Enhanced Catalytic Performance of Hierarchical MnOₓ/ZSM-5 Catalyst for the Low-Temperature NH₃-SCR

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Abstract: A ZSM-5 zeolite with a hierarchical pore structure was synthesized by the desilication-recrystallization method using tetraethyl ammonium hydroxide (TEAOH) and cetyltrimethylammonium bromide (CTAB) as the desilication and structure-directing agents, respectively. The MnOₓ/ZSM-5 catalyst was synthesized by the ethanol dispersion method and applied for the low-temperature selective catalytic reduction of NOₓ with NH₃. The results showed that NOₓ conversion of the hierarchical MnOₓ/ZSM-5 catalyst could reach 100% at about 120 °C and could be maintained in the temperature range of 120–240 °C with N₂ selectivity over 90%. Furthermore, the hierarchical MnOₓ/ZSM-5 catalyst presented better SO₂ resistance performance than the traditional catalyst in the presence of 100 ppm SO₂ at 120 °C. XRD, SEM, TEM, XPS, BET, NH₃-TPD, and TG were applied to characterize the structural properties of the MnOₓ/ZSM-5 catalysts. These results showed that the MnOₓ/ZSM-5 catalyst had micropores (0.78 nm) and mesopores (3.2 nm) leading to a larger specific surface area, which improved the mass transfer of reactants and products while reducing the formation of sulfates. The better catalytic performance over hierarchical MnOₓ/ZSM-5 catalyst could be attributed to the higher concentration of Mn⁴⁺ and chemisorbed oxygen species and higher surface acidity. The improved SO₂ resistance was related to the catalyst’s hierarchical pore structure.

Keywords: hierarchical pore structure; MnOₓ/ZSM-5; NH₃-SCR; SO₂ resistance

1. Introduction

Selective catalytic reduction of NOₓ by NH₃ (NH₃-SCR) is the most widely applied technology to remove NOₓ from stationary sources. The catalyst is the key factor that can determine the efficiency of the selective catalytic reduction system [1]. The temperature window of traditional commercial catalyst (V₂O₅-WO₃(MoO₃)/TiO₂) is 300–400 °C, and low-temperature NH₃-SCR catalysts, which can be placed downstream of the desulfurizer and electrostatic precipitator, have attracted increasing attention in recent years [2]. Research on the low-temperature NH₃-SCR reaction using transition metal oxides (MnOₓ [3], FeOₓ [4], CuOₓ [5], CeOₓ [6]) as the active components has become widespread. Among these metal oxides, MnOₓ exhibits excellent low-temperature catalytic activity, which can be attributed to the variable valence states of manganese and oxygen species [7]. However, there still remains a challenge of SO₂ poisoning for low-temperature NH₃-SCR catalysts. The deposition of sulfite and sulfate species and sulfate of manganese oxide on the catalysts’ surface lead to the inhibition of the
catalysts. Therefore, improving the SO$_2$ tolerance of catalysts is required. Many efforts have been made to promote SO$_2$ tolerance of NH$_3$-SCR catalysts. Yu et al. [8] demonstrated that Pr modification could enhance the sulfur dioxide resistance of MnO$_x$/SAPO-34 catalyst. Compared with manganese oxide, SO$_2$ preferentially combines with PrO$_x$ to form praseodymium sulfate and protecting the active sites of Mn. Fan et al. [9] demonstrated that when the cerium oxides were incorporated in the framework and the surface of the Mn/SAPO-34 catalyst, the sulfate of the manganese oxide and the formation of NH$_3$HSO$_4$ could be inhibited. In recent years, catalysts with hierarchical pore structures have attracted much attention for environmental catalytic applications. Due to their adjustable pore sizes and unique structural properties, Gao et al. [10] demonstrated manganese oxide nanoparticles with a hierarchical mesopore structure in the walls of the macroporous skeleton supported by three-dimensionally ordered macroporous carbon, which exhibited better low-temperature NH$_3$-SCR reaction activity, stability, as well as H$_2$O and SO$_2$ resistance. Fang et al. [11] prepared foam-like Fe$_2$O$_3$@CuO$_x$ monolith catalysts with a three-dimensional hierarchical structure and displayed a higher activity, stability, as well as SO$_2$ and H$_2$O resistance than the catalyst without Fe$_2$O$_3$. In addition, some research studies have also focused on the hierarchical zeolite supported metal oxides. Pt nanoparticles were encapsulated in a hollow ZSM-5 through a “dissolution-recrystallization” process [12]. The Pt hollow ZSM-5 catalyst showed excellent SO$_2$ and H$_2$O tolerance, but the active temperature range of the catalyst was very narrow. When the catalyst showed a maximum NO conversion at 90 °C, the activity then decreased with increasing temperature. Other catalysts like hierarchical Fe/ZSM-5 [13], hierarchical Fe-Beta [14], and hierarchical Fe-ZSM-5@CeO$_2$ [15] were synthesized and applied in the SCR reaction.

The ZSM-5 zeolite has adjustable surface acidity, shape selectivity, and a stable framework structure, which has been widely applied as a carrier in the SCR reaction. In this work, a hierarchical ZSM-5 zeolite was successfully prepared via a desilication-recrystallization method, and cetyltrimethylammonium bromide (CTAB) was used as the structure-directing agent. The hierarchical MnO$_x$/ZSM-5 catalyst was synthesized by the ethanol dispersion method and applied in the NH$_3$-SCR reaction. We studied the effect of the hierarchical pore structure on the catalytic performance through comparison with a traditional MnO$_x$/ZSM-5 catalyst. The hierarchical MnO$_x$/ZSM-5 catalyst showed better low-temperature NH$_3$-SCR catalytic activity and higher SO$_2$ tolerance. Furthermore, XRD, SEM, TEM, XPS, BET, NH$_3$-TPD, and TG were employed to explore the structural properties of the MnO$_x$/ZSM-5 catalyst. The results of comparable MnO$_x$/ZSM-5 catalysts demonstrated that a larger specific surface area and pore size, higher surface acidity, and higher concentration of Mn$^{4+}$ and chemisorbed oxygen species could be provided by the hierarchical pore structure, thus promoting the low-temperature NH$_3$-SCR catalytic performance.

2. Results and Discussion

2.1. XRD Results

The XRD patterns of MnO$_x$/HZ-ET (hierarchical MnO$_x$/ZSM-5, the treated ZSM-5 was denoted as HZ-ET) and MnO$_x$/Z-P (conventional MnO$_x$/ZSM-5, ZSM-5 zeolite without treatment was denoted as Z-P) are shown in Figure 1. Two diffraction peaks between 2θ = 7 and 10° and three diffraction peaks between 2θ = 22 and 25° were observed, and these peaks were attributed to the characteristic diffraction peaks of the MFI zeolite, indicating that the MFI characteristic structure of ZSM-5 was not destroyed after desilication-recrystallization. No peaks of manganese oxide could be seen in the XRD spectra, indicating that manganese oxide in the catalyst existed either in an amorphous or highly dispersed state. TEM images would be used to further elucidate the structure of the MnO$_x$. The relative crystallinity results of MnO$_x$/HZ-ET and MnO$_x$/Z-P are shown in Table 1. Compared with the parent ZSM-5 (Z-P), the lower relative crystallinity (R$_C$) of the MnO$_x$/HZ-ET was attributed to the desilication, which destroyed the crystal structure [16] and the interaction between the MnO$_x$ and the zeolite [17]. The R$_C$ of MnO$_x$/HZ-ET was higher than MnO$_x$/Z-P because of recrystallization, which indicated that the framework structure of MnO$_x$/HZ-ET was more complete.
were exhibited in MnO$_2$ (110) plane of MnO$_2$ and the (222) plane of Mn$_2$O$_3$, respectively. Combined with the XRD analysis, the results of TEM images showed that manganese oxide was not amorphous, but existed in the form of crystalline structures.

Figure 3 shows TEM images of MnO$_x$/HZ-ET catalysts. Regular mesopores are observed in Figure 3c,d. The micropores and regular/irregular mesopores were exhibited in MnO$_x$/HZ-ET with different size ranges. HRTEM images of MnO$_x$/HZ-ET catalyst are shown in Figure 3e,f. The lattice fringe spacing of 0.437 nm in Figure 3f corresponds to the (021) plane of Mn$_3$O$_4$, while the lattice fringe spacings of 0.690 nm and 0.272 nm in Figure 3e correspond to the (110) plane of MnO$_2$ and the (222) plane of Mn$_2$O$_3$, respectively. Combined with the XRD analysis, the

Table 1. Relative crystallinity (RC) of the catalysts.

| Samples        | RC (%) |
|----------------|--------|
| Z-P            | 100    |
| MnO$_x$/HZ-ET  | 81.4   |
| MnO$_x$/Z-P    | 79.3   |

2.2. SEM and TEM Results

Figure 2 shows the SEM images of MnO$_x$/Z-P and MnO$_x$/HZ-ET catalysts. The two catalysts showed a hexagonal morphology of the characteristic MFI structure. Compared with the smooth surface of the MnO$_x$/Z-P catalyst (Figure 2a), the surface of the MnO$_x$/HZ-ET catalyst (Figure 2b) was rougher, and the pore structure could be seen on the surface.

![Figure 2. SEM images of the catalysts. (a) MnO$_x$/Z-P, (b) MnO$_x$/HZ-ET.](image)

Figure 3 shows TEM images of MnO$_x$/HZ-ET catalysts. Regular mesopores are observed in Figure 3a,b. At the same time, some irregular, larger pore size mesopores compared with the above regular mesopores can be observed in Figure 3c,d. The micropores and regular/irregular mesopores were exhibited in MnO$_x$/HZ-ET with different size ranges. HRTEM images of MnO$_x$/HZ-ET catalyst are shown in Figure 3e,f. The lattice fringe spacing of 0.437 nm in Figure 3f corresponds to the (021) plane of Mn$_3$O$_4$, while the lattice fringe spacings of 0.690 nm and 0.272 nm in Figure 3e correspond to the (110) plane of MnO$_2$ and the (222) plane of Mn$_2$O$_3$, respectively. Combined with the XRD analysis, the
results of TEM images showed that manganese oxide was not amorphous, but existed in various forms of crystallization in highly dispersed states. The (110) planes of MnO$_2$ in Figure 3e was considered as the most active crystal plane in the NH$_3$-SCR reaction [18] and provided a large number of active sites and oxygen vacancies. This was one of the reasons why the MnO$_x$/HZ-ET catalyst showed better low-temperature SCR activity than MnO$_x$/Z-P.

![TEM images](image)

**Figure 3.** (a–d) TEM images of the MnO$_x$/HZ-ET, (e–f) HR-TEM images of the MnO$_x$/HZ-ET.

### 2.3. BET Results

Figure 4 shows the nitrogen adsorption-desorption isotherms and the pore size distribution curves of MnO$_x$/Z-P and MnO$_x$/HZ-ET catalysts. Figure 4a shows that MnO$_x$/Z-P exhibited type I isotherms with no distinct hysteresis loop, which indicated that MnO$_x$/Z-P was a typical microporous material, where MnO$_x$/HZ-ET displayed typical type I isotherms at low relative pressure ($P/P_0 < 0.01$) and type IV isotherms with a clear hysteresis loop at higher relative pressure ($P/P_0 > 0.4$), demonstrating the co-existence of micropores and mesopores created through the desilication-recrystallization processes. Figure 4b shows that the micropore size distributions of MnO$_x$/HZ-ET catalyst centered around 0.78 nm, which was larger than that of MnO$_x$/Z-P (around 0.73 nm). The enlargement of the micropores in MnO$_x$/HZ-ET may be due to the destruction of pore walls by treatment with TEAOH [19]. The pore size distribution of MnO$_x$/Z-P (Figure 4b) showed no obvious peaks in the range of 2–20 nm, and MnO$_x$/HZ-ET showed a narrow and intense peak at 3.2 nm. In addition, MnO$_x$/HZ-ET showed broad peaks between 4 and 15 nm, which possibly indicated that the intracrystalline mesopores were caused by desilication and existed in an irregular state [16]; this result was consistent with the TEM images.
2.4. XPS Results

The surface atomic composition was analyzed by XPS. Figure 5 shows the XPS spectra of Mn 2p and O 1s for the MnOx/Z-P and MnOx/HZ-ET catalysts. The XPS spectra of Mn 2p3/2 could be fit into three characteristic peaks ascribed to Mn2+ at 640.4 eV, Mn3+ at 642.0 eV, and Mn4+ at 644.1 eV. The XPS spectra of O 1s could be divided into two characteristic peaks ascribed to lattice oxygen species (Oα), around 529.7 eV, and chemisorbed oxygen species (Oβ), around 531.5 eV [20]. The corresponding results are summarized in Table 3. It was clear that the molar concentration of manganese on the surface of MnOx/HZ-ET (9.62%) was higher than MnOx/Z-P (8.47%), and the relative surface concentration ratios of Mn4+ (Mn4+/Mn) of MnOx/HZ-ET (49.09%) were much higher than MnOx/Z-P (36.36%). It was reported that Mn4+ could promote the oxidation of NO to NO2, and higher concentration ratios of Mn4+ species were beneficial for the improvement of their redox cycle, thus promoting the activity in the NH3-SCR reaction at low temperatures [21]. In addition, the percentage of chemisorbed oxygen species Oβ in MnOx/HZ-ET (87.09%) was much higher than MnOx/Z-P (75.41%). The chemisorbed oxygen species Oβ was reported to be more active than Oα because of their higher mobility. Higher percentage of Oβ was beneficial for the oxidation of NO to NO2, enhancing the low-temperature activity through the “fast SCR” reaction [22]. Therefore, the excellent low-temperature SCR activity of MnOx/HZ-ET was attributed to the higher percentage of active Mn4+ and chemisorbed oxygen species.
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The NH3 desorption of the catalysts. The NH3 desorption profiles of MnOx/HZ-ET and MnOx/Z-P exhibited two distinct desorption peaks. The desorption peaks below 350 °C were associated with the weakly acidic sites, while the desorption peaks ranging from 350 to 550 °C were associated with the strongly acidic sites [23]. The quantified results of NH3-TPD are summarized in Table 4, and the area of the peak was proportional to the amount of acid. It could be found that MnOx/Z-P, which may be ascribed to the higher specific surface area of the MnOx/HZ-ET catalyst. It could be concluded that MnOx/HZ-ET with a hierarchical pore structure could provide more strong surface acidity sites, which would be beneficial for the adsorption and activation of NH3, resulting in increased low-temperature NH3-SCR performance.

2.5. NH3-TPD Results

The surface acidity properties of the catalysts were analyzed by the NH3-TPD technique. Figure 6 shows that the NH3 desorption profiles of MnOx/HZ-ET and MnOx/Z-P exhibited two distinct desorption peaks. The desorption peaks below 350 °C were associated with the weakly acidic sites, while the desorption peaks ranging from 350 to 550 °C were associated with the strongly acidic sites [23]. The quantified results of NH3-TPD are summarized in Table 4, and the area of the peak was proportional to the amount of acid. It could be found that MnOx/HZ-ET showed more total acid amount than MnOx/Z-P. Although the weak acid amount of MnOx/Z-P was higher than MnOx/HZ-ET, the strong acid and total acid amount of MnOx/HZ-ET were both higher than MnOx/Z-P, which may be ascribed to the higher specific surface area of the MnOx/HZ-ET catalyst. It could be concluded that MnOx/HZ-ET with a hierarchical pore structure could provide more strong surface acidity sites, which would be beneficial for the adsorption and activation of NH3, resulting in increased low-temperature NH3-SCR performance.

Table 3. Surface atomic concentrations and relative concentration ratios of Mn and O.

| Sample       | Atomic Fraction(%) | XO/(%)    | Xmn/(%)  |
|--------------|---------------------|-----------|----------|
|              | Mn      | O        | Others  | Oα      | Oβ      | Mn2+     | Mn3+     | Mn4+     |
| MnOx/HZ-ET   | 9.62    | 58.51    | 31.87   | 12.91   | 87.09   | 9.78     | 41.12    | 49.10    |
| MnOx/Z-P     | 8.47    | 58.85    | 32.68   | 24.59   | 75.41   | 15.35    | 48.29    | 36.36    |

Figure 5. XPS spectra of Mn 2p (a), O 1s (b) of the catalysts.

Figure 6. NH3-TPD of the catalysts.
Low-temperature NH₃-SCR activities and N₂ selectivities of MnOₓ/HZ-ET and MnOₓ/Z-P were tested over the temperature range of 80–240 °C, and the results of the NOₓ conversion are shown in Figure 7. The MnOₓ/Z-P catalyst showed low NOₓ conversion in the temperature range of 80–180 °C, and 99% NOₓ conversion was obtained around 180 °C. Meanwhile, the N₂ selectivity of MnOₓ/Z-P was lower than 90% over the whole temperature range. Compared with MnOₓ/Z-P, MnOₓ/HZ-ET showed significantly higher NOₓ conversion over the temperature range of 80–120 °C. When the temperature reached 120 °C, nearly 100% NOₓ conversion could be obtained with a broader operating temperature window (120–240 °C). Over 90% N₂ selectivity could be maintained for the MnOₓ/HZ-ET catalyst throughout the entire temperature range. Conventional microporous catalysts were reported to have several drawbacks in the SCR reaction, such as diffusion limitations of the reactants and products [24]. Therefore, it was reasonable to deduce that the mass transfer of reactants and products could be enhanced with the existence of mesopores at low temperatures, and as a result of this, better low-temperature NH₃-SCR performance could be obtained using the hierarchical MnOₓ/HZ-ET catalyst.

2.6. SCR Performance

2.7. Effect of SO₂ on SCR Catalytic Activity

Figure 8 shows the NOₓ conversion for the MnOₓ/HZ-ET and MnOₓ/Z-P catalysts in the presence of 100 ppm SO₂ at 120 °C and 180 °C, respectively. The results showed that NOₓ conversion noticeably decreased with the addition of SO₂ into the feed gas. The SCR activity of the MnOₓ/Z-P catalyst decreased from 100% to 15% after 60 min of SO₂ addition. The NOₓ conversion of MnOₓ/HZ-ET decreased from 100% to 60% after the SO₂ was added for 1 h. The NOₓ conversion could not be recovered over the two catalysts when SO₂ was absent from the reaction mixture, which indicated that the deactivation was reversible. (NH₄)₂SO₄ or NH₄HSO₄ may be formed during the reaction when SO₂ was added into the reaction atmospheres. These species could only decompose over 300 °C and may block the zeolite channels, leading to reduced catalytic activities. At the same time, catalysts with a larger pore size could reduce the formation of sulfate species [25]. Comparing the SO₂ tolerance of MnOₓ/HZ-ET and MnOₓ/Z-P, the hierarchical pore structure MnOₓ/HZ-ET catalyst could provide larger specific surface area and larger pore size, which was beneficial for its SO₂ resistance.

### Table 4. The NH₃ desorption of the catalysts.

| Sample       | Area of Peak | Total Area of Peaks |
|--------------|--------------|---------------------|
|              | Peak 1       | Peak 2              |                      |
| MnOₓ/HZ-ET   | 1415         | 1671                | 3086                |
| MnOₓ/Z-P     | 1878         | 1042                | 2920                |

![Figure 7](image_url) SCR activity (a) and N₂ selectivity (b) of MnOₓ/HZ-ET and MnOₓ/Z-P catalysts with a Mn loading of 15 wt.%.
XRD and TG were applied to identify the formation of (NH₄)₂SO₄ or NH₄HSO₄. Figure 9 shows the XRD patterns of poisoned MnOₓ/HZ-ET and MnOₓ/Z-P catalysts. The peak at 2θ = 33° observed over the used MnOₓ/Z-P could be attributed to the phase of formed NH₄HSO₄. No obvious peaks of NH₄HSO₄ could be observed in the XRD pattern of used MnOₓ/HZ-ET, which may be because the NH₄HSO₄ formed existed in amorphous species or was below the detection limit. Figure 10 presents the XRD patterns of poisoned MnOₓ/HZ-ET and MnOₓ/Z-P catalysts. The first weight loss emerging at 80–110 °C could be due to the evaporation of water in the catalysts. Two other weight losses at about 250 °C and 350 °C were close to the decomposition temperature of (NH₄)₂SO₄ or NH₄HSO₄ [8]. For MnOₓ/HZ-ET, the intensities of two weight losses was lower than that of MnOₓ/Z-P. The XRD and TG results showed that the MnOₓ/HZ-ET with a larger pore size could reduce the deposition of (NH₄)₂SO₄ or NH₄HSO₄ on the catalyst surface during the NH₃-SCR reaction with SO₂, which was one of the reasons for the better SO₂ resistance of the MnOₓ/HZ-ET catalyst.

![Figure 9. XRD patterns of the catalysts used.](image-url)

Figure 8. The SO₂ tolerance tests over the MnOₓ/HZ-ET and MnOₓ/Z-P; reaction conditions: 800 ppm NH₃, 800 ppm NO, 100 ppm SO₂, 5 vol. % O₂, Ar to balance, gas hourly space velocity (GHSV) = 40,000 h⁻¹.
3. Materials and Methods

3.1. Catalyst Preparation

The hierarchical ZSM-5 was prepared from commercial MFI-type zeolites by sequential desilication-recrystallization based on previous studies [16,19,26]. The parent zeolite in this study was a commercial H form ZSM-5 with a Si/Al mass ratio = 38 (XFNANO Company, Nanjing, China). Typically, three grams of ZSM-5 zeolite and 1 g cetyltrimethylammonium bromide (CTAB, Aladdin, Shanghai, China) were dispersed in 30 mL of 1 M tetraethyl ammonium hydroxide (TEAOH, Aladdin, Shanghai, China), and the mixture was stirred at ambient temperature. The solution was transferred into a Teflon-lined autoclave and treated at 150 °C for 24 h. The product was washed with distilled water, filtered, dried, and calcined at 550 °C for 4 h to remove the templates. The treated sample was denoted as HZ-ET, and for comparison, the ZSM-5 zeolite without treatment was denoted as Z-P.

The catalysts were synthesized by the ethanol dispersion method, and manganese nitrate (50 wt.% in H2O, Aladdin, Shanghai, China) was used as a precursor. Typically, one-point-nine-five grams of 50 wt.% Mn(NO3)2 (Mn loading = 15 wt.%) were dissolved in 75 mL ethanol under stirring at ambient temperature. Subsequently, two grams of HZ-ET or Z-P powder were added and stirred. Then, the solution was treated with ultrasound for 0.5 h and stirred continuously at 85 °C until the solvent was completely evaporated. The products were dried at 80 °C and calcined at 400 °C for 3 h. The catalyst was denoted as MnOx/HZ-ET. For comparison, MnOx/Z-P was also prepared according to the same method.

3.2. Low-Temperature NH3-SCR Activity Measurements

The NH3-SCR activity tests were carried out in a fixed-bed quartz glass reactor. Five-hundred milligrams of 40–60 mesh catalysts were used in the test. The reaction temperature was increased from room temperature to 240 °C with a heating rate of 5 °C/min with an isotherm step of 20 °C. The gas was composed of 800 ppm NH3, 800 ppm NO, 5.0 vol% O2, and 100 ppm SO2 (when added), balanced by Ar. The flow rate was 600 mL/min with a gas hourly space velocity (GHSV) of 40,000 h−1. The concentrations of NO/NO2 were measured by a NO–NO2–NOx analyzer (Thermal Scientific, model 42i-HL, Waltham, USA), and N2 gas chromatography was used to analyze N2-selectivity. The NOx removal efficiency and the N2 selectivity are calculated as follows:

\[
\text{NOx conversion} = \frac{[\text{NOx}]_{\text{inlet}} - [\text{NOx}]_{\text{outlet}}}{[\text{NOx}]_{\text{inlet}}} \times 100\% \quad (1)
\]

\[
\text{N2 selectivity} = (1 - \frac{2[\text{N2O}]_{\text{outlet}}}{[\text{NOx}]_{\text{inlet}} + [\text{NH3}]_{\text{inlet}} - [\text{NOx}]_{\text{outlet}} - [\text{NH3}]_{\text{outlet}}} \times 100\% \quad (2)
\]

Figure 10. TG profiles of the catalysts used. (a) MnOx/Z-P-SO2, (b) MnOx/HZ-ET-SO2.
where $[\text{NO}_x]_{\text{inlet}}$ and $[\text{NH}_3]_{\text{inlet}}$ represent the inlet concentration (ppm) of NO$_x$ and NH$_3$, respectively. $[\text{NO}_x]_{\text{outlet}}$, $[\text{NH}_3]_{\text{outlet}}$, and $[\text{N}_2\text{O}]_{\text{outlet}}$ represent the outlet concentration (ppm) of NO$_x$ and NH$_3$ and N$_2$O, respectively.

3.3. Characterization

X-ray diffraction (XRD) patterns were recorded on a D8 Advance diffractometer (Bruker, Karlsruhe, Germany) with Cu Kα radiation. Chemical states of all elements were analyzed by X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD, Kratos, U.K.) with Al Kα radiation ($h\nu = 1253.6$ eV). NH$_3$-TPD analysis was performed on Tp 5080 (Xianquan Industrial and Trading Co., Ltd, Tianjin, China). A scanning electron microscope (SEM) was carried out on ZEISS Merlin instrument (Carl Zeiss AG, Jena, Germany). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed on TECNAI G2 F20 (FEI, Hillsboro, OR, USA). N$_2$ physisorption was performed at $-196^\circ$C using a surface analyzer (Micromeritics, ASAP 2020, Norcross, USA), and all samples were degassed in a vacuum at 30 $^\circ$C for 6 h prior to measurements. The Brunauer–Emmett–Teller (BET) method was used to calculate the specific surface area. The micropore surface area and micropore volume were evaluated using a $t$-plot. The Barrett–Joyner–Halenda (BJH) method was used to determine the pore size distributions from desorption branches. Thermogravimetric analysis (TG) was carried out in a static N$_2$ atmosphere using a TGA/DSC 3+ instrument (Mettler, Zurich, Switzerland). Fifteen milligrams of each sample were analyzed between 30 and 800 $^\circ$C at a rate of 10 $^\circ$C/min.

4. Conclusions

A MnO$_x$/HZ-ET catalyst, which possessed a hierarchical pore structure, was successfully prepared through desilication-recrystallization and ethanol dispersion methods. Compared with MnO$_x$/Z-P prepared using traditional microporous ZSM-5 as a support, MnO$_x$/HZ-ET showed better low-temperature NH$_3$-SCR activity with nearly 100% NO$_x$ conversion over a broad temperature window from 120 $^\circ$C to 240 $^\circ$C and above 90% N$_2$ selectivity throughout the entire temperature range. The low temperature NH$_3$-SCR performance of MnO$_x$/HZ-ET could be attributed to the hierarchical pore structure, higher concentration of chemisorbed oxygen and Mn$^{4+}$ species, as well as appropriate acid strengths and amounts. The MnO$_x$/HZ-ET catalyst also showed better SO$_2$ tolerance than the MnO$_x$/Z-P, and 60% NO$_x$ conversion could be maintained after the SO$_2$ was added for 1 h, which could be related to its larger specific surface area and larger pore size, which may reduce the deposition of ammonium sulfate.

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