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Deactivation Mechanism of SO\textsubscript{2} on the Cu/SAPO-34 NH\textsubscript{3}-SCR Catalysts: Structure and Active Cu\textsuperscript{2+}

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Abstract:

The deactivation mechanism of Cu/SAPO-34 ammonia selective catalytic reduction catalysts (NH\textsubscript{3}-SCR) by SO\textsubscript{2} poisoning has been systematically investigated using a range of analytical techniques in order to study the influence on both the zeolitic framework and the active Cu\textsuperscript{2+} ions. The different sulfate samples were obtain by SO\textsubscript{2} poisoning over Cu/SAPO-34 NH\textsubscript{3}-SCR catalysts as functions of the time and concentration in the feed. The obtained results reveal that the SO\textsubscript{2} poisoning could seriously decrease the NO conversion during the whole temperature range (100 \textdegree C-500 \textdegree C). The XRF result shows that there is almost no sulfur existing on the
SAPO-34 support. The ex-situ DRIFTS and BET results expose that the \( \text{SO}_2 \) poisoning does a less pronounced affect on its framework structure. The TPR and EPR results demonstrate that \( \text{SO}_2 \) poisoning does a significant influence on the coordination environment and the content of the active isolated \( \text{Cu}^{2+} \) species. The kinetic results demonstrate the \( \text{SO}_2 \) poisoning does not influence the apparent activation energy (Ea) of \( \text{NH}_3 \)-SCR reaction over \( \text{Cu/SAPO-34} \) catalysts. The decline of the \( \text{NH}_3 \)-SCR activity is due to the reduction of the number of isolated \( \text{Cu}^{2+} \) ions.

**Key words:** Cu/SAPO-34; \( \text{SO}_2 \) poisoning; Active \( \text{Cu}^{2+} \); Deactivation Mechanism

1. Introduction

World-wide news on poor air quality in Chinese cities was quite common since 2013. Some of the leading contributors are the pollutants emitted from increasing automotives. These environmental problems have resulted in a continuous decrease of the allowed NOx concentrations due to stringent emission regulations. Ammonia selective catalytic reduction (\( \text{NH}_3 \)-SCR) was considered as the technology with the highest potential to meet strict future diesel emissions standards in mobile applications.

Well established \( \text{NH}_3 \)-SCR technique uses either \( \text{V}_2\text{O}_5/\text{WO}_3/\text{TiO}_2 \) or Zeolite based catalysts. Zeolite-based catalysts promoted by transition metal such as Fe and Cu represent an excellent solution to overcome the stability problems of \( \text{V}_2\text{O}_5 \)-based catalysts but may show disadvantages in stability after hydrothermal ageing and sulphur poisoning\(^{[1-3]} \). Recently, Bull and Kwak et al \(^{[4-7]} \) reported the small-pore zeolite (\( \sim 3.8 \) A) with the CHA structure show significant promise as the new leading candidate among zeolite formulations compared to the Cu/ZSM-5 and Cu/Beta. Bull and Andersen et al \(^{[8, 9]} \) firstly reported the \( \text{NH}_3 \)-SCR activity of \( \text{Cu/SAPO-34} \) catalyst. In addition, Fickel and others found that \( \text{Cu/SAPO-34} \) catalysts perform superior \( \text{NH}_3 \)-SCR activity and prominent hydrothermal stability at 750 °C to that of Cu/zeolites was related to their unique microporous structure \(^{[5,7]} \). Meanwhile,
previous researches \cite{6,10-12} proved the isolated Cu$^{2+}$ species are the SCR active sites by EXAFS and kinetic tests.

A major problem in practical applications of SCR catalysts has been their deactivation by different components in the exhaust gas, which accumulate on the catalyst surface \cite{13,14}. Deactivation can also result from competitive adsorption of certain molecules on SCR sites, thereby inhibiting the SCR reaction. The main focus hereby was on the effect of sulfur poisoning. Because of its high chemical binding strength and the oxidative conditions in the exhaust stream, sulfur can readily react with Cu in a Cu/zeolite SCR catalyst forming stable CuSO$_4$-like compounds \cite{14-16}. This sulfur poisoning affects the redox properties of the Cu sites, severely inhibits NO oxidation and the subsequent formation of the adsorbed NOx complex, and ultimately decreases the SCR activity of the catalyst. Despite drastic reduction of sulfur content in diesel fuel in recent years, sulfur poisoning remains one of the most significant factors impacting the performance of Cu/zeolite catalysts. The poisoning effect of sulfur on the Cu/SAPO-34 catalyst has been reported by several groups \cite{17,18}. Zhang et al \cite{17} found the formation of (NH$_4$)$_2$SO$_4$ species that might poison the active sites and block the zeolite pores, which induce the inhibition of the SCR activity on Cu/SAPO-34 below 300 $^\circ$C. Kumar et al \cite{18} investigated the different impacts of SO$_2$ and SO$_3$ on Cu/SAPO-34 SCR catalysts. Obtained results indicated that the poisoning effect of different S species is almost identical or unobvious at low temperature (200 $^\circ$C). While, at high temperature (400 $^\circ$C), SO$_3$ has a substantial effect due to some temperature-activated chemical reaction taking place with catalyst material \cite{14,18}. Overall, based on the literature, different sulfur poisoning mechanisms of NH$_3$-SCR catalysts have been proposed. However the effect of sulphur poisoning on the structure and active sites of Cu/SAPO-34 has not been investigated. For direct automotive applications, it is very necessary to gain a better understanding of the sulphur poisoning properties for Cu/SAPO-34 catalyst. Understanding these properties would provide important information to improve the performance of sulphur resistance for meeting different fuel standards.

This study deals with an intensive investigation for the SO$_2$ poisoning on the
structure and active sites over Cu/SAPO-34 catalysts. The different sulphated samples were prepared by exposure to 112 ppm SO\textsubscript{2} for 5 h and 16 h, or 336 ppm SO\textsubscript{2} for 16 h with 10\% H\textsubscript{2}O at 250 °C respectively. The total sulfur throughput corresponded to 100,000 kilometre and 3,200,000 kilometre sulfur-equivalent miles (assuming 15 ppm S fuel) or 3,200,000 kilometre sulfur-equivalent miles (assuming 50 ppm S fuel)\textsuperscript{[15,16]}. The nature and structure of the Cu/SAPO-34 catalysts were characterized by XRD, ex-situ DRIFTS, H\textsubscript{2}-TPR and EPR. The kinetic analysis was used to study the influence of SO\textsubscript{2} poisoning of active sites. The mechanism of SO\textsubscript{2} poisoning over Cu/SAPO-34 catalysts was proposed.

2. Experimental

2.1. Catalyst preparation

The HSAPO-34 molecular sieve was synthesized by hydrothermal method from a gel with the molar composition Al\textsubscript{2}O\textsubscript{3}:SiO\textsubscript{2}:P\textsubscript{2}O\textsubscript{5}:Morpholine:H\textsubscript{2}O=1.0:0.6:1.0:2.0:60. Pseudoboehmite (68 wt\% Al\textsubscript{2}O\textsubscript{3}), orthophosphoric acid (85 wt\% H\textsubscript{3}PO\textsubscript{4}) and silica sol (25 wt\% SiO\textsubscript{2}) were used as the source of aluminium, phosphorus and silicon, respectively. Cu/SAPO-34 catalysts were synthesized by exchanging NH\textsubscript{4}-SAPOP34 in copper sulfate solution. The detail synthesis procedures of the Cu/SAPO-34 catalysts had been reported in our former study \textsuperscript{[19]}. The fresh supports or the Cu/SAPO-34 catalysts were hydrothermally treated at 750 °C for 4 h in 10\% H\textsubscript{2}O/air to get de-greened samples; the samples were named as SAPO-34 and Cu/SAPO-34, respectively.

In SO\textsubscript{2} poisoning process, Cu/SAPO-34 was heated from room temperature to 250 °C and exposed in 112 ppm SO\textsubscript{2} for 5 h or 16 h, or in 336 ppm SO\textsubscript{2} for 16 h with 10\% H\textsubscript{2}O/air at 250 °C respectively. The poisoned samples were named as Cu-112-5, Cu-112-16 and Cu-336-16 according to the concentration of SO\textsubscript{2} and treating time. Similarly, the support was heated from room temperature to 250 °C and exposed in 336 ppm SO\textsubscript{2}, 10\% H\textsubscript{2}O/air for 16 h. The SO\textsubscript{2} poisoned support was named as SAPO-34-336-16h.
2.2. NH$_3$-SCR performance evaluation

The NH$_3$-SCR activity was performed at atmospheric pressure in a three-sleeve quartz reactor. The 100 mg catalysts (powder 60-80 mesh) mixed with 900 mg quartz sands were packed in the plug flow reactor and the temperature was controlled by a type K thermocouple inserted into the centre of the catalysts. The gas flow and volume hourly space velocities in NH$_3$-SCR activity experiments was controlled at 500 ml/min and 300,000 h$^{-1}$, respectively. The inlets gases contained 500 ppm NO, 500 ppm NH$_3$, 5% O$_2$, 5% H$_2$O and 8% CO$_2$. The gas composition was controlled by mass flow controllers and the outlet concentrations were analysed by a Fourier Transform Infrared (FTIR) spectrometer (MKSP2030) equipped with a 5.11 m gas cell. The test temperatures were selected from 100 °C to 500 °C. The NOx conversions were calculated by Eq. (1) which based on the inlet and outlet gas concentrations.

$$\text{NO}_x \text{ Conversion} = \frac{(\text{NO} + \text{NO}_2)_{\text{inlet}} - (\text{NO} + \text{NO}_2)_{\text{outlet}}}{(\text{NO} + \text{NO}_2)_{\text{inlet}}} \times 100\% \; \text{ ................. (1)}$$

The NH$_3$-SCR kinetic results of Cu/SAPO-34 catalysts were obtained in a differential reactor fitted with 25 mg catalyst and 125mg quartz sand. The samples particles were 80-100 mesh and the volume hourly space velocities (VHSV) was 3,600,000 h$^{-1}$ to eliminate internal and external diffusion, respectively. The samples were pre-treated in 5% O$_2$/N$_2$ at 300 °C before kinetic experiments. Since negligible effects of H$_2$O (g) and CO$_2$ in our previous study [12], the SCR kinetic experiments were performed without H$_2$O (g) and CO$_2$. The reaction gas consisted of 500 ppm NO, 500 ppm NH$_3$, 5% O$_2$ with N$_2$ as the balance. The kinetic steady-state measurements were obtained from 170 °C to 230 °C at 20 °C intervals and kept at each temperature for at least 1.5 h. By assuming plug flow reactor and free of diffusion limitations, the NH$_3$-SCR reaction rates can be calculated from the NOx conversion by:

$$\text{rate} [\text{mol NO}_x \cdot \text{g}_{\text{cata}} \cdot \text{s}^{-1}] = \frac{X_{\text{NO}x} \times F_{\text{NO}} \times L_{(\text{NO}_2)} \times \text{min}^{-1}}{m_{\text{cata}} \times 60 \times \text{s} \cdot \text{min}^{-1} \times 22.4 \times \text{L} \cdot \text{mol}^{-1}} [\text{mol NO}_x \cdot \text{g}_{\text{cata}} \cdot \text{s}^{-1}] \; \text{ ................. (2)}$$
\[ X_{\text{NO}_x} = \text{NO}_x \text{ Conversion}, \% \]

\[ F_{\text{NO}_x} = \text{Flow Rate of NO}_x, [L \text{ (NO}_x \cdot \text{min}^{-1}] \]

2.3. Catalyst characterization

The Cu content was determined by ICP-AES (inductively coupled plasma and atomic emission spectrometry), and the Si, P, Al and S contents were determined by X-Ray Fluorescence (XRF). The Cu content of the Cu/SAPO-34 catalysts was 1.66 wt% and Al:Si:P ratio (1:0.22:0.83) was calculated by molar ratio of Al, Si and P by Al as the standard.

The XRD patterns were acquired using X’ Pert Pro diffractometer operating at 40 kV and 40 mA with nickel-filtered Cu Kα radiation (\( \lambda = 1.5418 \) Å) in the range 5° < 20 < 50° with a step size of 0.02°. The BET surface area was determined from the liner portion of the BET plot by measuring the N\(_2\) isotherm of the samples at 77 K using F-Sorb 3400 volumetric adsorption/desorption apparatus. Prior to the measurement, the samples were degassed at 150 °C under vacuum for 3 h (Table 1).

The Electron Paramagnetic Resonance (EPR) spectra were recorded on a Bruker ESP320 spectrometer. The Bruker ESP320E software and the special Bruker program were used for data analysis. Each spectrum was obtained by multiple scans to achieve a satisfied signal to noise ratio. Before these measurements, the samples were pre-treated in air at 300 °C for 1 h. Then X-band (\( v = 9.78 \) GHz) EPR spectra were recorded at room temperature and the magnetic field was swept from 2000 Gauss to 5000 Gauss. The standard sample DPPH (\( g = 2.0036 \)) was used for calibration of the instrument error before every measurement. The location and the intensity of g factors were determined by Bruker’s WINEPR program based on the \( h\nu = g\beta H \), where h was Planck constant, H was the actual magnetic field, and \( \beta \) is Bohr magneton.

Temperature Programmed Reduction (TPR) experiments were performed in a U-shaped tubular quartz reactor. Prior to reduction, the samples (100 mg) were first treated at 300 °C under a flow of 30 ml/min 2% O\(_2\)/N\(_2\) and kept for 30 minutes. Then, the samples were cooled down to room temperature following by purging in N\(_2\) with a
flow of 30 ml/min. In the temperature programmed reduction process, the samples were measured in a flow of 5% H\textsubscript{2}/N\textsubscript{2} (10 ml/min\textsuperscript{-1}) from 30 °C to 900 °C at a ramping rate of 10 °C·min\textsuperscript{-1}. The consumption of hydrogen was monitored by a thermal conductivity detector and combined by mass spectrometer (HIDEN HPR20). Diffuse reflectance infrared Fourier transform spectra (DRIFTS) was measured on a FTIR spectrometer (Nicolet 6700 FTIR) with a MCT detector at a resolution of 2 cm\textsuperscript{-1}, averaging 32 scans for each spectrum, using the OMNIC software. ZnSe windows were used in the commercial high-temperature vacuum diffuse reflectance chamber (Thermofisher). The ex-situ DRIFTS spectra were recorded in the range of 4000-400 cm\textsuperscript{-1}. Initially, the samples were treated at 300 °C in 1% O\textsubscript{2}/He/Ar for 1 h executing to remove the adsorbed water and clean the surface before each measurement. The spectra of the catalysts were recorded at 150 °C in He/Ar atmosphere and the spectrum of KBr under the same condition was used as the background. For the SO\textsubscript{2}-DRIFTS experiments, the fresh Cu/SAPO-34 was treated at 300 °C in 1% O\textsubscript{2}/He/Ar for 1 h and then the sample was exposed to 0.1% SO\textsubscript{2} with 2% O\textsubscript{2} until stable, the experiment was conducted at 250 °C.

3. Results

3.1. XRD&BET

Fig. 1 shows the XRD patterns of fresh and SO\textsubscript{2} poisoned samples. All the samples present the typical chabazite structure and keep a high crystallinity, which meant that SO\textsubscript{2} poisoning did not destroy the structure of molecular sieves\textsuperscript{[20,21]}. Sulfur oxides are expected to have larger affinity to copper species compared with strong acid sites originating from the SAPO-34. However the formation of ammonium sulfate or ammonium bisulfate species does not change the CHA structure due to the amount of sulfate species is too small (< 2µm) and well dispersed on the supports. Furthermore, Cu/SAPO-34 catalysts with relatively small pores and one-dimensional pore structure have shown certain poisoning resistance to these deposits. The results of the BET
surface area (Table 1) show that both fresh and SO$_2$ poisoned samples keep a high surface area (around 540m$^2$/g). It indicated that SO$_2$ poisoning does not obviously change the framework structure of Cu/SAPO-34 catalyst.

3.2. *Ex-situ* DRIFTS

In order to probe the effect of SO$_2$ poisoning on the SAPO-34 framework vibrations, the *ex-situ* DRIFT spectra was used to characterize the surface during exposure to SO$_2$ (As shown in Fig.2). The spectra in absorbance units are acquired after pretreating the samples at 300 °C to remove the adsorbed water and clean the surface. Peaks in the range of 2000 cm$^{-1}$-650 cm$^{-1}$ associated with the internal and external stretching vibrations of the SAPO-34 framework. The peaks in the 3800 cm$^{-1}$-3500 cm$^{-1}$ region are related to the OH group stretching vibration modes. The weaker bands at 3745 cm$^{-1}$ and 3678 cm$^{-1}$ are assigned to P-OH and Si-OH species located on the external surface of the sample particles, respectively. Two stronger bands at 3627 cm$^{-1}$ and 3600 cm$^{-1}$ are assigned as the stretching mode of bridged OH groups Al-(OH)-Si, which are related to the Brønsted OH groups [7]. The result illustrates that there is no significant difference between the spectra of fresh and SO$_2$ poisoning SAPO-34 (Fig. 2a). So it is suggested that SAPO-34 support are insensitive to sulfur, since both of them shows acidic.

For the DRIFT spectra of Cu/SAPO-34 samples (Fig. 2b), two bands at 891 cm$^{-1}$ and 844 cm$^{-1}$ appear, which are associated with an internal asymmetric framework vibration perturbed by copper cations [21, 22]. Noteworthy, the intensity of the two bands obviously decline with the different sulfide degree. It illustrates that sulfates/sulfites may combine with the copper cations, which influence the coordination environment and the content of active Cu$^{2+}$ species.

3.3. Catalyst activity

NH$_3$-SCR performance of various catalysts is shown in Fig. 3. It can be seen that the fresh Cu/SAPO-34 sample shows the superior SCR activity during the whole
temperature range (100 °C-500 °C), while the NO conversion of all the SO₂ poisoned samples decline obviously. The relation between the average NO conversion loss with the S content of the SO₂ poisoned samples is showed in Fig.4. The largest decline of the NO conversion is about 32% for Cu-336-16h sample, while the S content is 35.625 µmol/g catalysts. For all the samples, the Cu loading and Si: Al: P ratio is consistent, the XRD and BET results also show that the framework structure of the support does not change after SO₂ poisoning. It suggested that the decline of the NH₃-SCR activity is attributed to the reduction of the active Cu species. According to the previous results [14,17,18], some SO₂ are released during the TPD for Cu/SAPO-34 catalyst exposure to SO₂. And ammonium-sulfate or ammonium-bisulfate species would be formed in the presence of NH₃. However the decomposition temperature of (NH₄)₂SO₄ is at around 300 °C, which is far less than the desorption temperature of SO₂ for the sulphated Cu/SAPO-34 catalyst. So the influence of ammonium-sulfate formed during the SCR reaction on the activity was inconspicuously.

3.4. H₂-TPR

To obtain more information on the copper species, H₂-TPR was carried out on the fresh catalysts and SO₂ poisoned Cu/SAPO-34 catalysts (As shown in Fig. 5). Two main peaks (denoted as A and B) of H₂ consumption for Cu/SAPO-34 sample and three main peaks (denoted as A, B and C) of H₂ consumption for SO₂ poisoned catalysts from 150 °C to 600 °C are observed. The peak at the lower temperature (peak A) represents the reduction of isolated Cu²⁺ to Cu⁺ [23-25], the moderate one (peak B) represents the reduction of CuO to Cu⁰ [23, 24]. The peak at around 450 °C represent the reduction of the deactivated Cu²⁺ species, which are close to those observed from the reduction of CuSO₄·5H₂O [26]. The peak above 650 °C (peak D) can be attributed to the reduction of sulfate species. H₂S is detected at around 650 °C for the SO₂ poisoned samples by MS (see Fig.6). Hence, there are three types of Cu species in all the SO₂ poisoned samples, including external surface CuO, isolated Cu²⁺ and deactivated Cu²⁺. It is worth noting that the valence of sulfur species is difficult to
specify from TPR results. It is worth noting that the valence of sulfur species is difficult to specify from TPR results. But the TPR experiment shows that the sulfur species occur on copper sites of the Cu/SAPO-34 materials, and this phenomenon is corroborated with the TG and *ex-situ* DRIFTS results.

### 3.5. EPR

EPR is an excellent technique for quantitatively identifying the amount of isolated Cu$^{2+}$ ions and to probe the structure and coordination environment. Fig. 7 shows the EPR spectra of the fresh and SO$_2$ poisoned Cu/SAPO-34 catalysts performed at room temperature. Ham and Kim et al [27, 28] suggested that the isolated Cu$^{2+}$ ions was octahedral coordinated to three framework oxygen atoms and three water molecules in Cu/SAPO-34. As shown in Fig. 7, the Cu$^{2+}$ species load in all Cu/SAPO-34 samples display axial symmetry for all spectra. For all Cu/SAPO-34 samples, the characteristic signal peaks of isolated Cu$^{2+}$ at $g_\parallel$=2.373 and $g_\perp$=2.047 are observed, which is characteristic of the Cu$^{2+}$ species in site (Ⅰ) (Cu$^{2+}$ (Ⅰ)) [29, 30], it illustrates that the location of the Cu$^{2+}$ does not change after SO$_2$ poisoning. Four hyperfine splitting peaks (originated from the interaction of the Cu nuclear and unpaired electron) clearly observed from the spectra of the fresh Cu/SAPO-34. Simultaneously, the hyperfine splitting peaks of the SO$_2$ poisoned samples are not obvious. The strength of the peaks decline for the SO$_2$ poisoned samples, which mean the reduction of the content of the active isolated Cu$^{2+}$ species.

### 4. Discussion

#### 4.1 The effect of SO$_2$ poisoning on the structure of the Cu/SAPO-34

According to the sulfur content shown in Table 1 and the XRD patterns shown in Fig. 1, there is almost no sulfur exists on the SAPO-34 support after SO$_2$ exposure. In addition, the *ex-situ* DRIFT results illustrate that SO$_2$ poisoning has a less pronounced influence on the structure of the SAPO-34 support. It can be concluded that SO$_2$ could not influence the crystal and texture structure of the support because SO$_2$ is difficult to
interact with HSAPO-34. In good agreement with results of Kumar et al\cite{18}, very little SO$_2$ was absorbed on the SAPO-34 support due to both of them showing acidity. However, for the Cu/SAPO-34 catalysts, the coordination environment of Cu species has a significant change according to the decline of the strength of the two bands at 891 cm$^{-1}$ and 844 cm$^{-1}$ by the ex-situ DRIFT results (Fig. 2). It suggested that the varying states of copper species among the different sulfate samples resulted in noticeable SCR activity degradation.

4.2 The effect of SO$_2$ poisoning on the Cu species

According to the results of H$_2$-TPR, there are three types of copper species in all the SO$_2$ poisoned Cu/SAPO-34 samples. However, the intensity of each H$_2$ consumption peak is significantly different according to the degree of SO$_2$ treatment. It indicates that the SO$_2$ poisoning influence the distribution of Cu species. According to the TPR quantification results (As shown in Fig.8), all the samples show the similar total amount of copper. Noteworthy, the content of the CuO species is basically unchanged after SO$_2$ exposure. However the amount of the Cu$^{2+}$ decline with the aggravation of the SO$_2$ poisoning. In good agreement with EPR results, Cu$^{2+}$ is more active than CuO species, being thus it is easier for electrons transferring. Fig. 9 shows the concentration of isolated Cu$^{2+}$ ions semi-quantified by double integrating the EPR spectroscopy. It is observed that the amount of Cu$^{2+}$ decline apparently after SO$_2$ exposure. According to the TPR results, the reduced Cu$^{2+}$ is due to the partly deteriorated by the S species and eventually changed into the sulfate/sulfite species. Lavalley \cite{26} also found that the sulfates formed on copper sides by TPR. As the amount of S species is low in the SO$_2$ poisoned samples, the kind of sulfur species is difficult to specify from ex-situ DRIFTS results.

The thermal gravimetric experiments were conducted for all samples (As shown in Fig.S1). The amount of sulfate species for samples of different sulfate degree were calculated and shown in Fig 10. It is obviously that the amount of sulfate species increased with the time and the concentration of SO$_2$ exposure.

4.3 The effect of the SO$_2$ poisoning on the NH$_3$-SCR activity
The kinetic NH$_3$-SCR reaction was performed between 170 °C to 230 °C, at which temperatures the NO conversion is less than 20%. Fig. 11 presents the Arrhenius plots of the SCR reaction rates over SO$_2$ poisoned Cu/SAPO-34 samples. At each fixed temperature, the reaction rate decreases with increased sulfide degree. It indicates that SO$_2$ exposure makes part of active Cu$^{2+}$ deactivation. The relationship between the molar ratio of S/Cu$^{2+}$ and the rate of NO conversion over all Cu/SAPO-34 catalysts is shown in Fig.12. The result shows that the lowest occupation of S species per Cu$^{2+}$ ion on the catalysts is about 13%. However the reaction rate for NO conversion immediately decreases from $16.85 \times 10^{-5}$ to $8.61 \times 10^{-5}$ mmol/g/s. Further, the S/Cu$^{2+}$ ratio and the reaction rate maintain a linear regular on the SO$_2$ poisoned samples. It reveals that the catalyst is very sensitive to SO$_2$ exposure.

According to the kinetic results, all the samples present a similar apparent activation energy ($E_a=33.99kJ.mol^{-1}$), which is coincident with our previous result (33.6 kJ.mol$^{-1}$) for the ion-exchange Cu/SAPO-34 catalysts$^{[12]}$. It illustrates that SO$_2$ poisoning does not change the SCR reaction mechanism. Noteworthy, the samples show different pre-exponential factor (A), illustrating the decline of active sites content. According to our previous study, the isolated Cu$^{2+}$ is the activity site of Cu/SAPO-34 for NH$_3$-SCR reaction$^{[12]}$. So it can be concluded that SO$_2$ may attack the isolated Cu$^{2+}$ to form cupric sulfates/sulfites species, which result in the active Cu$^{2+}$ species lose its ability involving in the reaction.

Fig. 13 presents the results of SO$_2$-DRIFTS of Cu/SAPO-34, the two bands of Cu$^{2+}$ species at 890 cm$^{-1}$ and 845 cm$^{-1}$ occur at about 3 min. It illustrates that SO$_2$ adsorb on the Cu$^{2+}$ species immediately (3 min) as soon as SO$_2$ is exposure to the Cu/SAPO-34 sample. Combining the above data, it was concluded that the mechanism of SO$_2$ poisoning could be concluded as shown in Scheme 1. SO$_2$ is acidic and the isolated Cu$^{2+}$ is electronegative, the gaseous SO$_2$ molecule is easy to adsorb on Cu$^{2+}$. Then SO$_2$ may translate into sulfite on the Cu$^{2+}$ side. The Cu$^{2+}$ and sulfur species also contain the characteristic of the coordinate covalent bond, where Cu$^{2+}$ and sulfur species may act as a Lewis acid and base, respectively$^{[31]}$. Moreover, in the presence of gaseous oxygen, Cu$^{2+}$ firstly performs catalytic oxidation of SO$_2$ to SO$_3$, which
then forms sulfate on the copper site[32]. Kim et al[33] found that the translation of SO$_2$ to SO$_3$ is much higher reaction rate for copper containing catalyst than for copper free ones. So both sulfates and sulfites exist on the SO$_2$ poisoned samples. As we known, SAPO-34 is a structural equivalent of chabazite zeolite, which has channel dimensions 4.3 Å×4.3 Å and formed by 8-membered oxygen ring[34]. Since the bond distance between S and O atoms in SO$_4^{2-}$ is known to be 1.49 Å[35], the diagonal length of O-S-O bond in the SO$_4^{2-}$ anion is approximately 2.58 Å[33]. SO$_2$ is able to diffuse into the channels of SAPO-34 to interact with Cu$^{2+}$ (0.73 Å) and form SO$_4^{2-}$. Since Cu$^{2+}$ species in the cage of the zeolite exist in an isolated environment, they could interact with the sulfates/sulfites species to form cupric sulfates/sulfites at the original position of the catalyst.

5. Conclusions

The SAPO-34 support and the Cu/SAPO-34 catalysts prepared by ion-exchange method are treated with different SO$_2$ concentrations (112 ppm and 336 ppm) and time (5 h and 16 h) at 250 °C. The framework of SAPO-34 does not change after SO$_2$ poisoning. The NH$_3$-SCR performance deactivation observed in the current study is attributed to the loss of active Cu sites in the catalyst due to the presence of sulfur. And the coordination of Cu$^{2+}$ species in Cu/SAPO-34 samples is affected by SO$_2$ from ex-situ DRIFTS. The TPR and EPR results further confirm the amounts of Cu$^{2+}$ in SO$_2$ poisoned samples decline, and they may transform into cupric sulfates/sulfites. Moreover, the kinetic results demonstrate the SO$_2$ poisoning cannot influence the reaction mechanism of NH$_3$-SCR reaction over Cu/SAPO-34 catalysts.

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Supporting Information Available: Some related figures are shown in the supporting information.
References


Figure/Table Captions

Table 1 Sulfur content and BET area of all the samples

Fig. 1 XRD patterns of all the fresh samples and SO2 poisoned samples

Fig. 2 Ex-situ DRIFTs spectra of all the fresh samples and SO2 poisoned samples

Fig. 3 NO conversions as a function of reaction temperature; reaction condition: 500ppmNO, 500ppmNH3, 5% O2, 8% CO2, 3% H2O balanced with N2; the flow rate: 500 mL/min; GHSV: 300,000 h⁻¹, catalyst weight: 100mg

Fig. 4 The relationship between S content and average loss of NO conversion over SO2 poisoned Cu/SAPO-34

Fig. 5 H2-TPR profiles for the fresh sample and SO2 poisoned samples. Conditions: 5% H2 balanced with N2. Flow rate: 10 ml·min⁻¹. Ramping rate: 10 °C·min⁻¹. “Dash line” represents for the fitting results.

Fig. 6 The partial pressure of H2S for fresh and SO2 poisoned samples

Fig. 7 EPR spectra of fresh sample and SO2 poisoned samples at room temperature after pretreating 60 minutes at 300 °C.

Fig. 8 Amount of Cu species quantified by the H2-TPR profile.

Fig. 9 Concentration of isolated Cu²⁺ ions semi-quantified by double integrating the EPR spectroscopy

Fig. 10 The amount of sulfate species quantified by TG

Fig. 11 Arrhenius plots of the SCR reaction rates at 170 °C-230 °C over fresh and SO2 poisoned samples. The in-let gas composition: 500 ppm NO, 500 ppm NH3, 5% O2/N2.

Flow rate: 1.5 L·min⁻¹. GHSV: 3600,000 h⁻¹. Catalysts weight: 25 mg

Fig. 12 The relationship between the molar ratio of S/Cu²⁺ and the rate of NO
conversion over the SO₂ poisoned samples

Fig. 13 DRIFT spectra of Cu²⁺ species on Cu/SAPO-34 catalysts during exposure to SO₂ + O₂

Scheme 1 The mechanism of SO₂ poisoning on NH₃-SCR reaction over Cu/SAPO-34 catalysts
<table>
<thead>
<tr>
<th>Sample</th>
<th>Sulfur content (µmol/g Cu/SAPO-34)</th>
<th>BET area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAPO-34</td>
<td>0</td>
<td>539.5</td>
</tr>
<tr>
<td>SAPO-34-336-16</td>
<td>0</td>
<td>537.1</td>
</tr>
<tr>
<td>Cu/SAPO-34</td>
<td>0</td>
<td>570.7</td>
</tr>
<tr>
<td>Cu-112-5</td>
<td>11.3</td>
<td>557.7</td>
</tr>
<tr>
<td>Cu-112-16</td>
<td>23.9</td>
<td>546.1</td>
</tr>
<tr>
<td>Cu-336-16</td>
<td>35.6</td>
<td>538.2</td>
</tr>
</tbody>
</table>
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![Graph showing H₂ Consumption at different temperatures for various catalysts: Cu-336-16-h, Cu-112-16-h, Cu-112-5-h, and Cu/SAPO-34. The x-axis represents temperature in °C ranging from 100 to 900. The y-axis represents H₂ Consumption (a.u.).](image-url)
$E_a = 33.99 \pm 1.29 \text{kJ/mol}$
The graph shows the rate of NO conversion (10^-5 mol/g·s⁻¹) as a function of the molar ratio of S/Cu²⁺ (%). The rate decreases as the molar ratio increases.
Isolated Cu$^{2+}$ Gaseous SO$_2$

SO$_2$ $\rightarrow$ 250 °C

SO$_3^{2-}$ or SO$_4^{2-}$
Supporting information

Fig. 1 Derivative TGA data of weight loss of all SAPO-34 samples during temperature programmed process in 20% O₂/N₂ atmosphere

Thermal gravimetric experiments were conducted on METTLER TOLEDO thermal gravimetric analysis. 10 mg samples were heated in a mixture gas flow contained N₂ (25 ml/min) and O₂ (5 ml/min) at a heating rate of 10 °C/min from ambient temperature to 1000 °C.