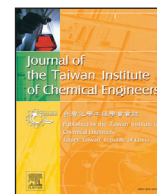




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Liquid phase oxidation of benzyl alcohol to benzaldehyde over sepiolite loaded chromium oxide catalysts

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ABSTRACT

Sepiolite loaded chromium oxide catalysts were prepared through the precipitation and characterized by physical techniques such as XRD, SEM, TEM BET, EDS, FT-IR, UV-vis, XPS, H₂-TPR... The experimental results indicated that Cr₂O₃ are major Cr-species finely distributed on the sepiolite nanofibers in addition to small amount of Cr(VI) on the catalyst surface. All catalysts have large surface area, high porosity, and good dispersion of Cr₂O₃ nanoxides on the support. The sepiolite-loaded-Cr catalysts have been tested for the partial oxidation of benzyl alcohol without any base or organic solvent and shown good conversion and very high selectivity to benzaldehyde at mild conditions. The catalytic activity was found to be related to the amount of transition metal oxide content, distribution of Cr(III) sites, oxidant behavior, and reaction variables... An increased calcination temperature of the catalysts leads to the distortion of sepiolite fibers, the interaction between Cr(III) and support, and the enhanced reusability of the catalysts.

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1. Introduction

The selective oxidation of alcohols to carbonyl compounds is an interesting process in both theoretical and practical fields. Among carbonyl aromatic compounds, benzaldehyde (BzH) is always high in demand because it is an important chemical feedstock for the production of pharmaceuticals, dyestuff, perfumery, and agro-chemistry [1,2]. In tradition, benzaldehyde can be usually produced through alkali hydrolysis of benzyl chloride, partial oxidation of alkyl benzene, benzyl alcohol (BzOH) using Cr-, Mn-, Co-, or Os-based reagents as homogeneous oxidants [1–4]. These oxidants usually yield a large amount of hazardous heavy metal waste causing serious environmental problems. Therefore, great efforts have recently been made to develop environmentally friendly catalytic oxidations and also to reduce the volume of byproducts and solvents used [5–12].

During the last decades, many studies have been reported on the oxidation of benzyl alcohol to benzaldehyde using novel homogeneous, immobilized, and heterogeneous catalysts under different conditions [3,4,7–10]. Among reported catalyst systems, precious metals such as Ni–Cu [3], Pt [11,13,14], Au [15–18], Ag [6,9,19–21], Ru [8,22] have been intentionally applied for the selective oxidation reaction of primary alcohols. These solid catalysts

normally showed good catalytic activity; but they often have some disadvantages such as the use of expensive noble metals and difficulty in preparation, performance fluctuation, and low recycling efficiency, sintering of metal oxides. Therefore, some cheaper metal-supported catalysts (Cu, Zn, Cr, Mn, Co, V, Bi...) have been developed as alternate ways to prepare oxidation–reduction catalyst systems [7,8,23–27]. For common transition metals, chromium was well known as an active component in metal-catalyzed oxidations inorganic synthesis [3,4,8,28–32]. However, reported Cr-based catalysts mostly exhibited a considerable initial loss in catalytic activity and poor-recycling ability. Thus, preparation of Cr-containing catalysts with enhanced structural stability is highly desirable. For instance, chromium ions was exchanged with zeolite, Cr-ZSM-5, Cr-MCM-41 [8,28,29]; doped in perovskite, LaCrO₃, [30] or molecular sieve materials, CrS-1, CrAPO-5, CrSAPO-37, Crβ [31]; inserted in spinel [8,32]. These catalysts showed somewhat the better resistance to deactivation during the oxidation reaction. However, Cr-containing molecular sieve catalysts are sometimes limited for the oxidation of bulkier substrates and usually worked in high polar organic solvent conditions [8,29,31].

Sepiolite is a fibrous clay mineral used as adsorbents and catalysts or metal support in many applications [33]. It is composed of blocks and tunnels that grow up in the fiber direction. Each block is constructed of an octahedral sheet of magnesium oxide/hydroxide inserting between two tetrahedral silica layers. The octahedral silica sheet discontinuity leads to the construction of structural channels and tunnels. As a result of the unique structure

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Table 1
Some physical properties of all catalyst samples.

| Catalyst batch | S_{BET} (m^2/g) | Cr^{3+} (wt%) |
|--------------------------------------|--|------------------------|
| Sepiolite | 166.2 | – |
| 1.0 wt% Cr^{3+} /sepiolite | 150.3 | 0.83 |
| 3.0 wt% Cr^{3+} /sepiolite | 130.6 | 2.91 |
| 5.0 wt% Cr^{3+} /sepiolite | 127.4 | 4.91 |
| 7.0 wt% Cr^{3+} /sepiolite | 192.5 | 6.89 |
| 10.0 wt% Cr^{3+} /sepiolite | 129.6 | 9.73 |
| 20.0 wt% Cr^{3+} /sepiolite | 100.2 | 20.64 |

and composition, sepiolite fibers possess huge specific surface area, high porosity and plentiful surface hydroxyl groups. In the present work, we distributed chromium oxides on sepiolite as an efficient catalyst for the liquid phase oxidation of benzyl alcohol. Obviously, sepiolite supported chromium catalysts could exhibit obvious advantages: low-cost and porous material, active function groups, basic support. It is expected that as-synthesized Cr-containing catalysts are highly active for the selective oxidation of benzyl alcohol.

2. Experimental

2.1. Preparation and characterization of the catalysts

4.0 g of sepiolite (Aldrich) were added into a 250 mL beaker containing 100 mL of aqueous solution of $\text{Cr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99%) with a given amount of Cr^{3+} (see Table 1S in Supplementary Materials). Then, a stoichiometric amount of NaOH solution was added dropwise to the beaker under vigorous stirring (see Table 1S in Supplementary Materials) to precipitate chromium (III) ions in the suspension. The suspension solution was further stirred for 2 h at room temperature. Then, the resultant slurry was then filtered, washed with distilled water several times, and then dried at 80 °C for 24 h in air before calcination at 410 °C for 2 h. All the prepared catalysts are summarized in Table 1.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a D8 Advance-Bruker instrument using $\text{CuK}\alpha$ radiation ($\lambda = 0.1549 \text{ nm}$). The scanning electron microscopy (SEM) microphotographs were obtained with a JEOS JSM-5410 LV. The nitrogen physisorption was

run on an Autochem II 2920 (USA). Energy-dispersive spectroscopy (EDS) data were obtained from Varian Vista Ax X-ray energy-dispersive spectroscope. Fourier transform infrared (FT-IR) spectra were obtained in 4000–400/ cm range on a FT/IR spectrometer (DX-Perkin Elmer, USA). The recorded spectral range was 100–2500/ cm and scanned 4 times with the wavelength of laser beam of 632 nm. UV–vis spectra were collected with UV-visible spectrophotometer, JASCO V-670. The spectra were recorded at room temperature in the wavelength range of 200–800 nm. The XPS analysis was made on a photoelectron spectrometer (VG Scientific Fison ESCA 210) with Mg $\text{K}\alpha$ radiation (1253.6 eV). Temperature Programmed Reduction (H_2 -TPR) of hydrogen experiments were carried out using a flow system GOW-MAC 69-350 with a thermal conductivity detector (TCD).

2.3. Catalytic performance

The catalytic oxidation of benzyl alcohol was carried out in a 100 mL three-neck glass flask fitted with a reflux condenser. For a typical run, 3 mL of benzyl alcohol and 0.20 g of catalyst were loaded into the flask. After the reaction mixture was magnetically stirred and heated to the desired temperature, then 6 mL of *t*-butyl hydrogen peroxide (TBHP, 70%, Sigma Aldrich) or hydrogen peroxide solution (H_2O_2 , 30%) or flow of air (3 mL/min) was conducted into stirred reaction mixture and the reaction time starts recorded. After the reaction, the mixture was quenched to room temperature and then catalyst was filtered off. The filtrate was analyzed by a GC-MS (HP-6890 Plus).

3. Results and discussion

3.1. Catalyst characteristics

Fig. 1 displays X-ray diffraction diagrams for all as-prepared samples while the XRD patterns of raw sepiolite and calcined samples are presented in Fig. 1S for comparison (Supplementary Materials). For the parent sepiolite, XRD pattern appears the 2-theta values at 7.31, 20.6, 23.8, 26.7, 28.1, 35.0, 36.9, 40.1°, which are typically characteristics for the sepiolite (JCPDS no. 01-075-1597) (Fig. 1S) [33–35]. The intensity of these peaks slightly decreases after sepiolite loading Cr_2O_3 . This observation is possibly explained by the dehydration and structural folding of the sepiolite (Figs. 1 and 2) [34,35]. In other context, no reflection of Cr_2O_3 are detected for the low-chromium content samples (1–5 wt% Cr_2O_3),

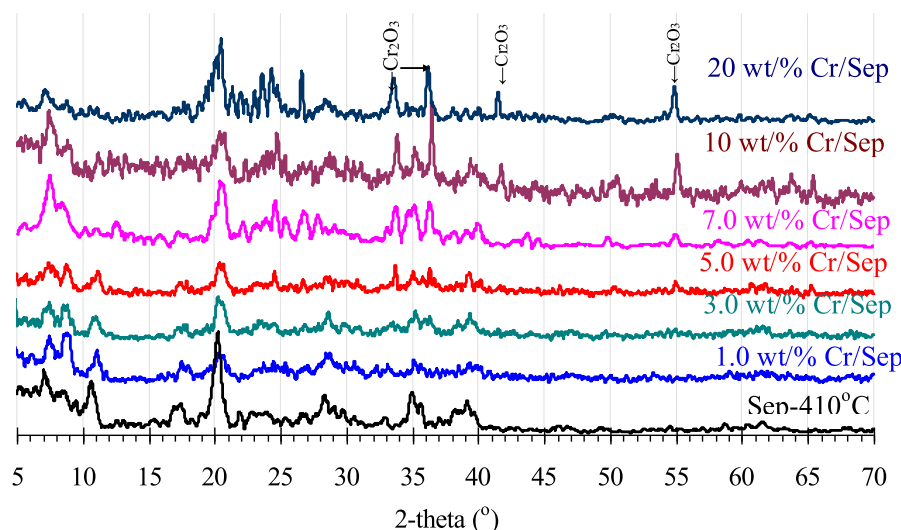


Fig. 1. XRD patterns for sepiolite parent calcined a 410 °C and chromium oxides/sepiolite catalysts.

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