Synthesis of mesoporous MnO₂ nanosheets and its application in toluene purification reaction

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Abstract. Mesoporous manganese dioxide (m-MnO₂) nanosheets were synthesized using octadecylamine (OTA) as template. The obtained m-MnO₂ has rich mesoporous structures, high pore volume of 0.323 cm³/g and high surface area of 125.7 m²/g. While using the as-synthesized m-MnO₂ as a carrier to support the noble metal active component of platinum, the obtained Pt-based supported catalyst exhibited excellent toluene purification activity: toluene conversion can be over 90% at low reaction temperature of 160°C.

1. Introduction
Volatile Organic Compounds (VOCs) is a kind of atmospheric pollutants which can cause great harm to the environment and human health. In recent years, it has become a global issue that has received increasing attention [1, 2]. Catalytic oxidation technology has received much attention as one of the most effective and economically viable methods for eliminating VOCs. The performance of VOCs oxidation catalysts is closely related to both the active metal and the support. Therefore, a better carrier is of great significance for the preparation of high-performance oxidation catalysts [3, 4].

Manganese dioxide nanosheets have edge-shared octahedral crystal structure and large surface area, which makes them have good adsorption and degradation ability for various organic pollutants, dyes and heavy metal ions. It is an ideal carrier material for VOCs oxidation catalyst [5]. In this study, MnO₂ nanosheets with rich mesoporous structure and high BET specific surface area were synthesized by using organic macromolecules as templates. The Pt/MnO₂ catalysts were prepared by in-situ growing method. The performance of the Pt/MnO₂ catalysts for VOCs oxidation was determined by using toluene as a probe molecule. The as-prepared catalysts exhibit good catalytic performance for toluene oxidation.

2. Experimental
2.1. Materials synthesis
A bottom-up self-assembly strategy was used to synthesize m-MnO₂ nanosheets. (Prepared according to a modified literature procedure [6]) First, 2 g OTA was dissolved in 100mL ethanol and 100mL deionized water to generate white layered micelle aggregation. After vigorous stirring, 50 mL 2 wt%
KMnO₄ aqueous solution was added to the above solution. Then, after continuous stirring, the solution turns brown to form MnO₂. Finally, m-MnO₂ nanosheets were obtained by centrifugation, repeatedly immediate filtration and drying. Traditionally, preparation of 1 wt% Pt/MnO₂ by chloroplatinic acid impregnation and sodium borohydride in situ reduction.

2.2. Materials characterization

The MnO₂ sample’s structure was analyzed by powder X-ray diffraction (XRD, Malvern Panalytical Aeras PANalytical’s) and transition electron microscopy (TEM, HITACHI HT7700). The specific surface area and pore volume of the catalysts were calculated from the nitrogen adsorption-desorption isotherms using the Brunner-Emmet-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods (Micromeritics ASAP 2020 HD88).

2.3. Catalytic test

The oxidation of toluene over the catalyst was carried out in an isothermal fixed-bed continuous-flow reactor (i.d. = 9.0 mm) to test catalytic reactivity using 0.1 g of catalysts (40–60 mesh) and 0.1 g Quartz sand giving a space velocities of 20,000 h⁻¹ with the total flow rate of 33.3 mL/min. The reactant was toluene/air mixture gas (4 g/m³ toluene in air, 0.1 MPa). Reactants and products were analyzed by gas chromatograph (HP6820, Agilent) with FID detector. The only products were CO₂ and H₂O, and other by-products were not found under most experimental conditions. Thus the conversion was calculated based on toluene consumption.

3. Result and discussion

The XRD pattern of the sample is presented in Fig. 1. It is found that the diffraction peaks at 25.0°, 37.0°, 65.7° were indexed to the (002), (110) and (020) reflections, respectively. This result confirmed the formation of δ-MnO₂ (JCPDS Card No. 87-1497) phase.

![Figure 1. XRD pattern of m-MnO₂ nanosheets.](image)

The TEM image (Fig. 2(a)) of the sample exhibit that the sample is a ultrathin and flat nanosheet-like structure with a size of hundreds of nanometers, but there are also the accumulation of nanosheets (in the darker position), which is related to the single-layer sheet structure. The TEM image also shows that there is a rich planar mesoporous structure in the MnO₂ nanosheet, so the prepared sample are m-MnO₂ nanosheets.

The surface area and pore structure of the MnO₂ nanosheets was analyzed by N₂ adsorption–desorption measurements, as shown in Fig. 2(b). It is identified from the figure that the isotherms of m-MnO₂ nanosheets was type IV, indicating that the mesoporous nature. Moreover, BJH results also indicate that the pores on the MnO₂ nanosheets are basically mesoporous larger than 5nm. The Brunauer-
Emmett-Teller surface area and pore volume of m-MnO$_2$ nanosheets were calculated to be 127.5 m$^2$/g and 0.323 cm$^3$/g, respectively.

![Figure 2. Characterizations of m-MnO$_2$ nanosheets. (a) TEM image of m-MnO$_2$ nanosheets, (b) N$_2$ adsorption/desorption isotherm and corresponding pore size distribution (inset).](image)

The toluene conversion as a function of reaction temperature is shown in Fig. 3. The toluene catalytic activity test of pure m-MnO$_2$ nanosheets without noble metal loading showed that the toluene conversion rate of the sample reached 90% at 240 °C. This indicates that pure m-MnO$_2$ nanosheets have toluene purification activity, but it is not a high-performance catalyst in toluene oxidation reaction.

After Pt was supported on m-MnO$_2$ nanosheets by a conventional in-situ growth method, the activity of catalytically oxidizing toluene obtained by 1.0 wt% Pt/MnO$_2$ was greatly improved, and toluene was completely converted at 170 °C. The m-MnO$_2$ nanosheets loaded with Pt exhibited superior performance in catalytic oxidation of toluene. This is due to the rich mesoporous structure and high BET specific surface area on the m-MnO$_2$ nanosheet, which is beneficial not only for the diffusion and adsorption of toluene in the catalyst, but also facilitates the uniform dispersion of Pt surface active components in the m-MnO$_2$ nanosheets carrier. This resulted in 1.0 wt% Pt/MnO$_2$ after loading Pt capable of catalytically oxidizing toluene at lower reaction temperatures.

![Figure 3. Toluene conversion as a function of reaction temperature on Pt/MnO$_2$ catalysts](image)

4. Conclusion
A kind of m-MnO$_2$ nanosheets containing a rich mesoporous structure was prepared by template method. The 1.0 wt% Pt/MnO$_2$ catalyst prepared by in-situ growth method on manganese dioxide has good catalytic activity for toluene oxidation, and conversion of toluene at a lower reaction temperature of 160 °C exceeds 90% (SV= 20,000 h$^{-1}$). The unique structure of m-MnO$_2$ nanosheets make it an excellent
carrier. The rich mesoporous structure and high surface area are conducive to the preparation of Pt/MnO$_2$ catalysts with high-performance for the toluene oxidation.

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