 F, using tungsten filament doped with lanthanumhexaboride (LaB6) as an X-ray source, fitted with an ETD detector with high vacuum mode using secondary electrons and an acceleration tension of 10 or 30 kV. Samples were

analyzed by spreading them on a carbon tape. Transmission electron microscopy (TEM) images were recorded using a JEOL JEM 2100 microscope, and samples were prepared by mounting an ethanol-dispersed sample on a lacey carbon Formvar coated Cu grid. The Raman spectrum was collected using a Labram HR 800 microspectrometer (Jobin Yvon) with a 785 nm laser excitation source at 100 mW. The surface area (BET) was measured using ASAP2020 by nitrogen adsorption at 77 K. Prior to measurements, the sample was pretreated at 353 K for 3 h under vacuum.

2.3. Catalytic oxidation

In a typical reaction, liquid-phase oxidation of cyclohexane was carried out in a neck round bottom flask equipped with a condenser. Successively, 0.05 g catalyst, 10 ml solvent, 0.5 ml cyclohexane and H_2O_2 (30% solution) were added into the flask. The reaction was carried out under continuous stirring for the required time and temperature. After reaction, the products were analyzed by a gas chromatograph (GC 9560) connected with a SE-54 capillary column. The identification of product was carried out by injecting the standard samples into GC. The catalyst was recovered via centrifugation, washed thoroughly with ethanol and reused for multiple circles.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. XRD measurements

As shown in (Fig. 1a, b, c), the samples are found to be amorphous before calcination. The characteristic peaks of Cu_2CrO_5 are attributed to the $\text{Cu}_2(\text{OH})_3\text{NO}_3$ (JCPDS: 75–1779). Due to the weak peak intensity, most of the metal is still in an amorphous structure (Fig. 1d). In addition, CuO_5 is also attributed to the $\text{Cu}_2(\text{OH})_3\text{NO}_3$ (JCPDS: 75–1779), whose crystallinity is obviously better than Cu_2CrO_5 , due to more characteristic peaks at $2\theta = 25.7^\circ$, 33.6° and 36.5° (Fig. 1e). On the curve of CuCr_2O_5 and CuCrO_5 , some weak diffraction peaks appear at lower angles, suggesting a small amount of copper species exists in these samples.

As can be seen from (Fig. 1f–i), the amorphous materials are transformed to the CuCr_2O_4 spinel (JCPDS: 88-0110) and metal oxide after calcination. The Cu^{2+} undergoes thermodynamic competition, resulting in more stable metal oxide during high temperature heating [30]. The diffraction peaks at $2\theta = 18.8^\circ$, 29.6° , 31.1° , 35.2° , 37.7° and 42.4° are attributed to the tetragonal structure of CuCr_2O_4 spinel (JCPDS: 88-0110). The diffraction peaks (Fig. 1g) at $2\theta = 24.5^\circ$, 33.5° ,

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