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# Location and nature of Cu species in Cu/SAPO-34 for selective catalytic reduction of NO with $\ensuremath{\mathsf{NH}_3}$

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# ABSTRACT

Cu/SAPO-34 catalysts have been reported to show much improved activities and durability for selective catalytic reduction (SCR) of NO<sub>x</sub>. In this work, we examined the nature of Cu species in SAPO-34 catalysts in order to shed light on the active site requirements. Cu/SAPO-34 catalysts, prepared by ion-exchange and precipitation methods, were characterized in detail. The results consistently indicate that Cu species exist predominantly as isolated ions at the exchange sites in the ion-exchanged sample, whereas in the precipitated sample CuO on the external surface is the dominant species. The ion-exchanged Cu/SAPO-34 was found to show superior  $NH_3$ -SCR activity than the precipitated sample, suggesting that isolated Cu ions at the exchange sites.

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# 1. Introduction

Selective catalytic reduction of  $NO_x$  with hydrocarbons (HC-SCR) or with ammonia (NH<sub>3</sub>-SCR) as the reducing agent has been extensively studied for lean  $NO_x$  control. HC-SCR technology was first reported on copper ion-exchanged zeolites by Iwamoto et al. [1,2]. NH<sub>3</sub>-SCR technology has been commonly used for  $NO_x$  control in stationary applications [3] and more recently for diesel vehicle emissions [4–10].

Copper-based zeolites have been investigated as the catalysts for direct decomposition of NO [11], HC-SCR [12–14], NH<sub>3</sub>-SCR [15–18], decomposition of N<sub>2</sub>O [19,20], and N<sub>2</sub>O reduction [21]. Cu ion-exchanged ZSM-5 zeolites exhibit high NO decomposition rates and SCR activities, but ZSM-5 zeolite possesses poor hydrothermal stability due to dealumination. Consequently, other types of zeolites have been explored to improve the activity and durability of the SCR catalysts. Cu-exchanged beta zeolite [22,23] has been shown to have excellent activity with better hydrothermal stability than ZSM-5 catalysts. Recently, it was reported that Cu ion-exchanged SSZ-*n* [24,25] showed higher NO<sub>x</sub> conversions over a broad temperature range with higher N<sub>2</sub> selectivities and hydrothermal stability compared with Cu/ZSM-5 and Cu/beta. Silico-alumino-phosphates (SAPO-*n*) possess ion-exchange properties as a result of the isomorphous substitution of P in AlPO<sub>4</sub> by Si, and SAPO-34, with a small-pore chabazite structure, exhibits high thermal stability even in the presence of water [12]. Cu ion-exchanged SAPO-*n* has been investigated for the selective reduction of NO by  $C_xH_y$  [12], N<sub>2</sub>O decomposition [19], and recently for NH<sub>3</sub> SCR [26].

The SCR catalytic performance of Cu-modified zeolites has been found to depend on the microstructure and the content of copper [2]. The SCR activity of exchanged Cu/ZSM-5 increased with increasing Cu exchange level and reached a maximum at the exchange level of 100% [27,28]. Several types of copper species, such as isolated Cu<sup>2+</sup> and Cu<sup>+</sup> ions [29,30], CuO or Cu<sub>2</sub>O clusters [31,32] and dimeric copper species ([Cu–O–Cu]<sup>2+</sup>) [33,34], have been proposed as the active sites over Cu/ZSM-5 catalysts. The most active species in Cu-Beta zeolites were found to be copper ions rapidly transitioning between Cu<sup>2+</sup> and Cu<sup>+</sup> species under SCR reaction conditions [35]. However, the active site requirements for Cu ionexchanged small-pore zeolites (e.g., Cu/SAPO-34), especially the location and state of the active Cu species, are not well understood.

The state of copper species could be strongly affected by the preparation method. With the coexistence of multiple copper species, it is difficult to distinguish the contribution of various copper species to the SCR activity separately. In addition, there has been no systematic study of the SCR activities of copper species at different locations over Cu/SAPO-34. In this work, Cu-modified SAPO-34 catalysts were prepared via liquid ion-exchange and precipitation methods, and the goal was to prepare samples with predominately single type of Cu species. Various techniques (XRD, H<sub>2</sub>-TPR, STEM, and DRIFTS) were used to probe the location and state of the Cu



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species in these samples. The impact of different Cu species on  $NH_3$  SCR activity was evaluated to shed insight on the active sites in these catalysts.

# 2. Experimental

# 2.1. Catalysts preparation

The ion-exchanged Cu/SAPO-34 catalyst was prepared by a two-step liquid ion-exchange method. A commercial H/SAPO-34 powder (Novel, Al/Si/P = 1:0.1:0.9, measured by inductively coupled plasma and atomic emission spectrometry) was ion exchanged using a NH<sub>4</sub>NO<sub>3</sub> (Alfa Aesar, >95%) solution at 80 °C for 1 h to obtain the  $NH_4^+$  form. Then, the solid was filtered and washed with distilled water. The  $NH_4^+/SAPO-34$  was dried at 100 °C for 16 h before repeating the ammonium exchange process for a total of two exchanges. Cu ion-exchange was performed by mixing the  $NH_4^+/SAPO-34$  with a Cu(CH<sub>3</sub>COO)<sub>2</sub> (Riedel de Haën, >99%) solution (0.05 mol/L) at ambient temperature for 6 h. A low-concentration copper solution was used for liquid ion exchange to avoid copper aggregating on the surface or in the pores. After the powder was filtered and thoroughly washed with distilled water, it was dried at 100 °C for 16 h and calcined at 550 °C for 4 h. This sample will be hereafter denoted as "Cu/SAPO-34-E," where "E" stands for the exchange method.

The CuO/SAPO-34 catalyst was prepared by precipitation of CuC<sub>2</sub>O<sub>4</sub> on H/SAPO-34 powder with Cu(CH<sub>3</sub>COO)<sub>2</sub> (Riedel de Haën, >99%) as the precursor and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (Fisher, >99%) as the precipitator. A Cu(CH<sub>3</sub>COO)<sub>2</sub> solution was added dropwise into a slurry of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> aqueous solution and H/SAPO-34 powder to minimize liquid ion exchange of Cu. The precipitate was filtered, washed and then dried at 100 °C overnight and calcined at 550 °C for 4 h. This sample will be hereafter denoted as "Cu/SAPO-34-P," where "P" stands for the precipitation method.

#### 2.2. NH<sub>3</sub>-SCR catalytic activity and NH<sub>3</sub> oxidation ability

The catalytic activity evaluation was carried out using a flowthrough powder reactor system equipped with a Fourier Transform Infrared (FT-IR) spectrometer (Nicolet 670) with a gas-sampling cell. The gas mixture consisted of 200 ppm NO, 200 ppm NH<sub>3</sub>, 8% O<sub>2</sub> balanced with N<sub>2</sub> for the NH<sub>3</sub>-SCR reaction and 200 ppm NH<sub>3</sub>,  $8\%~O_2$  balanced with  $N_2$  for the  $NH_3$  oxidation reaction.  $10\%~H_2O$ and 10% CO<sub>2</sub> were present all the time. The gas hourly space velocity (GHSV) was 300,000 h<sup>-1</sup> for the standard SCR and NH<sub>3</sub> oxidation measurements and 1,200,000  $h^{-1}$  for the rate measurements and activation energy evaluation. Prior to the activity measurements, the catalysts were pretreated at 550 °C for 30 min in 8%  $O_2/N_2$  flow. The catalytic activities were measured at temperatures varying from 180 to 550 °C. The NO and NH<sub>3</sub> conversions were calculated based on the inlet and outlet gas concentrations (Eqs. (1) and (2)) at steady state. The selectivity to  $N_2$  in the NH<sub>3</sub> oxidation was estimated based on nitrogen balance (Eq. (3)).

NO Conversion = 
$$\frac{[NO]_{inlet} - [NO]_{outlet}}{[NO]_{inlet}} \times 100\%$$
(1)

Chemical composition of the catalysts by ICP analysis.

Table 1

Sample	Concentration (wt.%)			
	Al	Р	Si	Cu
H/SAPO-34	18	19	2.1	0
Cu/SAPO-34-E	19	20	2.3	0.8
Cu/SAPO-34-P	17	19	2.1	0.8

$$\begin{split} \text{NH}_3 \, \text{Conversion} &= \frac{[\text{NH}_3]_{\text{inlet}} - [\text{NH}_3]_{\text{outlet}}}{[\text{NH}_3]_{\text{inlet}}} \times 100\% \end{split} \tag{2} \\ \text{N}_2 \, \text{Selectivity} &= \frac{[\text{NH}_3]_{\text{inlet}} - [\text{NO}]_{\text{outlet}} - [\text{NO}_2]_{\text{outlet}} - 2[\text{N}_2\text{O}]_{\text{outlet}} - [\text{NH}_3]_{\text{outlet}}}{[\text{NH}_3]_{\text{inlet}} - [\text{NH}_3]_{\text{outlet}}} \\ &\times 100\% \end{split}$$

(3)

# 2.3. Characterizations of Cu-modified SAPO-34 catalysts

The copper contents in the samples were determined by inductively coupled plasma and atomic emission spectrometry (ICP-AES), as shown in Table 1. The Cu loadings in the two samples were chosen to be similar to probe the effect of Cu species.

The phase compositions and structures of the catalysts were determined by X-ray diffraction (D8 advance diffractometer) using CuK $\alpha$  radiation ( $\lambda$  = 1.5418 Å). The X-ray powder diffractograms were recorded at 0.02° intervals in the 2 $\theta$  range from 10° to 40°. The transmission electron microscopy (TEM) images were measured on a Cs corrected JEOL 2100F TEM/STEM operated at 200 kV.

Temperature-programmed reduction by  $H_2$  ( $H_2$ -TPR) and temperature-programmed desorption of  $NH_3$  ( $NH_3$ -TPD) were carried out on a commercial instrument (Micromeritics, Autochem 2920) with a TCD detector. Before the TPR/TPD measurements, the samples were pre-oxidized at 500 °C followed by helium flow to purge the residual gaseous and weakly adsorbed oxygen. The  $H_2$ -TPR profiles were measured in a flow of 10 vol.%  $H_2/Ar$  (30 ml min<sup>-1</sup>) from room temperature to 800 °C at a rate of 10 °C min<sup>-1</sup>. For  $NH_3$ -TPD measurements, the catalysts were exposed to  $NH_3$  at 30 °C for 60 min, followed with a temperature ramp at a rate of 5 °C min<sup>-1</sup>.

Diffuse reflectance infrared Fourier transform spectra (DRIFTS) were measured on a FT-IR spectrometer (Thermo Nicolet Magna670) using a heatable environmental reaction cell with ZnSe windows, which was connected to a gas-dosing system. The oxidation pretreatments at 500 °C for 1 h were executed to remove the adsorbed water and clean the surface before each measurement. The DRIFTS spectra were recorded in the range of 4000-650 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. Nicolet OMNIC<sup>™</sup> software (Ver. 7.3) was used to convert the raw reflectance data (absorbance units) to Kubelka–Munk units. The *ex situ* spectra of the catalysts were recorded at 30°C and the spectrum of KBr under the same condition was used as the background. The in situ DRIFTS of chemisorption were performed to characterize the surface adsorbed species, and the background spectra were collected before the samples were exposed to the absorbates. CO chemisorption was performed in 1 vol.% CO/He (100 ml min<sup>-1</sup>) at room temperature. The spectra were recorded over the CO-saturated samples. A helium flow was introduced to purge the extra gas-phase CO molecules before the sampling. NH<sub>3</sub> chemisorption was operated at room temperature in 200 ppm  $NH_3/He$  (100 ml min<sup>-1</sup>). The spectra were recorded every 5 min during the NH<sub>3</sub> adsorption process. After saturated with NH<sub>3</sub>, the flow was switched to helium, and the samples were heated up to 500 °C at a rate of 10 °C min<sup>-1</sup> in the He flow. The spectra of the temperature-programmed desorption were collected every 50 °C.

# 3. Results

#### 3.1. NH<sub>3</sub>-SCR catalytic activity and NH<sub>3</sub> oxidation activity

NO and NH<sub>3</sub> conversions were measured on the Cu/SAPO-34 catalysts at reaction temperatures between 180 and 550 °C (Fig. 1). Due to the high activities of these catalysts, high space velocity conditions were used in order to differentiate the activities of the catalyst samples. The H/SAPO-34 itself showed very low



Fig. 1. NO (left) and NH<sub>3</sub> (right) conversions as a function of reaction temperature; reaction conditions: 200 ppm NO, 200 ppm NH<sub>3</sub>, 8% O<sub>2</sub>, 10% H<sub>2</sub>O, 10% CO<sub>2</sub> balanced with N<sub>2</sub>; flow rate: 1 L min<sup>-1</sup>; GHSV: 300,000 h<sup>-1</sup>.



**Fig. 2.** NH<sub>3</sub> oxidation conversions and N<sub>2</sub> selectivity as a function of reaction temperature; reaction conditions: 200 ppm NH<sub>3</sub>, 8% O<sub>2</sub>, 10% H<sub>2</sub>O, 10% CO<sub>2</sub> balanced with N<sub>2</sub>; flow rate:  $1 \text{ Lmin}^{-1}$ ; GHSV: 300,000 h<sup>-1</sup>.

activities in this temperature range; hence, the activities of the Cucontaining samples could be attributed to contribution of the copper species. The exchanged sample Cu/SAPO-34-E was much more active than the precipitated catalyst Cu/SAPO-34-P, even though the Cu loadings in these two samples were similar. NO<sub>2</sub> was only detected in H/SAPO-34 at low temperature. For the Cu-containing catalysts, there was no NO<sub>2</sub> formed during the NH<sub>3</sub>-SCR reaction in the whole temperature range, suggesting that either the catalysts have a low NO oxidation ability or the formed NO<sub>2</sub> was quickly reacting with NH<sub>3</sub> to form N<sub>2</sub>.

Fig. 2 shows the NH<sub>3</sub> oxidation performance of the catalysts as a function of temperature during the steady state reaction in the absence of NO. H/SAPO-34 not only exhibits low NH<sub>3</sub> oxidation ability, but also poor N<sub>2</sub> selectivity. However, after copper ion exchange, the NH<sub>3</sub> conversion could reach 40% at 550 °C with a N<sub>2</sub> selectivity of 90% (Fig. 2, Cu/SAPO-34-E). Consistent with the performance in SCR reaction, the precipitated sample Cu/SAPO-34-P shows a stronger NH<sub>3</sub> oxidation ability, but a lower N<sub>2</sub> selectivity compared with Cu/SAPO-34-E. Considering that different Cu species may be present in these two samples due to the different preparation methods, it seems that the location and the status of Cu species play a critical role in determining the catalyst activity and selectivity.



Fig. 3. XRD patterns of H/SAPO-34 (a), Cu/SAPO-34-E (b), Cu/SAPO-34-P (c).

#### 3.2. Structural properties

The XRD patterns of the Cu-containing samples show a chabazite phase (Fig. 3, labeled by solid circle symbols), which is consistent with the pattern of H/SAPO-34, suggesting that neither the ion-exchange nor the precipitation method significantly affects the SAPO-34 structure. No diffraction peak of copper species (Cu, Cu<sub>2</sub>O, CuO) was observed for the ion-exchanged sample Cu/ SAPO-34-E (Fig. 3b), suggesting that copper is either well dispersed or exists as isolated ions at the exchange sites. For Cu/SAPO-34-P (Fig. 3c), two diffraction peaks located at 35.29° and 38.49° (labeled by open diamond symbols) were observed, and these peaks can be related to a CuO phase. The CuO crystallite, estimated based on the Sherrer's equation, was found to have an average size of 5.0 nm, which is much too large to be inside the pores of SAPO-34 (pore diameter = 0.38 nm) [27]. Therefore, it can be inferred that CuO particles locate on the external surface of SAPO-34 in the precipitated sample.

Although the introduction of Cu ions does not significantly influence the crystal structure of the SAPO-34, different Cu species may affect the positions of the diffraction peaks. In comparison with H/SAPO-34, the peaks for the Cu ion-exchanged sample shifted to lower diffraction angles, suggesting a lattice expansion



Fig. 4. STEM images of Cu/SAPO-34-P.

of SAPO-34. This could be attributed to the incorporation of Cu ions inside the SAPO-34 pores. On the other hand, the diffraction peaks in the precipitated sample (Cu/SAPO-34-P) did not shift positions, consistent with the Cu species existing as CuO on the external surface of SAPO-34.

#### 3.3. Morphology of Cu/SAPO-34 catalysts

STEM images of Cu/SAPO-34 catalysts were taken (Fig. 4) to examine the morphology of Cu species and the support (SAPO-34). SAPO-34 showed the typical cubic crystals in the size of 1– 3  $\mu$ m. The isolated copper ions in the exchanged sample (Cu/ SAPO-34-E, not shown here) cannot be detected by the STEM technique. However, CuO particles (bright area) were indeed found to aggregate on the external surface of SAPO-34 over the precipitated catalyst (Cu/SAPO-34-P, Fig. 4), and the crystallite size of CuO observed in the image is in the range of 10–30 nm, which is higher than the averaged crystallite size value calculated by XRD. This suggests that either the observed CuO particles are agglomerates of smaller crystallites or there are probably smaller CuO particles that are invisible in the STEM images.

# 3.4. Reducibility of copper species

Temperature-programmed reduction (TPR) measurements were carried out using H<sub>2</sub> for the catalyst samples to probe the reducibility of Cu species. No reduction peak was observed for H/ SAPO-34 (Fig. 5), indicating that the H<sub>2</sub> consumption peaks for the Cu-containing samples are attributed to the reduction of copper species. The precipitated sample (Cu/SAPO-34-P) exhibited a sharp peak centered at 200 °C, attributed to the reduction of CuO<sub>x</sub> particles [36]. Contrary to that, a broad reduction peak in the temperature range of 150–350 °C was obtained in the ion-exchanged samples (Cu/SAPO-34-E). The reducibility of copper species at the ion-exchange sites is still under debate. According to the literature [36], the isolated Cu<sup>2+</sup> ions could be reduced in the temperature of 200–300 °C, but the Cu<sup>+</sup> ions at the ion-exchange sites could be reduced to Cu<sup>0</sup> at distinctly higher temperatures or too stabile to be reduced in the H<sub>2</sub>-TPR temperature range.

The amount of H<sub>2</sub> consumption during TPR provides quantitative information on the number of reducible Cu ions in the samples (Table 2). The H<sub>2</sub>/Cu ratio in the precipitated sample is close to 1, suggesting that the Cu ions mainly exist as Cu<sup>2+</sup>, which again confirms that CuO is the dominant species. As for the ion-exchanged sample, the amount of H<sub>2</sub> consumption is much less than the theoretical value, even if we assume that all the copper ions exist as Cu<sup>+</sup>. This indicates that some copper species (e.g., Cu ions at the ion-exchange sites) are too stable to be reduced to Cu<sup>0</sup> at temperatures below 800 °C.



Fig. 5. H<sub>2</sub>-TPR profiles of all the catalysts; conditions: 10 vol.% H<sub>2</sub>/Ar; ramp rate: 10  $^\circ C$  min $^{-1}.$ 

# Table 2 $H_2$ consumption and composition of copper ions in $H_2$ -TPR.

Catalyst	Cu loading <sup>a</sup> (wt.%)	$H_2$ consumption (ml/g)	H <sub>2</sub> /Cu
Cu/SAPO-34-E	0.8	0.67	0.24
Cu/SAPO-34-P	0.8	2.79	0.98

<sup>a</sup> Obtained by ICP.



**Fig. 6.** NH<sub>3</sub>-TPD profiles of all the catalysts; ammonia adsorbed at 30 °C for 60 min; temperature ramp rate: 5 °C min<sup>-1</sup>.

# 3.5. NH<sub>3</sub>-TPD

Temperature-programmed desorption of ammonia was carried out to determine the strength and amount of different acid sites. The normalized NH<sub>3</sub>-TPD profiles are displayed in Fig. 6. All the catalysts show similar NH<sub>3</sub> desorption curves with three peaks, corresponding to the acid sites with different acid strengths. The low-temperature (LT) desorption peak is centered at 80 °C with a shoulder peak at around 155 °C, which can be attributed to weakly adsorbed NH<sub>3</sub> or ammonium species adsorbed at weak Lewis acid sites [37]. The high-temperature (HT) desorption peak in the temperature range of 250–450 °C could be assigned to ammonia adsorbed at strong Brønsted acid sites [37,38]. H/SAPO-34 shows the most intense NH<sub>3</sub> desorption peaks at high temperature as well



Fig. 7. Ex situ DRIFT spectra of H/SAPO-34, Cu/SAPO-34-P and Cu/SAPO-34-E; units in absorbance.

as the precipitated catalyst (Cu/SAPO-34-P), suggesting the largest number of strong Brønsted acid sites. However, the ion-exchanged catalyst (Cu/SAPO-34-E) exhibits a stronger LT desorption peak and a slightly weaker HT desorption peak compared with H/SAPO-34. The difference in LT desorption peak could be attributed to the Cu species in the ion-exchanged sample, which will be further confirmed in the following section.

# 3.6. Diffuse reflectance infrared spectra

#### 3.6.1. H/SAPO-34 and Cu/SAPO-34

The *ex situ* DRIFT spectra of the Cu/SAPO-34 catalysts were measured to probe the effect of Cu on the SAPO-34 framework vibrations (Fig. 7). The spectra in absorbance units were acquired after pretreating the samples at 500 °C to remove the adsorbed water and clean the surface. Peaks in the range of 2000–650 cm<sup>-1</sup> are associated with the internal and external stretching vibrations of the SAPO-34 framework. The peaks in the 3500–3800 cm<sup>-1</sup> region are related to the OH group stretching vibration modes (vOH). The weaker bands at 3745 and 3678 cm<sup>-1</sup> are assigned to P–OH and Si–OH species located on the external surface of the sample particles, respectively. Two stronger bands at 3627 and 3600 cm<sup>-1</sup> are assigned as the stretching mode of bridged OH groups Al–(OH)–Si, which are related to the Brønsted OH groups [37,38].

Two new bands at 891 and 844 cm<sup>-1</sup> only appeared in the exchanged samples, which have been associated with an internal asymmetric framework vibration perturbed by copper cations [39,40]. It was proposed that the band at the lower wavenumber

Table 3	
Peak positions and assignments in the DRIFT spectra.	

is related to Cu<sup>2+</sup> (oxygen bridged) ions and the band at the higher wavenumber is related to Cu<sup>+</sup> (isolated) ions [39,40]. The presence of these two bands in the exchanged samples provides direct evidence for the Cu species occupying the exchange sites inside the SAPO-34 pores. These two bands were not detected for Cu/SAPO-34-P, which suggests that there were few copper ions at the exchange sites in the precipitated sample. The peak assignments and references for the DRIFT spectra are summarized in Table 3.

# 3.6.2. CO chemisorption

Diffuse reflectance IR spectra of CO adsorption were measured to probe the oxidation state and coordination of Cu ions in the catalysts. CO can absorb strongly on Cu<sup>+</sup> sites to form stable Cu<sup>+</sup>–CO species [41], while it does not interact with Cu<sup>2+</sup> cations at ambient temperature. The H/SAPO-34 zeolite does not show any CO adsorption in the range of 2200–2100 cm<sup>-1</sup> (Fig. 8). A band at around 2154 cm<sup>-1</sup>, characteristic of Cu<sup>+</sup>–CO carbonyls species on isolated Cu<sup>+</sup> sites, was observed on the exchanged catalysts (Cu/SAPO-34-E), consistent with isolated Cu cations occupying the exchange sites. For the precipitated sample (Cu/SAPO-34-P), in addition to the main band at 2154 cm<sup>-1</sup>, a shoulder at around 2134 cm<sup>-1</sup> was observed. This shoulder band has been assigned to CO adsorbed on dimeric Cu<sup>+</sup> sites (Cu<sup>+</sup>–CO–Cu<sup>+</sup> species) [41]. The presence of this lower frequency band may suggest the existence of CuO<sub>x</sub> aggregates, consistent with the XRD and STEM results.

# 3.6.3. NH<sub>3</sub> chemisorption

Ammonia has been extensively used as a probe molecule to identify the different types of surface acidic sites. Fig. 9 illustrates the DRIFT spectra of all the samples after  $NH_3$  adsorption at room temperature for 5 min and 30 min. Adsorbed species can be roughly divided into three regions:  $3800-3500 \text{ cm}^{-1}$  (O–H stretching mode region),  $3500-1800 \text{ cm}^{-1}$  (N–H stretching mode region) and  $1800-1200 \text{ cm}^{-1}$  (N–H deformation region) [37,38].

Generally, the similarity of NH<sub>3</sub> adsorption behaviors of H/ SAPO-34 and Cu/SAPO-34-P implies that the CuO<sub>x</sub> species on the external surface of SAPO-34 has little impact on the acidic property. At the beginning of NH<sub>3</sub> adsorption (Fig. 9, gray lines), they both show strong band at around 1465 cm<sup>-1</sup> assigned to asymmetric vibration of NH<sub>4</sub><sup>+</sup> adsorbed on the Brønsted acid sites ( $\sigma_{as}$ (NH<sub>4</sub><sup>+</sup>)), as well as the bands at 3377, 3335 and 3294 cm<sup>-1</sup> related to NH<sub>4</sub><sup>+</sup> [37]. Meanwhile, two distinct negative bands at 3600 and 3627 cm<sup>-1</sup>, assigned to OH vibrations at Brønsted acid sites, are progressively intensified and it is thus indicative of NH<sub>4</sub><sup>+</sup> adsorbed at these Brønsted acid sites over these two catalysts. With the increasing extent of ammonia chemisorption, ammonia is eventually adsorbed molecularly. Band at 3338 cm<sup>-1</sup> assigned as NH<sub>3</sub> molecule adsorption increases with band at 3293 cm<sup>-1</sup> intensified, then superimposed on bands of NH<sub>4</sub><sup>+</sup> groups.

Spectra	Wavenumber (cm <sup>-1</sup> )	Species	Reference
ex situ	3745	Si-OH on the external surface	[37,38]
	3678	P-OH on the external surface	[37,38]
	3627, 3600	Bridged Al-(OH)-Si Brønsted groups	[37,38]
	891, 844	Internal asymmetric framework vibration perturbed by copper cations	[39,40]
CO chemisorption	2154	Cu <sup>+</sup> -CO carbonyls	[41]
	2134	Cu <sup>+</sup> -CO-Cu <sup>+</sup> species	[41]
NH <sub>3</sub> chemisorption	3377, 3335, 3294	$NH_4^+$ species	[37,38]
	3338, 3293 (3344, 3286)	NH <sub>3</sub> molecules	[37,38]
	3179	$NH_3$ -Cu <sup>+</sup> species	[42]
	1617	$\sigma_{as}(NH_3)$ on Lewis acid sites	[37,38,42]
	1465–1496	$\sigma_{\rm as}({\rm NH}_4^+)$ on Brønsted acid sites	[37,38,42]



**Fig. 8.** DRIFT spectra of CO adsorption over H/SAPO-34, Cu/SAPO-34-P and Cu/SAPO-34-E; units in Kubelka–Munk; conditions: 1% CO/He, adsorption of CO for 15 min and purging with He at 30 °C.



**Fig. 9.** DRIFT spectra of NH<sub>3</sub> adsorption at room temperature for 5 min (gray lines) and 30 min (black line); units in Kubelka–Munk; a:H/SAPO-34; b:Cu/SAPO-34-E; c: Cu/SAPO-34-P.

NH<sub>3</sub> chemisorption spectra of Cu/SAPO-34-E are different from those of H/SAPO-34 and Cu/SAPO-34-P, which exhibit more intense bands at 1617 cm<sup>-1</sup>, assigned to asymmetric vibration of NH<sub>3</sub> adsorbed on Lewis acid sites ( $\sigma_{as}$ (NH<sub>3</sub>)) at the first stage of adsorption, but less intense bands in the range 1465–1496 cm<sup>-1</sup> assigned to NH<sub>4</sub><sup>+</sup> adsorbed on the Brønsted acid sites. A new band at 3179 cm<sup>-1</sup> corresponding to NH<sub>3</sub>–Cu<sup>+</sup> species on the exchanged sites was observed [42]. Concurrently, two obvious negative bands at 891 and 844 cm<sup>-1</sup> appeared which are associated with internal asymmetric framework vibrations perturbed by copper cations. This further confirms that Cu ions species in the framework were occupied by NH<sub>3</sub> with the formation of Cu–NH<sub>3</sub> species. As a result, Cu exchange enhances the NH<sub>3</sub> adsorption ability by introducing more Lewis acid sites and reduces the Brønsted acidic strength of zeolite.

# 3.6.4. NH<sub>3</sub> desorption

The decomposition behaviors of ammonium species over all the catalysts were also studied by DRIFT spectra as shown in Fig. 10. Contrary to what was observed during  $NH_3$  adsorption process, the adsorbed species are released at different temperatures while the intrinsic species of catalysts are restored, due to different acidic

strengths. Consistent with the NH<sub>3</sub> adsorption results, the spectra evolution during the NH<sub>3</sub> desorption process for Cu/SAPO-34-P (Fig. 10c) is much similar with that for H/SAPO-34 (Fig. 10a). The doublet bands at 3338 and 3293  $\text{cm}^{-1}$  (3344 and 3286  $\text{cm}^{-1}$  for Cu/SAPO-34-E) firstly decrease at lower temperatures (below 200 °C), and meanwhile, the negative band at 3678 cm<sup>-1</sup> assigned to the external hydroxyl groups (i.e., P-OH, Si-OH, and Al-OH) restores. This process is corresponding to the release of molecularly adsorbed NH<sub>3</sub>, which is the main product in the LT desorption peak of the NH<sub>3</sub>-TPD profiles (Fig. 6). For Cu/SAPO-34-E, an extra quantity of NH<sub>3</sub> comes from the contribution of copper species. As shown in Fig. 10b, the bands at 1617 and  $3179 \text{ cm}^{-1}$ , assigned to ammonia adsorbed on copper related Lewis sites, also decrease in this temperature range, mainly due to the release of NH<sub>3</sub> adsorbed on copper species. At the same time, the negative bands at 891 and 844 cm<sup>-1</sup> gradually restore, which reveals the available copper ions sites resumed. With further increasing the temperatures, the intensities of the spectra continue to decrease. The progressive disappearance of the complex bands in 1469–1496  $cm^{-1}$ , and 3377–3294 cm<sup>-1</sup>, indicates that adsorbed on the Brønsted acid sites are decomposed. Simultaneously, the bridged OH groups generally come out with the temperature increasing, as testified by the growth of the bands at 3627 and 3600 cm<sup>-1</sup>. This again confirms that the HT desorption peak in NH<sub>3</sub>-TPD process (Fig. 6) is assigned to ammonia adsorbed at strong Brønsted acid sites.

# 4. Discussion

# 4.1. The structure of copper species

The Cu species in Cu/SAPO-34 prepared by precipitation and liquid ion-exchange methods appear to exist in different forms. In Cu/SAPO-34-P, CuO<sub>x</sub> on the external surface is the dominant species. The XRD patterns (Fig. 3) prove that Cu ions in the precipitated sample (Cu/SAPO-34-P) exist as copper oxide phase and STEM images (Fig. 4) illustrate that these CuO particles locate on the external surface of SAPO-34 as expected. From the H<sub>2</sub>-TPR profile, the sharp reduction peak at low temperatures is due to the reduction of CuO<sub>x</sub> as reported in the literature [36].

In the ion-exchanged sample Cu/SAPO-34-E, Cu species exist predominantly as isolated Cu ions at the exchange sites. No feature peaks of copper species were detected by XRD, and no copper aggregation was observed over the entire zeolite in the STEM micrographs, which means the copper ions uniformly distribute over the SAPO-34 zeolite. However, the absence of Cu species phase in the XRD pattern of Cu/SAPO-34-E sample could not confidently prove the copper ions locate at the cation exchange sites. But the broad reduction peak in the H<sub>2</sub>-TPR profile suggests that the copper species in Cu/SAPO-34-E are much more difficult to reduce than the copper oxides. In addition, the appearance of two bands at 891 and 844 cm<sup>-1</sup> in the ex situ IR spectra of the exchanged samples (Fig. 7), which have been associated with an internal asymmetric framework vibration perturbed by copper cations, directly proves the occupancy of the ion-exchange sites by copper ions inside the framework. On the contrary, the absence of these two bands in the precipitated catalyst (Cu/SAPO-34-P, Fig. 7), the spectrum of which resembles that of the parent H/ SAPO-34, suggests that the Cu species in this sample do not affect the SAPO-34 framework, which again confirms that CuO species are mostly on the external surface of SAPO-34.

# 4.2. Relation between acidity and the structure of copper species

The acidity of the catalysts is considered as an essential factor for SCR reaction. Two stronger bands at 3627 and 3600 cm<sup>-1</sup> in



**Fig. 10.** DRIFT spectra of NH<sub>3</sub>-TPD over H/SAPO-34 (a), Cu/SAPO-34-E (b), and Cu/SAPO-34-P (c); units in Kubelka–Munk; a:50 °C; b:100 °C; c:200 °C; d:300 °C; e:400 °C; f:500 °C;

Table 4	
Amount of Brønsted acid sites in Cu/SAPO-34 measured by IR.	
	_

Catalyst	H/SAPO- 34	Cu/SAPO-34- P	Cu/SAPO-34- E
Integrated area (3560– 3660 cm <sup>-1</sup> )	105.60	95.54	72.87
[B <sub>Catal.</sub> ]/[B <sub>H/SAPO-34</sub> ]	-	0.90	0.69

the *ex situ* IR spectra (Fig. 7) are related to the Brønsted acid sites in the catalysts [37,38]. The integrated area in the range of 3560–3660 cm<sup>-1</sup>, calibrated by the intensity of the band at 1362 cm<sup>-1</sup> which is assigned to the framework vibration as an internal standard, represents the amount of the Brønsted acid sites in the samples. Normalized to that in H/SAPO-34, the relative amounts of Brønsted acid sites in Cu/SAPO-34 are listed in Table 4, suggesting that the ion-exchange consumed Brønsted acid sites to form isolated copper ions while precipitation maintained a large quantity

of Brønsted acid sites. It could also be concluded from the ammonia desorption results (Fig. 6) that the copper ion exchange enhances the Lewis acidity but reduces the Brønsted acidity of SAPO-34, due to the replacement of  $H^+$  by  $Cu^{x+}$  at the bridge hydroxyl sites Si–(OH)–Al, whereas the copper oxide loaded on the external surface has little impact on the acidity of zeolite, which could maintain a strong Brønsted acidity of the catalyst.

# 4.3. Relation between SCR activity and nature of copper species

The present work demonstrates that copper species could locate at different positions in SAPO-34 via different preparation methods, resulting in significant differences in both NH<sub>3</sub>-SCR activities and structural/chemical properties. The SCR activity results in Fig. 1 reveal that the Cu-modified SAPO-34 catalysts with different structures of copper species exhibit significant difference in NH<sub>3</sub>-SCR activities. Generally, the Cu ion-exchanged SAPO-34 is the most active catalyst for NH<sub>3</sub>-SCR reaction in the whole temperature range, while the precipitated catalyst Cu/SAPO-34-P shows

Table 5				
Reaction rates at	220 °C and	apparent	activation	energies.

Catalysts	Reaction rate (mol $g^{-1} s^{-1}$ )	Cu content (mol g <sup>-1</sup> )	TOF $(s^{-1})$	Apparent activation energy $E_a$ (kJ mol <sup>-1</sup> )
Cu/SAPO-34-E Cu/SAPO-34-P	$\begin{array}{l} 9.63\times 10^{-7} \\ 2.06\!\times\! 10^{-7} \end{array}$	$\begin{array}{c} 1.25{\times}10^{-4} \\ 1.25{\times}10^{-4} \end{array}$	0.0077 0.0017	9.8 16.8



**Fig. 11.** Arrhenius plots of the turnover frequency (TOF) with respect to the total Cu amount on Cu catalysts; conditions: 200 ppm NO, 200 ppm NH<sub>3</sub>, 8% O<sub>2</sub>, 10% H<sub>2</sub>O, 10% CO<sub>2</sub> balanced with N<sub>2</sub>; flow rate:  $1 \text{ Lmin}^{-1}$ ; GHSV: 1,200,000 h<sup>-1</sup>.

strong NH<sub>3</sub> oxidation ability rather than SCR activity at the high temperatures (>350 °C), suggesting that the isolated copper ions at the exchange sites are active for the SCR reaction and that copper oxide species could promote NH<sub>3</sub> oxidation reaction prior to SCR reaction.

In order to quantitatively estimate the contribution of different copper species to the SCR reaction. NO reaction rates were measured for the two Cu/SAPO-34 samples. A higher space velocity  $(1,200,000 h^{-1})$  was used to achieve the kinetically controlled conditions and keep the NO conversions low (less than 40%). As listed in Table 5, the reaction rate at 220 °C on the Cu ion-exchanged sample (Cu/SAPO-34-E) is  $9.63 \times 10^{-7}$  mol g<sup>-1</sup> s<sup>-1</sup>, which is more than four times of that on the Cu-precipitated catalyst  $(2.06 \times 10^{-7} \text{ mol g}^{-1} \text{ s}^{-1})$ . In addition, the turnover frequency (TOF), which is defined as the number of NO molecule converted per Cu per second, could be calculated with respect to the total copper contents and also shows the similar trend. These rates are comparable to those reported on Fe/ZSM-5 [43], but at much lower temperatures (220 °C versus 300 °C). Fig. 11 shows the Arrhenius plots of the turnover frequency (TOF) for the SCR reaction with respect to the total copper contents in the temperature range of 220–350 °C. Over this temperature range, the NH<sub>3</sub> conversions are consistent with the NO conversions for all the catalysts with no N<sub>2</sub>O and NO<sub>2</sub> detected, suggesting that the NH<sub>3</sub> oxidation, NO oxidation, and N<sub>2</sub>O formation are negligible. The apparent activation energy of the SCR reaction for Cu/SAPO-34-E is 9.8 kJ mol<sup>-1</sup>, which is lower than values reported for Cu/ZSM-5 catalysts  $(85 \text{ kJ mol}^{-1} [44] \text{ and } 49 \text{ kJ mol}^{-1} [45])$ . The reason for the difference is not clear and might suggest a different reaction mechanism on these catalysts. We examined the effect of external mass transport and found that the reaction rates were not affected by external mass transport (results are included in the Supporting Information). Small size (less than 200 mesh size) catalyst particles were used in this study and internal diffusion limitation was unlikely but could not be completely ruled out. It is important to note that the estimated apparent activation energy may be affected by factors such as NO or  $NH_3$  adsorption on the catalyst surface.

Although the CuO species on the external surface are capable of undergoing through reduction/oxidation cycles, their weak interaction with the zeolite acid sites may lead to lower NH<sub>3</sub>-SCR reaction rates and the stronger Brønsted acidity and external CuO species could accelerate the NH<sub>3</sub> oxidation at high temperatures. On the other hand, isolated Cu ions at the exchange sites are the predominant species in the exchanged sample, which show much faster rates of NH<sub>3</sub> SCR reactions. The Cu ions residing in the proximity of the acid sites in the zeolite with a stronger Lewis acidity could provide high catalytic reactivity even at low temperatures.

# 5. Conclusions

Ion-exchange and precipitation methods were used to prepare Cu-loaded SAPO-34 catalysts. Cu species existed as isolated cations inside the SAPO-34 pores in the ion-exchanged samples, whereas the predominant species in the precipitated sample were  $CuO_x$ clusters dispersed on the external surface of the zeolite. The ionexchanged sample was found to have superior catalytic activities for ammonia SCR. For Cu/SAPO-34, the active sites for NH<sub>3</sub>-SCR reactions are likely the isolated Cu ions inside the pores at the exchange sites, and copper oxide species could promote NH<sub>3</sub> oxidation reaction prior to SCR reaction at high temperatures.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2012.01.012.

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