Toluene Conversion by Using Different Morphology MnO₂ Catalyst

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ABSTRACT

MnO_x 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

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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 FeO_x (Wang *et al.*, 2021), CeO₂ (Fan *et al.*, 2020), Co₃O₄ (Zhang *et al.*, 2021), MnO_x (Yang *et al.*, 2020b), were deemed as the promising candidates owing to the advantage of highly catalytic performance for VOCs. MnO_x 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 MnO_2 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 MnO_2 displayed the excellent catalytic activity for toluene because it had the rich oxygen vacancies. Flower like MnO_2 showed the highest Sr^{2+} adsorption capacity as compared to MnO_2 nanotube (Asim *et al.*, 2021), and the hollow tube structure MnO_2 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 MnO_2 was related to their morphology, but no consistent results were obtained. Therefore, synthesized MnO_2 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, MnO_2 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, N_2 adsorption-desorption curve, H_2 -TPR and XPS.

2 EXPERIMENTS

2.1 MnO_2 Catalysts Preparation

- (1) nanotube: 0.900 g KMnO_4 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 KMnO_4 and 0.453 g MnSO_4 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 MnSO_4 and 0.429 g KClO_3 were dissolved into 20.0 mL deionized water, until completely dissolved, 4.5 mL CH_3COOH 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 KMnO_4 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).

N_2 adsorption-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 N_2 physisorption isotherms and the Barrett-Joyner-Halenda (BJH) model.

H_2 -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 H_2 -Ar mixture (10% H_2 by volume) was switched on, and the catalyst was heated to 700°C at a rate of $10^\circ\text{C min}^{-1}$. The H_2 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, ϕ 10 mm $\times$ 8 mm), which contained 0.065 g catalyst (40–60 mesh) and 0.260 g silicasand (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:

$$\text{Toluene conversion efficiency (\%)} = \frac{C_0 - C}{C_0} \times 100\% \quad (1)$$

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 MnO₂ were shown in the Fig. 1. MnO₂ nanotube was successfully prepared via the facile hydrothermal process with participation of KMnO₄ and HCl at the temperature of 110°C for 10 h (Figs. 1(A) and 1(B)), While MnO₂ flower could be synthesized at the temperature of 110°C and the condition of KMnO₄ and HCl (Asim *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 *et al.*, 2021), however, nanosheet could curl to format nanotube with the reaction time prolonged. The SEM images of MnO₂ 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 μ m, in addition, its size was relatively uniform.

MnO₂ nanowire was obtained through the hydrothermal treatment of a MnSO₄-KMnO₄ 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 μ m, respectively. MnO₂ nanocube was synthesized via the hydrothermal method in the presence of MnSO₄ and KClO₃ 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 MnO₂ were formed during the process of hydro-thermal synthesis. The MnO₂ flower was prepared via oxidation-reduction of KMnO₄ itself at the hydrothermal temperature of 160°C for 24 h (Figs. 1(G) and 1(H)).

3.2 XRD

XRD patterns of different MnO₂ nanomaterials were provided in Fig. 2. The results showed that MnO₂ nanotube and MnO₂ nanowire were correspond to the α -MnO₂ (PDF#44-0141), nanocube was correspond β -MnO₂(PDF#24-0735), while nanoflower was correspond to the α -MnO₂ and others phase. At the same time, different morphology MnO₂ all exhibited higher peak intensity and without any impurity, indicating that high purity and crystallinity of MnO₂ 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 MnO₂ 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-MnO₂. The temperature of 100% toluene conversion followed the sequence: MnO₂ nanotube (225°C) < MnO₂ nanowire (250°C) < MnO₂ nanoflower (275°C) < MnO₂ nanocube (325°C). Note that MnO₂ nanotube exhibited highest conversion rates of toluene.

Fig. 1. The SEM of different morphology MnO_2 : (A, B) nanotube, (C, D) nanowire, (E, F) nanocube, (G, H) nanoflower.

Since MnO_2 nanotube had the best catalytic activity, it was necessary to estimate the stability of the catalyst. Toluene conversion over MnO_2 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 MnO_2 nanotube did not significantly change during the specific period.

3.4 N_2 Adsorption-Desorption

The N_2 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 MnO_2 materials had mesoporous (Yamaguchi *et al.*, 2020).

Fig. 2. XRD patterns of different morphology MnO_2 .

Fig. 3. Profile of (a) toluene conversion over different morphology MnO_2 nanomaterials and (b) catalyst stability during 60 h continuous test over MnO_2 nanotube (The reaction condition: 500 ppm toluene + balance synthetic air with total flow rate of 200 mL min^{-1} , $0.065 \text{ g catalyst} + 0.26 \text{ g silica}$).

And all the catalyst possessed H_3 type hysteresis loop, while the relative pressure of hysteresis loop in nanoflower was high, which indicated that the MnO_2 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 MnO_2 nanotube ($55.47 \text{ m}^2 \text{ g}^{-1}$) > MnO_2 nanowire ($31.74 \text{ m}^2 \text{ g}^{-1}$) > MnO_2 nanoflower ($13.05 \text{ m}^2 \text{ g}^{-1}$) > MnO_2 nanocube ($2.91 \text{ m}^2 \text{ g}^{-1}$), 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 MnO_2 catalytic activity to toluene.

Fig. 4. N₂-adsorption/desorption isotherms of different morphology MnO₂ nanomaterials.

Table 1. Structural properties of different morphology MnO₂ nanomaterials.

	S_{BET} (m ² g ⁻¹)	Average pore size (nm)
nanotube	55.47	16.82
nanowire	31.74	13.11
nanocube	2.91	15.18
nanoflower	13.05	30.10

MnO₂ nanotube had a hollow structure, which was helpful to exposes 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 (O_{latt}), surface adsorbed (O_{ads}) and surface hydroxyl oxygen (O_{adsO-H}) peaks could be deconvoluted from the O1s spectra, peaks at 529.7 eV, 531.4 eV, 533 eV could be assigned to O_{latt}, O_{ads}, O_{adsO-H}, respectively (Chen *et al.*, 2020; Yang *et al.*, 2020b). From the result of Table 2, we could see that the proportion of O_{latt} followed the order of nanotube > nanowire > nanocube > nanoflower, which was agreement with the

Fig. 5. H₂-TPR profile of different morphology MnO₂ catalysts.

Fig. 6. XPS spectra of different morphology MnO₂ 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			Mn		
	O _{latt} (%)	O _{ads} (%)	O _{adsO-H} (%)	Mn ²⁺ (%)	Mn ³⁺ (%)	Mn ⁴⁺ (%)
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

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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