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The Cu migration of Cu-SAPO-34 catalyst for ammonia selective catalytic reduction of NO_x during high temperature hydrothermal aging treatment

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Abstract

Two kinds of Cu-SAPO-34 catalysts, prepared with a one-pot technique using Cu-tetraethylenepentamine as co-template and an ion-exchange method, were hydrothermally treated at 750 °C for at least 16 h. The migration of Cu species during hydrothermal treatment and the corresponding effect on the selective catalytic reduction (SCR) of NO_x were examined and characterized. A certain amount of CuO exists outside and inner the crystallites in the as prepared ion-exchanged sample, whereas copper is mainly atomically dispersed in the one-pot sample existing as isolated Cu²⁺. After hydrothermal treatment for 16 h, the amount of the inner nanosized CuO in the ion-exchanged sample reduced and the copper disperses to form more isolated Cu²⁺. However, surface CuO particles increase at the sacrifice of isolated Cu²⁺ with extending the hydrothermal treatment to 24 h. Aggregation of Cu²⁺ species also happens during the aging treatment over the one-pot prepared sample where the initial Cu is atomically

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dispersed as isolated Cu^{2+} . The increase of the amount of the isolated Cu^{2+} enhances the low-temperature ($< 350\text{ }^{\circ}\text{C}$) performance. However, the increase of the amount of surface CuO particles in the aged samples promotes the nonselective NH_3 oxidation reaction in the high temperature range and results in the lowering of the SCR activity by limiting NH_3 supply.

Keywords: NH_3 selective catalytic reduction; Hydrothermal treatment; Cu-SAPO-34 zeolite; One-pot synthesis; Ion-exchange preparation.

1. Introduction

Selective catalytic reduction by NH_3 (NH_3 -SCR) over zeolite catalysts has been extensively investigated to eliminate NO_x in stationary combustion and diesel vehicle emissions [1, 2]. Cu-based zeolite catalysts, i.e., Cu-Y, Cu-Beta, have been reported to exhibit high NO_x conversion and N_2 selectivity in the last two decades [3-5]. Unfortunately, these zeolites often show poor stability via dealumination in the inevitable harsh hydrothermal conditions, induced by upper stream processes such as the regeneration of catalysts in the diesel particulate filter [6-8]. In recent years, Cu-chabazite (CHA) catalysts including Cu-SSZ-13 and Cu-SAPO-34 have been successfully utilized as the major components of the catalyst in NH_3 -SCR of NO_x in the treatment of diesel vehicle exhausts. The small openings in those zeolites impedes the structural dealumination, thus improves the hydrothermal stability [9]. For example, Cu-SAPO-34, a P-containing silicoaluminophosphate molecular sieve with CHA structure, has been reported with high activity for De NO_x as well as high hydrothermal stability [10, 11].

Due to the concern on the hydrothermal stability, the migration of the cupric species in the Cu-SAPO-34 framework has been examined, and the change of the coordination number as well as the location of Cu^{2+} during hydrothermal treatment has been reported [12-18]. Cu^{2+} was found migrate from CuO and re-disperse to occupy the ion exchange sites in the crystal framework during hydrothermal treatment [13, 15-17]. There are also reports that for the catalyst with Cu well dispersed in the framework, the active Cu species were pulled out from the CHA framework during hydrothermal treatment and aggregated into CuO particles [12, 14, 18]. In short, the published results indicate that the initial state of the cupric species is critical for the migration of Cu during the hydrothermal treatment.

In this work, two Cu-SAPO-34 catalyst samples with an equivalent copper content have been prepared with a one-pot technique with Cu-TEPA as the template [19, 20] and an ion-exchange method [21], respectively. The initial state of the cupric species as well as the migration of the Cu species in the hydrothermal process is examined. The migration mechanism of the cupric species in the Cu-SAPO-34 framework is discussed.

2. Experimental

2.1. Catalyst preparation

Chemicals. Pseudo-boehmite (70 wt.% Al_2O_3) was bought from CNOOC, Tianjin. Silica sol (30 wt.%, dispersed in H_2O), phosphoric acid (85 wt.%, dissolved in H_2O), copper (II) sulfate (99 wt.%) and tetraethylenepentamine (TEPA, 93 wt.%) were purchased from Guangfu, Tianjin. Diethylamine (DEA, 99 wt.%) was obtained from Aladdin, Shanghai and H-SAPO-34 (mole ratio: $\text{P}_2\text{O}_5:\text{SiO}_2:\text{Al}_2\text{O}_3=1:1:1$) was ordered from Nankai, Tianjin as seed crystal.

An H-SAPO-34 sample was prepared with a hydrothermal method. 7.283 g pseudo-boehmite, 10.01 g silica sol and 21.48 g H_2O were mixed with 11.53 g phosphoric acid solution to form a slurry. Subsequently, 7.314 g diethylamine and 0.895 g SAPO-34 seeds (5 wt.% of expected final yield) were added into the slurry, followed by stirring for 30 min, forming a homogenous sol (Sol A). The Sol A was sealed into a 50 ml teflon-lined stainless-steel pressure vessel and kept at 150 °C for seven days. The crystalline product was collected with centrifugation, washed and dried at 100 °C for 12 h. Finally, the sample was heated to 550 °C with a ramp of 2 °C min^{-1} and calcined at the temperature for 6 h to remove the residual organic compound.

The ion-exchanged samples were prepared with the as-prepared H-SAPO-34, following the procedure reported in detail in our previous work [22]. Typically, 5 g of H-SAPO-34 zeolite was introduced into 50 ml ammonium sulfate solution (23.4 wt.%), and then the mixture was stirred at 80 °C for 2 h, with the pH adjusted to 3.0-4.0 via adding dropwise ammonium hydroxide solution (2 mol/l). Then, the solid was filtrated, washed and dried to obtain the resulting NH_4^+ /SAPO-34 sample. 50 ml cupric sulfate solution and the NH_4^+ /SAPO-34 was mixed and stirred at 70 °C for 8 h, with a PH 3.0-4.0. The product was filtrated, washed in water, and dried at 100 °C, followed by calcination at 550 °C for 6 h to obtain the final Cu-SAPO-34 catalyst.

The same structured zeolite was also prepared via a one-pot method with a modified procedure. Firstly, 0.757 g tetraethylenepentamine (TEPA) and 0.638 g copper sulfate was dissolved in 2.554 g H_2O under intensive stirring for 2 h to get the Cu-complex solution, followed by adding 11.53 g phosphoric acid solution. Then, 18.92 g H_2O ,

7.283 g pseudo-boehmite, 10.01 g silica sol, 7.021 g diethylamine and 0.927 g SAPO-34 seeds were mixed to form a slurry. Subsequently, the mixture was stirred at ambient temperature for 30 min to reach a homogeneous sol (Sol B). Sol B was then used to produce Cu-SAPO-34 following the same procedure as the preparation of H-SAPO-34 from Sol A.

To examine the migration of Cu species in Cu-SAPO-34 during hydrothermal aging, all the as-prepared catalyst samples were hydrothermally treated in 10% H₂O/air at 750 °C for 16 h. The ion-exchanged sample was further hydrothermally aged until 24 h. In this context, the sample notations are listed in Table 1.

2.2. Catalyst characterization

N₂ physisorption was performed on a Quantachrome Autosorb-1 at -196 °C, and the specific surface area was calculated using the Brunauer-Emmett-Teller (BET) equation for p/p_0 values between 0.009 and 0.05, and the micro pore volume was estimated using t-method for the isotherm desorption curve. The samples were outgassed in vacuum at 250 °C for 6 h before the measurement.

The elemental contents of the samples were analyzed with an inductively coupled plasma optical emission spectrometer (ICP-OES, VISTA-MPX, Varian).

Powder X-ray diffraction (XRD) patterns were recorded with a Bruker AXS instrument employing a Cu K α radiation ($\lambda = 0.15418$ nm). Data were collected in the 2θ range from 5° to 40° at room temperature with a scanning velocity of 5 min⁻¹.

Solid-state ²⁷Al and ³¹P MAS NMR experiments were carried out on Varian Infinity plus 300WB spectrometer. ²⁷Al and ³¹P MAS NMR spectra were obtained at resonance frequencies of 78.13 and 121.37 MHz, respectively, with a spinning speed of 8 kHz.

Transmission electron microscope (TEM) images were acquired with a JEOL JEM 2100F electron microscope. The histograms of the particle size distribution on CuO particles were obtained with the Image J software.

Electron paramagnetic resonance (EPR) spectra in the X-band were collected on a Bruker A300 instrument. 50 mg sample was loaded in a quartz tube. After the sample was cooled down to the temperature -183 °C, the magnetic field was swept from 2000 to 4000 G.

Temperature-programmed reduction by H₂ (H₂-TPR) was carried out using a home-made setup with a quartz tube reactor and a thermal conductivity detector. 70 mg catalyst sample was pre-treated in helium flow (50 ml/min) at 300 °C to remove the weakly adsorbed compounds. Then the catalyst was cooled to 50 °C in He flow. After that, H₂-TPR was performed in 10% H₂/Ar (50 ml/min) from 50 °C to 900 °C with a ramp of 10 °C/min.

2.3. Catalytic performance

NH₃ oxidation reaction was performed with 100 mg sample (40-60 mesh) under ambient pressure in a fixed bed quartz reactor. Prior to the reaction, the catalyst was activated at 550 °C in 5% O₂/N₂ flow for 1 h, and then cooled to 150 °C in N₂. The experiments were carried out with a gas mixture containing 500 ppm NH₃, 5% O₂ and N₂ as balance, with a total flow rate of 500 ml/min. The expected reaction is written as equation (1).

The reaction temperature was increased from 150 to 550 °C stepwise, with each step 50 °C. For product analysis an online FTIR spectrometer (Thermo Nicolet iS10) was used when the steady state was reached.

The activity of the catalyst for standard NH₃-SCR reaction was tested with a fixed-bed operation with steady flow. The reaction is written as equation (2).

100 mg catalyst (40-60 mesh) was packed in a quartz reactor (10 mm in diameter). The sample was pre-activated at 550 °C in 5% O₂/N₂ flow for 1 h, then cooled to 150 °C in N₂. After that, the reaction was carried out in the reactant gas (500 ml/min gas flow and 150,000 h⁻¹ GHSV) containing 500 ppm NH₃, 500 ppm NO, 5 vol% O₂ and N₂ as a balance, with the temperature increased from 150 °C to 550 °C stepwise with each 50 °C. The outlet gas was analyzed quantitatively with a same FTIR spectrometer (Thermo Nicolet iS10) equipped with a heated, multiple-path gas cell detector (2 m). The NO_x (NO_x = NO + NO₂) conversion was calculated with the total NO_x concentrations in the inlet and outlet gas at steady state using the following Equation (3):

$$\text{NO}_x \text{ conversion} = \left(1 - \frac{[\text{NO}_x]_{\text{out}}}{[\text{NO}_x]_{\text{in}}}\right) \times 100\% \quad (3)$$

The activity experiments were repeated and the difference of the data from two tests was less than 2%.

3. Results

3.1. Composition, structure and texture

The elemental contents are almost identical for all the samples according to the ICP results presented in table 2, with a Cu loading of around 2.5 wt.%. N₂ physisorption results also in Table 2 tell that the as-prepared Cu-OP-F and Cu-IE-F has comparable surface area and pore volume, and both the two values decrease slightly with the hydrothermal treatment for the two kinds of samples prepared with the two methods.

The XRD patterns of the fresh and aged Cu-SAPO-34 samples are shown in Fig. 1, using the as-prepared H-SAPO-34 as a reference. The sharp diffraction peaks of all the samples exhibit a typical CHA phase, agreeing well with the pattern of SAPO-34 in the literature [16, 23], suggesting no collapse of the crystalline structure during the hydrothermal treatments. The data in Fig. 1 also illustrate that the peak intensities of the ion-exchanged samples are lower slightly than those of the H-SAPO-34, indicating that the ion-exchange process has a minor effect on the structure, agreeing with literature [21]. Fig. 1 also shows that no diffraction peaks of cupric oxide exist for the samples used in this work as often appearing in the pattern of the reported Cu-SAPO-34 catalyst samples locating at 35.6° and 38.8° [24]. This is probably due to either the ultra-fine dispersion of cupric species or the fact that the small content of Cu in the samples used in this work is below the detecting limitation of the instrument [24].

The XRD results reflect the long-range structural information of samples, therefore, solid-state ²⁷Al and ³¹P MAS NMR spectroscopies are used to further obtain the microstructural information of samples before and after hydrothermal treatment. Two obvious peaks were observed in the Cu-SAPO-34 catalysts in Fig. 2. The peak of chemical shift at 39 ppm is attributed to the tetrahedral coordination of alumina in the zeolite framework [25], and the other peak centered at -10 ppm is assigned to octahedral coordinated aluminum atoms in the zeolite framework formed by an additional coordination of two water molecules to tetrahedrally coordinated framework aluminum atoms [26]. There was little difference amongst ²⁷Al MAS NMR spectra of the fresh and aged Cu-SAPO-34 samples, regardless of preparation methods. Similarly, the peak with chemical shift at -29 ppm in ³¹P MAS NMR spectra, in accordance with tetrahedral

framework P(4Al) environments [25, 26], had minor change after hydrothermal treatment, no matter which preparation method is used. Those observations show that the Cu-SAPO-34 was robust enough to resist the hydrothermal treatment and the structural integrity was maintained well.

3.2. The micrographs

Fig. 3 presents the TEM micrographs and the histograms of particle size distribution of CuO in the fresh and aged samples prepared with different methods. Many bulk-like CuO particles anchored on the Cu-OP-A-16h with particle size mainly around 4.5-6.5 nm and Cu-IE-A-24h samples with particle size mainly around 3.5-5.5 nm are clearly observed. The bulk-like CuO particles with size above 3.5 nm may not locate inside the small CHA cage in SAPO-34 due to the restriction of the hexagonal unit cell size with the parameters of $1.368 \times 2.369 \times 1.477 \text{ nm}^3$ [27]. Otherwise, the existence of bulk-like CuO particles would destroy the structure, which is contradict with our XRD and NMR results where the structure integrity of the samples was largely maintained. Herein, those bulk-like CuO particles are denoted as surface CuO particles. In contrast, highly dispersed nanosized CuO particles (with shadow area around 2 nm) locating inside the Cu-IE-F sample are much less clearly observed, locating inside of the Cu-IE-F crystal, which are denoted as inner nanosized CuO. No CuO particles with clear edges are found in the Cu-OP-F and Cu-IE-A-16h samples. As a consequence, the histograms of particle size distribution of CuO within the two samples are not be given herein.

3.3. Electron paramagnetic resonance

Isolated Cu^{2+} is the only cupric species sensitive to EPR in the Cu-SAPO-34 structure, because Cu (II) are paramagnetic and the antiferromagnetic effect renders the CuO clusters or particles EPR invisible [17, 20, 27, 28]. Fig. 4 illustrates the axially symmetrical signals with four hyperfine splitting peaks corresponding to the interaction of the unpaired electron with the Cu nuclear, and one large sharp peak in the vertical region with all the samples. The $g_{\parallel} = 2.39$, $A_{\parallel} = 122 \text{ G}$ and $g_{\perp} = 2.06$ are attributed to the isolated Cu^{2+} species which is octahedrally coordinated to three framework oxygen atoms and three water molecules in the Cu-SAPO-34 crystal cage [29].

Song *et al.* reported that the errors pertaining to repeated EPR measurements are

substantially lower than 5% and the EPR quantification of fresh Cu-SSZ-13 sample matches the ICP result very well [27]. Therefore, EPR measurement offers an effective method to quantitatively identify the amount of isolated Cu^{2+} over Cu-based zeolite Catalyst. The relative concentration of the isolated Cu^{2+} ions was semi-quantified with double-integrating the EPR signal and plotted in Fig. 5 [16]. Fig. 4 and 5 shows that the EPR signal intensity lowered for the one-pot sample after hydrothermal aging for 16 h, whereas the EPR signal intensity of the ion-exchanged sample is enhanced with the hydrothermal treatment for 16 h, indicating the increase of the amount of the isolated Cu^{2+} . Nevertheless, further prolonging of the hydrothermal aging treatment to 24 h decreased the EPR signal intensity. Fig. 5 gives also that the amount of isolated Cu^{2+} in the samples decreased with the following sequence: Cu-OP-F > Cu-IE-A-16h > Cu-IE-A-24h > Cu-IE-F > Cu-OP-A-16h.

3.4. Temperature-programmed reduction by H_2

The H_2 -TPR profiles are used to determine the reducibility of the different type copper species. Xu *et al.* reported that the sum of the isolated Cu^{2+} and CuO amounts in Cu-SAPO-34 sample quantified by deconvoluting the H_2 -TPR profiles are consistent with the total Cu loading quantified with ICP [30]. This indicates that H_2 -TPR results reflect not only the overall trend of copper species, but also provide the information of quantification of copper species over Cu/zeolite Catalyst [28, 31].

As depicted in Fig. 6, a large H_2 consumption peak is observed in the low temperature range (150-400 °C) with all the samples, which can be further de-convoluted into three peaks, locating at around 208, 246 and 316 °C, respectively. The first H_2 reduction peak at around 208 °C was ascribed to the reduction of the surface CuO particles to Cu^0 [17, 32]. The peak at around 248 °C was attributed to the reduction of the isolated Cu^{2+} to Cu^+ [12, 28], and the peak at 316 °C was assigned to the reduction of the inner nanosized CuO [16, 28, 33]. In addition, the peak at high temperature range, i.e. 700-900 °C was proposed due to the reduction of highly stable Cu^+ to Cu^0 [22, 28, 34, 35].

Fig. 6 also shows the evolution of the peak areas assigned to the cupric species with the change of the preparation method and the hydrothermal aging. The relative amount of the three kinds of cupric species was estimated with integrating the de-convoluted peaks

and is plotted in Fig. 7. Obviously, the isolated Cu^{2+} is the dominant cupric species, accounting for more than 70% of Cu^{2+} in all the samples. The as-prepared one-pot synthesized sample Cu-OP-F showed the largest amount of the isolated Cu^{2+} among all the samples which is also higher than that in the as-prepared sample via ion-exchange method, i.e. Cu-IE-F. Meanwhile, the amount of the inner nanosized CuO in the sample Cu-IE-F is the highest and is 3 times higher than that in the sample Cu-OP-F, which is in agreement with the results recently reported by Zhang *et al.* [33]. This difference is due to the different way of formation of the isolated Cu^{2+} in the two preparation procedures. The one-pot technique allows the direct incorporation of extra-framework copper species in the CHA cages via Cu-TEPA as the structure-directing reagent. Moreover, the Cu-TEPA has a higher directing effect toward CHA cages than DEA, therefore, the Cu-TEPA would disperse well in each unit cell during the crystal growth, resulting in the uniform distribution of copper species [20]. In contrast, the presence of CuO is inevitable in the sample prepared with the ion-exchange method, which forms due to the size of the hydrated Cu ion [21, 36]. After the hydrothermal treatment, the amount of the isolated Cu^{2+} (246 °C) decreased significantly with the increase of the surface CuO particles (208 °C) in the one-pot synthesized catalyst (Cu-OP-A-16h). In contrast, the amount of isolated Cu^{2+} increased in the catalyst prepared *via* ion-exchange method after the hydrothermal treatment for 16 h (Cu-IE-A-16h), while the inner nanosized CuO (316 °C) decreased from 22% to 7%. Nevertheless, the isolated Cu^{2+} decreased with further prolonging the hydrothermal aging to 24 h, while the surface CuO particles increased from 5% to 16%.

3.5. Activity in ammonia oxidation reaction

Fig. 8 shows that the NH_3 conversion increases with the increase of the reaction temperature in NH_3 oxidation for all the fresh and aged samples. Obviously, the NH_3 conversion was increased due to the hydrothermal treatment for the samples prepared with both the two methods. Furthermore, the NH_3 conversion also increased with prolonging the time of hydrothermal treatment from 16 h to 24 h.

3.6. NO_x reduction activity

As shown in Fig. 9, the as-prepared one-pot catalyst (Cu-OP-F) shows the best SCR

activity within the whole temperature range, with a complete conversion over a temperature range of 250-450 °C. Meanwhile, the activity of the as-prepared ion-exchanged sample Cu-IE-F is lower than that of the Cu-OP-F sample. After 16 h hydrothermal treatment, deactivation was observed with the aged one-pot catalyst (Cu-OP-A-16h). Interestingly, the activity of the ion-exchanged sample Cu-IE-A was enhanced with hydrothermal treatment in the low reaction temperature range, i.e. 150-350 °C, while the activity in high temperature range, 350-500 °C was slightly decreased, which is consistent with the literature by Wang *et al.* [15]. With prolonging the hydrothermal treatment to 24 h, the activity decreased slightly as compared to the sample treated for 16 h in the whole reaction temperature range tested, but still higher than the as prepared Cu-IE-F in the low reaction temperature range, 150-350 °C.

4. Discussion

4.1. Migration of cupric species

As the data in Table 2 shown, identical elemental contents are observed with the catalysts prepared with the two different preparation methods. Both EPR (Fig. 4 and 5) and H₂-TPR (Fig. 6 and 7) results show the highest isolated Cu²⁺ content exist in the as-prepared Cu-OP-F sample. As a comparison, the as-prepared Cu-IE-F sample contains less isolated Cu²⁺, as well as more surface CuO particles and inner nanosized CuO than those in the Cu-OP-F sample. Obviously, the one-pot synthesis facilitates the uniform dispersion of Cu species.

The N₂ physisorption (Table 2), XRD (Fig. 1) and NMR (Fig. 2) results show only minor differences exist of the texture and structure of all the samples both before and after the hydrothermal treatments, confirming that the framework of Cu-SAPO-34 is robust enough to resist the harsh hydrothermal condition, irrespective to the preparation method [14, 15]. Interestingly, after hydrothermal treatment for 16 h, the surface area even increased slightly for the ion-exchanged sample, i.e. Cu-IE-A-16h. This is likely because of the migration of cupric species from the inner nanosized CuO to the isolated Cu²⁺, as indicated both by the H₂-TPR and EPR results presented in Fig. 4-7, releasing the congestion of the porous channel. However, longer running hydrothermal aging for 24 h resulted in both the surface area and the pore volume decreasing for about 15%, probably caused by either the formation of CuO particles blocking the porous channel again, or minor change of the framework of the zeolite driven by the secession of Cu²⁺ from the framework [27].

After 16 h hydrothermal treatment, the distribution of the cupric species changed significantly for the one-pot synthesized sample. The amount of the isolated Cu²⁺ ions decreased significantly, while the amount of the surface CuO particles increased as indicated with the EPR and H₂-TPR shown in Fig. 4-7.

The distribution of the cupric species also changed for the ion-exchanged samples during hydrothermal aging. Interestingly, EPR or H₂-TPR shows the amount of the isolated Cu²⁺ ions increased significantly after aging for 16 h, while the amount of the inner nanosized CuO decreased for about 70% as compared with the as-prepared

sample. Simultaneously, the amount of the surface CuO particles increase slightly. Obviously, the rate of the increase of surface CuO particles is slower than that of redispersion of inner nanosized CuO. This is likely attributed to the excessive isolated Cu^{2+} ions formed via redispersion of the inner nanosized CuO, agreeing well with the observations reported by Fan *et al.* [37]. With prolonging the hydrothermal aging to 24 h, the amount of the inner nanosized CuO further decreased slightly, but the amount of the surface CuO particles increased obviously at the sacrifice of the amount of the isolated Cu^{2+} . This indicates that some isolated Cu^{2+} ions are pulled out from the framework and aggregate into surface CuO particles when the aging time is extended to 24 h. In summary, Cu first migrated from the inner nanosized CuO inside of the cages to form more isolated Cu^{2+} , and when the inner nanosized CuO decreased to thimbleful, the isolated Cu^{2+} would detach from the framework and aggregate into surface CuO particles through a pathway as follows:

where the whole procedure can be understood as Ostwald ripening, driven by the difference of the surface energy between the inner nanosized CuO and the surface CuO particles [38]. Cu^{2+} ions migrate from the inner nanosized CuO diffusing in the catalyst. Part of the mobile Cu^{2+} ions were trapped and stabilized on the ion-exchange sites in the zeolite, coordinating with O on the framework as well as H_2O from the atmosphere, as suggested by the EPR results [27]. Further aging results in the accumulation of Cu^{2+} to form CuO particles on the surface of the zeolite crystal and thus the slight increase of the amount of the surface CuO particles in the sample. Importantly, the initial amount of the inner nanosized CuO was significantly higher in the as-prepared Cu-IE-F sample than that in the Cu-OP-F sample, driving the formation of the isolated Cu^{2+} via Eq. 4. The decrease of the amounts of the isolated Cu^{2+} and inner nanosized CuO during the prolonged hydrothermal aging results in the aggregation of the Cu^{2+} species eventually to the surface CuO particles, which either blocking the cages or locating outside the pores (Fig. 3). Obviously, the rate of the second step, viz. from the isolated Cu^{2+} to surface CuO particles, is slower than that of the first step, inner nanosized CuO clusters

to the trapped isolated Cu^{2+} , based on the fact that the increasing amount of the surface CuO particles is far less the decreasing amount of the inner nanosized CuO over the ion-exchanged sample after aging for 16 h. This probably can be explained with the energy required by ion-exchange between H^+ and Cu^{2+} on the trapping sites and the high energy required by the transformation from the isolated Cu^{2+} to $\text{Cu}(\text{OH})_2$ [27].

4.2. Effect on the activity

It is known that nonselective ammonia oxidation occurs in parallel on copper oxides and ionic copper species, and CuO particles are more active than the isolated Cu^{2+} [27, 37, 39, 40]. Interestingly, the nonselective NH_3 oxidation activity of sample Cu-IE-A-24h is higher than that of the sample Cu-IE-F, even though the overall content of CuO, i.e. the sum of the inner nanosized CuO and surface bulk CuO particles, over sample Cu-IE-A-24h is lower than that in the sample Cu-IE-F, as measured both by EPR and TPR. This means that the state of CuO has a significant influence on the activity in nonselective NH_3 oxidation. After aging for 24 h, the amount of surface CuO particles increased accompanied by the decrease of the amount of the inner nanosized CuO in the ion-exchanged catalyst. This indicates that the surface CuO particles are more active than the inner nanosized CuO in NH_3 oxidation, which may be attributed to the higher dissociation energy needed for oxygen dissociation on inner nanosized CuO than that on the surface CuO particles [41]. The increase of the activity in nonselective NH_3 oxidation of sample Cu-IE-A-24h over the as prepared sample Cu-IE-F can be explained by the increase of the amount of the surface CuO particles. Similarly, the increase of the amount of the surface CuO particles at the sacrifice of the isolated Cu^{2+} leads to the enhancement of the activity in NH_3 oxidation of the sample Cu-OP-A-16h. NH_3 direct oxidation, i.e. Eq. 1, is a typical side-reaction occurring during NH_3 -SCR reaction [42]. All the samples exhibit NH_3 conversion lower than 20% in the temperature range below 350 °C, as shown in Fig. 8, suggesting that the non-selective NH_3 oxidation has negligible competitiveness with the NH_3 -SCR reaction at low temperatures (<350 °C) [43].

For Cu-CHA catalysts, isolated Cu^{2+} ions as the active sites for NH_3 -SCR reaction have been verified with operando UV-Vis spectroscopy and kinetics measurements [28, 44,

45]. For the standard SCR reaction, NO and NH₃ were both activated on isolated Cu²⁺ coordinating with paired Al to form Cu⁺-H₂NNO and a NH⁴⁺ in an adjacent Al site, and then the Cu⁺-H₂NNO complex decomposes into N₂ and H₂O. Subsequently, the Cu⁺ is recovered to Cu²⁺ with the oxidation of O₂ and NO [46]. The EPR and the H₂-TPR results presented in this work show that the content of isolated Cu²⁺ decreases in a sequence Cu-OP-F > Cu-IE-A-16h > Cu-IE-A-24h > Cu-IE-F > Cu-OP-A-16h. An identical sequence of the activity in NH₃-SCR reaction in the temperature range below 350 °C is observed. A simple relationship figure between the NO_x conversion in the low temperature range and the content of isolated Cu²⁺ is depicted in Fig. S2, and it shows that NO_x conversion is positively related the isolated Cu²⁺ content in the low-temperature range.

Above 350 °C, the NH₃ conversion due to non-selective oxidation increases significantly as shown in Fig. 8 and shows a non-negligible contribution in the NH₃-SCR reaction in the high temperature range, leading to a low observed overall conversion of NO_x [16, 37]. Cu-OP-A-16h shows an obviously low activity in the high-temperature range in NH₃-SCR reaction, which is explained that part of the isolated Cu²⁺ ions detach from the zeolite framework and form surface CuO particles. The NH₃-SCR activity of Cu-OP-A-16h is slightly superior to that of Cu-IE-A-16h, even though the former sample contains relatively low isolated Cu²⁺, which might be interpreted by its stronger acidity in the Cu-OP-A-16h than that in the Cu-IE-A-16h shown in Fig. S1. Cu-IE-A-16h sample shows only slightly decreased NH₃-SCR activity in the temperature range above 350 °C compared to the as prepared sample. The prolonging of the aging time further enhances the NH₃ non-selective oxidation activity, resulting in the decrease of performance in NH₃-SCR reaction above 350 °C.

5. Conclusion

All the Cu-SAPO-34 catalysts contain three cupric compounds such as the inner nanosized CuO, isolated Cu²⁺ and surface CuO particles.

The distribution of copper species in the Cu-SAPO-34 sample prepared with a one-pot technique is more uniform than that in the as prepared sample obtained via an ion-exchanged route. In the as prepared one-pot sample almost all the copper exists as isolated Cu²⁺, while the as-prepared ion-exchanged sample contains a certain amount of inner nanosized CuO.

Inner nanosized CuO migrates to cation exchange sites and transform into isolated Cu²⁺ during the hydrothermal treatment, improving the performance of ion-exchanged sample. As the aging time prolonged to 24 h, partial isolated Cu²⁺ transforms into surface CuO particles, consistent with the aggregation of Cu²⁺ during the aging treatment over the one-pot prepared sample. The migration of copper species during hydrothermal follows the route:

Isolated Cu²⁺ ions are the active sites for NH₃-SCR reaction, but surface CuO particles promote the side-reaction, viz. NH₃ direct oxidation reaction in the high temperature range above 350 °C, limiting the NH₃ supply and resulting in the decrease of NH₃-SCR activity over Cu-SAPO-34 catalysts.

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Table 1. The sample notation of the fresh and aged Cu-SAPO-34 catalyst samples.

Notation	Aging time/h	Synthetic method
Cu-OP-F	\	one-pot
Cu-OP-A-16 h	16	one-pot
Cu-IE-F	\	ion-exchange
Cu-IE-A-16 h	16	ion-exchange
Cu-IE-A-24 h	24	ion-exchange

Table 2. Element contents of the fresh and aged Cu-SAPO-34 samples prepared by different methods.

Catalyst	S_{BET} (m^2/g) ^{a)}	V_p (cm^3/g) ^{b)}	Chemical content (wt.%)				
			Cu ^{c)}	P ^{c)}	Al ^{c)}	Si ^{c)}	Si/Al
Cu-OP-F	380.3	0.198	2.52	15.4	20.4	5.65	0.267
Cu-OP-A-16h	356.4	0.188	2.50	15.6	20.2	5.40	0.258
Cu-IE-F	401.4	0.211	2.49	15.8	19.5	5.35	0.265
Cu-IE-A-16h	409.4	0.213	2.52	15.3	20.8	5.65	0.263
Cu-IE-A-24h	346.8	0.184	2.55	15.6	20.4	5.5	0.260

a) Calculated with Brunauer-Emmett-Teller (BET) equation

b) Obtained with t-plot method

c) Determined with ICP

Fig. 1. XRD patterns for the fresh and aged Cu-SAPO-34 catalyst samples prepared by different methods.

Fig. 2. ^{27}Al (a) and ^{31}P (b) MAS NMR spectra of the fresh and aged Cu-SAPO-34 catalyst samples prepared by different methods.

Fig. 3. TEM images of Cu-OP-F (a1), Cu-OP-A-16h (b1), Cu-IE-F (c1), Cu-IE-A-16h (d1), Cu-IE-A-24h (e1) catalyst samples in the left part. The histograms of particle size distribution of CuO of Cu-OP-A-16h (b2), Cu-IE-F (c2), Cu-IE-A-24h (e2) according to TEM are shown in the right part.

Fig. 4. EPR spectra of the fresh and aged Cu-SAPO-34 catalyst samples prepared by different methods.

Fig. 5. Relative concentration of isolated Cu^{2+} ions semi-quantified by double integrating the EPR spectra of the fresh and aged Cu-SAPO-34 catalyst samples prepared by different methods.

Fig. 6. H₂-TPR profiles of the fresh and aged Cu-SAPO-34 catalyst samples prepared by different methods.

Fig. 7. Ratio of different Cu species in the fresh and aged Cu-SAPO-34 catalyst samples prepared by different methods quantified by the H₂-TPR profile.

Fig. 8. NH₃ conversion in NH₃ oxidation experiment of the fresh and aged Cu-SAPO-34 catalyst samples prepared by different methods. Reaction conditions: 500 ppm NH₃, 5% O₂ and balance N₂; flow rate: 500 ml/min; GHSV: 150,000 h⁻¹.

Fig. 9. NO_x conversion during standard NH₃-SCR as a function of the temperature (150-550 °C) of the fresh and aged Cu-SAPO-34 catalyst samples prepared by different methods. Reaction conditions: 500 ppm NO, 500 ppm NH₃, 5% O₂ and balance N₂; flow rate: 500 ml/min; GHSV: 150,000 h⁻¹.

Fig. S1 NH₃-TPD profiles of fresh and aged Cu-SAPO-34 catalyst samples prepared by different methods. All figures have the same Y-scale length.

Temperature programmed desorption with NH₃ (NH₃-TPD) was conducted using 100 g sample in a bed quartz reactor. The adsorption was carried out at 50 °C by passing a gas mixture flow (500/min) containing 500 ppm NH₃ with N₂ as balance for 1 h. Then, the purge gas was switched to N₂ flow for 1 h, with a total flow rate of 500 ml/min to remove the weakly adsorbed NH₃. TPD measurements were performed at up 550 °C at a ramp rate of 10 °C/min with N₂ flow (500 ml/min). The concentrations of outlet NH₃ with recorded at 10 °C intervals with FTIR spectrometer (Thermo Nicolet iS10).

NH₃-TPD

As shown in Fig. S1, two peaks were evidently observed on H-SAPO-34 sample. The low-temperature peak at around 140 °C is ascribed to weakly adsorbed NH₃, such as physisorbed NH₃ and weakly Brønsted NH₃, and the high-temperature desorption centered at 340 °C is assigned to strong Brønsted NH₃ arising from Si-OH-Al bond [1-3]. A new NH₃ desorption peak around 250 °C appears on all Cu-SAPO-34 samples, which is related to the NH₃ desorbing from the Lewis acids arising from isolated Cu²⁺ [4]. After high-temperature hydrothermal treatment, the high-temperature NH₃ desorption peak around 340 °C barely changed, illustrating that the samples maintain its framework integrity during the hydrothermal aging process, irrespective of

preparation methods. However, the peak around 250 °C changed differently for one-pot and ion-exchanged prepared sample after hydrothermal treatment. The hydrothermal treatment results in a decrease in Lewis acidity for one-pot sample, which might be caused by the aggregation of copper species. Contrarily, the peak around 250 °C increases with the ion-exchanged prepared sample after hydrothermal treatment for 16 h, indicating that additional isolated Cu^{2+} ions were formed during the aging process. With aging time extended to 24 h, that intensity of the peak at 250 °C declines in the aged samples but is still higher than the fresh sample. This indicates that the Cu-OP-24 sample still contains a larger amount of isolated Cu^{2+} than that in the fresh counterpart.

Fig. S2. The relationship figure between catalyst activity NO_x conversion in NH_3 -SCR reaction and the content of Cu^{2+} over fresh and aged Cu-SAPO-34 catalysts prepared by one-pot method (a) and prepared by IE method (b).

The relationship figure between catalyst activity NO_x conversion in NH_3 -SCR reaction and the content of Cu^{2+} is depicted in Fig. S2 based on the NH_3 -SCR activity data in Fig. 9 and H_2 -TPR results in Fig. 4 and 5. Fig. S2 shows that NO_x conversion is positively related the isolated Cu^{2+} content in the low-temperature range. The unusual change in activity in 200 °C may be caused by the influence of diffusion [5].

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