Superior activity of iron–manganese supported on kaolin for NO abatement at low temperature

Xiaobo Wang¹,²,⁎, Jie Zhou¹, Tong Zhao¹, Keting Gui³, Jia Wang⁴,⁎, Hywel R. Thomas²

¹. School of Environmental Science, Nanjing Xiaozhuang University, Nanjing 211171, China
². Geoenvironmental Research Centre, School of Engineering, Cardiff University, Cardiff CF24 3AA, UK
³. School of Energy and Environment, Southeast University, Nanjing 210096, China
⁴. College of Chemical Engineering, Nanjing Forestry University, Nanjing 210037, China

ARTICLE INFO
Article history:
Received 2 May 2019
Revised 26 August 2019
Accepted 29 August 2019
Available online 5 September 2019

Keywords:
Kaolin
Low-temperature
Iron-based catalysts
NO abatement

ABSTRACT
A series of Fe–Mn catalysts was prepared using different supports (kaolin, diatomite, and alumina) and used for NO abatement via low-temperature NH₃-selective catalytic reduction (SCR). The results showed that 12Fe–10Mn/Kaolin (with the concentration of Fe and Mn 12 and 10 wt.%, respectively) exhibited the highest activity, and more than 95.8% NO conversion could be obtained within the wide temperature range of 120–300°C. The properties of the catalysts were characterized by inductively coupled plasma-atomic emission spectrometry (ICP-AES), thermogravimetry (TG), Brunner-Emmet-Teller (BET) measurements, X-ray diffraction (XRD), H₂-temperature programmed reduction (H₂-TPR), NH₃-temperature programmed desorption (NH₃-TPD), X-ray photoelectron spectroscopy (XPS), scanning electron microprobe (SEM) and energy dispersive spectroscopy (EDS) techniques. The support effects resulted in significant differences in the components and structures of catalysts. The 12Fe–10Mn/Kaolin catalyst exhibited better dispersion of active species, optimum low-temperature reduction behavior, the largest amount of normalized Brønsted acid sites, and the highest Mn⁴+/Mn and Fe³⁺/(Fe³⁺ + Fe²⁺), all of which may be major reasons for its superior catalytic activity.

© 2019 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

Introduction

Nitrogen oxides (NOₓ), emitted from both stationary and mobile sources, have led to such environmental problems as acid rain, photochemical smog and the greenhouse effect (France et al., 2017; Guo et al., 2018). The most common technology used for NOₓ removal is selective catalytic reduction (SCR) with ammonia, and the commercial catalysts commonly used for SCR are V₂O₅–WO₃/TiO₂ (Chen et al., 2018). However, there are several inevitable drawbacks linked to the existing commercial catalysts, such as the environmental toxicity of VOₓ species and the conversion of SO₂ into SO₃ at high temperatures (Guo et al., 2018). Therefore, many low-temperature SCR catalysts based on other transition metal oxides have been developed in recent years, including some that are vanadium-free and highly active at low temperatures.

Recent research on low-temperature SCR catalysts has mainly focused on Fe-based, Mn-based, and Ce-based catalysts (Chen et al., 2017; France et al., 2017; Huang et al., 2018; Kim et al., 2012; Wang et al., 2018, 2016b; Zhu et al., 2016; Zhuang et al., 2017). Among them, the Fe-Mn composite catalysts have attracted special attention due to their...
excellent low-temperature catalytic activity and nontoxicity. Wang et al. loaded Fe–Mn onto ZSM-5 via the impregnation method and found that Mn–Fe/ZSM-5 could achieve more than 96.15% NO\textsubscript{2} conversion at 100°C with the optimum molar ratio of Fe/Mn (Wang et al., 2018). Zhu et al. (2016) prepared Mn–Fe/TiO\textsubscript{2} catalysts for NO abatement with NH\textsubscript{3}-SCR and found that the Mn–Fe/TiO\textsubscript{2} (molar ratio of Mn/Fe/Ti = 4:1:10) catalyst synthesized by sol–gel method yielded the best SCR activity at low temperature. Putluru et al. (2015) synthesized a 25Mn0.75Fe0.25Ti (25 wt.% Mn and molar fractions of Mn: Fe = 0.75:0.25) catalyst by the deposition precipitation (DP) method and found its relative activity to be 26.9 times that of the standard VWTi (V\textsubscript{2}O\textsubscript{5}–WO\textsubscript{3}/TiO\textsubscript{2}) catalyst at 175°C. Wang et al. (2019) found that iron doping could greatly promote the SO\textsubscript{2} resistance of Fe–Mn/γ-Al\textsubscript{2}O\textsubscript{3} catalysts. Lin et al. (2010) loaded Fe–Mn on USY (ultra-stable Y zeolite) by the impregnation method to prepare SCR catalysts and found that Fe–Mn/USY yielded high catalytic activity at low temperature. Although the supported Fe–Mn catalysts exhibited high catalytic activity at low temperatures, ZSM-5, TiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, and USY, etc., were mainly selected as catalyst supports due to their large surface area. It is well known that kaolin and diatomite are also porous structured materials and thus may be suitable as catalyst supports. In previous studies, kaolin and diatomite have regularly been used as adsorbents for the removal of methylene blue and heavy metals in contaminated water (Mouni et al., 2018; Sheng et al., 2009; Yadav et al., 2019). However, studies on the SCR catalytic activity of Fe–Mn supported on kaolin or diatomite have not been reported in the literature so far. Different supports will lead to different physical and chemical properties for a catalyst, such as specific surface area and chemical stability, and thus lead to different catalytic activity. Therefore, it is worthwhile to study the catalytic performance of Fe–Mn supported on kaolin and diatomite for NO abatement at low temperature.

In the present study, kaolin and diatomite were selected as supports to prepare Fe–Mn-based catalysts. For comparison, Al\textsubscript{2}O\textsubscript{3} was also used as a catalyst support. The catalyst samples were tested in the NH\textsubscript{3}-SCR reaction to investigate the catalytic activity of the samples, and the relationships among the components, structure, and performance of catalysts were revealed by various characterization methods.

1. Materials and methods

1.1. Catalyst preparation

Kaolin (superfine, 5 μm), diatomite (CP), and Al\textsubscript{2}O\textsubscript{3} power (100–200 mesh) were used as catalyst support materials. The detailed properties of supports can be seen in Appendix A Table S1. Iron nitrate nonahydrate (Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O) and manganese nitrate (Mn(NO\textsubscript{3})\textsubscript{2}), analytical reagent (AR), 50 wt. % aqueous solution were selected as precursors for the iron oxides and manganese oxides, respectively. Ammonia solution (AR) was used as a precipitant. First, the precursors of iron, manganese, and kaolin were dissolved in distilled water, with stirring, to obtain a mixed solution. Then a solution of ammonia was gradually added to the mixture until the pH of the solution reached 9–10. After being stirred thoroughly, the mixture was filtered and the solid product was air-dried in an oven at 150°C for 5 hr until the sample dried completely. This process was followed by calcination in air at 450°C for 4 hr. The samples were denoted as yFe–zMn/Kaolin, where y and z were the respective weight percentages of Fe and Mn (e.g., 12Fe–10Mn/Kaolin). The amounts of Fe and Mn were based on the support. The samples based on diatomite and Al\textsubscript{2}O\textsubscript{3} supports were synthesized by the same process as described above. The mass percent (wt.% Fe and Mn in catalysts listed in Appendix A Table S2 were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Optima 7300 DV, PerkinElmer, USA), and the contents of Fe and Mn were basically the same as the theoretical values.

1.2. Catalyst characterizations

ICP-AES was executed to determine the element content of the catalysts on an inductively coupled plasma atomic emission spectrometer (Optima 7300 DV, PerkinElmer, USA). The thermogravimetry and differential thermogravimetry (TG–DTG) measurements were carried out by a thermogravimetric analyzer (TG 209 F3, Netzsch, Germany) with a heating rate of 20°C/min from room temperature to 900°C under nitrogen atmosphere.

N\textsubscript{2} adsorption/desorption isotherms at −196°C were measured using a Quantachrome (NOVA-400e, Quantachrome, Germany) instrument to determine the surface areas, pore volumes and pore size distributions of the samples. X-ray diffraction (XRD) patterns were obtained on an X-ray diffractometer (Smartlab 9, Rigaku, Japan) with CuK\textalpha\ radiation in the 2θ range from 10 to 90°.

H\textsubscript{2}-temperature programmed reduction (H\textsubscript{2}-TPR) experiments were carried out on a chemisorption analyzer (Chemisorbs 2720, Micrometrics, USA) connected with a thermal conductivity detector (TCD). Samples (50 mg) were pretreated in a N\textsubscript{2} stream at 200°C for 1 hr and then used for the experiment. The TCD signal was recorded from room temperature to 900°C at a heating rate of 10°C/min.

NH\textsubscript{3}-temperature programmed desorption (NH\textsubscript{3}–TPD) experiments were carried out using about 150 mg of catalyst on a Autochem II 2920 (Autochem II 2920, Micromeritics, USA) instrument. First, the sample was pretreated in He (40 mL/min) at 450°C for 1 hr and then cooled to room temperature. After that, it was treated with 10 vol.% NH\textsubscript{3} (40 mL/min) for 1 hr until saturated. Subsequently, the sample was flushed with He at 100°C for 1 hr. Finally, the TPD data were collected from 100 to 800°C with a heating rate of 10°C/min. X-ray photoelectron spectroscopy (XPS) analysis was performed to identify the surface elements and valence states of catalysts using a Thermo Fisher Scientific XPS (EXCALAB 250Xi, Thermo Fisher Scientific, USA) instrument. Scanning electron microprobe (SEM) analysis was conducted to investigate the morphology and structure of the catalysts by field emission scanning electron microscopy (S-4800, Hitachi, Japan).

Energy dispersive spectroscopy (EDS) mapping was conducted on a scanning electron microscope (Quanta FEG-250, FEI, USA) coupled with an energy dispersive spectrometer.
(INCA X-MAX50, Oxford, England) to obtain the dispersion of the Fe and Mn on the catalysts.

### 1.3. Catalytic activity evaluation

SCR activity evaluation was carried out in a fixed bed reactor using a sample of about 7 mL (30–60 mesh). The simulated gas was composed of 500 ppmV NH₃, 500 ppmV NO, 3 vol.% O₂, 50 or 100 ppmV SO₂ (when used), 5 vol.% H₂O and N₂ balance. A steady gas flow rate was maintained at 1.5 L/min. All the data were obtained online under a steady state using a flue gas analyzer (ECOM-J2KN, RBR, Germany). The NO₇ conversion \( C_{\text{NO}} \) was calculated as follows:

\[
C_{\text{NO}} = \frac{\text{[NO]}_{\text{inlet}} - \text{[NO]}_{\text{outlet}}}{\text{[NO]}_{\text{inlet}}} \times 100\% \tag{1}
\]

where, \([\text{NO}]_{\text{inlet}}\) and \([\text{NO}]_{\text{outlet}}\) are the inlet and outlet concentrations of NO, respectively.

### 2. Results and discussion

#### 2.1. Catalytic performance

Fig. 1 displays the NO conversion over different Fe/Kaolin catalysts. It can be seen that catalyst activities increased with increasing reaction temperature and that the sequence over different catalysts was ranked as 5Fe/Kaolin < 15Fe/Kaolin < 12Fe/Kaolin. The 12Fe/Kaolin catalyst yielded the highest NO conversion, which was only about 81% of the NO conversion at 300°C. Further increase of Fe loading did not increase the activity, which suggested that the optimal Fe loading was 12 wt.%.

Evidently, for catalysts with iron loading only, the catalytic activity was not sufficient, especially at low temperatures. To further promote the low-temperature catalytic activity, Mn was added to the 12Fe/Kaolin catalysts; the effects of Mn loading on activity are shown in Fig. 2. With the addition of Mn, the catalytic activity was greatly promoted as the reaction temperature increased, especially at low temperatures. The 12Fe–10Mn/Kaolin catalyst exhibited the highest activity, and more than 95.8% NO conversion could be gained within the temperature range of 120–300°C. Further increasing the Mn loading in the catalysts was not favorable to the catalytic activity. Compared with that of 12Fe/Kaolin, not only was the low-temperature catalytic activity of the 12Fe–10Mn/Kaolin catalysts significantly enhanced, but the active temperature window was also broadened.

After fixing the loading of Fe and Mn onto the catalysts at 12 and 10 wt.%, respectively, the effect of different supports on the SCR activity over the Fe–Mn catalysts was investigated and the results are shown in Fig. 3. It can be seen that the activity of Fe–Mn catalysts was closely related to the catalyst supports and the 12Fe–10Mn/Kaolin catalyst exhibited the highest catalytic activity. The order of the catalytic activity was as follows: 12Fe–10Mn/Kaolin > 12Fe–10Mn/Diatomite > 12Fe–10Mn/Al₂O₃ catalysts, which indicated that the catalytic activity greatly depended on the catalyst support, and that kaolin may be a promising alternative choice as an SCR catalyst support. Moreover, as shown in Appendix A Fig. S1, 12Fe–10Mn/Kaolin exhibited the best N₂ selectivity, and less N₂O was formed during SCR reaction. The excellent NO conversion and N₂ selectivity of the 12Fe–10Mn/Kaolin catalyst indicated its superior catalytic performance. In addition, compared with single loading of Fe or Mn displayed in Appendix A Fig. S2, the composite bimetallic 12Fe–10Mn/Kaolin catalyst yielded the best catalytic activity in the whole reaction temperature range, which demonstrated the existence of synergy between iron and manganese in the SCR reaction. Moreover, as shown in Appendix A Fig. S3, the catalytic activity of the 12Fe–10Mn/Kaolin catalyst at 180°C was maintained at 98.2% after 30 hr of continuous SCR reaction, which showed the superior stability of its catalytic activity.

---

**Fig. 1** – Effect of Fe loading on NH₃-SCR activity over iron-based catalysts. \( y \) in \( y\text{Fe} \) refers to weight percentage of Fe. NH₃-SCR: selective catalytic reduction of nitrogen oxides (NOₓ) with NH₃.

**Fig. 2** – Effect of Mn loading on NH₃-SCR activity over iron-based catalysts. \( y \) and \( z \) in \( y\text{Fe}_z\text{Mn} \) refer to weight percentages of Fe and Mn, respectively.
2.2. SO2 and H2O resistance

The effect of SO2 on the SCR activity of Fe–Mn catalysts on different supports was studied at 210°C, and the results are shown in Fig. 4. As can be seen, the introduction of 100 ppmV SO2 into the simulated flue gas led to a large activity drop over all three catalysts. The NO conversion of 12Fe–10Mn/Kaolin, 12Fe–10Mn/Al2O3, and 12Fe–10Mn/Diatomite decreased from 98.2%, 91.8%, and 96.5% to 43.5%, 39%, and 35.6%, respectively, on exposure to SO2 for 6 hr. This suggested that the SO2 resistance of 12Fe–10Mn/Kaolin was relatively better when compared to the two other catalysts prepared with Al2O3 and Diatomite supports.

The effect of H2O and the synergistic effects of SO2 and H2O on NO conversion were also investigated, and the results are displayed in Appendix A Figs. S4 and S5. It can be observed that after 5 vol.% H2O was introduced into the simulated gas, the NO conversion of the three catalysts markedly decreased. Subsequently, the NO conversion increased gradually and recovered to a level close to its original level when H2O was cut off. Meanwhile, the deactivation was significantly enhanced after the further addition of 50 ppmV SO2. When both SO2 and H2O were cut off, the NO conversion increased slowly but could not recover to its original level, which indicated that the deactivation was irreversible. The reason for the deactivation in the presence of SO2 was investigated by TG analysis. It can be clearly seen from Appendix A Fig. S6 that the TGA profiles of the three deactivated catalysts showed some weight loss in the temperature region of 260–500°C, which could be attributed to the decomposition of ammonium sulfate on the catalyst surface (Shen et al., 2013; Shu et al., 2014). The weight loss that occurred above 700°C could be assigned to the decomposition of metal sulfates (Shu et al., 2014). These results demonstrated that deactivation of the catalysts in the SCR reaction in the presence of SO2 was due to the formation of ammonium sulfate and metal sulfates on the catalyst surface, which would lead to the blocking of pore structures and the decrease of active sites, and thus inhibited the SCR reaction.

2.3. BET analysis

The textural properties of the three catalysts are listed in Table 1, which shows that the introduction of Mn into the 12Fe/Kaolin catalysts increased its specific surface area, pore volume, and pore diameter. The increased specific surface area might have been due to the strong interaction between the Fe and Mn species of the 12Fe–10Mn/Kaolin catalysts, which was confirmed by the results of SEM and EDS mapping discussed below (Sun et al., 2018). The interaction between Fe and Mn species could generate high dispersion of active species on the catalyst surface and therefore would contribute to the enlargement of specific surface area. In addition, with respect to the Fe–Mn catalysts based on different supports, the most active 12Fe–10Mn/Kaolin catalyst had the second-lowest specific surface area, while the 12Fe–10Mn/Al2O3 catalyst possessed the highest specific surface area and the lowest catalytic activity. These results suggested that the textural properties of catalysts were not a key factor in the enhanced low-temperature activity and that a complex interaction might exist between the composition and other properties, such as crystalline phases, amorphous phases, local surface structures, and the valence states of active species (France et al., 2017).

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>S BET (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12Fe/Kaolin</td>
<td>32.46</td>
<td>0.104</td>
<td>5.94</td>
</tr>
<tr>
<td>12Fe–10Mn/Kaolin</td>
<td>57.61</td>
<td>0.161</td>
<td>5.93</td>
</tr>
<tr>
<td>12Fe–10Mn/Al2O3</td>
<td>146.1</td>
<td>0.238</td>
<td>3.68</td>
</tr>
<tr>
<td>12Fe–10Mn/Diatomite</td>
<td>40.8</td>
<td>0.075</td>
<td>4.88</td>
</tr>
</tbody>
</table>

S BET: the specific surface area of catalysts.
Wu et al., 2008a). In the XRD profiles of 12Fe the existence of interaction between Fe and Mn (Li et al., 2019; Wang et al., 2018). Combining the results of XRD, SEM and EDS mapping, the decrease of crystallinity and the features also revealed that the Fe and Mn species in high dispersion or existed as amorphous phases (Guo et al., 2019; Li et al., 2018; Wang et al., 2016b). These features also revealed that the Fe and Mn species for the 12Fe/Kaolin catalyst, the corresponding reduction temperatures of Fe and Mn demonstrated the existence of interaction between Fe and Mn (Li et al., 2019; Wu et al., 2008a). In the XRD profiles of 12Fe-10Mn/Al2O3 and 12Fe-10Mn/Diatomite catalysts, only typical diffraction peaks assigned to Al2O3 and SiO2 were detected, and no peaks could be observed related to Fe or Mn species.

2.4. XRD results

XRD was used to characterize the crystal structures of the catalysts, and the results are shown in Fig. 5. In the XRD pattern of 12Fe/Kaolin, diffraction peaks corresponding to Fe2O3 and SiO2 could be detected. After the introduction of Mn, only the diffraction peaks related to SiO2 could be observed in 12Fe–10Mn/Kaolin; also, the peak intensities noticeably decreased, which suggested a decrease in crystallinity. These features also revealed that the Fe and Mn species in high dispersion or existed as amorphous phases (Guo et al., 2019; Li et al., 2018; Wang et al., 2016b). Combining the results of XRD, SEM and EDS mapping, the decrease of crystallinity and the high coincidence of dispersion for Fe and Mn demonstrated the step-wise reduction of Fe2O3 and SiO2 could be detected. After the introduction of Mn, only the diffraction peaks related to SiO2 could be observed in 12Fe–10Mn/Kaolin; also, the peak intensities noticeably decreased, which suggested a decrease in crystallinity.

12Fe-10Mn/ Kaolin
12Fe-10Mn/ Al2O3
12Fe-10Mn/ Diatomite
12Fe/Kaolin
12Fe-10Mn/ Diatomite

Temperature (°C)
100 200 300 400 500 600 700 800 900

Fig. 5 – X-ray diffraction (XRD) patterns of different catalysts.

2.5. H2-TPR results

The redox properties of each sample were investigated by H2-TPR analysis and the results after peak-fitting are depicted in Fig. 6 and Appendix A Table S3. In the H2-TPR trace of the 12Fe/Kaolin catalyst, four reduction peaks-centered at about 434, 649, 757, and 847°C were assigned to the reduction processes MnO2 → Mn3O4 → Mn2O3 → Mn3O4 → MnO, respectively (Ettireddy et al., 2007; Fang et al., 2018; France et al., 2017; Liu et al., 2018; Sun et al., 2018). For the 12Fe–10Mn/Al2O3 and 12Fe–10Mn/Diatomite catalysts, the redox behavior was similar to that of the 12Fe–10Mn/Kaolin catalyst except that the corresponding reduction temperatures shifted to higher values (listed in Appendix A Table S3). The redox behavior was similar to that of the 12Fe–10Mn/Kaolin catalyst except that the corresponding reduction temperatures shifted to higher values (listed in Appendix A Table S3). These findings coincide with the results of the XPS analysis. Compared with those of the 12Fe/Kaolin catalysts, the reduction peaks of Mn-doped catalysts shifted to low temperatures and the peak areas were greatly enhanced at low temperatures, especially for the 12Fe–10Mn/Kaolin catalysts, suggesting the increased reducibility of catalysts after Mn doping. The change may be due to the interplay between the Fe and Mn species and the enhanced mobility of surface oxygen after Mn doping (Shu et al., 2012; Wang et al., 2018). Moreover, the total H2 consumption of catalysts can be determined by calculating the peak area of the reduction peaks. The sequence of the total H2 consumption was calculated to be 12Fe–10Mn/Kaolin (Peak area 22,226) > 12Fe–10Mn/Diatomite (Peak area 19,920) > 12Fe–10Mn/Al2O3 (Peak area 14,939), respectively. Overall, among the three catalyst samples prepared with different supports, the 12Fe–10Mn/Kaolin catalyst exhibited the best low-temperature redox activity and thus yielded the highest catalytic activity in the whole temperature range.

2.6. NH3-TPD results

The adsorption of NH3 on a catalyst’s surface plays an important role in the SCR reaction. To gain further insight into the relationships between the structure and its activity, NH3-TPD experiments were carried out; the results are shown in Fig. 7. For the 12Fe/Kaolin catalyst, only small amounts of NH3 species desorbed from the catalyst surface, implying the catalyst’s weak surface acidity. After introducing Mn species, the surface acidity of the 12Fe–10Mn/Kaolin catalyst greatly increased. A broader and stronger peak in the low-temperature range (< 420°C) and two main signals, peaking at about 536 and 650°C in the high-temperature range (> 420°C), could be observed for the 12Fe–10Mn/Kaolin catalyst; these findings may be associated with the ammonia adsorbed on weak and medium acid sites and strong acid sites,
respectively (Wu et al., 2008b; Zhuang et al., 2017). For the NH3-TPD profile of the 12Fe–10Mn/Al2O3 catalyst, two strong ammonia desorption peaks in the range of 100–800°C were found, while three main NH3 desorption peaks were observed for the 12Fe–10Mn/Diatomite catalyst. For the purpose of comparison, the amounts of weak and medium acid, and strong acid of 12Fe/Kaolin catalyst were taken as 1, respectively; and the corresponding desorption peak area was calculated for each catalyst (shown in Table 2). Compared with those of the 12Fe/Kaolin catalyst, the acid amounts of the 12Fe–10Mn/Kaolin catalyst greatly increased, especially with respect to the strong acid amounts. Furthermore, despite having the same components, the NH3 adsorption properties differed on catalysts with different supports. The amount of strong acid was significantly increased for the 12Fe–10Mn/Kaolin and 12Fe–10Mn/Diatomite catalysts, while not only the amounts of weak and medium acid but also the amount of strong acid were greatly enhanced for the 12Fe–10Mn/Al2O3 catalyst.

In addition, the total amount of NH3 desorbed followed the order 12Fe/Kaolin (2.00) < 12Fe–10Mn/Diatomite (8.71) < 12Fe–10Mn/Kaolin (13.05) < 12Fe–10Mn/Al2O3 (17.80), which was not consistent with the catalytic activity. When we considered the amount of NH3 desorbed per unit surface area, the sequence of the normalized acidity of the catalyst followed 12Fe/Kaolin (0.06) < 12Fe–10Mn/Al2O3 (0.12) < 12Fe–10Mn/Diatomite (0.21) < 12Fe–10Mn/Kaolin (0.23), thus agreeing well with the catalytic activity. The higher normalized total acidity of the 2Fe–10Mn/Kaolin catalyst was believed to significantly contribute to the SCR performance.

Meanwhile, it was reported that the high-temperature desorption peaks could be attributed to the desorption of NH3 adsorbed on the strong Lewis acid sites, while the low-temperature desorption peaks were originated from the desorption of NH3 adsorbed on the weak Brønsted acid sites, which would be beneficial for the low-temperature catalytic activity of the catalyst (Jiang et al., 2019). The normalized amounts of low-temperature weak Brønsted acid sites were ranked as 12Fe–10Mn/Kaolin (0.032) > 12Fe–10Mn/Al2O3 (0.029) > 12Fe–10Mn/Diatomite (0.017). It can be clearly seen that the 12Fe–10Mn/Kaolin catalyst possessed the largest amount of normalized Brønsted acid sites, and thus could generate the best catalytic activity at low temperature. Although the 12Fe–10Mn/Al2O3 catalyst held much more Brønsted acid sites than that of 12Fe–10Mn/Diatomite, it yielded relatively lower catalytic activity than 12Fe–10Mn/Diatomite. This may mean that the surface acidity of the catalyst was not a key factor in the catalytic performance of the 12Fe–10Mn/Al2O3 catalyst at low temperature, and that the catalytic performance was affected by other factors such as the concentration and chemical valence of surface active species.

2.7. XPS results

The concentrations of the surface elements and their chemical states on each catalyst are crucial for SCR activity. Therefore, the surface atomic concentrations and valence states of the Fe, Mn, and O elements of the catalysts were characterized by XPS and the results are shown in Fig. 8 and Table 3.

Fig. 8a displays the Fe 2p spectra of the four studied catalysts. Two XPS peaks, located at around 711.5 and 725 eV, were observed for all the catalysts which could be assigned to Fe 2p3/2 and Fe 2p1/2, respectively (France et al., 2017; Xu et al., 2016). Deconvolution of the Fe 2p3/2 peak indicated the coexistence of the two different Fe species, Fe3+ (710.5–710.7 eV) and Fe2+ (712–712.9 eV) (Roosendaal et al., 1999; Shwan et al., 2012; Xu et al., 2016). The relative contents of Fe2+ were calculated from the area of the Fe 2p3/2 peak for Fe3+, and the ratios of Fe3+/Fe2+ are summarized in Table 3. There it can be seen that the ratios of Fe3+/Fe2+ for 12Fe/Kaolin and 12Fe–10Mn/Kaolin were 30.2% and 60.7%, respectively, which indicated that the introduction of Mn increased the relative contents of Fe3+. Furthermore, compared with those of 12Fe/Kaolin, the binding energies of Fe for 12Fe–10Mn/Kaolin shifted to lower values, which suggested that the Fe species on the catalyst surface were more active and thus would be more beneficial for promoting catalytic performance (Shen et al., 2014). For the catalysts with different supports, the ratios of Fe3+/Fe2+ were ranked as 12Fe–10Mn/Kaolin > 12Fe–10Mn/Diatomite > 12Fe–10Mn/Al2O3 and were highly consistent with the sequence of

![Fig. 7 – NH3-temperature programmed desorption (NH3-TPD) profiles of different catalysts.](image_url)
catalytic performance discussed above. It was noted that the oxidation of NO to NO₂ occurred over Fe³⁺ sites and that the conversion of this step would lead to a “fast SCR” reaction and thus significantly promote SCR activity (Delahay et al., 2005; Xia et al., 2018; Xu et al., 2016). The oxidation activity of NO to NO₂ over different Fe–Mn catalysts was studied and displayed in Appendix A Fig. S7. It can be clearly seen that the sequence of activity for the oxidation of NO to NO₂ ranked as 12Fe–10Mn/Kaolin > 12Fe–10Mn/Diatomite > 12Fe–10Mn/Al₂O₃, which agreed well with the order of low-temperature catalytic performance. Therefore, the 12Fe–10Mn/Kaolin catalyst possessed the highest ratio of Fe³⁺ among the three catalysts based on different supports, and could generate more NO₂ in the SCR reaction; thus this catalyst exhibited the best low-temperature catalytic activity.

The Mn 2p XPS spectra of the catalysts are illustrated in Fig. 8b. Two main peaks attributed to Mn 2p₂/₃ and Mn 2p½ are observed. By peak-fitting, the Mn 2p₂/₃ spectra of the three catalysts on different supports were separated into three peaks that could be ascribed to Mn²⁺, Mn³⁺, and Mn⁴⁺, respectively (France et al., 2017; Guo et al., 2018; Sun et al., 2018). The ratios of Mn⁴⁺/Mn for 12Fe–10Mn/Kaolin, 12Fe–10Mn/Diatomite, and 12Fe–10Mn/Al₂O₃ are 36.3%, 28.2%, and 18.7%, respectively. The catalyst prepared with the Kaolin support generated more Mn⁴⁺ species on the catalyst surface. It was noted that Mn⁴⁺ in the form of MnO₂ exhibited the best catalytic activity and redox ability among all the MnOₓ catalysts, and that Mn⁴⁺ could promote the oxidation of NO to NO₂, which was confirmed by experiments shown in Appendix A Fig. S7, and thus would open the “fast SCR” route for NOₓ removal and enhance catalytic activity (Kim et al., 2012; Li et al., 2016; Liu et al., 2018; Wang et al., 2016a). Therefore, the increase in Mn⁴⁺ species on the 12Fe–10Mn/Kaolin catalysts should contribute to its superior low-temperature catalytic performance.

Fig. 8c displays the O 1s XPS spectra of the four catalysts. The O 1s spectra of the studied catalysts were deconvoluted into two peaks. The peak centered on 529.7–530.2 eV was ascribed to the lattice oxygen, labeled as Oα; the peak centered on 531.7–532.3 eV was assigned to the surface adsorbed oxygen, denoted as Oβ (France et al., 2017; Liu et al., 2018; Xu et al., 2016). The relative concentration ratios of Oα/(Oα + Oβ) over different catalysts were calculated and the results are shown in Table 3. Clearly, a great increase of Oα was obtained after the introduction of Mn onto the 12Fe/Kaolin catalyst; this increase is also shown in Fig. 8c. For the catalysts prepared on the three different supports, the ratios of Oα/(Oα + Oβ) decreased in the following sequence: 12Fe–10Mn/Kaolin (37.7%) > 12Fe–10Mn/Diatomite (26.9%) > 12Fe–10Mn/Al₂O₃ (19.7%); the results agreed well with the observed catalytic performance. It was noted that surface chemisorbed oxygen species played an important role in the SCR reaction due to their higher mobility and greater reactivity compared with lattice oxygen (France et al., 2017; Kang et al., 2007; Xu et al., 2016). Therefore, it might be inferred that the catalysts with the best catalytic performance possessed the largest amount of surface chemisorbed oxygen species (France et al., 2017).

Table 3 – Surface atomic concentrations of the catalysts determined by XPS.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Fe</th>
<th>Mn</th>
<th>O</th>
<th>Fe³⁺/(Fe³⁺ + Fe⁴⁺)</th>
<th>Oα/(Oα + Oβ)</th>
<th>Mn⁴⁺/(Mn⁴⁺ + Mn³⁺ + Mn²⁺)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12Fe/Kaolin</td>
<td>5.76%</td>
<td>–</td>
<td>41.58%</td>
<td>30.2%</td>
<td>9.1%</td>
<td>–</td>
</tr>
<tr>
<td>12Fe–10Mn/Kaolin</td>
<td>4.88%</td>
<td>6.40%</td>
<td>48.61%</td>
<td>60.7%</td>
<td>37.7%</td>
<td>36.3%</td>
</tr>
<tr>
<td>12Fe–10Mn/Al₂O₃</td>
<td>2.37%</td>
<td>2.95%</td>
<td>36.18%</td>
<td>37.5%</td>
<td>19.7%</td>
<td>18.7%</td>
</tr>
<tr>
<td>12Fe–10Mn/Diatomite</td>
<td>4.49%</td>
<td>6.62%</td>
<td>41.19%</td>
<td>53.0%</td>
<td>26.9%</td>
<td>28.2%</td>
</tr>
</tbody>
</table>
However, this was not the case. Compared with the surface chemisorbed oxygen species, oxygen vacancies and lattice oxygen showed better low-temperature activity in the SCR reaction, promoting the possibility of NO oxidation to NO₂ forming nitrate species, and thus enhancing catalytic performance (Lin et al., 2010; Wang et al., 2018).

2.8. SEM and EDS mapping

SEM images were obtained at different magnifications to determine whether the catalyst support affected the morphologies of the catalysts and the dispersion of the active species. As shown in Fig. 9e–h, for the 12Fe–10Mn/Al₂O₃ catalyst, a lot of particles were observed on the support surface, which could be inferred to be active species. However, the particle size of active species was relatively large and the particle size distribution was uneven. Meanwhile, some agglomeration of particles could be observed in the local area shown in Fig. 9h. For the 12Fe–10Mn/Diatomite catalysts, a larger amount of active species particles could also be detected. Although the particles of active species were smaller than those of the 12Fe–10Mn/Al₂O₃ catalyst, the active species on the support surface displayed some noticeable

Fig. 9 – Scanning electron microprobe (SEM) images of (a–d) 12Fe–10Mn/Kaolin, (e–h) 12Fe–10Mn/Al₂O₃ and (i–l) 12Fe–10Mn/Diatomite.
agglomeration phenomena as well, as shown in Fig. 9i, which indicated a relatively poor dispersion of active species.

With respect to the 12Fe–10Mn/Kaolin catalyst prepared on the kaolin support, as displayed in Fig. 9a–d, the morphologies were much more regular and homogeneous and presented a sheet-like shape, which was attributed to the typical microstructure of kaolin. Moreover, no visible particles could be observed on the support surface, which might imply that the particles were too small to be detected at this magnification, and these smaller particles would generate better dispersion of active species on the catalyst surface. This was in good consistency with the XPS results, which demonstrated that more active species were accumulated on the catalyst surface. These features indicated that the catalyst support had a great effect on the dispersion of active species, and that the 12Fe–10Mn/Kaolin catalyst prepared with a kaolin support could generate better dispersion of active species on the catalyst surface, and therefore would exhibit superior catalytic activity.

On the other hand, the EDS mapping further provided evidence for the high dispersion of Fe and Mn species on the 12Fe–10Mn/Kaolin catalyst surface. As shown in Fig. 10, the Fe and Mn were highly dispersed on the 12Fe–10Mn/Kaolin catalyst, and the distribution regions of Fe and Mn coincident, indicating the existence of an interaction between Fe and Mn on the catalyst surface. With respect to the 12Fe–10Mn/Al2O3 and 12Fe–10Mn/Diatomite catalysts, Fe and Mn were dispersed unevenly and a certain degree of agglomeration could be observed.

3. Conclusions

The 12Fe–10Mn/Kaolin catalyst was found to yield superior activity, and more than 95.8% NO conversion could be obtained within a wide temperature range of 120–300°C. The support effect resulted in significant differences in the

Fig. 10 – Energy dispersive spectroscopy (EDS) mapping of (a) 12Fe–10Mn/Kaolin, (b) 12Fe–10Mn/Al2O3, and (c) 12Fe–10Mn/Diatomite.
components and structure of catalysts. The 12Fe–10Mn/Kaolin catalyst prepared using kaolin possessed better dispersion of active species, optimum low-temperature reduction behavior, the largest amount of normalized Brønsted acid sites, and the highest Mn\textsuperscript{4+}/Mn and Fe\textsuperscript{3+}/Fe\textsuperscript{3+} + Fe\textsuperscript{2+} ratios, and therefore exhibited superior catalytic activity at low temperature.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 51276039), a project supported by the Natural Science Foundation of the Jiangsu Higher Education Institutions of China (No. 17KJB610005) and a project funded by Nanjing Xiaozhuang University (No. 2016NYX41).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jes.2019.08.017.

REFERENCES


Chen, C., Jia, W., Liu, S., Cao, Y., 2018. Mechanism of Hg\textsubscript{2} oxidation in the presence of HCl over a CuCl\textsubscript{2}-modified SCR catalyst. J. Mater. Sci. 53, 10001–10012.


Lin, Q., Li, J., Ma, L., Hao, J., 2010. Selective catalytic reduction of NO with NH\textsubscript{3} over Mn-Fe/USY under lean burn conditions. Catal. Today 151, 251–256.


Shen, B., Zhang, X., Ma, H., Yao, Y., Liu, T., 2013. A comparative study of Mn/CoO\textsubscript{2}, Mn/ZrO\textsubscript{2} and Mn/Co/ZrO\textsubscript{2} for low temperature selective catalytic reduction of NO with NH\textsubscript{3} in the presence of SO\textsubscript{2} and H\textsubscript{2}O. J. Environ. Sci. 25, 791–800.


Shu, Y., AIkebaier, T., Quan, X., Chen, S., Yu, H., 2014. Selective catalytic reaction of NO\textsubscript{x} with NH\textsubscript{3} over Ce-Fe/TiO\textsubscript{2}-loaded wire-mesh honeycomb: resistance to SO\textsubscript{2} poisoning. Appl. Catal. B Environ. 150-151, 630–635.


Wang, X., Wu, S., Zou, W., Yu, S., Gui, K., Dong, L., 2016b. Fe-Mn/Al\textsubscript{2}O\textsubscript{3} catalysts for low temperature selective catalytic reduction of NO with NH\textsubscript{3}. Chin. J. Catal. 37, 1314–1323.


