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Facile synthesis of porous manganese oxide K-OMS-2 materials and their catalytic activity for formaldehyde oxidation

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ABSTRACT

Porous manganese oxide K-OMS-2 nanomaterials were successfully synthesized by a simple low-temperature method. Data collected from characterization methods affirmed the cryptomelane-type manganese oxide octahedral molecular sieve (OMS-2). With increase of reaction temperature, the nanoparticle morphology of K-OMS-2 with an average diameter of ca. 40 nm evolved into nanorod morphology with a diameter of ca. 40 nm and lengths of 50–500 nm. Results of catalytic tests revealed that K-OMS-2 nanoparticles show rather higher catalytic activity for complete oxidation of formaldehyde than K-OMS-2 nanorods. This simple, inexpensive, and environmentally friendly method may have the potential of being used in scaled-up of K-OMS-2 materials.

1. Introduction

Indoor air pollutants have been paid more and more attention with increasing awareness of the public environment and health, especially in urban cities. Gaseous pollutants, such as NO_x, SO_2, and VOCs (volatile organic compounds), which come from indoor decoration and vehicular emissions, are common hazardous species in indoor environment [1,2]. Formaldehyde (HCHO) is a major indoor air pollutant. Main emission sources are plywood, particle board and adhesives for wall clothes, commonly used in construction and furnishing. It has been the subject of numerous complaints regarding health disorders in residents which include nausea, chest tightness, skin rashes, and even lethiferous diseases such as nasopharyngeal cancer and probably leukemia if humans are exposed to an indoor environment polluted with elevated HCHO levels for an extended length of time [3,4]. Thus great efforts have been made to remove indoor HCHO.

To date, most of studies for the elimination of HCHO pollution have been focusing on two methods: adsorbing HCHO by an efficient adsorbent at ambient temperature and degrading HCHO into innocuous final products such as CO_2 and H_2O through a catalytic process at moderate temperature [5–8]. For eliminating HCHO of a very low concentration from indoor air, catalytic oxidation is believed to be an emerging and promising technology. Supported noble metals like Pd, Au, Ag and Pt [9,10] have been proved to be active for the HCHO emission control, but their high costs and lack of resources limit their widespread applications. Thus, the development of cheap and effective catalysts for the HCHO elimination at low temperatures is still the main challenge. It is reported that some transition metal oxides, such as TiO_2, MnO_x, CoO, CeO_2, or some binary oxides [11–13], show high performance in HCHO oxidation at low temperatures. Among them, manganese oxides have been demonstrated to be more promising for HCHO oxidation, and show catalytic activity as high as or slightly higher than those of the supported noble metals [12,14]. For example, cryptomelane exhibits much higher catalytic activity for HCHO oxidation, and complete conversion of HCHO could be achieved at low temperatures [15].

Manganese oxides have many forms, including one-dimensional tunnel structures, two-dimensional layer phases and three-dimensional spinels. Among the various manganese oxides studied, microporous manganese oxides with tunnel structure have received appreciable attention due to their excellent catalytic performances [16]. K-OMS-2 or manganese octahedral molecular sieve (mineral name is cryptomelane) is a type of manganese oxide with a one-dimensional tunnel structure composed of 2 × 2 edge-shared MnO_6 octahedral chains, which are corner connected to form 4.6 × 4.6 Å tunnels [17]. Manganese in K-OMS-2 are Mn^{2+}, Mn^{3+} and Mn^{4+} located in octahedral sites, and potassium ions reside in the tunnels along with a small amount of water to stabilize the tunnel structure [18]. Different K-OMS-2 morphologies have so far been prepared ranging from micrometer long fibers to nanorods, nanoneedles and paper like materials [16,18,19]. But there

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are few reports about the nanoparticle morphology, which exhibits more accessible structure for catalysants.

Methods reported for preparing K-OMS-2 include reflux, solid-state chemical reactions, sol–gel and hydrothermal treatment to produce nanofibers, nanorods and nanoneedles [15,19,20]. These synthesis methods usually require relatively long reaction times and complicated control of reaction conditions. Therefore, the development of rapid and simple synthetic means for large-scale production of K-OMS-2 nanomaterials with high purity, uniform shape and size, and excellent catalytic performance is still the major challenge for the elimination of HCHO and other VOCs.

In the current work, synthesis of K-OMS-2 nanomaterials by a novel and facile method is reported. Crystallographic and morphological properties of the products synthesized at different reaction temperatures were compared. The catalytic activities of selected K-OMS-2 nanomaterials in the reaction of HCHO oxidation were investigated, and the HCHO conversions over K-OMS-2 nanomaterials were also compared with those over conventional K-OMS-2 materials.

2. Experimental

2.1. Chemicals

All chemicals in this study were of commercially available analytical grade and used without further purification. All reactions were carried out using deionized water (18 MΩ) from a Millipore Milli-Q Plus 185 purifying system.

2.2. Catalyst synthesis

Previously, cryptomelane-type manganese oxide K-OMS-2 were usually obtained under acidic conditions [21,22]. In the current work, we showed that initially neutral media could also produce K-OMS-2 with different morphologies.

Porous K-OMS-2 nanoparticles were synthesized by a simple soft chemistry route at room temperature. Potassium permanganate ($KMnO_4$) was used as the starting material and benzyl alcohol was used as the reducing agent. In a typical procedure, 0.364 g (1 mmol) cetyltrimethylammonium bromide (CTAB) and 1.622 g (15 mmol) benzyl alcohol were dissolved in 100 mL of water under stirring. Then 1.580 g (10 mmol) of $KMnO_4$ was added in the mixture. The reaction proceeded with the appearance of a brown precipitate within a few minutes. After a reaction of 16 h at room temperature (ca. 25 °C), the precipitate was filtrated, washed several times with distilled water and alcohol, and dried overnight at 60 °C. Finally the product was calcined at 550 °C for 6 h to remove the surfactant.

To investigate the influence of the reaction temperature on the crystal phase and morphology of the final product, the temperature was varied from 80 to 120 °C. The precursor composition and amounts were identical to the previous synthesis. After stirring at room temperature for 1 h, the mixture was heated at different hydrothermal temperatures (80–120 °C) for 6 h in a Teflon bottle. The resulting samples were recovered by filtration, wash and drying at 60 °C as mentioned above, and finally were calcined at 550 °C for 6 h.

2.3. Characterization

X-ray diffraction (XRD) measurements were performed on a Bruker D8 Focus X-ray diffractometer using Cu Kα radiation (40 mA, 40 kV). Scanning electron microscopy (SEM) observations were carried out on a Hitachi S-4300 field emission scanning electron microscope operated at 10 kV. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2100F microscope. A typical TEM sample was prepared by depositing several droplets of a nanoparticles/ethanol mixture onto a carbon-coated Cu-grid. Fourier-transform infrared (FT-IR) spectra were recorded in the range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1} on a Varian Excalibur 3100 spectrometer. Specific surface area measurements were performed at 77 K using a Quadrasorb SI automated surface area and pore size analyzer. The surface areas were calculated by the Braunauer–Emmett–Teller (BET) method.

2.4. Catalytic activity

Catalytic activities of as-prepared K-OMS-2 for the HCHO oxidation were performed in a fixed-bed reactor under atmospheric pressure. The catalyst (100 mg, 40–60 mesh) was loaded in a quartz tube reactor (i.d. = 4 mm). Gaseous HCHO was generated by passing a purified air flow over HCHO solution in an incubator kept at 0 °C, leading to a feed gas with 460 ppm of HCHO. The total flow rate was 50 mL/min in a space velocity of 20,000 mL/(g_{cat} h). The effluents from the reactor were analyzed with an on-line Agilent 6890 gas chromatograph equipped with FID and Ni catalyst converter which was used for converting carbon oxides quantitatively into methane in the presence of hydrogen before the detector. In typical runs, the steady-state reaction data were taken after the catalytic reaction was performed for 2 h. No other carbon containing compounds except CO_2 in the products were detected for all tested catalysts. Thus, HCHO conversion was expressed in the yield of CO_2, and calculated as follows:

$$\text{HCHO conversion } (\%) = \text{CO}_2 \text{ yield } (\%) = \frac{[\text{CO}_2]_{\text{out}} \text{ vol.\%}}{[\text{HCHO}]_{\text{in}} \text{ vol.\%}} \times 100,$$

where $[CO_2]_{out}$ was the CO_2 concentration in the products (vol.%), and $[HCHO]_{in}$ was the HCHO concentration of the feed gas (vol.%).

3. Results and discussion

3.1. Features of materials

XRD patterns of as-prepared materials are shown in Fig. 1, corresponding to a well-crystallized cryptomelane structure characteristic of the octahedral molecular sieve material K-OMS-2. No additional phases are present for the material prepared at room

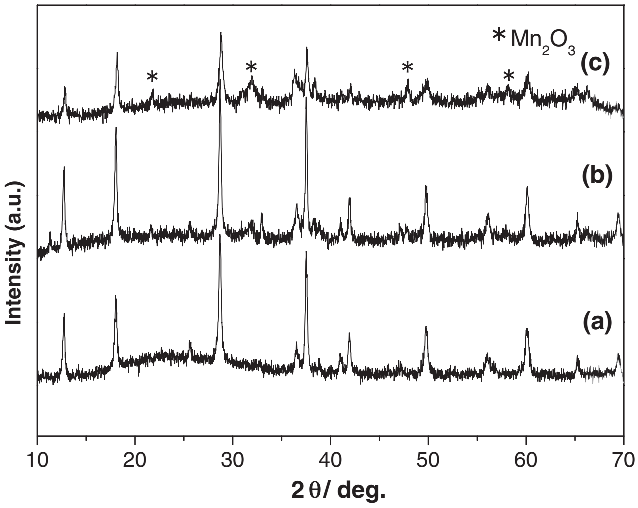

Fig. 1. XRD patterns of K-OMS-2 prepared at different temperatures: (a) 25 °C, (b) 100 °C, and (c) 120 °C.