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The Role of SO₃ Poisoning in Cu/SSZ-13 NH₃-SCR Catalysts

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Abstract: To reveal the role of SO₃ poisoning in Cu/SSZ-13 NH₃-SCR catalysts, fresh and sulfated Cu/SSZ-13 catalysts were prepared in the presence or absence of SO₃ flux. The deactivation mechanism is probed by the changes of structural, copper species, and selective catalytic reduction (SCR) activity. The variations concentrate on the changes of copper species as the Chabazite (CHA) framework of Cu/SSZ-13 catalysts could keep intact at high ratios of SO₃/SO_x. The thermal gravimetric analyzer (TGA) results reveal that the copper sulfate formed during sulfation and the amounts of sulfate species increased with an increase in the SO₃/SO_x ratio. In contrast to the changing trend of copper sulfate, temperature program reduction (H₂-TPR), and electron paramagnetic resonance (EPR) results manifest that, since the number of active copper ions declines with an increase of the SO₃/SO_x ratio, the active sites transform to these inactive species during sulfation. Due to the combination of NH₃-SCR activity and the kinetic tests, it is shown that the decreased number of active sites is responsible for the declined SCR activity at low temperature. As Cu/SSZ-13 catalysts show excellent acid-resistance ability, our study reveals that the Cu/SSZ-13 catalyst is a good candidate for NO_x elimination, especially when SO₃ exists.

Keywords: Cu/SSZ-13; NH₃-SCR; SO₃; deactivation mechanism; structural stability

1. Introduction

In the latest decade, the most effective post-processing technology for lean NO_x control in diesel is the selective catalytic reduction of NO_x with ammonia (NH₃-SCR). Cu/SSZ-13 catalysts, particularly in the last five years, have gained much attention because they exhibit excellent NH₃-SCR performance at low-temperature regions and outstanding N₂ selectivity. As a result, Cu/SSZ-13 catalysts could be a great SCR catalyst to meet with the strict emission regulations in diesel vehicles [1–5].

Actually, a number of essential conclusions and contributions have been made to properly understand the nature of copper ions and their impact on NH₃-SCR mechanisms over Cu/SSZ-13 catalysts [6–8]. When facing real applications; however, the Cu/SSZ-13 catalysts are invariably affected by impurities, like sulfur, phosphorus, or alkali metal ions, and hence, a deep comprehension of their impacts on catalysts is very useful for their application [9–15].

Among these impurities, sulfur poisoning is a common issue in SCR catalysts [16–18], and even when the amount of sulfur is quite low, sulfur exposure could result in serious deactivation of SCR activity [19]. Hence, in recent years, much work has focused on the sulfur impacts of NH_3 -SCR performance on Cu/SSZ-13 catalysts in diesel vehicles. Sandra et al. [10] investigated the effect of sulfur-exposure temperature on the adsorption of sulfur over Cu/SSZ-13 and found that lower temperature lead to the adsorption of more sulfur, as well as lower SCR activity. Wijayanti et al. [20,21] studied the effect of gas composition on SO_2 poisoning over Cu/SSZ-13 and found that the decrease in SCR activity is related to the formation of sulfate species and ammonium sulfate species. Luo et al. [22] identified the response of two types of copper sites upon sulfur poisoning, and they found that $\text{Cu}(\text{OH})^+$, compared with Cu^{2+} , easily combined with sulfur. Shih et al. [23] further used a theoretical method to support that $\text{Cu}(\text{OH})^+$ was more prone to SO_2 poisoning than Cu^{2+} . Yasser et al. [24] studied that SO_2 only adsorbed on Cu^{2+} when ammonia was present and formed ammonium sulfate as the main poisoning route on this site, while, SO_2 could react with $[\text{Cu}(\text{OH})]^+$ to form copper bisulfate. Wei et al. [25] studied the impact of hydrothermal aging on SO_2 poisoning over Cu/SSZ-13. The authors found that copper sulfate species decreased when aging at 750°C owing to copper migration and the contents of copper sulfate species increased at 850°C aging as $\text{CuO}_x/\text{CuAlO}_x$ species easy to react with SO_2 . Without any doubt, the above studies have provided important insights to understand SO_2 poisoning. However, the impact of SO_3 should not be overlooked because diesel oxidation catalysts (DOCs) will be applied upstream to SCR catalysts. As of yet, few studies have reported on the influence of SO_3 on Cu-loaded Chabazite (Cu/CHA) catalysts. Hammershøi et al. [26] found that the presence of SO_3 could lead to Cu-sulfate species formation and lead to higher deactivation on Cu/CHA catalysts. However, except for an increased loss of the number of active sites, the most important finding in our previous study is that SO_3 also had a serious impact on the structure of Cu/SAPO-34 catalysts [27]. The inconsistent conclusions above indicate that the mechanism of SO_3 poisoning on Cu/CHA catalysts is not well understood. Considering that no study has explicitly clarified the changes of Cu/SSZ-13 catalysts under sulfation in the presence of SO_3 , in this study, the following objectives are exclusively considered. (1) Whether the high content of SO_3 ions affected the integrity of the CHA structure, (2) whether SO_3 accelerates sulfate formation, and (3) what is the structural-activity relationship between SO_3 and SCR performance.

To properly address the above concerns and probe the deactivation mechanism, fresh Cu/SSZ-13 were sulfated in the presence or absence of SO_3 under a constant SO_x -containing stream. Using Brunauer–Emmett–Teller measurements (BET), X-ray diffraction (XRD), and nuclear magnetic resonance (NMR), a clear answer of whether SO_3 affects the framework on Cu/SSZ-13 could be obtained. Through a thermal gravimetric analyzer (TG), H_2 temperature-programmed reduction (H_2 -TPR), and electron paramagnetic resonance (EPR), the regulation of the variation in copper species during sulfation could be acquired. Furthermore, the structural-activity relationship is also monitored, combined with NH_3 -SCR and kinetic tests, as well as copper ions changes.

2. Results

2.1. Structural Characterization

2.1.1. BET and XRD Results

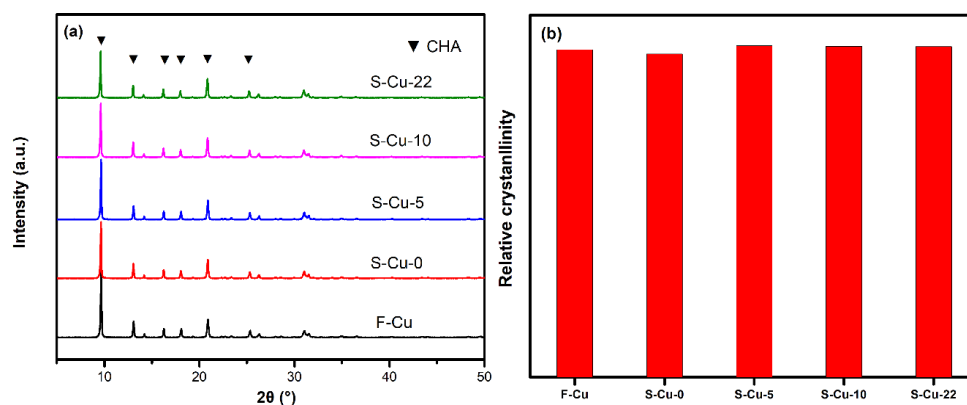
In order to investigate SO_3 effects, BET measurements were firstly performed on all catalysts, and the results are shown in Table 1. A continuous but slight reduction in the specific surface area of the sulfated samples relative to the fresh one was found. Only a 12.6% reduction in the specific surface area was found for S-Cu-22. The sulfur species formation, caused by pore blocking, accounts for the reduction in the specific surface area, which agrees with many other studies [20,28–30]. The result suggests that the CHA structure holds integrity during SO_x sulfation.

Table 1. The specific surface area of fresh and sulfated catalysts.

Samples' Name	Specific Surface Area (m ² /g)	ΔS (%) ¹
F-Cu	801	—
S-Cu-0	740	7.6
S-Cu-5	725	9.5
S-Cu-10	710	11.4
S-Cu-22	700	12.6

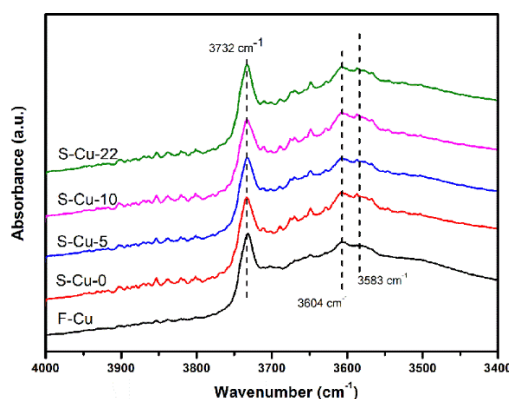
$$^1 \Delta S(\%) = \frac{S_{F-Cu} - S_{S-Cu-x}}{S_{F-Cu}} \times 100\%.$$

To verify the intact CHA framework under SO₃ poisoning, all samples were measured by XRD tests. As shown in Figure 1a, the fresh and sulfated catalysts show the typical Chabazite phase as the diffraction peaks at 9.6°, 13°, 16.3°, 18.0°, 20.9°, and 25.3° can be found [14,31,32]. To better reveal the changes in the framework variation, the relative crystallinity was calculated using the total areas of six peaks on F-Cu as a reference, and the results are shown in Figure 1b. The result in Figure 1b shows that the different catalysts have identical relative crystallinity, indicating that the CHA framework could hold the integrity of the framework after SO_x poisoning.

**Figure 1.** XRD pattern (a) and relative crystallinity (b) of fresh and sulfated catalysts.

2.1.2. Ex-Situ Diffused Reflectance Infrared Fourier Transform Spectroscopy (DRIFTs) Results

To further examine the changes in the framework, the OH vibrational region of the fresh sample with those of the sulfated catalysts were monitored using ex-situ DRIFTs, as shown in Figure 2. The infrared spectroscopy (IR) bands at 3732, 3604, and 3580 cm^{−1} are assigned to ν_{OH} features, which are related to the framework. The band at 3732 cm^{−1} corresponds to isolated silanols (SiOH) and two strong bands at 3604 and 3580 cm^{−1} are assigned to the Brönsted OH groups as (Si-O(H)-Al) [5,33].

**Figure 2.** Ex-situ DRIFTs results of the fresh and sulfated catalysts. Ex-situ DRIFTs results at 4000 and 3400 cm^{−1}, units in absorbance.

For the fresh and sulfated catalysts, the intensity of the three prominent bands on these catalysts are similar, which indicates that SO_3 poisoning could not influence the CHA structure of SSZ-13.

2.1.3. NMR Results

NMR measurements were used to gain insight into the SO_3 poisoning effect on the CHA framework, and hence, the chemical environment of ^{27}Al and ^{29}Si on F-Cu, S-Cu-0 and S-Cu-22 were measured. For the ^{27}Al NMR spectra (Figure 3a), one dominating peak at ~55 ppm is attributed to Al feature framework, while two peaks in the ^{29}Si NMR spectra (Figure 3b) at -105 and -111 ppm are assigned to Si(3Si, 1Al) and Si(4Si, 0Al), respectively [5,15,34].

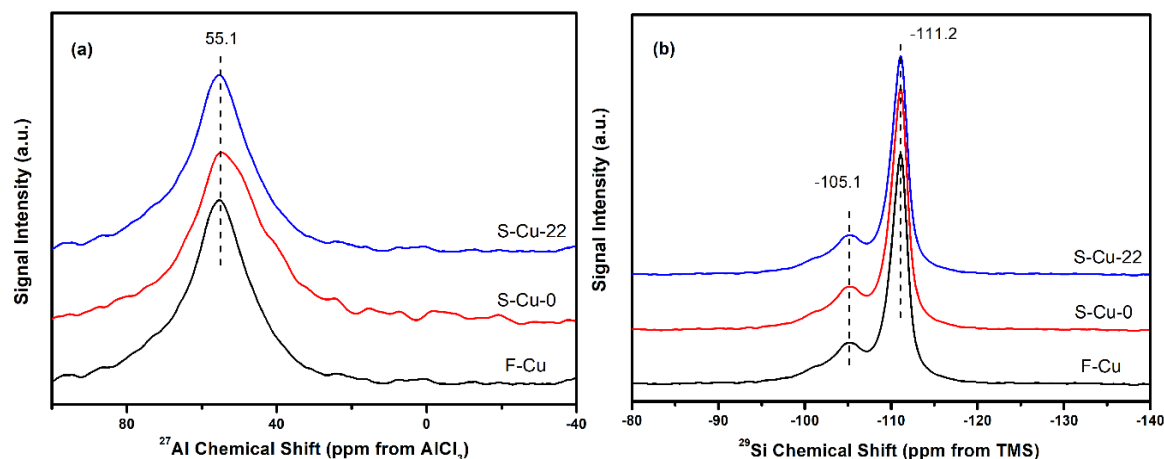


Figure 3. (a) ^{27}Al NMR and (b) ^{29}Si NMR spectra of F-Cu, S-Cu-0, and S-Cu-22.

It is worth noting that sulfation at SO_2 or SO_3 resulted in almost no changes in the ^{27}Al NMR spectra, and as a result, identical ^{29}Si NMR spectra are shown in Figure 3b. The results of NMR strongly support that the CHA framework of the SSZ-13 keep their integrity under SO_x poisoning, even though the ratio of SO_3/SO_x reached 22%.

2.2. Copper Species Variation on Cu/SSZ-13

As the CHA framework kept intact during sulfation, the variation of active sites and sulfur species should be considered. Consequently, in this part, semi-qualitative and qualitative methods to explore the regulatory change in Cu species are used.

2.2.1. TG Results

TG is a widely used method to identify the sulfur species and confirm their amounts; accordingly, all catalysts were performed using TG tests. As can be seen from Figure 4a, all samples showed weight loss at two temperature regimes. It is well-established that the weight loss below 300 °C is attributed to water evaporation [27,35]. Moreover, the weight loss between 300 and 800 °C, should be assigned to the decomposition of copper sulfate because sulfate catalysts have the similar derivative thermogravimetry (DTG) pattern at 600 to 800 °C with reference to the copper sulfate compound (the DTG pattern of copper sulfate is not shown in this study, but could be found in our previous study) [27,30,35]. The weight loss in this region decreases in the order: S-Cu-22 (~2.3 wt%) > S-Cu-10 (~2.1 wt%) > S-Cu-5 (~1.6 wt%) > S-Cu-0 (~1.3 wt%). It is interesting to note that the degree of weight loss is related to SO_3 exposure, and the higher ratio of SO_3/SO_x results in more weight loss.

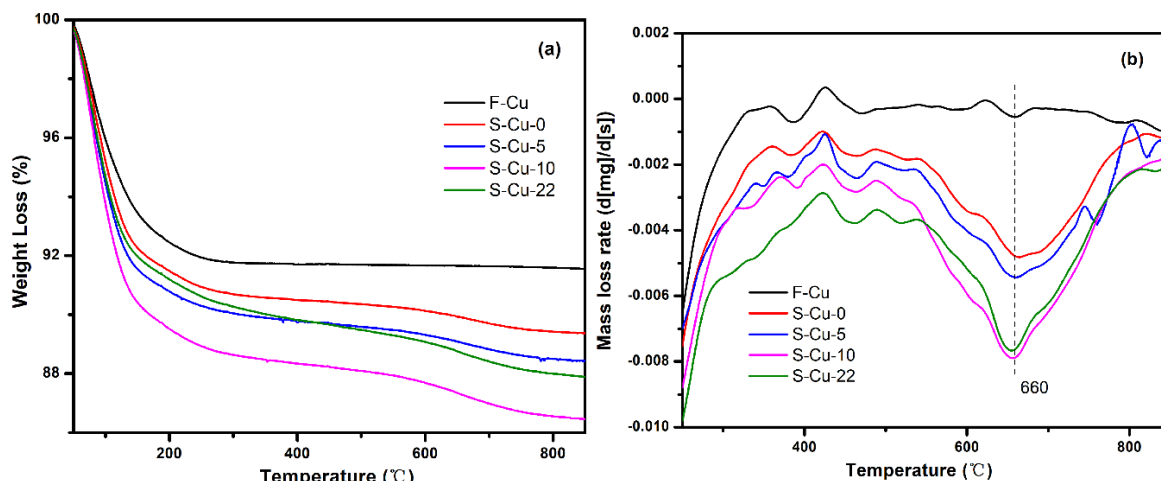


Figure 4. TG (a) and DTG (b) results of fresh and sulfated catalysts.

2.2.2. H₂-TPR Results

To investigate all the reducible copper species, the fresh and sulfated catalysts were tested using H₂-TPR measurements, and the results are shown in Figure 5. For F-Cu, two peaks centered at ~220 °C and ~340 °C represent the reduction of $[\text{Cu}(\text{OH})]^+$ to Cu^+ in 8 MR and the reduction of isolated Cu^{2+} to Cu^+ near 6 MR, respectively [1,3]. Furthermore, Cu^+ comes from the partial reduction of Cu^{2+} , and the reduction to Cu^0 usually appears above 600 °C [1]. When F-Cu went through sulfated treatments, four emerging peaks centered at ~270, ~400, ~500, and ~640 °C were presented on sulfated catalysts, which should be related to the reduction of copper-sulfur species. The reduction peak at ~270 °C is attributed to copper sulfate formed in 8 MRs [36], and the reduction peaks between 400 to 700 °C are related to copper sulfate in 6 MRs [27,35].

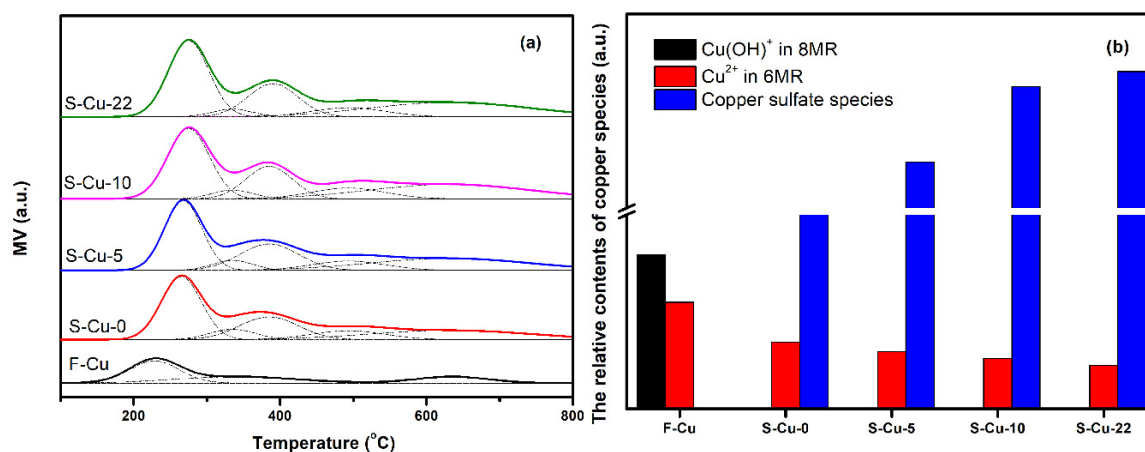


Figure 5. H₂-TPR results (a) and qualitative results (b) of fresh and sulfated catalysts.

Figure 5b shows the relative contents of the different copper species, active sites, and sulfate species, from the H₂-TPR results. It is worthy to mention that even though the reduction peak of copper sulfate centered at ~640 °C could contain the reduction area of Cu^+ , the Cu^+ reduction does not affect the semi-qualitative results of copper sulfate as small amounts of Cu^{2+} remained after sulfation. The amounts of Cu^{2+} decreased as sulfur oxide poisoning, and the contents of the isolated Cu^{2+} ions continuously decreased with the increase in the SO_3/SO_x ratio. In contrast, the copper sulfate largely forms on S-Cu-0 and the amounts of sulfate increase as SO_3 content increases.

2.2.3. EPR Results

To gain more insight into the contents of the active sites, EPR measurements were conducted on all the catalysts. As shown in Figure 6, fresh Cu/SSZ-13 shows two hyperfine structures ($g// = 2.39$, $A// = 128$ G; $g// = 2.36$, $A// = 135$ G), which attributed to copper ions in 6 MR and 8 MR [31,37]. For the sulfated samples, the hyperfine structure with $g// = 2.36$, $A// = 135$ G have a very weak signal, suggesting that copper ions in 8 MR are depleted, consistent with the results of the H_2 -TPR.

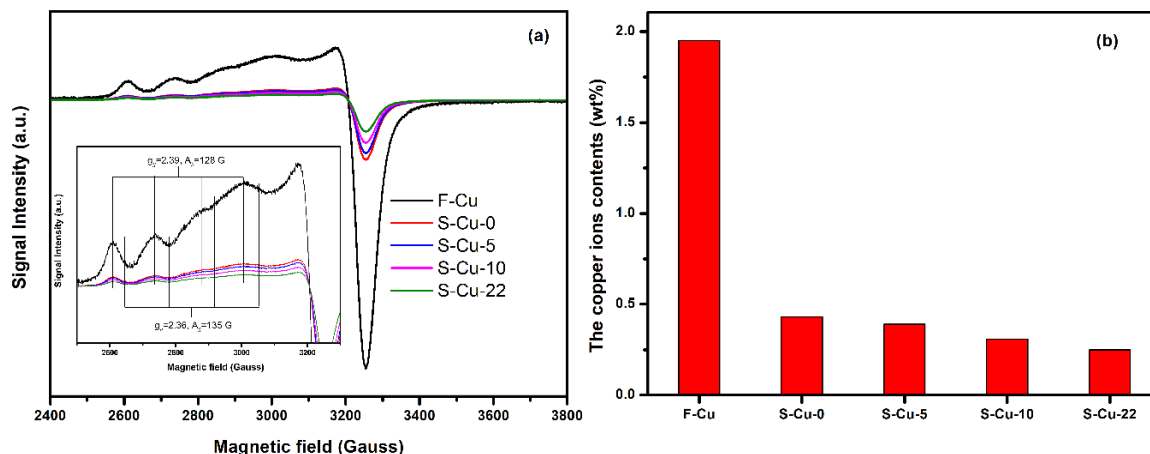


Figure 6. EPR spectra (a) and the quantitative results (b) of fresh and sulfated catalysts.

Figure 6b exhibits the number of Cu^{2+} ions on different catalysts. The number of active sites decreased in the following order: F-Cu (1.95%) > S-Cu-0 (0.43%) > S-Cu-5 (0.39%) > S-Cu-10 (0.31%) > S-Cu-22 (0.25%). The results are consistent with the variation tendency of copper ions in the H_2 -TPR results.

2.3. NH_3 -SCR Reactions over Cu/SSZ-13

2.3.1. NH_3 -SCR Activity

Figure 7a shows the NO_x conversion of fresh and sulfated Cu/SSZ-13 catalysts. Compared to F-Cu, the SCR activity of sulfated catalysts severely declined below 350 °C, but did not influence the NO_x conversion at high temperature (above 350 °C), which agrees with other findings [25,38]. The SCR performance below 350 °C decreases as follows: F-Cu > S-Cu-0 > S-Cu-5 > S-Cu-10 > S-Cu-22.

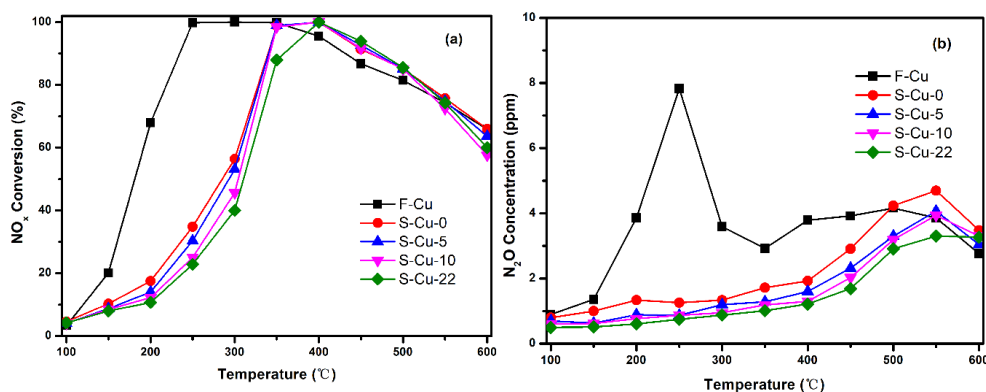


Figure 7. (a) NO_x conversion as a function of reaction temperature over catalysts; (b) N_2O formation during NH_3 -SCR reaction in the catalysts. The reaction was carried out with a feed containing 500 ppm NO_x , 500 ppm NH_3 , 10% O_2 , 3% H_2O , balance N_2 , and gas hourly space velocity (GHSV) = 80,000 h^{-1} .

As shown in Figure 7b, the highest N_2O concentration was found in the fresh catalysts at 250 °C (8 ppm). While, compared with F-Cu, the sulfated catalysts decreased the N_2O formation by ~7 ppm at 250 °C and increased the N_2O concentration by 2 to 3 ppm at high temperatures.

2.3.2. Activation Energy (E_a) Measurements

To probe whether the mechanism changes across different samples, kinetic measurements were performed, and the Arrhenius plots for the SCR reaction are shown in Figure 8. It is clearly seen that the SCR reaction rate decreased with an increase in SO_3 content. Besides that, it should be pointed out that the sulfated samples show similar apparent activation energies ($E_a = 35 \pm 1$ kJ/mol), which is considerably lower than that in F-Cu ($E_a = 64$ kJ/mol).

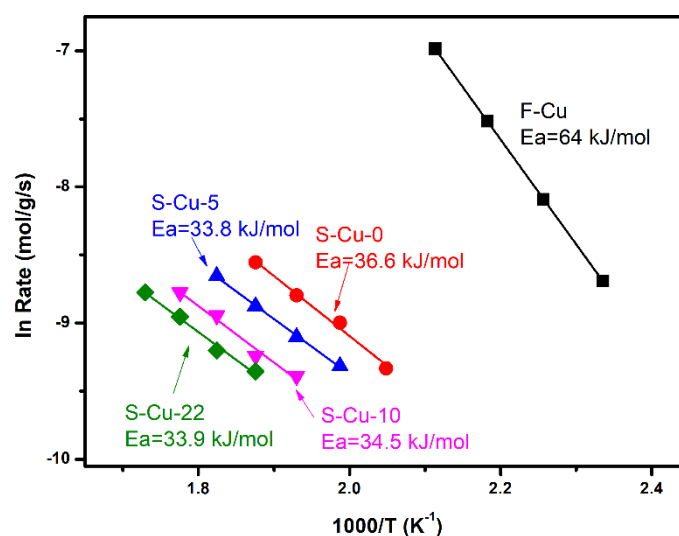


Figure 8. Arrhenius plots of the SCR reaction rates over fresh and sulfated catalysts. The reaction was carried out with a feed containing 500 ppm NO_x , 500 ppm NH_3 , 10% O_2 , 3% H_2O , balance N_2 , and GHSV = 316,800 h^{-1} .

3. Discussion

3.1. The Variation of the CHA Structure Under SO_3 Poisoning

It is generally accepted that SO_2 has no influence on the structure of zeolites as both SO_2 and zeolites show acidity [18]. Hence, no changes in the CHA framework on S-Cu-0 could be easily understood. Most importantly, in this study, the data of SO_x sulfated samples showed the identical results with S-Cu-0, indicating that the presence of SO_3 also had no influence on the CHA structure of SSZ-13. This is supported by the slight decline in the specific surface area, as well as the same relative crystallinity, the intensity of Si-O(H)-Al bonds and the chemical environment of Si and Al on the sulfated catalysts, as shown in Section 2.1.

It should be recalled from our previous study on SO_3 poisoning in Cu/SAPO-34 catalysts that the CHA structure of Cu/SAPO-34 was damaged during high contents of SO_3 poisoning (20% SO_3 in SO_x) as the process of dealumination occurred [27]. Considering the intact topological structure of SO_x sulfated Cu/SSZ-13, Cu/SSZ-13 catalysts show better acid resistance than Cu/SAPO-34. In fact, as SSZ-13 have a desorption peak of NH_3 at higher temperature compared with that of SAPO-34 (~420 °C for SSZ-13 vs. ~350 °C for SAPO-34) [15,39], SSZ-13 shows stronger acidity than SAPO-34. Similarly, with the mechanism of SO_2 effect on zeolites, the stronger acidity of SSZ-13 help withstand SO_3 with more acidity. Besides, this conclusion about SSZ-13 having good acid resistance could also be directly proved by running a comparative test using fresh Cu/SSZ-13 and Cu/SAPO-34 treated under identical H_2SO_4 solutions. As shown in Table 2, even though the solution of pH = 0.5 caused ~24% reduction in the specific surface area, Cu/SSZ-13 catalysts could stand the acid solution of pH = 1 as

only a 5.3% reduction in the specific surface area is shown in S-Cu-1 compared with the fresh one. However, a 41.3% reduction in the specific surface area was found for Cu/SAPO-34 when the acid solution was of pH = 2. Moreover, a severe reduction could be found for S-Cu-0.5 as only 8 m²/g remains in Cu/SAPO-34. The results indicate that Cu/SSZ-13 has great acid-resistance relative to Cu/SAPO-34. The XRD results in Figure 9 further support the above conclusion because the rate of decline relative to the crystallinity in Table 2 show a similar variation compared with that of the specific surface area.

Table 2. The specific surface area of different Cu/CHA catalysts.

CuSSZ-13s' Name	Specific Surface Area (m ² /g)	ΔS_{BET} (%) ¹	ΔS_{XRD} (%) ²	CuSAPO-34s' Name	Specific Surface Area (m ² /g)	ΔS_{BET} (%) ¹	ΔS_{XRD} (%) ²
F-Cu	791	—	—	F-Cu	733	—	—
Cu-80-2	763	3.5	2.1%	Cu-80-2	430	41.3	62.0
Cu-80-1	750	5.2	3.5%	Cu-80-1	306	58.3	83.5
Cu-80-0.5	600	24.1	20.1%	Cu-80-0.5	8	98.9	100.0

¹ The decline rate in the specific surface areas, $\Delta S_{BET} \% = \frac{S_{F-Cu} - S_{Cu-80-x}}{S_{F-Cu}} \times 100\%$; ² The decline rate in the relative crystallinity obtained from Figure 9 below, $\Delta S_{XRD} \% = \frac{1 - \frac{C_{Cu-80-x}}{C_{F-Cu}}}{1} \times 100\%$.

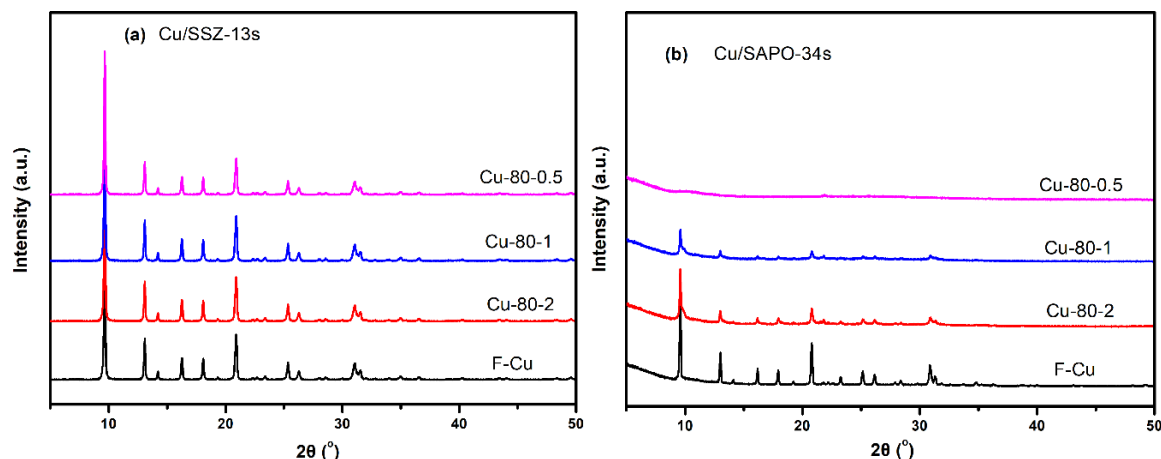


Figure 9. XRD results of fresh and different treated (a) Cu/SSZ-13s (b) and Cu/SAPO-34s.

3.2. The Structural-activity Relationship Over Cu/SSZ-13

As an obvious weight loss and reduction peak can be found in TG and TPR results (Figures 4 and 5), the results manifest that copper sulfate formed during sulfated treatment on Cu/SSZ-13. From the quantitative result of TG, more amounts of copper sulfate were found in the SO₃-treated samples compared with that in S-Cu-0. This result indicates that the presence of SO₃ accelerates the formation of copper sulfate. Besides, it clearly shows that the ratio of SO₃/SO_x plays a critical role in determining the amount of copper sulfate formation because more amounts of copper sulfate formed in the sulfated condition at a higher ratio of SO₃/SO_x.

As all the copper species in the fresh Cu/SSZ-13 catalyst are in their ionic state as shown in our H₂-TPR results (Figure 5), the increase in copper sulfate amounts during sulfation must impact on the number of copper ions. The change in the number of copper ions could be quantified by the EPR results. As shown in Figure 6, the number of copper ions change and the copper ion contents gradually decline when the SO₃/SO_x ratio increases, which is also justified by our H₂-TPR results. Besides, from part a in Figure 5 (H₂-TPR results), it must be mentioned that no reduction in the peak assigned to Cu(OH)⁺ in 8 MR was seen after SO₂ sulfation. The results indicate that Cu(OH)⁺ species have a stronger response to sulfur oxide than isolated Cu²⁺ ions, which is also supported by our EPR results. Taking the observation of variation of copper sulfate and copper ions contents into account, it shows

that the active copper species transform to inactive sulfate species during sulfation. To further prove this suggestion, the reduced contents of copper ions is correlated with the amount of sulfur on sulfated samples in Figure 10 (in the red square), and the linear relationship proves the validity.

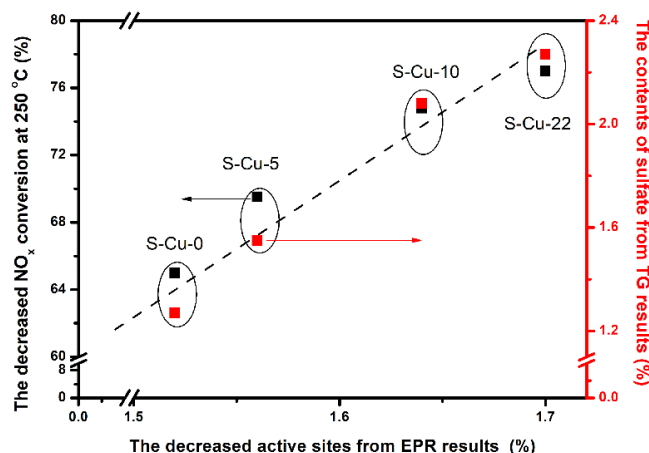


Figure 10. The relationship in decreased SCR activity and reduced copper ions (in the black square) and the contents of copper sulfate with the decreased copper ions (in the red square) on Cu/SSZ-13 catalysts.

Given all conclusions above, the structural-activity relationship at low-temperature in the fresh and sulfated catalysts could be addressed. According to the kinetic measurements results, all sulfated samples showed identical E_a values, but different pre-exponential factors (A). Given that A values reflect the contents of active sites, the kinetic results demonstrate that the change in catalytic activity on different sulfated samples is related to the variation of active site amounts when we notice the reduced order of A is the same as that of the SCR performance at low-temperature. Notably, the E_a of all sulfated samples is ~ 0.5 -fold that of fresh one (35 kJ/mol vs. 64 kJ/mol), indicating the mechanism of NH_3 -SCR reaction changes. When Cu/Al is lower than 0.1, it is well accepted the rate-determining step changes to the formation of Cu dimer species, $(\text{NH}_3)_2\text{Cu}^{\text{II}}\text{-O}_2\text{-Cu}^{\text{II}}(\text{NH}_3)_2$ [7], and hence, the change in the mechanism results from the rate-determining step changes. As clearly shown in our EPR results, the large portion of decreased contents in copper ions in the sulfated samples leads to a Cu/Al ratio less than 0.1 and uncovers this phenomenon. In a word, all the results above reveal that the decrease of catalytic activity at low-temperature is related to the reduction of active site numbers. To further confirm the validity of this conclusion, the decreased activity is correlated to the contents of the decreased active sites. As copper ions are responsible for the SCR performance at the low-temperature range, 250 °C is selected as the representative temperature to clarify the copper ions effect on SCR activity. In this calculation, the contents of copper ions and SCR activity at 250 °C on F-Cu are selected as the reference. As shown in Figure 10 in the black square, the linear relationship at 250 °C illustrates that the variable amounts of Cu ions determine the changes of SCR activity at the low-temperature range.

Based on our data, the structure of Cu/SSZ-13 is stable under the presence of SO_3 , which means we don't need to worry about its structural changes when it applied in the real application. The only thing needed to consider mainly is the decrease of copper ions and the corresponding copper sulfate formation. However, as the copper sulfate could decompose and the inactive copper species can back to exchange sites at appropriate condition [35], our study reveals that Cu/SSZ-13 catalyst is a good candidate for the elimination of NO_x , especially when SO_3 exists in the flux.

4. Materials and Methods

4.1. Materials

A normal ion exchange method was performed to get Cu/SSZ-13 with $\text{Si}/\text{Al} = \sim 12$. Briefly, Na/SSZ-13 were firstly synthesized using a hydrothermal method with the following compositions:

1 SiO₂: 0.04 Al₂O₃: 0.025 Na₂O: 0.1 SDA: 20 H₂O [40]. After the template agent removal, the power was further exchanged in a 1 M (NH₄)₂SO₄ solution at 80 °C for 4 h and 0.5 M Cu(NO₃)₂ at 80 °C for 1 h, respectively. The Cu/SSZ-13 catalysts were obtained by calcining at 550 °C for 6 h in a muffle furnace, and the total copper content was 1.95% that determined by ICP-AES (Thermo Fisher Scientific, Waltham, MA, USA).

To probe the nature of SO₃ poisoning on Cu/SSZ-13 catalysts, four different sulfur poisoned Cu/SSZ-13 catalysts with and without SO₃ were prepared. Briefly, 2 g of fresh Cu/SSZ-13 was sulfated at 250 °C with a feed containing 100 ppm SO_x (the ratio of SO₃/SO_x were 0, 5, 10 and 22%), 5% H₂O in air (total flow was 1000 sccm) for 8 h. Approximately 2.5% V₂O₅/10%WO₃/TiO₂ catalyst was used to inlet the stable SO₃ contents adjusting the bed temperature of catalyst, and the detailed instruments could be traced in our previous study [27]. The nomenclatures of the catalysts are shown in Table 1. The fresh catalyst was named “F-Cu” and the sulfated catalysts were denoted as “S-Cu-X,” where X stands for SO₃/SO_x ratio. To directly prove that the CHA structure of Cu/SSZ-13 had excellent acid-resistance, the catalysts were put into H₂SO₄ solutions with different pH values (2.0, 1.0, 0.5) at 80 °C for 12 h. The samples were named as ‘Cu-80-*y*’, where *y* stands for pH values. For better comparison, ‘One-pot’ synthesized Cu/SAPO-34 using morpholine as the templating agent was also treated under the same condition and had identical names.

4.2. Methods

The Cu/SSZ-13s needed to fully dehydrate (300 °C for 24 h under vacuum), and then, the specific surface area of Cu/SSZ-13s was measured using Brunauer–Emmett–Teller measurements (Micromeritics, Norcross, GA, USA).

The XRD spectra (Bruker, Billerica, MA, USA) were collected using an X’ Pert Pro diffractometer with nickel-filtered Cu K α radiation (λ = 1.5418 Å) and operated at 40 kV and 40 mA in the range of 5–50° with 0.01° step-size. The relative crystallinity of catalysts was calculated when the normalized total areas of six peaks relative to that for a fresh one.

A Nicolet 6700 FTIR (Thermo Fisher Scientific, Waltham, MA, USA) was used to probe the variation of -OH vibration on Cu/SSZ-13s. KBr was chosen as the standard substance to make the background for ex-situ tests.

²⁷Al and ²⁹Si NMR measurements were tested on a Varian Infinity plus 300 WB spectrometer (Palo Alto, CA, USA) at resonance frequencies of 59.57 and 78.13 MHz, respectively, with sample-spinning rates of 8 kHz for ²⁷Al and 4 kHz for ²⁹Si. Al(NO₃)₃ aqueous solutions and Tetramethylsilane (TMS) were used as a chemical reference for ²⁷Al and ²⁹Si NMR spectroscopy, respectively.

A Mettler Toledo thermal gravimetric analyzer (Zurich, Switzerland) was used to identify of sulfur species and give their amounts, and hence, 15 mg samples were examined within the temperature ranges from 40 to 850 °C at a ramping rate of 10 °C/min in a gas flow containing 10% O₂/N₂ (total flow was 50 sccm).

The overall copper species contents on Cu/SSZ-13s were probed by H₂-TPR methods. All samples were measured in a flow of 5% H₂/N₂ (10 sccm) from 40 °C to 800 °C at a ramping rate of 10 °C/min.

The contents of active sites were quantitative measured by EPR at −150 °C when hydrated Cu/SSZ-13s and dilute CuSO₄·5H₂O aqueous solution with known concentration were used as a reference to calibrate the copper amounts over Cu/SSZ-13.

NH₃-SCR activity at normal and kinetic conditions was performed on all Cu/SSZ-13 catalysts. The detailed description of the experimental process could be found in our previous studies [27,35].

5. Conclusions

The SO₃ effect on a Cu/SSZ-13 catalyst has been investigated as a function of SO_x contents. The main conclusions of this study are listed below:

1. As a good acid-resistant ability, even at a high ratio of SO₃/SO_x flux, the CHA structure of Cu/SSZ-13 keep intact.
2. Copper sulfate form during sulfation with SO₂ alone or SO_x at 250 °C and the contents of sulfate show the linear relationship with the SO₃ contents in SO_x.
3. Cu(OH)⁺ show the stronger response to sulfate, compared with Cu²⁺ ions, and no trace of Cu(OH)⁺ has been found during sulfation. The declined contents of copper ions depend on the ratio of SO₃/SO_x, and only ~13% copper ions remain after sulfation in 22% SO₃/SO_x stream.
4. For sulfated catalysts, the loss of Cu²⁺ contents contributed to the inferior SCR activity at low temperatures.

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