Effects of precursors for manganese-loaded γ-Al_2O_3 catalysts on plasma-catalytic removal of o-xylene
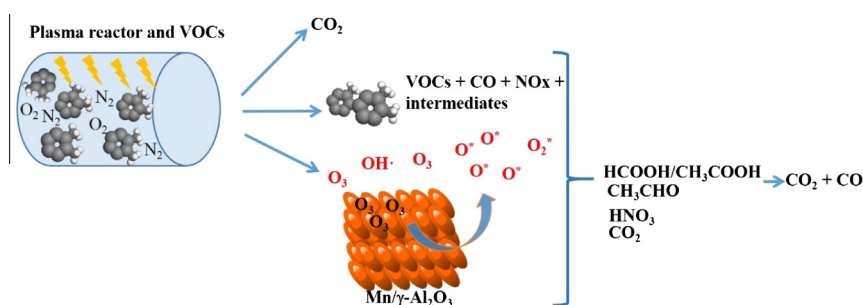
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HIGHLIGHTS

- Effects of precursors and loading amounts on Mn/Al_2O_3 catalysts were investigated.
- Catalyst prepared with manganese acetate had the greatest catalytic activity.
- The plasma-catalytic processes greatly decreased the concentrations of O_3 and NO_x.
- More Mn^{4+} and microcrystalline MnO_2 increased catalytic activity.
- Higher proportion of lattice oxygen was responsible for high catalytic activity.

GRAPHICAL ABSTRACT

ABSTRACT

The effects of precursors and Mn loading amounts on Mn/Al_2O_3 catalysts for plasma-catalytic removal of o-xylene were systematically investigated. Catalysts were characterized by XRD, XPS, and H_2-TPR. Experimental results show that o-xylene conversion was greatly increased even at very low specific energy density with addition of Mn/Al_2O_3 catalysts. The Mn/Al_2O_3 catalyst prepared with a manganese acetate precursor had the highest catalytic activity for o-xylene removal. Among tested loading amounts, 6 wt% Mn loading was the optimum condition for preparation of catalysts for o-xylene conversion. The presence of more Mn^{4+} species, higher proportion of lattice oxygen and microcrystalline MnO_2 phase on the surface of catalysts was responsible for the high catalytic activity for o-xylene removal. To compare with Mn/Al_2O_3 catalysts prepared with manganese acetate precursor, α-MnO_2/Al_2O_3 with more Mn^{4+} and lattice oxygen on the surface was also prepared. The o-xylene conversion, CO_2 selectivity, and $(CO + CO_2)$ (i.e. CO_x) yield increased with introduction of α-MnO_2/Al_2O_3 catalyst, which was due to the high oxidation ability of α-MnO_2/Al_2O_3 induced by higher amounts of Mn^{4+} and lattice oxygen. The concentrations of O_3 and NO_x byproducts greatly decreased when catalysts were used. The FT-IR spectrum show that CH_3CHO, O_3, NO_x and HNO_3 products were formed without catalyst, while $HCOOH$/CH_3COOH formation occurred with catalysts.

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1. Introduction

Benzene, toluene, and xylene (BTX) are the typical volatile organic compounds (VOCs) and harmful to the environment and human health. Removal of BTX for purification of indoor air and gaseous industrial streams is very important and necessary [1,2]. Recently, non-thermal plasma (NTP) technology is regard as a promising method since NTP could efficiently remove BTX at ambient conditions through generating strong oxidizing agents like ozone, hydroxyl radical, atomic oxygen, etc [3,4]. However, the main drawback of NTP for BTX removal is inevitable byproducts

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formation and low CO_2 selectivity because there is no enough energy of radicals for complete oxidation of BTX [4]. To overcome these disadvantages of NTP, the combination of NTP and catalysis has aroused great interesting to study the removal of BTX [4–16]. The byproducts formed during the plasma treatment could be oxidized by adding catalyst to abate the production of byproducts and increase CO_2 selectivity.

For plasma-catalytic process to remove BTX, one of the crucial issues is to find an appropriate catalyst with good catalytic performance. In recent years, Mn containing catalysts have been widely explored, which had high catalytic activity for BTX removal in plasma-catalytic process [5,6,8–10]. Manganese oxide (MnO_x) is the most active metal oxide catalyst for decomposition of ozone to generate atomic oxide species which play an important role for oxidation of VOCs [15–17]. Guo et al. have confirmed that manganese oxide/alumina/NF was the most effective catalyst for toluene removal among copper oxide, iron oxide, cobalt oxide, and manganese oxide loaded catalysts in plasma-catalytic process [8]. Zhu et al. have investigated the combination of NTP and MnO_x/Al_2O_3 catalysts for removal of BTX, and found that MnO_x/Al_2O_3 catalysts could lead to BTX total conversion and reduce the emission of O_3 and NO_2 [9]. MnO_x/SMF catalysts showed higher activity toward VOCs oxidation than CoO_x/SMF catalysts [10]. According to the above reports, MnO_x catalysts are promising to BTX conversion used in plasma-catalytic process. The catalytic activities of some transition metal doped Mn oxides have also been compared [18,19]. As the active species, the structure of Mn in catalyst was important for VOCs removal via combination of NTP and catalysis. Therefore, the effects of Mn valence and preparation conditions on BTX removal via combination of NTP and Mn catalysts need to be systematically investigated.

In this work, Mn/Al_2O_3 catalysts were prepared with different precursors and loading amounts, and α-MnO_2/Al_2O_3 was used for comparison. We also tested their activities for o-xylene removal in a dielectric barrier discharge (DBD) plasma system by introducing the above catalysts after the discharge zone. The conversion of o-xylene, CO_2 selectivity, carbon yield, decomposition products and discharge byproducts were investigated. Catalysts were characterized by XRD, XPS, and H_2-TPR methods. The effects of preparation condition on the chemical properties such as Mn valence, lattice oxygen contents, and redox properties were analyzed and subsequently correlated with their catalytic activities.

2. Experimental

2.1. Experimental setup and methods

A schematic diagram of the experimental setup is shown in Fig. 1, which includes a cylindrical plasma-catalysis reactor with inner high-voltage electrode, an o-xylene generator with reaction gas, and some analytical instruments for products measurements. The discharge-catalysis reactor had a coaxial geometry (inner diameter 8 mm, outer diameter 18 mm, and length 400 mm) with a quartz tube as dielectric between the inner high-voltage electrode (aluminum, diameter 8 mm and length 100 mm) and the grounded electrode (aluminum foil, diameter 18 mm and length 100 mm) on the outer quartz tube wall to form a 100 mm length DBD zone. The gas discharges were produced by a high-frequency AC high-voltage power supply source. In addition, catalysts (1.5 g, 40–60 mesh) were placed after the discharge zone. The gas o-xylene was produced by bubbling with N_2 and mixed with O_2 and N_2 before the reactor to achieve the mixed reactant feed that composed of 9 ppm o-xylene, 20 vol% O_2 and 80 vol% N_2 (total flow rate = 6 L min^{-1}). The AC power was supplied to start the electro-discharge and reaction when the concentration of

o-xylene reached a steady state. All experiments were repeated in triplicate.

Discharge power was measured by the V–Q Lissajous program. The charge Q was measured from the voltage across a capacitor of 100 nF connected in series to the ground electrode. The applied voltage was measured with a 1000:1 high-voltage probe (Tektronix TPP0201). The waveforms of the charge Q and the applied voltage were monitored using a digital oscilloscope (Tektronix TDS 2012c) and plotted to obtain the Lissajous diagram.

The o-xylene conversion, CO_2 selectivity, CO_x yield, and specific energy density in the gas phase were defined as follows:

o-xylene conversion efficiency (%)

$$= [\text{o-xylene}]_{outlet}/[\text{o-xylene}]_{inlet} \times 100$$

Carbon dioxide selectivity (%) $= [CO_2]/8[C_8H_{10}]_{conversion} \times 100$

Carbon dioxide and carbon monoxide yield:

CO_x yield (%) $= ([CO] + [CO_2])/8[C_8H_{10}]_{conversion} \times 100$

Specific energy density : SED (J/L)

$$= \text{discharge power} (W)/\text{gas flow rate} (L/min) \times 60$$

The o-xylene concentration was analyzed online by a GC–MS (Agilent 6890-5973 N, HP 5MS). CO_2 and CO concentrations were analyzed by a GC equipped with FID detector (Shangfen GC-112A, TDX-01 column). O_3 and NO_x concentrations were determined by an O_3 detector (Model 202, 2B Technology) and NO_x detector (Thermal 42i). Other oxidation products were detected by online FT-IR (Thermo Scientific Nicolet is 50).

2.2. Catalyst preparation

Mn/Al_2O_3 catalysts were prepared through an impregnation method by introducing an appropriate amount of γ-Al_2O_3 powder into manganese acetate, manganese chloride, manganese sulfate, or manganese nitrate precursor solutions, and the catalysts were designated as Mn/Al_2O_3-MA, Mn/Al_2O_3-MC, Mn/Al_2O_3-MS, and Mn/Al_2O_3-MN, respectively. The mixed solutions were stirred for 2 h at room temperature, followed by evaporation to dryness in a rotary evaporator at 60 °C. The obtained solids were dried at 100 °C overnight and calcined at 500 °C for 3 h in air.

The α-MnO_2 nanorods were synthesised by a hydrothermal method according to the literature [20]. For preparation of α-MnO_2 nanorods, 1.25 g $KMnO_4$ and 0.78 g $Mn(CH_3COO)_2 \cdot 4H_2O$ were mixed in 80 mL deionized water and stirred for 30 min. Then, the mixture was transferred into a Teflon-lined stainless steel autoclave (100 mL) and heated at 160 °C for 12 h. The product was washed and dried at 100 °C overnight. The α-MnO_2/Al_2O_3 catalyst was prepared by mixing the α-MnO_2 sample with γ-Al_2O_3 powder by ball-milling.

2.3. Catalyst characterization

The X-ray diffraction (XRD) patterns of catalysts were recorded on a PANalytical X'Pert PRO X-ray diffractometer (Japan) with Cu Kα radiation (λ = 0.154 nm) at a scan rate of 6 deg (2θ) min^{-1}. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo ESCALAB 250 spectrometer (Vacuum Generators, USA) using Al Kα radiation (1486.6 eV) with constant pass energy of 20 eV. The spectra were corrected by calibrating with the C1s peak at 284.8 eV. Temperature-programmed reduction of H_2 (H_2-TPR) was also performed on a Chemisorption Analyzer (AutoChem 2920). After the samples (100 mg) were pretreated at 400 °C in a flow of 20 vol% O_2/Ar (50 mL/min) for 1 h and cooled
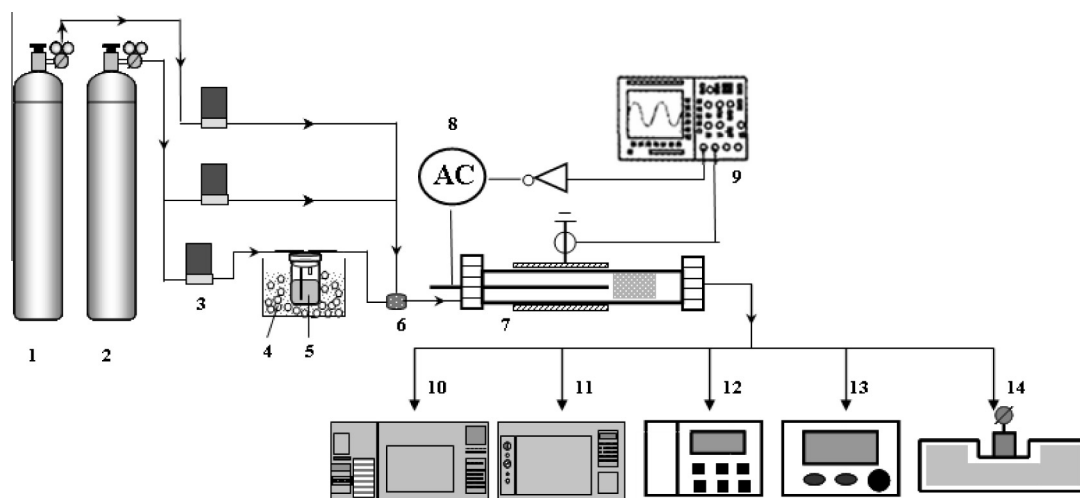
Fig. 1. A schematic diagram of experimental setup. (1) Oxygen, (2) nitrogen, (3) mass flow controller, (4) ice bath, (5) gas bubbler, (6) gas mixer, (7) plasma reactor, (8) AC high voltage supply, (9) oscilloscope, (10) GC–MS, (11) GC, (12) NO_x analyzer, (13) O_3 analyzer, (14) FT-IR.

down to room temperature, the samples were exposed to a flow of 10 vol% H_2/Ar (30 mL/min) at 30 °C for 1 h, followed by raising the temperature to 800 °C at a rate of 10 °C/min. To investigate the Mn content of Mn/Al_2O_3, catalysts were dissolved with concentrated HNO_3 and concentrated HCl with a volume ratio of 1:3. Then, the solution was diluted to 50 mL, followed by ICP-OES measurement on an Optima 2000 (Perkin–Elmer Co.). The actual contents of Mn in Mn/Al_2O_3 products were close to the nominal contents. Field emission scanning electronic microscopy (FE-SEM) measurements were performed on a SU-8000 electron microscope (Hitachi, Japan).

3. Results and discussion

3.1. Effect of manganese precursor

According to the literature, different precursors used to prepare MnO_x could influence on the dispersion of Mn on supports and activity of catalysts in catalytic oxidation of benzene by ozone [21]. Thus, it is necessary to investigate the effects of precursors used for preparation of Mn/Al_2O_3 catalysts on o-xylene removal in plasma-catalytic process. Fig. 2 shows o-xylene conversion, CO_2 selectivity, and CO_x yield on 6 wt% Mn/Al_2O_3 catalysts prepared with different manganese precursors and calcined at 500 °C in the plasma-catalytic system. As shown in Fig. 2, there was only 50% o-xylene conversion achieved with air plasma alone at specific energy density (SED) of 18 J/L. The conversion was greatly increased with addition of the Mn/Al_2O_3 catalysts. The Mn/Al_2O_3-MA catalyst showed the highest catalytic activity, with 100% conversion of o-xylene at a SED as low as 18 J/L. The sequence of catalytic activity was as follows: Mn/Al_2O_3-MA > Mn/Al_2O_3-MS > Mn/Al_2O_3-MN > Mn/Al_2O_3-MC > plasma alone. It is obvious that the o-xylene conversion was related to the precursors used for catalyst preparation. The CO_2 selectivity and CO_x yield using Mn/Al_2O_3-MN, Mn/Al_2O_3-MA, and Mn/Al_2O_3-MS catalysts were higher than those achieved using Mn/Al_2O_3-MC or plasma alone.

XRD and XPS experiments were carried out to characterize the structural and valence properties of catalysts. XRD patterns of catalysts prepared with different precursors are shown in Fig. 3. Compared with the typical diffraction peaks of γ-Al_2O_3, no new peak was observed for Mn/Al_2O_3-MC and Mn/Al_2O_3-MS catalysts. While a new peak appeared at 28.1° for Mn/Al_2O_3-MA, which is one of the diffraction peaks of microcrystalline MnO_2 (PDF#24-0735) [22]. For Mn/Al_2O_3-MN prepared with the manganese nitrate precursor,

sharp diffraction peaks at 28.7°, 32.9°, and 37.3° were observed, which indicated the appearances of MnO_2 and Mn_2O_3 (PDF#24-0735 and PDF#24-0508). The manganese nitrate precursor resulted in the formation of MnO_2 and Mn_2O_3 crystals, and the same result was reported by Rezaei et al. [23].

The XPS analysis was performed to investigate the state and atomic concentration of Mn and oxygen on the surface. Fig. 4 shows the XPS spectra of 6 wt% Mn/Al_2O_3. The binding energies at around 643.0 and 641.5 eV could be attributed to the presence of Mn^{4+} and Mn^{3+} species, respectively [22]. It is interesting to note that the Mn^{4+} ratios on the surfaces of Mn/Al_2O_3-MA and Mn/Al_2O_3-MS catalysts were more than 50%, while Mn^{3+} was the dominant species on the surfaces of the Mn/Al_2O_3-MN and Mn/Al_2O_3-MC catalysts, with small amounts of Mn^{4+} (Table 1). The ratio of lattice oxygen (O_α) to surface oxygen or defective oxides (O_β) was the highest for the Mn/Al_2O_3-MA catalyst and the second highest for Mn/Al_2O_3-MS. Thus, structure analysis by XRD and XPS revealed that microcrystalline MnO_2 was helpful for improving the catalytic activity of Mn/Al_2O_3-MA. More Mn^{4+} species and lattice oxygen (O_α) on the surface of the catalyst resulted in the much higher catalytic activity of Mn/Al_2O_3-MA and Mn/Al_2O_3-MS toward total oxidation of o-xylene. The reason might be that the effective decomposition of O_3 of MnO_2 (Mn^{4+}) to generate atomic oxide species. Tang et al. have also observed that more Mn^{4+} and the richer lattice oxygen in Mn–Ce composite catalysts were beneficial for the formaldehyde oxidation [24]. Generally, oxidation reactions such as CO and HCHO oxidation on MnO_x catalysts follow the Mars–van Krevelen mechanism [25,26]. The theory study implied that the lattice oxygen concentration could dominate the activity during the reaction [27].

The Mn/Al_2O_3 catalysts were subjected to FE-SEM measurements for their morphology. The FE-SEM micrographs displayed that the bulk size of Mn/Al_2O_3-MC was the largest, which might led to the lowest catalytic activity for o-xylene conversion in plasma-catalytic system (Fig. 5). Furthermore, the surface areas of Mn/Al_2O_3-MA, Mn/Al_2O_3-MC, Mn/Al_2O_3-MS, and Mn/Al_2O_3-MN were 298.2, 281.4, 284.8, 291.6 m^2/g, respectively. There were only minor differences in surface area among these catalysts, which was not the main effect factor in the different catalytic activity of these catalysts for o-xylene conversion.

To examine the redox ability of the catalysts, H_2-TPR experiments were carried out. Fig. 6 shows the H_2-TPR profiles of 6 wt% Mn/Al_2O_3. Two peaks of H_2 consumption were observed for

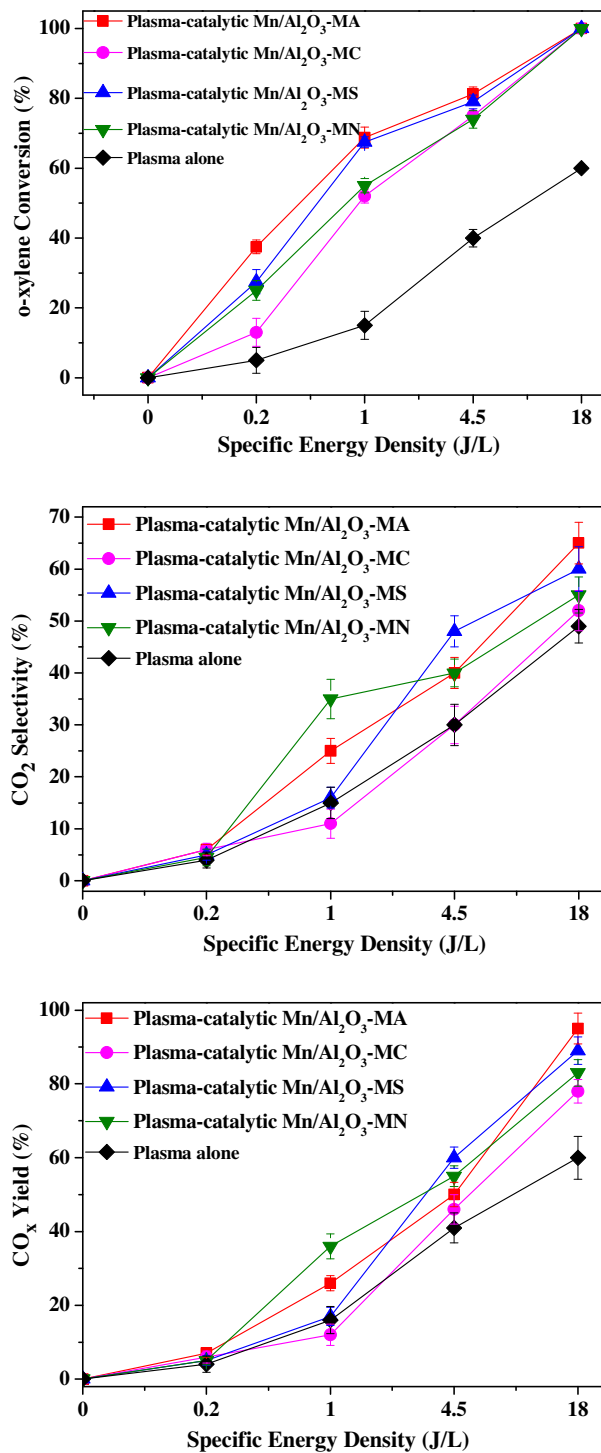**Fig. 3.** XRD patterns of 6 wt% Mn/Al_2O_3 catalysts prepared with different precursors.

Fig. 2. Effects of manganese precursor for preparation of 6 wt% Mn/Al_2O_3 catalysts on the o-xylene conversion, CO_2 selectivity, and CO_x yield.

Fig. 4. XPS spectra of 6 wt% Mn/Al_2O_3 catalysts prepared with different precursors (a) Mn 2p XPS spectra, (b) O1s XPS spectra.

Mn/Al_2O_3-MS and Mn/Al_2O_3-MN, and the ratio of the low-temperature peak at 320 °C to the high-temperature peak at 386 °C was about 2. According to the literature, the low-temperature peak should be attributed to reduction of MnO_2 to Mn_3O_4, whereas the high-temperature peak should be attributed to the reduction of Mn_3O_4 to MnO [28]. Only one peak appeared for Mn/Al_2O_3-MA and Mn/Al_2O_3-MC, which suggested that MnO_x (i.e. MnO_2 and Mn_2O_3) should be reduced to MnO directly. The temperature of the reduction peak of Mn/Al_2O_3-MS, Mn/Al_2O_3-
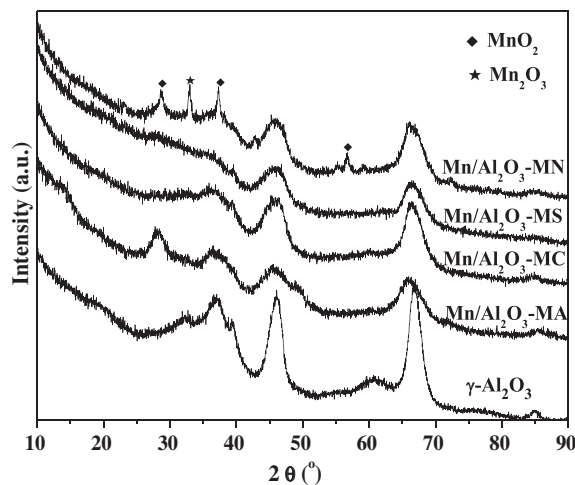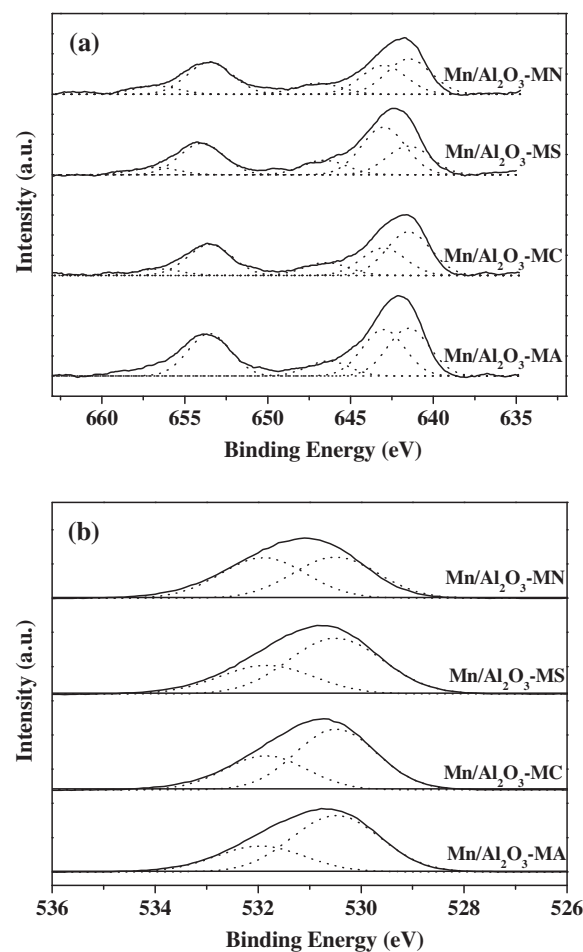
MN, and Mn/Al_2O_3-MA was lower than that of Mn/Al_2O_3-MC, which indicated that Mn/Al_2O_3-MS, Mn/Al_2O_3-MN, and Mn/Al_2O_3-MA had high oxidation–reduction ability, which was beneficial for the o-xylene conversion, CO_2 selectivity and CO_x yield.

Table 1
XPS results of the Mn/Al_2O_3 catalysts.

Sample	BE (eV)		$Mn^{4+}/(Mn^{4+} + Mn^{3+})$ (%)	BE (eV)		$O_\alpha/(O_\alpha + O_\beta)$ (%)
6 wt% Mn/Al_2O_3	Mn^{4+}	Mn^{3+}		O_α	O_β	
Mn/Al_2O_3-MA	643.0	641.5	54	530.5	532.1	75
Mn/Al_2O_3-MC	643.0	641.5	39	530.5	531.9	64
Mn/Al_2O_3-MS	643.0	641.5	63	530.5	532.0	71
Mn/Al_2O_3-MN	643.0	641.5	45	530.5	531.6	50

3.2. Effect of manganese loading amount

The effects of different Mn loading amounts of Mn/Al_2O_3-MA catalysts on the o-xylene conversion were investigated. In addition, the actual contents of Mn in all Mn/Al_2O_3 products were close to the prospective contents in the preparation process (Table 2). It was found that o-xylene conversion was the highest when 6 wt% Mn/Al_2O_3-MA was used (Fig. 7). XRD patterns showed that 2 and 4 wt% Mn/Al_2O_3-MA had no manganese-related peaks. 6 wt% Mn/Al_2O_3-MA exhibited a prominent MnO_2 microcrystal peak (Fig. 8). Furthermore, 8 wt% Mn/Al_2O_3-MA exhibited a weaker MnO_2 microcrystal peak than 6 wt% Mn/Al_2O_3-MA. XRD results also indicated that weak Mn_3O_4 crystal peaks appeared for 10 wt% Mn/Al_2O_3-MA, and the Mn_3O_4 peak intensity increased with increase of loading amount above 10 wt% Mn (not shown). These results suggested that there was a change of crystal form with increase of manganese loading amount. The analysis of XPS results revealed that 6 wt% Mn/Al_2O_3-MA had the highest Mn^{4+} ratio and O_α ratio among Mn/Al_2O_3-MA catalysts with different loading amounts (Table 2). The XRD and XPS results of Mn/Al_2O_3 prepared using different precursors and Mn/Al_2O_3-MA with different loading amounts all proved that the presence of microcrystalline MnO_2, more Mn^{4+}, and a higher proportion of O_α was beneficial to increase o-xylene conversion.
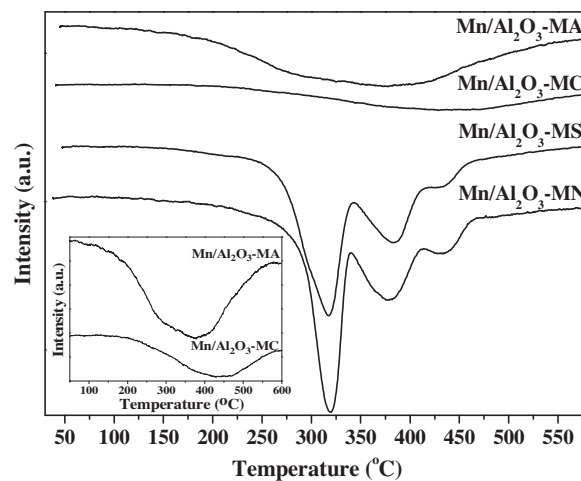

Fig. 6. H_2-TPR profiles of 6 wt% Mn/Al_2O_3 catalysts prepared with different precursors. The inset shows a magnification of the 6 wt% Mn/Al_2O_3-MA and Mn/Al_2O_3-MC profiles.
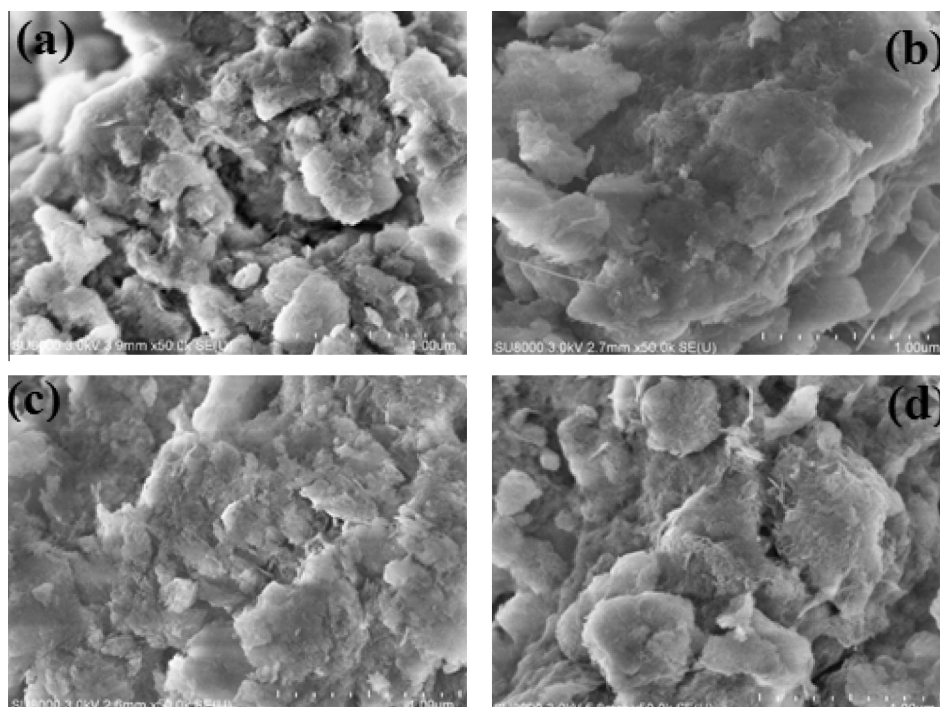

Fig. 5. FE-SEM micrographs of 6 wt% Mn/Al_2O_3 catalysts prepared with different precursors. (a) Mn/Al_2O_3-MA, (b) Mn/Al_2O_3-MC, (c) Mn/Al_2O_3-MS, and (d) Mn/Al_2O_3-MN.

Table 2
XPS and ICP-OES results of the Mn/Al$_2$O$_3$ catalysts.

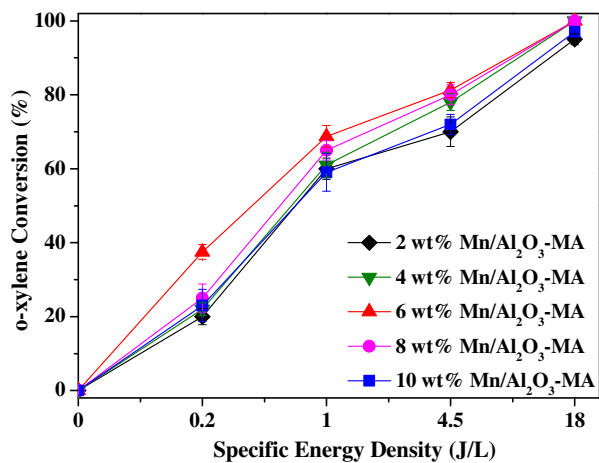| Sample	BE (eV)		Mn^{4+}/(Mn^{4+} + Mn^{3+}) (%)	BE (eV)		O$_\alpha$/(O$_\alpha$ + O$_\beta$) (%)	Mn content detected by ICP-OES (wt%)
Mn/Al$_2$O$_3$-MA	Mn^{4+}	Mn^{3+}		O$_\alpha$	O$_\beta$		
2 wt%	643.0	641.5	43	530.5	532.0	70	1.9
4 wt%	643.0	641.5	51	530.5	532.0	71	3.8
6 wt%	643.0	641.5	54	530.5	532.1	75	5.9
8 wt%	643.0	641.5	47	530.5	531.9	70	8.2
10 wt%	643.0	641.5	49	530.5	531.9	68	9.7
α-MnO$_2$/Al$_2$O$_3$	643.0	641.5	61	530.5	532.0	79	5.8

Fig. 7. Effects of loading amounts of Mn/Al$_2$O$_3$-MA on the o-xylene conversion.
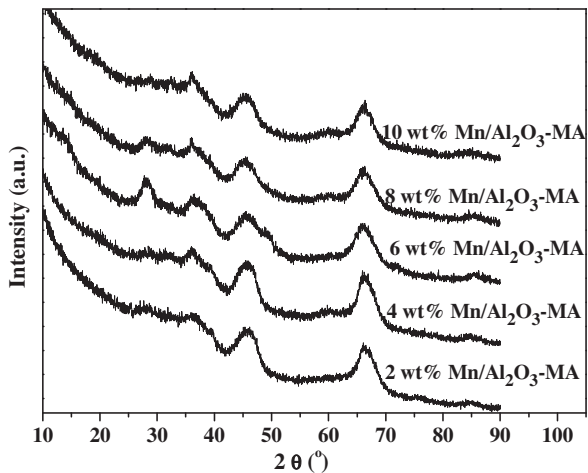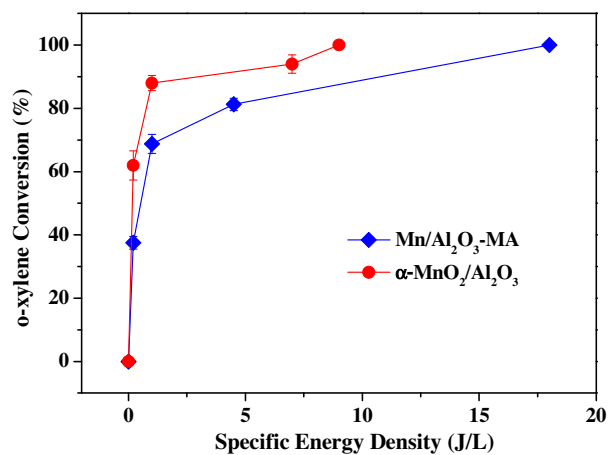

Fig. 8. XRD patterns of Mn/Al$_2$O$_3$-MA with different loading amounts.

3.3. Effect of Mn^{4+} ratio

According to the above results, it was found that Mn^{4+} and O$_\alpha$ on the surface of catalyst were helpful for o-xylene oxidation. Therefore, α-MnO$_2$/Al$_2$O$_3$, which had more Mn^{4+} and O$_\alpha$ (Table 2), was prepared with a hydrothermal method using manganese acetate as precursor. The catalytic activity of 6 wt% α-MnO$_2$/Al$_2$O$_3$ was compared with that of 6 wt% Mn/Al$_2$O$_3$-MA in plasma-catalytic system (Fig. 9). The XRD pattern of α-MnO$_2$/Al$_2$O$_3$ is shown in Fig. 10. Typical α-MnO$_2$ phases were found [20]. The o-xylene conversion efficiency using α-MnO$_2$/Al$_2$O$_3$ was higher than that using Mn/Al$_2$O$_3$-MA, and the CO$_2$ selectivity and CO$_x$ yield slightly increased using α-MnO$_2$/Al$_2$O$_3$ compared with those achieved using Mn/Al$_2$O$_3$-MA.

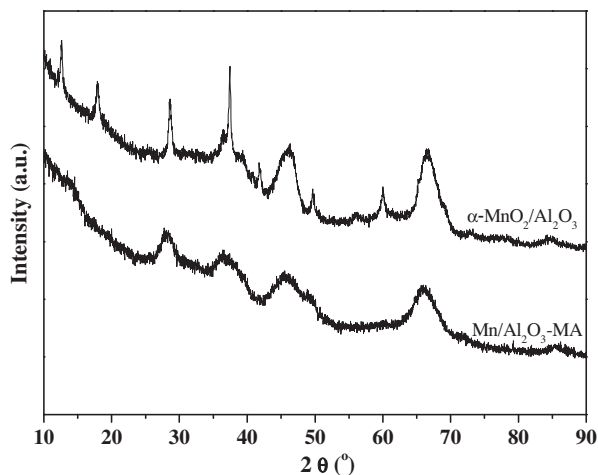**Fig. 9.** o-xylene conversion, CO$_2$ selectivity, and CO$_x$ yield using 6 wt% α-MnO$_2$/Al$_2$O$_3$.

Fig. 10. XRD patterns of 6 wt% α-MnO$_2$/Al$_2$O$_3$.

Fig. 11. H$_2$-TPR profiles of 6 wt% α-MnO$_2$/Al$_2$O$_3$.

Fig. 12. Byproducts of (a) O$_3$ and (b) NO$_x$ before and after addition of 6 wt% Mn/Al$_2$O$_3$-MA.

Fig. 11 shows the H$_2$-TPR profiles of 6 wt% α-MnO$_2$/Al$_2$O$_3$ compared with that of 6 wt% Mn/Al$_2$O$_3$-MA. The peak intensity of TPR profiles of α-MnO$_2$/Al$_2$O$_3$ at low temperature was much larger than that of Mn/Al$_2$O$_3$-MA. These results suggested that oxidation ability of α-MnO$_2$/Al$_2$O$_3$ was higher than that of Mn/Al$_2$O$_3$-MA, which was possibly induced by the higher amounts of Mn^{4+} and O$_\alpha$ for α-MnO$_2$/Al$_2$O$_3$ and responsible for the increase of o-xylene conversion, CO$_2$ selectivity and CO$_x$ yield when using α-MnO$_2$/Al$_2$O$_3$ catalyst. These results also confirmed the positive role of Mn^{4+} and O$_\alpha$.

3.4. Inhibiting formation of byproducts

To examine the effect of catalysts on suppression of byproduct formation, the outlet O$_3$ and NO$_x$ concentrations were measured. Fig. 12(a) gives the O$_3$ outlet concentrations with increase of SED for plasma alone and plasma-catalytic processes. With addition of 6 wt% Mn/Al$_2$O$_3$-MA catalyst, the O$_3$ outlet concentration was greatly decreased. It was clear that most ozone was catalytically decomposed to molecular and highly active atomic oxygen [29]. Those active oxygen species could oxidize o-xylene into CO$_2$. As another byproducts, NO and NO$_2$ were also monitored in this work. In the case of plasma alone, the NO$_x$ concentration increased to a maximum value of 2.7 ppm with a SED of 18 J/L (Fig. 11(b)). Below 4.5 J/L SED, there was no NO production. Some active molecules and radicals such as O$_3$, OH and O produced in the discharge
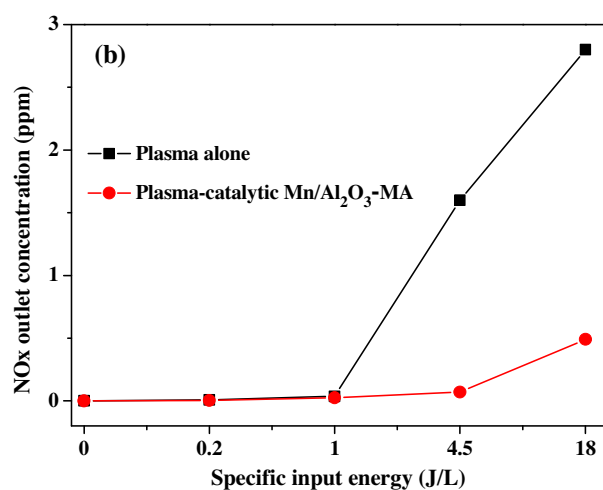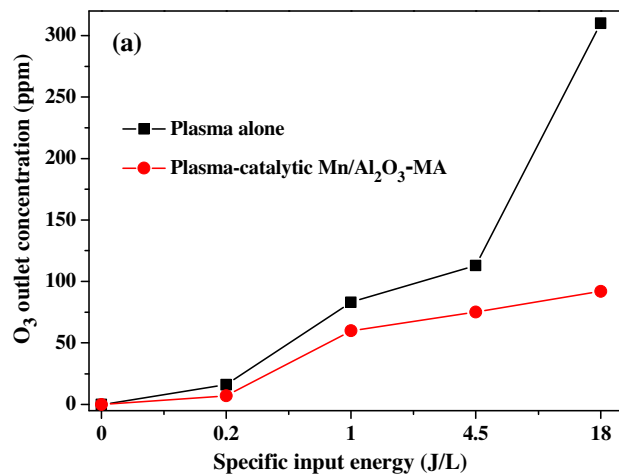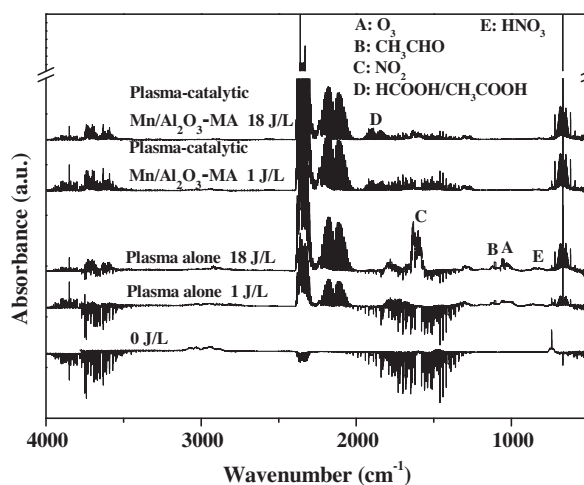

Fig. 13. FT-IR spectra in the processes of plasma and plasma-catalyst (6 wt% Mn/Al$_2$O$_3$-MA) oxidation of o-xylene.

process could oxidize NO to NO$_2$, which resulted in less NO production. In contrast, a much lower amount of NO$_x$ was detected with addition of the 6 wt% Mn/Al$_2$O$_3$-MA catalyst. Previous research reported that NO$_x$ could be oxidized to HNO$_2$ and HNO$_3$ due to oxidation of radicals [30].

Fig. 13 exhibits the main products for plasma and plasma-catalytic processes. Products including CO_2, CO, NO_2, O_3, CH_3CHO, and HNO_3 were observed in the case of plasma alone. The signal intensities of O_3, NO_2 and CH_3CHO increased with increase of SED, which was consistent with the results obtained by the O_3 and NO_x analyzers. The production of HNO_3 was also observed at about $850\ cm^{-1}$ at higher SED, which should be an oxidation product of NO_x [26]. Products including CO_2, CO, and $HCOOH/CH_3$ $COOH$, and HNO_3 were observed with addition of 6 wt% Mn/Al_2O_3-MA. The FT-IR waveform for $HCOOH$ is near to that of CH_3COOH, which is difficult to be distinguished. Comparing the major products in the case of plasma alone with the case of catalyst addition, it could be deduced that the Mn/Al_2O_3 catalyst could oxidize CH_3CHO to CH_3COOH, and then further oxidize CH_3COOH to CO or CO_2.

4. Conclusions

In this study, Mn/Al_2O_3 catalysts prepared with different precursors were introduced downstream of the discharge zone of DBD plasma system for removal of o-xylene. With the introduction of the catalysts, o-xylene removal efficiency, CO_2 selectivity and CO_x yield could be significantly improved. The byproducts such as O_3 and NO_x was remarkably reduced by the Mn/Al_2O_3 catalysts. The catalysts could oxidize o-xylene to CH_3COOH, and then further oxidize CH_3COOH to CO or CO_2. Among catalysts prepared with four kinds of precursors, the 6 wt% Mn/Al_2O_3 catalyst prepared by manganese acetate precursor exhibited the best catalytic activity for o-xylene removal, which is due to the presence of microcrystalline MnO_2, more Mn^{4+} species, and higher proportion of lattice oxygen on the surface of the catalyst, resulting in high oxidation activity. The o-xylene conversion, CO_2 selectivity, and CO_x yield increased with an α-MnO_2/Al_2O_3 catalyst that possessed more Mn^{4+} species and lattice oxygen on the surface compared with Mn/Al_2O_3 catalysts prepared with the manganese acetate precursor, which also confirmed the positive role of Mn^{4+} species and lattice oxygen.

Acknowledgements

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