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# The promotion effect of manganese on Cu/SAPO for selective catalytic reduction of NO<sub>x</sub> with NH<sub>3</sub>

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The activity and hydrothermal stability of Cu/SAPO and xMn–2Cu/SAPO for low-temperature selective catalytic reduction of NO<sub>x</sub> with ammonia were investigated. An ion-exchanged method was employed to synthesize xMn–2Cu/SAPO, which was characterized by N<sub>2</sub> adsorption, ICP-AES, X-ray diffraction (XRD), NH<sub>3</sub>-temperature programmed desorption (NH<sub>3</sub>-TPD), NO oxidation, X-ray photoelectron spectrum (XPS), UV-vis, H<sub>2</sub>-temperature programmed reduction (H<sub>2</sub>-TPR) and diffuse reflectance infrared Fourier transform spectra (DRIFTS). 2Mn–2Cu/SAPO and 4Mn–2Cu/SAPO showed the best SCR activity, in that at 150 °C NO conversion reached 76% and N<sub>2</sub> selectivity was above 95% for the samples. NO oxidation results showed that the 2Mn–2Cu/SAPO had the best NO oxidation activity and the BET surface area decreased as manganese loading increased. XRD results showed that the metal species was well dispersed. NH<sub>3</sub>-TPD showed that the acid sites have no significant influence on the SCR activity of xMn–2Cu/SAPO. H<sub>2</sub>-TPR patterns showed good redox capacity for xMn–2Cu/SAPO. UV-vis and H<sub>2</sub>-TPR showed that the ratio of Mn<sup>4+</sup> to Mn<sup>3+</sup> increased as manganese loading increased. XPS spectra showed a significant amount of Mn<sup>3+</sup> and Mn<sup>4+</sup> species on the surface and addition of manganese increased the ratio of Cu<sup>2+</sup>. The promotion effect of manganese to 2Cu/SAPO comes from the generation of Mn<sup>3+</sup> and Mn<sup>4+</sup> species. Deduced from the DRIFTS spectra, the Elay–Rideal mechanism was effective on 4Mn–2Cu/SAPO.

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## 1 Introduction

NO<sub>x</sub> consists of NO, NO<sub>2</sub>, N<sub>2</sub>O and their related derivatives, which can lead to numerous environmental and health hazards.<sup>1</sup> By forming nitric acid, NO<sub>x</sub> can lead to the generation of acid rain; by forming ammonium nitrate, it can accelerate the generation of PM<sub>2.5</sub>; by reacting with hydrocarbons under sunlight, it can cause the generation of photo chemical smog and ozone; by infiltrating into lungs, it can result in respiratory morbidity, like impaired host defense and lung inflammation. Thus, legislations on NO<sub>x</sub> emission are now becoming more and more stringent. In China, according to the emission standard of air pollutants for thermal power plants (GB 13223-2011), the NO<sub>x</sub> emission limit is 100 mg m<sup>−3</sup> for new natural gas-fired industrial boilers and all oil and coal-fired industrial boilers. For compression ignition and gas fueled positive ignition engines of vehicles, the NO<sub>x</sub> emission limit in Chinese National 5 standards is 57% of that in Chinese National 4 standards and 40% of that in Chinese National 3 standards.

The treatment of environmentally harmful NO<sub>x</sub> compounds emitted from mobile or stationary sources remains

a challenging task, especially for industrial applications such as cement plants or iron and steel plants, because the suitable process temperature for NO<sub>x</sub> abatement is usually around 150 °C, under which commercial SCR catalysts V<sub>2</sub>O<sub>5</sub>–MoO<sub>3</sub> (WO<sub>3</sub>)/TiO<sub>2</sub> cannot work well.

Manganese oxides were reported by Smirniotis *et al.* as potential catalysts for low-temperature NH<sub>3</sub>-SCR reactions.<sup>2–5</sup> They studied the promoted manganese oxides supported on TiO<sub>2</sub> systematically<sup>3–5</sup> and found that the surface Mn<sup>4+</sup> species was reported to be highly active for the SCR of NO reaction with ammonia at low temperatures.

Recently, copper modified zeolites with a CHA structure attracted much attention owing to their excellent activity, N<sub>2</sub> selectivity and hydrothermal stability for low temperature NH<sub>3</sub>-SCR reaction.<sup>6–8</sup>

However for the Cu/SAPO-34 catalyst, the oxygen activation of transiently formed Cu pairs [Cu<sup>I</sup>(NH<sub>3</sub>)<sub>2</sub>] to [(NH<sub>3</sub>)<sub>2</sub>Cu<sup>II</sup>-O<sub>2</sub>-Cu<sup>II</sup>(NH<sub>3</sub>)<sub>2</sub>] was rate-limiting in the catalytic cycle.<sup>8</sup> Feng Gao<sup>9</sup> also thought that the oxidation reaction of Cu<sup>+</sup> to Cu<sup>2+</sup> was the rate-determine step, so tuning the redox properties of the active site by introducing a second cation might be a promising approach. Li *et al.*<sup>10</sup> and Chen *et al.*<sup>11</sup> modified the Cu/SAPO catalyst with CeO<sub>x</sub> for SCR reaction; they found that the introduction of CeO<sub>x</sub> increased the SCR activity at high temperatures and cerium helped increase the amount of isolated Cu<sup>2+</sup> ions.

Leistner *et al.*<sup>12</sup> found that Cu in Cu/SAPO-34 was more easily reduced compared to Cu/SSZ-13, which could facilitate the

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redox processes and increase the SCR activity. Ma *et al.*<sup>13</sup> also found that Cu-SAPO-34 showed higher DeNO<sub>x</sub> catalytic activity than Cu-SSZ-13. The usage of SAPO-34 in low-temperature SCR might be favored in low temperature SCR reactions. When manganese is introduced into the Cu/SAPO system, it not only promotes the oxidation reaction of Cu<sup>+</sup>, but also acts as an active site for low temperature SCR reaction. Thus the manganese modified Cu/SAPO-34 catalyst would probably show better SCR activity.

In this work, the treatment of exhaust from a gas-fired boiler which contains a high concentration of H<sub>2</sub>O and a very low concentration of SO<sub>2</sub> was focused upon. xMn-Cu/SAPO catalysts with different manganese loadings were prepared and their performance in SCR reaction was discussed. Various characterization methods (XRD, XPS, H<sub>2</sub>-TPR, UV-vis) were used to probe the promotion effect of manganese on Cu/SAPO for low temperature SCR reaction.

## 2 Experimental

### 2.1 Catalyst preparation

xMn-2Cu/SAPO catalysts were prepared by an ion-exchange method. The alkali metals in commercial Na/SAPO-34 powder (Jiangsu XFNANO) would decrease SCR activities, so it was transformed to H<sup>+</sup>/SAPO as follows. Na/SAPO-34 powder was ion exchanged using 11% wt NH<sub>4</sub>NO<sub>3</sub> (Aladdin, >98.5%) solution whose pH value was adjusted to 3.0–4.0 by 2 M ammonium hydroxide (Aladdin, 25–28%) solution at 80 °C for 4 h. It was then filtered and washed with distilled water three times. Finally, it was dried at 110 °C for 16 h and calcined at 550 °C for 3 h.

xMn-2Cu/SAPO (x = 0, 1, 2, 4, 8) was prepared in two steps. Firstly, H<sup>+</sup>/SAPO was mixed with Cu(NO<sub>3</sub>)<sub>2</sub> (across, >95%) solution at 80 °C for 6 h under vigorous stirring. Then it was dried and calcined at 550 °C for 3 h. In the second step, it was mixed with Mn(NO<sub>3</sub>)<sub>2</sub> (across, >95%) solution at 80 °C for 6 h under vigorous stirring, and at last it was dried and calcined at 550 °C for 3 h.

### 2.2 SCR activity measurements

Catalytic activity evaluation was carried out using a flow-through powder reactor system equipped with a Fourier transform infrared (FT-IR) spectrometer (THERMO SCIENTIFIC IGS). In order to prevent condensation along upstream tubing, all the gas lines were heated and maintained at 120 °C. The gas mixture was 500 ppm NO + 500 ppm NH<sub>3</sub> + 3% vol O<sub>2</sub> balanced with N<sub>2</sub>. The gas hourly space velocity (GHSV) was 65 000 h<sup>-1</sup> for the standard SCR reaction. Prior to each activity measurement, the catalysts were pretreated at 500 °C for 30 min with 21% vol O<sub>2</sub>/N<sub>2</sub> flow. Catalytic activities were measured in the temperature range of 120 to 210 °C. The typical time to achieve the steady state was 2.5 h. NO conversion, promotion effect, and (*E<sub>p</sub>*) and N<sub>2</sub> selectivity were calculated at steady state using the equation below:

$$X_{\text{NO}} = \frac{C_{\text{NO},\text{in}} - C_{\text{NO},\text{out}}}{C_{\text{NO},\text{in}}} \times 100\% \quad (1)$$

$$E_p = (X_{\text{xMn-2Cu/SAPO}} - X_{\text{2Cu/SAPO}}) \times 100\% \quad (2)$$

$$\text{N}_2 \text{ selectivity} = \left(1 - \frac{2[\text{N}_2\text{O}]_{\text{outlet}}}{[\text{NO}_x]_{\text{inlet}} - [\text{NO}_x]_{\text{outlet}}}\right) \times 100\% \quad (3)$$

where *C*<sub>NO<sub>x</sub> in</sub> and *C*<sub>NO<sub>x</sub> out</sub> represent the inlet and outlet NO<sub>x</sub> concentration. *X*<sub>xMn-2Cu/SAPO</sub>, *X*<sub>2Cu/SAPO</sub> and *X*<sub>xMn/SAPO</sub> respectively represent the NO<sub>x</sub> conversion of xMn-2Cu/SAPO, 2Cu/SAPO and xMn/SAPO at 210 °C, and [N<sub>2</sub>O]<sub>outlet</sub> represents the outlet N<sub>2</sub>O concentration.

### 2.3 Characterization

X-ray diffraction patterns were collected on a bruker D8 Advance X-ray diffractometer with a Ni-Filtered Cu Kα with a step size of 0.02 in the 2θ range of 5° to 40°.

Ammonia temperature programmed desorption (NH<sub>3</sub>-TPD) experiments were carried out as follows. 150 mg sample was first pretreated in 21% vol O<sub>2</sub>/N<sub>2</sub> at 500 °C for 30 min and then cooled to 100 °C in N<sub>2</sub> and a total flow of 100 ml min<sup>-1</sup> containing 2500 ppm NH<sub>3</sub> in N<sub>2</sub> was injected into the reactor for 2 hours to achieve a steady state. Once the catalyst was saturated, NH<sub>3</sub> was switched off and the catalyst was swept by N<sub>2</sub> overnight. Finally, the catalyst was heated in N<sub>2</sub> at a temperature ramp to 700 °C with a heating rate of 10 °C min<sup>-1</sup>.

NO oxidation experiments were carried out as follows. 150 mg sample was first pretreated in 21% vol O<sub>2</sub>/N<sub>2</sub> at 500 °C for 30 min and then cooled to 210 °C in N<sub>2</sub>. Then a total flow of 100 ml min<sup>-1</sup> containing 500 ppm NO and 3% vol O<sub>2</sub> was injected into the reactor for 30 min to achieve the steady state.

The contents of the elements were determined by ion coupled plasma (ICP) optical emission spectroscopy (Thermo IRIS Intrepid II) after microwave digestion.

The BET surface area, pore volume and pore size of the catalyst samples were measured by N<sub>2</sub> adsorption using the MICROMERITICS ASAP 2020 surface area and porosity analyzer.

Diffuse reflectance UV-vis spectra were recorded in the range of 200–800 nm against a BaSO<sub>4</sub> as a reference standard on a HitachiU-3900 UV-vis spectrophotometer equipped with an integration sphere.

H<sub>2</sub>-TPR experiments were performed using 20 mg sample as follows. The catalysts were first pretreated at 500 °C for 30 min in a highly pure O<sub>2</sub> (40 ml min<sup>-1</sup>) stream. Then the furnace temperature was decreased to room temperature, and feed containing 5% vol H<sub>2</sub> in N<sub>2</sub> was fed at a flow rate of 40 ml min<sup>-1</sup>. H<sub>2</sub>-TPR runs were performed as the temperature increased from room temperature to 800 °C at a linear heating rate of 10 °C min<sup>-1</sup> and then the temperature was kept constant for 30 min at 800 °C to ensure complete reduction. Hydrogen was measured by TCD.

X-ray photoelectron spectroscopy (XPS) analyses were performed using PHI quantera SXM Scanning ESCA Microprobe (Physical Electronics) with a hemispherical detector operating at a constant pass energy (PE = 55 eV). An X-ray source at 210 W (*I* = 15 mA, *U* = 14 kV) and Al Kα radiation (1486.6 eV) were used. Intensities were estimated from the integration of each peak, after smoothening, subtracting the L-shaped background,



and fitting the experimental curve to a combination of Lorentzian and Gaussian lines of variable proportions. All binding energies were referenced to the C 1s line at 284.8 eV.

Diffuse reflectance infrared Fourier transform spectra (DRIFTS) were measured on an FT-IR spectrometer (Thermo Nicolet NEXUS870) with an MCT detector and high temperature reaction chamber (Harrick Scientific Praying Mantis) with ZnSe Windows, which was connected to a gas-dosing system. The powder sample was placed in a sample cup and heated by a cartridge heater underneath the sample. The temperature was adjusted using a K-type thermocouple connected to a Harrick temperature controller. Before each measurement, oxidation pretreatments were executed at 500 °C for 1 h. Background spectra were collected before adsorption for 32 scans with a resolution of 4 cm<sup>-1</sup> in N<sub>2</sub>. DRIFTS spectra were recorded in the range of 4000–650 cm<sup>-1</sup> for 32 scans with a resolution of 4 cm<sup>-1</sup>.

### 3 Results and discussion

#### 3.1 Low temperature NH<sub>3</sub>-SCR activity and N<sub>2</sub> selectivity

Fig. 1a shows the NO conversion of xMn-2Cu/SAPO. There was not much difference in the catalytic activity between 2Cu/SAPO and 1Mn-2Cu/SAPO, 2Mn-2Cu/SAPO and 4Mn-2Cu/SAPO. The activity of 8Mn-2Cu/SAPO was slightly lower than the activity of 2Mn-2Cu/SAPO. As manganese loading increased from 1% to 2%, the activity increased obviously and the SCR activity of 2Mn-2Cu/SAPO, 4Mn-2Cu/SAPO and 8Mn-2Cu/SAPO was much higher than that of 2Cu/SAPO and 1Mn-2Cu/SAPO.

For 2Mn-2Cu/SAPO and 4Mn-2Cu/SAPO, the conversion of NO at 120 °C was about 60%; as the temperature increased to 210 °C, the conversion reached 95%.

Fig. 1b shows the N<sub>2</sub> selectivity of xMn-2Cu/SAPO. Good N<sub>2</sub> selectivity was observed, being above 95% for all catalysts. Other researchers<sup>10,11</sup> also found good N<sub>2</sub> selectivity for the supported SAPO-34 catalysts.

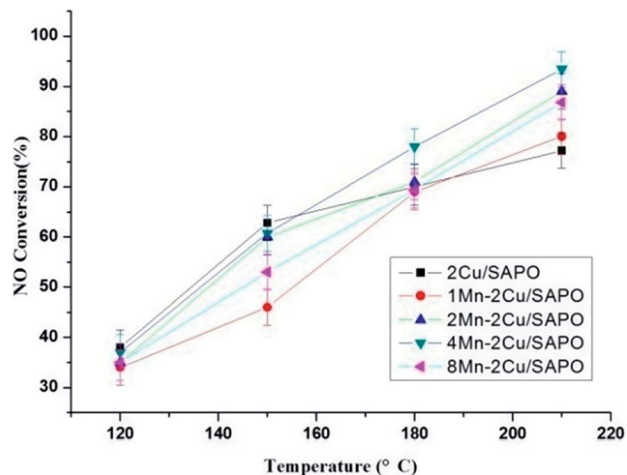


Fig. 2 Water resistance test of xMn-2Cu/SAPO for low-temperature SCR. Conditions: 500 ppm NO + 500 ppm NH<sub>3</sub> + 16.3% H<sub>2</sub>O + 3% vol O<sub>2</sub> + N<sub>2</sub> balance, GHSV = 65 000 h<sup>-1</sup>.

Compared with xMn/SAPO ( $x = 1, 2, 4, 8$ ), the previously prepared,<sup>14</sup> xMn-2Cu/SAPO showed better SCR activities, especially for 2Mn-2Cu/SAPO, indicating that the interactions between copper and manganese might increase its SCR activity.

#### 3.2 Water resistance test

Fig. 2 shows the water resistance test of xMn-2Cu/SAPO. The poison effect of water might come from the reversible adsorption of H<sub>2</sub>O<sup>15</sup> or irreversible dealumination process of zeolite.<sup>16</sup>

In Fig. 2, all catalysts showed strong resistance to water at high temperature. It could be caused by the lower adsorption capability of water at high temperature, since SAPO-34 was highly hydrothermally stable<sup>16</sup> and the poison effect might originate from the competitive adsorption of water with ammonia.

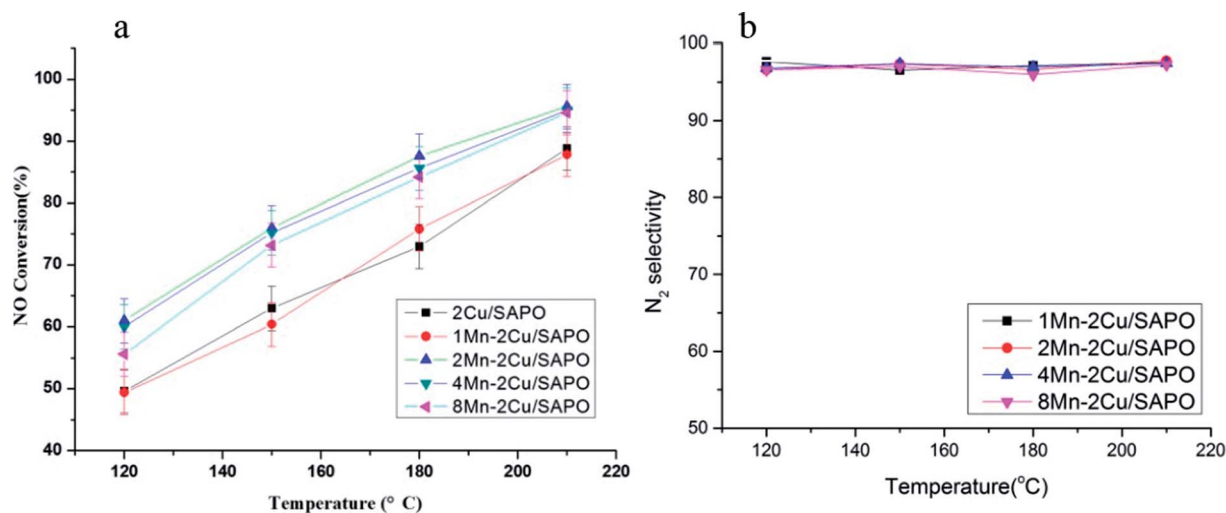


Fig. 1 (a) Catalytic activity and (b) N<sub>2</sub> selectivity of xMn-2Cu/SAPO. Conditions: 500 ppm NO + 500 ppm NH<sub>3</sub> + 3% vol O<sub>2</sub> + N<sub>2</sub> balance, GHSV = 65 000 h<sup>-1</sup>.



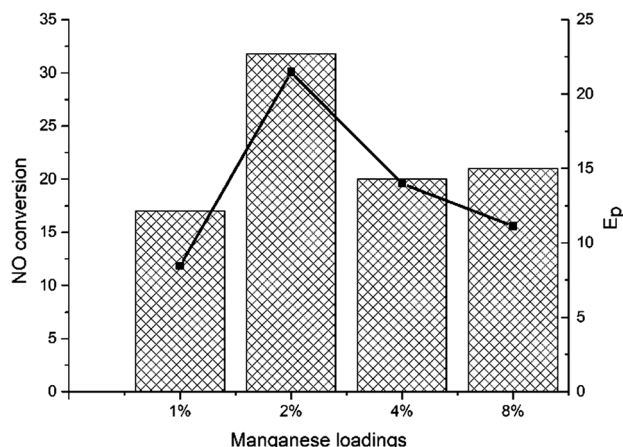


Fig. 3 NO oxidation activity and promotion effect of manganese.

### 3.3 NO oxidation activity and promotion effect

Fig. 3 showed the NO oxidation activity of  $x\text{Mn}-2\text{Cu}/\text{SAPO}$  and the promotion effect.  $2\text{Mn}-2\text{Cu}/\text{SAPO}$  had the best NO oxidation activity, indicating the interaction between copper and manganese elements, which accelerated the NO oxidation process. Good oxidation activity would certainly help the oxidation of  $\text{Cu}^+$  to  $\text{Cu}^{2+}$  in SCR reaction. The  $E_p$  profile was almost the same as the NO conversion profile, indicating that the increase in NO oxidation activity would promote the low-temperature SCR activity. Compared with the  $x\text{Mn}/\text{SAPO}$  ( $x = 1, 2, 4, 8$ ) previously prepared,<sup>14</sup> the NO oxidation activities of  $x\text{Mn}-2\text{Cu}/\text{SAPO}$  were much higher, which could be one reason for the increased SCR activity.

### 3.4 Physicochemical properties

As showed in Table 1, the BET surface area and micro pore volume decreased gradually as manganese loading increased; the surface areas of  $2\text{Mn}-2\text{Cu}/\text{SAPO}$ ,  $4\text{Mn}-2\text{Cu}/\text{SAPO}$  and  $8\text{Mn}-2\text{Cu}/\text{SAPO}$  were similar.  $x\text{Mn}/\text{SAPO}$  ( $x = 1, 2, 4, 8$ ) previously prepared<sup>14</sup> showed the same trend: the surface area and pore volume decreased as manganese loading increased.

The manganese loading, copper loading and Mn/Cu molar ratio from ICP result were almost the same as the set values. Meanwhile the Mn/Cu molar ratio from the XPS results was quite different from that of ICP results. Since XPS and ICP reflect the elemental information of the surface phase and the

bulk phase respectively, the difference might come from the enrichment of manganese on surface.

### 3.5 XRD

XRD patterns of  $x\text{Mn}-2\text{Cu}/\text{SAPO}$  are depicted in Fig. 4. The diffraction peaks of chabazite phase with the space group of  $R\bar{3}m$  were identified, indicating that the crystalline structure of SAPO-34 remained unchanged after catalyst preparation. When manganese loading increased from 0 to 4%, only the chabazite phase was detectable, indicating that the manganese species were well dispersed. As manganese loading reached 8%, the diffraction peaks of the  $\text{Mn}_2\text{O}_3$  phase appeared, indicating the aggregation of manganese species and decreased manganese dispersity. On  $x\text{Mn}/\text{SAPO}$  ( $x = 1, 2, 4, 8$ ), which was previously prepared,<sup>14</sup> there too were no peaks attributed to manganese oxides until manganese loading increased to 8%.

### 3.6 $\text{NH}_3$ -TPD

Fig. 5 showed the effluent  $\text{NH}_3$  profiles during the  $\text{NH}_3$ -TPD process. The amount of  $\text{NH}_3$  desorption was closely related to the amount of acid sites. As expected, when manganese loading increased, the amount of  $\text{NH}_3$  desorption decreased, which was caused by the replacement of  $\text{H}^+$  in the framework of SAPO by  $\text{Mn}^{x+}$  in the ion exchange process.

In Fig. 5 there are three  $\text{NH}_3$  desorption peaks, i.e. a low temperature peak at  $250^\circ\text{C}$ , a middle temperature peak at  $400^\circ\text{C}$  and a high temperature peak at  $500^\circ\text{C}$ , which could be assigned to the weak acid site, the middle strong acid site and the strong acid site, respectively.<sup>17</sup>

The shapes of  $1\text{Mn}-2\text{Cu}/\text{SAPO}$ ,  $2\text{Mn}-2\text{Cu}/\text{SAPO}$  and  $4\text{Mn}-2\text{Cu}/\text{SAPO}$  were similar while the activity differed a lot, indicating that the related acid sites might not have significant influence on the SCR activity for  $x\text{Mn}-2\text{Cu}/\text{SAPO}$ . For  $x\text{Mn}/\text{SAPO}$  ( $x = 1, 2, 4, 8$ ),<sup>14</sup> the amount of ammonia desorption also decreased as manganese loading increased.

### 3.7 $\text{H}_2$ -TPR

The  $\text{H}_2$ -TPR profiles of the four catalysts are depicted in Fig. 6. For  $8\text{Mn}-2\text{Cu}/\text{SAPO}$ , there were two sharp peaks at  $278^\circ\text{C}$  and  $327^\circ\text{C}$ , respectively. The former indicated the reduction of  $\text{MnO}_2$  to  $\text{Mn}_2\text{O}_3$ , while the latter indicated the reduction of  $\text{Mn}_2\text{O}_3$  to  $\text{Mn}_3\text{O}_4$ .<sup>3</sup> Compared with  $\text{Mn}/\text{TiO}_2$ ,<sup>18,19</sup> the reduction peaks moved to a lower temperature, indicating its good redox capacity.

Table 1 Physico-chemical properties

Sample	BET surface area ( $\text{m}^2 \text{g}^{-1}$ )	Micro pore volume ( $\text{cm}^3 \text{g}^{-1}$ )	Micro pore width (nm)	Mn loading <sup>a</sup> (wt%)	Cu loading <sup>a</sup> (wt%)	Mn/Cu molar ratio <sup>a</sup>	Mn/Cu molar ratio <sup>b</sup>
2Cu/SAPO	467	0.231	2.36		1.951		
1Mn-2Cu/SAPO	459	0.230	1.90	1.054	2.016	0.51	1.587
2Mn-2Cu/SAPO	430	0.228	2.53	2.108	1.998	1.055	2.594
4Mn-2Cu/SAPO	426	0.206	1.96	3.846	2.048	1.878	3.424
8Mn-2Cu/SAPO	424	0.196	2.54	8.306	1.848	4.495	9.104

<sup>a</sup> Determined by ICP. <sup>b</sup> Determined by XPS.





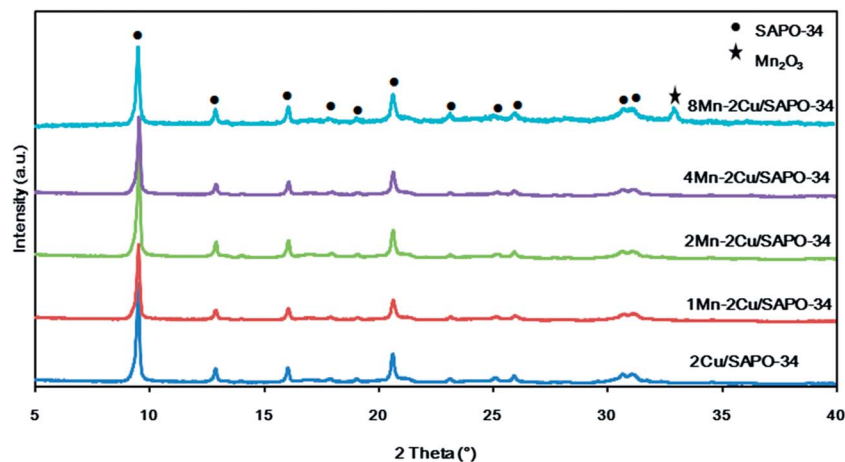


Fig. 4 XRD patterns of  $x\text{Mn}-2\text{Cu}/\text{SAPO}$ .

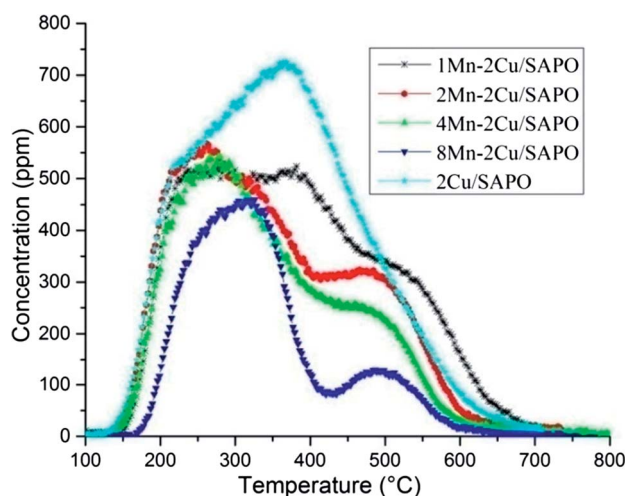


Fig. 5  $\text{NH}_3$ -TPD of  $x\text{Mn}-2\text{Cu}/\text{SAPO}$ .

In the TPR patterns, the reduction process of copper in SAPO-34 zeolite could be separated into two steps, *i.e.* the reduction of  $\text{Cu}^{2+}$  to  $\text{Cu}^+$  at about 300 °C and the reduction of  $\text{Cu}^+$  to  $\text{Cu}^0$  at about 440 °C,<sup>10</sup> while in Fig. 6 the peak strength of 1Mn-2Cu/SAPO was relatively low, indicating that the peak strength of 2Cu/SAPO was even lower, making the assignment of copper species difficult and unreasonable, so the assignment of copper was not discussed. The hydrogen consumption amount of copper reduction was relatively low, so the ignorance of copper species would not influence the discussion of manganese species.

As manganese loading increased, the peaks at 278 °C and 327 °C increased, indicating that the proportion of  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  species increased. For 1Mn-2Cu/SAPO catalysts, only one broad peak between 250 and 400 °C was detectable, indicating that most of the manganese species were  $\text{Mn}^{2+}$  since  $\text{Mn}^{2+}$  cannot be reduced below 700 °C. Since  $\text{Mn}^{2+}$  species were inactive for SCR reaction, addition of manganese did not help increase the activity for 1Mn-2Cu/SAPO, which was consistent

with  $E_p$  trends and NO oxidation results. For 2Mn-2Cu/SAPO the peaks belonging to  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  species started to generate, indicating its good redox capacity. For 4Mn-2Cu/SAPO and 8Mn-2Cu/SAPO, the peaks at 278 °C and 327 °C increased greatly, indicating that the ratio of  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  increased. When manganese loading was above 2%,  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  species began to generate, which is consistent with the  $E_p$  trends and NO oxidation results.

Compared with  $x\text{Mn}/\text{SAPO}$  ( $x = 1, 2, 4, 8$ ) previously prepared,<sup>14</sup> for which the temperature peak of  $\text{H}_2$ -TPR was about 353 °C and 442 °C, the peak temperature moved to a lower value, indicating that the interactions between copper and manganese species might accelerate oxidation reaction and increase the catalytic oxidation activity, which would promote low temperature SCR reaction.

Table 2 represents the hydrogen consumption of  $x\text{Mn}-2\text{Cu}/\text{SAPO}$  during TPR processes. As manganese loading increased, hydrogen consumption increased gradually, while the actual hydrogen consumption was much lower than the theoretical value. The ratio of experimental hydrogen consumption to

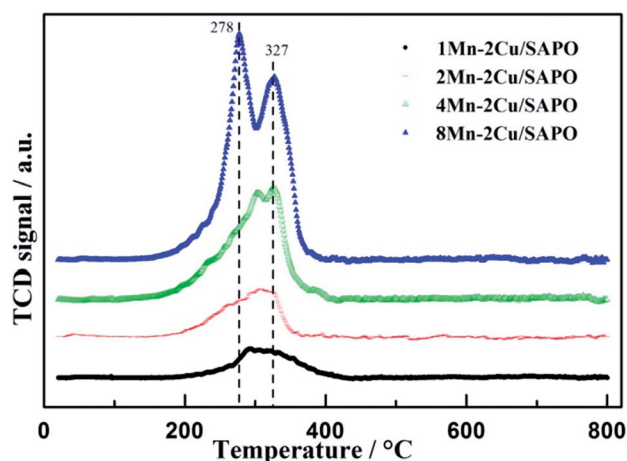


Fig. 6  $\text{H}_2$ -TPR of  $x\text{Mn}-2\text{Cu}/\text{SAPO}$ .



Table 2 Hydrogen consumption

	8Mn-2Cu/SAPO	4Mn-2Cu/SAPO	2Mn-2Cu/SAPO	1Mn-2Cu/SAPO
Hydrogen consumption <sup>a</sup> (10 <sup>-2</sup> mmol)	2.04	1.11	0.468	0.327
Hydrogen consumption <sup>b</sup> (10 <sup>-2</sup> mmol)	3.53	2.08	1.35	0.989
Hydrogen consumption <sup>a</sup> /hydrogen consumption <sup>b</sup> (%)	57.8	53.4	35.7	33.1

<sup>a</sup> The actual hydrogen consumption calculated from TPR profiles. <sup>b</sup> The theoretical hydrogen consumption, assuming all of the Cu species are Cu<sup>2+</sup> and reduced to Cu<sup>0</sup>, and all of the Mn species are Mn<sup>4+</sup> and reduced to Mn<sup>2+</sup> in TPR process.

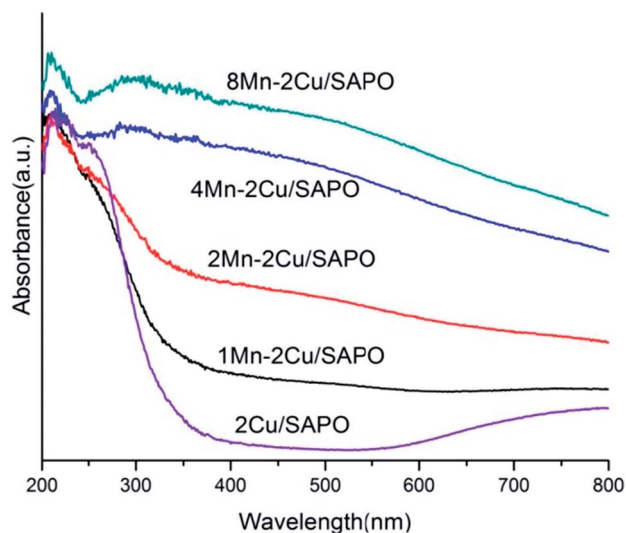


Fig. 7 DR UV-vis spectra recorded under ambient atmosphere of xMn-2Cu/SAPO.

theoretical hydrogen consumption of 8Mn-2Cu/SAPO and 4Mn-2Cu/SAPO was similar, as well as that of 1Mn-2Cu/SAPO and 2Mn-2Cu/SAPO. Since the ratio of experimental hydrogen consumption to theoretical hydrogen consumption was highly related to the proportion of Mn<sup>3+</sup> and Mn<sup>4+</sup>, the proportion of Mn<sup>3+</sup> and Mn<sup>4+</sup> for 1Mn-2Cu/SAPO and 2Mn-2Cu/SAPO were similar, as well as that of 8Mn-2Cu/SAPO and 4Mn-2Cu/SAPO.

### 3.8 DR UV-vis

The UV-vis spectra of the samples are given in Fig. 7. In Fig. 7, the absorption bands at 240 nm were related to the charge transfer processes between the framework aluminum and oxygen atoms of aluminophosphate.<sup>20</sup> The band at 220 nm was attributed to the oxygen-to-metal charge-transfer of the isolated Cu<sup>+</sup>/Cu<sup>2+</sup> bound on the framework of zeolites.<sup>21,22</sup> The bands at 280–300 nm were assigned to copper oxide clusters.<sup>23,24</sup> The bands at 700–800 nm were assigned to the d-d transition of isolated Cu<sup>2+</sup> in weak disordered octahedral coordination of O-containing ligands.<sup>23,25</sup>

The broad bands in the range 320–380 nm were attributed to the Mn<sup>3+</sup> ← O<sup>2-</sup> charge transfer transition superimposed on the <sup>5</sup>B<sub>1g</sub> → <sup>5</sup>B<sub>2g</sub> crystal field d-d transition.<sup>26</sup> The band at 322 nm was tentatively assigned to the Mn<sup>3+</sup> ← O<sup>2-</sup> charge transfer in Mn<sub>3</sub>O<sub>4</sub> in which manganese was octahedrally coordinated with oxygen.<sup>27–29</sup> The band at 255–276 nm could be assigned to the Mn<sup>2+</sup> ← O<sup>2-</sup> charge transfer transition in tetrahedral oxygen coordination.<sup>27,28</sup> In the α-Mn<sub>2</sub>O<sub>3</sub> structure, Mn<sup>3+</sup> ions occupied octahedral sites and, if highly symmetric, a single spin-allowed absorption band in the d-d transition region was expected similarly to [Mn(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> at 500 nm.

As manganese loading increased, the band at 320–380 nm increased gradually especially when the manganese loading changed from 2% to 4%, indicating that the percentage of Mn<sup>3+</sup> increased.

Meanwhile the bands at 255–276 nm were generated, indicating that the percentage of Mn<sup>2+</sup> decreased. Consistent with

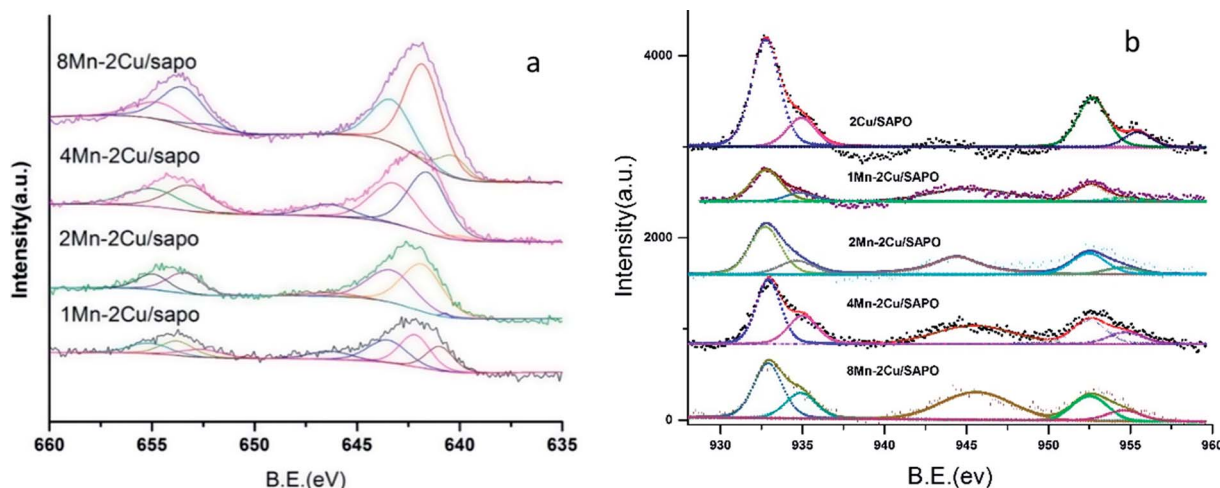


Fig. 8 XPS spectra of (a) Mn 2P and (b) Cu 2P.



**Table 3** Binding energies (eV) of  $\text{Mn}^{x+}$  2P<sub>3/2</sub> and the percentage of  $\text{Mn}^{x+}$ 

Compound	$\text{Mn}^{2+}$		$\text{Mn}^{3+}$		$\text{Mn}^{4+}$	
	Peak (eV)	%	Peak (eV)	%	Peak (eV)	%
1Mn-2Cu/SAPO	640.97	26.3	642.19	38.8	643.51	34.9
2Mn-2Cu/SAPO	640.69	0.5	641.83	55.8	643.36	44.2
4Mn-2Cu/SAPO	639.99	0.1	641.58	56.2	643.18	43.8
8Mn-2Cu/SAPO	640.42	9.0	641.83	60.7	643.44	30.3

**Table 4** Binding energies (eV) of  $\text{Cu}^{x+}$  2P<sub>3/2</sub> and the percentage of  $\text{Cu}^{x+}$ 

Compound	$\text{Cu}^+$		$\text{Cu}^{2+}$	
	Peak (eV)	%	Peak (eV)	%
2Cu/SAPO	932.75	78.3	934.93	21.7
1Mn-2Cu/SAPO	932.75	79.9	934.81	20.1
2Mn-2Cu/SAPO	932.64	75.6	934.56	24.4
4Mn-2Cu/SAPO	932.84	65.7	934.93	34.3
8Mn-2Cu/SAPO	932.82	67.2	934.80	32.7

the H<sub>2</sub>-TPR result, the UV-vis results showed the partial oxidation of  $\text{Mn}^{2+}$  to  $\text{Mn}^{3+}$  or  $\text{Mn}^{4+}$ , when manganese loading increased.

The UV-vis spectra of  $x\text{Mn-2Cu/SAPO}$  were similar to that of  $x\text{Mn/SAPO}$  ( $x = 1, 2, 4, 8$ )<sup>14</sup> in that the percentage of  $\text{Mn}^{3+}$  increased suddenly as manganese loading increased from 2% to 4%, indicating that the distribution of manganese species might not have been influenced by the copper species.

### 3.9 XPS

Fig. 8a shows the XPS spectra of Mn 2P of  $x\text{Mn-2Cu/SAPO}$ . Two main peaks assigned respectively to Mn 2P<sub>3/2</sub> at 642.5 eV and Mn 2P<sub>1/2</sub> at 654 eV were observed.

By performing peak-fitting deconvolution, the Mn 2P<sub>3/2</sub> peak could be separated into three peaks, *i.e.* 640.8–640.9 eV, 642.1–642.3 eV and 643.8–644.1 eV, which correspond to the  $\text{Mn}^{2+}$  species,  $\text{Mn}^{3+}$  species and  $\text{Mn}^{4+}$  species,<sup>3,30</sup> respectively. The atomic percentages of manganese species in different valence states are shown in Table 3.

When manganese loading increased from 1% to 2%, the percentage of  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  increased and the percentage of

$\text{Mn}^{2+}$  decreased a lot, while when manganese loading kept increasing, the percentage of manganese species did not change much. This was consistent with the NO oxidation, H<sub>2</sub> TPR and UV-vis results.

As manganese loading increased, the percentage of  $\text{Mn}^{3+}$  species increased, and the percentage of  $\text{Mn}^{4+}$  species also increased, except for 8Mn-2Cu/SAPO. This was consistent with the UV-vis and H<sub>2</sub>-TPR results. Though H<sub>2</sub>-TPR, UV-vis and XPS all showed that there were many  $\text{Mn}^{4+}$  and  $\text{Mn}^{3+}$  species on 8Mn-2Cu/SAPO, the XRD patterns showed the  $\text{Mn}_2\text{O}_3$  phase, which indicated the aggregation of manganese species and decreased manganese dispersity, and the NH<sub>3</sub>-TPD results showed that there were much less acid sites. The decreased manganese dispersity and the less acid sites could lead to the lower SCR activity. The XPS spectra of  $x\text{Mn/SAPO}$  ( $x = 1, 2, 4, 8$ )<sup>14</sup> also showed that most of the manganese species were  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$ .

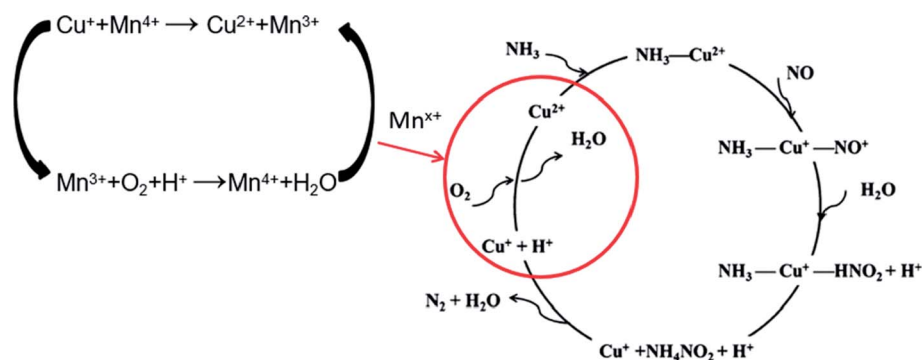
Fig. 8b shows the XPS spectra of Cu 2P; two peaks respectively attributed to Cu 2P<sub>3/2</sub> at 932.6 eV and Cu 2P<sub>1/2</sub> at 952.7 eV were observed. The shake-up satellite was found at about 945 eV, indicating the presence of  $\text{Cu}^{2+}$  species. As manganese loading increased, the shake-up satellite increased, indicating that the amount of  $\text{Cu}^{2+}$  species increased.

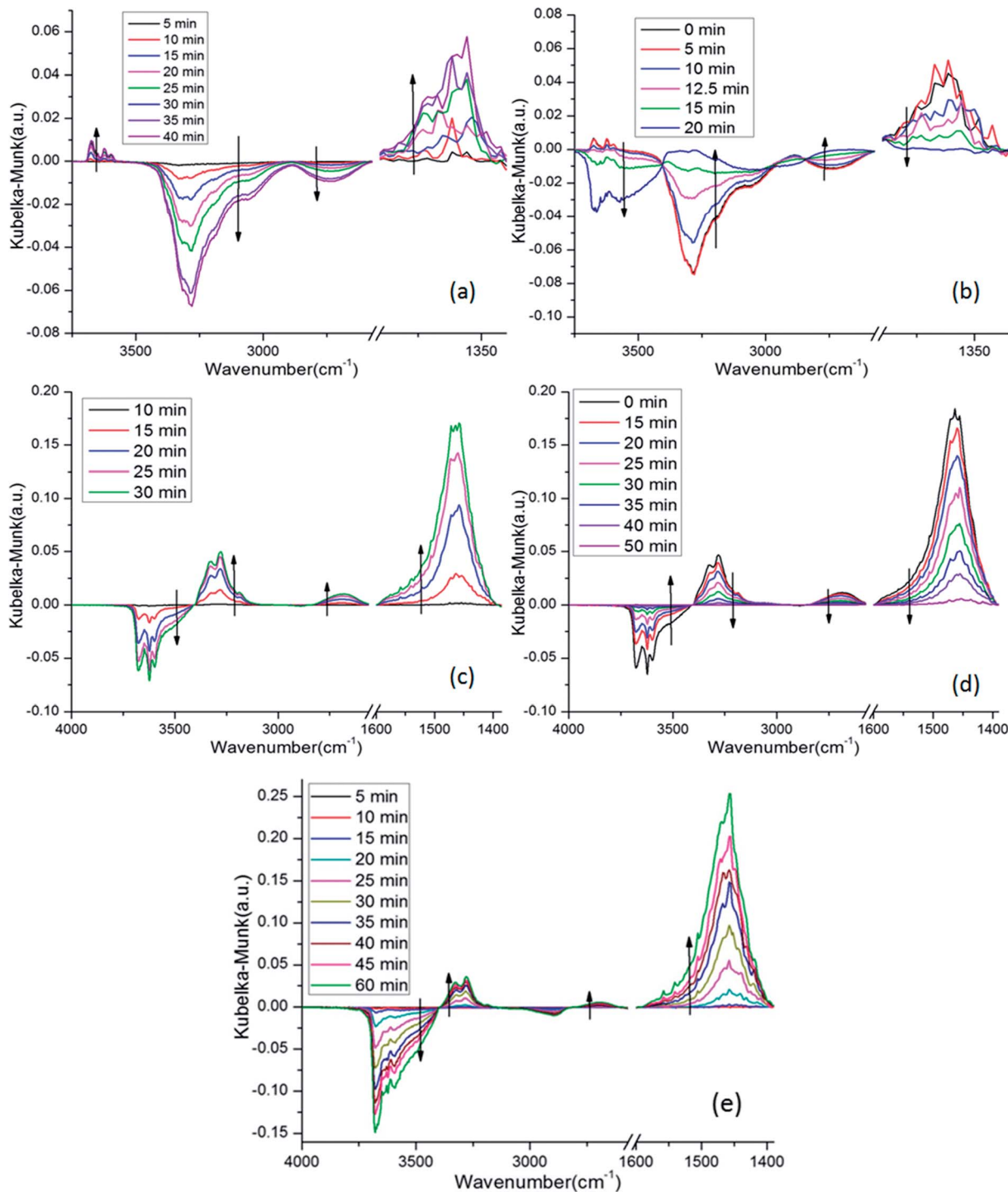
By performing peak-fitting deconvolution, the Cu 2P<sub>3/2</sub> peak could be separated into two peaks, at about 932.7 eV and 934.8 eV respectively, which was ascribed to the  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  species.<sup>31</sup> The atom percentage of  $\text{Cu}^+$  and  $\text{Cu}^{2+}$  is shown in Table 4. As manganese loading increased, the ratio of  $\text{Cu}^{2+}$  increased, indicating that the addition of manganese might oxidize  $\text{Cu}^+$  into  $\text{Cu}^{2+}$ , which was strong evidence that there was strong interaction between the copper and manganese species.

According to the results above and referring to the mechanism of SCR on Cu/SAPO Feng Gao<sup>9</sup> had put forward, the mechanism of SCR on 2Mn-2Cu/SAPO could be proposed. Fig. 9 showed the proposed low temperature SCR mechanism on 2Mn-2Cu/SAPO. In the catalytic cycle,  $\text{Mn}^{x+}$  acts as a catalyst for the oxidation step of  $\text{Cu}^+$  to  $\text{Cu}^{2+}$  in low temperature SCR reaction.

### 3.10 DRIFTS

*In situ* DRIFTS was performed to identify the adsorbed NO species. Fig. 10 shows the DRIFTS spectra of 4Mn-2Cu/SAPO at 150 °C exposed to different gas phases. In Fig. 10a, there was only one positive band at 1360 cm<sup>-1</sup> in the range of 1200–

**Fig. 9** The proposed low temperature SCR mechanism on 2Mn-2Cu/SAPO.



**Fig. 10** DRIFTS spectra of 4Mn-2Cu/SAPO at 150 °C exposed to gas phase of (a) 500 ppm NO + 3% vol O<sub>2</sub> + N<sub>2</sub> (balance); (b) 500 ppm NH<sub>3</sub> + 3% vol O<sub>2</sub> + N<sub>2</sub> (balance) after saturation with NO; (c) 500 ppm NH<sub>3</sub> + 3% vol O<sub>2</sub> + N<sub>2</sub> (balance); (d) 500 ppm NO + 3% vol O<sub>2</sub> + N<sub>2</sub> (balance) after saturation with NH<sub>3</sub>; (e) 500 ppm NO + 500 ppm NH<sub>3</sub> + 3% vol O<sub>2</sub> + N<sub>2</sub> (balance).

1600 nm, which belongs to nitrite groups,<sup>32,33</sup> suggesting that those NO species were nitrite groups. The negative bands at 3280 cm<sup>-1</sup> and 2730 cm<sup>-1</sup> might be attributed to the depletion of Brønsted base sites by the nitrite groups. Three bands at 3675 cm<sup>-1</sup>, 3623 cm<sup>-1</sup> and 3598 cm<sup>-1</sup> could be attributed to the appearance of O-H bond of nitrite groups (-N-O-H) in different

chemical environments. When NH<sub>3</sub> was introduced into the system, as shown in Fig. 10b, the bands associated with nitrite groups decreased rapidly, indicating reaction between NH<sub>3</sub> and NO related species.

In Fig. 10c, when NH<sub>3</sub> was introduced into the system, the bands at 1463 cm<sup>-1</sup> increased greatly, indicating the generation





of  $\text{NH}_3$  species on the Brønsted acid sites,<sup>22</sup> while the bands at  $1210\text{ cm}^{-1}$  increased slightly, which was consistent with the fact that most of the acid sites on SAPO-34 were Brønsted acid sites. The negative bands at  $3681\text{ cm}^{-1}$ ,  $3625\text{ cm}^{-1}$  and  $3600\text{ cm}^{-1}$  were attributed to the depletion of Brønsted acid sites, which was caused by the adsorption of  $\text{NH}_3$ . Specifically, the negative bands at  $3681\text{ cm}^{-1}$  were assigned to the occupation of P–OH sites by  $\text{NH}_3$ . The other two bands were related to the depletion of Si–OH–Al acid sites. The band at  $3147\text{--}3396\text{ cm}^{-1}$  was attributed to the N–H stretching vibrations of  $\text{NH}_4^+$ .<sup>22</sup> When NO was introduced into the system, as shown in Fig. 10d, the bands related to the  $\text{NH}_3$  species decreased gradually, which was caused by the reaction between NO and  $\text{NH}_3$ .

Fig. 10e and c are similar in that only bands related to  $\text{NH}_3$  are visible, while no other bands appeared, especially the negative bands at  $2700\text{ cm}^{-1}$  and  $3000\text{--}3400\text{ cm}^{-1}$  were invisible.

This was strong evidence that only the Elay–Rideal mechanism was effective on the 4Mn–2Cu/SAPO at  $150^\circ\text{C}$ . Since if Langmuir–Hinshelwood mechanism was effective, the adsorbed and well activated NO and  $\text{NH}_3$  related species would react with each other, while the NO species not well activated would accumulated and be detectable for DRIFTS, leading to the appearance of negative bands at  $2700$  and  $3000\text{--}3400\text{ nm}^{-1}$ , as Fig. 10a and b show. Due to the fact that those peaks were not observed in Fig. 10e, all these observations lead to the exclusion of the Langmuir–Hinshelwood mechanism and the assurance of the Elay–Rideal mechanism. In the Elay–Rideal mechanism, NO molecules from gas phase directly react with the well activated  $\text{NH}_3$  species adsorbed on the surface and leave as products to gas phase with the active site left.

## 4 Conclusion

In this work, the SCR activity and physicochemical properties of xMn–2Cu/SAPO were investigated. The  $\text{H}_2$ -TPR, UV-vis and XPS results showed that  $\text{Mn}^{4+}$  and  $\text{Mn}^{3+}$  species began to appear when manganese loading reached 2%. The NO oxidation results showed that 2Mn–2Cu/SAPO had the best NO oxidation activity, indicating that good interaction existed between copper and manganese, which was consistent with the XPS results of Cu 2p binding energy.

The graph of the promotion effect of manganese showed that for 2Mn–2Cu/SAPO, manganese had a good promotion effect on 2Cu/SAPO. According to  $\text{H}_2$ -TPR, UV-vis, XPS and NO oxidation results, the promotion effect of manganese on 2Cu/SAPO comes from the generation of  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  species. The addition of manganese increased the ratio of  $\text{Cu}^{2+}$ . The  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  species might take part in the catalytic cycle and accelerate the oxidation of  $\text{Cu}^+$  to  $\text{Cu}^{2+}$ .

From the *in situ* DRIFTS results, the acid sites on the surface were mainly Brønsted acid sites, the main mechanism on 4Mn–2Cu/SAPO-34 at low temperature was the Elay–Rideal mechanism.

## Conflicts of interest

There are no conflicts to declare.

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