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Short communication

Fabrication of hollow-structured FeO_x-MnO_x oxidative catalysts with ultra-large surface area

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ABSTRACT

In this work, hollow-structured MnO_x and FeO_x-MnO_x were synthesized by self-template route and applied for CO oxidation. FeO_x-MnO_x exhibited better catalytic activity than MnO_x. It could convert 79.1% CO at 20 °C and had a higher CO conversion during the temperature ramping. The FeO_x species could react with HCl and greatly helped to increase the specific surface area (428.5 $m^2 g^{-1}$) and pore volume (0.82 $cm^3 g^{-1}$) of the catalyst. The reserved FeO_x in the FeO_x-MnO_x sample enhanced the redox properties and increased the amount of reactive oxygen species.

1. Introduction

MnO_x has been extensively researched as an inexpensive and environmental-friendly material applied in catalytic oxidation of CO, NO, VOCs, *etc.*[1,2]. Given the fact that the morphologies and structure properties could significantly influence the catalytic performance of the material, remarkable progress has been made for the synthesis of MnO_x. Various morphologies and phase structures were successfully obtained, including nanostructures (nano-tubes/− belts/− rods/− flakes, *etc.*) [3–6], ordered mesoporous structures [7], and some hierarchical structures (urchin-like/hollow sphere, *etc.*) [8–11].

Among the methods for preparing MnO_x materials, acid treatment was a simple and effective way to create defects and porous structures [1,12,13]. Si et al. [13] selectively removed La^{3+} cations from the $LaMnO_{3+\delta}$ perovskite using diluted HNO_3 and obtained a γ-MnO_2-like material. Such an oxide had a specific surface area of about 250 $m^2 g^{-1}$ and showed higher CO oxidation activity than the normal $LaMnO_{3+\delta}$ and γ-MnO_2 synthesized by traditional methods. On the other hand, the self-template route using acid solution was a method to synthesize MnO_x with hollow structures [14]. Dispersed $MnCO_3$ particles were firstly synthesized and an oxide shell was formed by the oxidation of carbonate using $KMnO_4$. Then the carbonate core was selectively removed by acid solution. The as-prepared hollow MnO_x was used in water treatment [15–17], supercapacitors [18], and Li-ion batteries [19,20]. The most attractive feature of the hollow MnO_x prepared by such a self-template method was their high surface area. Cao et al. [17] calcined the samples at 400 °C for 4 h after acid leaching and got a kind of γ-MnO_2/α-MnO_2 ellipsoids with a specific surface area of ~100 $m^2 g^{-1}$. Yu and co-workers [18] obtained MnO_2 hollow structures without calcination and the samples had a specific surface area of about 300 $m^2 g^{-1}$. However, few literature were focused on the behavior of manganese carbonate that mixed with other metal elements in the self-template route. A mixed oxide shell should be formed over the carbonate after the reaction with $KMnO_4$. It is, therefore, possible that the specific surface area of the final oxide product would be further increased if some less acid-stable metal oxide such as FeO_x and CoO_x are chosen. And the physicochemical properties of the base material MnO_x may also be tuned.

In the present study, we fabricated hollow MnO_x and FeO_x-MnO_x structures with large specific surface areas and evaluated their catalytic performance for CO oxidation. With Fe doping into the carbonate precursor, the specific surface area and pore volume of the final FeO_x-MnO_x product were remarkably increased. The physicochemical properties of the catalysts were also studied.

2. Experimental

2.1. Synthesis of MnO_x and FeO_x-MnO_x

In this work, the hollow structures were synthesized in the way that was similar to the literature [15], and a scheme of the preparation was shown in Fig. S1. The $MnCO_3$ and Fe-doped carbonate (Mn/Fe = 4/1, denoted as $Fe_{0.2}Mn_{0.8}CO_3$) were served as precursors and they were prepared using $MnSO_4{\cdot}H_2O$ (99%, Aladdin, China), $FeSO_4{\cdot}7H_2O$ (99%, Aladdin, China), and $NaHCO_3$ (99.8%, Aladdin, China). For the preparation of $MnCO_3$, 0.01 mol $MnSO_4{\cdot}H_2O$ and 0.01 mol $NaHCO_3$ were

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separately dissolved in 700 mL deionized water. Then the $NaHCO_3$ solution was added into the $MnSO_4$ solution under stirring. The mixture was stirred for 12 h at room temperature. Finally, the suspension was filtered and washed with deionized water, followed by drying at 80 °C in an oven overnight. For the preparation of $Fe_{0.2}Mn_{0.8}CO_3$, 0.008 mol $MnSO_4{\cdot}H_2O$ and 0.002 mol $FeSO_4{\cdot}7H_2O$ were dissolved to form a homogeneous solution. The following steps were same to those of the preparation of $MnCO_3$.

For the preparation of MnO_x and FeO_x-MnO_x, 1 g of the as-prepared precursor of $MnCO_3$ or $Fe_{0.2}Mn_{0.8}CO_3$ was dispersed in 40 mL deionized water. Then 5 mL $KMnO_4$ solution (0.032 mol L^{-1}) was added under stirring. After being reacted for 40 min, 5 mL HCl solution (2.4 mol L^{-1}) was added into the above solution, and the suspension was stirred for another 2 min. The precipitate was centrifuged and washed with deionized water and ethanol for several times and dried at 110 °C overnight. Finally, the products were calcined in a muffle furnace at 300 °C for 3 h in static air.

2.2. Catalyst characterization

The bulk compositions of the catalysts were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES). X-ray diffraction (XRD) was performed to determine the phase structures. The morphologies and sizes of the samples were observed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The pore volume and specific surface area were determined by N_2 adsorption/desorption experiments. The X-ray photoelectron spectroscopy (XPS) analysis was carried out to get the surface properties. The redox properties were measured by H_2 temperature programmed reduction (H_2-TPR). All of the characterizations mentioned above can be found in detail in our previous work [1,21,22].

2.3. CO catalytic oxidation tests

The CO catalytic oxidation activity was evaluated in a fixed-bed reactor with an inner diameter of 12 mm. 50 mg catalyst was put into the reactor and fixed by quartz wool on both ends. Before each test, the catalyst was pretreated at 300 °C for 30 min in 10% O_2/N_2 (100 mL min^{-1}). Then the reactant gas mixture (5000 ppm CO, 10% O_2, balanced with N_2) was introduced into the reactor system, with a total flow rate of 100 mL min^{-1}, corresponding to a gas hourly space velocity (GHSV) of 120,000 mL g_{cat}^{-1} h^{-1}. The temperature was increased from 20 to 250 °C with a heating rate of 10 °C min^{-1}. The component concentrations in the effluent gas were detected by a Fourier-transform infrared spectrometer (Thermal Nicolet iS10) with a spectral resolution of 0.5 cm^{-1}. The pretreatment and temperature ramping test were performed twice for each catalyst and the CO conversion was calculated according to $(1\text{-}[CO]_{outlet}/[CO]_{inlet}) \times 100\%$.

3. Results and discussion

3.1. Phase structures and morphologies

The XRD patterns of the two carbonates in Fig. S2 show sharp characteristic peaks of rhombohedral $MnCO_3$ phase (JCPDS No. 44–1472) without any impurities [18]. The diffraction peaks of $Fe_{0.2}Mn_{0.8}CO_3$ slightly shift to higher angle positions; this indicates that the Fe ions are doping into the carbonate structure since the radius of Fe^{2+} (0.65 Å) is smaller than that of Mn^{2+} (0.83 Å) [23]. The XRD patterns shown in Fig. 1(a) correspond to the oxides derived from the carbonate precursors. They both match the pattern of the birnessite MnO_2 (JCPDS No. 18–0802) [18,24,25]. The peaks centered at $2\theta = 36.9°$ and 66.0° could be well assigned to the (006) and (119) planes of MnO_2. However, the low intensities and broadening of the peaks reveal an amorphous or poorly ordered polycrystalline nature of the catalysts. For the XPS spectra of Mn 2*p* in Fig. 1(b), the two catalysts

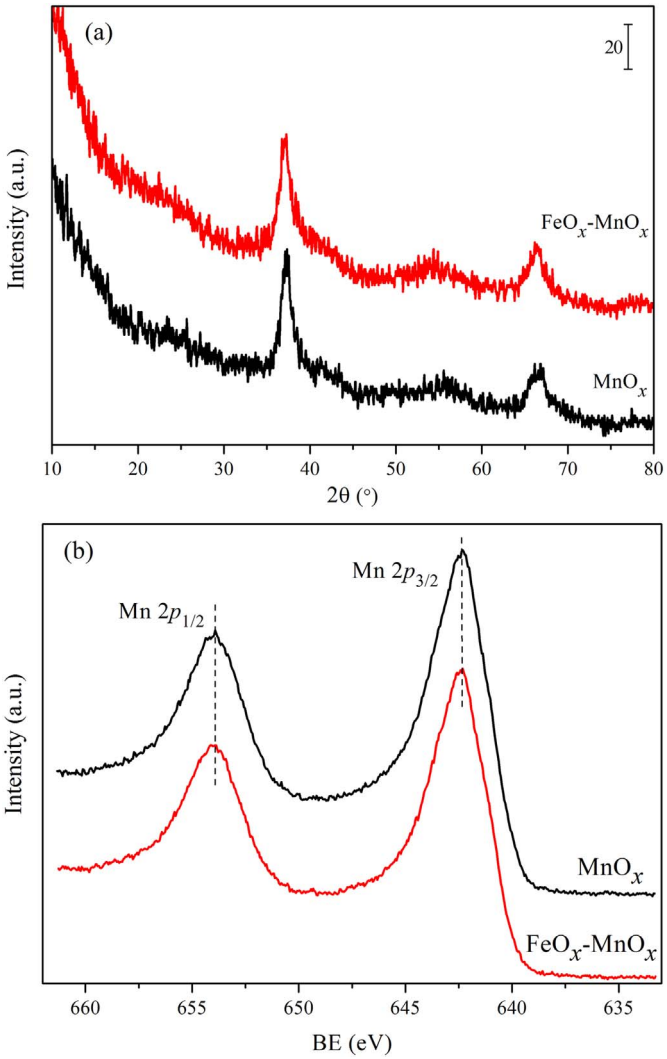

Fig. 1. (a) X-ray diffraction patterns and (b) Mn 2*p* XPS spectra of the catalysts.

have very similar spectra and two peaks centered at 653.9 and 642.3 eV can be found in each of the spectra, which are assigned to the Mn $2p_{1/2}$ and Mn $2p_{3/2}$, respectively. That further proves the dominance of MnO_2 in the catalysts [24,25].

Fig. 2 shows the SEM images of the oxides. As can be seen from their overall appearance in Fig. 2(a) and (b), the samples preserve the shapes and sizes of $MnCO_3$ and $Fe_{0.2}Mn_{0.8}CO_3$ precursors. The hollow structures of the MnO_x and FeO_x-MnO_x were created after the acid treatment. Some of the broken samples present the "shell-like" appearance, and the cavity inside the shell can be clearly seen in the magnified SEM images as insets in Fig. 2(a) and (b). The surface of the shells consists of a lot of curly sheets with a thickness in nanoscale. The formation of the oxide shells and nano-sheets proceeded simultaneously during the reaction between $KMnO_4$ and carbonates [16]. For clearly explaining the formation of such a characterized morphology, more microscopic images are given in the "Supporting Information". Fig. S3 presents the typical SEM images of the $MnCO_3$ and $Fe_{0.2}Mn_{0.8}CO_3$ particles. The $MnCO_3$ particles have a uniform solid spherical morphology with an average size of ~3.5 μm. After doping Fe into the carbonate, the particles tend to grow into elliptic shapes which are not standard spheres, with a size ranging from 4 to 6 μm. As shown in Fig. S3(b), the surface of the as-prepared $MnCO_3$ microsphere is composed of triangular edges and corners. It seems like that in the solution the crystals are in a radially growing method to form $MnCO_3$. As for the high-magnification image of $Fe_{0.2}Mn_{0.8}CO_3$ in Fig. S3(d), it looks different with that of