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# Catalytic oxidation of toluene over MnO<sub>2</sub> catalysts with different Mn (II) precursors and the study of reaction pathway



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## GRAPHICAL ABSTRACT



#### ARTICLE INFO

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 $MnO_2$ -Ac,  $MnO_2$ -N,  $MnO_2$ -Cl and  $MnO_2$ -S samples were prepared by the redox reaction between potassium permanganate and manganese acetate, manganese nitrate, manganese chloride and manganese sulfate and the effect of Mn (II) precursor on the toluene oxidation was studied. The physicochemical properties of these samples were characterized by XRD, TEM,  $N_2$  asdorption-desorption isotherms,  $H_2$ -TPR and XPS. Results showed that the catalytic activity of the four samples decreased in the order of  $MnO_2$ -Ac  $> MnO_2$ -N  $> MnO_2$ -Cl  $> MnO_2$ -S, which was highly related to the specific surface areas, oxygen vacancy concentration and the content of adsorbed oxygen.  $MnO_2$ -Ac owned potential for practical applications. It showed superior toluene oxidation activity with  $T_{90}$  of 200 °C, as well as excellent water-resistance and stability during 50 h at 300 °C. The good catalytic activities under high WHSV and high toluene concentration were also observed over  $MnO_2$ -Ac. Moreover, the reaction pathway of toluene oxidation was presented with the aid of In-situ DRIFTS.

#### 1. Introduction

Volatile organic compounds (VOCs), such as formaldehyde, ethane, acetone, toluene, are a major class of air pollutants. They are mainly emitted from petrochemical industries, chemical industries, processing industries, and transport processes [1,2]. Many environmental issues, such as offensive odors, ozone generation, petrochemical smog and

haze, are related to the emissions of VOCs [3]. Meanwhile, exposure to VOCs can cause all kinds of physical discomfort or even induce teratogenicity, carcinogenicity and mutagenicity [4]. Therefore, strict legislation laws and regulations have been established in many countries. Now it is urgent to exploit effective techniques to control VOCs emissions.

Up to now, many environmental technologies have been developed

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to control VOCs, including absorption, adsorption, condensation, membrane separation, biodegradation, thermal combustion, catalytic oxidation, plasma catalysis, and photo-catalysis [1]. Amongst, catalytic oxidation is focused to be a promising technology owing to the absence of toxic by-products, low operating cost, and wide application scope. As is well-known, the economical and efficient catalyst is the core of catalytic oxidation technology. Based on active component, catalysts are usually classified into two major groups: supported noble metal catalysts and non-noble metal oxide catalysts. Supported noble metal catalysts (Pt, Pd, Rh etc.) usually showed excellent activities in the removal of VOCs [5], but their widespread application was limited by the high price, easy poisoning and bad thermal stability [6]. Alternatively, non-noble metal oxides, such as CeO<sub>2</sub>, MnO<sub>x</sub>, CuO, Co<sub>3</sub>O<sub>4</sub>, FeO<sub>x</sub>, etc. and their composite oxides, have received increased attention because of their sufficient activity, low costs, and better thermal stability [6]. Among them, MnO<sub>2</sub> catalysts are known as one of the most promising non-noble metal oxide catalysts owing to its unique physicochemical properties, such as multivalent nature, nonstoichiometric composition, poly-morphism, high redox potential and environmental friendliness [7,8]. Up to now, numerous studies showed that MnO<sub>2</sub> catalysts performed well in the removal of VOCs, including alkanes [9], alcohols [10], aldehydes [11], ketones [12], ethers [13], aromatic hydrocarbons [8], chlorinated VOCs [14] etc. For example, Lahousse et al. [15] observed  $\gamma$ -MnO<sub>2</sub> showed better activity than Pt/TiO<sub>2</sub> for the removal of various VOCs. Sekine et al. [16] found MnO2 showed the best activity for the removal of formaldehyde at room temperature among 13 commercial non-noble metal oxides. Huang et al. [8] reported the hierarchically  $\alpha@\beta-MnO_2$  nano-catalyst prepared via hydrothermal method could completely convert toluene to CO2 at about 205 °C owing to its mixed phase interfacial structure.

The performance of MnO<sub>2</sub> generally depends on various factors, such as crystalline structure, particle size, morphology, specific surface area, low-temperature reducibility, and surface defect, etc. It is wellknown that these factors can be controlled by changing preparation methods or adjusting preparation conditions. The popular preparation methods include hydrothermal method [8,17], redox method [18,19], template method [20], selective atom removal method [7,21], etc. The preparation conditions include acid treatment, choice of reactant precursor, reactant ratio, template, pH, reaction time and temperature, calcination time and temperature, etc. Recently, many efforts have been made in this respect. Yang et al. [14] compared catalytic activity of hexachlorobenzene over  $\alpha$ -MnO<sub>2</sub>,  $\beta$ -MnO<sub>2</sub> and  $\delta$ -MnO<sub>2</sub>, prepared by adjusting the reactant ratio and hydrothermal temperature. The catalytic activity decreased in the order of  $\delta$ -MnO<sub>2</sub> >  $\alpha$ -MnO<sub>2</sub> >  $\beta$ -MnO<sub>2</sub>, which was related to the surface area, pore volume, surface acid sites, catalyst reducibility and the amount of surface labile oxygen. Jiang et al. [13] studied the effect of reaction temperature and acid treatment on the catalytic activity of MnO2 in dimethyl ether combustion. The reaction temperature affected the crystal phase of MnO<sub>2</sub>, and MnO<sub>2</sub> prepared at the room temperature exhibited better activity. Acid treatment enhanced the surface oxygen species, reductivity, and acidic sites of MnO<sub>2</sub>, and hereby the catalytic activity was improved. By altering the reactant ratio of KMnO<sub>4</sub> and (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, Wang et al. [22] obtained birnessite MnO<sub>2</sub> samples with different content of manganese vacancies, which induced unsaturated oxygen species, and hereby enhanced the catalytic activity for HCHO oxidation. Du et al. [20] prepared MnO<sub>2</sub>-KIT6 and MnO<sub>2</sub>-SBA16 using different hard templates (SBA-16 and KIT-6). Results showed MnO<sub>2</sub>-KIT6 with a three-dimensional ordered mesoporous structure performed better than MnO2-SBA16 with a wormhole-like mesoporous structure in the removal of toluene. Unfortunately, we found that there were still few reports referring to the effects of Mn (II) precursors on the MnO<sub>2</sub> catalysts for VOCs oxidation. In addition, the reaction pathway about the oxidation of most of VOCs over the MnO2 catalyst was still not very clear.

Therefore, in this study,  $MnO_2$  samples were prepared by the redox reaction between potassium permanganate ( $KMnO_4$ ) and various Mn

(II) precursors. Toluene was selected as the target pollutant because it is widely used as solvents and has been classified as a priority pollutant. The influences of Mn (II) precursors on the physicochemical characteristics and catalytic activities for toluene oxidation of these  $MnO_2$  samples were studied. Then the effects of flue gas component ( $O_2$  and  $H_2O$ ), weight hourly space velocity (WHSV) and toluene concentration as well as long-term stability over the optimum samples were investigated. Moreover, the catalytic reaction pathway for toluene oxidation over the optimum samples was also presented with the help of in situ DRIFTS technique.

### 2. Experimental section

#### 2.1. Catalyst preparation

To study the effect of Mn (II) precursor on the catalytic performance in toluene oxidation, the MnO2 catalysts were prepared by a facile redox reaction between potassium permanganate (KMnO<sub>4</sub>) and manganese acetate (Mn(CH<sub>3</sub>COO)·4H<sub>2</sub>O), manganese nitrate (50 wt% Mn (NO<sub>3</sub>)<sub>2</sub> solution), manganese chloride (MnCl<sub>2</sub>·4H<sub>2</sub>O), or manganese sulfate (MnSO<sub>4</sub>·H<sub>2</sub>O) at room temperature. Note that all the chemicals used in this study were of analytical grade, and were used without further purification. The process was as follows: the Mn (II) precursor solution was dropped into the KMnO<sub>4</sub> solution under vigorous stirring, and stirred continuously for 24 h at room temperature, then filtered and washed three times with deionized water. The obtained solid sample was dried at 105 °C for 12 h and followed by calcined in air at 300 °C for 2 h. Finally, the sample was grinded to powder (40-60 mesh). These synthesized samples were donated as MnO2-Ac (manganese acetate as precursor), MnO<sub>2</sub>-N (manganese nitrate as precursor), MnO<sub>2</sub>-Cl (manganese chloride as precursor), and MnO<sub>2</sub>-S (manganese sulfate as precursor).

#### 2.2. Catalyst characterization

The X-ray diffraction (XRD) was tested between 5° and 80° (2 $\theta$ ) using a Riguku D/Max 2550 (Rigaku Corporation, Japan) diffractometer with Cu Ka radiation (40 kV and 250 mA). The transmission electron microscopy (TEM) was recorded using TECNAL G2 F20 high resolution transmission electron microscope (FEI 207 Company, USA) with an accelerating voltage of 200 kV. The N2 adsorption-desorption tests were performed on a Quadrasorb SI-3MP (USA) instrument at 77 K. The specific surface areas and pore structure parameters were calculated by the Brunauer-Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) method. The H2-temperature-programmed reduction (H2-TPR) was performed on an AutoChem 2920 (China) automated adsorption analyzer equipped with a TCD detector. 50 mg sample was first treated in Ar stream (30 mL min<sup>-1</sup>) at 300 °C for 1 h, and then cooling down to room temperature. After that, the reducing gas (5% H<sub>2</sub>/Ar) at a flow rate of  $30 \text{ mLmin}^{-1}$  was introduced and the samples were heated up to 600 °C at a rate of 10 °C min<sup>-1</sup>. The X-ray photoelectron spectroscopy (XPS) analyses were carried out on a K-Alpha 1063 spectrometer (Thermo Fisher Scientific, USA), using Al Ka as the X-ray radiation source. The In-situ DRIFTS experiments were performed in an FT-IR spectrometer (Thermo Fisher Nicolet iZ10) equipped with an in-situ cell and a liquid N2-cooled MCT detector to study the intermediates in toluene oxidation over  $MnO_2$ -AC. The spectra were recorded at a resolution of  $2 \text{ cm}^{-1}$  in the range of 500–4000  $\text{cm}^{-1}$ . The sample was first pretreated under air at 300 °C and cooled down to test temperature. Then, the adsorption followed under a flow of toluene/air (toluene = 1000 ppm).

#### 2.3. Catalytic performance test

The experimental setup of toluene oxidation on  $MnO_2$  is shown in Fig. 1. The catalytic activity measurement was carried out in a fixed bed



Fig. 1. Schematic diagram of the experimental setup.



Fig. 2. The effect of  $Mn^{2+}$  precursors on toluene oxidation activities over  $MnO_2$  samples (Reaction conditions: 1000 ppm toluene, 21 vol%  $O_2$ ,  $N_2$  as balance, WHSV = 90,000 mL/(g h)).

continuous flow quartz reactor (i.d. = 6.0 mm, length = 600 mm) at atmospheric pressure. 0.1 g of catalysts (40-60 mesh) was loaded in the reactor for each run. The simulated flue gas contains 1000 ppm toluene generated by passing N<sub>2</sub> through toluene bubbler cooled in an ice-water isothermal bath, 21 vol% O2 and balanced N2. And all gas flows were controlled by mass flow controller, respectively, at a total flow rate of 150 mL min<sup>-1</sup>, corresponding to WHSV of 90,000 mL/(g h). The effect of WHSV on toluene conversion efficiency was investigated by altering the catalyst dosage to make different space velocity. The effect of toluene inlet concentration on toluene conversion efficiency was investigated by altering the flow of N<sub>2</sub> used to carry toluene to make different inlet toluene concentration. The performance was evaluated at the temperature range of 140-300 °C. The reaction temperature was controlled by a digital temperature controller. Each sampling temperature was stabilized for 30 min prior to measuring the toluene concentration in effluent gas. The concentration of toluene in feed gas and effluent gas were analyzed on-line by gas chromatography (GC-2014C, Shimadzu, Japan) equipped with a flame ionization detector (FID). The conversion of toluene (X<sub>tol</sub>) and the specific reaction rates (R,

per unit surface area of catalyst,  $\mu mol\ m^{-2}\ h^{-1})$  was calculated via the following equation:

$$X_{tol} = \frac{C_{in} - C_{out}}{C_{in}} \times 100\%$$
$$R(\mu \text{mol } \text{m}^{-2} \text{h}^{-1}) = \frac{C_{in} \div 22.4 \times \text{Fx} X_{tol}}{\text{Sx} \text{ m}}$$

where  $C_{\rm in}$  and  $C_{out}$  represent the inlet concentration and the outlet concentration of toluene, respectively. F is the flow rate (L h^{-1}), S is the specific surface area of sample (m<sup>2</sup> g<sup>-1</sup>) and m is the sample weight (g).

#### 3. Results and discussion

#### 3.1. Catalytic performance

#### 3.1.1. The effect of Mn (II) precursors

A blank experiment (only quartz wool was loaded) was performed at first to exclude any interference of the reactor. No significant conversion of toluene was detected below 300 °C, indicating that there was no occurrence of homogeneous reactions under the adopted reaction conditions. The catalytic conversion of toluene versus reaction temperature over the four MnO<sub>2</sub> samples prepared using diffident Mn (II) precursors was presented in Fig. 2. The conversion of toluene at  $T_{10}$ ,  $T_{50}$ and  $T_{90}$  (the temperature at 10%, 50% and 90% of conversion, respectively) as well as specific reaction rates (R) were listed in Table 1. Obviously, higher toluene conversion of the four samples was obtained at higher reaction temperature and nearly 100% toluene conversion was reached at 300 °C for all samples. Besides, it could be seen that the activity of toluene oxidation was influenced by the Mn precursors to a

Table 1		
Catalytic activities	for various	s catalysts.

Samples	Toluene conversion temperature		erature	Specific reaction rates $(\text{upol}\text{m}^{-2}\text{h}^{-1})$
	T <sub>10</sub> (°C)	T <sub>50</sub> (°C)	T <sub>90</sub> (°C)	
MnO <sub>2</sub> -Ac	160	183	200	4.33
MnO <sub>2</sub> -N	163	188	210	3.35
MnO <sub>2</sub> -Cl	180	207	225	1.72
MnO <sub>2</sub> -S	190	215	236	1.57

Note: The specific reaction rates were calculated at 170 °C.



Fig. 3. The effect of (a) WHSV and (b) toluene inlet concentration on tolueneoxidationactivitiesover $MnO_2$ -Acsample(Reactionconditions:1000–3000 ppmtoluene,21 vol% $O_2$ , $N_2$ asbalance,WHSV = 30,000–200,000 mL/(g h)).

large extent. MnO<sub>2</sub>-Ac showed the best activity among the four samples with  $T_{10}, T_{50}$  and  $T_{90}$  of 160, 183 and 200 °C, respectively as well as R of 4.33  $\mu mol \ m^{-2} \ h^{-1}$ . The catalytic activity order of the four samples decreased as follows: MnO<sub>2</sub>-Ac > MnO<sub>2</sub>-N > MnO<sub>2</sub>-Cl > MnO<sub>2</sub>-S. Therefore, MnO<sub>2</sub>-Ac sample was used in the following study based on the experimental result.

#### 3.1.2. The effect of WHSV and toluene concentration

As is well-known, WHSV is a crucial parameter in actual industrial application. So the effect of WHSV on the catalytic activity of toluene oxidation over  $MnO_2$ -Ac catalyst was studied, and the results are displayed in Fig. 3a. As expected, the catalytic activity of  $MnO_2$ -Ac decreased as WHSV increasing from 30,000 to 200,000 mL/(g h), because a longer residence time of toluene on the catalyst surface benefits catalytic oxidation. However, even at WHSV of 200,000 mL/(g h), the 90% toluene conversion was also achieved at a relative low temperature (247 °C).

Pollutant concentration is also an important factors in practical application. Fig. 3b exhibits the influence of toluene concentration on the catalytic activity of  $MnO_2$ -Ac catalyst for toluene oxidation. It is obvious that inlet toluene concentration has negligible effect on the catalytic activity. The catalytic activity of  $MnO_2$ -Ac decreased slightly with toluene concentration increasing from 1000 ppm to 3000 ppm. The above results suggested that  $MnO_2$ -Ac can work well under high WHSV and high toluene concentration.



Fig. 4. The effect of  $O_2$  on toluene oxidation activities over  $MnO_2$ -Ac sample (Reaction conditions: 1000 ppm toluene, 0–21 vol%  $O_2$ ,  $N_2$  as balance, WHSV = 30,000 mL/(g h), T = 300 °C).

#### 3.1.3. The effect of $O_2$

As a crucial gas component, the effect of  $O_2$  on toluene oxidation over MnO<sub>2</sub>-Ac was investigated. The results are exhibited in Fig. 4. Prior to the reaction without gas-phase O<sub>2</sub>, the reactor was firstly pretreated with pure N2 for 1 h at 300 °C to remove the physical adsorbed oxygen, and then followed under a flow of toluene/N2 (toluene = 1000 ppm) at 300 °C. It could be seen from Fig. 4 that the conversion of toluene was 47.8% at exposure time of 10 min, and then the conversion of toluene gradually decreased to nearly zero with the time increasing. The result demonstrated that the limited surface adsorbed oxygen and lattice oxygen involved in the toluene oxidation, consisting with the previous results [23]. After the reaction without gas-phase O2 continued for 90 min, 21% O2 was added in flue gas. There was an evident change for the toluene conversion. It could be clearly seen that the conversion of toluene quickly rose to 96.4% at exposure time of 100 min, and then stabilized at nearly 100%. The above results revealed that gas-phase O2 significantly affected toluene oxidation. It might play an important role in the replenishment of the adsorbed oxygen and the regeneration of lattice oxygen. Besides, the very rapid increase of the toluene conversion efficiency after the addition of 21% O<sub>2</sub> might also be related to the high content of oxygen vacancy on the MnO<sub>2</sub>-Ac surface, which would be discussed in later section.

#### 3.1.4. The effect of $H_2O$

In the real exhaust gas,  $H_2O$  is one of the inevitable components. The presence of  $H_2O$  usually lead to an inhibiting effect for removal of VOCs, and rarely a promoting effect [6]. In this study, the influence of  $H_2O$  on toluene oxidation over  $MnO_2$ -Ac was investigated in the presence of  $H_2O$  with different concentrations from 0% to 15%, and the results were displayed in Fig. 5a. It can be clearly seen that  $H_2O$  had an inhibiting effect on the catalytic activity of  $MnO_2$ -Ac. The catalytic activity decreased with the increasing of  $H_2O$  content in feed gas. This inhibiting effect may be due to the competitive adsorption of  $H_2O$  and toluene on surface active sites of  $MnO_2$ -Ac [24]. Remarkably, nearly 100% toluene conversion was achieved at 300 °C for all different moisture levels, indicating that the  $MnO_2$ -Ac sample possessed good water-resistance at sufficiently high temperature.

To evaluate the catalytic performance of  $MnO_2$ -Ac comprehensively, the 50 h stability test for toluene oxidation was performed at 300 °C. The feed gas contained 5% H<sub>2</sub>O. As shown in Fig. 5b, the toluene conversion was always remained at about 100% during 50 h tests, indicating that  $MnO_2$ -Ac has excellent water-resistance and stability for toluene oxidation at 300 °C.



**Fig. 5.** (a) The effect of H<sub>2</sub>O on toluene oxidation activities over MnO<sub>2</sub>-Ac sample (Reaction conditions: 1000 ppm toluene, 21 vol% O<sub>2</sub>, 0–15 vol% H<sub>2</sub>O, N<sub>2</sub> as balance, WHSV = 90,000 mL/(g h)); (b) The long-term stability test over MnO<sub>2</sub>-Ac sample (Reaction conditions: 1000 ppm toluene, 21 vol% O<sub>2</sub>, 5 vol% H<sub>2</sub>O, N<sub>2</sub> as balance, WHSV = 30,000 mL/(g h), T = 300 °C).

#### 3.2. Catalyst characterization

#### 3.2.1. Textural and structural characterization



XRD analysis is usually used to determine crystal composition and crystallize parameters of catalysts. Fig. 6 shows the XRD patterns of the four MnO<sub>2</sub> samples. All samples presented three peaks at  $2\theta = 37.4^\circ$ ,

Fig. 6. XRD patterns of  $MnO_2$  samples.

42.3° and 66.5°, corresponding to birnessite-type  $MnO_2$  [25]. The three peaks were broad and weak, meaning the low crystallinity nature and approximately amorphous nature of these samples. In addition, it can be observed that  $MnO_2$ -Ac owned weaker diffractions than other samples, suggesting lower crystallinity which benefits the toluene oxidation.

Fig. 7 shows the TEM images of these  $MnO_2$  samples. All  $MnO_2$  samples were with mixed crystalline and amorphous parts, and amorphism was the main part. This was consistent with the results of XRD characterization. In addition, these samples possessed different morphology.  $MnO_2$ -Ac has no special morphology, it consisted of closely packed nanosheets with a few nanometers in size.  $MnO_2$ -Cl and  $MnO_2$ -N showed flower-like morphology consisting of nanosheets, and the diameter was about 90 nm.  $MnO_2$ -S displayed spherical morphology composed by nanosheets, with diameter of about 150 nm. The TEM images indicated that the Mn (II) precursors visibly acted a vital role in determining the morphology of  $MnO_2$  catalysts.

Fig. 8a shows the  $N_2$  adsorption–desorption isotherms of these  $MnO_2$  samples. Obviously, all of the samples exhibited a type IV sorption isotherm with a hysteresis loop at  $p/p_0 = 0.4-0.7$  for  $MnO_2$ -Ac and 0.4–1.0 for other three samples, suggesting the presence of mesoporous structures. In Fig. 8b, the presence of mesoporous structures was substantiated by the pore size distributions measurements calculated from the desorption isotherm using the Barrett–Joyner–Halenda (BJH) method. For  $MnO_2$ -Ac sample, there was one sharp peak at ca. 3.6 nm, indicating that its pore size was relatively uniform. Compared with  $MnO_2$ -Ac,  $MnO_2$ -N and  $MnO_2$ -Cl possessed one smaller peak at ca. 3.6 nm. For the  $MnO_2$ -S sample, there were two small broad peaks at ca. 3.6 nm and ca. 5.3 nm, respectively, indicating that its pore size distribution was relatively wide.

The pore parameters and specific surface areas of these MnO<sub>2</sub> samples were summarized in Table 2. MnO<sub>2</sub>-Ac owned the largest specific surface area of 231 m<sup>2</sup> g<sup>-1</sup>, followed by MnO<sub>2</sub>-N, MnO<sub>2</sub>-Cl and  $MnO_2$ -S with this values of 186, 140 and 77 m<sup>2</sup> g<sup>-1</sup>, respectively. This is probably related to the lower crystallinity of MnO<sub>2</sub>-Ac sample that demonstrated by the XRD results. MnO<sub>2</sub>-S owned the largest average pore diameter of 10.497 nm, followed by MnO2-N, MnO2-Cl and MnO2-Ac with that of 8.848, 7.553, and 4.396 nm, respectively. The total pore volume of  $MnO_2$ -N was 0.410 cm<sup>3</sup> g<sup>-1</sup>, much higher than the values of 0.264, 0.254 and 0.202 cm<sup>3</sup> g<sup>-1</sup> of MnO<sub>2</sub>-Cl, MnO<sub>2</sub>-Ac and MnO<sub>2</sub>-S, respectively. It could be found that the order of the specific surface areas of the four MnO<sub>2</sub> samples was highly correlated with that of catalytic activities, which meant that specific surface areas was an key factors affecting the reaction activities of toluene oxidation. The large surface area of MnO2-Ac benefited the exposure of active sites and could enhance contact efficiency between gaseous toluene and catalyst surface.

#### 3.2.2. Surface chemical properties

H<sub>2</sub>-TPR is an effective tool to investigate the low-temperature reducibility of solid oxide catalysts. The better low-temperature reducibility is normally advantageous to enhance the mobility of oxygen species and hereby promote the redox process [8]. Fig. 9 displays the H<sub>2</sub>-TPR profiles of the four MnO<sub>2</sub> samples. In general, the H<sub>2</sub>-TPR profiles of MnO<sub>2</sub> catalysts exhibited two peaks related to the following two processes: the reduction of  $Mn^{4+}$  to  $Mn^{3+}$  and the reduction of  $Mn^{3+}$  to  $Mn^{2+}$  [8]. Herein,  $MnO_2$ -S showed two reduction peaks at 362 °C and 417 °C, while MnO<sub>2</sub>-Ac, MnO<sub>2</sub>-N and MnO<sub>2</sub>-Cl displayed an overlapping peak at above 362 °C, 378 °C and 385 °C, respectively. Obviously, the low-temperature reducibility decreased in the trend of  $MnO_2-S > MnO_2-Ac > MnO_2-N > MnO_2-Cl$ , which was not in good accordance with the catalytic activities. This result suggested that there was no direct correlation between the low-temperature reducibility of MnO<sub>2</sub> samples and catalytic activity for toluene oxidation. The effect of low-temperature reducibility on toluene oxidation activity thereby could be ruled out.



Fig. 7. TEM images of (a, b) MnO<sub>2</sub>-Ac, (c, d) MnO<sub>2</sub>-N, (e, f) MnO<sub>2</sub>-Cl, (g, h) MnO<sub>2</sub>-S.



**Fig. 8.** (a) Nitrogen adsorption-desorption isotherms and corresponding (b) pore size distribution curves.

 Table 2

 Specific surface area and pore parameters of various samples.

Samples	Specific surface area (m <sup>2</sup> /g)	Total pore volume (cm <sup>3</sup> /g)	Average pore diameter (nm)
MnO <sub>2</sub> -Ac	231	0.254	4.40
MnO <sub>2</sub> -N	186	0.410	8.85
MnO <sub>2</sub> -Cl	140	0.264	7.55
MnO <sub>2</sub> -S	77	0.202	10.50

The oxidation states of surface elements on these  $MnO_2$  samples were clearly differentiated by XPS measurements. Fig. 10a and 10b presents the XPS spectra of O 1s and Mn 2p, respectively. The corresponding surface information was compared in Table 3. The Mn 2p peaks were made up of two spin-orbital lines of Mn 2p<sub>3/2</sub> and Mn 2p<sub>1/2</sub>, with binding energies of 642.5–642.7 eV and 654.2 eV, respectively. The spin-energy separation between the two peaks was about 11.5–11.7 eV for these MnO<sub>2</sub> samples, indicating the presence of mostly Mn<sup>4+</sup> [26]. The Mn2p<sub>3/2</sub> spectra of all samples were deconvoluted into three peaks with binding energy of 642.1 eV, 643.3 eV and 645.7–646.1 eV, representing surface Mn<sup>3+</sup> species, surface Mn<sup>4+</sup> species and the satellite, respectively [27,28]. The coexistence of Mn<sup>3+</sup> and Mn<sup>4+</sup> benefited the transfer and transformation of electrons, which could facilitate the redox properties of samples and hence improved its



Fig. 9. H<sub>2</sub>-TPR profiles of MnO<sub>2</sub> samples.

catalytic performance. The differences in  $Mn^{3+}/Mn^{4+}$  area ratios of these  $MnO_2$  samples were observed in Table 3, indicating that Mn (II) precursor had an influence on  $Mn^{3+}/Mn^{4+}$  area ratios. The  $Mn^{3+}/Mn^{4+}$  area ratios declined as follows:  $MnO_2$ -Ac >  $MnO_2$ -N >  $MnO_2$ -Cl >  $MnO_2$ -S. According to the principle of electrostatic balance, the presence of  $Mn^{3+}$  in  $MnO_2$  samples means that oxygen vacancies are created [26,29]. In other words, the higher surface concentration of  $Mn^{3+}$  implies the higher oxygen vacancies defect. Therefore, we can reach that  $MnO_2$ -Ac had the highest content of oxygen vacancies. The content of oxygen vacancies is an important impact factor for oxidation reaction. Previous experimental studies and theoretical calculations revealed that abundant oxygen vacancies can facilitate the rapid adsorption and activation of  $O_2$  molecules, enhance oxygen storage capacity and reduce oxygen migration activation energy [30–32].

For all samples, O 1 s was fitted in two peaks at 530.0–530.2 eV and 531.2–532.3 eV, attributed to surface lattice oxygen ( $O_L$ ) existed as  $O^{2-}$  and surface adsorbed oxygen ( $O_A$ ) such as  $O_2^{2-}$ ,  $O_2^-$ ,  $O^-$  and terminal OH group, respectively [33]. Both kinds of surface oxygen can affect the VOCs oxidation efficiency. It has been demonstrated that catalytic oxidation of VOCs over non-noble metal oxides usually followed Marsvan Krevelen mechanism [8]. In this mechanism, the surface lattice oxygen play an important role in reacting with adsorbed VOCs. Relevant literature mentioned that surface adsorbed oxygen owned higher mobility than surface lattice oxygen, and tended to replenish the lattice oxygen via a series of migrations and transformation [31,34]. As shown



Fig. 10. XPS analysis of fresh  $MnO_2$  samples and used  $MnO_2$ -Ac sample: (a) fitted Mn 2p photoelectron peaks; (b) fitted O 1s photoelectron peaks.

# Table 3

Surface element molar ratios of various catalysts.

Samples	Surface element area ratio		
	Mn <sup>3+</sup> /Mn <sup>4+</sup>	$O_A/O_L$	
MnO <sub>2</sub> -Ac	0.892	1.192	
MnO2-N	0.846	1.109	
MnO2-Cl	0.760	1.083	
MnO <sub>2</sub> -S	0.685	0.883	
U-MnO <sub>2</sub> -Ac	0.709	0.965	

in Table 3, Mn (II) precursor also affected  $O_A/O_L$  area ratios. The  $O_A/O_L$  area ratios declined in the order of  $MnO_2\text{-}Ac > MnO_2\text{-}N > MnO_2\text{-}Cl > MnO_2\text{-}S$ . The result agreed well with the Mn  $2p_{3/2}$  spectra. This is because surface adsorbed oxygen species usually locates in oxygen vacancies of catalysts, and they are mainly influenced by surface oxygen vacancies.

According to the above results, it was clear that the trend of the  $Mn^{3+}/Mn^{4+}$  area ratios and the  $O_A/O_L$  area ratios of the four  $MnO_2$  samples were highly correlated with that of catalytic activities. That is, the content of oxygen vacancies and adsorbed oxygen on  $MnO_2$  surface played an important role in toluene oxidation.

As shown in Fig. 10, the XPS measurements of used MnO<sub>2</sub>-Ac was



Fig. 11. DRIFTS spectra of  $MnO_2$ -Ac (a) at room temperature and (b) at elevated temperature in a flue gas containing 1000 ppm toluene.

also performed. The used MnO<sub>2</sub>-Ac obtained after the stability test at 300 °C. Compared with fresh MnO<sub>2</sub>-Ac, the Mn<sup>3+</sup>/Mn<sup>4+</sup> and O<sub>A</sub>/O<sub>L</sub> area ratios of used MnO<sub>2</sub>-Ac decreased by 0.183 and 0.227, respectively. The declined ratio confirmed the important role of oxygen vacancies and surface adsorbed oxygen species.

#### 3.3. The reaction pathway for toluene oxidation

Catalytic oxidation of toluene is a sophisticated process. Many intermediates can be generated before complete oxidation into  $CO_2$  and  $H_2O$ . Up to now, the exact reaction pathway for toluene oxidation on Mn-based catalysts was not well understood. In this study, the in-situ DRIFT was used to study the reaction process of toluene oxidation over  $MnO_2$ -Ac.

The DRIFT spectra of toluene adsorbed with the increase of time at room temperature are shown in Fig. 11a. The bands at 1619, 1604, 1495 and 1462 cm<sup>-1</sup> belonged to the typical aromatic ring skeletal vibrations [35]. The bands at 3084, 3030 and 1030 cm<sup>-1</sup> were ascribed to the C–H stretching vibration and C–H in plane bending vibrations of aromatic rings, respectively [35–37]. And the symmetric bending vibration of methyl (–CH<sub>3</sub>) at 1380 cm<sup>-1</sup> was also observed [35]. With time increasing, the intensity of these bands increased initially, and did not increase obviously after 12 min. These observations indicated that toluene could be adsorbed easily on the surface of MnO<sub>2</sub>-Ac and the aromatic nucleus remained intact. Besides, the weak bands ascribed to C–O stretching vibration modes appeared at 1179, 1156 and 1082 cm<sup>-1</sup> [38,39], and the bands at 2925 and 2879 cm<sup>-1</sup> were



Fig. 12. Reaction pathway for toluene oxidation over MnO<sub>2</sub>-Ac sample.

assigned to C–H asymmetric or symmetric stretching vibration of methylene (–CH<sub>2</sub>) rather than methyl (–CH<sub>3</sub>) [40]. So it can be inferred that part of adsorbed toluene interacted with the active oxygen on MnO<sub>2</sub>-Ac surface by abstracting an H of the methyl group to generate benzoyl oxide species (C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>-O). The band at 1655 cm<sup>-1</sup> could be ascribed to aldehydic species [36], suggesting benzoyl oxide species were further oxidized even at room temperature.

To further illuminate the evolution of adsorption species on the surface of MnO<sub>2</sub>-Ac, the spectra at elevated temperatures were recorded after MnO<sub>2</sub>-Ac was exposed to toluene for 30 min. The results are shown in Fig. 11b. Compared to the spectra at room temperature, the spectrum at the temperature of 220 °C changed dramatically. The intensity of the bands related to aldehydic species increased, meaning that almost all adsorbed toluene interacted with the active oxygen on MnO<sub>2</sub>-Ac surface to form benzoyl oxide species. The bands belonging to an aromatic ring shifted to lower wavenumber (1596, 1491 and  $1445 \text{ cm}^{-1}$ ), which might be due to that there were some interactions between aromatic ring and MnO2-Ac surface at 220 °C and hereby led to the changes in electronic distribution and the symmetry of the aromatic ring [41]. Similar changes were reported previously [38]. The bands at 1540 and 1412 cm<sup>-1</sup> were assignable to asymmetric and symmetric stretching vibration of carboxylate group, respectively, indicating the formation of benzoate species [42]. And it can be seen that benzoate species was the dominant intermediates. The frequency separation of the two bands is  $128 \text{ cm}^{-1}$ , manifesting the benzoate species was bonded to the sample in a bridging bidentate configuration [43].

At the temperature of 260 °C, the bands implying the cleavage of aromatic ring appeared. The bands at 1745, 1436 and 1319 cm<sup>-1</sup> were assignable to maleic anhydride [44,45]. The band at 1574 cm<sup>-1</sup> was designated to long-chain carboxylate [46]. Moreover, the bands corresponding to CO<sub>2</sub> (2445 and 2331 cm<sup>-1</sup>) and the crystallization bending vibration of H<sub>2</sub>O (1640 cm<sup>-1</sup>) suggested that these intermediates without aromatic ring were further oxidized into CO<sub>2</sub> and H<sub>2</sub>O [38,47].

Based on the discussion above and Mars-van Krevelen mechanism, the pathway of toluene oxidation was purposed and depicted in Fig. 12. Initially toluene was adsorbed on lattice oxygen species on the catalyst surface to form benzoyl oxide species ( $C_6H_5$ - $CH_2$ -O) by abstracting an H of the methyl group, and benzoyl oxide species successively transformed into aldehydic species and benzoate species. Then, the aromatic ring was opened, and maleic anhydride and long-chain carboxylate were generated. Finally, the intermediates without aromatic ring were oxidized to  $CO_2$  and  $H_2O$ . Meanwhile, the consumed lattice oxygen could be replenished with the incessant dissociation of gaseous oxygen through the redox couple  $Mn^{3+}/Mn^{4+}$  and the abundant oxygen vacancies.

#### 4. Conclusion

Four MnO<sub>2</sub> samples were prepared by the redox reaction between KMnO<sub>4</sub> and various Mn (II) precursors for the toluene oxidation. The catalytic activities for toluene oxidation and physicochemical characteristics of these samples were affected by the nature of Mn (II) precursors. MnO<sub>2</sub>-Ac showed optimal toluene oxidation activity with T10, T50 and T90 of 160, 183 and 200 °C, respectively, followed by MnO2-N, MnO2-Cl and MnO2-S. In addition, MnO2-Ac also worked well under high WHSV and high toluene concentration. This was highly relative to the specific surface areas, the content of vacancy defects and the content of adsorbed oxygen species. Gas-phase O<sub>2</sub> played a significant role in the replenishment of the adsorbed oxygen and the regeneration of lattice oxygen. The presence of H<sub>2</sub>O had an inhibition effect on toluene oxidation when the reaction temperature was lower than 300 °C, and the inhibition effect was enhanced with the increase of H<sub>2</sub>O content. However, the presence of H<sub>2</sub>O had little effect on toluene oxidation at 300 °C for all the different H2O contents, and MnO2-Ac showed excellent stability during 50 h at 300 °C when 5% H<sub>2</sub>O in exhaust gas. The above results indicated MnO2-Ac is a robust catalyst and have potential for practical applications. Furthermore, the reaction pathway of toluene oxidation was presented with the help of In-situ DRIFTS experiments. Benzoyl oxide, benzaldehyde, benzoate, maleic anhydride and long-chain carboxylate were the main intermediates before toluene was oxidized to CO2 and H2O.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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