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Catalytic properties of manganese oxide polyhedra with hollow and solid morphologies in toluene removal

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ABSTRACT

In order to develop an efficient and active catalyst to degrade the toxic volatile organic compounds, manganese oxide polyhedra with hollow and solid morphologies were synthesized by a convenient hydrothermal route without any surfactants or templates. The catalytic performances of the two manganese oxides were assessed in the oxidation reaction of toluene. Compared with the solid polyhedral manganese oxide, an excellent catalytic activity of the hollow one has been found, resulting from its cavity nature, the high content of active oxygen and the high manganese oxidation state of hollow MnOx. Meanwhile, the probable reaction pathway for toluene oxidation over the hollow polyhedral manganese oxide was initially discussed by means of in situ FTIR.

1. Introduction

Volatile organic compounds (VOCs) are among the most toxic pollutants of the air. They often include a large of hydrocarbons with several functional groups, which are not only harmful to human health but also hazardous to the environment [1–3]. Therefore, destruction of VOCs has become an important issue. Catalytic oxidation is one of the most attractive methods for VOCs degradation [4–8] in that VOCs can be converted into environmentally neutral products [9].

The catalytic performance of materials is regarded as a key factor to determine the efficiency of catalytic oxidation method [10]. Noble metals and metal oxides are the two main kinds of materials for the complete oxidation of VOCs. It is generally known that noble metals exhibit high activities for VOCs oxidation. However, the high cost limits their wide application. In the recent years, metal oxides have proved to be active for total oxidation of VOCs, which are expected to be a better alternative to take the place of noble metal.

As an important transition metal oxide, manganese oxides (MnOx) are one of the most active oxide catalysts in the destruction of VOCs, NOx and automobile exhaust. Bastos [11] revealed that manganese oxides were able to oxidize ethanol into 100% of CO_2 at 240 °C. Study of catalytic combustion of VOCs over a series of manganese oxide catalysts (Mn_3O_4, Mn_2O_3 and MnO_2) stated that Mn_3O_4 showed the best performance due to the oxygen mobility, and the reaction temperature for T_{50} and T_{90} conversion of toluene are 245 °C and 270 °C [12]. Santos [13] reported that ethyl acetate was completely oxidized to CO_2 at 213 °C over MnOx catalyst, while at 280 °C for toluene and 215 °C for ethanol. Beyond it, a lot of efforts have been spent on the control of morphology and structure of metal oxides in their preparations. Wang [14] prepared the manganese oxides with rod-, wire-, tube-, and flower-like morphologies, which were then evaluated for toluene oxidation. It was showed that the catalytic performance of these samples decreased in the order of rod-like α-MnO_2 > tube-like α-MnO_2 > flower-like Mn_2O_3 > wire-like α-MnO_2. Li [15] investigated the effect of MnO_2 morphology on the catalytic oxidation of toluene over Ag/MnO_2 catalyst. The Ag/MnO_2 nanowires sample exhibited the highest reactivity for toluene oxidation with a complete conversion at 220 °C. That is, the morphology was an important factor influencing their performance. At present, the hollow structures have attracted significant attention in the modern materials research, since the hollow structures possessing special properties, such as high specific surface area, porosity, lower density, or good permeation. Particularly, hollow metal oxides are drawn much more interest due to their potential applications [16–19]. Yet, besides the tubular and hollow sphere as the hollow materials to be studied, few studies about other special morphological materials

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with hollow structure and their corresponding catalytic properties have been reported.

In the present work, a convenient hydrothermal route without any surfactants or templates has been developed to prepare the special morphological MnOx, that is, the hollow and solid polyhedra, respectively. Both of them were employed as the catalysts for toluene oxidation. An excellent catalytic activity of the hollow polyhedral MnOx has been found, compared with the solid one. And the catalytic reaction pathway for toluene oxidation was also obtained by the in situ technique.

2. Material and methods

2.1. Synthesis of MnOx catalysts

In a typical procedure, 5 mmol manganese acetate ($Mn(CH_3COO)_2{\cdot}4H_2O$) was dissolved in distilled water (20 mL) under magnetic stirring, followed by adding 60 mL NaOH solution. After being stirred for 30 min, the transparent solution was taken into a Teflon-lined stainless steel autoclave (100 mL) and then maintained at 130 °C in an electric oven for 5 h. After the hydrothermal treatment the product was cooled down to the room temperature. The precipitate was separated by centrifugation, washed with distilled water and absolute alcohol several times until neutral and then dried overnight at 100 °C. Finally, calcination was carried out at 400 °C for 4 h. The sample was signed as MnOx-Hollow. To compare the catalytic activities of the MnOx with different morphology, another MnOx sample was synthesized via the same route with manganese sulfate ($MnSO_4{\cdot}H_2O$) as the source and the hydrothermal reaction time for 48 h. The resultant sample was signed as MnOx-Solid.

2.2. Characterization

Scanning electron microscopy (SEM) images were obtained on the Ultra55 electron scanning microscopy (ZEISS, Germany). Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were recorded on JEM-2100HR (JEOL, Japan). Wide-angle power X-ray diffraction (XRD) patterns were performed on a D8 ADVANCE diffractometer (Bruker, Germany) using Cu Kα radiation ($\lambda = 0.154056$ nm, 40 kV, 40 mA, scanning step = 0.02°). N_2 adsorption-desorption measurements were carried out at 77 K on an ASAP2020M analyzer (Micromeritics, USA). Before measurement, the samples were outgassed at 100 °C in vacuum for 4 h. The specific surface area was calculated by the BET method. Temperature-programmed reduction profiles were obtained by using Auto Chem II Chemisorption Analyzer (Micromeritics, USA). In TPR experiments, 100 mg of sample was used and pretreated in Ar gas at 300 °C for 30 min. After the sample was cooled down to 60 °C, 10%H_2/Ar mixture gas was introduced and the reactor was heated at a flow rate of 10 °C min^{-1} to 850 °C. Temperature-programmed desorption with O_2 (O_2-TPD) was measured by Auto Chem II Chemisorption Analyzer (Micromeritics, USA). 100 mg sample was used and pretreated with He gas at 300 °C for 60 min. After the sample was cooled down to 50 °C, 5%O_2/He mixture gas was introduced for 60 min. Then the reactor was heated with He at a rate of 10 °C min^{-1} to 800 °C. The XPS spectra and images were acquired on ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific, USA). Charge effects of samples were corrected by setting the binding energy of adventitious carbon (C1s) at 284.8 eV. The spectra were deconvoluted using the XPSPEAK 41 program by the curve fitting with a Gaussian/Lorentaian ratio of 80/20 after the Shirley-type background substraction. The average oxidation state (AOS) of manganese was gained from Mn 3s XPS analysis, which was also performed on ESCALAB 250 photoelectron spectrometer (Thermo Fisher Scientific, USA).

2.3. Catalytic activity evaluation

Toluene was selected as the representative VOCs pollutant. Catalytic activity evaluation was determined in a fixed-bed reactor with a quartz tube of 8 mm, in which 300 mg of catalysts (40–60 mesh) were loaded. Catalytic activity was measured over the range of 150–280 °C, the temperature was obtained by a K type thermocouple in the catalyst bed. Gaseous toluene was generated by passing dry air flow over toluene solution in an incubator kept at 0 °C. The feed flow was set with the concentration of toluene 1000 ppm that was metered by a mass flow controller, and the weight hourly space velocity at 32,000 ml g^{-1} h^{-1}. The conversion measurement was taken after 30 min at steady state. The concentration of the inlet and outlet gas stream was analyzed on-line by gas chromatography (GC-2014C, Shimadzu, Japan) equipped with FID for the quantitative analysis of toluene. The conversion of toluene (X) was calculated as $X = 1 - C_{toluene}/C_{toluene,\ in}$, where $C_{toluene}$ is the mean concentration of toluene at steady state; $C_{toluene,\ in}$ is the inlet concentration of toluene at steady state.

2.4. Reactions without oxygen in the feed

The aim of this test was to study the role of the active oxygen of catalyst on the mechanism for toluene oxidation. The experimental procedure used here was the same as the specification in Section 2.3. Before the reaction, the catalysts were heated with dry air up to 280 °C for 60 min. The reactor was then blown with pure N_2 at the same temperature for 2 h so as to remove the physical adsorption of oxygen, and the experiment began by delivering liquid toluene with pure N_2. The exact concentration of carbon oxides was detected once every 6 min by another FID equipped in GC with a nickel catalyst converter used for converting CO and CO_2 quantitatively into methane. Hardly any CO can be detected in the outlet gas stream. The amounts of active oxygen were calculated in accordance with the amounts of the resultant CO_2. The calculation equation was as follows.

$$n = (m \times 10^{-6} \times 2 \times 10^{-3}/22.4)/0.3 \times 2$$

n is the amount of the oxygen atom, mol/g; m is the amount of CO_2, ppm; The volume of quantitative loop in the detector of GC is 2 mL; The weight of MnOx is 0.3 g.

Moreover, the total amount of active oxygen was quantified by integrating the curve of the amount of active oxygen as a function of reaction time.

2.5. Stability test

An on-stream reaction experiment was performed for toluene oxidation at 280 °C lasting for 150 h to examine the catalytic stability of the hollow polyhedral MnOx. In addition, the gas mixture was introduced with different inlet concentration of toluene in order to determine the durability of the catalyst.

2.6. Catalytic pathway for toluene oxidation

The reaction pathway for toluene oxidation was discussed by means of in situ Fourier Transform Infrared Spectroscopy (Nicolet 6700, Thermo, USA). The resolution ratio was 4 cm^{-1}. The samples were put into the in situ reaction equipment, and were swept with Ar for 60 min at 300 °C before being cooled down to 100 °C to obtain the background. At first, toluene with carrier gas (Ar) was introduced into the reaction system. Then change the carrier gas by dry