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Synthesis of three-dimensional ordered mesoporous MnO_2 and its catalytic performance in formaldehyde oxidation

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ABSTRACT

Three-dimensional (3D) ordered mesoporous MnO_2 was prepared using KIT-6 mesoporous molecular sieves as a hard template. The material was used for catalytic oxidation of HCHO. The material has high surface areas and the mesoporous characteristics of the template, with cubic symmetry (ia3d). It consists of a β-MnO_2 crystalline phase corresponding to pyrolusite, with a rutile structure. Transmission electron microscopy and X-ray photoelectron spectroscopy showed that the 3D-MnO_2 catalyst has a large number of exposed Mn^{4+} ions on the (110) crystal plane surfaces, with a lattice spacing of 0.311 nm; this enhances oxidation of HCHO. Complete conversion of HCHO to CO_2 and H_2O was achieved at 130 °C on 3D-MnO_2; the same conversions on α-MnO_2 and β-MnO_2 nanorods were obtained at 140 and 180 °C, respectively, under the same conditions. The specific mesoporous structure, high specific surface area, and large number of surface Mn^{4+} ions are responsible for the catalytic activity of 3D-MnO_2 in HCHO oxidation.

Manganese oxides, including MnO, MnO_2, Mn_2O_3, and Mn_3O_4, are important in a range of applications such as ion exchange, molecular adsorption, catalysis, electrochemical reactions, batteries, and magnetic processes, because of their structural flexibility and novel chemical and physical properties [1–5]. Three-dimensional (3D) ordered mesoporous MnO_2 has disordered polycrystalline walls and a unit cell parameter of 20.85 nm; it has a large number of exposed (110) crystal planes, with a lattice spacing of 0.311 nm, and more Mn^{4+} ions are present on these than on other planes [6]. 3D-MnO_2 has been used as an effective environmentally friendly material for ethanol, carbon monoxide, benzene, and toluene oxidation, and in electronic components [6–9]. The catalytic oxidation of volatile organic compounds (VOCs) over 3D-MnO_2 shows the potential usefulness of this novel material. It has excellent hydrophobicity and a strong affinity toward VOCs, and can selectively adsorb VOC molecules and oxidize VOCs to CO_2 and H_2O even in the presence of water vapor [10,11].

The development of effective catalysts for complete oxidation of low concentrations of HCHO at low temperatures is still a challenge. In this study, an ordered mesoporous 3D-MnO_2 material was synthesized using a nanocasting method, and its catalytic performance in HCHO oxidation was evaluated. This work was motivated by the fact that HCHO is becoming a major indoor pollutant. It is emitted from widely used construction and decorating materials, and long-term exposure to indoor air

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containing even a very low concentration of HCHO is potentially harmful to human health [12,13].

The 3D-MnO_2 was prepared using KIT-6 mesoporous silica as a hard template [11,13]. After KIT-6 sample was synthesized, KIT-6 molecular sieves (4.0 g) were added to a solution of $Mn(NO_3)_2·4H_2O$ in ethanol (0.91 mol/L, 40 mL). The sample was evaporated to dryness at 80 °C and calcined at 200 °C for 6 h. These casting and evaporating steps were repeated. Finally, the material was calcined at 400 °C for 6 h. The KIT-6 hard template was removed using a NaOH solution (2 mol/L). Centrifugal separation was used to remove sodium silicate, and the samples were dried at 100 °C and calcined at 400 °C to yield 3D-MnO_2. 3D-MnO_2 grain growth is related to the initial crystallite size of the KIT-6 template and calcination temperature [2]; for example, 3D-Mn_2O_3 can be obtained by increasing the calcination temperature.

α-MnO_2 and β-MnO_2 nanorods were prepared using the method reported in the literature [14]. $MnSO_4·H_2O$ (0.008 mol) and an equal amount of $(NH_4)_2S_2O_8$ were added to distilled water at room temperature to form a homogeneous solution. The solution was transferred to a 40-mL Teflon-lined stainless-steel autoclave, and the autoclave was sealed and maintained at 140 °C for 12 h. After the reaction was complete, the solid product was filtered, washed with distilled water to remove any ions in the final product, and dried at 120 °C to yield β-MnO_2. α-MnO_2 was prepared by adding analytical grade $(NH_4)_2SO_4$ (0.015 mol) to the reaction system.

Powder X-ray diffraction (XRD) was performed using a TTR3 X-ray diffractometer with a Cu K_α radiation source, at a scanning speed of 0.05°/min, 40-kV tube voltage, and 40-mA tube current. The pore size distribution and N_2 adsorptiondesorption isotherms of the sample were investigated using an Autosorb-1MP instrument. Transmission electron microscopy (TEM) was performed using a JEM-2011 instrument at a voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was performed using a PHI-5300 instrument at 300 W, with Mg K_α X-rays as the excitation source. HCHO oxidation tests were performed in a fixed-bed quartz-tube reactor (ϕ10 mm) using 0.2 g of catalyst (40–60 mesh). HCHO gas was generated and injected using a N_2 bubbler in a low-temperature thermostatic bath at 0 °C; the N_2 was passed through a container filled with formalin (a HCHO aqueous solution (37%)). The total gas flow rate through the reactor was kept at 100 mL/min using mass-flow meters; the gas consisted of 400 ppm HCHO, 20% of O_2, and balance N_2. The space velocity was 30000 mL g^{-1} h^{-1}). The reaction products were detected online using an Agilent 7890A gas chromatograph, with a thermal conductivity and mass-selective detector connected to Porapak-Q and HP-INNOWAX columns, respectively. No carbon products other than CO_2 were detected.

Fig. 1(a) shows the N_2 adsorption-desorption isotherms. The isotherm has a hysteresis ring and is a type IV adsorption isotherm; this indicates the presence of mesopores [9,13]. Fig. 1(b) shows the Barrett-Joyner-Halenda pore size distribution of 3D-MnO_2 calculated from the desorption isotherm. The 3D-MnO_2 pore size distribution is 3.7–11.4 nm, therefore the material has a mesoporous structure. 3D-MnO_2 has a high specific surface area (87 m^2/g), which is consistent with previous literature reports [6].

Fig. 2 shows the XRD patterns of 3D-MnO_2. The low-angle diffraction peaks at 2θ = 1.00° and 1.04° correspond to the (211) and (332) planes (Fig. 2(a)), indicating that 3D-MnO_2 has the 3D ordered mesoporous structure with cubic symmetry (ia3d) of its template. The wide-angle diffraction peaks at 2θ = 28.7°, 37.3°, 42.8°, 56.7°, 59.4°, 64.8°, and 72.3°, corresponding to the (110), (101), (111), (211), (220), (002), and (301) planes, respectively, are attributed to the crystalline phase of β-MnO_2 pyrolusite [8,9]. This indicates that the 3D-MnO_2 has a rutile structure.

Fig. 3 shows TEM images of 3D-MnO_2, and α-MnO_2 and β-MnO_2 nanorods. The α-MnO_2 (Fig. 3(c)) and β-MnO_2 (Fig. 3(d)) nanorods are both nonporous materials, and have one-dimensional single-crystal nanostructures of diameters about 10 and 100 nm, respectively. The α-MnO_2 nanorod diameter is much smaller than that of the β-MnO_2 nanorods. Ordered mesoporous structures can be clearly observed in Fig. 3(a) and (b). The 3D-MnO_2 has exposed (110) crystal planes with a lattice spacing of 0.311 nm. In the β-MnO_2 unit cell, more Mn^{4+} ions are exposed on the (110) crystal planes than on the other planes [15,16]. The different structures of the samples may result from the different amounts of Mn^{4+} exposed on the (110) crystal facets.

Fig. 4 shows that the Mn $2p_{2/3}$ XPS profiles have two components, at binding energy of 641.6 and 642.9 eV, corresponding to surface Mn^{3+} and Mn^{4+} ions, respectively. The peak areas indicate that the surface Mn^{4+}/Mn^{3+} molar ratios for 3D-MnO_2,

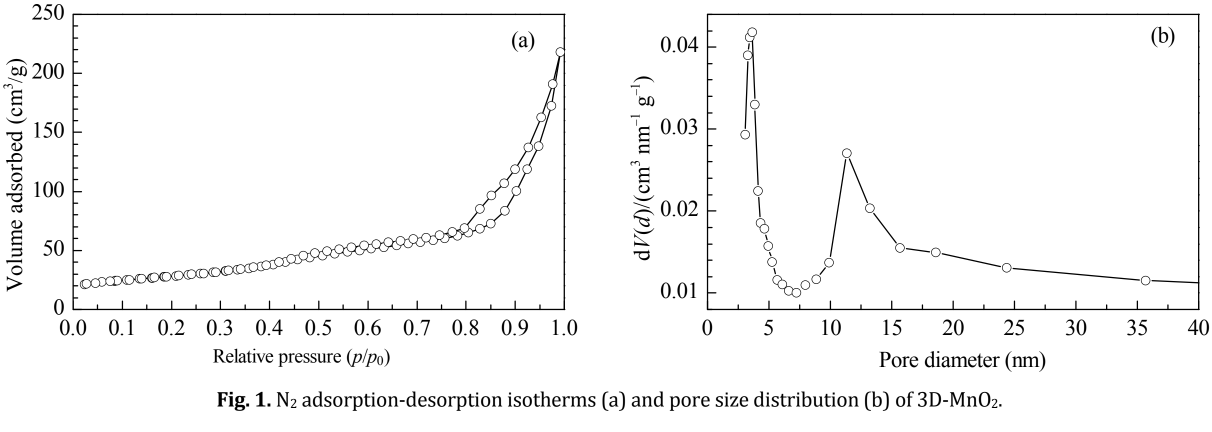

Fig. 1. N_2 adsorption-desorption isotherms (a) and pore size distribution (b) of 3D-MnO_2.