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In-plasma catalytic degradation of toluene over different MnO₂ polymorphs and study of reaction mechanism

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ABSTRACT

α -, β -, γ - and δ -MnO₂ catalysts were synthesized by a one-step hydrothermal method, and were utilized for the catalytic oxidation of toluene in a combined plasma-catalytic process. The relationship between catalytic performance and MnO₂ crystal structures was investigated. It was noted that the toluene removal efficiency was 32.5% at the specific input energy of 160 J/L when non-thermal plasma was used alone. The α -MnO₂ catalyst showed the best activity among the investigated catalysts, yielding a toluene conversion of 78.1% at the specific input energy of 160 J/L. For β -MnO₂, γ -MnO₂ and δ -MnO₂, removal efficiencies of 47.4%, 66.1% and 50.0%, respectively, were achieved. By powder X-ray diffraction, Raman spectroscopy, transmission electron microscopy, scanning electron microscopy, Brunauer-Emmett-Teller, H₂ temperature-programmed reduction and X-ray photoelectron spectroscopy analyses, it was concluded that the tunnel structure, the stability of the crystal in plasma, the Mn–O bond strength of MnO₂ and the surface-chemisorbed oxygen species played important roles in the plasma-catalytic degradation of toluene. Additionally, the degradation routes of toluene in non-thermal plasma and in the plasma-catalytic process were also studied. It was concluded that the introduction of MnO₂ catalysts enabled O₃, O₂, electrons and radical species in the gas to be adsorbed on the MnO₂ surface via a facile interconversion among the Mn⁴⁺, Mn³⁺ and Mn²⁺ states. These four species could then be transported to the toluene or intermediate organic by-products, which greatly improved the toluene removal efficiency and decreased the final output of by-products.

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1. Introduction

Toluene, a typical volatile organic compound (VOC), is

emitted from architectural coatings, motor vehicles and various industrial processes [1,2], and is an important precursor for forming PM_{2.5}, O₃ and photo-chemical smog, which are harm-

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ful to the environment and human health [3–5]. Over the decades, numerous technologies have been developed to limit the emission of VOCs, using techniques such as adsorption, photocatalysis, catalytic combustion, bio-decomposition and membrane separation [6–9]. In recent years, non-thermal plasma (NTP) for the degradation of VOCs has attracted significant attention because of its high efficiency in the removal of VOCs at ambient temperature and pressure. This technology functions through the generation of hard electrons, active oxygen species, hydroxyl radicals and energetic nitrogen species to oxidize the VOCs [10–12]. However, high energy consumption by the plasma and large amounts of by-products have significantly limited its industrial applications [13,14]. A promising strategy to overcome these drawbacks is the combination of NTP and catalysis, which has the potential to enhance the reaction rate, product selectivity and energy utilization ratio [15–17]. The catalysts used thus far in combined plasma-catalytic systems include various metallic oxides, such as those of Mn [13,15–18], Co [19,20], Ni [18], Ti [13,19], Cu [18,20], Ag [16,17], Fe [11,18] and Ce [18–20]. The active oxygen species generated from the decomposition of O_3 , such as atomic oxides and superoxide radicals, are reported to play important roles in the oxidation of VOCs in plasma-catalytic processes [10,21], while among the transition metal oxides, MnO_2 is among the most active for the decomposition of O_3 [22,23]. MnO_2 shows a wide diversity of phase structures, crystal morphologies and tunnel structures, which significantly influence its catalytic performance [24–27]. As such, the effect of MnO_2 phase structures on the plasma-catalytic degradation of VOCs merits detailed investigation.

In this work, α -, β -, γ - and δ - MnO_2 catalysts were synthesized by a one-step hydrothermal method. The relationship between the plasma-catalytic performance of toluene degradation and the different phase structures of MnO_2 was investigated. A surface dielectric barrier discharge (SDBD) reactor was utilized to produce the plasma. The catalysts and plasma were then combined in an in-plasma catalytic system by placing the catalysts in the SDBD reactor. Powder X-ray diffraction (XRD), Raman spectroscopy (Raman), scanning electron microscopy (SEM), transmission electron microscopy (TEM), the Brunauer-Emmett-Teller (BET) method, H_2 temperature-programmed reduction (H_2 -TPR) and X-ray photoelectron spectroscopy (XPS) were used to evaluate the relationship between the phase structure and plasma-catalytic performance. The by-products of toluene degradation in the plasma-catalytic system were analyzed to deduce the reaction mechanism of toluene over the MnO_2 catalysts.

2. Experimental

2.1. Catalyst preparation

Four different phase structures of MnO_2 were synthesized by the hydrothermal process as described in previous reports [25,27,28]. All reagents were of analytical grade and used without further treatment. For the preparation of α - MnO_2 [29], 2.37 g $KMnO_4$ was dissolved in 0.4 mol/L CH_3COOH solution

(150 mL). After stirring magnetically for about 0.5 h to form a homogeneous solution, it was transferred to a Teflon-lined stainless steel autoclave (200 mL), sealed and maintained at 140 °C for 12 h in an oven. Thereafter, the autoclave was naturally cooled to room temperature and the sediment in the solution was washed with distilled water and ethanol several times, and dried at 80 °C for about 12 h. Similar to the α - MnO_2 , for the preparation of β - MnO_2 , 6.42 g $(NH_4)_2S_2O_8$ and 3.17 g $MnSO_4 \cdot H_2O$ were mixed in 150 mL distilled water at 150 °C for 16 h. To obtain γ - MnO_2 [30], 6.32 g $MnSO_4 \cdot H_2O$ was reacted with 8.578 g $(NH_4)_2S_2O_8$ at 90 °C for 24 h. The δ - MnO_2 was obtained from the reaction of 0.52 g $MnSO_4 \cdot H_2O$ and 2.81 g $KMnO_4$ at 200 °C for 24 h [27].

2.2. Catalyst characterizations

Nitrogen adsorption apparatus (JW-BK132F, Beijing JWGB Sci. & Tech. Co., Ltd, Beijing, China) was used to measure the specific surface area and pore characteristics by the multipoint BET method. The samples were preprocessed at 200 °C prior to the measurements.

The microstructures and morphologies of the prepared samples were investigated by SEM (Ultra 55, Carl Zeiss AG, USA) and TEM (JEM-2010, Japan). Samples were prepared by coating the powder onto a conductive tape for the SEM measurements. For the TEM measurements, samples were prepared by dispersing the powder in ethanol solvent and dropping onto the membrane.

Powder XRD was conducted using a powder diffractometer with $Cu K\alpha$ radiation (Model D/max RA, Rigaku Co., Japan). The data were collected at scattering angles (2θ) ranging from 10° to 80° with a step size of 0.02°.

H_2 -TPR measurements were conducted on a Chemisorption Analyzer equipped with a custom-made thermal conductivity detector (TCD). Prior to the measurement, a precisely weighed 50 mg sample was purged with He at 200 °C for 1 h and then naturally cooled to room temperature, then purged with N_2 containing 6% H_2 (30 mL/min) and heated from 100 to 600 °C at a linear heating rate of 10 °C/min.

XPS was performed using a Thermo ESCALAB 250 instrument, with Al $K\alpha$ X-ray radiation ($h\nu = 1486.6$ eV) at 150 W as the excitation source. The data were corrected by setting the binding energy of adventitious carbon (C 1s) at 285.0 eV.

Raman spectroscopy was performed at room temperature with a resolution of approximately 0.6 cm^{-1} using an SPEX-1403 laser. A back-scattering configuration was used to excite the crystals with an Ar-ion laser at a wavelength of 514.5 nm (Raman: Lab RAM-HR, SPEX-1403, France).

2.3. Plasma-catalytic activity and by-product measurements

Fig. 1 shows a schematic diagram of the experimental setup, which consisted of three parts: a tubular plasma-catalytic reactor (volume = 140 mm × 50 mm × 30 mm), a reaction gas supply system and an analytical instrument. Two planar SDBD generators were installed on the top and bottom plates of the tubular plasma-catalytic reactor, respectively. The SDBD gen-

Fig. 1. Schematic diagram of the experimental setup.

erator (Fig. 2) consisted of three parts: a quartz glass plate (170 mm × 80 mm × 1 mm) as the dielectric, a high-voltage electrode (copper plate, 140 mm × 50 mm × 1 mm) and a grounded electrode (stainless steel net, 160 mm × 70 mm × 1 mm). The SDBD plasma was generated using a pulsed power supply system created in-house. Fig. 3 shows a simplified circuit diagram of the system, which was based on fast MOSFETs, and could produce high-voltage pulses with a peak voltage up to 6 kV and a width of 1–4 μs at a repetition rate of up to 30 kHz. The pulse energy was up to 30 mJ/pulse, and the average power was up to 1 kW. Twelve frosted-glass slides (160 mm × 28 mm × 1.25 mm) for the loading of catalysts were vertically placed in the cavity of the tubular plasma-catalytic reactor. The catalysts were coated onto the glass slides using a dip-coating method, with 0.3 g catalyst used for each glass slide in each test. The gas stream was composed of $(120 \pm 5) \times 10^{-4}\%$ toluene, 20 vol% O₂ and 80 vol% N₂ (total flow rate = 2 L/min), and was mixed in a mixing chamber (0.5 L) before entering the reactor. The experiments were carried out at atmospheric pressure and ambient temperature, and the decomposition experiments using the plasma were initiated when the concentration of toluene at the outlet reached a steady state (i.e., the concentration at the outlet was approximately the same as at the inlet). The results of blank experiments indicated that the four catalysts had no capacity for the catalytic oxidation of toluene when used alone.

The concentration of toluene and production of CO/CO₂ were evaluated on-line using a chromatograph (GC, PuxiG5, China) equipped with two flame ionization detectors and a

Fig. 3. Simplified circuit diagram of pulsed power supply.

nickel converting equipment for the determination of CO/CO₂. The O₃ and NO_x concentrations were determined by an O₃ detector (UV-100, Eco Sensors, USA) and NO_x detector (Photon II + PGD100, Madur, Austria).

The off-gas contained various gaseous products, which were captured using an adsorption tube (Tenax TA/Tenax GR) at the specific input energy (SIE) of 160 J/L for 30 min. The adsorbed compounds were released and injected into a GC/MS (Agilent 7890A GC equipped with an Agilent 5975C MS) using a thermal desorption instrument (TDI, PERSEE-TP7, China).

The SIE in the tubular plasma-catalytic reactor, toluene removal efficiency (η , %), carbon dioxide yield and carbon monoxide yield (CO_x yield, %) were calculated as follows. The waveform, current and voltage were obtained using a digital oscilloscope (TDS 2012C, Tektronix), current probe (CP8030A, Zhiyong) and high-voltage probe (P6015A, Tektronix), respectively.

$$\text{SIE (J/L)} = P/Q = \text{discharge power (W)} \times 60 \text{ (s/min)} / \text{total flow rate (L/min)} \quad (1)$$

$$P \text{ (W)} = E \times f = \text{input energy (J)} \times \text{frequency (Hz)} \quad (2)$$

$$E(\text{J}) = \int_0^T u(t) \times i(t) dt = \int_0^{\text{one-pulse time}} \text{transient voltage (V)} \times \text{transient current (A)} dt \quad (3)$$

$$\eta = [C(\text{C}_7\text{H}_8)_{\text{inlet}} - C(\text{C}_7\text{H}_8)_{\text{outlet}}] / C(\text{C}_7\text{H}_8)_{\text{inlet}} \times 100\% \quad (4)$$

$$\text{CO}_x \text{ yield} = [C(\text{CO}) + C(\text{CO}_2)] / 7C(\text{C}_7\text{H}_8)_{\text{inlet}} \times 100\% \quad (5)$$

3. Results and discussion

3.1. Toluene decomposition performance

3.1.1. Toluene removal efficiency

The toluene removal efficiencies of the four MnO₂ polymorphs via plasma-catalytic degradation are depicted in Fig. 4 as a function of the SIE. In this figure, we can see that the removal efficiencies improved as the SIE was increased, regardless of the catalyst. When the NTP was used alone, the toluene removal efficiency was 32.5 % at the SIE of 160 J/L. In comparison, when the four MnO₂ polymorphs were introduced, the removal efficiencies over α -MnO₂, β -MnO₂, γ -MnO₂ and δ -MnO₂ increased to ca. 78.1%, 47.4%, 66.1% and 50.0%, respectively, at the SIE of 160 J/L. Thus, the introduction of catalysts into the plasma significantly improved the toluene removal efficiency, with α -MnO₂ affording the greatest improvement.

3.1.2. CO_x yield, NO_x concentration and O₃ concentration

The CO_x yield, the amount of NO_x generated and the concen-

Fig. 2. (a) General scheme for plasma; (b) Photograph of plasma in planar reactor.

Fig. 4. Toluene removal efficiency in the plasma-catalytic systems and plasma alone.

tration of O_3 generated by plasma alone and by the plasma-catalytic processes with different catalysts are illustrated in Fig. 5. Like the toluene removal efficiencies, the CO_x yields also increased with increasing SIE, regardless of the catalyst (Fig. 5(a)). With the introduction of the MnO_2 catalysts, the CO_x yields of the plasma-catalytic systems were greatly improved, in particular for α - MnO_2 . The generation of NO_x and O_3 with and without the catalysts are shown in Figs. 5(b) and (c), respectively. NO_x was generated by the reaction between N_2 and O_2 in the discharge zone of the NTP reactor [31,32], and the amount increased with increasing SIE. The concentration of NO_x generated in our experiments was similar to previously reported values [33,34]. Fig. 5(c) presents the O_3 production in the plasma system and the amount of residual O_3 in the plasma-catalytic systems as a function of the SIE, showing positive correlations between the O_3 production and the SIE values. The O_3 production increased from $200 \times 10^{-4}\%$ to $1000 \times 10^{-4}\%$ when the SIE was increased from 50 to 350 J/L. O_3 is reported [10] to play a significant role in the degradation of toluene. The in-situ decomposition of O_3 leads to the formation of atomic oxygen, which can react with pollutants. However, the residual

O_3 in the exhaust gas is itself a source of secondary air pollution, so its amount must be carefully controlled. As shown in Fig. 5(c), the introduction of the MnO_2 catalysts heavily reduced the concentration of residual O_3 , except in the case of β - MnO_2 . Comparison of the toluene removal efficiencies in Fig. 4 with the residual O_3 concentrations in Fig. 5c indicates that the adsorption of O_3 at the catalyst surface played a key role in the degradation of toluene. The decomposition of O_3 proceeds through two kinetically irreversible steps, i.e., the adsorption of O_3 on the catalyst surface and the desorption of O_2 . The intermediate products of this reaction are peroxide species, which in turn react with toluene [22].

3.2. Characterizations

3.2.1. Tunnel structure, crystal structure and morphology of MnO_2 catalysts

The catalytic performances of the MnO_2 catalysts were closely related to their physical and chemical properties. As reported [26,35], all of the different MnO_2 polymorphs are built from units of edge-sharing MnO_6 octahedra. Depending on the different ways in which the MnO_6 octahedra are interlinked, the resulting crystal phase structures are composed of different proportions of tunnels or interlayers [26,35]. The crystal phase structure of α - MnO_2 consists of one-dimensional (2×2) and (1×1) tunnels, which are composed of double chains of edge-sharing MnO_6 octahedra, and stabilized by K^+ or H_3O^+ [36,37]. The pyrolusite form, β - MnO_2 ($P4_2/mnm$), is the densest and most stable polymorph of MnO_2 , having a rutile-type structure with an infinite chain of MnO_6 octahedra sharing opposite edges. Each chain is corner-linked with four like chains, as a consequence of the formation of (1×1) channels in the β - MnO_2 structure [37,38]. The structure of γ - MnO_2 is characterized by the random intergrowth of pyrolusite layers (1×1 channels) and a ramsdellite matrix (2×1 channels), in which the basic building blocks of MnO_6 octahedra share the edges and corners. As a result, the structure of γ - MnO_2 is the most complex [30,39]. Finally, δ - MnO_2 is constructed from sheets of edge-sharing MnO_6 octahedra forming a 2D layer structure, separated by layers of OH^- , K^+ or H_2O [40].

Fig. 5. Toluene degradation in the plasma-catalytic systems or plasma alone. (a) CO_x yield; (b) Amount of NO_x generated; (c) O_3 concentration.

Chen *et al.* [24] have suggested that the channel structure of MnO_2 catalysts influences their capacity to adsorb oxygen at the surface, which is directly related to the oxidation of NO. Liang *et al.* [25] found that CO molecules were chemisorbed onto MnO_2 nanorods via direct contact with the tunnel structure of the rods, thus greatly influencing the catalytic performance for CO oxidation. Zhang *et al.* [27] concluded that the interlayer structure of MnO_2 was beneficial for the diffusion and adsorption of HCHO molecules, and promoted their oxidation more strongly than the (2×2) tunnel structure. Indeed, our experimental results were in agreement with these reports, the tunnel structure will influence the performance of the catalysts. The toluene removal efficiencies of the different MnO_2 catalysts were linked to the tunnel structure, as discussed below.

The crystallographic structures of the various MnO_2 catalysts were investigated by XRD. The XRD patterns of the used MnO_2 catalysts were also recorded. As shown in Fig. 6, the four MnO_2 catalysts showed different reflections, all of which could be indexed to the respective pure crystal phase (i.e., α - MnO_2 [JCPDS Card No. 44-0141], β - MnO_2 [JCPDS Card No. 24-0735], γ - MnO_2 [JCPDS Card No. 14-0644] and δ - MnO_2 [JCPDS Card No. 80-1098]). The diffraction peaks for α - MnO_2 and β - MnO_2 were much greater in intensity and narrower in width compared with those for γ - MnO_2 and δ - MnO_2 . The poor crystallinity of γ - MnO_2 was mainly attributed to the incorporation of defects during synthesis, which involved a random intergrowth of pyrolusite layers within the ramsdellite matrix [39]. As for δ - MnO_2 , the large set of diffraction peaks indicated a high degree of structural disorder in certain crystallographic directions [41]. The characteristic diffraction peaks remained present in the XRD profiles of all the used catalysts. This verified that the crystal phases of MnO_2 were retained after the plasma-catalytic reaction. However, the positions of the diffraction peaks for δ - MnO_2 were shifted to higher diffraction angles by about 0.2° , revealing a decrease in the d spacing.

Raman spectroscopy was also performed to investigate in more detail the crystal structures of α -, β -, γ - and δ - MnO_2 before and after the reaction. As shown in Fig. 7, the peaks between

Fig. 6. XRD patterns of the four MnO_2 catalysts before and after the reaction.

Fig. 7. Raman spectra of the four MnO_2 catalysts before and after the reaction.

500 and 700 cm^{-1} were assigned to the stretching modes of MnO_6 octahedra. The Raman scattering spectrum of α - MnO_2 , containing K^+ , contained bands at 183, 192, 384, 572, 628 and 748 cm^{-1} [36,42]. The bands at 572 and 628 cm^{-1} originated from the breathing vibrations of MnO_6 octahedra within a tetragonal hollandite-type framework. For β - MnO_2 , one strong band at 643 cm^{-1} and two weak bands at 529 and 750 cm^{-1} were identified as the stretching modes of MnO_6 octahedra [36]. Since the synthetic process for γ - MnO_2 results in a random intergrowth of pyrolusite layers (β - MnO_2) within a ramsdellite (R-MnO_2) matrix, the spectra of γ - MnO_2 consisted of a superposition of the peaks of these two crystal forms of MnO_2 . The sharp band at 630 cm^{-1} and the weak band at 575 cm^{-1} corresponded to R-MnO_2 , and the strong band at 656 cm^{-1} along with the weak band at 530 cm^{-1} corresponded to β - MnO_2 [38]. The Raman spectra of δ - MnO_2 displayed two main bands at around 570 and 638 cm^{-1} . The band at 638 cm^{-1} may have originated from the symmetric stretching vibration (Mn-O) of the MnO_6 groups, and the band at 570 cm^{-1} was identified as the Mn-O stretching of the baseline plane of the MnO_6 sheet [40]. Comparing the Raman spectra of the MnO_2 catalysts before and after the plasma-catalytic reaction, it was found that the peak at around 570 cm^{-1} , which was considered as the Mn-O lattice vibration in the MnO_2 octahedral lattice, decreased in intensity for δ - MnO_2 and increased for γ - MnO_2 . Additionally, the band at around 637 cm^{-1} , which can be assigned to the Mn_3O_4 structure, increased greatly in intensity for β -, γ - and δ - MnO_2 [43]. In contrast, no significant structural change was observed for α - MnO_2 before and after the plasma-catalytic reaction.

The BET specific surface areas (A_{BET}), total pore volumes (V_{pore}) and average pore sizes (D_{pore}) of the different MnO_2 catalysts are summarized in Table 1. It can be seen that δ - MnO_2 had the highest specific surface area and total pore volume among the investigated catalysts, while γ - MnO_2 had the highest average pore size.

The surface structure and morphology of the MnO_2 catalysts were studied by SEM and TEM analyses. As shown in Figs. 8 and Fig. 9, α - MnO_2 , which was composed of uniform nanorods

Table 1

Specific surface areas (A_{BET}), pore volumes (V_{pore}) and average pore sizes (D_{pore}) of the α -, β -, γ - and δ - MnO_2 catalysts.

Catalyst	A_{BET} (m^2/g)	V_{pore} (cm^3/g)	D_{pore} (nm)
α - MnO_2	42.64	0.13	11.35
β - MnO_2	10.02	0.05	10.38
γ - MnO_2	60.89	0.27	14.23
δ - MnO_2	115.98	0.38	10.78

acting as dispersive nanowires, displayed a dendritic nanostructure. The lengths of the nanowires ranged from 0.4 to 1.6 μm , with the diameters ranging from 20 to 40 nm. The panoramic morphology of the β - MnO_2 powder consisted of rod-like crystals, which were 40–200 nm in diameter and 0.4–2 μm in length. As for γ - MnO_2 , it consisted of microparticles with a morphology resembling sea urchins, covered with numerous crystalline and well-ordered nanowires. The nanowires had lengths ranging from 0.9 to 2.0 μm and diameters of around 10–20 nm. δ - MnO_2 displayed a hierarchical architecture with microspherical cores and nanosheet coronas, forming a globular morphology with diameters of 1–2 μm and widths of 10–20 nm.

3.2.2. H_2 -TPR and XPS analyses

The H_2 -TPR profiles of the four MnO_2 catalysts were measured to explore the redox potentials of the catalysts. As shown

in Fig. 10(a), the β - MnO_2 contained two narrow peaks at 314 and 330 $^\circ\text{C}$ and a broad peak at 438 $^\circ\text{C}$. The hydrogen consumption calculated from the lower-temperature peak was double that of the higher-temperature peak. According to previous reports [44,45], the low-temperature peaks originate from the reduction of MnO_2 to Mn_2O_3 and of Mn_2O_3 to Mn_3O_4 , whereas the high-temperature peak was attributed to the reduction of Mn_3O_4 to MnO . The profile of γ - MnO_2 contained three reduction peaks, which were all shifted to slightly to lower temperatures, i.e., 280, 288 and 403 $^\circ\text{C}$, but was otherwise qualitatively similar to that of β - MnO_2 . The areal ratio of the higher-temperature peak to the lower-temperature peak was measured to be around 1:1. The low-temperature peaks and high-temperature peak in this catalyst can be attributed to the reduction of MnO_2 to Mn_2O_3 and of Mn_2O_3 to MnO , respectively. In contrast, the TPR profiles of α - and δ - MnO_2 were very different from those of β - and γ - MnO_2 . α - MnO_2 showed two reduction peaks at 316 and 326 $^\circ\text{C}$. Similarly, δ - MnO_2 exhibited two overlapping reduction peaks at 280 and 300 $^\circ\text{C}$. The detailed reduction process giving rise to these peaks is not clear, but probably involved the reduction of MnO_2 to MnO with the simultaneous reductions of Mn_2O_3 and Mn_3O_4 . For all four MnO_2 polymorphs, the main reduction product was MnO . This was deduced from the observation of green powders after the H_2 -TPR experiments [25]. Based on the H_2 -TPR analyses, it was concluded that the initial reduction temperatures of the four

Fig. 8. SEM images of α - (a), β - (b), γ - (c) and δ - (d) MnO_2 catalysts at different magnifications.

Fig. 9. TEM images of α - (a), β - (b), γ - (c) and δ - (d) MnO_2 catalysts at different magnifications.

Fig. 10. H_2 -TPR profiles (a) and initial H_2 consumption rates (b) of α -, β -, γ - and δ - MnO_2 catalysts.

MnO_2 catalysts decreased in the order of $\gamma \approx \delta > \alpha \approx \beta$. However, the initial H_2 consumption rate per mole of Mn is considered a better indicator for comparing the reducibility of the catalysts [46]. Fig. 10(b) shows the initial H_2 consumption rates per mole of Mn before reduction reached 20% (i.e., before any phase transformation) versus inverse temperature. The results indicate that the initial H_2 consumption rates decreased in the order of $\alpha\text{-MnO}_2 > \beta\text{-MnO}_2 > \delta\text{-MnO}_2 > \gamma\text{-MnO}_2$. Thus, even though $\gamma\text{-MnO}_2$ and $\delta\text{-MnO}_2$ had shown the lowest initial reduction temperatures, $\alpha\text{-MnO}_2$ achieved the highest initial H_2 consumption rate. This might imply that $\alpha\text{-MnO}_2$ possessed better oxygen mobility, allowing more oxygen to be produced and adsorbed on the surface of the catalyst and become available to the plasma-catalytic reaction.

XPS analyses were conducted to identify the superficial elemental species for each catalyst, specifically the surface content of Mn and O. As shown in Fig. 11(a), each catalyst showed two dissymmetric peaks located at 642.2 (Mn $2p_{3/2}$) and 653.9 eV (Mn $2p_{1/2}$). The Mn $2p_{3/2}$ and Mn $2p_{1/2}$ peaks could each be decomposed into two sub-peaks, corresponding to different Mn oxidation states. The sub-peaks located at 641.9 (or 642.1) and

at 653.5 (or 653.7) eV were assigned to $\text{Mn}^{3+}(2p_{3/2})$ and $\text{Mn}^{3+}(2p_{1/2})$ ions, respectively, while the sub-peaks situated at 642.8 and 654.2 eV were assigned to $\text{Mn}^{4+}(2p_{3/2})$ and $\text{Mn}^{4+}(2p_{1/2})$ ions, respectively [27,47]. By quantitative analysis of the Mn $2p$ spectra, the molar ratios of $\text{Mn}^{4+}/\text{Mn}^{3+}$ on the surface were calculated, as presented in Table 2. The different crystal phase structures of the MnO_2 catalysts exhibited clearly different surface $\text{Mn}^{4+}/\text{Mn}^{3+}$ molar ratios, which followed the sequence $\delta\text{-MnO}_2 > \alpha\text{-MnO}_2 > \gamma\text{-MnO}_2 > \beta\text{-MnO}_2$.

The XPS spectra of O 1s are shown in Fig. 11(b). The O 1s spectra could be divided into three regions, wherein the binding energy (BE) in the range of 529.2–530.8 eV was denoted O_{lat} (Mn–O–Mn bond), corresponding to lattice oxygen species; the BE at 531.0–532.6 eV was assigned to oxide defects or surface-chemisorbed oxygen species (O_{sur} , Mn–OH bond), which originated from surface oxygen vacancies; and the BE at 532.6–534.0 eV corresponded to adsorbed molecular water (O_{ads} , H–O–H bond) [48–50]. From Fig. 11(b), it can be seen that O_{lat} , O_{sur} and O_{ads} were located at 529.8 ± 0.2 , 531.6 ± 0.2 and 533.1 ± 0.3 eV, respectively. Relative to the other three catalysts, the O 1s peak of $\beta\text{-MnO}_2$ was shifted by 0.4 eV toward

Fig. 11. XPS spectra of α -, β -, γ - and δ - MnO_2 catalysts. (a) Mn 2p; (b) O 1s.

Table 2Mn 2p binding energy and surface atomic Mn⁴⁺/Mn³⁺ ratio of the α -, β -, γ - and δ -MnO₂ catalysts.

Catalyst	Binding energy (eV)				Molar ratio of Mn ⁴⁺ /Mn ³⁺
	Mn ⁴⁺ (2p _{3/2})	Mn ⁴⁺ (2p _{1/2})	Mn ³⁺ (2p _{3/2})	Mn ³⁺ (2p _{1/2})	
α -MnO ₂	642.8	654.2	642.1	653.7	4.03
β -MnO ₂	642.8	654.2	641.9	653.5	2.40
γ -MnO ₂	642.8	654.2	641.9	653.5	2.99
δ -MnO ₂	642.8	654.2	642.1	653.7	4.25

lower binding energies [24,25,27]. It is well known that surface-chemisorbed oxygen species are more active than lattice-bound oxygen species, and play critical roles in oxidation reactions because of their higher mobility [48,51]. Therefore, the molar ratios of surface-bound oxygen, i.e., $O_{\text{sur}}/O_{\text{lat}}$, were also measured and are given in Table 3. The ratios $O_{\text{sur}}/O_{\text{lat}}$ decreased in the order γ -MnO₂ > α -MnO₂ > β -MnO₂ > δ -MnO₂, which is consistent with the sequence of catalytic activities for toluene oxidation for the four MnO₂ catalysts. In addition, some hydroxyl species were also present on the surface of α -MnO₂.

3.3. Catalytic performance of MnO₂

From the aforementioned results, it can be concluded that the catalytic performance of the different MnO₂ catalysts in the plasma-catalytic reaction was related to the variations in their tunnel structure, crystal phase and other physicochemical properties. The XPS results indicated that the molar ratios of $O_{\text{sur}}/O_{\text{lat}}$ on the catalyst surface decreased in the sequence γ -MnO₂ > α -MnO₂ > β -MnO₂ > δ -MnO₂. The H₂-TPR experiments revealed that α -MnO₂ possessed the highest oxygen mobility. The tunnel structure analyses showed that α -MnO₂ was composed of one-dimensional channels with (2 × 2) and (1 × 1) tunnels, which was beneficial for the adsorption and diffusion of toluene to active sites. The XRD and Raman spectra of fresh and used MnO₂ catalysts suggested that all of the polymorphs except α -MnO₂ underwent structural changes during the plasma-catalytic reaction. All of these results support the designation of α -MnO₂ as the best-performing catalyst in the plasma-catalytic degradation of toluene.

Moreover, it has been reported that the Mn–O bond strength of MnO₂ can also affect the catalytic performance of MnO₂ catalysts [25,37,39]. An increase of the Mn–O bond length indicates a decrease of the bond strength [25]. The average Mn–O bond lengths of the α -, β -, γ - and δ -MnO₂ catalysts [25,37,39] were calculated as 1.98, 1.88, 1.91 and 1.94 Å, respectively. This implies that the Mn–O bond strengths increase in the order: α -

δ - < γ - < β -MnO₂. Thus, the Mn–O bond is most easily broken in the reaction of α -MnO₂, which hence showed the best catalytic performance among the tested MnO₂ oxides.

3.4. By-product generation in off-gases and proposed degradation mechanism of toluene in plasma-catalytic process

To identify the by-products generated in the off-gases from the toluene degradation process, GC-MS measurements were conducted during the reactions with sole NTP or the combined plasma-catalysts with α -, β -, γ - and δ -MnO₂. The reaction SIE was set at 160 J/L to ensure the conversion of toluene and the generation of sufficient detectable by-products. In each experiment, an adsorption column was used to collect the outlet gas for 30 min, and the gas was then desorbed in a thermal analyzer equipped with a GC-MS for subsequent analyses. As shown in Fig. 12, the main products included carbon dioxide (CO₂), 2-methylpropene (C₄H₈), ethane (C₂H₆), furan (C₄H₄O), water (H₂O), benzene (C₆H₆), methyl formate (HCOOCH₃), acetaldehyde (CH₃CHO), toluene (C₇H₈) and acetone (CH₃COCH₃). Previous studies have identified the by-products formed in the NTP process [12,52]. In the present study, both the number of species detected and the total amounts of the organic by-products were heavily reduced with the introduction of the α -, β -, γ - and δ -MnO₂ catalysts (Fig. 12). The lower levels of organic by-products in the combined plasma-catalytic process implied that the toluene had been deeply oxidized to CO₂ and CO in this process.

In the plasma reactor (i.e., NTP alone), the major reaction pathways of toluene degradation were initiated by high-energy electrons, hydroxyl radicals, excited nitrogen species and active oxygen species (i.e., $\cdot\text{OH}$, N , N_2^* , O^* , O_2^* , O_2^-). The degradation of toluene proceeded via two processes: direct degradation and secondary oxidation. Direct degradation was induced by the collision of toluene molecules with electrons and by the reaction between toluene and gas-phase radicals, as illustrated in Fig. 13(a). In direct degradation, the collision between toluene molecules and high-energy electrons triggered the excitation of toluene into an activated state, accompanied by opening of the aromatic ring. Then, the reaction proceeded by a series of oxidation steps by O^* , $\cdot\text{OH}$, etc., leading to the generation of CO₂ and H₂O. In the secondary oxidation process, radicals such as $\cdot\text{OH}$, N , N_2^* , O^* , O_2^* and O_2^- were generated in the plasma process and reacted with toluene molecules in the activated state. This resulted in opening of the aromatic ring, followed by a suite of hydroxylation steps, which eventually led to the formation of CO₂ and H₂O [1].

Table 3O 1s binding energy and surface atomic $O_{\text{sur}}/O_{\text{lat}}$ ratio of the α -, β -, γ - and δ -MnO₂ catalysts.

Catalysts	Binding energy (eV)			Molar ratio of $O_{\text{sur}}/O_{\text{lat}}$
	O_{lat}	O_{sur}	O_{ads}	
α -MnO ₂	530.0	531.6	533.4	0.282
β -MnO ₂	529.6	531.4	532.8	0.270
γ -MnO ₂	529.9	531.5	532.8	0.350
δ -MnO ₂	530.0	531.8	533.4	0.211

Fig. 12. GC-MS measurements of the off-gases from toluene oxidation by NTP or the combined plasma-catalysts with α -, β -, γ - and δ - MnO_2 at the SIE of 160 J/L.

Fig. 13. Proposed degradation routes of toluene in plasma and in the plasma-catalytic process.

In the plasma-catalytic process, the major pathways of toluene degradation were likewise initiated by high-energy electrons and radical species. As shown in Fig. 13(b), the proposed reaction mechanism could be divided into two parts [11]: reactions in the gas phase and reactions at the catalyst surface. The former involved the direct degradation of toluene through collision with electrons followed by oxidation driven by the active free radicals ($\cdot\text{OH}$, N , N_2^+ , O , O_2^+ , O_2^-). The latter involved the oxidation of adsorbed toluene and its intermediate by-products

(2-methylpropene, ethane, furan, benzene, methyl formate, acetaldehyde and acetone) by active species (such as O and $\cdot\text{OH}$). The reactions at the catalyst surface depended on the chemisorption of toluene, the Mn–O bond strength of MnO_2 , the amounts of chemisorbed oxygen species and the transformations among MnO_2 , Mn_2O_3 , Mn_3O_4 and MnO . In the plasma-catalytic process, the O_3 , O_2 and electrons in the gas stream could be adsorbed and transported to the toluene or intermediate by-products at the catalyst surface via a facile intercon-

version among Mn^{4+} , Mn^{3+} and Mn^{2+} states, which then promoted the deep oxidation of toluene to produce greater amounts of CO_2 . Furthermore, MnO_2 is the most active metal oxide for the decomposition of O_3 [22,23], thereby producing O_2 and $\text{O}^\bullet$, which can also oxidize toluene and intermediate organic by-products.

4. Conclusions

α -, β -, γ - and δ - MnO_2 catalysts were synthesized by a hydrothermal method, and their performance in the plasma-catalytic oxidation of toluene was evaluated. When NTP was used alone, the toluene removal efficiency was 32.5% with the SIE of 160 J/L. Among the investigated catalysts, α - MnO_2 showed the best activity, increasing the toluene conversion from 32.5% to 78.1% at the SIE of 160 J/L. For β - MnO_2 , γ - MnO_2 and δ - MnO_2 at the same SIE, their toluene conversion efficiencies were measured at 47.4%, 66.1% and 50.0%. Among the four MnO_2 polymorphs, α - MnO_2 possessed a double-tunneled structure, the most stable crystal phase in the plasma and the weakest Mn–O bond strength. α - MnO_2 contained a larger content of surface-adsorbed oxygen than β - and δ - MnO_2 , but slightly lower than γ - MnO_2 . Thus, α - MnO_2 achieved by far the most impressive catalytic performance for the degradation of toluene among the four tested polymorphs. In addition, the degradation routes of toluene in the plasma-only and plasma-catalytic processes were investigated and a mechanism was proposed. The introduction of MnO_2 catalysts promoted the adsorption of O_3 , O_2 , electrons and radical species in the gas stream, which were

then transported to molecules of toluene (or its intermediate by-products) at the catalyst surface through facile interconversion among Mn^{4+} , Mn^{3+} and Mn^{2+} states. This promoted the deep oxidation of toluene to produce greater amounts of CO_2 .

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Graphical Abstract

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In-plasma catalytic degradation of toluene over different MnO_2 polymorphs and study of reaction mechanism

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In a combined plasma-catalytic process for toluene degradation, α - MnO_2 presented the wonderful catalytic performance because of the double tunneled structure, the best stability of crystal in plasma, the Mn–O bond intension and the surface adsorbed oxygen.

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低温等离子体场内复合不同晶型氧化锰催化降解甲苯性能和机理

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摘要: 作为典型的挥发性有机化合物, 甲苯通常来源于建筑涂料、交通运输和各种工业生产过程, 是PM_{2.5}、臭氧和光化学烟雾的重要前驱体, 对环境和人类健康造成巨大影响。近年来, 低温等离子体技术因具有在常温常压下就能通过高能电子、活性物种和羟基等活性粒子有效降解挥发性有机物的优点而受到广泛关注。然而, 高能耗和大量副产物的产生是等离子体技术工业化应用的巨大障碍。当前最有效的策略之一是将等离子体技术与催化技术结合, 从而加快反应速率, 提高产品的选择性和能源利用率。在所应用的催化剂中, MnO₂因具有较好的O₃分解效率而成为最有潜力的催化剂之一。但是MnO₂具有不同的晶型结构、隧道结构和形貌, 这些均会显著影响MnO₂的催化活性。本文通过一步水热法制备了 α -, β -, γ -和 δ -MnO₂四种MnO₂催化剂, 并将其用于等离子体催化降解甲苯研究, 在此基础上系统考察了等离子体催化降解性能和MnO₂不同晶型之间的关系。

结果表明, 当能量密度为160 J/L时, 等离子体单独降解甲苯去除效率为32.5%。引入催化剂能够显著提高甲苯的降解效率, 其中 α -MnO₂效果最显著, 甲苯降解效率能够提升至78.1%, β -, γ -和 δ -MnO₂能够相应提升至47.4%, 66.1%和50.0%。采用X射线衍射、拉曼光谱、扫描电子显微镜、透射电子显微镜、比表面积-孔结构分析、氢气程序升温还原和X射线光电子能谱等手段研究了催化剂的理化特性。结果表明, 隧道结构、催化剂在等离子体中的稳定性、Mn–O键能和催化剂表面

吸附氧均在等离子体催化降解甲苯中发挥了重要作用。在此基础上,通过GC-MS分析降解产生的气相副产物推断甲苯在等离子体和等离子体催化体系中的降解机理。在等离子体催化体系中,通过 Mn^{4+} , Mn^{3+} 和 Mn^{2+} 价态的变化,等离子体产生的 O_3 , O_2^* 和其他活性自由基会被吸附到催化剂表面,随后与催化剂吸附的甲苯或中间副产物发生氧化还原反应,将甲苯氧化为 CO_2 等小分子物质。此外, MnO_2 作为分解 O_3 最有效的催化剂,可以吸附 O_3 并将其分解为 O^* 或者与 H_2O 生成 OH^* 参与到反应中,从而提高甲苯的降解效率。

关键词: 甲苯; 催化氧化; 低温等离子体; 氧化锰; 晶型结构

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