Mn$_2$NiO$_4$ spinel catalyst for high-efficiency selective catalytic reduction of nitrogen oxides with good resistance to H$_2$O and SO$_2$ at low temperature

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Abstract

Mn–Ni oxides with different compositions were prepared using standard co-precipitation (CP) and urea hydrolysis-precipitation (UH) methods and optimized for the selective catalytic reduction of nitrogen oxides (NO$_x$) by NH$_3$ at low temperature. Mn$_{2+}$Ni$_{1-}$O$_x$-CP and Mn$_{2+}$Ni$_{1-}$O$_x$-UH (with Mn:Ni molar ratio of 2:1) catalysts showed almost identical selective catalytic reduction (SCR) catalytic activity, with about 96% NO$_x$ conversion at 75°C and ~99% in the temperature range from 100 to 250°C. X-ray diffraction (XRD) results showed that Mn$_{2+}$Ni$_{1-}$O$_x$-CP and Mn$_{2+}$Ni$_{1-}$O$_x$-UH catalysts crystallized in the form of Mn$_2$NiO$_4$ and MnO$_2$ respectively. The latter gave relatively good selectivity to N$_2$, which might be due to the presence of the MnO$_2$ phase and high metal–O binding energy, resulting in low dehydrogenation ability. According to the results of various characterization methods, it was found that a high density of surface chemisorbed oxygen species and efficient electron transfer between Mn and Ni in the crystal structure of Mn$_2$NiO$_4$ played important roles in the high-efficiency SCR activity of these catalysts. Mn$_{2+}$Ni$_{1-}$O$_x$ catalysts presented good resistance to H$_2$O or/and SO$_2$ with stable activity, which benefited from the Mn$_2$NiO$_4$ spinel structure and Eley-Rideal mechanism, with only slight effects from SO$_2$.

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Introduction

Selective catalytic reduction (SCR) by ammonia is the most efficient technique for eliminating nitrogen oxides (NO$_x$, which includes NO and NO$_2$) from coal-fired industrial thermal power sources. In the past decades, vanadium-based catalysts have been widely adopted in SCR reactors operating in the temperature range of 300–400°C (Chen et al., 2018; Lai and Wachs, 2018; Yan et al., 2018). Recently, in China, there has been an urgent demand for the abatement of NO$_x$ from low-temperature (100–280°C) flue gases in steel, cement, glass and other industries, resulting in a high level of research on the investigation and development of efficient and stable SCR
catalysts capable of operating at low temperature (<280°C) (Gao et al., 2017a, 2017b).

Mn-based catalysts, including multi-component oxides (doped with Ce (Wei et al., 2017; Yao et al., 2017), Fe (Zhan et al., 2014; Wang et al., 2016), Co (Zhang et al., 2014a; Tang et al., 2018), W (Ma et al., 2015), Sn (Chang et al., 2012), Cr (Gao et al., 2017a, 2017b), etc.), novel supports (Duan et al., 2018; Liu et al., 2017, 2014) and special structural assemblies of special crystals or/and morphologies (such as nanocage (Zhang et al., 2014a), core-shell (Liu et al., 2015; Zhang et al., 2017), Mn/Co metal organic frameworks (MOF-74) (Jiang et al., 2016), 3-dimensional flower-like NiMnFe (Li et al., 2012), etc.), as we reviewed (Gao et al., 2017b), have been investigated in order to improve the H2O and SO2 resistance and N2-selectivity at low temperature. These catalysts show relatively high SCR activity and improve the resistance to H2O or/and SO2 because of the pre-sulfating of dopants to protect MnOx. In our research work (Gao et al., 2017a), Co/Ni modified MnOx-CeO2 catalysts were found to present higher SCR performance than unmodified MnOx-CeO2 catalysts due to the higher Brunner-Emmet-Teller (BET) surface, greater amount of chemisorbed oxygen, and more active sites. We further found that the Co and Ni elements were effective in delaying the SO2 poisoning, while the catalysts would still be deactivated after the postponement. In spite of this, the design of Co/Ni doped Mn-based catalysts with special crystal morphologies (core-shell (Liu et al., 2015), microsheet (Li et al., 2016), spinel crystal (Qiu et al., 2015; Meng et al., 2018), etc.) rather than simple mixed components is an attractive option to overcome such poisoning.

Thus, in this study, we continued to investigate Ni-modified MnOx catalysts with the spinel structure to obtain high-efficiency SCR activity and improve the hydrogen-sulfide-precipitation (H2S-P) method. Various characterization methods such as X-ray diffraction (XRD), inductively coupled plasma (ICP), BET and X-ray photoelectron spectroscopy (XPS) were utilized to analyze the chemical and physical properties to help understand the essential reasons for the efficient SCR activity at low temperature. The adsorption behaviors of NH3 and NOx + O2 were studied using diffuse reflectance infrared transform spectroscopy (DRIFTS) to analyze the SCR reaction mechanism, and the influence of SO2 on the surface of the Mn–Ni spinel catalyst on the reaction pathways was also investigated.

1. Materials and methods

1.1. Catalyst preparation

All reagents were of analytical grade and used without further purification. Mn(CH3COO)2 · 4H2O (≥99.0%), Ni(NO3)2 · 6H2O, and (NH4)2CO3 (≥40.0%, in NH4) were purchased from Sinopharm (Beijing, China). Urea (CO[NH2]2, ≥99.0%) was purchased from Beijing Chemical Works (Beijing, China). The deionized water was made by an ultrapure water manufacturing system (UPT, Sichuan Ulupure Co., Ltd, China). Ni-MnOx catalysts prepared by a standard co-precipitation (CP) method were denoted as Mn(Ni)yNiOz−CP (T/t), where ‘y’ and ‘z’ represent the molar ratio of Mn and Ni, and ‘T’ and ‘t’ represent the calcination temperature and time, respectively. In a typical process, the molar ratio of (NH4)2CO3 (solution A: 0.5 mol/L) to total metal cations (solution B: 0.5 mol/L, Mn/ Ni = y/z) for complete precipitation was set at 1.0. Solution A was dipped into Solution B under magnetic stirring at 1000 r/min. The solution mixture was stirred for 2 hr and aged for 3 hr at room temperature, then filtered and washed to pH ≈ 7 with deionized water. The obtained samples were dried at 120°C for 12 hr and calcined in air at the designed temperature for 6 hr. Finally, the powders were pressed and sieved to 20–40 mesh for testing.

For comparison purposes, Ni-MnOx catalysts were prepared by the urea hydrolysis-precipitation (UH) method and denoted as Mn(Ni)yNiOz−UH (urea/M, T/t), where ‘urea/M’ represents the molar ratio of urea to total cations, and ‘T’ and ‘t’ represent the hydrolysis temperature and time, respectively. The details are shown in Appendix A. Supplementary data.

1.2. Catalytic activity tests

The NH3-SCR tests were carried out in a fixed-bed quartz reactor (inner diameter 7 mm) with the following conditions: [NO] = [NH3] = 500 ppmV, [O2] = 5 vol.%, [H2O] = 8 vol.% (when used), [SO2] = 150 ppmV SO2 (when used), balanced by N2 with gas flows of 100 mL/min, and Gaseous hourly space velocity (GHSV) of 10 000 hr−1. For comparison purposes, Ni-MnOx catalysts were prepared by the urea hydrolysis-precipitation (UH) method and denoted as Mn(Ni)yNiOz−UH (urea/M, T/t), where ‘urea/M’ represents the molar ratio of urea to total cations, and ‘T’ and ‘t’ represent the hydrolysis temperature and time, respectively. The details are shown in Appendix A. Supplementary data.

1.3. Catalyst characterization

X-ray diffraction (XRD) patterns were recorded on a system (D8 ADVANCE, Bruker, Germany) with Cu Kα radiation (40 kV and 40 mA) scanning from 10 to 90° at 6°/min. N2 adsorption and desorption isotherms were obtained with an analyzer (ASAP 2020, Micromeritics, USA) at 77 K after pretreating at 400°C for 3 hr. X-ray photoelectron spectra (XPS) were carried out on a system (ESCALAB 250Xi, Thermo, USA) with Al Kα radiation, and the spectra were calibrated against the C1s peak at 284.6 eV.

The in situ DRIFTS were acquired on a spectrometer (IS50, Thermo, USA) equipped with a detector (MCT/A, Thermo, USA) cooled by liquid nitrogen and an in situ DRIFT reaction cell with ZnSe windows. Prior to each experiment, the sample was pretreated at 400°C for 1 hr with N2. Reaction conditions were set as follows: 500 ppmV NO, 500 ppmV NH3, 5 vol.% O2, 400°C.
2. Results and discussion

2.1. NH3-SCR performance of various Mn(2)Ni(O)Ox catalysts

Fig. 1a shows the NOx conversion in NH3-SCR reaction over various Ni-MnOx-CP catalysts with different molar ratios of Mn/Ni under a GHSV of 32,000 hr⁻¹. At the calcination temperature of 450°C, the Mn(2)Ni(O)Ox-CP and Mn(2)Ni(O)Ox-CP catalysts obtained the highest SCR activities in a wide operating temperature window, with about 96% NOx conversion at 75°C and ~99% in the temperature range from 100 to 250°C. The pure MnO2 catalyst showed 92% NOx conversion at 100°C and presented a maximum NOx conversion of nearly 100% from 125°C on up. With the increase of Ni content, the SCR activity at temperatures below 150°C decreased markedly. The Mn(2)Ni(O)Ox-CP and Mn(2)Ni(O)Ox-CP catalysts achieved NOx conversion of approximately 99% and 97% at 150 and 175°C, respectively. The pure NiO catalyst showed an equilibrium NOx conversion of ~66% from 150 to 250°C. Fig. 1b gives the N2 selectivity over the corresponding catalysts in the SCR reaction. Pure MnO2 and NiO catalysts showed poor selectivity to N2, while Ni-modified MnO2 catalysts had improved selectivity, especially for the Mn(2)Ni(O)Ox-CP and Mn(2)Ni(O)Ox-CP catalysts. Nevertheless, the selectivity to N2 needed further improvement. Overall, the molar ratio of Mn/Ni was set as 2 (Mn:Ni = 2:1), and the optimized calcination temperature was 450°C (as shown in Appendix A Fig. S1).

To identify the phases in the Ni-MnOx-CP catalysts calcined at 450°C, XRD measurements were performed, as shown in Fig. 2. The pure MnO2 and NiO catalysts presented the phases Mn3O4 (JCPDS 24-0734) and NiO (JCPDS 01-1239), respectively. The Mn(2)Ni(O)Ox-CP catalyst exhibited diffraction peaks at 30.1, 35.5, 43.3, 57.2, 62.7 and 74.0°, which are in good agreement with the phase of Mn3NiO4 (JCPDS 74-1865, space group Fd-3m), corresponding to the lattice planes of (220), (311), (400), (511), (440) and (533), respectively. For the Mn(2)Ni(O)Ox-CP catalyst, the pattern exhibited peaks corresponding to the phases Mn3NiO4, NiO and Mn2NiO4. With further increase in the Ni content, the Mn(2)Ni(O)Ox-CP catalyst presented the main peak of NiO, with some Mn3NiO4. These results suggested that the decreased amount of active compounds and excessive non-active NiO may be one reason for the decrease of SCR activity over the nickel-enriched catalysts as the Ni content increased, which can be verified by the ICP results showing that the mass content of Mn was 483.5 mg/g in Mn(2)Ni(O)Ox-CP, 359.5 mg/g in Mn(2)Ni(O)Ox-CP and 245.3 mg/g in Mn(2)Ni(O)Ox-CP, while the combined (Mn + Ni) mass contents were 75.1, 74.2 and 76.2 wt.% for the above three catalysts, respectively. Meanwhile, the Mn3NiO4 phase, which has a typical spinel structure, may be a beneficial structure for good SCR activity.

In this study, we also prepared the Mn(2)Ni(O)Ox-CP catalyst by a urea hydrolysis-precipitation (UH) method to conduct a comparative study with the Mn(2)Ni(O)Ox-CP catalyst. As shown in Appendix A Fig. S2, it was found that the optimized preparation parameters for good SCR performance (activity and selectivity) of Mn(2)Ni(O)Ox-CP were value 3 for the molar ratio of urea to total cations (Urea/M, M for metal), and 130°C and 24 hr for the hydrolysis temperature and time, respectively. Comparisons of the NOx conversion and N2 selectivity over the MnO2-CP, Mn(2)Ni(O)Ox-CP and Mn(2)Ni(O)Ox-CP catalysts are shown in Fig. 3. It can be seen that the SCR activity of Mn(2)Ni(O)Ox-CP was slightly better than that of Mn(2)Ni(O)Ox-CP, and much better than the MnO2-CP catalyst. Nevertheless, the three catalysts all showed approximately 98% NOx conversion from 125 to 250°C. In addition, Mn(2)Ni(O)Ox-CP had better N2 selectivity than the MnO2-CP catalyst, with similar...
near-linear dependence on temperature, declining to 48% at 250 °C from 96.3% at 50 °C. It is noteworthy that the Mn(2)Ni(1)-Ox-UH catalyst obtained the best selectivity to N2, which was 100% below 100 °C and near-linear decline to 81.5% at 250 °C.

2.2. Crystal structure and pore parameters

Fig. 4 shows the XRD patterns of MnOx-CP, Mn(2)Ni(1)Ox-CP and Mn(2)Ni(1)Ox-UH catalysts. The pure MnOx catalyst prepared by the co-precipitation method presented the pattern of Mn3O4 (JCPDS 24-0734). The Mn(2)Ni(1)Ox-CP catalyst exhibited diffraction peaks at 30.1, 35.5, 43.3, 57.2, 62.7 and 74.0 °C, which are in good agreement with the phase of Mn2NiO4 (JCPDS 74-1865, space group Fd-3m), corresponding to the lattice planes of (220), (311), (400), (511), (440) and (533), respectively. The Mn(2)Ni(1)Ox-UH catalyst displayed diffraction peaks at 37.3, 43.3 and 63.2 °C. The strongest peak at 37.3 °C was characteristic of MnO2 (101), and the latter two peaks corresponded to spinel structure Mn2NiO4. The strongest peak at 35.5 °C corresponding to Mn3NiO4 (JCPDS 74-1865) was not observed for the Mn2NiOx-UH catalyst, which might be due to the lack of exposure of the (311) face in the mixture of MnO2 and Mn2NiO4 spinel. To further determine the crystal structure, ICP and XPS measurements were performed. The results showed that the Mn/Ni ratio of the Mn(2)Ni(1)Ox-CP catalyst was about 1.9, which was very close to 2. For the Mn(2)Ni(1)Ox-UH sample, the Mn/Ni ratio was slightly higher than 2, indicating the existence of other Mn-containing phases. Based on the above analysis, we believe that the Mn(2)Ni(1)Ox-CP and Mn(2)Ni(1)Ox-UH catalysts can be defined as Mn2NiO4 and MnO2-Mn2NiO4 spinel.

The data for specific surface area, pore volume and average pore size are listed in Table 1. It is evident that the Mn(2)Ni(1)-Ox-UH catalyst had a larger BET surface area and greater pore volume than the Mn(2)Ni(1)Ox-CP or MnOx-CP catalysts. The high surface area could generally contribute to the adsorption of NH3 and NOx, resulting in high activity (Boxiong et al., 2014). However, the SCR activity of the Mn(2)Ni(1)Ox-UH catalyst was inferior to that of Mn(2)Ni(1)Ox-CP while superior to the MnOx catalyst. In conclusion, it is suggested that the apparent surface area of Mn(2)Ni(1)Ox catalysts is related to the activity to some extent, but is not a crucial influencing factor (Liu et al., 2014).

2.3. XPS analysis

XPS measurements of the O 1s, Mn 2p and Ni 2p spectra of MnOx-CP, Mn(2)Ni(1)Ox-CP and Mn(2)Ni(1)Ox-UH catalysts were conducted to obtain the surface chemical states and understand the interaction between Mn and Ni. As shown in Fig. 5a, according to our previous studies (Gao et al., 2017a, 2018; Tang et al., 2015), the two peaks in the O 1s spectrum can be divided into lattice oxygen (denoted as O\textsubscript{L}, such as O\textsuperscript{2-}) at 529.2–530.2 eV and chemisorbed oxygen (denoted as O\textsubscript{C}, such as O\textsuperscript{2-}, O\textsuperscript{-}, OH\textsuperscript{-}, etc.) at a higher binding energy of around 531.3–532.2 eV. It has been reported that surface chemisorbed oxygens (O\textsubscript{C}) are the most active oxygen species and play an indispensable role in SCR catalysis (Koebel et al., 2002; Long...
et al., 2002; Qi et al., 2017). However, the SCR activity results showed that Mn2NiO4-CP had better activity than Mn2NiO4-CP, Ni2O3-UH and Mn3O4-CP, although the O2 ratio of Mn2NiO4-CP (33.9%) was higher than that of the Mn2NiO4-CP (29.1%) and MnO2-CP (25.8%) catalysts. Thus, we proposed that while high O2 content is beneficial to the SCR reaction, the SCR activity and chemisorbed oxygen do not follow an absolutely linear relationship (Liu and He, 2010b). In our previous study (Gao et al., 2019, 2018), we found that Mn–O binding energies of manganese oxides play an important role in the SCR reaction, and that the active oxygen species of manganese oxides with lower Mn–O binding energy facilitate the cleavage of more N–H bonds in the NH3 molecule to form more adsorbed nitrogen atom species, which leads to greater amounts of the more highly oxidized product (N2O).

As shown in Fig. 5b, the binding energies of Mn 2p1/2 and Mn 2p3/2 were centered at ~653.5 and ~642.0 eV. To analyze the valence states, the spectrum of Mn 2p3/2 was split into three peaks at 641.2, 642.4 and 644.0 eV, which were attributed to Mn2+, Mn3+ and Mn4+, respectively (Zhang et al., 2014a, 2013). It can be observed that the Mn3+ contents for the three catalysts were higher than 50%, and the total concentrations of Mn3+ and Mn4+ increased while that of Mn2+ decreased. As we all know, Mn2+ and Mn4+ are regarded as active sites for the adsorption and activation of species during the SCR reaction, with the redox couples of Mn3+ → Mn2+ and Mn2+ → Mn4+ (Cai et al., 2014; Chang et al., 2013). Thus, the high ratio of Mn2+ could enhance the ability of Mn species to transform between various valence states, promoting the catalytic cycles and the performance. Further, the spectra for Ni 2p over Mn2NiO4-CP and Mn2NiO4-UH catalysts are presented in Fig. 5c, which were fitted into Ni2+ at 854.8 eV, Ni3+ at 856.1 eV and a shake-up satellite peak at 861.5 eV (Wan et al., 2014; Gao et al., 2018). It is evident that Mn2NiO4-CP had a Ni3+/Ni2+ ratio of 1.67, which was higher than that of Mn2NiO4-UH, with 1.03. It is generally recognized that a greater number of Ni3+ species is beneficial for the redox properties and plays a critical role in the enhancement of catalytic activity (Gao et al., 2018). Wan et al. (2014) reported that a strong Mn–Ni interaction expressed as Ni3+ + Mn2+ ↔ Ni2+ + Mn4+ could play a synergistic role in the reducibility of the catalysts, leading to the enhancement of the catalytic cycle during the SCR reaction. Thus, it is clear that there are electronic interactions between Mn and Ni in the SCR reaction over Mn2NiO4-CP and Mn2NiO4-UH catalysts. The electronic transfer is closely related to the activation of NO and NH3 during the SCR process. Furthermore, in-situ DRIFTS experiments were performed to elucidate the SCR mechanism over the MnO2, Mn2NiO4 spinel catalysts in the following study.

### 2.4. In-situ DRIFTS for SCR reaction pathways

The above results showed that Mn2NiO4-CP contained a relatively pure phase of Mn2NiO4 spinel compared to the Mn2NiO4-UH catalyst; thus, in this section, Mn2NiO4-CP and MnO2-CP catalysts were selected to investigate the SCR reaction pathways over Mn2NiO4 and Mn2NiO4 spinel catalysts.

Fig. 6a and b shows the DRIFTS for the adsorption of NH3 and NO + O2 performed at the temperature of 175 °C over MnO2 and Mn2NiO4 spinel catalysts, respectively. In Fig. 6a, prominent peaks at 3306, 3138, 2228, 1146, 1033 cm⁻¹, and weak peaks at 966 and 931 cm⁻¹ were observed over the Mn2NiO4 spinel catalyst. According to the reports, the peaks at 3306, 3138, 1228 and 1146 cm⁻¹ can be ascribed to the N–H stretching vibration modes of coordinated NH3 linked to Lewis sites (Chen et al., 2014; Liu et al., 2012), while the peak at 3034 cm⁻¹ was due to NH3 species adsorbed onto Brønsted sites (Liu and He, 2010a). The peak at 1033 cm⁻¹ was attributed to bidentate nitrate, which might be a product of the oxidation of adsorbed NH3 species (Meng et al., 2015). For the Mn2NiO4 spinel catalyst, the adsorbed-NH3 species consisted of NH4+ species on Lewis sites (3036, 3199, 3138, 1601 and 1212 cm⁻¹), NH2+ species at 1317 cm⁻¹ might be attributed to monodentate nitro species (M–NO3) from the oxidation/decomposition of adsorbed ammonia species (Yang et al., 2011). The adsorption spectra of NO + O2 presented in Fig. 6b shows that the main adsorbed-NOx species was monodentate nitro at 1371 cm⁻¹ on both MnO2 and NiMn2O4 spinel catalysts (Zhou et al., 2011), while a strong peak for −NO3 species at 1317 cm⁻¹ (Lin et al., 2010; Zhang et al., 2014b; Meng et al., 2015) and weak peak for −N2O4 species at 1756 cm⁻¹ (Zhou et al., 2011) were also observed over the NiMn2O4 spinel catalyst.

Fig. 7a and b shows the alternant and transient adsorption behaviors between NO + O2 with pre-adsorbed NH3 over

<table>
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<tr>
<th>Table 1</th>
<th>Pore structure results of MnO2-CP, Mn2NiO4-CP and Mn2NiO4-UH catalysts.</th>
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<td>Catalysts</td>
<td>Brunner-Emmet-Teller (BET) specific surface area (m²/g)</td>
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<td>MnO2-CP</td>
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</tr>
<tr>
<td>Mn2NiO4-CP</td>
<td>53.9</td>
</tr>
<tr>
<td>Mn2NiO4-UH</td>
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a Mn:Ni molar ratio obtained by inductively coupled plasma (ICP). b Mn:Ni molar ratio obtained by X-ray photoelectron spectroscopy (XPS).
Mn$_3$O$_4$ and Mn$_2$NiO$_4$ spinel catalysts process, respectively. As shown in Fig. 7a, the pre-adsorbed coordinated NH$_x$ species on Lewis sites (3306, 3138, 1601, 1228 and 1146 cm$^{-1}$) declined significantly within 1 min after the introduction of NO$^+$O$_2$ and the peak for NO$_2$ species continued to increase over the Mn$_3$O$_4$ catalyst. This result indicated that all the coordinated NH$_x$ species gave good reactivity for the SCR reaction. Similarly, in Fig. 7b, coordinated NH$_x$ on Lewis sites, NH$_4^+$ on Brønsted sites and weakly adsorbed NH$_3$ species exhibited rapid reactivity on the surface of the Mn$_2$NiO$_4$ spinel catalyst. Fig. 7c and d shows the adsorption and reaction between NH$_3$ with pre-adsorbed NO$^+$O$_2$ over Mn$_3$O$_4$ and Mn$_2$NiO$_4$ spinel catalysts, respectively. As shown in Fig. 7a, the pre-adsorbed coordinated NH$_x$ species on Lewis sites (3306, 3138, 1601, 1228 and 1146 cm$^{-1}$) declined significantly within 1 min after the introduction of NO$^+$O$_2$ and the peak for NO$_2$ species continued to increase over the Mn$_3$O$_4$ catalyst. This result indicated that all the coordinated NH$_x$ species gave good reactivity for the SCR reaction. Similarly, in Fig. 7b, coordinated NH$_4^+$ on Lewis sites, NH$_4^+$ on Brønsted sites and weakly adsorbed NH$_3$ species exhibited rapid reactivity on the surface of the Mn$_2$NiO$_4$ spinel catalyst. 

Fig. 5 – X-ray photoelectron spectroscopy (XPS) spectra of (a) O 1s, (b) Mn 2p and (c) Ni 2p for MnO$_x$-CP, Mn$_{20}$Ni$_{10}$O$_x$-CP and Mn$_{20}$Ni$_{10}$O$_x$-UH. O$_\text{c}$: chemisorbed oxygen; O$_\text{l}$: lattice oxygen; Sat.: satellite peak.

Fig. 6 – Diffused Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) spectra of (a) NH$_3$ and (b) NO$^+$O$_2$ adsorption behaviors taken at 175°C over Mn$_3$O$_4$ and Mn$_2$NiO$_4$ catalysts.
−NO3 species at 1317 cm−1 over Mn2NiO4 spinel showed a small decrease but did not disappear, illustrating that these nitrate species may have only a certain reactivity, but their activation capacity was limited, possibly due to their slow activation rate or the poor adsorption capacity of the adjacent sites for NH3 adsorption, which was not sufficient to supply the reaction.

Thus, it can be concluded that the SCR reactions of NO with NH3 over Mn2O4 and Mn2NiO4 spinel catalysts mainly follow the typical Eley-Rideal mechanism while the Langmuir-Hinshelwood (L-H) mechanism could be ignored, which was consistent with the behavior of CrMn2O4 (Gao et al., 2019) spinel and Ni/Co-MnOx catalysts reported in our latest research, as presented in the following Eqs. (3)–(8) (Jiang et al., 2013; Yang et al., 2016, 2011).

\[ \text{NH}_3^\text{(gas)} + NO^\text{(gas)} \rightarrow \text{NH}_2\text{NO}^\text{(ads)} + \text{H}_2\text{O} \]  \hspace{1cm} (6)
\[ \text{NO}^\text{(gas)} + [\text{O}] \rightarrow -\text{NO}_2^\text{(ads)} \]  \hspace{1cm} (7)
\[ \text{NH}_3^\text{(gas)} + M - O - H \xrightarrow{\text{B sites}} M - O + \text{NH}_2^+ \]  \hspace{1cm} (8)

where \([\text{O}]\) is the reactive oxygen, \(M-\text{OH}\) is the metal bonded hydroxyl, \(M-O\) is the metal bonded oxygen, B sites are the Brønsted acid sites, \(-\text{NO}_2^\text{(ads)}\) is the adsorbed nitro species, and the subscripts (ads) and (gas) refer to the adsorption and gaseous state, respectively.

### 2.5. H2O and SO2 resistance and influencing behaviors

SO2 resistance tests were performed during the SCR reaction over Mn3O4-CP and Mn2NiO4-CP spinel catalysts, as shown in Fig. 8. MnOx gave poor activity, with a sustained loss to below 40% within 1 hr in the presence of 150 ppmV SO2, both at 125 and 175°C. The Mn2NiO4-CP spinel catalyst presented steady NOx conversion of about 58% and 79% within 6 hr after the introduction of SO2 at 125 and 175°C, respectively. This result indicated that the modification of the MnOx catalyst with Ni.

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**Fig. 7** – In-situ DRIFT spectra of (a, b) NO + O2 introduced to pre-adsorbed NH3 and (c, d) NH3 introduced to pre-adsorbed NO + O2 over Mn3O4 and Mn2NiO4 catalysts at 175°C.
has an extremely significant enhancement effect on the SO2 resistance, which was evidenced in our previous research (Gao et al., 2017a, 2018). What must be remembered is that, in the mixed oxides of MnO and NiO, Ni is effective in delaying the SO2 poisoning but the catalyst is still deactivated after the postponement. We proposed that a good approach to overcoming the SO2 poisoning problem is to design Co/Ni doped Mn-based catalysts with special crystal structures (Gao et al., 2018). In this study, the Mn(2)Ni(1)O4-CP catalyst exhibited sustained resistance to SO2, which might have largely been due to the special spinel structure, which was similar to the results of our latest study on CrMn2O4 spinel for SCR (Gao et al., 2019).

Fig. 8 compares the resistance to H2O or/and SO2 of Mn3O4-CP and Mn2NiO4-CP at 125 and 175 °C. Reaction conditions: [NO] = [NH3] = 500 ppmV, [O2] = 5 vol.%, [SO2] = 150 ppmV, N2 balance, GHSV 32,000 hr⁻¹.

Fig. 9 compares the resistance to H2O or/and SO2 of Mn(2)Ni(1)O4-CP and Mn(2)Ni(1)O4-UH catalysts at the test temperature of 175°C over an 11 hr period. Mn(2)Ni(1)O4-CP showed stable activity with 83% NOx conversion for 8 vol.% H2O, and stable activity with 82% conversion in 150 ppmV SO2 (the repeated test is comparable to the data in Fig. 8b), and 75% NOx conversion with co-existing 8 vol.% H2O and 150 ppmV SO2.

The XRD results in Fig. 4 gave evidence that the Mn(2)Ni(1)O4-CP and Mn(2)Ni(1)O4-UH catalysts contained the phases Mn3NiO4 spinel and mixed MnO2−Mn2NiO4. Thus, it was not difficult to understand why the Mn(2)Ni(1)O4-UH catalyst exhibited...
relatively weaker resistance toward H₂O, SO₂, and H₂O + SO₂ than MnₓNiₓO₄-CP. These results provided further evidence that the crystal structure of MnₓNiₓO₄ spinel plays a very important role in the resistance of the catalyst to H₂O or/and SO₂, which provides a potential strategy for the synthesis of novel Mn-based SCR catalysts with good poisoning resistance and stability.

In our previous study (Gao et al., 2017a), we found that the adsorption of monodentate nitrite (-NO₂) species was significantly inhibited by SO₂. However, MnₓNiₓO₄ spinel showed almost no reaction activity between the adsorbed NOx-species and ammonia (according to the DRIFTS experiments in Fig. 7c and d), while giving obvious SCR activity mainly obeying the Eley-Rideal mechanism. Although the majority of adsorbed NH₃ species were in the form of monodentate nitrite, the influence of SO₂ could be ignored on the surface of the MnₓNiₓO₄ spinel catalyst. Thus, the effect of SO₂ on the adsorption behavior of NH₃ on MnₓNiₓO₄ spinel was investigated via DRIFT spectra, as shown in Fig. 10. The spectrum was obtained 30 min after the introduction of the corresponding atmosphere.

In the spectra in Fig. 10a, the adsorbed species of SO₂/O₂ were assigned to the S=O and S–O vibrations of the surface or bulk sulfate species at 1196, 1131, 1050 and 976 cm⁻¹ (Abdelhamid et al., 2006; Gao et al., 2019; Jin et al., 2010). In Fig. 10b, it can be observed that there was no significant weakening of the main adsorbed NH₃ species on MnₓNiₓO₄ spinel under the coexistence of NH₃ + SO₂ + O₂. It should be noted that the peaks at 1371 cm⁻¹ for monodentate nitrite and at 1212 cm⁻¹ for the coordinated NH₃ species were almost completely shifted to higher wavenumbers. This might be due to interference by adsorbed SO₂, such that the adsorbed SOₓ species donated electrons to the adsorption sites, increasing the electron-withdrawing properties of the sites and resulting in electron transitions and blue-shifting of bonding states (Vélez et al., 2017). It should be pointed out that SO₂ had a more limited impact on the adsorption of NH₃, and even the peaks for coordinated NH₃ species at 1212/1228 cm⁻¹ and gas-phase or weakly adsorbed NH₃ species (966 and 931 cm⁻¹) were enhanced to a certain extent. These results indicated that the Eley-Rideal mechanism (reaction pathways between the adsorbed NH₃-species and gaseous NO) was only slightly affected by SO₂, which was an important reason for the good SO₂ resistance of the MnₓNiₓO₄ spinel catalyst.

3. Conclusions

In this study, a series of Ni-MnOₓ catalysts was prepared by standard co–precipitation (CP) and urea hydrolysis–precipitation (UH) methods for comparative studies on the selective catalytic reduction of NOₓ by NH₃ at low temperature (50–250°C). The MnₓNiₓOₓ-CP (Mn:Ni as 2:1, calcined at 450°C for 6 hr) catalyst was optimized for SCR, with about 96% NOₓ conversion at 75°C and ~99% in the temperature range from 100 to 250°C, while the selectivity to N₂ needed further improvement. The optimized MnₓNiₓOₓ-CP catalyst was optimized for SCR activity to that of MnₓNiₓOₓ-CP in the whole test temperature range, and obtained the best selectivity to N₂, with about 100% below 100°C and a near-linear decline to 81.5% at 250°C. The XRD results showed that MnₓNiₓOₓ-CP and MnₓNiₓOₓ-UH catalysts could be defined as MnₓNiₓO₄ and MnO₂–MnₓNiₓO₄ spinel, respectively. The characterization results demonstrated that the excellent SCR activity of MnₓNiₓOₓ catalysts was due to the high density of surface chemisorbed oxygen species and efficient electron transfer between Mn and Ni within the crystal structure of MnₓNiₓO₄ spinel. Good resistance to H₂O or/and SO₂ was obtained with stable activity over the MnₓNiₓO₄ catalyst, which was benefited by the MnₓNiₓO₄ spinel structure and Eley-Rideal mechanism, which was only slightly affected by SO₂.

Conflict of interest

No conflict of interest exits in the submission, and the manuscript is approved by all authors for publication. I would like to declare on behalf of my co-authors that the work described was original research that has not been published previously in whole or in part. All the authors listed have approved the manuscript that is enclosed.
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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jes.2019.10.010.

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