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

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ABSTRACT

Birnessite - type manganese oxides with very high surface areas (up to 154 m²/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 H₂-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.

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1. Introduction

Due to stringent environmental regulations for human health protection, low-temperature catalytic oxidation of formaldehyde (HCHO) to CO₂ and H₂O 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/CeO₂ catalysts. An et al. [10] found that Pt/Fe₂O₃ 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 m²/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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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/H₂O in the system was 30:16:84. 3.16 g of KMnO₄ 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 K α 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 (H₂-TPR) was carried out in a microreactor using 50 mg of sample for each run. At constant temperature of 50 °C, the flow of H₂/Ar (5% H₂, 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 H₂ 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 CO₂ in the products were detected for all tested catalysts. Thus, HCHO conversion was expressed in the yield of CO₂, 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 [CO₂]_{out} was the CO₂ 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 Mn₃O₄ (Fig. 1d), which is due to the excessive reduction of Mn⁷⁺ 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 Mn⁷⁺ ions were reduced to Mn in lower oxidation states such as Mn²⁺ and Mn³⁺.

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 Mn⁴⁺ 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 Mn³⁺ to Mn⁴⁺, which leads to the phase transformation from the layered structure to the α -MnO₂ 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.

Fig. 2. TG and DTA curves of BSW-120 catalyst.

appear, which are probably assembled from smaller flakes. The widening of the XRD peaks (Fig. 1b and c) supports this speculation. With further increasing the synthesis temperature to 140 °C, however, the nanospheres disappear, and a novel nano-octahedra structure is observed (Fig. 3d, pointed by arrow). This nano-octahedra structure corresponds to the Mn_3O_4 phase [24], in accordance with those revealed by XRD for BSW-140.

It is well known that microemulsion systems have different phase structures such as lamellar liquid crystal region (L_c), hexagonal liquid crystal region (Hex) and isotropic liquid regions (L_1 , o/w structure and L_2 , w/o structure). Among them, L_1 region consists of three subregions: rod, spherical and bicontinuous regions. These

structures can be obtained by changing the amount of each component [25]. Xu and Liu [26] reported that in the SDS/BA/ H_2O system, when the weight ratio of SDS/ H_2O was 16:84, the structure of system appeared as rod ($\text{BA} < 1.0 \text{ wt\%}$), spherical ($1.0 \text{ wt\%} < \text{BA} < 16.0 \text{ wt\%}$) and bicontinuous ($\text{BA} > 16.0 \text{ wt\%}$), respectively. It is evident from these results that the composition used the current work (SDS/ H_2O = 16:84, $\text{BA} = 23 \text{ wt\%}$) should exhibit the bicontinuous structure. It is further noted that in the bicontinuous structure, both water and BA are the solubilized phase and continuous phase, simultaneously, and the SDS aggregate shows a network structure. Hence, cotton-like nanospheres and flake architectures of manganese oxides are obtained when the synthesis temperatures are not too high. While the synthesis temperature rises to 120 °C, BA, which was used as a microemulsion component and reducing agent, simultaneously, may be consumed faster than that at lower temperature, leading to the formation of spherical region in microemulsion. In this case, nanosphere-like manganese oxide appears. However, further increasing the synthesis temperature to 140 °C will destroy the microemulsion system [27], leading to the formation of scattered flake manganese oxide again.

Fig. 5 shows the N_2 adsorption isotherms of manganese oxide materials. There is no clear capillary condensation and hysteresis loop at high p/p_0 for the BSW-80 sample, indicating its poorly porous nature. In contrast, type II adsorption isotherms with capillary condensation at high p/p_0 can be observed for BSW-100, BSW-120 and BSW-140, respectively. A hysteresis loop of type H3, according to the IUPAC classification of types of hysteresis loops [28], occurs at high p/p_0 close to saturation, suggesting the existence of slit-shaped mesopores with nonuniform sizes, probably due to the aggregation of nanoparticles. BSW-100 adsorbs apparently more nitrogen molecules than other products, indicating its larger pore

Fig. 3. TEM images of varied manganese oxide catalysts: (a) BSW-80, inset: HRTEM image, (b) BSW-100, inset: HRTEM image, (c) BSW-120, and (d) BSW-140.

Fig. 4. SEM images of varied manganese oxide catalysts: (a) BSW-80, (b) BSW-100, (c) BSW-120, and (d) BSW-140.

Fig. 5. N₂ adsorption-desorption isotherms of varied manganese oxide catalysts: (a) BSW-80, (b) BSW-100, (c) BSW-120, and (d) BSW-140.

volumes. But the hysteresis loop of BSW-100 is also relatively broader, which demonstrates that the bottle-neck effect of the BSW-100 pores becomes much more evident.

All the textural properties of the as-prepared materials are summarized in Table 1. The BET surface area and total pore volume of BSW-80 is 28 m²/g and 0.039 cm³/g respectively, much lower than those of BSW-100, BSW-120 and BSW-140. These results match the XRD (Fig. 1) and N₂ adsorption isotherm (Fig. 5) data. The nearly amorphous nature of BSW-80 leads to its poor pore structure, and eventually to the low surface area and pore volume. BSW-100 has the highest surface area (154 m²/g) and the largest pore volume (0.984 cm³/g). The BET surface areas of BSW-120 and BSW-140 are 138 and 145 m²/g, respectively, lower than that of BSW-100 but still much higher than those of reported for crystallized K-type birnessite to date. These results are consistent with the TEM observations (Fig. 3). BSW-100 consists of well-crystallized flakes, whereas some nanospheres and nano-octahedra appear in BSW-120 and BSW-140, respectively, all of which are accompanied by a decrease in the surface area.

According to Table 1, the micropores only contribute 1–2% of total pore volume. The most probable pore size in the micropore range is around 0.6 nm. Compared to BSW-80, the other three products prepared at higher temperatures have larger most probable mesopore sizes (14–26 nm, compared to 5.4 nm of BSW-80) and pore volumes. The mesopore size and pore volume of BSW-100 is found to be the highest among others, as well as its surface area.

Table 1
Textural properties and catalytic performance of manganese oxide catalysts.

Sample	S_{BET}^a (m ² /g)	Pore size (nm)		Pore volume (cm ³ /g)		%V _{mic}	HCHO oxidation activity (°C)	
		D_{mic}^b	D_{mes}^c	V_{mic}^d	V_{total}^e		T_{30}	T_{50}
BSW-80	28	0.6	5.4	0	0.039	0	83	100
BSW-100	154	0.6	25.6	0.013	0.984	1.3	77	92
BSW-120	138	0.6	16.6	0.007	0.572	1.2	68	83
BSW-140	145	0.5	14.1	0.010	0.511	2.0	64	86

^a Total surface area obtained by the BET method.

^b The most probable micropore size based on the HK method.

^c The most probable mesopore size based on the BJH method.

^d Micropore (<2 nm) volume calculated using the t-plot method.

^e Total pore volumes obtained by N₂ adsorption at $p/p_0 = 0.99$.

3.2. Activity test

Results for the HCHO oxidation over the manganese oxide catalysts prepared at varied temperatures are shown in Fig. 6. In all cases, in order to check for the complete oxidation of HCHO as accurately as possible, only CO₂ was detected as the oxidation product of HCHO. It is noted that CO₂ yield increases with the rise of oxidation temperature over the catalysts. Among all the catalysts tested, BSW-120 gives the highest catalytic activity. A 100% yield of CO₂ over BSW-120 was achieved at 100 °C which is much lower as compared to other manganese oxides reported elsewhere under similar conditions [3,11,29,30], indicating that the porous manganese oxide BSW-120 is an excellent catalyst for HCHO oxidation. These catalysts should measure even better when the HCHO conversion is determined by the decrease of HCHO concentration, as reported in some literatures [15]. Because the conversion obtained by this method includes the amount of adsorbed HCHO during the catalytic reaction, and thus gives a conversion probably higher than the real value.

The temperatures of 30% CO₂ yield (T_{30}) and 50% CO₂ yield (T_{50}) over different catalysts are presented in Table 1. The T_{50} decreases greatly with increasing the synthesis temperature from 80 to 120 °C. However, further increasing the temperature (from 120 to 140 °C) leads to the slight decrease of the catalytic activity. Moreover, it is interesting that BSW-140 with T_{30} of 64 °C shows slightly higher activity than BSW-120 with T_{30} of 68 °C, as shown in Fig. 6. Clearly, the discrepancies in the structural and chemical properties of these catalysts greatly affect the catalytic behavior.

The porous structure of the catalyst may facilitate the diffusion of the HCHO molecules. An earlier study on VOCs oxidation revealed that high surface area is much crucial for high catalytic activity of catalyst [31,32]. It is mentioned above that BSW-80 consists of agglomerated nanospheres, showing much lower surface area than those of BSW-100, BSW-120 and BSW-140, and thus naturally has a lower activity. BSW-100 and BSW-120 have comparable surface areas, but compared with BSW-100, BSW-120 has smaller pore size and consists of some nanospheres of ca. 500 nm, which could prolong the stay time of HCHO molecules in the catalyst, and enhance HCHO oxidation. Our previous work [15] also showed that the morphology largely affected on the catalytic activity of MnO₂ nanomaterials. Hollow K_xMnO₂ nanospheres exhibited larger catalytic activity than honeycomb K_xMnO₂ nanospheres because the former could adsorb and retain HCHO for a longer period of time than the latter, and eventually

enhanced the HCHO oxidation. All of these results indicate that the morphology, pore size and the surface area of catalysts are among the major factors governing their high catalytic activity. The surface area of BSW-140 is higher than that of BSW-120 though they have similar pore sizes, however, at elevated temperature (>70 °C) the catalytic activity of BSW-140 slightly decreases, which may be due to the presence of nano-octahedral Mn₃O₄ in the BSW-140 material.

3.3. Redox properties

To further investigate the relationship between chemical property and catalytic activity, the as-prepared manganese oxides were measured using H₂-TPR, and the results are showed in Fig. 7. According to the literature [33], the reduction procedure of manganese oxides can be described by three steps:

Fig. 7 shows that two or three peaks at 250–500 °C are observed in each H₂-TPR profile, depending on the sample, and the corresponding positions are summarized in Table 2.

The reduction spectrum of BSW-100 is characterized by three peaks at ca. 324, 365 and 462 °C. The first sharp peak may correspond to the transformation of MnO₂ to Mn₂O₃, while the second peak is assigned to the subsequent reduction to Mn₃O₄. The third peak (highest temperature peak, maximum near 462 °C) is less intense but broad, and attributed to the reduction of Mn₃O₄ to MnO.

A similar reduction pattern was observed for the BSW-120 sample, but the peak positions shift to lower temperatures, indicating higher reducibility. In addition, the intensities of reduction peaks are much higher in comparison to BSW-100, showing higher relative amounts of reducible species (thus, more reactive species and higher reactivity). However, when the synthesis temperature of the sample is increased to 140 °C, the temperatures of three reduction peaks slightly shift to higher temperatures (see Table 2), meaning lower reducibility.

The H₂-TPR spectrum of BSW-80 is different from the others. Just two major peaks at ca. 308 °C and 424 °C were observed. The low temperature peak represents the reduction of MnO₂ to Mn₂O₃. The broad high temperature peak with a maximum at ca. 424 °C may be deconvoluted into two overlapping components, indicating that the intermediate reduction from Mn₂O₃ to Mn₃O₄

Fig. 6. HCHO conversions on manganese oxide catalysts prepared at varied temperatures. Catalyst: 100 mg, space velocity: 30,000 mL/(g_{cat} h), HCHO 460 ppm, O₂ 21 vol.%.

Fig. 7. H₂-TPR profiles of varied manganese oxide catalysts.

Table 2Peak positions (°C) of the H₂-TPR spectra for the manganese oxide catalysts.

Sample	Peak I ^a	Peak II ^b	Peak III ^c
BSW-80	308	424	
BSW-100	324	365	462
BSW-120	296	342	432
BSW-140	314	362	460

^a The first reduction peak in each H₂-TPR profile.^b The second reduction peak in each H₂-TPR profile.^c The third reduction peak in each H₂-TPR profile.

may finish at a relatively high temperature, and thus the corresponding component overlaps with the component ascribed to the reduction of Mn₃O₄ to MnO.

As far as we know, the surface redox property of catalyst profoundly influences heterogeneous catalytic reactions because the reactions mainly occur on the catalyst surface. Kapteijn et al. [33] reported that manganese oxide with a lower onset temperature of reduction showed a higher catalytic activity in the NO reduction by NH₃. Chen et al. [34] found that the facile reduction feature of manganese oxide implied the easy activation for CO oxidation. It is clear that high surface reducibility results in high catalytic activity in that the reduction of surface species frequently occurs at relatively low temperatures.

In the current work, the order of reducibility of all samples derived from the low temperature reduction peak is BSW-120 > BSW-80 > BSW-140 > BSW-100, similar to the order of catalytic activity (BSW-120 > BSW-140 > BSW-100 > BSW-80) except BSW-80. The H₂-TPR results indicate that though the first peak reduction temperature of BSW-80 is lower than those of BSW-140 and BSW-100, its intensity is much lower, meaning consequently lower relative amounts of surface reactive species and lower reactivity. Meanwhile, as compared to BSW-140 and BSW-100, BSW-80 has worse pore structure and lower surface area, all of which leads to its lower catalytic activity for the HCHO oxidation.

It is clear that the catalytic activity of birnessite manganese oxides for HCHO oxidation is influenced by a combination of factors including morphology, surface area and surface reducibility. High surface area and high reducibility increase the catalytic activity of the synthesized manganese oxides, while poor pore structure has the opposite effect. The optimal catalyst obtained is BSW-120.

4. Conclusion

We have demonstrated a facile route to synthesizing birnessite manganese oxides in a microemulsion system. The morphology, crystal phase, surface area, pore size, and even the chemical property of manganese oxides were tailorable via controlling the synthesis temperature. By this method, porous birnessite materials were obtained with very high specific surface areas ranging from 138 to 154 m²/g. This strategy can be extended to the preparation of other useful manganese oxide nanomaterials. The catalytic activity of obtained birnessite manganese oxides for HCHO oxidation is excellent, and is highly dependent on their morphology, surface area and surface reducibility. The most active catalyst

(BSW-120) could completely oxidize HCHO into CO₂ and H₂O at 100 °C. This value is significantly superior to those of previously reported manganese oxides under similar conditions.

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