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SSZ-13-supported manganese oxide catalysts for low temperature selective catalytic reduction of NO_x by NH₃

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Abstract. A series of Mn/SSZ-13 catalysts of varying Mn content were synthesized by hydrothermal and co-precipitation methods. Their performances for the selective catalytic reduction (SCR) of NO_x with NH₃ were evaluated. The results indicate that over 95% NO_x conversion was achieved at a low temperature of 150°C with an Mn loading of 4.74 wt%. Meanwhile, the NO_x conversion rate remained greater than 90% at 450°C. The Mn/SSZ-13 catalysts were characterized by X-ray diffraction, ultraviolet–visible diffuse reflectance spectroscopy, Raman spectroscopy, transmission electron microscopy, N₂-adsorption, temperature-programmed desorption, and X-ray photoelectron spectroscopy. The analysis indicates that Mn₂O₃, Mn₃O₄, and amorphous MnO₂ coexist on the surface of the Mn/SSZ-13 catalysts, with MnO₂ comprising the largest proportion, which may contribute to the high SCR activity. Additionally, the specific surface area and pore volume both decrease with increasing Mn loading. The Mn/SSZ-13 catalyst with 4.74 wt% of Mn has a high concentration of lattice oxygen, a high amorphous MnO₂ content, and greatest number of strong Lewis acid sites, which are beneficial to the adsorption of NH₃, and may account for its superior catalytic activity.

Keywords. Selective catalytic reduction; NO; Mn/SSZ-13; SCR activity.

1. Introduction

Nitrogen oxides (NO_x) are produced from mixtures of oxygen and nitrogen in the combustion process, such as in air-breathing engines, and easily react to form harmful environmental pollutants. The selective catalytic reduction (SCR) of NO_x with ammonia (NH₃) is the most effective means of removing NO_x emissions from the tail exhaust of diesel engines. Commercial V-Ti catalysts (V₂O₅/TiO₂) are commonly employed for this purpose.¹ However, V-Ti catalysts suffer from various drawbacks such as the low N₂ selectivity used in the automotive apparatus at high temperature, and an active temperature window between 300 to 400°C, which limits its practical application. Recently, ZSM-5 zeolite catalysts have received considerable attention.^{2,3} Moreover, catalysts composed of chabazite (CHA) have been found to be a possible alternative to V-Ti catalysts^{4,5} due to its high activity, wide reaction temperature window, suitable acidity, and good hydrothermal stability.

Transition metal exchanged zeolite-based catalysts, such as those involving isolated Cu²⁺ sites located in small pore-sized molecular sieves of a CHA framework structure, have also received considerable attention in

recent years for SCR applications. Fickel *et al.* investigated the NH₃ selective reduction activity of isolated Cu²⁺ exchanged zeolite molecular sieves, and Cu/SSZ-13 catalysts were demonstrated to provide an NO_x conversion rate approaching 100% in the temperature range of 200–450°C.⁶ Ma *et al.*, analyzed the activity of Cu/SSZ-13 catalysts by means of *in situ* IR spectroscopy and temperature programmed technology, and determined that the NH₃-SCR of Cu/SSZ-13 catalysts is facilitated by a Cu²⁺/Cu⁺ redox process, with the Cu⁺ oxidized to Cu²⁺ by oxygen to complete the catalytic cycle.⁷ The hydrothermal stability of Cu/SSZ-13 catalysts was found to be excellent after treatment with ammonium hexafluorosilicate.⁸ Moreover, after hydrothermal aging at 850°C for 12 h, Cu/SSZ-13 catalysts exhibited high NO_x conversion (>90%) with a wide temperature window (200–400°C).

While the temperature range provided by Cu/SSZ-13 catalysts is good, extending the low temperature SCR activity threshold of SSZ-13 type molecular sieves would be extremely valuable in terms of expanding its potential applications. In that regard, the richly variable valence states of manganese and its oxide species would be beneficial to the SCR reaction cycle. In fact, Mn and its oxide species supported on SSZ-13

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molecular sieves have shown superior low temperature activity. For example, Mn/ZSM-5 catalysts have exhibited good SCR reaction activity in the low temperature range of 170–350°C.⁹ Wang *et al.*, reported that catalysts composed of MnO_x and multi-walled carbon nanotube (MWCNT) composites demonstrated excellent low-temperature activity, and the NO_x conversion rate was greater than 90% at 190°C.¹⁰ The above studies demonstrated that the loading of SSZ-13 type molecular sieves with Mn compounds can be expected to extend the low temperature threshold of SCR activity.

In the present study, a family of Mn/SSZ-13 catalysts with varying Mn loading was prepared by the co-precipitation method. The SCR activities were evaluated, and the structure of the Mn/SSZ-13 samples was characterized by X-ray diffraction (XRD), UV-Visible diffuse reflectance spectroscopy (DRS), UV-Raman spectroscopy, high-resolution transmission electron microscopy (HRTEM), N₂-adsorption, temperature-programmed desorption (TPD), and X-ray photoelectron spectroscopy (XPS). We examine and discuss the effects of different Mn loadings on the structure of Mn/SSZ-13 catalysts, the specific surface area, the pore size distribution, the composition of the Mn species, the dispersion of Mn loadings, and the acidity of the Mn loading over the SSZ-13 molecular sieve. In addition, the catalytic mechanism of the SCR reaction for the Mn/SSZ-13 catalysts and the factors influencing the SCR reaction are discussed.

2. Experimental

2.1 Preparation of Mn/SSZ-13 catalysts

Silica sol was obtained from Sigma-Aldrich (30%, St. Louis, MO). Aluminum sulfate, and Sodium hydroxide were obtained from Sinopharm (AR, Shanghai, China). N,N,N-trimethyl-1-adamantyl ammonium hydroxide was obtained from Sichuan Zhong Bang Technology Development Co. Ltd (AR, Sichuan, China). Deionized water was used. For the synthesis of the Mn/SSZ-13 catalyst series, SSZ-13 was prepared from synthetic gel compositions of proportions 15–20 Na₂O : 1 Al₂O₃ : 800–1600 H₂O :

6 R₂O : 30–80 SiO₂ with aluminum sulfate, silica sol, deionized water, and sodium hydroxide as raw materials, and N,N,N-trimethyl-1-adamantyl ammonium hydroxide as the structure-directing agent. SSZ-13 was prepared as follows. N,N,N-trimethyl-1-adamantyl ammonium hydroxide was dissolved in deionized water together with aluminum sulfate and sodium hydroxide under stirring for 30 min. Silica sol was subsequently added slowly to obtain a gel mixture under stirring for 30 min. The gel mixture was transferred to a Teflon-lined autoclave reactor, sealed, and heated at 155°C under static conditions for 2 to 4 days. The synthesis product was filtered and thoroughly washed with distilled water and dried at 100°C for 12 h. The synthesis product was then ion-exchanged using an NH₄NO₃ solution at 80°C for 24 h. The sample was filtered and washed with abundant distilled water and dried at 100°C for 6 h. The NH₄⁺/SSZ-13 product was calcined at 550°C for 6 h in air to remove the organic template. The detailed synthesis procedure for Cu/SSZ-13 catalysts was reported in our previous work.⁸ Mn/SSZ-13 catalysts were similarly prepared by precipitation with NH₃ as a precipitant. A specific proportion of the SSZ-13 molecular sieve sample was ion-exchanged with different concentrations of manganese acetate under magnetic stirring at room temperature for 24 h. Subsequently, NH₃ was slowly added to adjust the pH of the resulting solution to 11. Then, the solution was filtered and washed with deionized water and dried at 100°C overnight, followed by calcination at 550°C for 2 h. The synthesized catalyst samples are hereafter denoted as Mn/SSZ-13-x, where x represents the sample number. The Mn content of the samples was measured by a Varian Vista-AX inductively coupled plasma optical emission spectrometer (ICP-OES), and the results are listed in Table 1.

2.2 The characterization of catalysts

XRD patterns of the products were obtained using a Rigaku D/MAX2500 diffractometer with a Cu K_α radiation source (λ = 0.154 nm), a tube voltage of 40 kV, and a tube current of 100 mA in the 2θ range of 5–70° at a scanning rate of 3° per min. N₂ adsorption-desorption isotherms were determined using a Quantachrome Autosorb-iQ2-MP N₂ adsorption instrument. All the samples were held in a vacuum at 300°C for 5 h prior to measurement to ensure the elimination of water and other superfluous species. The micropore volume was measured by means of the t-plot

Table 1. Textural properties of Mn-SSZ-13 catalysts.

Sample	BET surface area (m ² /g)	Pore size (nm)	Pore volume (cm ³ /g)	Mn (wt%)
Mn/SSZ-13-1	223.5	2.1	0.14	0.9
Mn/SSZ-13-2	219.3	2.3	0.13	2.4
Mn/SSZ-13-3	217.4	2.5	0.12	4.7
Mn/SSZ-13-4	190.8	2.8	0.11	7.8
Mn/SSZ-13-5	119.2	3.4	0.10	28.9

method. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method. UV-Raman spectroscopy was conducted on a Thermo Fisher Scientific DXR Raman spectrometer. A laser line at 325 nm was employed as the excitation source. UV-Vis DRS spectra were obtained on a Shimadzu UV-2450 UV-Vis spectrophotometer in the range of 200–800 nm. The atomic concentrations on the sample surfaces were evaluated using XPS conducted on a Kratos Analytical AXIS Ultra DLD spectrometer. The binding energy of the C 1s peak (284.8 eV) was used as an internal standard. The TPD of NH_3 (NH_3 -TPD) was employed to determine the number of different acid sites and their strengths for the catalysts using a Micromeritics AutoChem 2920 automated catalyst characterization system. Prior to testing, approximately 30 mg of catalyst samples were pretreated with high-purity N_2 under a flow rate of $40 \text{ mL} \cdot \text{min}^{-1}$ at 500°C for 60 min. Then, physisorbed ammonia was removed by means of helium under equivalent conditions. The TPD operation was subsequently conducted at a heating rate of $10^\circ\text{C} \cdot \text{min}^{-1}$ in the temperature range of 100 to 800°C . The amount of NH_3 desorbed was determined by a thermal conductivity detector (TCD).

2.3 NH_3 -SCR activity testing

The catalytic activities of the Mn/SSZ-13 samples were investigated using a custom-made fixed bed. For each sample, $\sim 500 \text{ mg}$ of the catalyst was placed in a quartz tube reactor with a diameter of 1 cm, and mixed with a given amount of quartz sand to ensure the smooth passage of the reaction gas through the reactor. The reaction gas was composed of 8% ppm O_2 , 600 ppm NO , 600 ppm NH_3 , 5% H_2O , and the balance N_2 , at a total flow rate of $300 \text{ mL} \cdot \text{min}^{-1}$ and a gas hourly space velocity (GHSV) of $36,000 \text{ h}^{-1}$ was employed. The concentration of NO in the outlet gas from the reactor was analyzed by means of a gas analyzer.

The NO_x conversion rate and N_2 selectivity were respectively calculated as follows.

$$\text{NO}_x \text{ conversion} = \frac{C_1 - C_0}{C_1} \times 100\% \quad (1)$$

$$\text{N}_2 \text{ selectivity} = \frac{C_1 + C_2 - C_3 - 2C_4}{C_1 + C_2} \times 100\% \quad (2)$$

Here, C_1 and C_0 are the respective concentrations of NO_x at the inlet and the outlet of the reactor, C_2 is the concentration of NH_3 at the inlet, C_3 is the concentration of NO_2 at the outlet, and C_4 is the concentration of N_2O at the outlet.

3. Results and Discussion

3.1 NH_3 -SCR activity performance

The NO_x conversion rates for the SCR were measured on Cu/SSZ-13 catalysts and Mn/SSZ-13 catalysts with different Mn loadings at temperatures between 100°C

Figure 1. (A) Catalytic performance for SCR of NO_x with ammonia in the temperature range of 100 – 550°C ; (B) N_2 selectivity of catalysts.

and 550°C , and are shown in Figure 1A. Compared with Cu/SSZ-13 catalysts, the Mn/SSZ-13 catalysts exhibit higher SCR activity at low temperatures. The NO_x conversion rate varies with increasing Mn loading. It is noted that the low temperature NO_x reduction (DeNO_x) activity of Mn/SSZ-13 increases with increasing Mn loading from 0.91 wt% to 4.74 wt%, whereas the trend is reversed for Mn loadings above 4.74 wt%. In particular, the catalytic activity of Mn/SSZ-13-5 dramatically decreases across the entire temperature window. Mn/SSZ-13-3 exhibits the best catalytic performance with an NO_x conversion above 90% from 150°C to 450°C , and attains an NO_x conversion rate greater than 95% from 150°C to 350°C , which demonstrates its excellent low-temperature performance over a wide temperature window. Figure 1B shows the N_2 selectivity for these catalysts, all of which exhibit high selectivity along the entire temperature range.

3.2 XRD patterns

The XRD patterns of pure SSZ-13 and Mn/SSZ-13 samples with the various Mn loadings are shown in Figure 2A. The figure indicates that all samples have a relatively high crystallinity. The Mn/SSZ-13 samples exhibit the typical peaks of SSZ-13 zeolite,¹¹ and the original structure remains intact with different Mn loadings. Interestingly, the intensities of the principal diffraction peaks of SSZ-13 decrease with

increasing Mn loading. In addition, the XRD pattern for the Mn/SSZ-13-3 catalyst shown in Figure 2B indicates that the characteristic reflection peaks of crystalline Mn_2O_3 and Mn_3O_4 phases¹² are observed, while the MnO_2 phase is not detected. Moreover, the XRD pattern for the Mn/SSZ-13-5 catalyst shown in Figure 2C exhibits a greater baseline noise, which is possibly due to an excessive Mn loading, resulting in clogged channels. Alternately, the noise may be due to the higher absorption of Mn compounds for X-ray radiation.

3.3 UV-Raman spectroscopy and UV-Vis DRS results

The UV-Raman spectra of the catalyst samples were employed to detect the framework of the metal sites in SSZ-13 zeolite and the extra-framework Mn species. The Raman spectra of pure SSZ-13 and the Mn/SSZ-13 samples are shown in Figure 3. The bands at 336 cm^{-1} are assigned to the T-O-T (with T being Si or Al) vibration mode of the six-membered building unit of the CHA-structured zeolite. The characteristic peak at 476 cm^{-1} assigned to the Vs(T-O-T) mode is a typical peak for the SSZ-13 framework, where it is noted that SSZ-13 consists of four- or six- and eight-membered rings.¹³ The weak and broad peaks centered at 810 cm^{-1} and 1205 cm^{-1} are, respectively, ascribed to the characteristic symmetric and asymmetric Si-O bond vibration modes of the CHA-type structure.^{14,15} Comparing the SSZ-13 and Mn/SSZ-13 spectra, we observe a new band at 582.2 cm^{-1} , which is a band associated with Mn complexes found in the presence of extra-framework Mn species,¹⁶ as also indicated by the XRD results.

Figure 2. XRD patterns. (A) pure SSZ-13 (a); Mn-SSZ-13-1 (b); Mn-SSZ-13-2 (c); Mn-SSZ-13-3 (d); Mn-SSZ-13-4 (e); Mn-SSZ-13-5 (f). (B) Mn-SSZ-13-3. (C) Mn-SSZ-13-5.

Figure 3. (a) Raman spectra of Mn-SSZ-13-1; (b) Mn-SSZ-13-2; (c) Mn-SSZ-13-3; (d) Mn-SSZ-13-4; (e) Mn-SSZ-13-5; (f) SSZ-13.

Figure 4. (a) UV-Vis DRS spectra of Mn-SSZ-13-3; (b) SSZ-13. (Details: 20 mg of sample spread on 1.7 g BaSO₄ powder. BaSO₄ powder is the blank sample).

However, when the Mn loading is excessive, the SSZ-13 zeolite peaks are difficult to observe.

UV-Vis DRS was applied to understand the nature and coordination of Mn species in the catalysts. The UV-Vis absorption spectra of the Mn/SSZ-13 catalysts are shown in Figure 4. The spectra exhibit three different bands: a narrow band at about 270 nm and two broad bands with their respective centers at about 360 nm and 800 nm. The narrow band at 270 nm is attributed to electron transfer from O²⁻ to tetrahedral Mn³⁺. The 360 nm and 800 nm absorption bands are assigned to the d-d transition of either the framework or the extra-framework Mn species of different valences.¹⁷ Therefore, the results reveal that different Mn species are either on the surface of the SSZ-13 samples or within the framework.

3.4 HRTEM results

Figure 5 presents the HRTEM images of the Mn/SSZ-13-3 catalyst. Nanoparticles, representative of Mn species, are clearly observed on the surface of the catalyst, and MnO_x particles with different sizes are observed to be aggregated on the surface of SSZ-13 samples. The lattice fringes of the MnO_x particles are measured to be 1.8 Å indexed as (520) and 2.8 Å indexed as (222), which can be assigned to the Mn₃O₄ and Mn₂O₃ phases, respectively. This also independently verifies the existence of Mn species with different valences, which is consistent with the XRD results.¹⁸

The results of XRD, UV-Raman spectroscopy, UV-Vis DRS, and HRTEM clearly show that MnO_x species exists in the form of Mn₂O₃ and Mn₃O₄ on the surface and in the interior of the Mn/SSZ-13 catalysts.

Figure 5. The HRTEM images of Mn-SSZ-13-3.

3.5 XPS results

The catalysts were characterized by XPS to evaluate the oxidation states of Mn, and to estimate the concentration of Mn on the surface of the Mn/SSZ-13 catalysts.¹⁹ Figure 6 presents the Mn 2p peaks, which consist of asymmetrical Mn 2p_{3/2} and Mn 2p_{1/2} peaks with binding energies of about 642.3 eV and 653.8 eV, respectively.^{20–22} The energy difference between the Mn 2p_{3/2} and Mn 2p_{1/2} peaks is 11.5 eV, which is consistent with previous reports.³⁶ Deconvolution fitting of the Mn 2p_{3/2} and Mn 2p_{1/2} peaks yields four distinct peaks centered at 655.1 eV or 653.4 eV, and 643.8 eV or 642.1 eV, which are slightly shifted relative to standard reported values,^{37,38} indicating a varying valence state for Mn. The Mn 2p_{3/2} peak at about 655.1 eV and Mn 2p_{1/2} peak at about 643.8 eV are assigned to Mn(+4), proving the presence of the MnO₂ species on the catalyst surface. Considering that the crystal MnO₂ was not detected on all the catalysts by XRD, it is deduced that the MnO₂ species might be in amorphous state on the catalyst surface. The Mn 2p_{3/2} and Mn 2p_{1/2} peaks at approximately 653.4 eV and 642.1 eV are assigned to Mn(+3), proving the presence of Mn₂O₃ species on the

Figure 6. (a) XPS results of Mn 2p of Mn-SSZ-13-1; (b) Mn-SSZ-13-3; (c) Mn-SSZ-13-5.

catalyst surface. The characterization of XRD and TEM also demonstrated the presence of Mn_2O_3 species. As listed in Table 2, the $\text{Mn}^{4+}/\text{Mn}^{3+}$ ratios of the samples are all greater than 1, indicating that MnO_2 is the major species.²³

Figure 7 presents the O 1s core level peaks of the Mn/SSZ-13 catalysts. From the deconvolution fitting of the O 1s spectra, two distinct peaks with binding energies of about 532.2 eV and 529.9 eV are observed, which are respectively assigned to the weakly surface-adsorbed oxygen ions ($\text{O}_{\text{adsorbed}}$) and the lattice oxygen ($\text{O}_{\text{lattice}}$).^{9,24,25} As given in Table 2, the ratio of $\text{O}_{\text{lattice}}/\text{O}_{\text{adsorbed}}$ increases with increasing Mn loading, indicative of an increase in $\text{O}_{\text{lattice}}$ component in the samples.

3.6 BET results

The N_2 adsorption/desorption isotherms of Mn/SSZ-13 catalysts are shown in Figure 8. When the relative pressure $P/P_0 < 0.1$, the amount of adsorbed N_2 increases rapidly, and then slowly increases in the relative pressure range of $0.1 < P/P_0 < 0.9$. This demonstrates that the Mn/SSZ-13 catalysts have a typical microporous structure. With increasing Mn loading, the pore size distribution of the catalysts generally becomes increasingly uniform. However, the Mn/SSZ-13-5 sample presents a

Figure 7. (a) XPS results of O 1s of Mn-SSZ-13-1; (b) Mn-SSZ-13-3; (c) Mn-SSZ-13-5.

wider pore distribution. The BET surface areas, pore sizes, and pore volumes are listed in Table 1. The BET surface area and pore volume of the Mn/SSZ-13 catalysts are clearly affected by the degree of Mn loading. With increasing of Mn loading over the entire range, the BET surface area is observed to decrease from $223.5 \text{ m}^2 \cdot \text{g}^{-1}$ to $119.2 \text{ m}^2 \cdot \text{g}^{-1}$, while the pore volume decreases from $0.14 \text{ cm}^3 \cdot \text{g}^{-1}$ to $0.10 \text{ cm}^3 \cdot \text{g}^{-1}$, suggesting that the micropores are blocked with Mn species or MnO_x species are aggregated on the surfaces of the catalysts.

3.7 NH_3 -TPD results

The surface acidity of the catalysts is one of the important factors in NH_3 -SCR. The NH_3 -TPD curves of the SSZ-13 and Mn/SSZ-13 catalysts are shown in Figure 9. Two desorption peaks are observed from the NH_3 -TPD profiles, corresponding to the acid strengths of the different acid sites.²⁶ The peak centered at about 210°C can be assigned to the weakly adsorbed NH_3 , which involves physisorbed NH_3 or NH_3 adsorbed at weak Lewis acid sites. The desorption peak at a temperature between 350°C to 550°C is assigned to NH_3 strongly adsorbed at strong Lewis acid sites.²⁷ However,

Table 2. Surface element composition of Mn-SSZ-13 catalyst with different loadings.

Sample	Mn/SSZ-13-1	Mn/SSZ-13-3	Mn/SSZ-13-5
$\text{O}_{\text{lattice}}/\text{O}_{\text{adsorbed}}$	2.11	9.31	40.4
$\text{Mn}^{4+}/\text{Mn}^{3+}$	1.03	1.14	1.38

Figure 8. Nitrogen adsorption–desorption isotherms and pore size distribution (inset) of (A) Mn-SSZ-13-1; (B) Mn-SSZ-13-3; (C) Mn-SSZ-13-5.

three peaks can be observed in the NH_3 -TPD results for the Mn/SSZ-13-5 catalyst. Here, a desorption peak is located at about 600°C , which can be attributed to NH_3 adsorbed at Brønsted acid sites.²⁸ Comparing SSZ-13 and Mn/SSZ-13 catalysts, the strong Lewis acid sites increased with the increase of Mn loading, indicating that the loading of manganese could increase the number of the strong Lewis acid sites, and the strong Lewis acid sites are beneficial to the adsorption and activation

Figure 9. NH_3 -TPD profiles of Mn-SSZ-13-1 (a); Mn-SSZ-13-3 (b); Mn-SSZ-13-5 (c); SSZ-13 (d).

of NH_3 . The NO_x conversion rate was affected by different acid sites. Both weak and strong Lewis acid sites can enhance the NH_3 -SCR reaction at low temperatures, while the stronger Brønsted acid sites can accelerate the oxidation of NH_3 to a certain extent, which results in a decreased SCR reaction activity, and leads to a lower catalytic efficiency.

Comparing the three Mn/SSZ-13 catalysts considered, increasing Mn loading corresponds to a decreasing number of weak Lewis acid sites, while the intensity of strong Lewis acid sites increases. The Mn/SSZ-13-3 catalyst demonstrates the largest number of strong Lewis acid sites, and consequently, exhibits the best low temperature catalytic activity. For the Mn/SSZ-13-5 catalyst, the number of weak and strong Lewis acid sites are relatively decreased, and Brønsted acid sites are observed, which are not conducive to the catalytic reaction, resulting in a reduced catalytic activity.

3.8 Catalytic mechanism of Mn/SSZ-13 catalysts

With regard to the role of lattice oxygen in the Mn/SSZ-13 catalysts, it is thought that the lattice oxygen has two functions; firstly, lattice oxygen can dehydrogenate NH_3 to form NH_2 species; and, secondly, lattice oxygen plays an important role in the formation of nitrite and nitrate species.^{29,30} The XPS results showed that the $\text{O}_{\text{lattice}}/\text{O}_{\text{adsorbed}}$ value of the Mn/SSZ-13-3 catalyst was larger. It is widely accepted that a high lattice oxygen content contributes to the SCR reaction.⁹

Based on the above results, we speculate that the NH_3 -SCR reaction of the Mn-supported catalysts proceeds according to the following pathway. (1) NH_3

Figure 10. NH_3 -SCR reaction process of Mn/SSZ-13 catalyst.

adsorbs on the Lewis acid sites of the Mn-based catalysts, and undergoes dehydrogenation by lattice oxygen and other surface atoms to form NH_2 surface species. (2) NH_2 surface species react with NO and N_2O to form nitrites or nitrates followed by transformation into amide intermediates, which then decompose into N_2 and H_2O .^{31,32} The possible reaction process is illustrated in Figure 10.

3.9 Factors affecting the catalytic performance of Mn/SSZ-13

The XRD and HRTEM results showed that the Mn species of the Mn/SSZ-13 catalysts consist of Mn_2O_3 and Mn_3O_4 species, and that no MnO_2 species were observed in the catalysts. Clear evidence, however, of extra amorphous MnO_2 on the surface of the catalysts was provided by XPS. Tang *et al.*, reported that, compared with crystalline manganese oxides, amorphous manganese oxides provide better SCR activity.³³ The NH_3 -SCR activity of manganese oxides in the Mn/SSZ-13 catalysts decreases in the following order: $\text{MnO}_2 < \text{Mn}_3\text{O}_4 < \text{MnO}$. Because amorphous MnO_2 possesses abundant oxygen vacancies and a high surface area, the NH_3 -SCR reaction demonstrates high catalytic activity at low temperature. Zhang *et al.*, reported that amorphous MnO_2 favors the introduction and release of protons, and this can accelerate the chemical adsorption/desorption and redox properties of the surfaces and interiors of the catalysts.³⁴ It is believed that the amorphous MnO_2 species on the Mn/SSZ-13 catalysts are beneficial to the SCR reaction.

XPS results showed that the Mn/SSZ-13 catalysts have high oxygen concentration on their surfaces, and previous research has reported that the presence of lattice oxygen plays an important role in the SCR.³⁵ Comparing Mn/SSZ-13-1 and Mn/SSZ-13-3 catalysts,

the increased value of $\text{O}_{\text{lattice}}/\text{O}_{\text{adsorbed}}$ corresponds with an increased NH_3 -SCR activity. While the value of $\text{O}_{\text{lattice}}/\text{O}_{\text{adsorbed}}$ for the Mn/SSZ-13-5 catalyst was the highest, the NH_3 -SCR conversion rate was observed to decrease sharply. The NH_3 -TPD results indicate that the acidity of the Mn/SSZ-13 catalysts affects SCR activity. The Mn/SSZ-13-3 catalyst was found to have the greatest number of weak and strong Lewis acid sites, which is conducive to the NH_3 -SCR reaction. However, while Mn/SSZ-13-5 has the greatest concentration of lattice oxygen with enhanced SCR activity, it also includes Brønsted acid sites, which can accelerate the oxidation of NH_3 , and is therefore not conducive to the formation of NH_2 intermediates, thereby reducing the SCR activity.

The distribution of metal particles on the surface of zeolite is usually related to the catalytic activity of its SCR reaction. Some degree of Mn loading is favorable for the SCR reaction, while excessive loading will reduce the dispersion of Mn in the material.

The larger specific surface area contributes to the dispersion of the active component and makes the active site of the catalyst exposed to the surface of the catalyst, which is more likely to react with the reactants. According to the BET results, when the Mn loading is less than 7.8%, the specific surface area of Mn-SSZ-13 catalyst is more than $217.4 \text{ m}^2 \cdot \text{g}^{-1}$, and the active component is well dispersed on the catalyst surface. However, the specific surface area of Mn-SSZ-13-5 catalyst is $119.2 \text{ m}^2 \cdot \text{g}^{-1}$. We know that the BET surface area and the pore volume decreased sharply with excessive Mn loading owing to channel blockage by Mn species or by the accumulation of Mn species on the surface of the catalysts, which leads to a reduced SCR activity. The Mn/SSZ-13-3 catalyst had a larger BET surface area and pore volume than the Mn/SSZ-13-5 catalyst. The catalyst also had a greater number of active components than the Mn/SSZ-13-1 catalyst, which is another important reason for the excellent catalytic activity observed.

When a relatively large Mn loading and lattice oxygen concentration are balanced with a relatively large BET surface area, conditions are most favorable for the NH_3 -SCR reaction, particularly for its low temperature catalytic activity. Wang *et al.*, reported that the NO_x conversion rate of an $\text{MnO}_x/\text{MWCNTs}$ catalyst attained 90% at 260°C .³⁶ However, in the present work, the NO_x conversion rate of the Mn/SSZ-13 catalysts attained 90% at a temperature of 150°C . The comparison indicates that the Mn/SSZ-13 catalyst has excellent low-temperature NH_3 -SCR activity, which provides very promising prospects for future applications.

4. Conclusions

In summary, Mn/SSZ-13 catalysts prepared by a co-precipitation method with a 4.74 wt% of Mn loading (*i.e.*, Mn/SSZ-13-3) showed the best NH₃-SCR activity among the prepared catalysts, as demonstrated by the high NO_x conversion rate with a wide temperature window (150–450°C). Higher Mn loading reduced the dispersion of the Mn species; thus, blocking the zeolite channels or causing agglomeration on the catalyst surface, which led to a decreased catalytic activity. Mn/SSZ-13 catalysts with an appropriate Mn loading demonstrated excellent physical and chemical properties such as a large pore volume and specific surface area. The Mn species in the Mn/SSZ-13-3 catalysts are mainly in the form of crystalline Mn₃O₄ and amorphous MnO₂, which are beneficial to the SCR reaction. However, the excessive Mn loading of the Mn/SSZ-13-5 catalyst led to decreased catalytic activity due to the aggregation or agglomeration of Mn species on the catalyst surface, and the formation of Brønsted acid sites, which are not conducive to the catalytic reaction. In addition, the good performance of the Mn/SSZ-13-3 catalyst, particularly its excellent low-temperature catalytic activity, was also related to the concentration of lattice oxygen, which is beneficial to the SCR reaction.

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