Toluene Conversion by Using Different Morphology MnO₂ Catalyst

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ABSTRACT

MnO₂ was one of the important catalysts for the degradation of organic compounds. MnO₂ with different morphology (nanotube, nanowire, nanocubic and nanoflower) were synthesized by hydrothermal method using KMnO₄ and MnSO₄ as precursors. Firstly, their structures were studied by X-ray diffraction (XRD), N₂ adsorption desorption curve, H₂ temperature programmed reduction (H₂-TPR) and X-ray electron spectroscopy (XPS). Next, their catalytic conversion test for toluene was carried out under the condition of toluene concentration of 500 ppm and gas flow rate of 200 mL min⁻¹. The results showed that the crystal structure of nanotube and nanowire were α-MnO₂, nanoflower was α-MnO₂ phase and other crystalline, the nanocube was β-MnO₂. For the different morphology MnO₂, their catalytic conversion activity for toluene were increased with the rise of temperature. Nanotube, nanowire, nanoflower and nanocube reached 100% toluene conversion at 225°C, 250°C, 275°C and 325°C, respectively. MnO₂ nanotube showed the highest activity for toluene among all the samples, which attribute to the larger specific surface area, better low-temperature reduction performance and higher the Mn⁴⁺ content.

Keywords: MnO₂ nanotube, MnO₂ nanowire, MnO₂ nanocube, MnO₂ nanoflower, Toluene conversion

1 INTRODUCTION

Volatile organic compounds (VOCs) emission amount sharply increase, and cause many environmental problems (Liu et al., 2021), such as photochemical smog, haze and so on. Long-terms exposure to the atmospheric environment containing VOCs would cause the damage of respiratory, nervous system, and seriously threaten to the human health (KP Veerapandian et al., 2019). Simultaneously, there are many difficulties in governance them due to their numerous emission sources, multiple levels of emission concentrations and large emissions amount. Therefore, VOCs control has become one of the most important issues on air pollution control. Among the numerous VOCs, toluene was one of the most important contaminants due to its high emission and difficulty of degradation (Schmid et al., 2010). So, it was selected as the target pollutant.

Catalytic oxidation technology, as a high efficient method, was widely used for VOCs elimination. The catalyst was the core part and played critical role in this method. Metallic oxides, such as FeO₃ (Wang et al., 2021), CeO₂ (Fan et al., 2020), Co₃O₄ (Zhang et al., 2021), MnO₂ (Yang et al., 2020b), were deemed as the promising candidates owing to the advantage of highly catalytic performance for VOCs. MnO₂ had catalytic activity toward the VOCs oxidation, which attributed to the variable electronic structure, including the multiple valences of manganese (Mn²⁺, Mn³⁺, and Mn⁴⁺) (Yang et al., 2021a), and the properties of the low cost and environmental compatibility (Phakkhawan et al., 2018).

The catalytic property of MnO₂ was determined by its morphology. The previous work found that the nano-rod MnO₂ had the best-performing catalytic property for the toluene at lower
temperatures due to its higher oxygen species concentration and better low-temperature reducibility (Wang et al., 2012). However, Yang et al. (2020c) research showed that the polymerized flower-like nanosheets MnO₂ presented the higher toluene oxidation activity than nanorod, because this structure was beneficial to the oxygen vacancy formation. While Yang et al. (2021b) revealed that the flower-ball MnO₂ displayed the excellent catalytic activity for toluene because it had the rich oxygen vacancies. Flower like MnO₂ showed the highest Sr²⁺ adsorption capacity as compared to MnO₂ nanotube (Asim et al., 2021), and the hollow tube structure MnO₂ displayed the most active catalyst for phenol removal because of more active sites (Huang et al., 2021). The previous results indicated that the catalytic activity of MnO₂ was related to their morphology, but no consistent results were obtained. Therefore, synthesized MnO₂ nanomaterials with high stability and efficient catalytic activity was conducive to its further application in the VOCs degradation.

To explore the relationship between catalyst morphology and catalytic activity for toluene, MnO₂ nanomaterials with different morphologies were prepared using hydrothermal method, and their conversion for toluene were carried under the different temperatures. At the same time, their morphology and the structure were studied regarding to SEM, XRD, N₂ adsorption-desorption curve, H₂-TPR and XPS.

2 EXPERIMENTS

2.1 MnO₂ Catalysts Preparation

(1) nanotube: 0.900 g KMnO₄ were added to 80 mL deionized water, until completely dissolved, added 2.0 mL hydrochloric acid (37%) under vigorous stirring, the mixed solution was transferred into 100 mL Teflon-lined stainless steel autoclave. and then hydrothermal crystallization was conducted at 110°C for 10 h. The products were washed with deionized water and dried at 80°C overnight.

(2) nanowire: 0.316 g KMnO₄ and 0.453 g MnSO₄ were respectively dissolved into a certain amount of deionized water to obtain 40.0 mL solution A and 40.0 mL solution B. The A solution was added quickly to the B solution under vigorous stirring, then the mixed solution was transferred into 100 mL Teflon-lined stainless steel autoclave, keeping at the temperature of 160°C for 8 h. The products were washed with deionized water and dried at 80°C overnight.

(3) nanocube: 0.679 g MnSO₄ and 0.429 g KClO₃ were dissolved into 20.0 mL deionized water, until completely dissolved, 4.5 mL CH₃COOH were dropwise added into it under the condition of stirring, then constant volume to 60.0 mL, the mixed solution was transferred into 100 mL Teflon-lined stainless steel autoclave, keeping at the temperature of 160°C for 12 h. The products were washed with deionized water and dried at 80°C overnight.

(4) nanoflower: 1.276 g KMnO₄ were dissolved into 20.0 mL deionized water, until completely dissolved, constant volume to 66.0 mL with deionized water, then transferred into 100 mL Teflon-lined stainless steel autoclave, keeping at the temperature of 160°C for 24 h. The products were washed with deionized water and dried at 80°C overnight.

2.2 Characterization

SEM images were obtained from S-3400N electron microscope (Hitachi, Japan).

X-ray powder diffraction (XRD) patterns were gained on the ADVANCE D8 X-ray diffractometer (Bruker, Germany).

N₂ absorption-desorption isotherms were obtained from the BELSORP-mini II (BEL, Japan) at −196°C. Specific surface area was calculated based on Brunauer-Emmett-Teller (BET), the pore size was calculated from the adsorption branches of N₂ physiosorption isotherms and the Barrett-Joyner-Halenda (BJH) model.

H₂-TPR was carried on the Chemisorb 2920 chemical adsorption analyzer (Micromeritics, USA). 50 mg catalyst was pretreated at 300°C using high-purity He for 60 min and then cooled to 60°C. Subsequently, the flow of a H₂-Ar mixture (10% H₂ by volume) was switched on, and the catalyst was heated to 700°C at a rate of 10°C min⁻¹. The H₂ consumption was monitored using a thermal conductivity detector (TCD).

XPS were characterized on ESCALAB 250XI photoelectron spectrometer (Thermo Scientific, USA).
2.3 Catalyst Activity Evaluation

Toluene conversion test was performed in a fixed-bed flow reactor (U-tube, \( \Phi 10 \text{ mm} \times 8 \text{ mm} \)), which contained 0.065 g catalyst (40–60 mesh) and 0.260 g silica sand (40–60 mesh). The toluene vapor was prepared by bubbling dry air into pure liquid toluene (99.5%) kept in constant temperature incubator. Gaseous toluene was fed into mixing chamber and was diluted to 500 ppm by dry air, the mixture gas flow rate was controlled at 200 mL min\(^{-1}\), and then was introduced into the reactor. The gas in the outlet reactor was analyzed by an online GC-MS system (GC-7890B MS-5977B, Agilent) equipped with TG-BOND Q pillar (30 m, 0.32 mm) (Column box temperature: 60°C).

The toluene conversion was calculated as:

\[
\text{Toluene conversion efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100\%
\]

where \( C_0 \) and \( C \) were the inlet and outlet concentrations of toluene, respectively.

3 RESULTS AND DISCUSSION

3.1 SEM

The SEM of different morphology MnO\(_2\) were shown in the Fig. 1. MnO\(_2\) nanotube was successfully prepared via the facile hydrothermal process with participation of KMnO\(_4\) and HCl at the temperature of 110°C for 10 h (Figs. 1(A) and 1(B)), While MnO\(_2\) flower could be synthesized at the temperature of 110°C and the condition of KMnO\(_4\) and HCl (Asim \textit{et al.}, 2021), but that the reaction time was only 40 min, which was much lower than 10 h in this study. This may be explained that the particles rapid self-assembly around the small nuclei and formatted the amorphous spheres in the short time (Asim \textit{et al.}, 2021), however, nanosheet could curl to format nanotube with the reaction time prolonged. The SEM images of MnO\(_2\) nanotube also showed that the pipe orifice was smooth and flat, the inner and outer diameter was respective about 30 nm and 70 nm, and the length of nanotube was about 1.07 \( \mu \text{m} \), in addition, its size was relatively uniform.

MnO\(_2\) nanowire was obtained through the hydrothermal treatment of a MnSO\(_4\)-KMnO\(_4\) mixture at the temperature 160°C for 8 h (Figs. 1(C) and 1(D)), and showed that its size was relatively uniform, the diameter and the length was about 40 nm and 2.5 \( \mu \text{m} \), respectively. MnO\(_2\) nanocube was synthesized via the hydrothermal method in the presence of MnSO\(_4\) and KClO\(_3\) under the temperature of 160°C for 12 h (Figs. 1(E) and 1(F)), but the size was uneven, and a certain number of particles appeared around the cube, indicating that a certain amount of amorphous MnO\(_2\) were formed during the process of hydro-thermal synthesis. The MnO\(_2\) flower was prepared via oxidation-reduction of KMnO\(_4\) itself at the hydrothermal temperature of 160°C for 24 h (Figs. 1(G) and 1(H)).

3.2 XRD

XRD patterns of different MnO\(_2\) nanomaterials were provided in Fig. 2. The results showed that MnO\(_2\) nanotube and MnO\(_2\) nanowire were correspond to the \( \alpha \)-MnO\(_2\) (PDF#44-0141), nanocube was correspond \( \beta \)-MnO\(_2\) (PDF#24-0735), while nanoflower was correspond to the \( \alpha \)-MnO\(_2\) and others phase. At the same time, different morphology MnO\(_2\) all exhibited higher peak intensity and without any impurity, indicating that high purity and crystallinity of MnO\(_2\) were prepared by the one-step hydrothermal method under the condition of facile.

3.3 Catalytic Performance and Catalytic Stability

The toluene conversion efficiency in the range of 150°C–325°C on the surface of different morphology MnO\(_2\) were shown in the Fig. 3(a). With temperature increased, the toluene conversion efficiency also increased, and reached 100% conversion efficiency within 225°C–275°C. However, the performance on the different catalysts showed the significant difference, the nanocube reached the 100% conversion efficiency was at 325°C, which was higher than others nano-MnO\(_2\). The temperature of 100% toluene conversion followed the sequence: MnO\(_2\) nanotube (225°C) < MnO\(_2\) nanowire (250°C) < MnO\(_2\) nanoflower (275°C) < MnO\(_2\) nanocube (325°C). Note that MnO\(_2\) nanotube exhibited highest conversion rates of toluene.
Since MnO₂ nanotube had the best catalytic activity, it was necessary to estimate the stability of the catalyst. Toluene conversion over MnO₂ nanotube was carried out at the temperature of 225°C for 60 h, and the result was displayed in Fig. 3(b). With increasing the reaction time, toluene conversion efficiency did not appear obvious attenuation during 60 h-test, indicating that the activity of MnO₂ nanotube did not significantly change during the specific period.

3.4 N₂ Adsorption-Desorption

The N₂ adsorption-desorption isotherms were shown in the Fig. 4, their BET specific surface areas and diameter were summarized in Table 1. All the catalysts showed the typical type IV isotherm, indicated that the synthesized MnO₂ materials had mesoporous (Yamaguchi et al., 2020).
Fig. 2. XRD patterns of different morphology MnO₂.

Fig. 3. Profile of (a) toluene conversion over different morphology MnO₂ nanomaterials and (b) catalyst stability during 60 h continuous test over MnO₂ nanotube (The reaction condition: 500 ppm toluene + balance synthetic air with total flow rate of 200 mL min⁻¹, 0.065 g catalyst + 0.26 g silica).

And all the catalyst possessed H₃ type hysteresis loop, while the relative pressure of hysteresis loop in nanoflower was high, which indicated that the MnO₂ channel in nanoflower was wide and the channel structure was irregular.

The results showed that the specific surface areas (Table 1) decreased the order of MnO₂ nanotube (55.47 m² g⁻¹) > MnO₂ nanowire (31.74 m² g⁻¹) > MnO₂ nanoflower (13.05 m² g⁻¹) > MnO₂ nanocube (2.91 m² g⁻¹), which was consistent with the conversion of toluene. In general, for a catalyst, the larger specific surface area might have more active site, resulted the better of catalytic activity (Yang et al., 2020a), which benefit to the toluene conversion. This result indicated that the larger specific surface area was a main reason for MnO₂ catalytic activity to toluene.
MnO₂ nanotube had a hollow structure, which was helpful to expose more active sites, so it showed the best catalytic activity for toluene. In addition, compared with other MnO₂ crystal forms, α-MnO₂ had the rich lattice oxygen species and reducible properties, therefore MnO₂ nanotube (α-MnO₂, Fig. 2) had the highest activity for the toluene conversion.

### 3.5 H₂-TPR

The reduction ability of the different morphology MnO₂ catalysts were conducted by H₂-TPR (Fig. 5). For all the catalysts, there were two H₂ consumption peaks occurring at 150°C–300°C and 300°C–400°C, which were attributed to stepwise reduction of MnO₂ to Mn₃O₄ and, ultimately, to MnO. The temperature of first reduction peaks followed the sequence of nanoflower (271°C) < nanotube (278°C) < nanowire (285°C) < nanocube (292°C), while the H₂ consumption amount was lower for nanoflower than nanotube, thus nanotube had the better low temperature redox performance than nanoflower. Another hand, the temperature of second reduction peak followed the sequence nanotube (289°C) < nanowire (300°C) < nanoflower (348°C) < nanocube (385°C), which was consistent with the performance of toluene conversion (Fig. 3(a)). Notably, the reduction temperature of Mn species in MnO₂ nanotube were lower than others MnO₂ nanomaterials, demonstrating that the MnO₂ nanotube catalyst displayed better low-temperature reducibility performance, which was favorable for the toluene decomposition.

### 3.6 XPS

XPS spectra was employed to study the oxygen species and chemical states of Manganese ions on the catalyst surface. The oxygen species of these different morphology MnO₂ were shown in Fig. 6(a) and Table 2. As displayed in Fig. 6(a), lattice oxygen (O₉₅), surface absorbed (O₉₆) and surface hydroxyl oxygen (O₉₇) peaks could be deconvoluted from the O1s spectra, peaks at 529.7 eV, 531.4 eV, 533 eV could be assigned to O₉₅, O₉₆, O₉₇, respectively (Chen et al., 2020; Yang et al., 2020b). From the result of Table 2, we could see that the proportion of O₉₅ followed the order of nanotube > nanowire > nanocube > nanoflower, which was agreement with the
Fig. 5. H$_2$-TPR profile of different morphology MnO$_2$ catalysts.

Fig. 6. XPS spectra of different morphology MnO$_2$ nanomaterials (a) O 1s and (b) Mn 2p$_{3/2}$. 
Table 2. The chemical state of Mn and O in different morphology MnO2 catalysts.

|          | O latt (%) | O ads (%) | Oads-OH (%) | Mn2+ (%) | Mn3+ (%) | Mn4+ (%) |
|----------|------------|-----------|-------------|----------|----------|----------|
| nanotube | 79.54      | 15.7      | 4.76        | 6.17     | 51.54    | 42.29    |
| nanowire | 76.04      | 23.96     | ——          | 9.15     | 52.97    | 37.88    |
| nanocube | 74.57      | 25.43     | ——          | 39.14    | 33.89    | 26.96    |
| nanoflower | 73        | 23.15     | 3.87        | 13.22    | 50.63    | 36.15    |

Table 2. The chemical state of Mn and O in different morphology MnO2 catalysts.

Toluene conversion efficiency. Researches indicated that the surface adsorbed oxygen played a decisive role in the degradation of VOCs (Du et al., 2018; Sun et al., 2018), due to its better mobility than the lattice oxygen. While the Mn4+ on surface of catalyst might result in the charge imbalance, could produce a large amount of adsorbed oxygen species and unsaturated chemical bonds on the catalyst surface (Zhao et al., 2019; Mo et al., 2020), consequently promoted the oxidation of pollutants. Therefore, even the proportion of surface adsorbed oxygen in the nanotube was the lowest (Table 2), while the Mn4+ proportion on the MnO2 nanotube surface was the highest (Table 2), resulted the nanotube had the best catalytic conversion for toluene. Tang et al. (2006) and Huang et al. (2019) also found the Mn4+ species could promoted complete HCHO oxidation on the catalyst of Ag/MnO2 surface.

At the same time, the O latt peak of MnO2 nanocube slightly shifted to lower binding energy, indicating that the electron cloud density of oxygen was greater, this phenomenon would result the inertization of surface oxygen species (Wang et al., 2017; Yang et al., 2020c). Therefore, the catalytic performance of MnO2 nanocube for toluene was lower than others MnO2 catalysts. Surface hydroxyl oxygen might also play an important role in VOCs oxidation (Chen et al., 2020), so although the surface adsorbed oxygen in nanoflower had no significant higher than that in nanocube, there was no hydroxyl oxygen in the nanocube, therefore the conversion efficiency of nanoflower for toluene was higher than nanocube.

4 CONCLUSION

1) Nanotube, nanowire, nanocube and nanoflower were prepared by hydrothermal method using KMnO4 and MnSO4 as precursors. The crystal structure of nanotube and nanowire were α-MnO2, nanoflower was α-MnO2 phase and others crystalline, and the nanocube was β-MnO2.

2) The toluene conversion efficiency increased with the increase of temperature. Nanotube, nanowire, nanoflower and nanocube reached 100% toluene conversion at 225°C, 250°C, 275°C and 325°C, respectively. MnO2 nanotube showed the highest activity for toluene conversion among all samples, which probably due to the larger of specific surface area, the better of low-temperature reduction and the higher of Mn4+ content.

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