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# Insight into the promotional effect of $\mathrm{NO}_2$ on toluene oxidation over MnCe/ HZSM-5 catalyst

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# ABSTRACT

A thorough probe into the activation mechanism of NO<sub>2</sub> on toluene oxidation during co-removal of toluene in NH<sub>3</sub>-SCR unit is imperative but still lacking. This study unraveled the promotional effects of NO<sub>2</sub> on toluene conversion, CO<sub>2</sub> selectivity and catalytic stability over a MnCe/HZSM-5 catalyst. 1000 ppm NO<sub>2</sub> was sufficient for complete oxidation of 50 ppm toluene into CO<sub>2</sub> at 280 °C in the absence of O<sub>2</sub> (C<sub>7</sub>H<sub>8</sub> + 18NO<sub>2</sub>  $\rightarrow$  7CO<sub>2</sub> + 4H<sub>2</sub>O + 18NO). NO<sub>2</sub> had stronger oxidizing ability than O<sub>2</sub>, while O<sub>2</sub> re-oxidized NO to NO<sub>2</sub>, resulting in a synergistic contribution to toluene conversion. NO<sub>2</sub> participated in toluene oxidation producing predominant NO and negligible organic N-byproducts. The N in NO<sub>2</sub> scarcely took part in the organic synthesis process. NO<sub>2</sub> gave one of its O easily to provide additional O<sub>sur</sub> and improved mobility and activity of O<sub>lat</sub>, hence speeding up the reoxidation of reduced metal sites. The activation of NO<sub>2</sub> on toluene oxidation predominantly followed Mars-van Krevelen mechanism. The Langmuir-Hinshelwood mechanism also existed but was less important.

#### 1. Introduction

Solid waste incineration emits NO<sub>x</sub> and VOCs (e.g., toluene) simultaneously, arising serious threats to the environment and human health. Catalytic method of reducing NO<sub>x</sub> to N<sub>2</sub> and oxidizing VOCs to CO<sub>2</sub> is effective and clean. In recent years, NH<sub>3</sub>-SCR technology for NO<sub>x</sub> abatement has been explored to co-remove VOCs successfully [1–7], thereby hopefully cutting the investment and land-use for the flue gas treatment system of incineration plants. The understanding of interaction between SCR reaction and VOCs oxidation provides theoretical guidance to rationally design bifunctional catalysts [8].

Several studies already investigated the impacts of  $NH_3$ -SCR reactants on VOCs oxidation.  $NH_3$  delivered negative effects on VOCs oxidation due to the formation of N-byproducts (e.g., benzonitrile and nitrobenzene) and the competitive adsorption between  $NH_3$  and VOCs [9–13]. Whereas, NO possessed a positive effect derived from its oxidizing product  $NO_2$ . NO itself and the adsorbed nitrates or nitrites were not able to play the role of oxidants for VOCs catalytic oxidation [14]. Bertinchamps et al. [15,16] proposed an activation mechanism induced by  $NO_x$  on the performances of  $VO_x/TiO_2$  catalysts in

chlorinated VOCs oxidation. Briefly, chlorobenzene was oxidized on VO<sub>x</sub> site through Mars-van Krevelen (MvK) mechanism. NO was catalytically oxidized to NO<sub>2</sub> in the same time. The *in-situ* generated NO<sub>2</sub> assisted O<sub>2</sub> in the reoxidation of V<sup>4+</sup>O<sub>x</sub> to V<sup>5+</sup>O<sub>x</sub>, thus accelerating the oxidation cycle of catalyst. This activation mechanism has been well accepted and cited in many works related to the simultaneous removal of NO and VOCs [3,17–19]. However, details to further explain this phenomenon are lacking and urgently need more investigation.

First, the mechanism of toluene oxidation by  $O_2$  has been widely researched [20,21]. The MvK mechanism is mostly recognized, where toluene is first oxidized to  $CO_2$  and  $H_2O$  by lattice oxygen, leading to the reduction of metal oxides, then the reduced sites are re-oxidized by gaseous  $O_2$  [22,23]. The aforementioned activation process also presumed a MvK mechanism of VOCs oxidation by  $NO_2$  [15,16]. Nevertheless, more and more researchers revealed the existence of a Langmuir-Hinshelwood (L-H) mechanism especially at relatively low temperatures, where toluene reacted with adsorbed peroxide [24,25]. It is reasonable to re-consider and further clarify the reaction mechanism of toluene oxidation by  $NO_2$ . Second, the  $NO_x$  concentration is usually 1–2 orders of magnitude higher than toluene concentration in industrial

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## Table 1

Characterization parameters of obtained catalysts.

Sample	Activation energy (kJ/ mol)	Surface area <sup>a</sup> (m <sup>2</sup> /g)	H <sub>2</sub> consumption <sup>b</sup> (mmol/g)	Mn content <sup>c</sup> (wt%)	Peak area of O <sub>2</sub> - TPD <sup>d</sup>
MnO <sub>x</sub> /HZSM- 5	37.89	240.8	1.08	9.02	165
Mn <sub>0.8</sub> Ce <sub>0.2</sub> O <sub>2</sub> / HZSM-5	27.62	267.9	0.87	5.81	313
Mn <sub>0.5</sub> Ce <sub>0.5</sub> O <sub>2</sub> / HZSM-5	23.97	261.3	0.68	3.23	2011
Mn <sub>0.2</sub> Ce <sub>0.8</sub> O <sub>2</sub> / HZSM-5	31.62	256.2	0.93	1.24	437
CeO <sub>2</sub> /HZSM-5	/	199.4	/	/	/

<sup>a</sup> determined by the BET method.

<sup>b</sup> H<sub>2</sub> consumption obtained from 50 to 800 °C in TPR profiles.

<sup>c</sup> Mn content obtained from ICP-OES.

<sup>d</sup> Peak area of O<sub>2</sub>-TPD below 300 °C.

flue gas [12,26]. The *in-situ* generated NO<sub>2</sub> hopefully oxidizes toluene completely. A quantitative analysis of the NO<sub>2</sub> contribution to toluene oxidation in the presence/absence of O<sub>2</sub> is imperative, but has rarely been reported in literature. Third, the organic byproducts during toluene oxidation in NH<sub>3</sub>-SCR unit are undesirable. The solid byproducts cover the catalyst surface, leading to deactivation. The hazardous benzamide and benzonitrile in the off-gas may cause health risks [9,14]. Special care should be considered towards the organic byproducts generated from toluene oxidation by NO<sub>2</sub>.

MnCe/HZSM-5 catalyst delivered excellent activities towards NH3-SCR and VOCs oxidation due to good redox ability, superior oxygen storage capability, adjustable acid sites, large surface area and thermal stability [27-32], hence being a potential bifunctional catalyst for coremoval of NOx and toluene. In this work, MnCe/HZSM-5 catalyst was utilized to explore the impacts of NO2 on the performance of toluene catalytic oxidation. Activity test, thermal desorption instrument coupled with a gas chromatography-mass spectrometer (TD-GC-MS), in-situ diffuse reflectance infrared Fourier transforms (DRIFTs) coupled with Fourier transform infrared spectroscopy (FTIR), together with other characterization methods were applied. Special attention has been paid to the NO<sub>2</sub> contribution, byproduct information and reaction mechanism of toluene oxidation by NO<sub>2</sub>. The findings will contribute to a deep understanding of the activation mechanism of NO<sub>x</sub> on toluene oxidation and shed lights on the design of bifunctional catalysts, which may achieve mutual promotion in simultaneous removal of NO<sub>x</sub> and VOCs.

# 2. Experimental

# 2.1. Catalyst preparation

The  $Mn_xCe_{1-x}O_2/HZSM$ -5 catalyst with various Mn/Ce molar ratios (100Mn-0Ce, 80Mn-20Ce, 50Mn-50Ce, 20Mn-80Ce and 0Mn-100Ce) were synthesized by wet impregnation method. The mass ratio and the SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio of HZSM-5 support were 80 wt% and 25, respectively. Preparation details can be found in our previous work [9].

#### 2.2. Activity measurement

The catalyst was sieved to a particle size of 40–60 mesh and placed in a quartz fixed-bed reactor (i.d. = 8 mm). The reaction temperature was monitored by a thermocouple located in the center of the catalyst bed. 200 mL/min feed gas consisted of 50 ppm toluene ( $C_7H_8$ ), 500 ppm NO<sub>2</sub> (when used), 10 vol% O<sub>2</sub> and balance of N<sub>2</sub>, passing through 0.2 g catalyst with a gas hourly space velocity (GHSV) of 60,000 mL/(g·h). The inlet and outlet gas compositions ( $C_7H_8$ , CO<sub>2</sub>, CO, NO<sub>2</sub>, NO and N<sub>2</sub>O) were continuously detected by an on-line FTIR spectrometer (GASMET DX-4000). Toluene conversion and CO<sub>2</sub> selectivity were calculated as Eqs. (1) and (2). The methods for kinetic analysis and turnover frequency (TOF) determination were supplied in the Supporting Information.

$$Toluene \ conversion \ (\ \ )) = \left(1 - \frac{C_{toluene}^{out}}{C_{toluene}^{in}}\right) \times 100\%$$
(1)

$$CO_2 \ selectivity \ (\ \%)) = \frac{C_{CO2}}{7(C_{toluene}^{in} - C_{toluene}^{out})} \times 100\%$$
(2)

The apparent activation energies (E<sub>a</sub>) of the obtained catalysts for toluene oxidation were in the order of  $Mn_{0.5}Ce_{0.5}O_2/HZSM-5 < Mn_{0.8}Ce_{0.2}O_2/HZSM-5 < Mn_{0.2}Ce_{0.8}O_2/HZSM-5 < MnO_x/HZSM-5 (Fig. S1 and Table 1). Mn_{0.5}Ce_{0.5}O_2/HZSM-5 (denoted as MnCe/HZSM-5) delivered the lowest E<sub>a</sub> value of 23.97 kJ/mol, indicating that the coexistence of Mn and Ce oxides were beneficial for toluene catalytic oxidation.$ 

# 2.3. Byproduct identification

The used catalyst was collected and analyzed using TD (APL-TD-2)-GC-MS (Agilent 6890 N GC-5975B MSD). The outlet gas was collected using a sampling bag (Teflon FEP) and analyzed by GC-MS. TD was operated over 100 mg sample at 300 °C to desorb the deposited organic byproducts. The released species then entered the GC-MS system for identification. The GC oven increased to 150 °C with a heating rate of 5 °C/min and held for 7 min. Afterwards, the GC oven increased to 200 °C with a heating rate of 10 °C/min and held for 4 min. The quadrupole and ion source temperatures were set as 150 °C and 230 °C, respectively.

# 2.4. Catalyst characterization

Temperature programmed desorption (TPD) experiments were carried out by the same equipment as activity measurement. First, 100 mg sample was pretreated in high purity N<sub>2</sub> at 350 °C for 1 h. Second, the sample was exposed to the experimental atmosphere at 50 °C for 1 h and to the N<sub>2</sub> for another 1 h, sequentially. Finally, the sample was heated up to 800 °C at a rate of 10 °C/min in N<sub>2</sub> to record the TPD profiles. The first step of surface desorption (SD)-TPD was the same. Then, the sample was treated in the experimental atmosphere at 250 °C for 3 h and cooled down to 50 °C. Finally, the sample was heated up to 800 °C at a rate of 10 °C/min in 10 vol% O<sub>2</sub> (balance of N<sub>2</sub>).

The *in-situ* DRIFTs experiments were conducted using a FTIR spectrometer (Bruker VERTEX 70). First, the sample was pretreated in N<sub>2</sub> at 350 °C for 1 h. Then, the sample was treated in the experimental atmosphere for 0.5 h to pre-adsorb at a setting temperature and purged the weakly physically adsorbed gases in N<sub>2</sub> for 10 min. Finally, the sample was exposed to the reaction atmosphere for 0.5 h. The spectra were collected by accumulating 64 scans with a resolution of 4 cm<sup>-1</sup>. During the DRIFTs experiments, an on-line FTIR spectrometer (GASMET DX-4000) was connected to monitor the composition of outlet gas.

X-ray photoelectron spectroscopy (XPS) spectra were obtained by Thermo Scientific ESCALAB 250 with Al K $\alpha$  X-ray radiation (1486.6 eV) operated at 150 W. Powder X-ray diffraction (XRD) patterns were recorded using a model D/max RA (Rigaku Co., Japan) in the 2 $\theta$  range of 20–70° with a step size of 0.02°. The N<sub>2</sub> adsorption–desorption experiments were conducted on a chemisorption analyzer (Micromeritics ASAP 2020, USA). The specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) model. The scanning electron microscope (SEM) and energy dispersive spectrometer (EDS) were conducted on ZEISS Gemini SEM 300 coupled with INCA X-Max 80. The highresolution transmission electron microscope (HRTEM) images were obtained via FEI Tecnai G2 F20. The contents of active metal components were analyzed by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES, Agilent Technologies 700 Series).



**Fig. 1.** (a) Toluene conversion and CO<sub>2</sub> selectivity, (b) long-term experiments at 280 °C, (c) N distribution and NO<sub>2</sub> conversion and (d) NO<sub>2</sub> contribution during toluene catalytic oxidation. Reaction conditions:  $[C_7H_8] = 50 \text{ ppm}$ ,  $[NO_2] = 500 \text{ ppm}$ ,  $[O_2] = 10 \text{ vol}\%$ ,  $[H_2O] = 5 \text{ vol}\%$ , Q = 200 mL/min, GHSV = 60,000 mL/(g·h).

Thermogravimetric analysis (TGA) under air atmosphere was conducted on a DSC/DTA-TG instrument (STA 449 F3 Jupiter, NETZSCH). Pyridine adsorbed IR spectroscopy (Py-IR) experiments were carried out by an FTIR spectrometer (PerkinElmer). H<sub>2</sub> temperature programmed reduction (H<sub>2</sub>-TPR) and O<sub>2</sub> temperature programmed desorption (O<sub>2</sub>-TPD) analyses were carried out using an AutoChem II 2920 instrument. The details of TGA, Py-IR, H<sub>2</sub>-TPR and O<sub>2</sub>-TPD were described in the **Supporting Information**.

# 3. Results and discussion

# 3.1. Basic information of obtained catalysts

The XRD pattern of MnO<sub>x</sub>/HZSM-5 catalyst presented diffraction peaks of Mn<sub>2</sub>O<sub>3</sub> at  $2\theta = 32.9^{\circ}$ ,  $37.2^{\circ}$  and  $55.3^{\circ}$  (JCPDS: 41-1442) (Fig. S2a). The Mn<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>2</sub>/HZSM-5 catalyst showed typical diffraction peaks of CeO<sub>2</sub> at  $2\theta = 28.7^{\circ}$ ,  $33.2^{\circ}$ ,  $47.3^{\circ}$  and  $56.5^{\circ}$  (JCPDS: 34-0394), representing the crystal planes of (111), (200), (220) and (311) [33,34]. Mn<sup>x+</sup> may enter the lattice of CeO<sub>2</sub> to form a solid solution. No distinct peaks of MnO<sub>x</sub> or CeO<sub>2</sub> were observed for MnCe/HZSM-5 catalyst, implying that these oxides were well dispersed on HZSM-5 support. SEM-EDS images (Fig. S3f-h) confirmed this result. HRTEM images of MnCe/HZSM-5 catalyst (Fig. S3e) presented nanolattices of CeO<sub>2</sub> with different lattice spacing, such as (200) and (111) planes.

The N<sub>2</sub> adsorption–desorption results were presented in Fig. S2b and Table 1. The co-existence of Mn and Ce resulted in larger specific surface areas (256.2–267.9 m<sup>2</sup>/g) comparing with MnO<sub>x</sub>/HZSM-5 or CeO<sub>2</sub>/HZSM-5. The reducibility of the catalysts was investigated by H<sub>2</sub>-TPR (Fig. S4a and Table 1). The reduction peak located at 250–400 °C (Mn<sub>2</sub>O<sub>3</sub> reduction to Mn<sub>3</sub>O<sub>4</sub>) of MnCe/HZSM-5 broadened and shifted to a lower temperature (351 °C), indicating the existence of strong interaction between Mn and Ce [28,35]. For O<sub>2</sub>-TPD results (S4b), The low temperature region (<300 °C) can be attributed to the desorption of active physical/chemical absorbed or active lattice oxygen species on the catalyst surface [36], which were known to play an important role in

toluene oxidation [37]. Among the obtained catalysts, MnCe/HZSM-5 possessed the largest area and lowest temperature of oxygen desorption peaks below 300 °C (Table 1), indicating more active oxygen species and higher oxygen mobility [28].

# 3.2. Catalytic performance

Effect of NO2 on catalytic oxidation of toluene was evaluated over MnCe/HZSM-5 catalyst. As presented in Fig. 1a, the temperatures at which the toluene conversions were 50% and 90% ( $T_{50}$  and  $T_{90}$ ) were 230 °C and 278 °C, respectively. When 500 ppm  $NO_2$  was present, the toluene conversion increased quickly even at a relatively low temperature of 150 °C. The T<sub>50</sub> and T<sub>90</sub> decreased to 201 °C and 229 °C, accordingly. In the meantime, CO2 selectivity was promoted. The TOF increased as the reaction temperature increased (Fig. S5). The TOF values in the presence of NO<sub>2</sub> were larger than the values without NO<sub>2</sub> especially at 200-260 °C, as verified by the catalytic activity measurements. The long-term experiments clearly showed that NO<sub>2</sub> had a positive effect on the catalytic stability of MnCe/HZSM-5 catalyst (Fig. 1b). The toluene conversion remained  $\sim 100\%$  in the presence of 500 ppm  $NO_2$  at 280 °C, while it gradually decreased to ~70% without  $NO_2$ within 500 min. Moreover, the addition of 5 vol% of water had negligible effect on the catalytic stability. Water was found conducive to the adsorption of toluene and oxygen [28]. The protonated species (e.g., HNO3 and/or OH<sup>-</sup> species) formed by reactions between H<sub>2</sub>O and NO<sub>2</sub> may enhance the oxidation reaction [38].

During the toluene oxidation process, NO<sub>2</sub> was reduced. The N distribution in Fig. 1c showed the dominant product of NO<sub>2</sub> conversion was NO. The NO<sub>2</sub> was capable to give one of its O to participate in the toluene oxidation. The other N may transfer into the adsorbed nitrates/ nitrites and organic byproducts. When temperature increased from 200 to 260 °C, the NO<sub>2</sub> conversion reached the maximum value of 97.3%. It's worth noting that the toluene was almost completely converted at 260 °C. Presuming the O for complete oxidation of 50 ppm toluene all came from NO<sub>2</sub>, 900 ppm NO<sub>2</sub> was required (Eq. (3)), which was larger than the actual NO<sub>2</sub> concentration of 500 ppm. Besides, the O<sub>2</sub>



**Fig. 2.** (a) toluene conversion and (b) NO<sub>2</sub> contribution at varied temperatures in the absence of O<sub>2</sub> ( $[C_7H_8] = 50$  ppm, Q = 200 mL/min, m = 0.2 g, GHSV = 60,000 mL/(g·h)), (c) toluene conversion rate and (d) NO<sub>2</sub> contribution with varied NO<sub>2</sub> concentrations ( $[C_7H_8] = 50$  ppm,  $[O_2] = 10$  vol% (when used), T = 300 °C, Q = 300 mL/min, m = 0.02 g, GHSV = 900,000 mL/(g·h)).

concentration of 10 vol% was much higher than the theoretical value of 450 ppm. These results proved toluene was prone to being oxidized by NO<sub>2</sub> and both NO<sub>2</sub> and O<sub>2</sub> contributed to the toluene oxidation (**Eq. (4)**). The stoichiometric number x ( $0 \le x \le 18$ ) in **Eq. (4)** represented the NO<sub>2</sub> contribution in the complete oxidation of toluene, which was the ratio of converted NO<sub>2</sub> (ppm) and converted toluene (ppm). The NO<sub>2</sub> contribution increased from 7.9 at 220 °C to 9.0 at 260 °C (Fig. 1d). When temperature was above 260 °C, the re-oxidation of NO to NO<sub>2</sub> (**Eq. (5)**) became more pronounced. This explained the drop of both NO<sub>2</sub> conversion and NO<sub>2</sub> contribution, also guaranteed the NO<sub>2</sub> level in the gas was maximized. The co-existence of NO<sub>2</sub> and O<sub>2</sub> showed a synergistic effect on toluene oxidation.

$$C_7H_8 + 18NO_2 \rightarrow 7CO_2 + 4H_2O + 18NO$$
 (3)

$$C_7H_8 + xNO_2 + \frac{18 - x}{2}O_2 \rightarrow 7CO_2 + 4H_2O + xNO$$
 (4)

$$2NO + O_2 \rightarrow 2NO_2 \tag{5}$$

The toluene oxidation by NO<sub>2</sub> in the absence of O<sub>2</sub> was further carried out (Fig. 2a). 500 ppm NO<sub>2</sub> gave a maximum toluene conversion of 66.8% due to the insufficient supply of O. NO<sub>2</sub> concentration of 1000 ppm was larger than the theoretical value of 900 ppm, hence completely converting toluene at 280 °C with ~100% CO<sub>2</sub> selectivity. The utilization ratio of O in NO<sub>2</sub> for toluene oxidation was pretty high. NO<sub>2</sub> contributions (Fig. 2b) with 500 ppm NO<sub>2</sub> were ~13.5. The x cannot reach the theoretical value of 18 due to the participation of oxygen on the catalyst and the formation of byproducts (e.g., CO, coke). NO<sub>2</sub> contributions with 1000 ppm NO<sub>2</sub> were much larger than that with 500 ppm NO<sub>2</sub> and increased as the temperature rose. The maximum x of 17.9 at 280 °C was very close to the theoretical value of 18.

Toluene conversion rates ( $\delta_{toluene}$ ) with different NO<sub>2</sub> concentrations in the presence/absence of O<sub>2</sub> were then evaluated. When NO<sub>2</sub> concentration increased from 200 to 800 ppm,  $\delta_{toluene}$  increased from 8.6 to 18.1 µmol·g<sup>-1</sup>·min<sup>-1</sup> (Fig. 2c). The promotional effect of NO<sub>2</sub> on toluene oxidation was more obvious with a higher concentration of NO<sub>2</sub>. This tendency remained in the absence of O<sub>2</sub>.  $\delta_{toluene}$  of 200 ppm NO<sub>2</sub> without O<sub>2</sub> (5.4 µmol·g<sup>-1</sup>·min<sup>-1</sup>) was even larger than the  $\delta_{toluene}$  of 10 vol% O<sub>2</sub> without NO<sub>2</sub> (4.8 µmol·g<sup>-1</sup>·min<sup>-1</sup>), proving again the strong oxidizing ability of NO<sub>2</sub>. Nevertheless, the toluene conversion rates without O<sub>2</sub> were smaller than those with O<sub>2</sub>. The x values without O<sub>2</sub> were larger than the results in the presence of O<sub>2</sub> (Fig. 2d), proving again the cocontribution of NO<sub>2</sub> and O<sub>2</sub> to toluene oxidation.

# 3.3. Byproduct identification

The used catalysts after reactions at 250 °C were analyzed by TG (Fig. S6a). The weight loss ratios of used catalysts within 200-800 °C were 3.4% and 5.9% without and with 500 ppm NO<sub>2</sub>, respectively, which were much larger than that of fresh catalyst (0.9%). This result suggested that the consumption of deposited coke derived from toluene oxidation was the major reason for the weight loss of used catalysts. The SD-TPD results in Fig. S6b showed that the used catalyst in the presence of NO<sub>2</sub> yielded more CO<sub>2</sub> and CO (1364 µmol/g) than the used catalyst in the absence of NO<sub>2</sub> (1209  $\mu$ mol/g). The weight loss in TGA and the generation of CO2 and CO in SD-TPD were attributed to the deposited solid byproducts on catalyst surface. NO2 enhanced the toluene conversion significantly and slightly increased the CO2 selectivity at 250 °C (Fig. 1a). As a consequence, more solid byproduct may be generated. However, more deposited coke did not cause a faster deactivation (Fig. 1b). It could be speculated that the positive effect of  $NO_2$  was greater than the negative effect aroused by coke, which was further



Fig. 3. (a) TD-GC-MS results of deposited solid byproducts and (b) GC-MS results of gaseous byproducts after reaction at 250 °C.



Fig. 4. Compositions of (a) deposited solid byproducts and (b) gaseous byproducts after reaction at 250 °C.



Fig. 5. (a) Py-IR spectra of fresh and used catalysts after desorption of pyridine at 200 °C and (b) amount of acid sites.

explored in the following sections.

The composition of deposited solid byproducts was analyzed by TD-GC-MS. Benzene was the predominant byproduct and its proportion was much larger than the others (Fig. 3a, 4a). The formation of benzene followed the route: toluene  $\rightarrow$  benzyl alcohol  $\rightarrow$  benzaldehyde  $\rightarrow$  benzoic acid  $\rightarrow$  benzene [36,39,40]. The further oxidation of benzene to small molecular species (e.g., maleic anhydride species, carbonate and acetic acid) may be the rate-determining step of toluene mineralization. Benzene series (e.g., p-Xylene, styrene and ethylbenzene) were detected. Oxygen-containing compounds (O-compounds) such as benzaldehyde and phenol were also observed. When 500 ppm NO<sub>2</sub> was added, the proportion of organic nitrogen-containing compounds (N-compounds, e. g., nitrobenzene, benzonitrile) in deposited coke was only 0.24%. This result was consistent with the N distribution in Fig. 1c. The N in NO<sub>2</sub> scarcely participated in organic synthesis process. The content of

toluene in coke was obviously reduced, while the contents of benzene and others (e.g., benzene series and O-compounds) were increased. The presence of NO<sub>2</sub> promoted the conversion of toluene to CO<sub>2</sub> (Fig. 1a) and benzene. The composition of gaseous byproducts was presented in Fig. 3b, Fig. 4b. Fewer species were identified, such as benzene, styrene and benzaldehyde. Considering the higher conversion of toluene in the presence of NO<sub>2</sub> (Fig. 1a), the increased toluene content in outlet gas demonstrated that less gaseous byproducts were generated. In addition, the proportion of organic N-compounds (mainly benzonitrile) in gaseous products was also negligible (0.15%).

# 3.4. Mechanism investigation

*3.4.1.* Physicochemical properties of fresh and used catalysts The used catalysts after reaction at 250 °C were characterized by PyP. Lu et al.



Fig. 6. O 1 s XPS spectra of fresh and used catalysts after reaction at 250 °C.

IR to verify the change of acid sites. There were 5 bands in the spectra of fresh and used catalysts (Fig. 5a). The bands at 1635 and 1543  $\text{cm}^{-1}$ were corresponded to the pyridine adsorbed on Brønsted acid sites [9,41,42]. The bands at 1607 and 1447 cm<sup>-1</sup> were related to the pyridine adsorbed on Lewis acid sites. The other band at 1490 cm<sup>-1</sup> was assigned to Brønsted and Lewis acid sites. After toluene oxidation, the amount of Brønsted acid sites of catalyst decreased slightly, while the amount of Lewis acid sites decreased more significantly (Fig. 5b). Lewis acids were believed to play the core role in toluene oxidation [29], which were continuously consumed. The deposited coke could also lead to the loss of acids. The amount of Lewis acids on  $C_7H_8 + O_2 + NO_2$ -used catalyst (0.08 mmol/g) was much smaller than fresh (0.17 mmol/g) and  $C_7H_8 + O_2$ -used catalysts (0.15 mmol/g). The faster loss of Lewis acids was due to the higher toluene oxidation rate in the presence of NO2 (Fig. 2a) and more coke deposited. The amount of Brønsted acids on  $C_7H_8 + O_2 + NO_2$ -used catalyst (0.12 mmol/g) was more than two times larger than fresh (0.05 mmol/g) and  $C_7H_8$  +  $O_2$ -used catalysts (0.05

Table 2				
Quantitative	e analysis of TI	PD results (	µmol/g).	
TPD	C-Hau	C-Hai	COat	cc

TPD	C <sub>7</sub> H <sub>8ads</sub>	C <sub>7</sub> H <sub>8des</sub>	CO <sub>2des</sub>	CO <sub>des</sub>	NO <sub>2des</sub>	NO <sub>des</sub>
$\begin{array}{l} C_7H_8\\ C_7H_8+NO_2 \end{array}$	101.2	55.3	122.6	14.6	/	/
	91.2	7.2	373.1	144.3	147.3	92.8

mmol/g). The dissociated free H atoms from toluene could be captured by the catalyst surface and converted into Brønsted acids ( $C_6H_5CH_3^* + O^* \rightarrow C_6H_5CH_2^* + Brønsted$ ) [19]. NO<sub>2</sub> may promote the dissociation and the capture of H atom from the methyl group of toluene to form additional Brønsted acids by suppling more surface available O [15,16].

The O 1 s XPS spectra of used catalysts were deconvoluted into three bands (Fig. 6) [43,44]. The band at 532.8 eV was assigned to hydroxyl species or adsorbed water (Oads). The band at 531.9 eV belonged to surface chemisorbed oxygen ( $O_{sur}$ ), such as  $O^{2-}$ ,  $O_2^{2-}$  and  $O^-$ . The band at 529.8 eV was attributed to the lattice oxygen (Olat). The percentages of Osur and Olat decreased from 35.2% and 17.9% to 33.9% and 17.5% accordingly after toluene oxidation. Both Osur and Olat took part in the reaction. The addition of NO2 in the atmosphere enhanced the consumption of lattice oxygen, which played an important role in toluene deep oxidation through the MvK mechanism [24]. Since more lattice oxygen was consumed, oxygen vacancies were generated. Thus, more chemisorbed oxygen was required for the filling of oxygen vacancies from the uptake of NO<sub>2</sub> or O<sub>2</sub> [12]. This explained the increase of O<sub>sur</sub> content from 35.2% on fresh catalyst to 35.8% on  $C_7H_8 + O_2 + NO_2$ -used catalyst. NO2 was much easier to give one of its O than O2 to supplement the consumed lattice oxygen through the following path:  $NO_{2ads} \rightarrow O_{ads}$  $\rightarrow$  O<sub>sur</sub>  $\rightarrow$  O<sub>lat</sub>. The beneficial effect of NO<sub>2</sub> could be explained by two reasons [38]. First, the strength of O-NO bond in NO<sub>2</sub> (305 kJ/mol) is much weaker than the strength of the O—O bond in  $O_2$  (498.36 kJ/mol). Second, NO<sub>2</sub> is a radical species that decomposes to NO and O radical with relative ease, especially on catalyst surface. In addition, the Olat band of  $C_7H_8 + O_2 + NO_2$ -used catalyst shifted to a higher binding energy (529.7 eV) compared with  $C_7H_8 + O_2$ -used catalyst (529.5 eV),



Fig. 7. Desorbed concentrations of (a) toluene, (b) NO<sub>x</sub>, (c) CO<sub>2</sub> and (d) CO recorded in C<sub>7</sub>H<sub>8</sub>-TPD and C<sub>7</sub>H<sub>8</sub> + NO<sub>2</sub>-TPD experiments.



Fig. 8. In-situ DRIFTs spectra of (a) NO2 adsorption and (b) toluene adsorption.

indicating a lower electron density and therefore a higher mobility of lattice oxygen species [45]. Thus,  $NO_2$  enhanced the consumption, replenishment and mobility of lattice oxygen.

# 3.4.2. TPD analysis

 $C_7H_8\text{-}TPD$  and  $C_7H_8+NO_2\text{-}TPD$  results were shown in Fig. 7 and Table 2. The adsorption amounts of toluene were 101.2 and 91.2  $\mu\text{mol/g}$  without and with 500 ppm NO<sub>2</sub> (Fig. S7), respectively. The competitive adsorption between toluene and NO<sub>2</sub> was identified. Toluene could be oxidized by oxygen on catalyst surface during desorption process even

no oxidant (e.g.,  $O_2$  and  $NO_2$ ) was added. The desorbed  $CO_2 + CO$  was 137.2 µmol/g. The initial temperature of  $CO_2/CO$  production was as high as ~300 °C (Fig. 7c, d), indicating limited amount and activity of oxygen on catalyst itself. The mobility and activity of lattice oxygen became stronger at a higher temperature. The desorption behavior of toluene was dramatically influenced by  $NO_2$ . The desorbed toluene was reduced from 55.3 to 7.2 µmol/g, whereas the desorbed  $CO_2 + CO$  increased to 517.4 µmol/g. The initial temperature of  $CO_2/CO$  production was significantly reduced to ~100 °C, suggesting that the light-off of toluene occurred at much lower temperatures in the presence of



Fig. 9. (a), (b) DRIFTs spectra, (c) outlet gas composition when passing toluene over NO<sub>2</sub> pre-adsorbed catalyst, (d), (e) DRIFTs spectra, (f) outlet gas composition when passing NO<sub>2</sub> over toluene pre-adsorbed catalyst, (g), (h) DRIFTs spectra, (i) outlet gas composition when passing NO<sub>2</sub> and toluene simultaneously. Reaction conditions:  $[C_7H_8] = 50$  ppm,  $[NO_2] = 500$  ppm, T = 250 °C, Q = 100 mL/min.



Fig. 10. Summary of the productions of (a) NO and (b)  $CO_x$  ( $CO_2$  + CO) at 150 °C and 250 °C.

NO<sub>2</sub>. The temperatures corresponding to the maximum CO<sub>2</sub>/CO concentration below 500 °C were 328 and 327 °C, respectively, which were significantly lower than that in C<sub>7</sub>H<sub>8</sub>-TPD (416 and 463 °C). NO<sub>2</sub> not only provided more surface oxygen species, but also improved the activity of lattice oxygen, hence promoting the light-off and mineralization of toluene.

The desorption profiles of NO<sub>x</sub> were presented in Fig. 7**b**. Only NO<sub>2</sub> and NO were detected, while N<sub>2</sub>O was negligible. NO started to be produced at ~90 °C, which was a little bit earlier than the production of CO<sub>2</sub>/CO. It is interesting to see there were two peaks in NO curve located at 115 and 261 °C. The desorbed NO amounts in the two stages were similar. But the produced CO<sub>2</sub> + CO in the first stage was far less than the second stage. These results suggested that the toluene oxidation by NO<sub>2</sub> may follow different mechanisms at various temperature ranges [24,25].

# 3.4.3. In-situ DRIFTs coupled with FTIR

The mechanism of toluene oxidation by NO2 was further investigated by in-situ DRIFTs coupled with FTIR experiments. Several bands appeared in the NO<sub>2</sub> adsorption spectra (Fig. 8a). The band at 1595  $cm^{-1}$  was corresponded to adsorbed NO<sub>2</sub> [14]. The bands at 1572, 1548, 1530 and 1513 cm<sup>-1</sup> were recognized as nitrate species [46,47]. Besides, the linear nitrite (1445  $\text{cm}^{-1}$ ) and chelating nitrite (1285  $\text{cm}^{-1}$ ) were detected [47]. With the increase of temperature, the intensity of all bands decreased. The surface adsorbed NO<sub>2</sub> species were unstable at high temperatures. Especially, the nitrites disappeared within 200 °C. The spectra of toluene adsorption varied in different temperature ranges (Fig. 8b). The band at 1641  $\text{cm}^{-1}$  was ascribed to the C=O stretching vibration of aldehyde group [45]. The bands at 1496, 1430 and 1284  $cm^{-1}$  were assigned to the C=C stretching vibration of aromatic ring, C-H bending vibrations of methylene group and C-H bending vibration of methyl group [45], respectively, indicating that toluene was adsorbed on the catalyst at a low temperature. At 100  $^\circ$ C, the intensities of bands belonging to vibration of aromatic ring, methylene and methyl groups (1496, 1430 and 1284 cm<sup>-1</sup>) decreased, suggesting a weaker adsorption. In the meantime, the intensity of aldehyde group (1641 cm<sup>-1</sup>) increased slightly. The toluene oxidation became stronger, producing more byproduct (e.g., benzaldehyde). When temperature further raised to 250 °C, these bands disappeared, while some new bands were observed, such as the bending vibration of H-O-H in water (1625 cm<sup>-1</sup>), the stretching vibration of -COO<sup>-</sup> in carboxylate (1591 and 1547 cm<sup>-1</sup>), the stretching vibration of -COO<sup>-</sup> in carbonate (1575 and 1521 cm<sup>-1</sup>) [35,44,45]. The appearance of these species indicated a deeper oxidation of toluene because more lattice oxygen was activated and involved at a high temperature.

During the adsorption of NO<sub>2</sub> at 250 °C, NO was identified (Fig. 9ac). NO<sub>2</sub> could oxidize the metals of catalyst with a relatively low valence state (e.g.,  $Mn^{3+}$  and  $Ce^{3+}$ ), resulting in the reduction to NO. Passing toluene over NO<sub>2</sub> pre-adsorbed catalyst, the adsorbed NO<sub>2</sub> (1595 cm<sup>-1</sup>) disappeared, whereas the nitrates (1572 and 1548 cm<sup>-1</sup>) barely changed within the first two minutes. It was consistent with our previous finding that the nitrates were inactive for toluene oxidation [14]. Five minutes later, the bands of  $C_7H_{8ads}$  overlapped the NO<sub>2</sub> adsorption species. Comparing with Fig. 8b, the intensity of band related to water (1625 cm<sup>-1</sup>) was much stronger. The adsorption of NO<sub>2</sub> promoted the deep oxidation of toluene. Moreover, the gas composition revealed that a small amount of NO was produced (Fig. 9c). The highest NO concentration was only 15.2 ppm. Adsorbed NO<sub>2</sub> species may directly oxidize toluene into aldehyde species following the L-H mechanism.

 $CO_2$  and CO were barely identified during the adsorption of toluene at 250 °C (Fig. 9d-f). Passing NO<sub>2</sub> over toluene pre-adsorbed catalyst, the intensities of aldehyde (1668 cm<sup>-1</sup>), water (1625 cm<sup>-1</sup>), carboxylate (1591 cm<sup>-1</sup>) and carbonate (1575 and 1531 cm<sup>-1</sup>) reached maximum values in two minutes. Afterwards, these bands gradually decreased due to the consumption of toluene adsorption species. The productions of NO, CO<sub>2</sub> and CO during this process were significantly larger than that in Fig. 9c. The highest concentrations of these gases reached 181.1, 56.3 and 11.7 ppm, respectively.

When NO<sub>2</sub> and toluene passed the catalyst simultaneously (Fig. 9**g**i), the consumed toluene could be replenished continuously. More byproduct aldehydes (1668 cm<sup>-1</sup>) were generated comparing with passing NO<sub>2</sub> over toluene pre-adsorbed catalyst (Fig. 9**d**-f). However, the presence of NO<sub>2</sub> restricted the toluene adsorption (Fig. S7). The highest concentrations of NO, CO<sub>2</sub> and CO were pretty much the same (187.4, 47.6 and 13.9 ppm) as passing NO<sub>2</sub> over toluene pre-adsorbed catalyst.

The above in-situ DRIFTs couple with FTIR experiments were also carried out at 150 °C (Fig. S8a-i). The trends in DRIFTs spectra were similar with the spectra at 250 °C. The composition of outlet gas was different. The productions of NO and  $CO_x$  (CO<sub>2</sub> + CO) at different temperatures were summarized in Fig. 10. At 150 °C (Fig. 10a), the production of NO was 8.7 µmol in the situation of passing NO2 over toluene pre-adsorbed catalyst (denoted as C7H8-NO2), which was much larger than the NO production  $(1.0 \,\mu mol)$  after passing toluene over NO<sub>2</sub> pre-adsorbed catalyst (denoted as NO2-C7H8) and close to the NO production (11.2 µmol) after passing NO2 and toluene simultaneously (denoted as  $NO_2 + C_7H_8$ ). The yield of  $CO_x$  was low (0.12–0.48 µmol) but delivered the same tendency (Fig. 10b). At 250 °C, the NO productions of  $C_7H_8\text{--}NO_2$  and  $NO_2+C_7H_8$  increased to 18.1 and 21.8  $\mu\text{mol}$ respectively. Whereas, the NO production of NO2--C7H8 decreased slightly to 0.9 µmol. These results suggested that toluene was oxidized by NO<sub>2</sub> following both L-H and MvK mechanisms. The adsorption of NO<sub>2</sub> was proved to be more difficult than toluene and O2 on MnOx-CeO2 composites by DFT calculation [14]. The NO<sub>2</sub> adsorption species became unstable (Fig. 8a) but the mobility and activity of lattice oxygen were enhanced at a high temperature [24,45]. The adsorbed nitrates and



Scheme 1. Mechanism of toluene oxidation by NO<sub>2</sub> in the absence of O<sub>2</sub>.

nitrites were not easy to give their O to oxidize toluene (Fig. 9a, b). These factors led to a predominant MvK mechanism of toluene oxidation by NO<sub>2</sub>, especially at a high temperature, resulting in much higher yields of CO<sub>x</sub> (0.90–6.81  $\mu$ mol).

# 3.4.4. Reaction mechanism

The proposed toluene oxidation by NO<sub>2</sub> in the absence of O<sub>2</sub> was presented in Scheme 1. A competitive adsorption between NO<sub>2</sub> and toluene was found, slightly restricting the toluene adsorption. Adsorbed NO2 species reacted with toluene via the L-H mechanism. However, this mechanism was less important because NO2 adsorption was not easy and the adsorbed nitrates/nitrites were inactive. Instead, the promotional effect of NO<sub>2</sub> on toluene oxidation mainly followed the MvK mechanism. The mobility and activity of lattice oxygen played an important role in this process, especially for the ring-opening and mineralization reactions [24,45]. Toluene was adsorbed and oxidized on metal oxides to produce benzaldehyde, benzoic acid, CO2, H2O and so on. The metal oxides were reduced to lower valance states at the same time. NO<sub>2</sub> has a stronger oxidizing ability than O2, hence speeding up the re-oxidation of the reduced sites. NO<sub>2</sub> was prone to giving one of its O in this reaction to become NO. The N in NO<sub>2</sub> barely participated in toluene oxidation, thus the production of organic N-byproducts was negligible.

# 4. Conclusions

In summary, NO<sub>2</sub> promoted the toluene conversion, CO<sub>2</sub> selectivity and catalytic stability. There were some negative impacts of NO2 included: (1) competitive adsorption between  $NO_2$  and toluene; (2) generating more coke and faster consumption of Lewis acids. However, the positive impacts of NO2 were more pronounced, such as (1) stronger oxidizing ability than O2 and improving the mobility and activity of Olat; (2) generating additional  $\mathrm{O}_{sur}$  and Brønsted acids, hence accelerating the redox cycle of catalyst. NO2 contribution to toluene oxidation was quantitatively analyzed, which was more pronounced with higher NO2 contribution no matter  $O_2$  was present or not. As the temperature rose, the NO<sub>2</sub> contribution first increased then decreased owing to the reoxidation of NO back to NO2. The N-containing organic byproducts in solid and gas were negligible, indicating that the N in NO2 scarcely participated in organic synthesis process. The mechanism of toluene oxidation by NO<sub>2</sub> was determined by the stability of NO<sub>2</sub> adsorption species and the mobility of lattice oxygen, which were significantly influenced by temperature. MvK mechanism was dominant especially at a high temperature because NO<sub>2</sub> adsorption species became unstable and the mobility of lattice oxygen was promoted.

# CRediT authorship contribution statement

**Peng Lu:** Conceptualization, Investigation, Methodology, Writing – original draft. **Lyumeng Ye:** Methodology, Validation. **Xianhui Yan:** Investigation, Methodology. **Xiongbo Chen:** Resources. **Ping Fang:** Resources. **Dingsheng Chen:** Resources. **Dongyao Chen:** Resources. **Chaoping Cen:** Supervision, Funding acquisition, Methodology.

# **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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#### Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apsusc.2022.154161.

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