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New Insight into the In Situ SO₂ Poisoning Mechanism over Cu-SSZ-13 for the Selective Catalytic Reduction of NO_x with NH₃

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Abstract: To reveal the nature of SO₂ poisoning over Cu-SSZ-13 catalyst under actual exhaust conditions, the catalyst was pretreated at 200 and 500 °C in a flow containing NH₃, NO, O₂, SO₂, and H₂O. Brunner–Emmet–Teller (BET), X-ray diffraction (XRD), thermo gravimetric analyzer (TGA), ultraviolet Raman spectroscopy (UV Raman), temperature-programmed reduction with H₂ (H₂-TPR), temperature-programmed desorption of NO+O₂ (NO+O₂-TPD), NH₃-TPD, in situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS), and an activity test were utilized to monitor the changes of Cu-SSZ-13 before and after in situ SO₂ poisoning. According to the characterization results, the types and generated amount of sulfated species were directly related to poisoning temperature. Three sulfate species, including (NH₄)₂SO₄, CuSO₄, and Al₂(SO₄)₃, were found to form on CZ-S-200, while only the latter two sulfate species were observed over CZ-S-500. Furthermore, SO₂ poisoning had a negative effect on low-temperature selective catalytic reduction (SCR) activity, which was mainly due to the sulfation of active sites, including Z₂Cu, ZCuOH, and Si-O(H)-Al. In contrast, SO₂ poisoning had a positive effect on high-temperature SCR activity, owing to the inhibition of the NH₃ oxidation reaction. The above findings may be a useful guideline to design excellent SO₂-resistant Cu-based zeolite catalysts.

Keywords: NH₃-SCR; Cu-SSZ-13; in situ SO₂ poisoning; copper sulfate; ammonium sulfate

1. Introduction

For a decade or so, Cu-SSZ-13 zeolite with a chabazite (CHA) topological structure has been extensively used/investigated for the ammonia selective catalytic reduction of NO_x (NH₃-SCR) from diesel engine emissions [1–3]. In general, Cu-SSZ-13 is prepared by solution ion-exchange method using NH₄-SSZ-13 and Cu salts [1,4] and one-pot methods [5–7]. According to recent research findings, active Cu species in Cu-SSZ-13 are present as two types [8,9]: (1) Cu²⁺ ions balanced by two adjacent negative framework charges (Z₂Cu) of the 6-membered ring; (2) [Cu(OH)]⁺ species balanced by one negative framework charge (ZCuOH) of the 8-membered ring. Furthermore, these active Cu species could transform into other active-type species under different conditions, such as [(NH₃)₂Cu^{II}-O₂-Cu^{II}(NH₃)₂] species [10].

Despite the above achievements, there are still some questions existing about Cu-SSZ-13 under actual exhaust conditions. Among them, SO_2 poisoning deactivation has been recognized as a substantial barrier for its wide practical application. To date, the impact of SO_2 poisoning on the selective catalytic reduction (SCR) performance of Cu-SSZ-13 and the corresponding deactivation mechanism have been investigated and can be summarized as follows: (1) low-temperature SCR activity was severely influenced, while high-temperature SCR activity seemed almost unaffected [11]. Nevertheless, low-temperature SCR activity is rather important because of the increased challenge in reducing NO_x emission during a cold start period or low-load condition [12]. (2) Three sulfate species, namely sulfuric acid (H_2SO_4), copper sulfate (CuSO_4), and aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$), formed on Cu-SSZ-13 when it was exposed to $\text{SO}_2 + \text{O}_2$ atmosphere [13]. Note that two active Cu species, i.e., Z_2Cu and ZCuOH , poisoned by SO_2 were very different. ZCuOH species more easily interacted with SO_2 to form CuSO_4 [14]. Furthermore, ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) would generate in case of the coexistence of SO_2 and NH_3 [15]. This poisoning behavior exhibited a reversible nature and had a threshold of about 350°C due to decomposition of $(\text{NH}_4)_2\text{SO}_4$ [14]. (3) The presence of SO_3 was found to cause more serious deactivation over Cu-SSZ-13 [16]. Moreover, the active sites interacted with SO_2 and SO_3 via different reaction mechanisms [17]. (4) The SCR activity of poisoned Cu-SSZ-13 could be partially recovered using a high-temperature treatment [18].

Overall, previous studies have systematically investigated the effect of SO_2/SO_3 poisoning on Cu-SSZ-13. However, little attention has been paid to the impact of SO_2 poisoning on Cu-SSZ-13 under actual exhaust conditions. Herein, a deactivation study of Cu-SSZ-13 was conducted using SO_2 exposure under SCR conditions at 200 and 500°C . The effect of in situ SO_2 poisoning on SCR performance was investigated. Furthermore, various techniques were employed to reveal the underlying in situ SO_2 poisoning mechanism.

2. Results

2.1. Catalyst Characterization

2.1.1. BET Results

The N_2 adsorption–desorption isotherms of Cu-SSZ-13 before and after in situ SO_2 poisoning are shown in Figure 1. All the isotherms can be ascribed to type I, the characteristic physical adsorption of microporous materials, according to Brunauer–Deming–Deming–Teller (BDDT) classification. Furthermore, the N_2 physisorption results of the investigated samples are summarized in Table 1. It can clearly be seen that in situ SO_2 poisoning had a significant impact on the surface area and pore volume of CZ-F, possibly due to the blocking effect of sulfate species [19]. Furthermore, the decrease degree of S_{BET} and V_{total} for CZ-S-200 was more serious than that for CZ-S-500, possibly due to the fact that more sulfate species were generated during the in situ SO_2 poisoning process.

Figure 1. N_2 adsorption–desorption isotherms of Cu-SSZ-13 before and after in situ SO_2 poisoning.

Table 1. Textural properties and NH_3 and NO_x capacities of Cu-SSZ-13 before and after in situ SO_2 poisoning.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{total} ($\text{cm}^3 \text{g}^{-1}$)	NH_3 Storage Capacity ($\mu\text{mol g}^{-1}$)	NO_x Storage Capacity ($\mu\text{mol g}^{-1}$)
CZ-F	543	0.31	250.8	36.6
CZ-S-200	439	0.26	325.5	6.1
CZ-S-500	509	0.30	308.5	22.8

2.1.2. XRD Results

The XRD patterns of Cu-SSZ-13 before and after in situ SO_2 poisoning were characterized and the results are shown in Figure 2. CZ-F showed typical chabazite (CHA) structure (PDF #52-0784). Furthermore, no diffraction peaks of CuO phases (PDF #48-1548) were observed, suggesting that Cu species in this sample were (1) in the form of isolated Cu^{2+} ions; (2) highly defective and non-crystalline; (3) crystalline but with particle sizes lower than the XRD detection limit. After in situ SO_2 poisoning at 200 and 500 °C, no diffraction peaks of sulfate species were observed over CZ-S-200 and CZ-S-500. Meanwhile, the relative crystallinities of these two samples were still high, indicating that SO_2 poisoning did not damage the CHA structure.

Figure 2. XRD patterns of Cu-SSZ-13 before and after in situ SO_2 poisoning.

2.1.3. TGA Results

Figure 3 shows the TGA profiles of Cu-SSZ-13 before and after in situ SO_2 poisoning. Sample weight loss was found in one temperature regime over CZ-F, while it was found in three and four temperature regimes over CZ-S-200 and CZ-S-500, respectively. The dramatic weight loss below 200 °C observed over all the samples can be assigned to the evaporation of adsorbed H_2O [20]. Weight loss at 300–500 °C was only found over CZ-S-200, which can be attributed to the decomposition of $(\text{NH}_4)_2\text{SO}_4$ species [21]. Weight loss at 500–800 °C was observed over CZ-S-200 and CZ-S-500, which can be ascribed to the decomposition of CuSO_4 species [14]. Note that the weight loss in this temperature region for CZ-S-500 was obviously higher than that for CZ-S-200, indicating that more copper sulfate species were formed as SO_2 poisoning temperature increased, well consistent with the previous study [22]. Furthermore, a slight weight loss above 800 °C was observed over CZ-S-200 and CZ-S-500, which can be due to the decomposition of $\text{Al}_2(\text{SO}_4)_3$ species [13]. Furthermore, the weight loss above 300 °C decreased in the order of CZ-S-200 (2.32 wt%) > CZ-S-500 (1.88 wt%), thereby proving that more sulfate species were generated during the in situ SO_2 poisoning process.

Figure 3. TGA profiles of Cu-SSZ-13 before and after in situ SO_2 poisoning. All the samples were tested in a flow of air.

2.1.4. UV Raman Results

UV Raman spectra were collected for Cu-SSZ-13 before and after in situ SO_2 poisoning. As shown in Figure 4, the spectrum of CZ-F mainly contained five bands at 330, 475, 800, 1060, and 1200 cm^{-1} . The band at 330 cm^{-1} can be assigned to the T-O-T vibration mode of the 6-membered rings of CHA structure, while the band at 475 cm^{-1} can be attributed to the $\nu_s(\text{T-O-T})$ mode of a combination of 4-, 6-, and 8-member rings of CHA structure [23,24]. Meanwhile, the bands at 800 and 1060/1200 cm^{-1} were typical symmetric and nonsymmetric Si-O stretching vibration modes of zeolite SSZ-13 [25]. Note that no bands related to copper species were observed over CZ-F. Specially, the absence of a band at 350 cm^{-1} indicates that this sample does not contain Cu-O-Cu species [26]. After in situ SO_2 poisoning, except for the above bands, a new band at 1142 cm^{-1} due to asymmetric S-O stretching vibrations appeared over CZ-S-200 and CZ-S-500 [27], further confirming that surface sulfate species exist in these two samples.

Figure 4. UV Raman spectra of Cu-SSZ-13 before and after in situ SO_2 poisoning: (a) CZ-F, (b) CZ-S-200, and (c) CZ-S-500.

2.1.5. H₂-TPR Results

Temperature-programmed reduction with H₂ (H₂-TPR) measurements were carried out to characterize the redox property of Cu-SSZ-13 before and after in situ SO₂ poisoning. According to previous studies, for Cu-SSZ-13, the reduction of isolated Cu²⁺ to Cu⁺ occurs below 600 °C, while the reduction of Cu⁺ to Cu⁰ occurs at much higher temperatures [4]. It is important to note that the reduction of CuO to Cu⁰ occurs at about 300 °C [7]. As shown in Figure 5, the main existence of Cu species in CZ-F was in the form of Cu²⁺ ions. After in situ SO₂ poisoning, two new H₂ consumption peaks were observed over CZ-S-200 and CZ-S-500. The peak around 200–300 °C can be assigned to the reduction of Cu²⁺ in CuSO₄, while the peak around 400–600 °C can be attributed to the reduction of SO₄^{2−} in CuSO₄ and (NH₄)₂SO₄ [22]. Note that the peak intensity below 200 °C decreased distinctly after in situ SO₂ poisoning, due to the fact that Cu²⁺ ions, including ZCuOH and Z₂Cu species, can interact with SO₂ to form CuSO₄ species. Furthermore, the reduction of Cu²⁺ in CuSO₄ to Cu⁰ only required one single step [28], which led to significantly higher H₂ consumption over CZ-S-200 and CZ-S-500 compared to CZ-F.

Figure 5. Temperature-programmed reduction with H₂ (H₂-TPR) profiles of Cu-SSZ-13 before and after in situ SO₂ poisoning.

2.1.6. NO+O₂-TPD Results

Figure 6 shows the temperature-programmed desorption of NO+O₂ (NO+O₂-TPD) profiles of Cu-SSZ-13 before and after in situ SO₂ poisoning. The desorbed NO_x species (NO and NO₂) over CZ-F, CZ-S-200, and CZ-S-500 were mainly from weakly adsorbed NO_x, surface nitrite, and nitrate species. Furthermore, the NO_x storage capacities of the catalysts were calculated from Figure 6 and the results are shown in Table 1. Compared to CZ-F, the NO_x storage capacities of CZ-S-200 and CZ-S-500 decreased significantly. Based on the above characterization results, it is reasonable to presume that the formation of sulfate species suppressed the adsorption of NO_x species on the catalyst surface. Note that except for weakly adsorbed NO, the formation of other adsorbed NO_x species starts with NO oxidation to produce gaseous NO₂, which then adsorbs on the catalyst surface in the form of weakly adsorbed NO₂, nitrite, and nitrate species [29]. Therefore, for CZ-S-200, the degradation of NO_x storage capacities could be owing to (1) the coverage of adsorption sites by the generated (NH₄)₂SO₄ species; and (2) the inhibition of oxidation of NO to NO₂ by Cu species interacting with SO₂ to form CuSO₄ species. Nevertheless, the degradation of NO_x storage capacities for CZ-S-500 could be caused by point (2). Furthermore, from Table 1, it could also be concluded that the influence of point (1) on NO_x storage capacity was obviously stronger than point (2).

Figure 6. Temperature-programmed desorption of NO+O₂ (NO+O₂-TPD) profiles of Cu-SSZ-13 before and after in situ SO₂ poisoning.

2.1.7. NH₃-TPD Results

NH₃-TPD experiments were performed to investigate the Brønsted and Lewis acid sites of Cu-SSZ-13 before and after in situ SO₂ poisoning. As shown in Figure 7, three main NH₃ desorption states were observed over CZ-F, CZ-S-200, and CZ-S-500: a low-temperature feature below 250 °C assigned to physisorbed NH₃, a medium-temperature feature at about 250–425 °C attributed to NH₃ adsorbed on Lewis acid sites (i.e., Cu²⁺ ions), and a high-temperature feature above 425 °C due to NH₃ adsorbed on Brønsted acid sites (i.e., Si-O(H)-Al sites) [30,31]. In addition, NH₃ storage capacities of the catalysts were calculated from Figure 8 and the results are shown in Table 1. Obviously, NH₃ storage capacity was improved after in situ SO₂ poisoning, which might be due to (1) newly generated acidic sites in the form of S-OH; and (2) decomposition of formed (NH₄)₂SO₄ species (only for CZ-S-200). Note that the Brønsted acid sites decreased significantly after in situ SO₂ poisoning, suggesting the bond breakage of Si-O(H)-Al sites and the corresponding Al atoms transforming into Al₂(SO₄)₃ [32]. However, the amount of reduction in Brønsted acid sites was almost unchanged as SO₂ poisoning temperature increased, indicating that the amount of Al₂(SO₄)₃ species generated at different SO₂ poisoning temperature remain constant. Note that as a result of the coaction of the abovementioned reasons, CZ-S-200 had much stronger NH₃ storage capacity in comparison with CZ-S-500.

Figure 7. NH₃-TPD profiles of Cu-SSZ-13 before and after in situ SO₂ poisoning.

Figure 8. In situ DRIFTS spectra of Cu-SSZ-13 before and after in situ SO_2 poisoning using NH_3 as probe molecule.

2.1.8. In Situ DRIFTS Results

To further investigate the changes of Cu species in SO_2 poisoning samples, in situ DRIFTS measurements were carried out using NH_3 as a probe molecule. It is well known that the symmetric and asymmetric T-O-T vibrations of zeolite SSZ-13 disturbed by Cu species are in the band range of $850\text{--}1000\text{ cm}^{-1}$ [33]. As shown in Figure 8, two negative bands were obviously observed over CZ-F. Based on the previous research, the band at about 898 cm^{-1} can be assigned to Z_2Cu ions, i.e., Cu^{2+} , located in the 6-member rings [34], while the band at about 950 cm^{-1} can be ascribed to ZCuOH ions, i.e., $[\text{Cu}(\text{OH})]^+$, located in the 8-member rings of CHA cages [8]. After SO_2 poisoning at $200\text{ }^\circ\text{C}$, the band intensity of both ZCu and ZCuOH decreased dramatically over CZ-S-200. This may be due to (1) the two Cu species being able to interact with SO_2 and ZCuOH being more reactive with SO_2 [14]; and (2) the two Cu species being partially covered by the generated $(\text{NH}_4)_2\text{SO}_4$. As a result, the above possible reasons led to reducing the disturbing influence of the Cu species on T-O-T vibrations. Note that the band assigned to ZCu species almost disappeared, indicating that the coverage of $(\text{NH}_4)_2\text{SO}_4$ had a far greater impact on ZCu sites. By contrast, Cu species interacting with SO_2 were mainly a reason that accounted for the decrease in band intensity over CZ-S-500, because $(\text{NH}_4)_2\text{SO}_4$ had decomposed completely at $200\text{ }^\circ\text{C}$ (Figure 3). Note that the degree of decrease in ZCuOH species was obviously higher than that for Z_2Cu , further confirming that ZCuOH was more reactive with SO_2 .

2.2. NH_3 -SCR and NH_3 Oxidation Performances

The standard NH_3 -SCR light-off curves of NO_x for Cu-SSZ-13 before and after in situ SO_2 poisoning are depicted in Figure 9a, in which their corresponding N_2 selectivity is also shown. CZ-F exhibited over 80% NO_x conversion at about $200\text{--}550\text{ }^\circ\text{C}$. After in situ SO_2 poisoning, CZ-S-200 and CZ-S-500 had obviously lower NO_x conversions below $300\text{ }^\circ\text{C}$, while they showed higher NO_x conversions above $350\text{ }^\circ\text{C}$. Note that the impact of in situ SO_2 poisoning on low-temperature SCR activity was lower than the simple sulfation at same temperature [17]. This may be due to the competitive adsorption between SO_2 and NH_3/NO on the active sites, which could slow the formation of sulfate species on the catalyst surface. As for the improved high-temperature SCR activity, we will discuss it in detail below. In addition, Cu-SSZ-13 before and after in situ SO_2 poisoning showed high N_2 selectivity, over 98%, in the whole temperature range, illustrating that SO_2 poisoning had little effect on its N_2 selectivity.

Figure 9. (a) NO_x conversion and N₂ selectivity of Cu-SSZ-13 before and after in situ SO₂ poisoning. Reaction conditions: [NO]_{inlet} = 500 ppm, [NH₃]_{inlet} = 500 ppm, [O₂]_{inlet} = 5%, [H₂O]_{inlet} = 5%, N₂ as balance gas, total gas flow rate—200 mL/min, and gas hourly space velocity (GHSV) = 200,000 h^{−1}. (b) NH₃ conversion of Cu-SSZ-13 before and after in situ SO₂ poisoning. Reaction conditions: [NH₃]_{inlet} = 500 ppm, [O₂]_{inlet} = 5%, [H₂O]_{inlet} = 5%, N₂ as balance gas, total gas flow rate—200 mL/min, and GHSV = 200,000 h^{−1}. 2

To further investigate the impact of in situ SO₂ poisoning on the active Cu species, NH₃ oxidation tests were performed. As shown in Figure 9b, for CZ-F, NH₃ conversions started at 200 °C and increased as reaction temperature rose. In contrast, NH₃ conversions significantly declined over CZ-S-200 and CZ-S-500. According to the previous studies, only ZCuOH species, among all active species for NH₃-SCR reaction, were mainly active sites for NH₃ oxidation reaction [35]. Therefore, the above results indicate that partial ZCuOH sites on CZ-S-200 and CZ-S-500 were poisoned, well consistent with the in situ DRIFTS results.

3. Discussion

Based on the above findings, a straightforward in situ SO₂ poisoning mechanism could be proposed and is illustrated in Figure 10. For in situ SO₂ poisoning at 200 °C, three reaction routes coexisted: (1) SO₂ interacted with NH₃ to form (NH₄)₂SO₄, which could cover the active sites and cause pore blocking (Table 1). Furthermore, this species affected more Z₂Cu than ZCuOH (Figure 8). (2) SO₂ interacted with both Z₂Cu and ZCuOH to form CuSO₄ (Figures 3 and 5), only the interaction with Z₂Cu species was slight (Figure 8). (3) SO₂ broke Si-O(H)-Al bonds and interacted with Al atoms to form Al₂(SO₄)₃ (Figure 3), leading to the decrease in Brønsted acid sites (Figure 7). For in situ SO₂ poisoning at 500 °C, only reaction routes (2) and (3) coexisted. Note that as SO₂ poisoning temperature increased, more CuSO₄ species were formed (Figure 3), while the amount of Al₂(SO₄)₃ species generated was almost unchanged (Figure 7). In particular, the crystal structure of Cu-SSZ-13 was not damaged during in situ SO₂ poisoning process, whether at 200 or 500 °C.

Combined with the reactive results shown in Figure 1, the effect of in situ SO₂ poisoning on the SCR performance of Cu-SSZ-13 could fall into two categories. At low-temperature regimes, there was a certain loss in SCR performance in comparison with that of fresh sample, and this loss increased with the increase in SO₂ poisoning temperature. The main reasons may be as follows: (1) the formation of CuSO₄ species resulted in the reduction in active Cu sites (i.e., Z₂Cu and ZCuOH), which were more susceptible to be sulfur-poisoned with the increasing temperatures; (2) for the NH₃-SCR reaction, Brønsted acid sites play an important and beneficial role at both low- and high-temperature regimes [31]. Therefore, the decrease in Brønsted acid sites after SO₂ poisoning inevitably led to the deterioration of SCR performance. Note that the decrease degrees of *S*_{BET} and *V*_{total} for CZ-S-200 were more serious than for CZ-S-500 (Table 1), which appeared contradictory to their low-temperature SCR performance, implying that the decrease in surface area and pore volume was not a dominant deactivation factor for Cu-SSZ-13 after SO₂ poisoning. At high-temperature regimes, the NH₃ oxidation reaction would compete with the NH₃-SCR reaction for the consumption of -NH₂, an intermediate

active NH_3 species [36]. That is the major reason why high-temperature activities decrease over SCR catalysts. From the in situ DRIFTS (Figure 8) and NH_3 oxidation test (Figure 9b) results, for Cu-SSZ-13, ZCuOH species were active sites for the NH_3 oxidation reaction, which was also very easily reactive with SO_2 . Therefore, the sulfation of ZCuOH species could inhibit the occurrence of the NH_3 oxidation reaction to some extent. From Figure 9a, it can be seen that although partial active sites, including Cu species and Brønsted acid sites, were lost during the SO_2 poisoning process, the residual active sites can suffice to sustain the NH_3 -SCR reaction proceeding. Even improved SCR performances were observed over CZ-S-200 and CZ-S-500 at high temperatures. Among the three catalysts, CZ-S-500 exhibited the best SCR activity at high temperatures as most ZCuOH species in it were sulfated during the in situ SO_2 poisoning process at 500 °C.

Figure 10. Schematic diagram of the in situ SO_2 poisoning mechanism over Cu-SSZ-13 at 200 and 500 °C.

4. Materials and Methods

4.1. Catalyst Preparation

The Cu-SSZ-13 sample (labeled as CZ-F) used in this study was supplied by China Catalyst Holding Co., LTD (Beijing, China). The Si/Al ratio was 13.5 and the Cu content was 2.67 wt%. In situ poisoning samples were prepared by being treated in a gas flow of 500 ppm NO, 500 ppm NH_3 , 5% O_2 , 50 ppm SO_2 , 5% H_2O , and N_2 balance for 24 h at 200 and 500 °C. They were labeled as CZ-S-200 and CZ-S-500, respectively.

4.2. Catalytic Performance

The NH_3 -SCR and NH_3 oxidation performance measurements were carried out in a fixed quartz microreactor setup (Beijing, China). Prior to testing, 0.04 g catalysts was sieved to 40–60 mesh. The standard SCR feed gas was composed of 500 ppm NH_3 , 500 ppm NO, 5% O_2 , 5% H_2O , and N_2 balance. Nevertheless, the NH_3 oxidation feed gas was composed of 500 ppm NH_3 , 5% O_2 , 5% H_2O , and N_2 balance. The total flow rate was 200 mL/min, and the gas hourly space velocity (GHSV) was 200,000 h^{-1} . For ensuring the stability of the testing results, each temperature test point was kept for 30 min before data were recorded. The concentrations of NH_3 , NO, NO_2 , and N_2O were continuously monitored by an MKS instrument (Shanghai, China). NO_x and NH_3 conversions were calculated based on the

inlet and outlet gas concentrations at steady state, as shown in Equations (1) and (2), respectively. N_2 selectivity was calculated from Equation (3).

$$NO_x \text{ Conversion} = \frac{[NO_x]_{\text{inlet}} - [NO_x]_{\text{outlet}}}{[NO_x]_{\text{inlet}}} \times 100\% \quad (1)$$

$$NH_3 \text{ Conversion} = \frac{[NH_3]_{\text{inlet}} - [NH_3]_{\text{outlet}}}{[NH_3]_{\text{inlet}}} \times 100\% \quad (2)$$

$$N_2 \text{ Selectivity} = \left(1 - \frac{2[N_2O]_{\text{outlet}}}{[NO_x]_{\text{inlet}} + [NH_3]_{\text{inlet}} - [NO_x]_{\text{outlet}} - [NH_3]_{\text{outlet}}} \right) \times 100\% \quad (3)$$

4.3. Physical and Chemical Characterization

Powder X-ray diffraction (XRD) patterns were taken in the 2θ range of $5\text{--}50^\circ$ at steps of $10^\circ \text{ min}^{-1}$, using an X-ray diffractometer (SmartLab 3 KW, Tokyo, Japan) with Cu $K\alpha$ ($\lambda = 0.15405 \text{ nm}$) radiation.

The N_2 sorption isotherms were measured at 77 K using a Micromeritics 3020 instrument (Waltham, MA, USA) in static mode. Prior to the measurements, the samples were degassed at 300°C for 4 h.

TGA patterns were obtained within the temperature range from room temperature (RT) to 1000°C by a Mettler Toledo TGA/DSC 3 instrument (Zurich, Switzerland).

UV Raman spectra were obtained on a Jobin-Yvon T64000 (Paris, France) spectrometer with a triple-stage spectrograph at a resolution of 2 cm^{-1} . The excitation laser line at 325 nm from a Kimmon He-Cd laser was used as the exciting source. The power of the laser on the sample was approximately 4 mW.

Temperature-programmed reduction with H_2 (H_2 -TPR) experiments were carried out on a chemisorption analyzer (Micromeritics Chemisorb, 2920, Waltham, MA, USA) in order to obtain the reducibility of samples and the valence of active sites. The samples in a quartz reactor were tested in 10% H_2 /Ar gas flow of 100 mL/min at a heating rate of $10^\circ\text{C min}^{-1}$. The temperature was raised from 100 to 1000°C , and the signal of hydrogen consumption was detected by the thermal conductivity detector (TCD).

Temperature-programmed desorption (TPD) of NH_3 or $NO+O_2$ was carried out using an MKS instrument to detect different nitrogen-containing species, including NH_3 , NO, and NO_2 . Adsorption was carried out directly at room temperature. After adsorption saturation, the NH_3 concentration was purged to below 10 ppm, and then the data of temperature-rising desorption were recorded. The temperature-programmed desorption experiments were conducted at a heating rate of $10^\circ\text{C min}^{-1}$ from RT to 700°C in N_2 (100 mL min^{-1}).

In situ DRIFTS experiments were performed on an FT-IR spectrometer (Nicolet 6700, Waltham, MA, USA) equipped with a Smart Collector and an MCT/A detector. Prior to each experiment, the catalyst was pretreated at 500°C for 30 min in N_2 at a flow of 100 mL min^{-1} . The DRIFTS spectra were collected by accumulating 32 scans with a resolution of 4 cm^{-1} .

5. Conclusions

In this study, the in situ SO_2 poisoning mechanism on Cu-SSZ-13 at 200 and 500°C was investigated. Three sulfate species, including $(NH_4)_2SO_4$, $CuSO_4$, and $Al_2(SO_4)_3$, were found to form on CZ-S-200, while only the latter two sulfate species were observed over CZ-S-500. The deterioration of low-temperature SCR activity was mainly due to the sulfation of active Cu species (i.e., Z_2Cu and $ZCuOH$) and the decrease in Brønsted acid sites. As such, the sulfation degree of active Cu species increased with the increasing in situ SO_2 poisoning temperature, whereas the amount of Brønsted acid sites was almost unchanged. Furthermore, the blocking effect of $(NH_4)_2SO_4$ was relatively small. In contrast, the improvement of high-temperature SCR activity was owing to the inhibition of the NH_3 oxidation reaction, from which active Cu species (i.e., $ZCuOH$) were very easily sulfated under the in situ SO_2 poisoning condition.

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