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# Mechanism and regeneration of sulfur-poisoned Mn-promoted calcined NiAl hydrotalcite-like compounds for C<sub>3</sub>H<sub>6</sub>-SCR of NO

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The selective catalytic reduction of NO with propene (C<sub>3</sub>H<sub>6</sub>-SCR) in the presence of SO<sub>2</sub> was investigated over a series of Mn-promoted calcined NiAl hydrotalcite-like compounds. The obtained 5% MnNiAlO catalyst exhibits superior NO conversion efficiency (95%) at 240 °C, and excellent sulfur-poisoning resistance. The possible reaction pathways of the catalytic process were proposed according to several characterization measurements. It is demonstrated that Mn-promoted NiAlO catalysts enhance the Brønsted acid sites and surface active oxygen groups, and improve the redox properties by the redox cycle (Ni<sup>3+</sup> + Mn<sup>2+</sup> ↔ Ni<sup>2+</sup> + Mn<sup>4+</sup>). Thus, the amount of the reaction intermediates is improved, and the reactivities between C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> species and nitrite/nitrate species are promoted. Furthermore, in the presence of SO<sub>2</sub>, the MnNiAlO samples can give rise to minor formation of sulfate and inhibit the competitive adsorption effectively due to their nitrite/nitrate species being more abundant and stable. Finally, regeneration was studied using *in situ* FTIR and the water washing method showed the best performance on the regeneration of S-poisoned catalysts.

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## 1. Introduction

Among the many problems related to air pollution, nitrogen oxides (NO<sub>x</sub>) from stationary and mobile fuel combustion sources, due to its ever-increasing environmental concerns and more serious harm, have attracted more and more attention from society.<sup>1,2</sup> The stringent environmental regulations require limiting NO<sub>x</sub> emissions and promote research into reducing or capturing NO<sub>x</sub>. The selective catalytic reduction of NO<sub>x</sub> by hydrocarbons (HC-SCR), which can eliminate NO<sub>x</sub> and unburnt hydrocarbons simultaneously, is regarded as an economical, effective and energy-saving technique for the removal of NO<sub>x</sub> from automotive exhaust gases,<sup>3,4</sup> and propylene has become the most widely used hydrocarbon.<sup>5</sup>

However, an inevitable problem of SCR is the deactivation of catalysts by SO<sub>2</sub>, owing to its permanent existence in typical diesel fired exhausts.<sup>6</sup> Thus, it is important to develop environmental-friendly SCR catalysts with excellent resistance against SO<sub>2</sub> poisoning. In addition, a mechanistic investigation is highly desired to exploit new catalysts with high sulfur-resistance.

Metal oxide catalysts have attracted much attention due to their high specific surface area, acid–base bifunctionality, synergistic effects and memory effects.<sup>7,8</sup> In previous reports,

hydrotalcite derivatives such as La–Mg–Al,<sup>9</sup> K/Mg–Al<sup>10</sup> and Co–Ce<sup>11</sup> all exhibited performance in NO removal. Xu *et al.*<sup>12</sup> recently reviewed the progress over hydrotalcite-derived NiTi mixed oxide in NO<sub>x</sub> removal by selective catalytic reduction with ammonia. However, the sulfur resistance of the hydrotalcite-based catalyst is rarely studied. Previous literature analyzed the competitive adsorption between SO<sub>2</sub> and NO. The deactivation mechanism of catalysts caused by SO<sub>2</sub> reflects on two aspects.<sup>13–16</sup> Zhang *et al.*<sup>13</sup> reported that SO<sub>2</sub> could react with reduction gas to form sulfate species which did not decompose at low temperature and finally deposited on the catalyst surface. Wu *et al.*<sup>14</sup> demonstrated that the active phase on catalyst was sulfated by SO<sub>2</sub> to form sulfate species, which competed with the formation of nitrogenous species. Crittenden, Li, and co-workers have also achieved great progress in the development of SCR catalysts with excellent sulfur-poisoning resistance.<sup>15,16</sup>

It has shown that the introduction of a metal adjuvant in the metal oxide can further improve the catalytic activity, selectivity and anti-poisoning properties of the original catalyst.<sup>17</sup> According to the reports, manganese oxides have attracted special attention owing to their different types of labile oxygen and oxidation states,<sup>18</sup> which are necessary and important for completing a catalytic cycle.<sup>18,19</sup> Moreover, a series of manganese-containing metal oxide catalysts also show a significant enhancement of catalytic activity at low temperature.<sup>20</sup> In brief, it is inevitable for the deactivation of catalysts caused by SO<sub>2</sub>. Therefore, the regeneration for catalysts is a very important process during SCR method. However the effect of SO<sub>2</sub> on their generation and transformation, has not been systemically addressed.

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Herein, we synthesized  $x\%$  MnNiAlO catalysts and examined their against  $\text{SO}_2$ -poisoning performance in the  $\text{C}_3\text{H}_6$ -SCR reaction. The reaction mechanism was investigated by *in situ* FTIR. The regeneration methods of deactivated catalyst were selected and investigated. The poisoning mechanism was analyzed by FTIR, XPS and Py-FTIR.

## 2. Experimental

### 2.1. Catalyst preparation

NiAl and ZrNiAl hydrotalcite were fabricated by a urea hydrolysis method according to the previous study.<sup>21</sup> NiAl-based hydrotalcite precursors were prepared by hydrothermal method. Different proportions of Mn were loaded in the preparation process, followed by calcined to prepare catalyst samples of  $x\%$  MnNiAlO. The  $x$  stands for the atomic number of Mn in the whole of Mn, Ni and Al. For example, 1% MnNiAlO indicates Mn : (Mn + Ni + Al) atomic ratio of 1 : 100.

### 2.2. Catalyst characterization

The powder X-ray diffraction (XRD) were manufactured by Rigaku D/max- $\gamma$ b X-ray diffractometer with a  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), operated at 40 kV and 100 mA. Thermogravimetry analysis (TGA) was rendered on a NETZSCH STA 409 PC/PG simultaneous thermal analyses from 30–1000 °C in flowing air atmosphere. FTIR and Pyridine chemisorption spectra were obtained on a VERTEX 70 infrared spectrometer. The morphology of the catalysts was characterized by virtue of scanning electron microscopy (SEM, S-4800, Japan). The X-ray photoelectron spectroscopy (XPS) experiments were undertaken on an ESCALAB XI photoelectron spectrometer with Al  $K\alpha$  radiation. Curve fitting was conducted by use of XPSPEAK 4.1 with a Shirley background. Hydrogen temperature programmed reduction ( $\text{H}_2$ -TPR) was carried out in a Quantachrome Chem-BET Pulsar TPR (p/n 02139-1).  $\text{O}_2$ -TPD experiments were started from 30–1000 °C with a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  under Ar flow. A mass spectrometer (Hiden HPR20) was used for on-line monitoring of the  $\text{O}_2$ -TPD effluent gas.

### 2.3. Catalytic performance test

The de- $\text{NO}_x$  efficiency of the  $\text{C}_3\text{H}_6$ -SCR catalysts was evaluated employing a fixed-bed quartz tube reactor with the effluent gas of NO detected by gas chromatograph. Samples of 200 mg were applied to evaluate the catalytic performance under the following conditions: 1000 ppm NO, 1000 ppm  $\text{C}_3\text{H}_6$ , 5 vol%  $\text{O}_2$ , He as balance, and the total gas flow rate was  $100 \text{ mL min}^{-1}$ , the GHSV was  $30\,000 \text{ h}^{-1}$ . Before each experiment, the catalyst was heated to 350 °C under He stream and held for 1 h, and the activity measurement was carried out at the heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  from 150 °C to 350 °C. The conversion of NO was calculated as follows:

$$\text{NO conversion} = \frac{([\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}})/[\text{NO}]_{\text{in}} \times 100\%}{(1)}$$

### 2.4. *In situ* FTIR measurements

The *in situ* FTIR experiments were performed on a VERTEX 70 infrared spectrometer. Before each experiment, the sample was pretreated at 400 °C in helium gas atmosphere for 60 min to remove trace impurities. When not specified, the test gas conditions were:  $[\text{O}_2] = 5 \text{ vol}\%$ ,  $[\text{NO}] = [\text{C}_3\text{H}_6] = [\text{SO}_2] = 1000 \text{ ppm}$ , He was a balance gas.

### 2.5. Regeneration of deactivated catalysts

**2.5.1. Water washing.** The deactivated catalysts were regenerated by washing with deionized water. 1 g deactivated sample was washed in 20 mL aqueous solution under continuous stirring for 2 h. Then the catalyst was filtered and dried at 110 °C.

**2.5.2. Thermal regeneration in air.** The deactivated catalysts were placed in a quartz tube ( $\Phi 6 \text{ mm}$ ) by packing quartz in air. The regeneration experiments were carried out by heating the samples with a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  in air. Then the samples were heated at 500 °C for 2 h purging with the air.

## 3. Results and discussion

### 3.1. Catalytic test

The NiAlO and MnNiAlO catalysts were tested in  $\text{C}_3\text{H}_6$ -SCR with and without  $\text{SO}_2$ . The NO conversion results in the temperature range of 150–350 °C without  $\text{SO}_2$  are shown in Fig. 1(A). In these experiments, the NO conversion changed with the reaction temperature increasing over all the samples. The NiAlO sample achieved the maximum NO conversion of 43% at 250 °C. For Mn doped samples, their activities improved obviously, as well as the temperature corresponding to the maximum NO conversion shifted to a lower temperature. The 5% MnNiAlO exhibited the best catalytic performance with NO conversion which promptly reached about 95% at 240 °C. When the Mn amount is increased above 5% and further to 7%, the activity is declined. This phenomenon is owing to the excessive deposition of Mn, which leads to the agglomeration. Hence, we selected the 5% MnNiAlO catalyst as the target catalyst for further investigation.

The effects of the  $\text{SO}_2$  on catalytic activity was investigated over NiAlO and 5% MnNiAlO catalysts at 240 °C, and the results are shown in Fig. 1(B). After introduction of  $\text{SO}_2$  (100 ppm), the catalysts exhibit different sulfur-poisoning resistant properties.

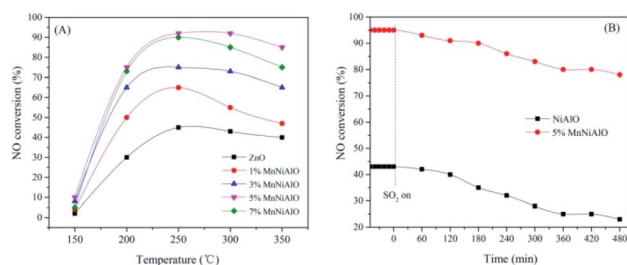


Fig. 1 (A) NO conversion as a function of temperatures over NiAlO and  $x\%$  MnNiAlO catalysts. (B)  $\text{NO}_x$  conversion of NiAlO and 5% MnNiAlO catalysts in the presence of 100 ppm  $\text{SO}_2$  at 240 °C.



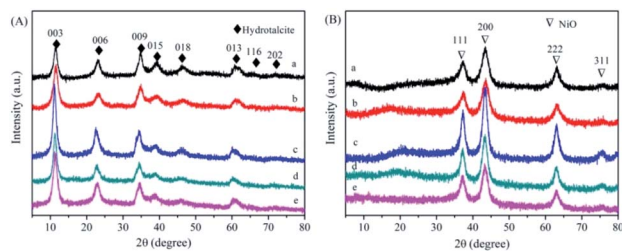


Fig. 2 (A) XRD patterns of NiAl-HT and MnNiAl-HT precursor. (a) NiAl-HT precursor; (b) 1% MnNiAl-HT precursor; (c) 3% MnNiAl-HT precursor; (d) 5% MnNiAl-HT precursor; (e) 7% MnNiAl-HT precursor. (B) XRD patterns of NiAlO and *x*% MnNiAlO samples. (a) NiAlO; (b) 1% MnNiAlO; (c) 3% MnNiAlO; (d) 5% MnNiAlO; (e) 7% MnNiAlO.

In terms of NiAlO sample, the  $\text{NO}_x$  conversion dropped significantly from 43% to 23% after 8 h. In contrast, the 5% MnNiAlO catalyst maintained high activity (from 95% to 88%) and excellent stability in the first 8 h, implying that Mn introduction could enhance  $\text{NO}_x$  reduction and maintain excellent catalytic activity in the presence of  $\text{SO}_2$ .

### 3.2. Morphology and physical properties of the catalysts

Fig. 2(A) shows the XRD spectra of NiAl-HT and four different Mn loadings samples. The characteristic peaks located at 11, 22, 35, 38, and  $46^\circ$  are assigned to the hydrotalcite structure (JCPDS 22-700).<sup>22–24</sup> Meanwhile, there are no additional peaks derived from Mn species for MnNiAl-HT samples, suggesting that Mn is well dispersed on the surface of the carrier. The unit cell parameters *a* and *c* of the hydrotalcite can be calculated assuming a 3R stacking sequence; therefore,  $a = 2d_{110}$  and  $c = d_{003} + 2d_{006} + 3d_{009}$ , where the value of *a* is the average distance of two metal cations in adjacent unit cells and *c* is the interlayer distance regulated by the size and charge of the anion placed between the brucite-like layers. The structural parameters of the hydrotalcite-like samples are listed in Table 1. Both *a* and *c* remained unchanged with increasing Mn loading due to the ion radius disparity similarity between  $\text{Ni}^{2+}$  (56 Å) and  $\text{Mn}^{4+}$  (54 Å).

The XRD patterns of derived oxides (Fig. 2(B)) show the complete transformation from HT phase to oxide phase after calcination. The characteristic diffraction peak of the hydrotalcite disappeared, implying that the hydrotalcite structure collapses. Meanwhile, all samples show four distinctive peaks at about  $37.4$ ,  $43.0$ ,  $63.4$  and  $75.2^\circ$ , which are corresponding to the

Table 1 Structural properties of the MnNiAl hydrotalcite

Sample	D-value				Lattice parameter	
	$d_{003}$	$d_{006}$	$d_{009}$	$d_{110}$	<i>a</i>	<i>c</i>
NiAl-HT	7.621	3.81	2.565	1.514	3.029	22.936
1% MnNiAl-HT	7.576	3.767	2.558	1.518	3.036	22.783
3% MnNiAl-HT	7.724	3.952	2.588	1.534	3.068	22.913
5% MnNiAl-HT	7.724	3.876	2.588	1.539	3.078	23.240
7% MnNiAl-HT	7.724	3.866	2.592	1.538	3.076	23.238

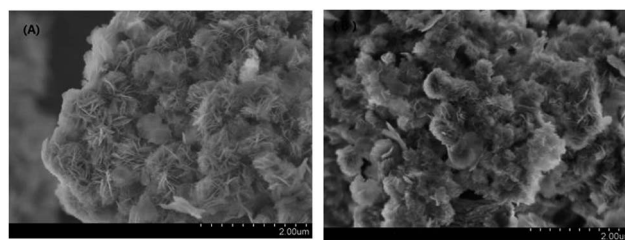


Fig. 3 SEM images of NiAlO and 5% MnNiAlO catalysts calcined at 500 °C.

NiO (111), (200), (220) and (311) crystal planes (JCPDS 47-1049), respectively. No diffraction peaks corresponding to crystalline Mn phase can be observed, due to the low Mn content or the high dispersion of Mn oxide.

SEM of NiAlO and 5% MnNiAlO catalysts is presented in Fig. 3. Two samples both exhibited pompon shape. Moreover, it can be found that the exposed crystal face of MnNiAlO was larger than NiAlO, which could provide more active sites for catalytic reaction.

The infrared spectra of NiAlO and *x*% MnNiAlO are shown in Fig. 4. The strong and wide absorption band located at  $3484\text{ cm}^{-1}$  is attributable to the superposition of the stretching vibration between the interlayer  $\text{H}_2\text{O}$  and the layer-OH. The absorption band at  $1648\text{ cm}^{-1}$  is attributed to the physically adsorbed water on the surface of the sample,<sup>25</sup> and the absorption band at  $1384\text{ cm}^{-1}$  is attributed to  $\text{CO}_3^{2-}$ .<sup>25</sup> The absorption peak at  $819\text{ cm}^{-1}$  is mainly caused by the vibration of the skeleton of the metal bond.

The  $\text{H}_2$ -TPR technology was employed in evaluating the reducibility of the catalysts. For all samples (Fig. 5), there are two reduction peaks centered at  $675^\circ\text{C}$  and  $780^\circ\text{C}$ . The former is related to the reduction of Ni species which has a low interaction with  $\text{Al}_2\text{O}_3$  or small Ni particles, and the latter belongs to the reduction of a stable  $\text{Ni}^{2+}$  compound ( $\text{NiO-Al}_2\text{O}_3$  or  $\text{NiAl}_2\text{O}_4$  formed during calcination) which strongly reacts with  $\text{Al}_2\text{O}_3$ .<sup>26</sup> In the terms of *x*% MnNiAlO samples, they presented two new reduction peaks around  $365^\circ\text{C}$  and  $505^\circ\text{C}$ , although the peak signals were very weak. According to the previous literature, the

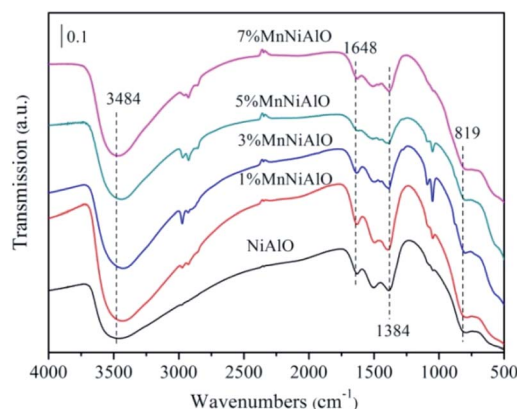


Fig. 4 FTIR spectra of the calcined NiAlO and MnNiAlO catalysts.



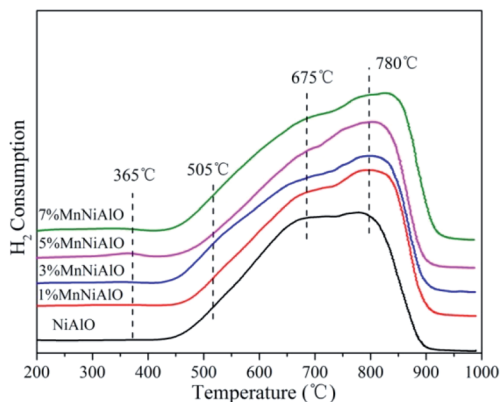


Fig. 5 H<sub>2</sub>-TPR patterns of calcined NiAlO and MnNiAlO samples.

two peaks can be attributed to the two-step reduction of MnO<sub>2</sub>: the first step corresponds to the reduction of MnO<sub>2</sub> to Mn<sub>3</sub>O<sub>4</sub>, and the second step is the further reduction of Mn<sub>3</sub>O<sub>4</sub> to MnO.<sup>27</sup> The total H<sub>2</sub> consumption increased at the same time as Mn-loading increased from 0 to 7 wt% as listed in Table 2, indicating that Mn doping can enhance the redox capacity of the samples, and finally accelerate the oxygen transfer and the oxidation process of NO to NO<sub>2</sub>.

As shown in the O<sub>2</sub>-TPD experiment (Fig. 6), three main characteristic peaks are clearly observed over each sample, which locate at 200–400 °C, 400–750 °C and above 750 °C, corresponding to the physically/chemically adsorbed oxygen O<sub>2</sub> (α), dissociated oxygen O<sup>2-</sup>/O<sup>-</sup> at the vacancy sites (β), and bulk lattice oxygen (γ), respectively.<sup>28</sup> We also quantified the oxygen desorption peaks (Table 2), which suggested Mn incorporation obviously enhanced all the oxygen desorption peaks, especially the peak β, implying positive effects for the mobility of the active oxygen species of these catalysts. Besides, the physically/chemically adsorbed oxygen O<sub>2</sub> (α) and dissociated oxygen O<sup>2-</sup>/O<sup>-</sup> at the vacancy sites (β) are found to be the most abundant over the 5% MnNiAlO catalyst, which reflect more active oxygen species. This is concordant with the catalytic test results (Fig. 1(A)). In fact, the first two kinds of oxygen species (α and β) are more crucial for the oxidation reaction during the C<sub>3</sub>H<sub>6</sub>-SCR.<sup>4</sup> It is beneficial to the oxidation following the steps C<sub>3</sub>H<sub>6</sub> → C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>/carbonates (adsorption and oxidation) → CO/CO<sub>2</sub> (desorbed species).<sup>4</sup>

### 3.3. DRIFTS studies

**3.3.1. Co-adsorption of NO + O<sub>2</sub>.** The *in situ* FTIR spectra of NO + O<sub>2</sub> on catalysts at 200 °C are presented in Fig. 7. As shown

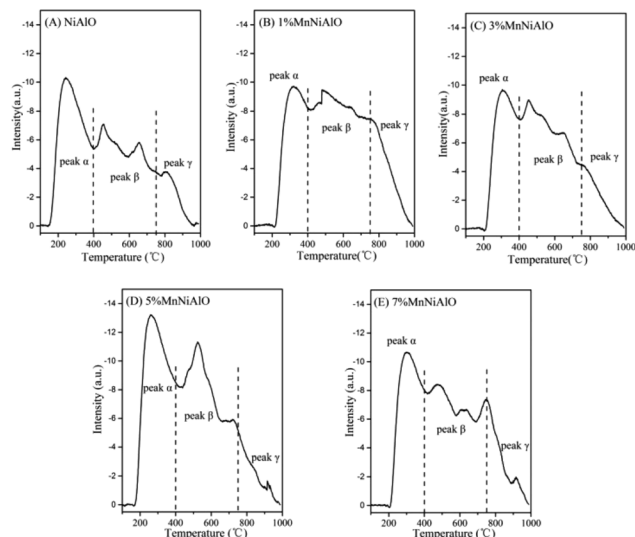


Fig. 6 O<sub>2</sub>-TPD profiles of calcined NiAlO and MnNiAlO samples. (A) NiAlO; (B) 1% MnNiAlO; (C) 3% MnNiAlO; (D) 5% MnNiAlO; (E) 7% MnNiAlO.

in Fig. 7(A), over NiAlO catalyst, nitrate species with different configurations appeared after introduction of NO/O<sub>2</sub> for 2 min, the bands at 1580 and 1349 cm<sup>-1</sup> were assigned to adsorbed nitrate ion,<sup>29</sup> and the band at 1209 cm<sup>-1</sup> was attributed to bridge bidentate nitrates.<sup>29</sup> The weak bands at 1449 and 1020 cm<sup>-1</sup> belonged to *trans*-N<sub>2</sub>O<sub>2</sub><sup>2-</sup> and bidentate nitrates, respectively.<sup>30</sup> Along with the time increasing, nitrate ion (1580, 1349 cm<sup>-1</sup>) and bridging bidentate nitrate (1209 cm<sup>-1</sup>) were pronounced at first and grew rapidly, and then decreased significantly over time. Meanwhile, *trans*-N<sub>2</sub>O<sub>2</sub><sup>2-</sup> (1449 cm<sup>-1</sup>) and bidentate nitrate (1020 cm<sup>-1</sup>) increased continuously.<sup>30</sup> More important, monodentate nitrate species (1279 cm<sup>-1</sup>) appeared after 10 min and accumulated greatly.<sup>30</sup> Taken together, we could infer the co-adsorption process of NO + O<sub>2</sub> on the catalyst surface. Firstly, NO was adsorbed onto the surface of the catalyst to form nitrate ion (1580, 1349 cm<sup>-1</sup>), bridging bidentate nitrate (1209 cm<sup>-1</sup>) and part of bidentate nitrate (1449, 1020 cm<sup>-1</sup>). After the complete conversion of NO in the reaction cell, the absorption peaks of the bidentate nitrate species (1449 and 1020 cm<sup>-1</sup>) still increased rapidly, whereas adsorbed nitrate ion species (1580 and 1349 cm<sup>-1</sup>) gradually weakened. This indicates that the surface nitrate ion species could be transformed to bidentate nitrate over time. As the reaction progressed, the absorption peak of bridged bidentate

Table 2 The O<sub>2</sub> desorption peak area and total H<sub>2</sub> consumption of NiAlO and MnNiAlO catalysts

Sample	Peak α area (<400 °C)	Peak β area (400–750 °C)	Peak γ area (>750 °C)	Total area	Total H <sub>2</sub> consumption (μmol g <sup>-1</sup> )
NiAlO	1781.0	1897.3	505	4181.3	478.6
1% MnNiAlO	1365.6	2422.2	667.2	4455.0	574.9
3% MnNiAlO	1561.5	2485.2	513.8	4560.5	589.1
5% MnNiAlO	1866.7	2914.5	422.6	5203.8	704.6
7% MnNiAlO	1630.6	2594.8	498.6	5324.0	757.0





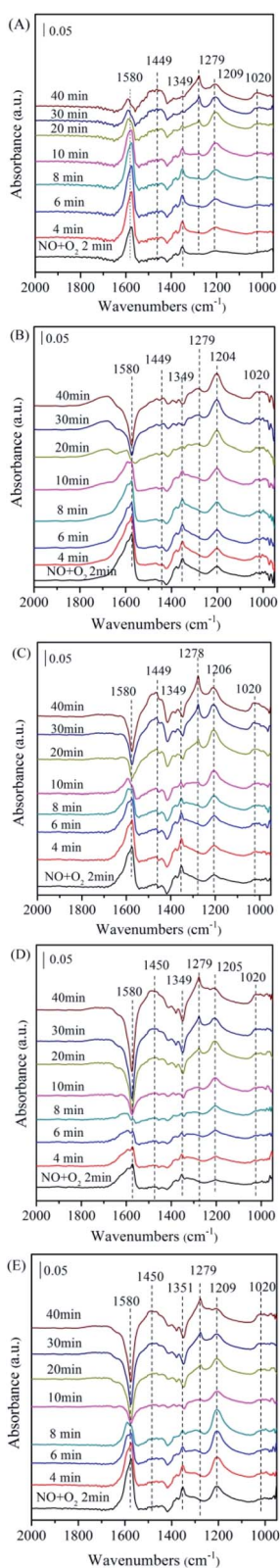


Fig. 7 The *in situ* FTIR spectra of the NiAlO and *x*% MnNiAlO catalysts reacting with NO + O<sub>2</sub> at 200 °C. (A) NiAlO; (B) 1% MnNiAlO; (C) 3% MnNiAlO; (D) 5% MnNiAlO; (E) 7% MnNiAlO.

nitrate (1209 cm<sup>-1</sup>) gradually enhanced to the maximum value, after which bridged bidentate nitrate was decreasing accompanied by the appearance and strengthening of monodentate nitrate (1279 cm<sup>-1</sup>). It is demonstrated that monodentate nitrate was converted from part of bridged bidentate nitrate.

In the case of MnNiAlO catalysts (Fig. 7(B)–(E)), the reaction process is basically similar to that of NiAlO catalyst. By comparing the adsorption amount of nitrogen-containing species, it can be concluded that the introduction of Mn into NiAlO sample promotes the adsorptive and active ability of catalyst for NO. This fact indicates that the synergetic effect between Ni and Mn facilitates the formation of different adsorbed NO<sub>x</sub> species. It is worth noting that for 7% MnNiAlO catalyst (Fig. 7(E)), its adsorbed NO species calculated by the band intensities were less than those of other MnNiAlO catalysts.

### 3.3.2. Reactions between C<sub>3</sub>H<sub>6</sub> and pre-adsorbed NO + O<sub>2</sub>.

In order to clarify the surface reactions and intermediates, the FTIR experiments in a flow of C<sub>3</sub>H<sub>6</sub>/O<sub>2</sub> after the catalyst was pre-adsorbed NO + O<sub>2</sub> followed by He purging at 200 °C were performed. In the case of NiAlO catalyst (Fig. 8(A)), NO and O<sub>2</sub> flushing at 200 °C produced adsorbed nitrate ion (1580 cm<sup>-1</sup>), monodentate nitrate (1279 cm<sup>-1</sup>), bidentate nitrates (1020 and 1482 cm<sup>-1</sup>), and bridge bidentate nitrate (1209 cm<sup>-1</sup>). A further switching the gas to C<sub>3</sub>H<sub>6</sub> and O<sub>2</sub> led to a disappearance in nitrate ion and bridge bidentate nitrates, and also resulted in a decrease in monodentate nitrate species. This suggests that these adsorbed NO<sub>x</sub> species are active. Simultaneously, there is no significant change for bidentate nitrates (at 1020 and 1482 cm<sup>-1</sup>), indicating that they were inert under this reaction condition. More important, the C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> adsorbed species formed by adsorption of C<sub>3</sub>H<sub>6</sub> (1574 and 1352 cm<sup>-1</sup>) become

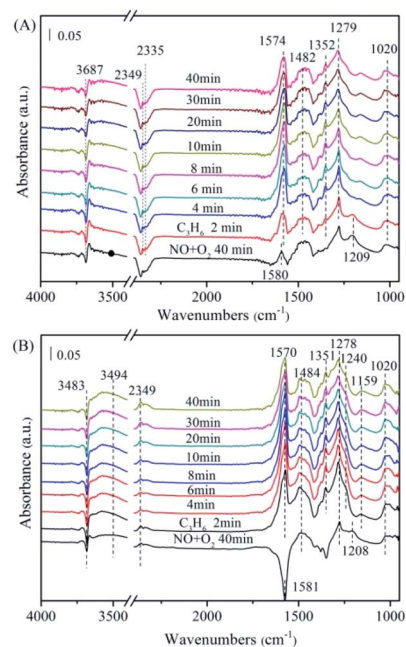


Fig. 8 The *in situ* FTIR spectra of the NiAlO and 5% MnNiAlO catalysts reacting with NO + O<sub>2</sub> and C<sub>3</sub>H<sub>6</sub> at 200 °C. (A) NiAlO; (B) 5% MnNiAlO.



visible and accumulate considerably over time. The band recorded at  $1574\text{ cm}^{-1}$  is assigned to formic acid or acetic acid.<sup>31</sup> The band at  $1352\text{ cm}^{-1}$  belongs to carboxylate or enolic species ( $\text{RCH}=\text{CH}-\text{O}^-$ ).<sup>31</sup> It is worth noting that these surface  $\text{C}_x\text{H}_y\text{O}_z$  adsorbed species grew rapidly within 10 min and then declined gradually, accompanied with a decrease in the signal of monodentate nitrate species ( $1279\text{ cm}^{-1}$ ). Besides, a large amount for gas phase  $\text{CO}_2$  was observed at  $2335\text{ cm}^{-1}$  and  $2349\text{ cm}^{-1}$ .<sup>32</sup> The peak at  $3687\text{ cm}^{-1}$  is attributed to the  $\nu(\text{OH})$  stretching of adsorbed  $\text{H}_2\text{O}$ .<sup>32</sup> It is evident that the intensities of these bands are increased with time passing, implying some amount of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are generated during the  $\text{C}_3\text{H}_6$ -SCR reaction process. This result is in agreement with previous work.<sup>31</sup> It is reported that the interactions of adsorbed NO species and  $\text{C}_x\text{H}_y\text{O}_z$  species are key steps for  $\text{C}_3\text{H}_6$ -SCR.  $\text{C}_x\text{H}_y\text{O}_z$  amounts decreased by reaction with NO species and  $\text{O}_2$  though carbonate species, directly gave rise to  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{H}_2\text{O}$ .

Fig. 8(B) displayed the FTIR spectrum of 5% MnNiAlO, respectively. The MnNiAlO catalyst exhibited the similar trend to NiAlO sample. The main species on the samples after  $\text{NO}/\text{O}_2$  adsorption are nitrate ion ( $1581\text{ cm}^{-1}$ ), monodentate nitrate ( $1278\text{ cm}^{-1}$ ), bidentate nitrates ( $1020$  and  $1484\text{ cm}^{-1}$ ), and bridge bidentate nitrates ( $1208\text{ cm}^{-1}$ ). Switching to  $\text{C}_3\text{H}_6$  atmosphere, the surface nitrate ion, bridge bidentate nitrate and monodentate nitrate species are observed to decline gradually. Surprisingly, the signal for chelating nitrite (at  $1240$  and  $1159\text{ cm}^{-1}$ ) were recorded at the same time, which differs from what occurs over NiAlO sample, suggesting the enhanced adsorption ability of NO on 5% MnNiAlO catalyst. General speaking, a higher NO conversion of one catalyst depends on a lower accumulation of  $\text{adNO}_x$  and a stronger generation of  $\text{C}_x\text{H}_y\text{O}_z$  species during  $\text{C}_3\text{H}_6$ -SCR. Compared to NiAlO catalyst, Mn doping samples showed much more concentration of  $\text{C}_x\text{H}_y\text{O}_z$  surface species, which is indeed advantageous to the further  $\text{deNO}_x$  process. This phenomenon may be due to the excellent redox and oxygen storage/release ability of Mn that can strongly activate  $\text{adNO}_x$  for conversion, which is correlated to the  $\text{H}_2$ -TPR and  $\text{O}_2$ -TPD results (Fig. 5 and 6). Additionally, by comparing the amount of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  produced, it can be judged that Mn incorporation promoted the reactivity of  $\text{C}_x\text{H}_y\text{O}_z$  species with nitrite/nitrate species, decomposing to more  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{H}_2\text{O}$ . These results are consistent with  $\text{C}_3\text{H}_6$ -SCR catalytic test (Fig. 1(A)).

### 3.4. $\text{SO}_2$ poisoning experiments

It is known that flue gas contains  $\text{SO}_2$ , the sulfate species with  $\text{S}=\text{O}$  bond can be formed on the surface of catalyst.<sup>33</sup> Moreover,  $\text{SO}_2$  competes with NO for active sites to form sulfate species, thereby reducing the activity of catalyst. Meanwhile,  $\text{SO}_2$  can react with the reducing gas for poisoning catalyst. Thus, we infer the poisoning mechanism for (Mn)NiAlO catalysts as follows.  $\text{SO}_2$  mainly affects  $\text{C}_3\text{H}_6$ -SCR process through the following two aspects: one is the adsorption and activation of  $\text{SO}_2$  on the surface of catalyst competes with adsorption and activation of NO. The other is the reaction between sulfate/sulfite and  $\text{C}_3\text{H}_6$  competes with the reaction between nitrate/nitrite and  $\text{C}_3\text{H}_6$ . Both 5% MnNiAlO and

NiAlO catalysts are selected to compare their sulfur poisoning situation.

The FTIR experiments in a flow of  $\text{NO}/\text{O}_2$  after the catalyst pre-adsorbed  $\text{SO}_2/\text{O}_2$  were performed and the results were presented in Fig. 9. In the case of NiAlO sample (Fig. 9(A)), the catalyst surface was mainly covered by sulfite (at  $1035\text{ cm}^{-1}$ ),<sup>34</sup> sulfate (at  $1165$ ,  $1243$  and  $1340\text{ cm}^{-1}$ )<sup>35,36</sup> and molecular water (at  $1601\text{ cm}^{-1}$ ) after  $\text{SO}_2/\text{O}_2$  adsorption. These species were bound to the catalyst surface strongly as the subsequent  $\text{N}_2$  purging couldn't change their intensity of absorption bands. Switching to  $\text{NO}/\text{O}_2$ , no significant adsorbed  $\text{NO}_x$  species could be detected, indicating that  $\text{SO}_2$  competes with NO to adsorb over the NiAlO catalyst and occupies active sites preferentially through forming sulfite and sulfate species.

For 5% MnNiAlO catalyst (Fig. 9(B)), introduction of  $\text{SO}_2/\text{O}_2$  resulted in the appearance of less sulfate species according to reducing the peak intensity of sulfate (at  $1156$  and  $1245\text{ cm}^{-1}$ ) compared with NiAlO sample. It is demonstrated significant decline of sulfate formation on 5% MnNiAlO sample. The results infer adding Mn could protect the active site of catalysts and improve resistance of catalysts towards  $\text{SO}_2$ . Herein, we think there are two reasons to explain this phenomenon. (i) Mn loading inhibits the formation of sulfate; (ii) the sulfate species formed on MnNiAlO present lower thermal stability and easier to be decomposed. Subsequently under  $\text{NO}/\text{O}_2$  atmosphere, the peaks intensities of  $1032$ ,  $1156$  and  $1245\text{ cm}^{-1}$  were increased obviously due to forming bidentate nitrate, chelating nitrite and monodentate nitrate, respectively, which differ from what occurs over NiAlO catalyst. This is clearly observed the adsorbed NO species were generated much greater over  $\text{SO}_2$ -poisoned MnNiAlO catalyst than over  $\text{SO}_2$ -poisoned NiAlO. Based upon these results, it can be indicated that Mn addition gives rise to minor formation of sulfate after exposure to  $\text{SO}_2$  and improves the resistance of catalyst towards  $\text{SO}_2$ . Moreover, the competitive adsorption phenomenon is dramatically inhibited over MnNiAlO samples due to their nitrite/nitrate species are more abundant and stable in comparison to NiAlO catalyst.

### 3.5. Regeneration of $\text{SO}_2$ -poisoned catalysts

**3.5.1. Thermal regeneration.** After pre-adsorption of  $\text{SO}_2$ , the catalysts were heated and regenerated at  $400\text{ }^\circ\text{C}$ . The infrared spectrum of the reaction of NiAlO and 5% MnNiAlO catalyst with  $\text{NO} + \text{O}_2$  and  $\text{C}_3\text{H}_6$  after thermal regeneration is

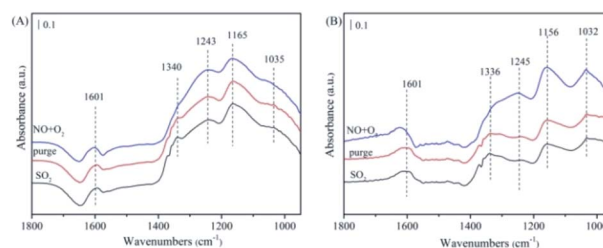


Fig. 9 The FTIR spectra of the catalysts with pre-adsorbed  $\text{SO}_2/\text{O}_2$  upon exposing in  $\text{NO}/\text{O}_2$ , followed by  $\text{C}_3\text{H}_6/\text{O}_2$  at  $200\text{ }^\circ\text{C}$ . (A) NiAlO; (B) 5% MnNiAlO.



shown in Fig. 10. In the term of NiAlO sample (Fig. 10(A)), the absorption peaks belonging to sulfates (1160 and 1341  $\text{cm}^{-1}$ ) decreased, while the absorption peaks belonging to sulfites (1032 and 1240  $\text{cm}^{-1}$ ) increased after regeneration, which proves that the method of thermal regeneration could not reduce the amount of sulfate adsorbed on the surface of the catalyst. This phenomenon may be due to the fact that thermal regeneration converts partially unstable adsorbed sulfate into  $\text{SO}_2$  at 400  $^\circ\text{C}$  and some  $\text{SO}_2$  is quickly activated to form a more thermally stable sulfate species adsorbed on the catalyst, resulting in more severe clogging. After introduction of  $\text{NO}/\text{O}_2$ , there is no absorption peak attributed to nitrate. After passing into  $\text{C}_3\text{H}_6$ , no change was observed in any peak. These results suggest that the thermal regeneration method could not regenerate the catalytic activity of NiAlO sample.

In the case of 5% MnNiAlO (Fig. 10(B)), the results were the same as those presented in the previous discussion. After thermal regeneration at 400  $^\circ\text{C}$ , the peaks of sulfite (1032  $\text{cm}^{-1}$ ) and some sulfates (1160  $\text{cm}^{-1}$ ) decreased, whereas that of sulfate at 1338  $\text{cm}^{-1}$  increased slightly. The result demonstrated that after high-temperature regeneration, the 5% MnNiAlO catalyst had fewer types of sulfate species and smaller quantities than the NiAlO catalyst. After passing  $\text{NO}/\text{O}_2$ , the absorption peaks at 1032 and 1156  $\text{cm}^{-1}$  were enhanced, which were attributed to the presence of bidentate nitrate species. In addition, the absorption peak at 1240  $\text{cm}^{-1}$  moved toward a low wavenumber because of the formation of a monodentate nitrate. After passing through  $\text{C}_3\text{H}_6$ , no change was observed in any peak. This proved that for the 5% MnNiAlO catalyst, thermal regeneration could partially restore the activation and adsorption capacity of  $\text{NO}$  but could not restore the reaction ability of  $\text{C}_3\text{H}_6$  with these produced nitrogen oxides.

**3.5.2. Water washing regeneration.** After pre-adsorption of  $\text{SO}_2$ , the catalysts were regenerated by water washing. The infrared spectrum of the reaction of NiAlO and 5% MnNiAlO catalyst with  $\text{NO} + \text{O}_2$  and  $\text{C}_3\text{H}_6$  after washing regeneration is shown in Fig. 11. For the NiAlO catalyst (Fig. 11(A)), after washing regeneration, the peaks of sulfite (1031  $\text{cm}^{-1}$ ) and sulfates (1168 and 1245  $\text{cm}^{-1}$ ) reduced, whereas that of sulfate at 1340  $\text{cm}^{-1}$  maintained stable. Moreover, a new absorption peak at 1425  $\text{cm}^{-1}$  is attributed to sulfate. This phenomenon may be due to the fact that during the washing process, part of the sulfate is washed away, whereas partially unstable adsorbed sulfate is converted into  $\text{SO}_2$  and then some  $\text{SO}_2$  is quickly

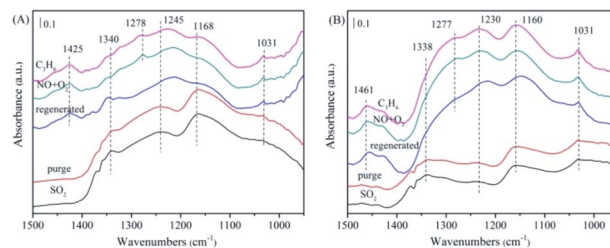


Fig. 11 The *in situ* FTIR spectra of the NiAlO and 5% MnNiAlO catalysts after washed regeneration reacting with  $\text{NO} + \text{O}_2$  and  $\text{C}_3\text{H}_6$  at 200  $^\circ\text{C}$ . (A) NiAlO; (B) 5% MnNiAlO.

activated to form a more thermally stable sulfate species adsorbed on the catalyst, resulting in more severe clogging. After the introduction of  $\text{NO}/\text{O}_2$ , the characteristic peak (at 1278  $\text{cm}^{-1}$ ) belonging to monodentate nitrates appeared, and after introduction of  $\text{C}_3\text{H}_6$ , the peak disappeared. It is shown that the method of washing regeneration can restore partial activity of catalyst.

For 5% MnNiAlO catalyst (Fig. 11(B)), the peaks of sulfite (1031  $\text{cm}^{-1}$ ) decreased, whereas that of sulfate at 1160  $\text{cm}^{-1}$  increased. In addition, 5% MnNiAlO catalyst had fewer types of sulfate species and smaller quantities. More important, the sulfate peak at 1338  $\text{cm}^{-1}$  disappeared. After injecting  $\text{NO}/\text{O}_2$ , it also appeared the characteristic peak at 1277  $\text{cm}^{-1}$ , attributing to monodentate nitrate. After introduction of  $\text{C}_3\text{H}_6$ , the monodentate nitrate disappeared. According to the results, the method of washing regeneration can expose more active sites so as to facilitate the progress of adsorption and activation of  $\text{SO}_2$ . It also can restore the ability of reaction between sulfate/sulfite and  $\text{C}_3\text{H}_6$  of all catalysts, showing remarkable recovery ability over the MnNiAlO catalyst.

### 3.6. Study on the poisoning mechanism of S

XPS spectra were employed to further characterize the surfaces. The XPS spectra of Mn 2p are illustrated in Fig. 12(A). After a peak fitting deconvolution, the Mn 2p XPS spectra could be separated into two peaks of  $\text{Mn}^{2+}$  (639.8 eV) and  $\text{Mn}^{4+}$  (645.5 eV).<sup>37</sup> From the results of XPS analysis, it is clearly to find that the quantity of  $\text{Mn}^{4+}$  in the S-poisoned catalyst was lower than that in the fresh catalyst. In contrast, in the regenerated catalyst, the  $\text{Mn}^{4+}$  peak intensity was greater. These results indicate that S poisoning resulted in a distinct decrease of surface  $\text{Mn}^{4+}$ . It is proposed that high  $\text{Mn}^{4+}$  concentration could promote the oxidation of  $\text{NO}$  to  $\text{NO}_2$ , while  $\text{SO}_2$  could be oxidized to  $\text{SO}_4^{2-}$  using the oxygen supplied by  $\text{Mn}^{4+}$  species, leading to the partial reduction of  $\text{Mn}^{4+}$ .<sup>38</sup>

The O 1s spectra (Fig. 12(B)) can be deconvoluted with two peaks, referred to as the surface chemisorbed oxygen  $\text{O}_A$  (532.0 eV), and lattice oxygen  $\text{O}_L$  (530.6 eV), respectively.<sup>39</sup> It is well known that  $\text{O}_A$  is much more active than  $\text{O}_L$  in oxidation reactions because of its higher mobility.<sup>40</sup> Liu *et al.*<sup>41</sup> showed that  $\text{O}_A$  was the most active oxygen species which were deciding to the oxidation of  $\text{NO}$ , then the SCR reaction was enhanced by “fast SCR” reaction. We compared the quantity of  $\text{O}_A$  *via* calculating

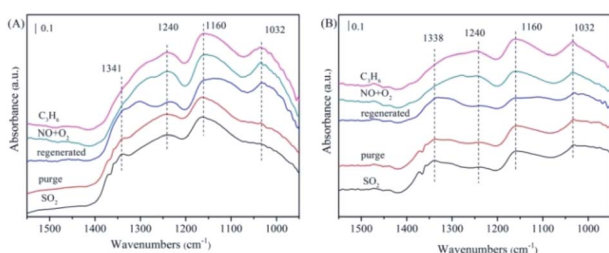


Fig. 10 The FTIR spectra of the NiAlO and 5% MnNiAlO catalysts after thermal regeneration at 200  $^\circ\text{C}$ . (A) NiAlO; (B) 5% MnNiAlO.





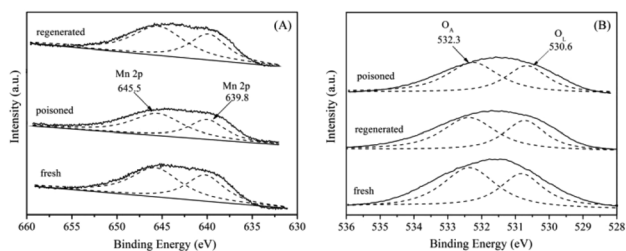


Fig. 12 XPS spectra of the fresh, S-poisoned and washing regenerated 5% MnNiAlO catalysts. (A) Mn XPS spectra; (B) O XPS spectra.

the ratio of peak area:  $O_A/(O_A + O_L)$ . It can be seen that the  $O_A/(O_A + O_L)$  ratio over  $SO_2$  poisoned sample (59.1%) was less than that of fresh sample (65.9%), because surface chemisorbed oxygen could be consumed by  $SO_2$ . Further, the ratio of  $O_A/(O_A + O_L)$  was recovered to 62.3% after washing regenerating, indicating that washing regeneration can restore partial surface chemisorbed oxygen of catalyst.

To further analysis the poisoning mechanism of the 5% MnNiAlO catalyst, we performed FTIR experiments on the fresh, S-poisoned and washing regenerated catalysts (Fig. 13). One peak appeared for the S-poisoned catalyst located at  $1129\text{ cm}^{-1}$ , which can be attributed to sulfate species. Importantly, there is an obvious decrease in the intensity of  $1129\text{ cm}^{-1}$  peak over the washing regenerated samples. The results indicate that most of sulfate species deposited on the S-poisoned catalyst could be removed by water washing.

To distinguish the acidity styles and acid sites of the catalysts, the Py-IR characterization was performed. As shown in Fig. 14(A), the bands attributed to pyridine adsorbed on Brønsted acid sites ( $1576\text{ cm}^{-1}$ ) and Lewis acid sites ( $1491$  and  $1604\text{ cm}^{-1}$ ) were detected. Another band ( $1448\text{ cm}^{-1}$ ) due to pyridine interacting with both Brønsted and Lewis acid sites was also observed.<sup>42,43</sup> Comparatively, the amount of Brønsted acid sites on fresh catalyst declined dramatically with  $SO_2$  poisoning treatment; whereas the amount of Lewis acid sites showed a slight increase.

This result implies that  $SO_2$  can increase the Lewis acid sites but decrease the Brønsted acid sites. Previous studies reported

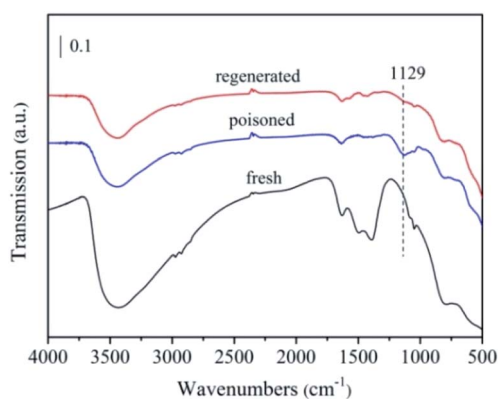


Fig. 13 FTIR spectra of the fresh, S-poisoned and washing regenerated 5% MnNiAlO catalysts.

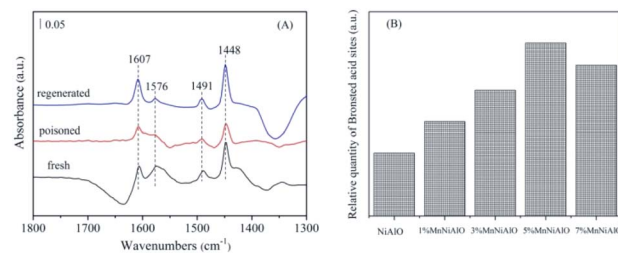


Fig. 14 (A) FTIR spectra of pyridine adsorption on 5% MnNiAlO catalysts. (B) Brønsted acid sites quantification of NiAlO and MnNiAlO catalysts.

that Brønsted acid sites are important SCR active sites for NO reduction.<sup>44</sup> The  $SO_2$ -poisoned sample exhibited relatively weak NO adsorption strength and NO reduction ability, which agreed with the results of the FTIR spectra (Fig. 11). In addition, the Brønsted acid sites could be recovered to almost the same level as the fresh catalyst after washing regenerating. Meanwhile, from the Brønsted acid sites quantification analysis (Fig. 14(B)), we can see that the amount of Brønsted acid sites over MnNiAlO catalysts were more abundant than that of NiAlO sample.

On the basis of the above studies, some possible reaction mechanisms for improved NO reduction in the absence and presence of  $SO_2$  are provided as follows. On one hand, the NiAlO catalyst shows relatively poor activity owing to the weak redox, oxygen storage/release ability and less surface Brønsted acid sites, which lead to insufficient accumulation of  $adNO_x$  and generation of  $C_xH_yO_z$  species during  $C_3H_6$ -SCR. In the case of MnNiAlO catalysts, Mn doping enhances the Brønsted acid sites and active oxygen groups, and improves the redox property by the redox cycle ( $Ni^{3+} + Mn^{2+} \leftrightarrow Ni^{2+} + Mn^{4+}$ ). Subsequently, the reaction intermediates and the reactivity between  $C_xH_yO_z$  species and nitrite/nitrate species are promoted, which contribute to excellent  $C_3H_6$ -SCR performance. On the other hand, in the presence of  $SO_2$ , for the NiAlO catalyst,  $SO_2$  strongly competes with NO to adsorb on the catalyst surface to form stable  $NiSO_4$  or  $Al_2(SO_4)_3$  compounds, which can impair the amount of active sites and decline the occurrence of  $C_3H_6$ -SCR reactions. After Mn addition, the  $SO_2$ -poisoned MnNiAlO catalysts generate much greater adsorbed NO species than over  $SO_2$ -poisoned NiAlO sample.  $SO_2$  reacts with Mn in the outer layer from the formation of  $MnSO_4$  which can protect the reaction active sites Ni–O–Al. It has been demonstrated that Mn addition gives rise to minor formation of sulfate after exposure to  $SO_2$  and improves the resistance of catalyst towards  $SO_2$ . Furthermore, the competitive adsorption phenomenon is dramatically inhibited over MnNiAlO samples due to their nitrite/nitrate species are more abundant and stable in comparison to NiAlO catalyst. As a result, the  $C_3H_6$ -SCR of NO in the presence of  $SO_2$  has been significantly improved.

## 4. Conclusions

The various manganese amounts loaded NiAl hydroxalite-like compounds were developed for selective catalytic reduction of NO with  $C_3H_6$ . Among them, 5% MnNiAlO catalyst exhibited





more than 95% and 88% NO<sub>x</sub> conversion in the presence and absence of SO<sub>2</sub>, respectively. The Mn doping enhances the Brønsted acid sites and surface active oxygen groups, and improves the redox property by the redox cycle (Ni<sup>3+</sup> + Mn<sup>2+</sup> ↔ Ni<sup>2+</sup> + Mn<sup>4+</sup>). *In situ* FTIR experiments showed that loading Mn on catalysts could improve the reaction intermediates and promote the reactivities between C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> species and nitrite/nitrate species, which contributes to excellent C<sub>3</sub>H<sub>6</sub>-SCR performance. In addition, in the presence of SO<sub>2</sub>, the XPS and FTIR results showed that sulfur species and nitrogen species were deposited on the catalyst surface, which made the catalyst poisoned. The MnNiAlO samples can give rise to minor formation of sulfate and inhibit the competitive adsorption effectively due to their nitrite/nitrate species are more abundant and stable. Finally, water washing method showed best performance on the regeneration of deactivated catalysts. The Brønsted acid sites could be recovered to almost the same level as the fresh catalyst after washing regenerating.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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## References

- S. X. Cai, J. Liu, K. Zha, H. Li, L. Shi and D. Zhang, *Nanoscale*, 2017, **9**, 5648–5657.
- T. Boningari and P. G. Smirniotis, *Chem. Eng.*, 2016, **13**, 133–141.
- X. Y. Li, G. Lu, Z. P. Qu, D. K. Zhang and S. M. Liu, *Appl. Catal., A*, 2011, **398**, 82–87.
- W. Yang, R. D. Zhang, B. H. Chen, D. Duprez and S. Royer, *Environ. Sci. Technol.*, 2012, **46**, 11280–11288.
- I. Sobczak, K. Musialska, H. Pawlowski and M. Ziolek, *Catal. Today*, 2011, **176**, 393–398.
- S. Putluru, L. Schill, A. Jensen, B. Siret, F. Tabaries and R. Fehrmann, *Appl. Catal., B*, 2015, **165**, 628–635.
- L. Fin, X. D. Wu and S. Liu, *Chem. Eng.*, 2013, **226**, 105–112.
- R. Jin, Y. Liu, Z. B. Wu, H. Q. Wang and T. T. Gu, *Chemosphere*, 2010, **78**, 1160–1166.
- Q. Li, M. Meng, H. Xian, N. Tsubaki, X. G. Li and Y. Xie, *Environ. Sci. Technol.*, 2010, **44**, 4747–4752.
- Z. L. Zhang, Y. Zhang, Q. Y. Su, Z. P. Wang, Q. Li and X. Y. Gao, *Environ. Sci. Technol.*, 2010, **44**, 8254–8258.
- L. Xue, H. He and C. Liu, *Environ. Sci. Technol.*, 2009, **43**, 890–895.
- X. Wu, R. N. Wang, Y. L. Du and X. J. Li, *New J. Chem.*, 2019, **43**, 2640–2648.
- L. F. Zhang, X. L. Zhang, S. S. Lv, X. P. Wu and P. M. Wang, *RSC Adv.*, 2015, **5**, 82952–82959.
- Z. B. Wu, R. B. Jin, H. Q. Wang and Y. Liu, *Catal. Commun.*, 2009, **10**, 935–939.
- Y. Peng, D. Wang, B. Li, C. Z. Wang, J. H. Li, J. Crittenden and J. M. Hao, *Environ. Sci. Technol.*, 2017, **51**, 11943–11949.
- Y. Peng, W. Z. Si, X. Li, J. Chen, J. H. Li, J. Crittenden and J. M. Hao, *Environ. Sci. Technol.*, 2016, **50**, 9576–9582.
- H. Zhou, Y. X. Su, W. Y. Deng and F. C. Zhong, *Environ. Sci. Technol.*, 2016, **39**, 93–100.
- Y. J. Kim, H. J. Kwon, I. S. Nam, J. W. Choung, J. K. Kil, H. J. Kim, M. S. Cha and G. K. Yeo, *Catal. Today*, 2010, **151**, 244–250.
- W. Tian, H. S. Yang, X. Y. Fan and X. B. Zhang, *J. Hazard. Mater.*, 2011, **188**, 105–109.
- S. C. Deng, T. T. Meng, B. L. Xu, F. Gao, Y. H. Ding, L. Yu and Y. N. Fan, *ACS Catal.*, 2016, **6**, 5807–5815.
- L. Zhao, X. Y. Li and J. Zhao, *Chem. Eng. J.*, 2013, **223**, 164–171.
- L. Chmielarz, P. Kustrowski, A. R. Lasocha and R. Dziembaj, *Thermochim. Acta*, 2002, **395**, 225–236.
- J. S. Valente, M. S. Cantu, J. G. H. Cortez, R. Montiel, X. Bokhimi and E. López-Salinas, *J. Phys. Chem. C*, 2007, **111**, 642–651.
- N. T. Nivangune and V. V. Ranade, *Catal. Lett.*, 2017, **147**, 2558–2569.
- A. C. Vieira, R. L. Moreira and A. Dias, *J. Phys. Chem. C*, 2009, **113**, 13358–13368.
- A. Djaidja, S. Libs and A. Kiennemann, *Catal. Today*, 2006, **113**, 194–200.
- K. Ramesh, L. Chen and F. Chen, *Catal. Today*, 2008, **131**, 477–482.
- Z. Q. Liu, J. H. Li, M. Buettner, R. V. Ranganathan, M. Uddi and R. Wang, *ACS Appl. Mater. Interfaces*, 2019, **11**, 17035–17049.
- L. Chen, J. H. Li and M. Ge, *Environ. Sci. Technol.*, 2010, **44**, 9590–9596.
- A. L. Goodman, E. T. Bernard and V. H. Grassian, *J. Phys. Chem. A*, 2001, **105**, 6443–6457.
- T. I. Halkides, D. I. Konaridis and X. E. Verykios, *Catal. Today*, 2002, **73**, 213–221.
- H. Zhou, Y. X. Su, W. Y. Liao and F. C. Zhong, *Fuel*, 2016, **182**, 352–360.
- A. L. Goodman, P. Li, C. R. Usher and V. H. Grassian, *J. Phys. Chem. A*, 2001, **105**, 6109–6120.
- Y. Liu, E. Lotero and J. G. Goodwin, *Appl. Catal., A*, 2007, **331**, 138–148.
- V. G. Milt, M. A. Ulla and E. E. Miro, *Appl. Catal., B*, 2005, **57**, 13–21.
- L. Zhao, J. Duan, S. W. Yang, X. Y. Li, Q. F. Liu and C. J. Martyniuk, *Sep. Purif. Technol.*, 2018, **207**, 231–239.
- C. Z. Sun, H. Liu, W. Chen, D. Z. Chen, S. H. Yu, A. N. Liu, L. Dong and S. Feng, *Chem. Eng. J.*, 2018, **347**, 27–40.
- C. Fang, D. Zhang, S. Cai, L. Zhang, L. Huang, H. Li, P. Maitarad, L. Shi, R. Gao and J. Zhang, *Nanoscale*, 2013, **5**, 9199–9207.



## Paper

- 39 K. J. Lee, P. A. Kumar, M. S. Maqbool, K. N. Rao, K. H. Song and H. P. Ha, *Appl. Catal., B*, 2013, **142–143**, 705–717.
- 40 S. Zhan, H. Zhang, Y. Zhang, Q. Shi, Y. Li and X. Li, *Appl. Catal., B*, 2017, **203**, 199–209.
- 41 F. Liu, H. He and Y. Ding, *Appl. Catal., B*, 2009, **93**, 194–204.
- 42 N. Jagtap, S. B. Umbarkar and P. Miquel, *Appl. Catal., B*, 2009, **90**, 416–425.
- 43 D. Yuan, X. Y. Li, Q. D. Zhao, J. J. Zhao and S. M. Liu, *Appl. Catal., A*, 2013, **451**, 176–183.
- 44 L. Kang, L. P. Han, J. B. He, H. R. Li, T. T. Yan, G. R. Chen, J. P. Zhang, L. Y. Shi and D. S. Zhang, *Environ. Sci. Technol.*, 2019, **53**, 938–945.

