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Highly active manganese oxide catalysts for low-temperature oxidation of formaldehyde

Hua Tian [a], Junhui He [a,*], Linlin Liu [a], Donghui Wang [b], Zhengping Hao [c], Chunyan Ma [c]

[a] *Functional Nanomaterials Laboratory, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, China*
[b] *Research Institute of Chemical Defence, Beijing 100083, China*
[c] *Department of Environmental Nano-materials, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China*

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ABSTRACT

Birnessite - type manganese oxides with very high surface areas (up to 154 m^2/g) were successfully prepared using a microemulsion process. The morphology, surface area, pore size, and the surface reducibility of these materials were readily tailored via the synthesis temperature. The physiochemical properties of the manganese oxides were characterized by means of XRD, TEM, SEM, BET and H_2-TPR techniques. These materials were also catalytically tested in HCHO oxidation, showing significantly high catalytic activity. It was found that the differences in catalytic performance of these materials were jointly attributed to the effects of the morphology, surface area and surface reducibility. The highly porous feature of the catalyst with nanospheres could allow HCHO molecules to easily diffuse onto catalytically active sites, which endows the nanospheres with high catalytic activity. The higher the surface area, the higher its catalytic activity. A higher surface reducibility offered a lower temperature of HCHO oxidation. The most active manganese catalyst (BSW-120) showed a 100% HCHO conversion at 100 °C.

1. Introduction

Due to stringent environmental regulations for human health protection, low-temperature catalytic oxidation of formaldehyde (HCHO) to CO_2 and H_2O has become an attractive research topic [1–5]. In the past decades, a variety of catalysts, including metal oxides [3,6], composite oxides [7], and supported noble metals [8] have been investigated for the HCHO emission control. Among them, catalysts made of noble metals (Au, Ag, Pd, and Pt) supported on metal oxides have been proved to be highly active at relatively low reaction temperatures. For instance, Zhang et al. [9] observed a 100% HCHO conversion at ~75 °C over three-dimensionally ordered macroporous Au/CeO_2 catalysts. An et al. [10] found that Pt/Fe_2O_3 prepared by a colloid deposition route performed highly active for HCHO oxidation at ambient temperature. However, the scarcity and high cost of these noble metals have long motivated the research for substitute catalysts. Recently, considerable efforts have been devoted to the design of catalysts based on transition metal oxides, like MnO_x, which exhibit catalytic activity for HCHO oxidation as high as or even slightly higher than those of the supported noble metals [3,11].

Layered birnessite manganese oxides, as environmental-friendly materials, have been extensively studied for the catalytic reduction of NO_x [12], decomposition of phenol [13], or the catalytic combustion of volatile organic compounds (VOCs) [14] because of their high catalytic activity and low cost. We recently reported that birnessite catalysts exhibited excellent catalytic activity for the complete oxidation of HCHO at relatively low temperatures [15]. It is well-known that catalytic activities are associated with the surface area, pore size and transition metal ion redox ability (surface reducibility) of the catalyst. Although a considerable number of strategies have been explored for tailoring their morphology, particle size, and framework substitution [16–19], to the best of our knowledge, there have been reported few birnessite materials, especially crystalline K-type birnessite materials with very high surface areas (>100 m^2/g). In a very recent work, we reported a novel microemulsion method for synthesis of birnessite manganese oxides [20]. Well-crystallized birnessite materials with varied morphologies and crystalline phases were obtained. Among them, a novel morphology of acanthosphere shape has a large specific surface area, and would be very promising for catalytic decomposition of HCHO.

In this work, we optimized the synthesis conditions, investigated the catalytic activity for HCHO oxidation, and found it is in fact the case, i.e., the acanthosphere birnessite manganese oxide showed excellent catalytic activity for HCHO decomposition.

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* Corresponding author. Tel./fax: +86 10 82543535.
E-mail address: jhhe@mail.ipc.ac.cn (J. He).

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2. Experimental

2.1. Synthesis of catalysts

In a typical synthesis, 23 g of benzyl alcohol (BA) and 12.32 g sodium dodecyl sulfate (SDS) were dissolved in 64.68 g of distilled water under vigorous stirring. The weight composition of BA/SDS/H_2O in the system was 30:16:84. 3.16 g of $KMnO_4$ was then added in the solution. The reaction proceeded with the appearance of a brown precipitate within a few minutes. After stirring at room temperature for 0.5 h, the mixture was heated at 80 °C for 2 h in a Teflon lined autoclave. The resulting product was collected, and washed several times with distilled water and absolute alcohol, respectively. Finally, the product was dried overnight at 60 °C, and labeled as BSW-80. Manganese oxide products obtained by heating at 100, 120 and 140 °C under otherwise identical conditions are denoted as BSW-100, BSW-120 and BSW-140, respectively.

2.2. Characterization of catalysts

The structure of the prepared materials was first analyzed with X-ray diffraction (XRD) using a Bruker D8 Focus diffractometer with a Cu Kα X-ray source (40 mA, 40 kV). The thermal stability was accessed by thermogravimetric analysis and differential thermal analysis (TGA–DTA), which were performed on a SDT Q600 thermal gravimetric analyzer in dry air with a heating rate of 10 °C/min. The morphologies of the products were studied by transmission electron microscopy (TEM) on a JEOL JEM-2100F electron microscope. Scanning electron microscopy (SEM) images were obtained on a Hitachi S-4300 electron microscope operating at 10 kV. The Braunauer–Emmett–Teller (BET) surface area measurements were carried out at 77 K using a Quadrasorb SI automated surface area and pore size analyzer. Hydrogen temperature-programmed reduction (H_2-TPR) was carried out in a microreactor using 50 mg of sample for each run. At constant temperature of 50 °C, the flow of H_2/Ar (5% H_2, 30 mL/min) was switched to the sample, and after 30 min the temperature-programmed reduction was started from 50 °C to 900 °C with a temperature ramp of 5 °C min^{-1}. The consumption of the reducing agent H_2 was measured on-line by a gas chromatograph equipped with a TCD.

2.3. Catalytic test

Catalytic activities were evaluated 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 30,000 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. 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:

$$\text{HCHO conversion } (\%) = CO_2 \text{ yield } (\%) = \frac{[CO_2]_{out} \text{ vol.\%}}{[HCHO]_{in} \text{ vol.\%}} \times 100,$$

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

The XRD patterns of as-prepared manganese oxide materials are displayed in Fig. 1, and confirm the formation of K-birnessite phase [21]. Broad peaks in Fig. 1a relate to the poorly-crystallized nature of the sample. When the synthesis temperature rises to 100 °C, the XRD peak intensities increase greatly (Fig. 1b and c). Clearly, transformation occurs from the poorly-crystallized initial aggregates into a well-crystallized structure. Further increase of the temperature to 140 °C would decompose part of the formed birnessite to Mn_3O_4 (Fig. 1d), which is due to the excessive reduction of Mn^{7+} by BA. The reduction ability of BA was previously utilized by Xiao et al. and our group to synthesize metal oxides [20,22]. It was reported that higher temperature would lead to a higher reduction ability of BA, and more Mn^{7+} ions were reduced to Mn in lower oxidation states such as Mn^{2+} and Mn^{3+}.

The TGA–DTA measurement of a selected manganese oxide sample is shown in Fig. 2. The profile reveals three weight losses in the temperature range of 25–800 °C. (i) The first weight loss of 11.0% in the range of 25–205 °C is attributed to physisorbed and interlayer water in birnessite nanostructure. (ii) The second weight loss of 2.9% in the 205–510 °C range is slightly complicated. In the 205–260 °C range, an exothermic peak appears at ca. 233 °C on the DTA curve, while the weight loss is not significant. This likely corresponds to the decomposition of tiny residual SDS in birnessite pores. The weight loss in the range of 260–510 °C is related to the oxygen release due to the partial reduction of the Mn^{4+} cations to their trivalent state [23]. (iii) Above 510 °C, the gained weight is possibly due to the compensation of released oxygen produced by the oxidation of Mn^{3+} to Mn^{4+}, which leads to the phase transformation from the layered structure to the α-MnO_2 phase [23]. The exothermic peak at 533 °C is related to this phase transformation. In addition, below 250 °C, no significant endothermic peak and weight loss of BA (its boiling point is 205 °C) appears, suggesting that BA should have been removed during the synthesis process.

The nanostructures of manganese oxides prepared at different temperatures were observed using TEM and SEM. BSW-80 shows agglomerated cotton-like nanospheres that consist of ultrafine crystals (Figs. 3a and 4a). It is poorly-crystallized, as was confirmed by the XRD analysis. When the temperature rises to 100 °C, flake architectures are represented with some twisting fiber-like manner (Figs. 3b and 4b). It is interesting to learn that when up to 120 °C, in addition to the flakes, some nanospheres of ca. 500 nm

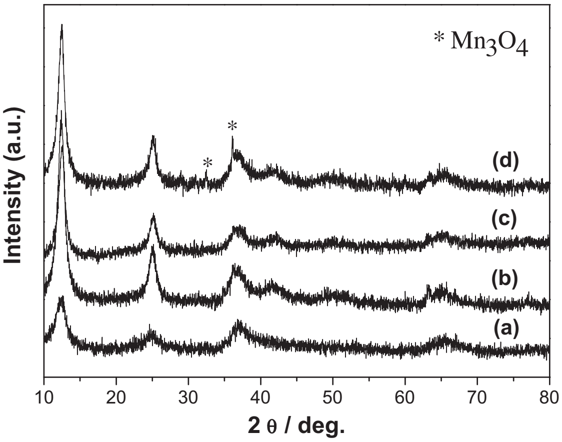

Fig. 1. XRD patterns of varied manganese oxide catalysts: (a) BSW-80, (b) BSW-100, (c) BSW-120, and (d) BSW-140.