Synthesis and kinetics investigation of meso-microporous Cu-SAPO-34 catalysts for the selective catalytic reduction of NO with ammonia

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A B S T R A C T

A series of meso-microporous Cu-SAPO-34 catalysts were successfully synthesized by a one-pot hydrothermal crystallization method, and these catalysts exhibited excellent NH3-SCR performance at low temperature. Their structure and physic chemical properties were characterized by means of X-ray diffraction patterns (XRD), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), N2 sorption-desorption, nuclear magnetic resonance (NMR), Inductively Coupled Plasma-Atomic Emission spectrometer (ICP-AES), X-ray absorption spectroscopy (XPS), Temperature-programmed desorption of ammonia (NH3-TPD), Ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis DRS) and Temperature programmed reduction (TPR). The analysis results indicate that the high activities of Cu-SAPO-34 catalysts could be attributed to the enhancement of redox property, the formation of mesopores and the more acid sites. Furthermore, the kinetic results verify that the formation of mesopores remarkably reduces diffusion resistance and then improves the accessibility of reactants to catalytically active sites. The 1.0-Cu-SAPO-34 catalyst exhibited the high NO conversion (>90%) among the wide activity temperature window in the range of 150–425°C.

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I N T R O D U C T I O N

The catalytic elimination of environmentally harmful NOx compounds (NO, NO2, and N2O) emitted from mobile or stationary power sources is an important and challenging task. The conventional three-way catalysts used in the exhaust after-treatment devices of gasoline engines were ineffective when the engine is operated under highly oxygen enrichment conditions. Numerous approaches have been proposed for lean-NOx abatement, each of them with its own technical advantage. The most promising technology seems to be the selective catalytic reduction either with hydrocarbons (HC-SCR) or with ammonia (NH3-SCR) due to their high efficiency and low cost.

Cu-ZSM-5 is representative catalyst for NH3-SCR (Boubnov et al., 2014; Ochońska et al., 2013; Zhang et al., 2014a, 2014b),
which has shown the excellent deNOx activity at low temperature as well as suitable operating temperature window (200–400°C) (Metkar et al., 2013). However, the poor hydrothermal stability of ZSM-5-based catalyst still remains a primary concern in its commercial application (Berggrund et al., 2009; Fickel et al., 2011; Shi et al., 2013). Therefore, it is imperative to develop new catalyst materials with excellent NH3-SCR activity and highly hydrothermal stability. Only such catalyst systems are qualified to respond to more stringent NOx emission standards. Recently, chabazite (CHA)-structured small-pore zeolite catalysts such as Cu–SSZ-13 have been reported to be the most attractive and highly promising commercial catalyst for the urea/SCR reaction owing to their excellent low-temperature activity and robust hydrothermal stability (Martínez-Franco et al., 2012; Xue et al., 2013; Xie et al., 2014a, 2014b, 2014c, 2015). Metkar et al. (2013) reported that Cu–SSZ-13 catalyst showed much higher deNOx activity than Cu-ZSM-5 catalyst even after hydrothermal aging at 750°C, although its fresh activity was similar to that of Cu-ZSM-5 catalyst. Hereafter, the F-containing silicaaluminophosphate molecular sieves with copper catalysts supported by CHA crystalline structure, such as Cu/SAPO-34, were proved to be another promising candidate for SCR of NOx by ammonia (Xue et al., 2013; Zhang et al., 2014a, 2014b). Traditionally, Cu/SAPO-34 catalysts were prepared by post-synthesis cationic exchange-impregnation methods introducing copper species into small pore zeolites (Moliner et al., 2014; Kwak et al., 2012a, 2012b, 2012c, 2012d). However, the distribution of Cu within the zeolitic crystals following these procedures can be limited due to the presence of small pores (openings 3.8 Å), being the metal preferentially located close to the external surface (Zhan and Iglesia, 2007). Gao et al. (2013b) found that kinetically limited at low reaction temperature was remarkable over Cu-SAPO-34 catalysts.

As we all know that the primary factors of porous diffusion in catalyst particles can be explained by the Thiele modulus ($\phi$) (Eq. (1)) (Perez-Ramirez et al., 2008):

$$\phi = \frac{\text{Intrinsic}}{\text{Diffusion}} = L \cdot \sqrt{\frac{k_v}{D_{\text{eff}}}}$$

where, $L$ (m) is the diffusion length; $k_v$ (sec$^{-1}$) is the intrinsic rate coefficient and $D_{\text{eff}}$ (m$^2$/sec) is the effective diffusivity. When $\phi$ is high, most of the catalyst particle is rendered and unutilized. However, when $\phi$ is close to 0, the entire particle is fully made use of. According to this formula, there are two ways to improve mass transfer. The first one is to decrease diffusion length and the other one is to increase the degree of diffusivity, which commonly involves in modifying the pore structure of catalysts. It needs to introduce meso- or/and macropores into the microporous zeolite crystals and obtain a hierarchical structure. The chemical reaction still takes place into the micropores, but the accessibility of catalyst active sites is improved.

In recent decades, some methods have been successfully employed for the preparation of hierarchical porous aluminosilicate zeolites, such as post-treatment method (Shin et al., 2011), hard-templating method (Jacobsen et al., 2000) and soft-templating method (Wu et al., 2012). Sommer et al. prepared hierarchical SSZ-13 treated with sodium hydroxide solutions of various concentrations (Sommer et al., 2010). Schmidt et al. (2012) synthesized hierarchical SAPO-34 by using carbon materials as hard templates. However these methods are too complicated and need two steps, which hamper its industrial evolution. Notably, Ryoo’s group demonstrated a soft-templating synthesis of zeolites by introducing organosilane surfactants as the mesopore director into conventional zeolite synthesis compositions (Choi et al., 2006a, 2006b). They further extended this strategy to the synthesis of mesoporous alumino-phosphate molecular sieves (Choi et al., 2006a, 2006b). Nevertheless, high cost and complex template synthesis method also limit its further application.

Herein, meso-microporous Cu-SAPO-34 was directly synthesized to obtain a highly efficient catalyst for NH3-SCR of NO. A rationalized cooperative organic structure direct agent (OSDAs) was used, and it consisted of an organometallic Cu-complex ($\text{Cu}^{+}$ with tetraethylpentamine (TEPA)) and another organic molecule N,N-diisopropylethylenediamine (DIPEA) which can direct the crystallization toward Cu-SAPO-34. Very interestingly, the direct synthesis of Cu-SAPO-34 materials allows the crystallization of catalysts with the high solid yields and the controllable location for the isolated Si species and extra-framework copper ions. The excellent NH3-SCR performances were also obtained.

### 1. Materials and methods

#### 1.1. Materials

Firstly, 20 wt.% of an aqueous solution of copper(II) sulfate (98 wt.%, Alfa, USA) was mixed with the required amount of tetraethylpentamine (TEPA, 98 wt.%, Aldrich, USA) to prepare Cu-complex with mole ratio of Cu/TEPA = 1, and then this mixture was stirred for 4 hr until complete dissolution. Secondly, distilled water and phosphoric acid (85 wt.%, Aldrich, USA) were added to the above solution successively and stirred for 0.5 hr. Thirdly, Co-OSDA organic molecule N,N-diisopropylethylenediamine (DIPEA, 99 wt.%, Aldrich, USA) was introduced in the gel mixture and stirred for 4 hr. Finally, pseudo-boehmite (75 wt.%, Condrea, Gemany) and silica gel (Ludox AS40 40 wt.%, Aladdin, China) were added in the gel and stirred for 12 hr. The final molar composition of the zeolite gel was: 1 Al$_2$O$_3$: 0.85 P$_2$O$_5$: 3.7 DIPEA: 0.185 Cu-TEPA: 0.30–2.0 SiO$_2$: 111 H$_2$O.

The resulting gel was hydrothermally crystallized in a Teflon-lined stainless-steel autoclave at 170°C and autogenous pressure for 48 hr. After filtration, the samples were washed with deionized water and dried at 110°C for 12 hr. These samples were calcined at 550°C for 6 hr in air to remove the template. The catalysts were denoted as x-Cu-SAPO-34, where, $x$ represents the mole ratio of Si/Al in the synthesis gel.

For comparison purpose, conventional Cu/SAPO-34 was synthesized by the following steps. H-SAPO-34 was synthesized according to the procedure described in Ref (Moliner et al., 2014). An ion-exchange (IE) step was applied using an excess amount of 0.1 mol/L NH$_4$NO$_3$ (99 wt.%, Aladdin, China).
at 50°C for 5 hr to generate NH₄/SAPO-34. Subsequently, centrifugation separation and washing cycles were employed. Then, NH₄/SAPO-34 was further exchanged with 0.01 mol/L Cu(OAc)₂ (98 wt. %, Aladdin, China) at 50°C for 2 hr to generate the resulting Cu/SAPO-34. The amount of Cu(OAc)₂ solution, assuming complete Cu exchange, was allowed 4.5 wt.% Cu loading in the final product. Finally, the as-synthesized Cu/SAPO-34 was separated, washed and dried at 110°C, and then calcined at 550°C for 6 hr.

The hydrothermal treatment of metal-containing zeolite catalysts was carried out on a flow set-up with 100% H₂O in air at 750°C for 16 hr.

1.2. Analytical methods
X-ray diffraction (XRD) experiments were performed on a Bruker D8 Advance diffractometer (Bruker D8 Advance, Germany) equipped with Cu Kα radiation (wavelength 1.5406 Å) with working voltage of 40 kV and current of 40 mA. The surface morphology of the catalyst was observed by field emission scanning electron microscopy (FESEM) on a Quanta 200F instruments (FEI Quanta 200F, Japan) using accelerating voltages of 5 kV. Transmission electron microscopy (TEM) pictures were taken on a FEI Tecnai 20 at 200 kV (FEI F20, Japan). The catalysts were suspended in ethanol and dispersed over a carbon-coated holey Cu grid with a film prior to measurements. The specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) method and the pore size distributions were obtained using the Barret–Joyner–Halenda (BJH) method. The element content of as-made materials was determined by a Varian 715-ES Inductively Coupled Plasma-Atomic Emission spectrometer (ICP-AES) (OPTIMA 7300V, Perkin Elmer, USA). X-ray absorption spectroscopy (XPS) was taken using a commercial VG Multilab 2000 system (Thermo Fisher K-Alpha, Japan). ²⁹Si, ²⁷Al and ³¹P magic angle spinning nuclear magnetic resonance (MAS NMR) were recorded on a standard Bruker MAS probe head at a spinning rate of 20 kHz (JNM-LA300FT-NMR, Japan). Temperature-programmed desorption of ammonia (NH₃-TPD) measurements were carried out on a conventional flow apparatus in the range of 100–600°C. UV–Vis diffuse reflectance spectroscopy (UV–Vis DRS) experiments were performed on a UV–Vis spectrophotometer Hitachi U-4100 with the integration sphere diffuse reflectance attachment (Hitachi U-4100, Japan). Temperature programmed reduction (TPR) experiments were performed in a home-made apparatus. Prior to reduction, the samples (50 mg) were treated from room temperature to 600°C under a flow rate of 30 mL/min N₂ and then cooled down to 100°C in a purging N₂ flow. The temperature programmed reduction process were carried out in 30 mL/min flow of 10% H₂/N₂ at a ramp rate of 10°C/min up to 700°C.

1.3. NH₃-SCR activity evaluation
SCR activity tests of the catalysts were performed in a fixed-bed quartz flow reactor at atmospheric pressure. The gas compositions were as follows: 1000 ppm NO, 1000 ppm NH₃, 3 vol% O₂, balance N₂, and the gas flow rate was 500 mL/min. Different gas hourly space velocities (GHSV) were obtained by changing the volume of catalysts. Catalyst samples (20–400 mg, 20–40 mesh) were loaded in a quartz tube and placed inside an electric tube furnace. The effluent gas including NO, O₂, NH₃ and N₂ was analyzed by a NEXUS 670-FTIR spectrometer equipped with a smart collector and an mercury cadmium tellurium/A (MCT/A) detector (NEXUS 670FT-IR, USA). The NO conversion, NH₃ conversion and N₂ selectivity were calculated as Eqs. (2)–(4):

\[
C_{\text{NO}} = \frac{\left[\text{NO}\right]_{\text{inlet}} - \left[\text{NO}\right]_{\text{outlet}}}{\left[\text{NO}\right]_{\text{inlet}}} \times 100\% \tag{2}
\]

\[
C_{\text{NH₃}} = \frac{\left[\text{NH₃}\right]_{\text{inlet}} - \left[\text{NH₃}\right]_{\text{outlet}}}{\left[\text{NH₃}\right]_{\text{inlet}}} \times 100\% \tag{3}
\]

\[
S_{\text{N₂}} = \left(1 - \frac{2\left[\text{N₂O}\right]_{\text{outlet}} + \left[\text{NO}\right]_{\text{outlet}} - \left[\text{NH₃}\right]_{\text{outlet}}}{\left[\text{NO}\right]_{\text{inlet}} + \left[\text{NH₃}\right]_{\text{inlet}} + \left[\text{NO}\right]_{\text{outlet}} - \left[\text{NH₃}\right]_{\text{inlet}} - \left[\text{NH₃}\right]_{\text{outlet}} - \left[\text{NO}\right]_{\text{outlet}} - \left[\text{N₂O}\right]_{\text{outlet}} - \left[\text{NH₃}\right]_{\text{inlet}} - \left[\text{NH₃}\right]_{\text{outlet}} - \left[\text{NO}\right]_{\text{inlet}} - \left[\text{NO}\right]_{\text{outlet}} - \left[\text{N₂O}\right]_{\text{inlet}} - \left[\text{N₂O}\right]_{\text{outlet}}}ight) \times 100\% \tag{4}
\]

where, \(C_{\text{NO}}\) (%) means the NO conversion, \(C_{\text{NH₃}}\) (%) means the NH₃ conversion; \(S_{\text{N₂}}\) means the N₂ selectivity. Turnover frequencies (TOF) were evaluated by dividing the moles of NO
molecules converted per second by the moles of Cu atoms in the catalysts.

2. Results and discussion

2.1. XRD results

By adjusting the chemical composition of the starting gels, Cu-SAPO-34 catalysts with various Si/Al ratios were successfully synthesized. The XRD patterns of the as-synthesized fresh and aged Cu/SAPO-34 and Cu-SAPO-34 catalysts are shown in Fig. 1. It can be seen from Fig. 1a that all of the samples exhibit identical characteristic peaks of the CHA structure in good agreement with those patterns of SAPO-34 (Martínez-Franco et al., 2012; Ma et al., 2013). Moreover, with the increasing of Si/Al ratio from 0.30 to 2.0, the intensity of typical peaks ascribed to the CHA structure firstly grows stronger. It is mainly due to the improvement of crystallinity degree of catalysts. And then it slightly becomes lower, which may be due to the decreasing of crystallinity degree or crystal size. Fig. 1b displays the XRD patterns of Cu/SAPO-34 and Cu-SAPO-34 catalysts aged at 750°C for 16 hr. Compared with the fresh samples, the crystal structure of the aged catalysts are hardly unchanged except the intensity of typical peaks slightly reduced. It indicates that the original zeolite structure is maintained and the highly hydrothermal stability of Cu-SAPO-34 catalysts is demonstrated. Furthermore, there is no obvious diffraction peaks with respect to CuOx (2θ = 35.6, 36.4 and 38.8°) and CuAl2O4 (2θ = 37.1°) species observed in the XRD pattern, revealing that the Cu species are well dispersed on SAPO-34 (Gao et al., 2015; Kwak et al., 2012a, 2012b, 2012c, 2012d).

2.2. SEM and TEM results

Scanning electron microscopy (SEM) images of Cu/SAPO-34 and Cu-SAPO-34 catalysts with various Si/Al ratios are shown in Fig. 2. It can be seen that Cu-SAPO-34 samples consist of large spherical particles with diameters about 20 μm. Notably, it is different from the conventional microporous Cu/SAPO-34 (Fig. 2a) with a smooth crystal surface and size around 5 μm, Cu-SAPO-34 are observed to be an intergrowth of small cubic-like zeolite crystals with sizes in the range of 4–10 μm. Furthermore, with the increasing of Si/Al ratio from 0.30 to 1.0, the cubic structure of catalysts become more regular, but further increasing Si/Al ratio from 1.0 to 2.0, it changes to irregular again.

A selection of representative TEM images 1.0-Cu-SAPO-34 catalyst is given in Fig. 2e. The micrographs clearly reveal the existence of intracrystalline mesopores with different sizes on the surface of 1.0-Cu-SAPO-34 catalysts, which should be beneficial to the catalytic reactions, especially those diffusion-controlled reactions.

2.3. N2 adsorption-desorption results

N2 adsorption-desorption isotherms and derived pore size distributions of the fresh and aged Cu/SAPO-34 and Cu-SAPO-34 catalysts are depicted in Fig. 3. In contrast to
conventional microporous Cu/SAPO-34 (Fig. 3a1) showing the type-I N\textsubscript{2} adsorption–desorption isotherms, Cu-SAPO-34 catalysts exhibit type-IV isotherms with a large hysteresis loops in the region 0.90 < P/P\textsubscript{0} < 1.0 due to the capillary condensation in the mesopores. Furthermore, the isotherms of Cu-SAPO-34 samples exhibit a clearly steep increase in N\textsubscript{2} adsorption volume in the region P/P\textsubscript{0} < 0.05 due to the presence of microporosity. Particularly, Cu-SAPO-34 catalysts exhibit a significantly increased external surface area (37.8–65.9 m\textsuperscript{2}/g) and mesopore volume (0.16–0.39 cm\textsuperscript{3}/g) as compared with the conventional microporous Cu/SAPO-34 catalyst (Table 1). Meanwhile, the pore-size distribution of the fresh samples displayed in Fig. 3b clearly shows the presence of mesopore structure with pore sizes centered at 21.2–33.3 nm and the pore distribution is relatively concentrated. Additionally, it is noted that the pronounced peak at 3.8 nm in the BJH desorption pore size distribution does not show the real pore. It is due to the tensile strength effect (TSE) of the adsorbed phase (Groen et al., 2003). Furthermore, the adsorption–desorption isotherm shape remains unchanged after the catalysts being aged at 750°C for 16 hr, and higher microporosity, i.e., higher total surface areas and total pore volumes for aged Cu-SAPO-34 samples were reserved (as shown in Table 1 and Fig. 3c), indicating the good hydrothermal stability of catalysts.

**Table 1 – Textural properties of Cu/SAPO-34 and Cu-SAPO-34 before and after hydrothermal aging (HT) at 750°C.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>S\textsubscript{BET}\textsuperscript{a} (m\textsuperscript{2}/g)</th>
<th>S\textsubscript{mic}\textsuperscript{b} (m\textsuperscript{2}/g)</th>
<th>S\textsubscript{ext}\textsuperscript{b} (cm\textsuperscript{3}/g)</th>
<th>V\textsubscript{t}\textsuperscript{b} (cm\textsuperscript{3}/g)</th>
<th>D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/SAPO-34</td>
<td>429</td>
<td>422</td>
<td>7.0</td>
<td>0.04</td>
<td>–</td>
</tr>
<tr>
<td>0.30-Cu-SAPO-34</td>
<td>370</td>
<td>323</td>
<td>47.0</td>
<td>0.24</td>
<td>23.2</td>
</tr>
<tr>
<td>1.0-Cu-SAPO-34</td>
<td>471</td>
<td>433</td>
<td>38.0</td>
<td>0.16</td>
<td>21.2</td>
</tr>
<tr>
<td>2.0-Cu-SAPO-34</td>
<td>377</td>
<td>311</td>
<td>66.0</td>
<td>0.39</td>
<td>33.3</td>
</tr>
<tr>
<td>Cu/SAPO-34-HT</td>
<td>410</td>
<td>402</td>
<td>8.0</td>
<td>0.04</td>
<td>–</td>
</tr>
<tr>
<td>0.30-Cu-SAPO-34-HT</td>
<td>303</td>
<td>266</td>
<td>37.0</td>
<td>0.22</td>
<td>38.3</td>
</tr>
<tr>
<td>1.0-Cu-SAPO-34-HT</td>
<td>408</td>
<td>373</td>
<td>35.0</td>
<td>0.13</td>
<td>20.6</td>
</tr>
<tr>
<td>2.0-Cu-SAPO-34-HT</td>
<td>339</td>
<td>287</td>
<td>52.0</td>
<td>0.35</td>
<td>32.9</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Calculated by BET method.
\textsuperscript{b} Calculated by t-plot method.
\textsuperscript{c} Can’t be measured by this BET method.
Together with the abovementioned SEM and TEM analysis, the nitrogen adsorption results strongly demonstrate that the existence of hierarchical porosity in the three Cu-SAPO-34 samples (Table 1 and Fig. 3b). Therefore, a pore system consisting of meso-micropore structure can greatly improve the accessibility of catalytically active sites between the microporous channels to reactants, especially for the reactions taking place in mass transfer limited regime (Kustova et al., 2006).

2.4. NMR results

$^{29}$Si NMR, $^{27}$Al NMR and $^{31}$P NMR spectroscopy are especially useful information for following changes in the structure of alumino-silicate zeolites. Fig. 4a presents the $^{29}$Si spectra of 0.30-Cu-SAPO-34, 1.0-Cu-SAPO-34, 2.0-Cu-SAPO-34 and marked differences occur among the three samples. Two distinctly resolved features are observed at $-90$ and $-110$ ppm. The first one is assigned to isolated Si, that is, Si (OAl)$_4$ species. The second one at $-110$ ppm is attributed to the Si (3OAl) (Sastre et al., 1997). The Si ($n$OAl, $n$: 0–3) structures imply the SM3 substitution (Si replaces P and Al) mechanism happens during SAPO-34 synthesis, and it may lead to the formation of Si island (Sastre et al., 1997; Xu et al., 2008). It can affect the acidity of SAPO-34 support, because the Si (OAl) structures in Si islands cannot generate acid site (Sastre et al., 1997; Xu et al., 2008). Furthermore, with the increasing of mole ratio of Si/Al in the synthesis gel, the relative intensity of the peak ascribed to Si islands increases and the intensity of the peak attributed to isolated Si species decreases simultaneously.

$^{27}$Al NMR spectra of the fresh (full line) and aged (dotted line) Cu/SAPO-34, 0.30-Cu-SAPO-34, 1.0-Cu-SAPO-34 and 2.0-Cu-SAPO-34 are presented in Fig. 4b. There are three primary features at 38, ca., 14 and $-11$ ppm observed, corresponding to tetrahedrally, pentahedrally and octahedrally coordinated Al, respectively, revealing the existence of various coordinated Al species in Cu-SAPO-34 catalysts. Additionally, it is reported that the formation of pentahedrally and octahedrally coordinated Al features is due to reversible SAPO-34 hydrolysis, and these features disappear upon dehydration (Gao et al., 2013a, 2013b). Moreover, it is noted that the relative intensity of the peak that corresponds to octahedrally coordinated Al is the lowest for Cu-SAPO-34 catalyst. It demonstrated that the different ratio of Si/Al in the synthesis gel can remarkably affect the distribution of aluminum in Cu-SAPO-34 catalysts. Furthermore, some subtle differences can be noticeable that the relative intensity of all peaks for the fresh Cu-SAPO-34 slightly decreased after being aged at 750°C for 16 hr. The reduction of the intensity of the tetrahedrally coordinated Al$^{3+}$ ions should be due to the dealumination of Al$^{3+}$ ions from their tetrahedral positions in the zeolite framework. The decreased intensity of pentahedrally and octahedrally coordinated Al features may be ascribed to that the interaction is more strongly between the paramagnetic Cu ions and the forming octahedral aluminum than that between zeolitic Cu ions and framework aluminum (Kwak et al., 2012a, 2012b, 2012c, 2012d; Vennestrøm et al., 2014).

Fig. 4c presents the $^{31}$P NMR data of 0.30-Cu-SAPO-34, 1.0-Cu-SAPO-34 and 2.0-Cu-SAPO-34. It can be seen that all samples exhibit similar two resonance peaks at $-26.5$ and $-15$ ppm. The former one is attributed to tetrahedral P. The latter one is assigned to disordered P formed by SAPO-34 hydrolysis (Simmen et al., 1991). Furthermore, no other clear differences are observed for Cu-SAPO-34 catalysts.
ICP and XPS measurements were also carried out to determine the composition and elements distribution of these samples, and the results are summarized in Table 2. It can be seen that the concentration of Al gradually decreases and the corresponding Si increases with the increasing of Si/Al ratio in the synthesis gel. Moreover, for all of Cu-SAPO-34 samples, the surface Cu/Al ratio was much lower than that in the bulk, indicating that the Cu ions are predominantly at the exchanged sites inside SAPO-34 pores. While with the increasing of the mole ratio of Si/Al in the synthesis gel of Cu-SAPO-34 catalysts, the Si/Al ratio on surface of the catalysts gradually increase, when Si/Al ≥ 1.0, the mole ratio of Si/Al on the surface is bigger than that in the bulk. Thus, by adjusting the ratio of Si/Al in the synthesis gel, Cu-SAPO-34 catalysts can be effectively controlled to the location of Si species, and then the catalytic performances are affected.

### 2.5. NH$_3$-TPD results

Temperature-programmed desorption of ammonia performed to determine the acid property. The strength of the acid sites in Cu-SAPO-34 catalysts is shown in Fig. 5, and the result of deconvolution of NH$_3$-TPD profiles is displayed in Table 3. For Cu/SAPO-34 catalyst, three desorption peaks are observed at around 200, 280 and 405°C, respectively. The first one is assigned to physisorbed NH$_3$ or ammonium species adsorbed at the Lewis acid sites. The second one centered at 280°C can be attributed to NH$_3$ adsorbed at the moderate acid sites and the third one centered at 405°C is attributed to NH$_3$ adsorbed at the strong acid sites (Ma et al., 2014; Wang et al., 2012). For Cu-SAPO-34 catalysts, the intensity of desorption peaks firstly increases and then decreases. When Si/Al is 1.0, the peak area reaches the largest (Table 3), and the peak temperatures, especially the moderate acid sites, are shifted to a higher temperature than that of 0.30-Cu-SAPO-34 with the increasing of mole ratio of Si/Al in synthesis sol. It indicates that the strength of acid is favorable for the adsorption and activation of NH$_3$. This gradual temperature variation for Cu-SAPO-34 catalysts may be due to the changing of Si/Al ratio in the synthesis sol, which results in the change of location of Si and Al species in Cu-SAPO-34 catalysts and causes the change of the amount of active species, and then leads to the change of catalyst acidity.

### 2.6. UV–Vis DRS results

In order to understand the coordination and dispersion of Cu species in Cu-SAPO-34 catalysts with varying Si/Al ratio, UV–Vis DRS spectra were investigated and the results are shown in Fig. 6. Two main characteristic absorption bands for all of the samples were observed. The one centered at ca. 240 nm is attributed to charge transfer lattice O$^-$→Cu$^{2+}$ (Wang et al., 2012; Gao et al., 2013a, 2013b; Debeček et al., 1999), and the other one observed in the 600-800 nm region centered at 750 nm is ascribed to d–d Cu$^{2+}$ transition in dispersed CuO particles (Ma et al., 2015; Zamadics et al., 1992). Moreover, the band at 650 nm bands related to bulk CuO is not detected (Yu et al., 1996), which is in accordance with the results of XRD. A red shift of the Cu absorption edge between 250 and 500 nm is observed with the increasing of mole ratio of Si/Al from 0.30 to 1.0 in synthesis sol, reflecting a

### Table 2 – Chemical composition of the catalysts obtained by ICP and XPS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration (wt.%)</th>
<th>Mole ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
<td>P</td>
</tr>
<tr>
<td>Cu/SAPO-34</td>
<td>19.8</td>
<td>9.8</td>
</tr>
<tr>
<td>0.30-Cu-SAPO-34</td>
<td>19.6</td>
<td>9.9</td>
</tr>
<tr>
<td>1.0-Cu-SAPO-34</td>
<td>18.7</td>
<td>10.5</td>
</tr>
<tr>
<td>2.0-Cu-SAPO-34</td>
<td>13.5</td>
<td>5.3</td>
</tr>
</tbody>
</table>

* a Obtained by ICP.
  b Obtained by XPS.

### Table 3 – Acid properties of Cu-SAPO-34 catalyst.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak1 (ca., 200°C)</th>
<th>Peak2 (ca., 300°C)</th>
<th>Peak3 (&gt;400°C)</th>
<th>Total area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/SAPO-34</td>
<td>1712.5</td>
<td>1641.4</td>
<td>1419.7</td>
<td>4773.6</td>
</tr>
<tr>
<td>0.30-Cu-SAPO-34</td>
<td>1702.4</td>
<td>1674.4</td>
<td>1394.9</td>
<td>4825.5</td>
</tr>
<tr>
<td>1.0-Cu-SAPO-34</td>
<td>2255.5</td>
<td>2139.5</td>
<td>1889.7</td>
<td>6284.7</td>
</tr>
<tr>
<td>2.0-Cu-SAPO-34</td>
<td>1923.8</td>
<td>1891.0</td>
<td>1296.8</td>
<td>5111.6</td>
</tr>
</tbody>
</table>

*a Ammonium desorption calculated from NH$_3$-TPD results.
decrease in the dispersion of Cu (Td) species. It may be beneficial to the reduction of Cu species and NH3-SCR activity. While further increasing the Si/Al from 1.0 to 2.0, a blue shift of the Cu absorption edge between 250 and 500 nm is observed, indicating an increase in dispersion of Cu species.

2.7. H2-TPR results

To further probe the redox properties of Cu-SAPO-34 catalysts, H2-TPR measurements were carried out. Owing to no clear H2 consumption signal was detected for the pure H-SAPO-34, it was used as the baseline. For Cu-SAPO-34 catalyst, there are three H2 consumption signals in the range of 100 to 700°C (Fig. 7). Gao et al. (2013a, 2013b) reported that the reduction peak centered at 210 and 260°C are ascribed to isolate copper ions and nano-sized CuO crystallites, respectively. In this work, Cu-SAPO-34 samples showed a very similar hydrogen reduction peak. Consequently, for 0.30-Cu-SAPO-34 catalyst, the peak observed at 220°C is assigned to the reduction of isolated Cu2+ (Cu2+ → Cu+) and the peak at 292°C to the reduction of nano-sized CuO crystallites (Cu2+ → Cu+). The H2 consumption peak at around 464°C is attributed to the reduction of Cu+ to Cu0. In addition, due to [Cu-O-Cu]2+ dimmers were not detected from UV–Vis DRS spectra (Fig. 6) and the peak temperature attributed to the reduction of isolate copper ions on Cu-SAPO-34 samples was similar. Therefore, it can be deduced that there is no remarkable difference on the distribution of isolate copper ions over Cu-SAPO-34 catalysts. Moreover, marked distinctions can be observed with the increasing of Si/Al ratio in Cu-SAPO-34 catalysts that the peak temperature at 220°C almost remains unchanged, but the area of this peak firstly increase and then sharply decrease. When Si/Al is 1.0, it reaches the largest. And the peak temperature with respect to the reduction of nano-sized CuO crystallites is obviously shifted to a lower temperature. It’s reported that the CuO nanoparticles and Cu (II) with tetrahedral coordination were considered as active sites in the NH3-SCR reaction, and the CuO nanoparticles favored the reduction of NO at lower temperature, due to it could promote the oxidation of NO to NO2 thus facilitating the “fast SCR” process (Xue et al., 2013; Wang et al., 2014). Consequently, by changing Si/Al ratio in Cu-SAPO-34 catalysts, the distributions of Cu species on Cu-SAPO-34 were altered, therefore the redox properties was different. Furthermore, in contrast to Cu-SAPO-34 catalyst, it is notable that the reduction peak attributed to the reduction of isolated Cu2+ (Cu2+ → Cu+) are shifted to a high temperature, which may be unfavorable for the enhancement of NH3-SCR performance of Cu/SAPO-34 catalysts.

2.8. NH3-SCR reaction results

The NO conversion over fresh and aged Cu-SAPO-34 catalysts was tested and the results are depicted in Fig. 8. The catalytic activity of conventional Cu/SAPO-34 catalyst is also investigated for comparison. It can be seen that 1.0-Cu-SAPO-34 catalyst exhibited the highest NO conversion at low temperature (<200°C) and the widest activity temperature windows in the range of 100–550°C (Fig. 8a1). Meanwhile, the conventional Cu/SAPO-34 catalyst showed relatively lower catalytic activity, which maintained NO conversion below 90% until 200°C. Fig. 8a2 shows that the ammonia oxidation abilities of the meso-micropore Cu-SAPO-34 catalysts are much higher than conventional Cu/SAPO-34 catalyst, and the ammonia oxidation abilities of the series of Cu-SAPO-34 catalysts are almost the same over the whole temperature range. The stoichiometric relationship between NH3 and NO conversion was 1:1 below 375°C, which indicated that “standard SCR” took place at this temperature range. However, at the high temperature range, ammonia conversions obviously became much higher than NO conversions, which indicated that ammonia oxidation reaction occurred. N2O formation is one of the important practical aspects for SCR catalysts and the result is shown in Fig. 8a3. It was observed that the trend of N2O formation of Cu/SAPO-34 and Cu-SAPO-34 catalysts are almost the same over the whole test temperature range, and the N2O concentration increased with the increasing of reaction temperature. The N2 selectivity of the fresh Cu/
Fig. 8 – NO conversions over fresh and aged Cu-SAPO-34 catalysts as a function of reaction temperature (a1, b1), NH₃ conversions (a2, b2), N₂O formation (a3, b3), and N₂ selective (a4, b4). Reaction condition: 1000 ppm NO, 1000 ppm NH₃, 3% O₂ balanced with N₂; GHSV = 50,000 hr⁻¹.
SAPO-34 and Cu-SAPO-34 catalysts is shown in Fig. 8a4. It shows that the value of N$_2$ selectivity of all catalysts is above 90%, and the value gradually decreased when the reaction temperature over 400°C, which should be due to the ammonia oxidation reaction. In addition, after being aged at 750°C for 16 hr, the NO conversion of all the catalysts (Fig. 8b1) slightly decreases at the low and high temperature, and the N$_2$O concentration increased compared with the fresh samples. It is due to the decrease of isolated Cu species resulting from hydrothermal treatment and the formation of CuO particles, which aggravates the overoxidation of NH$_3$. However, the active window is still wide. It indicates that a highly hydrothermal stability for hierarchical Cu-SAPO-34 materials have been obtained by the “one-pot” synthesis method.

The results of activity test indicate that Cu-SAPO-34 catalysts with meso-micropore structure are more active than conventional Cu/SAPO-34. The formation of mesopores, which may reduce diffusion resistance and improve the accessibility of reactants to catalytically active sites in the microporous channels, may be the main reason for the discrepancies in NH$_3$-SCR performances between Cu/SAPO-34 and Cu-SAPO-34 catalysts. The reaction kinetics results in the following section will account for this.

2.9. Reaction kinetics results

To understand the intrinsic effect of mesopore on the activity of Cu-SAPO-34 catalysts, the catalytic activity data are quantitatively analyzed using the reaction-kinetic approach. For ion-exchanged zeolite catalysts, the standard NH$_3$-SCR rate ($R_{SCR}$, sec$^{-1}$) can be presented using the following power-law model (Brandenberger et al., 2008; Olsson et al., 2008; Metkar et al., 2011) at steady state:

$$-R_{SCR} = k[NO]^{\alpha}[NH_3]^{\beta}[O_2]^{\gamma}$$  (5)

The power-law dependences on NO, NH$_3$ and O$_2$ concentration are probed over 1.0-Cu-SAPO-34 sample at 150, 175, and 200°C, as shown in Fig. 9. The different power-law values can be obtained for $\alpha \approx 1.0$, $\beta \approx 0$, $\gamma \approx 0$. These same power-law dependences are also found for other Cu-SAPO-34 samples (Gao et al., 2013a, 2013b, 2015). Therefore, the standard NH$_3$-SCR reaction on 1.0-Cu-SAPO-34 catalyst can be considered as a first order reaction with respect to NO. According to the first-order power-law rate equation:

$$-R_{SCR} = k_0[NO]$$  (6)

Fig. 9 – (a) NO conversions (in TOF) as a function of NO input for standard SCR over 1.0-Cu-SAPO-34 catalyst at 150–200°C. Reaction mixtures contain x ppm NO, 1000 ppm NH$_3$, 3% O$_2$ balanced with N$_2$, at a gas hourly space velocities (GHSV) = 800,000 hr$^{-1}$. (b) NO conversions (in TOF) as a function of NH$_3$ input for standard SCR over 1.0-Cu-SAPO-34 catalyst at 150–200°C. Reaction mixtures contain 1000 ppm NO, x ppm NH$_3$, 3% O$_2$ balanced with N$_2$, at a GHSV = 800,000 hr$^{-1}$. (c) NO conversions (in turnover frequencies) as a function of NH$_3$ input for standard SCR over 1.0-Cu-SAPO-34 catalyst at 150–200°C. Reaction mixtures contain 1000 ppm NO, 1000 ppm NH$_3$, x% O$_2$ balanced with N$_2$, at a GHSV = 800,000 hr$^{-1}$. 


where, $k_a$ (mL/(g·sec)) is the apparent rate constant.

The correlation between $k_a$ and NO conversion ($X$) can be expressed as follows:

$$k_a = -\frac{F_0}{[NO]_0 W} \ln(1-X)$$

(7)

where, $F_0$ (mol/min) is the molar NO feed rate; $[NO]_0$ (mol/mL) is the molar NO concentration; $W$ (g) is the catalyst amount. At the same temperature and NO concentrations, $-\ln(1-X)$ should be proportional to $W/F_0$. Using 1.0-Cu-SAPO-34 sample, NH3-SCR reactions were carried out at various space velocities and the results are listed in Table 4 and displayed in Fig. 10. It is clear that the increase of GHSV from 100,000 to 1,000,000 hr$^{-1}$ resulted in the decrease of NH3-SCR performance at low temperatures (150, 175 and 200°C). According to the data in Table 4, the plots of $-\ln(1-X)$ ($X$ is the NO conversion) versus $W/F_0$ are shown in Fig. 11. $k_a$, with units of mL/(g·sec), need to be converted to the units sec$^{-1}$ by dividing by the pore volume, and the $k_a$ values at 150, 175 and 200°C are calculated when the slopes of the lines are 209, 372 and 713 sec$^{-1}$, respectively. It is higher $k_a$ value than conventional Cu-CHA at the low temperature (Kwak et al., 2012a, 2012b, 2012c, 2012d).

The extent to the diffusion transport limiting the reaction rate can be quantified using Thiele relationship, giving the catalyst effectiveness factor ($\eta$), as a function of Thiele modulus $\phi$ (Grünert, 1998). The functional relationship between the effectiveness factor and the parameter $\phi$ depends on the geometry of the crystal and the kinetic order of the reaction. For Cu-SAPO-34 catalysts used in our work, the crystal geometry can be approximated as spheres with a radius of 1 μm (1 $\times$ 10$^{-6}$ m). For the spherical catalyst particles and first-order reaction, the effectiveness factor ($\eta$) is given as follows (Schirmer, 1995):

$$\eta = \frac{3}{\phi} \left( \frac{1}{\tanh \phi} - \frac{1}{\phi} \right)$$

(8)

Thiele modulus is defined by

$$\phi = R \sqrt{\frac{k}{D}}$$

(9)

where, $R$ (m) is the average radius of the catalyst particles crystals; $k$ (sec$^{-1}$) is an intrinsic reaction rate constant; $D$ (m$^2$/sec) is an effective diffusivity. The intrinsic and apparent reaction rate constants follow a very simple relationship (Huang et al., 2002):

$$k = \frac{k_a}{\eta}$$

(10)

For catalysts in powder form, inter-particle diffusivity generally falls in between $1 \times 10^{-6}$ and $1 \times 10^{-8}$ m$^2$/sec, while intra-particle diffusivity varies widely from $1 \times 10^{-8}$ to $1 \times 10^{-20}$ m$^2$/sec (Wang et al., 2012). For NH3-SCR, intra-particle diffusion limitations may also be the dominating limitation factor for zeolite powder catalysts. In the following, effective diffusivity of the reaction gas molecules within the channels of 1.0-Cu-SAPO-34 sample is estimated, using a reaction temperature of 150°C as the example.

It is known that the sizes of NH3, H2O, NO, O2 and N2 molecules are close or smaller as compared with CH4, and the diffusivity (D) of CH4 in ZSM-5 is $10^{-9}$ m$^2$/sec (Demontis et al., 1990). It is reasonable to use $10^{-9}$ m$^2$/sec as an estimate for the pore diffusivities. Next, by using $R = 1 \times 10^{-6}$ m and $k =$

<p>| Table 4 – NH3-SCR activity on 1.0-Cu-SAPO-34 catalyst. |</p>
<table>
<thead>
<tr>
<th>Catalyst amount (mg)</th>
<th>NO conversion at different temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>150°C</td>
</tr>
<tr>
<td>20</td>
<td>8.2%</td>
</tr>
<tr>
<td>25</td>
<td>14.3%</td>
</tr>
<tr>
<td>50</td>
<td>28.7%</td>
</tr>
<tr>
<td>100</td>
<td>48.5%</td>
</tr>
<tr>
<td>200</td>
<td>69.5%</td>
</tr>
</tbody>
</table>

Fig. 10 – NO conversions over 1.0-Cu-SAPO-34 catalyst under different GHSVs over 150, 175 and 200°C. GHSVs: gas hourly space velocities.

Fig. 11 – First-order plots with respect to NO for the data of Table 4. W is the catalyst amount, F is the feed rate of ammonia and X is the NO conversion.
209 s\(^{-1}\) at 150°C, as well as Eqs. (8), (9) and (10), effective factor for 1.0-Cu-SAPO-34 sample is obtained. Using Eqs. (9) and (10), the Thiele moduli and intrinsic reaction rate constant for 1.0-Cu-SAPO-34 sample are then calculated. Table 5 lists the catalyst effectiveness factors \(\eta\), Thiele moduli \(\phi\) and effective diffusivities \(D\) (m\(^2\)/sec) in NH\(_3\)-SCR for 1.0-Cu-SAPO-34 catalyst at 150°C. In general, when \(\phi \leq 0.40\), the effect of intra-particle diffusion limitations can be excluded (Grüner, 1998). These values in Table 5 demonstrate that the presence of mesopores in Cu-SAPO-34 catalysts indeed greatly reduces the diffusion resistance and then improves the accessibility of reactants to catalytically active sites.

### 3. Conclusions

Meso-microporous Cu-SAPO-34 catalysts were directly synthesized by the combination of an organic-metallic Cu-complex and DIPEA. These catalysts exhibited excellent performances at low-temperature for NH\(_3\)-SCR reaction. When the ratio of Si/Al is 1.0, a wide activity temperature window of 1.0-Cu-SAPO-34 catalyst can be obtained, and NO conversion is >90% in the temperature range of 150–425°C. NMR and NH\(_3\)-TPD results indicated that 1.0-Cu-SAPO-34 catalyst possesses the strongest acid sites than Cu/SAPO-34 and the other Cu-SAPO-34 catalysts, which is favorable for the adsorption and activation of NH\(_3\), but the acid strength is not the decisive factor resulting in the difference of NH\(_3\)-SCR performance between Cu/SAPO-34 and Cu-SAPO-34 catalysts. UV-Vis DRS results demonstrated that the dispersion of copper species decreased with the increasing of mole ratio of Si/Al in Cu-SAPO-34. H\(_2\)-TPR results suggest that the isolated Cu\(^{2+}\) in 1.0-Cu-SAPO-34 catalyst should be abundant, which accounts for its highly catalytic activity. Moreover, H\(_2\)-TPR results demonstrated that the enhancement of redox property should be one of the reasons giving rise to the discrepancy on NH\(_3\)-SCR performance between Cu/SAPO-34 and Cu-SAPO-34 catalysts.

The formation of mesopores remarkably reduces diffusion resistance, and greatly improves the accessibility of reactants to catalytically active sites in the microporous channels. Thus, Cu-SAPO-34 catalysts exhibit the higher catalytic activities compared to the conventional Cu/SAPO-34 catalysts.

### Acknowledgments

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