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Migration, reactivity, and sulfur tolerance of copper species in SAPO-34 zeolite toward NO_x reduction with ammonia[†]

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Cu/SAPO-34 catalysts were prepared by wet impregnation and ion-exchange methods, and both the catalysts were hydrothermally treated at 750 °C in 10 vol% $\text{H}_2\text{O}/\text{air}$ for 24 h. Subsequently, the as-received and hydrothermally treated catalysts were exposed to a sulfur poisoning treatment at 350 °C in 100 ppm $\text{SO}_2/10$ vol% $\text{H}_2\text{O}/\text{air}$ for 24 h and examined for NO_x conversion. Sulfur poisoning considerably decreased the NO_x conversion efficiency of the catalysts at low temperatures. In contrast, it improved the high-temperature selective catalytic reduction (SCR) activities of the as-received catalysts. The ion-exchange-prepared catalysts displayed higher sulfur tolerance than the impregnation-prepared catalysts at 150–350 °C. The electron paramagnetic resonance, X-ray photoelectron spectroscopy, energy-dispersive X-ray spectroscopy and H_2 -temperature-programmed reduction results showed that sulfur poisoning significantly influenced the migration of the copper species and thereby the amount of active isolated Cu^{2+} . More dispersed CuSO_4 was produced on the ion-exchange-prepared catalysts than on the impregnation-prepared catalysts after sulfur poisoning. The dispersed CuSO_4 showed considerably higher SCR activity than the crystalline CuSO_4 . Both the dispersed CuSO_4 and remaining isolated Cu^{2+} determined the low-temperature SCR behavior of the sulfur-poisoned catalysts.

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1. Introduction

Sulfur is always present in vehicle exhausts arising from residues in the fuel and lubricant oils. It is therefore essential to examine the effect of sulfur on different catalysts involved in NH_3 -selective catalytic reduction (SCR) after-treatment systems. Despite the considerable reduction in the content of sulfur in diesel fuel in recent years, especially with the implementation of China IV standard diesel in China, sulfur poisoning remains one of the most significant deactivation factors for SCR catalysts employed in heavy-duty diesel motor exhaust after-treatment systems. Although China IV standard diesel contains less than 50 ppm sulfur, the cumulative lifetime exposure of catalysts may amount to kilograms of sulfur.

Several studies^{1–9} have addressed the effects of sulfur poisoning on different NH_3 -SCR catalysts. Vanadium-based

catalysts were found to have a greater tolerance toward SO_2 poisoning than metal zeolite catalysts.^{1–4,5} Among the zeolite-based catalysts, Cu zeolites are more sensitive to sulfur dioxide than Fe zeolites,^{1–3} and the deactivation effect is more pronounced at low temperatures.^{2,4}

In recent years, Cu-exchanged zeolite catalysts of the chabazite family with unique microporous structures have emerged as a leading candidate among zeolite formulations when compared to Cu/ZSM-5 and Cu/beta owing to their superior NH_3 -SCR activity and prominent hydrothermal stability at 750 °C.^{10,11} Previous research studies^{12–16} demonstrated that isolated Cu^{2+} species are the active sites for SCR reaction, as determined by extended X-ray absorption fine structure and kinetic tests. Zhang *et al.* concluded that SO_2 inhibited the SCR activity at low temperatures owing to the formation of ammonium sulfates as well as the onset of competitive adsorption between SO_x and NO_x on the Cu sites.¹⁷ Kumar *et al.*¹⁸ compared the effects of SO_2 and SO_3 on Cu/SAPO-34 catalyst and found that poisoning with SO_3 at 400 °C resulted in a more severe deactivation when compared with that with SO_2 . Because of its strong chemical binding strength and the oxidative conditions in diesel exhaust streams, sulfur can react readily with Cu in a Cu/zeolite SCR catalyst to form stable CuSO_4 -like compounds.^{3,6,7} Such a sulfur poisoning phenomenon affects the redox properties of the Cu sites, severely inhibits NO oxidation and subsequent formation of the adsorbed NO_x

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complex, and ultimately decreases the SCR activity of the catalyst.^{19,50}

Although some sulfur poisoning mechanisms of NH₃-SCR catalysts have been proposed, little information on the effects of sulfur poisoning on different copper species and the location of sulfur has been reported to date.

In the present study, different preparation methods and a hydrothermal treatment were applied to generate different distributions of Cu species on SAPO-34 support. Various techniques (*i.e.*, X-ray photoelectron spectroscopy, electron paramagnetic resonance, H₂ temperature-programmed reduction, and NH₃ temperature-programmed desorption) were used to probe the location and state of Cu species before and after sulfur poisoning. The evolution of different copper species was examined, and their sulfur tolerance was determined, which is rarely reported.

2. Experimental

2.1. Catalyst preparation

Cu/SAPO-34 catalysts were synthesized by wet impregnation²⁰ and ion-exchange¹⁵ methods, respectively.

Cu(CH₃COO)₂·H₂O (Ling Feng Chemical Reagent, China) was dissolved in deionized water and mixed with commercial H-SAPO-34 molecular sieve (Al₂O₃/SiO₂/P₂O₅ = 1 : 0.3 : 0.8) powders using a wet impregnation method. The liquid was then dried at 80 °C using a rotary evaporator employing a vacuum pump. The powders were dried at 100 °C for 12 h and calcined at 550 °C for 4 h, and the as-received catalyst was denoted as CuiF.

The H-SAPO-34 was ion-exchanged using a NH₄NO₃ (99% NH₄NO₃, Aladdin, China) solution at 80 °C for 2 h to obtain the NH₄-SAPO-34. Then, the solid was filtered and rinsed with deionized water, and was dried at 100 °C for 12 h. Cu ion-exchange was performed by mixing the NH₄-SAPO-34 with a Cu(CH₃COO)₂ (Ling Feng, China) solution at 60 °C for 4 h. After filtered and washed with deionized water, the powders were dried at 100 °C for 12 h and calcined at 550 °C for 4 h, and the as-received catalyst was denoted as CueF.

The nominal content of Cu in the catalysts was 2 wt%. Additionally, the as-received catalysts were hydrothermally treated at 750 °C in 10 vol% H₂O/air for 24 h, and the resulting catalysts were denoted as CuiA and CueA, respectively.

In SCR reactions on many catalysts, the SO₂ effects involve competitive adsorption of SO₂ and the reactants, physical coverage of active sites by ammonium sulfates and formation of active metal sulfates. The last one was irreversible and paid attention to in the present study. To simplify the study, the accumulation of ammonium sulfates and the introduction of SO₂ in SCR reaction were not involved. The as-received and hydrothermally treated catalysts were subjected to a sulfur poisoning treatment in 100 ppm SO₂/10 vol% H₂O/air for 24 h at 350 °C which was located within the normal diesel exhaust temperature and commonly applied in the literature,⁶ and the obtained samples were denoted with a “-s” suffix.

For comparison, CuSO₄/SAPO-34 catalysts were synthesized by mechanical mixing and wet impregnation methods using CuSO₄ solution as the precursor, and the obtained samples

Table 1 The abbreviations of the samples

Sample	Unpoisoned	Abbreviation	Sulfur poisoned
SAPO-34 support	SAPO-34	SAPO-34-s	
Impregnated Cu/SAPO-34, as-received	CuiF	CuiF-s	
Ion-exchanged Cu/SAPO-34, as-received	CueF	CueF-s	
Impregnated Cu/SAPO-34, hydrothermally aged	CuiA	CuiA-s	
Ion-exchanged Cu/SAPO-34, hydrothermally aged	CueA	CueA-s	
Impregnated CuSO ₄ /SAPO-34	—	Cui-s	
Mechanically mixed CuSO ₄ /SAPO-34	—	Cum-s	

were denoted as Cum-s and Cui-s, respectively. The nominal mass content of Cu in the catalysts was also 2 wt%. The comparison of sample and abbreviation were listed in Table 1.

2.2. Activity measurement

The NH₃-SCR activity was evaluated in a fixed bed quartz reactor, and the effluent gases were monitored by infrared spectroscopy (Thermo Nicolet 380). The reaction gas consisted of 500 ppm NO, 500 ppm NH₃, 5% O₂, 10% H₂O, and N₂ in balance. The flow rate of the reaction gas was 1000 mL min⁻¹, the amount of catalyst (sieved to 50–80 mesh) used was 300 mg, and the gas hourly space velocity was kept at 100 000 h⁻¹. The concentration of NO_x (NO, N₂O, and NO₂) was detected at the ppm level. The NO_x conversion of the catalysts was calculated using eqn (1):

$$\text{NO}_x \text{ conversion } (\%) = \frac{\text{NO}_{\text{in}} - \text{NO}_{\text{out}} - \text{NO}_2_{\text{out}} - 2\text{N}_2\text{O}_{\text{out}}}{\text{NO}_{\text{in}}} \times 100, \quad (1)$$

2.3. Characterization

X-ray powder diffraction (XRD) patterns were recorded on a diffractometer (D8 ADVANCE, Bruker, Germany) employing Cu K α radiation ($\lambda = 0.15418$ nm). Data were collected in the range of $5^\circ \leq 2\theta \leq 50^\circ$ with a scanning velocity of 6° min^{-1} .

Textural properties were determined by nitrogen physisorption at -196°C using a JW-BK122F (Beijing JWGB, China) instrument. Prior to the measurements, the samples were degassed at 0.01 Pa at 220°C . The specific surface area and desorption pore volume were assessed using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda methods, respectively.

The actual contents of Cu, Si, Al, P and S were determined on an Agilent 5100 ICP-OES instrument.

Electron paramagnetic resonance (EPR) spectra in the X-band were recorded on a CW spectrometer JES-FA200 (JEOL) at microwave power of 1 mW, modulation frequency of 100 kHz, and central field of 300 mT. Before the measurements, the samples were heated in vacuum from room temperature to 100 °C for 30 min. The samples were then cooled to -150°C .

Mn^{2+} was used as an external reference sample, and the *g* value and EPR spectral intensity of Cu^{2+} were determined.

Transmission electron microscopy (TEM) image and composition of the catalysts were taken on a JEM-2100F (JEOL, Japan) high resolution transmission electron microscope equipped with energy dispersive X-ray spectroscopy (EDX, Oxford EDX System). The catalysts were suspended in ethanol and dispersed over a carbon-coated holey Ni grid with a film prior to measurements.

Hydrogen temperature-programmed reduction (H_2 -TPR) was performed on a Micromeritics Auto Chem II. Prior to the H_2 -TPR experiment, the test sample (50 mg) was treated with He at a total flow rate of 50 mL min^{-1} at $300\text{ }^\circ\text{C}$ for 30 min and subsequently cooled to room temperature and flushed with He for 10 min. The atmosphere was then changed to 10% H_2 /Ar (50 mL min^{-1}), and the reactor temperature was raised to $600\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. H_2 consumption during the experiment was monitored with a thermal conductivity detector.

Sulfate decomposition tests were performed using a mass spectrometer (Omni-star TM). In a typical test, the test sample (50 mg) was treated with He at a total flow rate of 50 mL min^{-1} at $300\text{ }^\circ\text{C}$ for 30 min and subsequently cooled to room temperature and flushed with He for 10 min. Finally, the atmosphere was changed to 10% H_2 /Ar (50 mL min^{-1}), and the reactor temperature was raised to $1000\text{ }^\circ\text{C}$ using a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. The intensities of the *m/z* ratios 64 (SO_2) and 34 (H_2S) in the outlet gas were monitored as a function of temperature.

Ammonia temperature-programmed desorption (NH_3 -TPD) analysis was performed using a TP 5000-II multiple adsorption apparatus (Xianquan, China). The samples (~ 50 mg) were pretreated in He at $500\text{ }^\circ\text{C}$ for 30 min. When the temperature decreased to $50\text{ }^\circ\text{C}$, NH_3 was introduced until adsorption on the samples was saturated. The samples were then purged with He to remove residual NH_3 from the surface of the samples. The samples were then heated in He from 100 to $500\text{ }^\circ\text{C}$ at a rate of $10\text{ }^\circ\text{C min}^{-1}$ for subsequent NH_3 desorption.

The thermal behavior of the catalysts was evaluated on a Mettler Toledo TG/DSC instrument from room temperature to $1000\text{ }^\circ\text{C}$ in N_2 (50 mL min^{-1}) at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. The test powders (30 mg) were loaded in individual alumina sample cells.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a ThermoFisher ESCALAB 250Xi high performance electron spectrometer using non-monochromated Al $K\alpha$ excitation source ($h\nu = 1486.6\text{ eV}$). Binding energies were calibrated using the contaminant carbon (C 1s = 284.6 eV).

3. Results

3.1. Structural properties

The effects of hydrothermal treatment and sulfur poisoning on the structures of the Cu species and SAPO-34 were investigated by XRD, and the results are shown in Fig. 1. For comparison, the diffraction pattern of SAPO-34 zeolite was included. The diffraction peaks of SAPO-34 were consistent with that of single-phase chabazite.²⁰ The chabazite structure of SAPO-34 remained

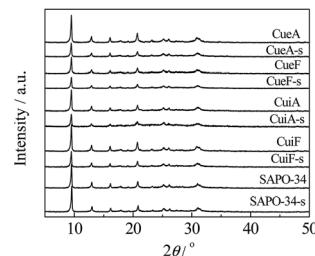


Fig. 1 XRD patterns of the SAPO-34 zeolites and Cu/SAPO-34 catalysts.

intact after copper loading, and no copper-related phases (e.g., Cu, Cu_2O and CuO) were detected for all the catalysts. These results indicated that the copper species were highly dispersed or existed in the form of Cu^{2+} ions.¹⁵ After sulfur poisoning, the intensity of the diffraction peaks of the catalysts decreased, which was mainly attributed to the slight skeleton damage of SAPO-34 upon the treatment.²¹

The specific surface area (S_{BET}), micropore surface area (S_{micro}), external surface area (S_{ext}), and micropore volume of the catalysts were determined and summarized in Table 2. The S_{ext} of the Cu/SAPO-34 catalysts were lower than that of the SAPO-34 support owing to coverage of CuO on the external surface of the zeolite. Interestingly, the S_{BET} and pore volume of the as-received catalyst CuiF, obtained after copper impregnation of the SAPO-4 support, was higher than those of the support. This increase could be related to the generation of small defects in the SAPO-34 crystals (following Cu impregnation).²² After hydrothermal treatment and sulfur poisoning, the copper species and metal sulfates blocked some of the zeolite channels, thus inducing changes in the textural properties of the zeolite.^{20,23} Moreover, as indicated by the XRD patterns in Fig. 1, skeleton damage of SAPO-34 led to decreases in the BET surface areas and pore volumes of the poisoned catalysts. Nevertheless, these changes of the textural properties for the catalysts should not be important factors responsible for their different catalytic behaviors.

As indicated by the inductively coupled plasma optical emission spectrometry (ICP-OES) results in Table 2, the obtained Cu contents in the catalysts were very close to the nominal value, and no loss of copper occurred after hydrothermal treatment. The sulfur content in the poisoned Cu/SAPO-34 catalysts ranged from 0.77 to 0.87 wt%.

3.2. Catalytic activity

The temperature dependency of NO_x conversion during the NH_3 -SCR reaction over the catalysts is shown in Fig. 2. The as-received Cu/SAPO-34 catalysts showed superior SCR activity at low temperatures ($150\text{--}350\text{ }^\circ\text{C}$) as shown in enlarged figure, and the differences were small. The reduced activities at higher temperatures were mainly caused by the competitive reactions between NH_3 -SCR and NH_3 oxidation.^{24,25} After the hydrothermal treatment, the catalysts showed high SCR activity at $200\text{--}500\text{ }^\circ\text{C}$, which are in consistence with the previous report.²⁶ Sulfur poisoning reduced the low-temperature ($150\text{--}350\text{ }^\circ\text{C}$) activities of the catalysts to different degrees; however, it



Table 2 Textural properties and chemical composition of the samples

Sample	S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	S_{micro} ($\text{m}^2 \text{ g}^{-1}$)	S_{ext} ($\text{m}^2 \text{ g}^{-1}$)	Pore volume ($\text{cm}^3 \text{ g}^{-1}$)	Concentration ^a (wt%)				
					Al	P	Si	Cu	S
SAPO-34	651	607	44	0.267	22	21	3.9	—	—
SAPO-34-s	638	599	39	0.262	22	21	3.9	—	0.23
CuiF	676	636	40	0.273	22	21	3.9	1.99	—
CuiF-s	620	575	45	0.253	21	20	3.7	1.95	0.77
CuiA	620	586	34	0.241	22	21	3.8	1.99	—
CuiA-s	575	525	50	0.184	21	20	3.7	1.96	0.81
CueF	618	582	36	0.238	22	21	3.8	2.04	—
CueF-s	569	534	35	0.219	22	21	3.8	2.00	0.85
CueA	621	583	38	0.240	22	21	3.8	2.04	—
CueA-s	560	524	36	0.216	22	21	3.8	1.99	0.87

^a Obtained by ICP-OES.

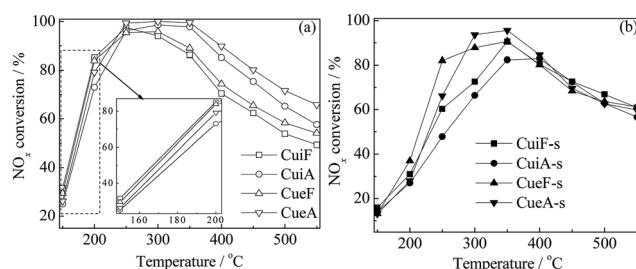


Fig. 2 NH₃-SCR curves of the (a) as-received and hydrothermally treated and (b) poisoned Cu/SAPO-34 catalysts. Reaction conditions: [NO] = [NH₃] = 500 ppm, O₂ = 5%, [H₂O] = 10%, N₂ in balance, and GHSV = 100 000 h⁻¹.

improved the high-temperature (350–550 °C) activities of the as-received catalysts. The concentration of N₂O was always lower than 10 ppm in the whole temperature range (not shown). Such results are discussed further in the following sections.

3.3. EPR studies

The hyperfine structure of isolated Cu²⁺ species was characterized by EPR analysis. In contrast, other copper species do not produce any EPR signals.¹⁵ Therefore, EPR is an effective method to quantitatively determine the amount of isolated Cu²⁺ on Cu-zeolite catalysts. Fig. 3 shows the EPR spectra of the non-poisoned (as-received and hydrothermally treated) and poisoned Cu/SAPO-34 catalysts. Four adsorption peaks were detected in the parallel region, and a sharp peak was observed in the vertical region. The EPR signals at $g_{\parallel} = 2.392$, $A_{\parallel} = 12.958$ mT, and $g_{\perp} = 2.074$ mT could be ascribed to Cu²⁺ species on the site (I) displaced from the six-ring structure into the ellipsoidal cavity of the SAPO-34 zeolite.^{26,27} Furthermore, the intensity of the hyperfine splitting peaks of the sulfur-poisoned samples was lower, indicating a reduction in the number of isolated Cu²⁺ active species.

3.4. EDX studies

In order to examine the effects of the hydrothermal aging and sulfur poisoning on the distributions of copper species on the

external surface of SAPO-34, EDX measurements were carried out based on TEM images and spectra in Fig. S1,† and the results were listed in Table 3. It can be seen that the hydrothermal treatment promoted the migration of Cu from the zeolite external surface to the ion-exchanged sites, which was similar to our previous report.¹⁶ After the sulfur poisoning, the surface Cu concentration increased again for all the catalysts as well as the accumulation of sulfur, suggesting that the sulfur poisoning can provide the driving force for copper migration.

3.5. H₂-TPR studies

H₂-TPR is commonly used for determining types of copper species and the redox properties of catalysts. Fig. S2† shows the TPR curves of the unpoisoned Cu/SAPO-34 catalysts. Four reduction peaks were observed in the temperature range of 50–600 °C. The first peak observed at 100–150 °C was attributed to the reduction of surface CuO clusters on the external surface of the zeolite framework, proceeding *via* a one-step reduction with the stoichiometry of one mole of H₂ for one mole of CuO clusters.²⁷ The second peak was attributed to the reduction of isolated Cu²⁺ in the zeolite framework to Cu⁺. The third peak was attributed to the reduction of CuO crystallites from CuO to Cu⁰. The fourth peak was attributed to the reduction of Cu⁺ to Cu⁰,¹¹ including that of Cu⁺ ions obtained from the reduction of isolated Cu²⁺ and that of original Cu⁺ ions in the framework of

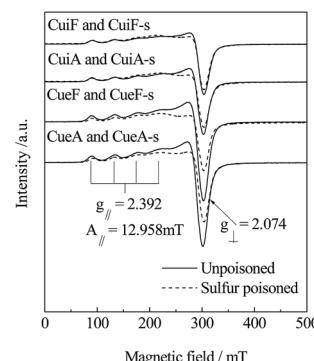


Fig. 3 EPR spectra of the Cu/SAPO-34 catalysts measured at -150 °C.



Table 3 Chemical composition of the Cu/SAPO-34 catalysts obtained by EDX

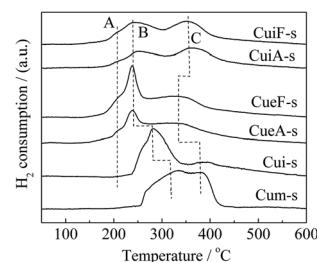
Catalysts	Concentration (wt%)					
	O	Al	P	Si	Cu	S
CuiF	44.09	24.98	23.82	4.25	2.86	—
CuiF-s	46.03	23.11	22.54	4.09	3.28	0.94
CuiA	44.23	25.06	25.30	3.84	1.57	—
CuiA-s	45.77	22.74	23.45	3.51	4.01	0.53
CueF	46.09	23.82	23.41	3.56	3.13	—
CueF-s	42.87	24.30	24.04	3.26	3.65	0.93
CueA	47.60	23.32	23.42	3.70	1.96	—
CueA-s	42.18	24.67	25.21	4.11	2.50	1.32

SAPO-34. According to the literature,²⁸ the isolated Cu²⁺ ions was reducible in the temperature range 200–300 °C, but the reduction of Cu⁺ ions at the ion-exchange sites to Cu⁰ occurred at distinctly higher temperatures, or they were too stable to be reduced in the H₂-TPR temperature range. Table 4 lists the amounts of different reducible Cu^{x+} species on the catalysts based on the TPR curves. The H₂ consumption was much less than the theoretical value, even if we assumed that all the copper ions existed as Cu⁺. This indicated that some copper species (Cu ions at the ion-exchange sites) were too stable to be reduced to Cu⁰ at temperatures below 800 °C. As observed, the isolated Cu²⁺ ions were more abundant on the ion-exchanged catalysts, and reached the maximum on CueA. Contrarily, more surface CuO clusters were found on the impregnated catalysts, and reached the maximum on CuiF. Furthermore, the strong interaction of copper ions with the zeolite framework, upon the hydrothermal treatment, produced more reducible copper species and especially isolated Cu²⁺ ions.²⁹

Surface CuO clusters are more active toward the oxidation of NO to NO₂ than isolated Cu²⁺ ions,³⁰ which favor low-temperature reactions *via* the so-called fast SCR reaction.^{20,30} In contrast, surface CuO clusters inhibit the high-temperature SCR activity owing to their high catalytic activity toward NH₃ oxidation.^{20,30} The isolated Cu ions are always active within a wide temperature range (150–550 °C). Hence, the surface CuO clusters and isolated Cu²⁺ ions synergistically determine the SCR performance of Cu/SAPO-34 catalysts, resulting in trends in catalytic activity in two temperature regions. The trend in low-temperature activity is in good agreement with the amount of

surface CuO clusters as shown in the enlarged figure in Fig. 2a, although the difference is not obvious. For the impregnated catalysts, abundant surface CuO clusters play a more crucial role in the low temperature range than isolated Cu²⁺.^{30,31} Isolated Cu²⁺ ions are abundant in the ion-exchanged catalysts and dominate the activity at low temperatures. Both types of copper species can act as active sites for the low-temperature SCR reaction. The active surface CuO clusters is absent in some studies,^{32,33} due to the specific SAPO-34 supports and preparation methods adopted, and the hydrothermal treatment will increase the amount of Cu²⁺ and improve the activity at low temperatures.

H₂-TPR analysis was also conducted on the sulfur-poisoned catalysts. Three peaks of H₂ consumption were observed (Fig. 4). The peak observed at the lowest temperature (peak A) was attributed to the reduction of isolated Cu²⁺ to Cu⁺.^{34,35} The peaks observed at 230–350 °C (peak B) and 350–450 °C (peak C) were attributed to the reduction of dispersed CuSO₄, and overlapping of the reduction of crystalline CuSO₄ (ref. 36 and 50) and Cu⁺ to Cu⁰, respectively.^{31,50} Assignments of these reduction peaks were confirmed by the TPR curves of reference samples Cui-s and Cum-s. Specifically, peak A was absent for these mixed catalysts using CuSO₄ as the precursor. Cui-s displayed a dominant peak B, which was assigned to the reduction of dispersed CuSO₄. Cum-s displayed a bimodal peak distribution that accounts for the reduction of dispersed CuSO₄ and crystalline CuSO₄ at 320 and 380 °C,^{31,36} respectively. The reducibility of CuSO₄ species followed the order of dispersed CuSO₄ > crystalline CuSO₄. The results agreed with the XRD results, which indicated that the dispersion of CuSO₄ in Cui-s and Cum-s is different. Compared with the unpoisoned catalysts

Fig. 4 H₂-TPR curves of the poisoned catalysts.**Table 4** Amounts of different copper species on the Cu/SAPO-34 catalysts

Sample	Amount of copper ^a (μmol Cu per g cat.)	Amount of reducible copper species ^b (μmol Cu per g cat.)					Total ^c
		Surface CuO clusters	Isolated Cu ²⁺	CuO crystallites	Cu ⁺		
CuiF	310.9	47.7	30.5	61.9	56.9	140.1 (166.5)	
CuiA	310.9	10.9	65.3	96.8	148.3	173.0 (256.0)	
CueF	318.8	32.9	208.1	56.0	120.6	297.0 (209.5)	
CueA	318.8	9.9	255.1	67.2	177.4	332.2 (254.5)	

^a Calculated based on the ICP results in Table 2. ^b Obtained by H₂-TPR curves. ^c The data outside and inside the brackets were estimated based on the sum of surface CuO clusters, isolated Cu²⁺ and CuO crystallites (that of surface CuO clusters, CuO crystallites and Cu⁺).





(Fig. S2†), the reduction peak associated with surface CuO clusters (at 100–150 °C) disappeared completely after sulfur poisoning owing to accessibility to SO₂ and transformation to copper sulfates. In contrast, some isolated copper ions remained as the small pores (0.43 nm) of SAPO-34 protected the isolated Cu²⁺ from attack by SO₂, which has a similar kinetic diameter of 0.411 nm.³⁷ As determined from the H₂-TPR curves, CuSO₄ was highly dispersed on the poisoned ion-exchange-prepared catalysts. In contrast, the metal sulfates was much larger on the poisoned impregnation-prepared catalysts, and hence, CuSO₄ was not as highly dispersed in the poisoned impregnation-prepared catalysts.

Surface CuO clusters and crystallites are more abundant on the impregnation-prepared catalysts. After sulfur poisoning, surface CuO clusters and crystallites tended to transform to dispersed CuSO₄ and crystalline CuSO₄, respectively, and the generated dispersed CuSO₄ would sinter to form crystalline CuSO₄, too. Thus, it appeared to be easier for surface copper species to form crystalline sulfates upon the sulfur poisoning treatment since they were exposed on the catalyst surface. As shown in Table 4 and Fig. S2,† the isolated Cu²⁺ ions were much more abundant on the ion-exchanged catalysts (CueF and CueA). On the other hand, the reduction peak B of the corresponding sulfated catalysts (CueF-s and CueA-s) in Fig. 4, which was attributed to the reduction of dispersed CuSO₄, was much intenser than those of the sulfated impregnated catalysts (CuiF-s and CuiA-s). Based on kinetic and thermodynamic theories, it is easier for isolated Cu²⁺ to migrate onto the catalyst surface to form dispersed CuSO₄ than CuSO₄ crystallites under the same poisoning treatment condition. Previous studies also have elucidated the impact of sulfur poisoning on Cu dispersion. Cheng *et al.*⁷ used XANES/EXAFS analyses to investigate properties of the copper species in Cu/SAPO-34 before and after sulfur poisoning. The Cu K-edge XANES spectra for the Cu/SAPO-34 before and after sulfur poisoning, as well as the spectra for CuSO₄ as a reference. The XANES spectra between 8975 and 8985 eV were similar for both the unsulfated and sulfur-poisoned catalysts, but quite different from the spectrum of crystalline CuSO₄. This suggests that the sulfate formation resulting from sulfur poisoning does not induce any macroscopic changes in the Cu species; in other words, Cu remains in a highly dispersed state as its initial ion-exchange locations. A similar phenomenon was observed by Hamada *et al.*³⁸ over a Cu-ZSM-5 catalyst after SO₂/O₂ treatment.

As observed in Fig. 5, a bimodal SO₂ release distribution was detected within 250–500 °C by mass spectrometry analysis. The low-temperature peak was ascribed to the decomposition/reduction of dispersed CuSO₄ was centered at 310 and 330 °C for the poisoned ion-exchange- and impregnation-prepared catalysts, respectively. The high-temperature peak was located at 380 °C and ascribed to the decomposition/reduction of crystalline CuSO₄. Moreover, the poisoned ion-exchange-prepared catalysts displayed a stronger dispersed CuSO₄-related peak. As noted, the temperatures at which the dispersed CuSO₄-related SO₂ peak was observed were somewhat higher than those of the corresponding H₂ peak B. This difference was attributed to the re-adsorption of the SO₂ released from the decomposition/

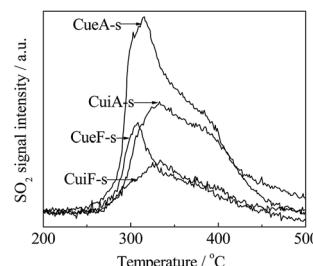


Fig. 5 The outlet SO₂ signals detected from the H₂-TPR tests of the poisoned catalysts.

reduction of CuSO₄ on the catalyst.^{39,40} No H₂S was detected at 50–1000 °C for all the poisoned catalysts. The formation of elemental sulfur on the catalyst surface cannot be completely excluded or some of the reduction products were not detected by MS, which may be responsible for the differences between the sulfate amounts determined by ICP-OES, TGA and MS. In this sense, the ICP-OES results appear to be more reliable.

3.6. NH₃-TPD studies

Ammonia is widely used as a probe molecule to identify types of surface acidic sites.^{41–43} In this study, the acid properties of the non-poisoned and poisoned catalysts were studied by NH₃-TPD. Fig. 6 shows the NH₃-TPD profiles of the different catalysts. Two broad bands at 120–260 and 320–460 °C could be observed, which could be deconvoluted into three desorption peaks (A, B, and C).⁴⁴ Peaks B and C observed at the higher temperatures could possibly be assigned to structural Brønsted acid sites, which can be correlated to moderate and strong acidity.^{37,45–48} After copper loading, considerable changes in peaks A, B, and C were observed. Peak A could be attributed to the adsorption of NH₃ molecules on weak Brønsted acid sites on the zeolite and weak Lewis acid sites related to Cu species. Peak B was ascribed to structural Brønsted acid sites on the zeolite and moderate Lewis acid sites related to Cu species. Peak C was related to the adsorption of NH₃ molecules on both strong Brønsted acid sites on the SAPO-34 support and new Lewis acid sites created by the Cu species.⁴¹ The assignments of different peaks are supported by the DRIFTS results as shown in Fig. S3.† Table 4 lists the amount of the different acid sites calculated from the NH₃-TPD results. As observed, the loading of Cu reduced the surface acidity

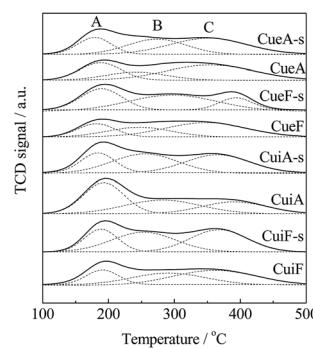


Fig. 6 NH₃-TPD profiles of the Cu/SAPO-34 catalysts.

Table 5 Acidity of the Cu/SAPO-34 catalysts and zeolite determined by NH₃-TPD analysis

Sample	Acidity (mmol NH ₃ per g cat.)			
	Weak	Moderate	Strong	Total
CuiF	0.0163	0.0302	0.0425	0.0890
CuiF-s	0.0255	0.0424	0.0433	0.1112
CuiA	0.0425	0.0350	0.0260	0.1035
CuiA-s	0.0226	0.0443	0.0399	0.1068
CueF	0.0166	0.0211	0.0399	0.0776
CueF-s	0.0298	0.0491	0.0134	0.0923
CueA	0.0243	0.0168	0.0453	0.0864
CueA-s	0.0189	0.0308	0.0417	0.0914
SAPO-34	0.0356	0.0421	0.0391	0.1168

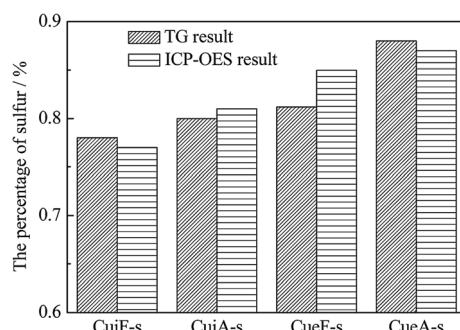


Fig. 7 The percentages of sulfur on the poisoned catalysts determined by TG and ICP-OES analyses.

of HSAP-34 mainly because of the substitution of the support proton ($-\text{Si-OH-Al}$) by Cu^{2+} ions. Table 5 also shows that more acid sites were created after sulfur poisoning. For the poisoned catalysts, the deposited sulfates could serve as moderate acid sites. Combined with the SCR performance in Fig. 2, the high NH₃ adsorption capacity of the poisoned catalysts may facilitate the SCR reaction at high temperatures. When compared with the as-received catalysts, the hydrothermally treated catalysts featured more Lewis acid sites. Sulfur poisoning also led to a decrease in the amount of weak acid sites, which could be related to the reduced amount of Lewis acid sites created by Cu species owing to the formation of copper sulfates.

Thermogravimetric analysis was conducted on the sulfated catalysts. The percentages of sulfur on the poisoned catalysts were calculated from the thermogravimetric analysis obtained in the temperature range of 450–1000 °C shown in Fig. 7 (estimated by SO₃), which decreased in the order of CueA-s > CueF-s > CuiA-s > CuiF-s. The TG results are in good agreement with the ICP-OES results, and minor differences determined by two methods may be caused by the incomplete decomposition or dissolution of some sulfate species.¹⁹

4. Discussion

4.1. Effects of sulfur poisoning on Cu species

The amount of isolated Cu^{2+} ions was calculated by integrating the EPR curves in the magnetic field range of 0–500 mT and

setting the value of CuiF as the standard. As shown in Fig. 8, the amount of isolated Cu^{2+} decreased after sulfur poisoning to different degrees, and the reduction in the amount of isolated Cu^{2+} (relative to that prior to sulfur poisoning) decreased in the order of CueA-s > CueF-s > CuiA-s > CuiF-s. This result was consistent with the EPR and H₂-TPR results. As the attack of SO₂ on the isolated Cu^{2+} ions is limited owing to the similarity in the pore size of SAPO-34 and kinetic diameter of SO₂, the decreased amount of isolated Cu^{2+} may be due to the migration of isolated Cu^{2+} to the surface and the formation of the dispersed sulfates.

To confirm the migration of the copper species during the hydrothermal and sulfur poisoning treatments, the Cu/Si atomic ratios on the surface and in the bulk were calculated. As listed in Table 6, the as-received catalysts featured a higher Cu/Si ratio on the surface than that in the bulk, indicating the enrichment of copper on the external surface of SAPO-34. As noted further, the ion-exchange catalyst CueF featured a higher surface Cu concentration than the impregnated sample, CuiF. This result was attributed to the relatively low calcination temperature (550 °C) employed, which did not allow sufficient diffusion of surface CuO into the ion-exchanged sites. After hydrothermal treatment, the surface Cu/Si ratios of the catalysts decreased and were lower than the bulk values. This result confirmed the migration of the surface copper ions to the internal region of SAPO-34 zeolite during hydrothermal treatment.^{16,49} The sulfur-poisoned catalysts featured considerably higher surface Cu/Si ratios than the non-poisoned catalysts, thus confirming that sulfur poisoning promotes the migration of isolated Cu^{2+} back to the surface to form copper sulfates. Based on the combined EPR, H₂-TPR, EDX and TG results, it is reasonable to suggest that the dispersed CuSO_4 species are mainly formed upon migration of isolated Cu^{2+} , whereas the crystalline CuSO_4 species are mainly produced from surface CuO clusters upon sulfation.

4.2. Effects of sulfur poisoning on NH₃-SCR activity

It has been reported that the types of copper species are critical to the NH₃-SCR activity of the zeolite catalysts and the formation of metal sulfates would deactivate the catalysts. Luo *et al.*²⁹ found that both surface Cu species and isolated Cu^{2+} were active

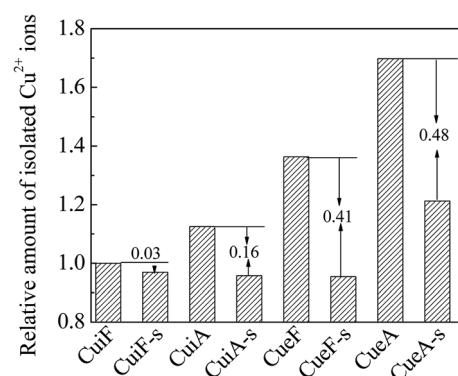


Fig. 8 Relative concentration of isolated Cu^{2+} ions determined from the EPR results.



Table 6 Chemical composition of the Cu/SAPO-34 catalysts

Sample	Cu/Si in the bulk ^a	Cu/Si on the surface ^b	S/Si in the bulk ^a	S/Si on the surface ^b
CuiF	0.23	0.29	—	—
CuiF-s	0.22	0.44	0.18	0.21
CuiA	0.23	0.21	—	—
CuiA-s	0.22	0.30	0.19	0.19
CueF	0.23	0.33	—	—
CueF-s	0.22	0.48	0.20	0.16
CueA	0.23	0.22	—	—
CueA-s	0.22	0.34	0.20	0.11

^a Obtained by ICP-OES. ^b Obtained by XPS.

for SCR reactions, while surface Cu species appeared to be more active for NO oxidation and NH₃ oxidation. After sulfur poisoning, both types of Cu species decreased significantly in the population due to the combination with sulfur. In a recent study by Shen *et al.*,⁵⁰ both copper sulfate and ammonia sulfate species decrease the SCR reaction rate of the Cu/SAPO-34 catalysts by reducing the number of isolated Cu²⁺ species, and the copper sulfate is harder to decompose than ammonia sulfate. However, the states of the copper sulfate and their contribution to activity were not involved in these studies.

To clarify the roles of the dispersed CuSO₄ and crystalline CuSO₄ in NH₃-SCR reaction, the CuSO₄/SAPO-34 catalysts were synthesized by mechanical mixing and wet impregnation methods using CuSO₄ solution as the precursor. As observed in the XRD patterns in Fig. 9, Cum-s displayed Cu(SO₄)·(H₂O) diffraction peaks. In contrast, those peaks were absent in Cui-s. These results agreed with the H₂-TPR results (Fig. 4), indicating that CuSO₄ is finely dispersed on SAPO-34 for Cui-s. As shown in Fig. 10, Cui-s displays much higher SCR activity at low temperatures (150–450 °C) than Cum-s. This demonstrates the dependency of catalytic activity on the dispersion of copper sulfates. It should be noted that the reference catalyst Cui-s even shows higher SCR activity than CuiF-s and CuiA-s in the whole temperature range measured, which may be due to the different status of the impregnated and *in situ* formed CuSO₄, and the detailed mechanism remains to be investigated.

Thus, the SCR reactions at low and high temperatures over the non-poisoned and poisoned Cu/SAPO-34 catalysts are

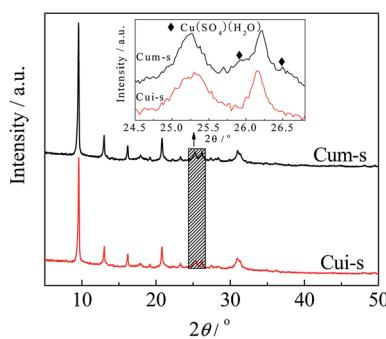
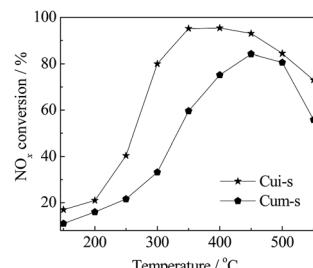
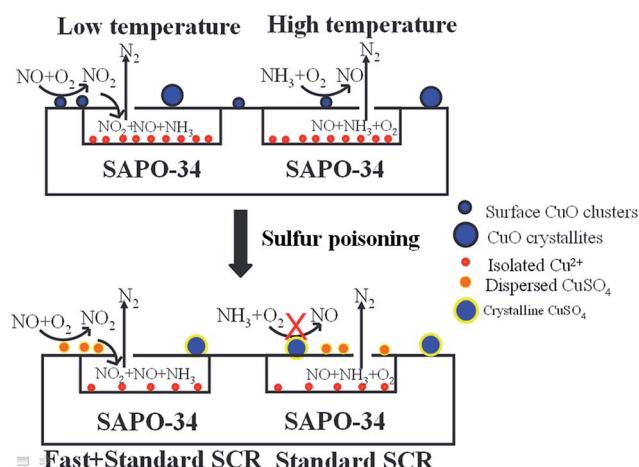
Fig. 9 XRD spectra of CuSO₄/SAPO-34 catalysts.

Fig. 10 NH₃-SCR curves of CuSO₄/SAPO-34 catalysts. Reaction conditions: [NO] = [NH₃] = 500 ppm, O₂ = 5%, [H₂O] = 10%, N₂ in balance, and GHSV = 100 000 h⁻¹.

dominated by different active species as presented in Scheme 1. Surface CuO clusters and isolated Cu²⁺ act synergistically at low temperatures *via* fast SCR reaction, which occurs mainly on isolated Cu²⁺ active sites with NO₂ generated from the oxidation of NO on surface CuO clusters. Upon hydrothermal treatment, a decrease in the amount of surface CuO clusters is observed, which leads to reduced low-temperature activities. At high temperatures, the competitive oxidation of NH₃ is weakened *via* sintering of the surface CuO clusters to CuO crystallites, resulting in improved high-temperature SCR activities. In this temperature range, the isolated Cu²⁺ ions serve as main active sites *via* the standard SCR reaction. For the sulfur-poisoned catalysts, the catalytic activity depends not only on the sulfur loading but also on the dispersion of the generated CuSO₄. As shown in Fig. 10, the dispersed CuSO₄ species on Cui-s show much higher activity than the crystalline CuSO₄ on Cum-s with the same sulfur loading. Based on the H₂-TPR result, the migrated isolated Cu²⁺ tends to form dispersed CuSO₄ species, which are more active for SCR reaction, on the ion-exchanged catalysts after sulfur poisoning. Meanwhile, the surface CuO clusters and crystallites tend to produce crystalline CuSO₄ species, which are less active for NH₃-SCR. The intensity of reduction peak of dispersed CuSO₄ follows the sequence of



Scheme 1 Roles of different copper species on the non-poisoned and poisoned Cu/SAPO-34 catalysts in NH₃-SCR reactions at different temperatures.

CueF-s > CueA-s > CuiF-s > CuiA-s, which is in good consistence with the low-temperature activity of the sulfated catalysts. Additionally, the sulfur poisoning improves the high-temperature activities of the as-received catalysts by inhibiting NH_3 oxidation.

5. Conclusions

The application of different preparation methods and the hydrothermal treatment in this work allowed us to obtain different distributions of Cu species on a zeolite support, and the catalytic activities and sulfur tolerance of those copper species were examined. Sulfur poisoning was found to promote the migration of isolated Cu^{2+} back to the surface as highly dispersed CuSO_4 , and the small pores of SAPO-34 appeared to protect the isolated Cu^{2+} from attack by SO_2 to some extent. Crystalline CuSO_4 formed mainly from sulfation of surface CuO clusters and crystallites, and contributed little to the low-temperature SCR activity. As a result, the operation window of the Cu/SAPO-34 catalysts shifted toward high temperatures after exposure in 100 ppm SO_2 at 350 °C for 24 h. The migration of copper was observed by XPS and EDX analysis, and a possible mechanism of Cu migration in sulfur poisoning was proposed on the basis of this observation.

The present study allowed us to learn the relationship between the formation of copper sulfates and the active copper species upon sulfur poisoning, and the contribution of CuSO_4 in different dispersion states to the NH_3 -SCR activity. It provided a strategy to develop anti-sulfur de NO_x catalysts for industrial applications.

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