available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

Synthesis of a chabazite-supported copper catalyst with full mesopores for selective catalytic reduction of nitrogen oxides at low temperature

Jixing Liu, Jian Liu*, Zhen Zhao, Weiyu Song, Yuechang Wei, Aijun Duan, Guiyuan Jiang

State Key Laboratory of Heavy Oil and Beijing Key Lab of Oil & Gas Pollution Control, China University of Petroleum, Beijing 102249, China

ARTICLE INFO

Article history:

Received 10 January 2016

Accepted 22 February 2016

Published 5 May 2016

Keywords:

One-pot synthesis

Meso-microporous Cu-SAPO-34

Low temperature

Selective catalytic reduction

Nitrogen oxides

ABSTRACT

A series of meso-microporous copper-supporting chabazite molecular sieve (Cu-SAPO-34) catalysts with excellent performance in low-temperature ammonia selective catalytic reduction (NH₃-SCR) have been synthesized *via* a one-pot hydrothermal crystallization method. The physicochemical properties of the catalysts were characterized by scanning electron microscopy, transmission electron microscopy, N₂ adsorption-desorption measurements, X-ray diffraction, ²⁷Al magic angle spinning nuclear magnetic resonance, diffuse reflectance ultraviolet-visible spectroscopy, inductively coupled plasma-atomic emission spectroscopy, X-ray photoelectron spectroscopy, temperature-programmed reduction measurements, and electron paramagnetic resonance analysis. The formation of micro-mesopores in the Cu-SAPO-34 catalysts decreases diffusion resistance and greatly improves the accessibility of reactants to catalytic active sites. The main active sites for NH₃-SCR reaction are the isolated Cu²⁺ species displaced into the ellipsoidal cavity of the Cu-SAPO-34 catalysts.

© 2016, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.
Published by Elsevier B.V. All rights reserved.

1. Introduction

Automobiles and industrial combustion of fossil fuels produce harmful nitrogen oxides (NO_x) [1]. The abatement of NO_x released from diesel engines remains a challenge in the field of environmental catalysis. One of the most promising technologies for NO_x emission control is the selective catalytic reduction (SCR) of NO_x with NH₃ [2].

Conventional three-way catalysts used in the exhaust after-treatment devices of internal combustion engines proved ineffective when the engine was operated under highly oxidizing conditions [3]. Copper-based zeolite catalysts, such as

Cu-Beta [4–6], Cu-ZSM-5 [7,8], Cu-SSZ-13 [9,10], have excellent catalytic activity and are drawing interest from the auto industry as potential catalysts for the urea-SCR system. Phosphorus-containing silicoaluminophosphate crystalline chabazite (CHA) molecular sieves supporting a copper catalyst (Cu-SAPO-34) are another promising candidate for NH₃-SCR of NO_x. Post-synthesis cationic exchange-impregnation methods have traditionally been used to prepare Cu-SAPO-34 catalysts, which involve introducing copper species into small-pore zeolites. However, the small pores (~0.38 nm) can limit the distribution of Cu within the zeolitic crystals, resulting in the metal preferentially locating close to the external surface [11]. Mar-

* Corresponding author. Tel: +86-10-89732326; Fax: +86-10-69724721; E-mail: liujian@cup.edu.cn

This work was supported by the National Natural Science Foundation of China (21376261, 21173270), the National High Technology Research and Development Program of China (863 Program, 2015AA034603), the Beijing Natural Science Foundation (2142027), and the China University of Petroleum Fund (20130007110007, 2462015QZDX04).

DOI: 10.1016/S1872-2067(15)61072-5 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 5, May 2016

tfnez-Franco *et al.* [12] have reported a direct preparation of Cu-SAPO-34 zeolite using a low-cost copper-amine complex (Cu^{2+} with tetraethylenepentamine, Cu-TEPA) as the template and diethanolamine as a co-template. This methodology allowed the introduction of extra-framework copper species in the CHA cages, and Cu-SAPO-34 is promising for the SCR of NO_x .

Peden' group [13] reported that Cu-SAPO-34 catalysts are kinetically limited in the NH_3 -SCR of NO_x at low reaction temperatures because their small pore sizes dramatically restricting reactant accessibility to the microporous channels of the catalytically active sites. To improve their catalytic performance, it is imperative to develop meso-microporous Cu-SAPO-34 catalysts that have less diffusion limitation for the NH_3 -SCR of NO_x . Internal mesopores can be created among the microporous particles during the synthesis of meso-microporous Cu-SAPO-34 catalysts. Chemical reactions still take place in the micropores of meso-microporous catalysts, but the accessibility to the catalytic active sites is improved.

In this work, a series of meso-microporous Cu-SAPO-34 catalysts are prepared *via* a one-pot hydrothermal crystallization synthesis method. Cu-TEPA is used as the template and *N,N'*-diisopropylethylamine (DIPEA) as a cooperative organic structure-directing agent. The molar ratio of DIPEA to Cu-TEPA is varied and the Si/Al ratio is fixed. The one pot synthesis of Cu-SAPO-34 is used to prepare catalysts with high solid yields and controlled locations of the Si species and extra-framework copper ions. The prepared Cu-SAPO-34 catalysts possess excellent low-temperature NH_3 -SCR performance.

2. Experimental

2.1. Cu-SAPO-34 synthesis

1.3 g tetraethylenepentamine (TEPA, 98 wt%, Aldrich, Beijing, China) was added to an aqueous solution containing 1.56 g copper (II) sulfate (98 wt%, Alfa, Shanghai, China) and 6.24 g distilled water, and the mixture was stirred for 1 h to ensure complete dissolution. 60.36 g distilled water and 6.53 g phosphoric acid (85 wt%, Aldrich, Beijing, China) were added to the solution successively and stirred for 5 min to give a gel. A certain amount of DIPEA (99 wt%, Aldrich, Beijing, China) was introduced to the gel mixture and stirred for 4 h. 4.59 g pseudo-boehmite (75 wt%, Condea, Beijing, China) and 1.50 g silica gel (Ludox AS40 40 wt%, Aladdin, Beijing, China) were added to the gel and stirred for another 12 h. The final molar composition of the zeolite gels were: 1 Al_2O_3 :0.85 P_2O_5 :(5–40) DIPEA:0.185 Cu-TEPA:1 SiO_2 :111 H_2O .

The gel was reacted in a stainless-steel autoclave at 175 °C and under autogenous pressure for 6 days. The crystalline product was filtered, washed with deionized water and dried at 110 °C overnight. The organic template was removed by heating in air at 550 °C for 6 h. Four hierarchical Cu-SAPO-34 samples were prepared and are as H-Cu-SAPO-34-*x*, where, *x* represents the molar ratio of DIPEA/Cu-TEPA used in the synthesis of the gel. For comparison, conventional Cu/SAPO-34 catalyst was synthesized according to a previously published method [14].

2.2. Catalyst characterization

The morphology of samples was observed by scanning electron microscopy (SEM) on an FEI Quanta 200F microscope (Oregon, USA) operating at 20 kV with a working distance of 11 mm. Transmission electron microscopy (TEM) images were obtained with an FEI Tecnai 20 (Oregon, USA) at 200 kV. The Brunauer-Emmett-Teller surface area and pore volume of the samples were measured by N_2 adsorption-desorption on an ASAP 2010 (Georgia, USA) analyzer (Micromeritics). Powder X-ray diffraction (XRD) measurements were undertaken using Cu K_α radiation ($\lambda = 0.15406$ nm) on a Bruker D8 Advance diffractometer (Germany) in the scanning range of 5°–50° (2θ) to identify the phase and determine the relative crystallinity. ^{27}Al magic angle spinning nuclear magnetic resonance (MAS NMR) was recorded using a standard Bruker MAS probehead at a spin rate of 20 kHz (Georgia, USA). Diffuse reflectance ultraviolet-visible spectra (UV-Vis DRS) were recorded with a Hitachi U-4100UV-Vis spectrophotometer (Tokyo, Japan) between 200–800 nm using dehydrated BaSO_4 as the internal reference standard. Elemental analysis of the materials prepared was determined by a Varian 715-ES inductively coupled plasma-atomic emission spectrometer (ICP-AES) (California, USA). X-ray photoelectron spectroscopy (XPS) experiments were conducted on a commercial VG Multilab 2000 system (UK). Temperature-programmed reduction (TPR) experiments were performed in a custom-made apparatus (China University of Petroleum, Beijing). Prior to reduction, the samples (50 mg) were heated from room temperature to 600 °C under N_2 flow rate of 30 mL/min and then cooled down to 100 °C with a purging N_2 flow. The TPR process was carried out with 10% H_2 -90% N_2 at a flow rate of 30 mL/min and a temperature ramp rate of 10 °C/min up to 700 °C. Electron paramagnetic resonance (EPR) spectra were obtained using a Bruker EMX EPR spectrometer (Germany) in the microwave region of 1–3 cm using a high-frequency modulation of magnetic field of 100 kHz, and magnetic field of up to 5000 G at –173 and 22 °C in a quartz glass ampoule with an internal diameter of 3 mm.

2.3. NH_3 -SCR activity evaluation

SCR activity tests of the catalysts were performed using a fixed-bed quartz flow reactor at atmospheric pressure. The gas composition was as follows: 0.1% NO , 0.1% NH_3 , 3% O_2 , with N_2 balance. The gas flow rate was 500 mL/min. Different gas hourly space velocities (GHSV) were obtained by changing the amount of catalyst (20–400 mg, 40–60 mesh). The effluent gases, including NO , O_2 , NH_3 and N_2 , were analyzed by a NEXUS 670-FTIR spectrometer (Wisconsin, US) equipped with a multiple-path gas cell (2 m). NO conversion was calculated according to the following equation:

$$\text{NO conversion} = \frac{[\text{NO}]_{\text{inlet}} - [\text{NO}]_{\text{outlet}}}{[\text{NO}]_{\text{inlet}}} \times 100\%$$

Turnover frequencies (TOF) were evaluated by dividing the moles of NO molecules converted per second by the moles of Cu atoms in the catalysts.

3. Results and discussion

3.1. SEM imaging

A series of H-Cu-SAPO-34 catalysts were prepared using varying amounts of DIPEA in the gel synthesis. Conventional Cu/SAPO-34 catalyst was synthesized for comparison. SEM was used to observe the morphology of the Cu/SAPO-34 and H-Cu-SAPO-34 samples (Fig. 1). The H-Cu-SAPO-34-5 sample consists of irregular particles with different diameters (Fig. 1(b)). Increasing the molar ratio of DIPEA to Cu-TEPA resulted in large spherical particles with diameters between 20 and 30 μm for H-Cu-SAPO-34-10 (Fig. 1(c)). Higher magnification images (not shown here) revealed that the large particles are made from the intergrowth of small cubic-like zeolite crystals with sizes in the range of 3–6 μm . Further increasing the molar ratio of DIPEA to Cu-TEPA from 10 to 40 during gel synthesis decreased the sizes of the agglomerated crystals to about 10 μm with well-defined morphology (Fig. 1(d) and (e)). This demonstrates an improvement in the level of crystallinity. The morphology of the H-Cu-SAPO-34 catalysts is notably different from the conventional microporous Cu/SAPO-34 particles, which have a smooth crystal surface and a size of approximately 5 μm (Fig. 1(a)).

3.2. TEM imaging

A selection of representative TEM images of the H-Cu-SAPO-34-20 catalyst is given in Fig. 2. The mesopores with different sizes are distributed homogeneously on the surface of the H-Cu-SAPO-34-20 crystals [15,16], and CuO_x nanoparticles are present on the surface of the catalyst. Furthermore, Cu ions do not migrate and aggregate inside the exchange sites to form CuO_x particles.

3.3. Brunauer-Emmett-Teller surface area analysis

Fig. 2. TEM images of H-Cu-SAPO-34-20 sample.

Fig. 3 displays the N_2 adsorption-desorption isotherms and the BJH pore size distributions of the Cu/SAPO-34 and H-Cu-SAPO-34 catalysts. Conventional microporous Cu/SAPO-34 (Fig. 3(a-1)) shows type-I N_2 adsorption-desorption isotherms. The H-Cu-SAPO-34 catalysts showed the representative characteristics of type-IV adsorption-desorption, with a sharp inflection at a relative pressure of $0.85 < p/p_0 < 1.0$ and a well-defined hysteresis loop, indicating well-formed mesoporous structural frameworks [17]. Furthermore, the isotherms of H-Cu-SAPO-34 samples exhibited a clear, steep increase in N_2 adsorption volume in the region of $p/p_0 < 0.05$. This increase suggests the presence of microporosity in the four H-Cu-SAPO-34 samples. The pore size distribution of H-Cu-SAPO-34 samples (Fig. 3(b)) illustrates the existence of a mesopore structure with pore sizes of approximately 25 nm. Combined with the SEM and TEM analyses, the N_2 adsorption-desorption results strongly suggest that a full meso-microporous structure exists in the four H-Cu-SAPO-34 samples (Table 1 and Fig. 3(b)).

Importantly, changes in the preparation conditions leads to a systematic change of the textural properties of H-Cu-SAPO-34 samples (Table 1). Increasing the molar ratio of DIPEA to Cu-TEPA for the gel synthesis increased the micropore surface area markedly from 180 m^2/g for H-Cu-SAPO-34-5 to 370 m^2/g

Fig. 1. SEM images of Cu/SAPO-34 samples. (a) Cu/SAPO-34; (b) H-Cu-SAPO-34-5; (c) H-Cu-SAPO-34-10; (d) H-Cu-SAPO-34-20; (e) H-Cu-SAPO-34-40.

Fig. 3. N_2 adsorption-desorption isotherms (a) and pore size distributions (b) of Cu-SAPO-34 samples. (1) Cu-SAPO-34; (2) H-Cu-SAPO-34-5; (3) H-Cu-SAPO-34-10; (4) H-Cu-SAPO-34-20; (5) H-Cu-SAPO-34-40.

for H-Cu-SAPO-34-20 and then resulted in a slight decrease to $361 \text{ m}^2/\text{g}$ for H-Cu-SAPO-34-40.

3.4. XRD analysis

The XRD patterns of Cu-SAPO-34 and H-Cu-SAPO-34 catalysts are displayed in Fig. 4. Characteristic diffraction peaks belonging to a CHA-type structure, which are in good agreement with those of SAPO-34, were present for all of the crystalline samples [18]. An additional characteristic peak attributed to SiO_2 was present in the pattern obtained for H-Cu-SAPO-34-5. The intensity of the peaks ascribed to the CHA-type structure increased slightly relative to the molar ratio of DIPEA to Cu-TEPA. There were no peaks related to CuO_x or CuAl_2O_4 species in the catalysts [19,20]. Combined with the TEM results, this demonstrates that most of the Cu species are well dispersed on the H-Cu-SAPO-34 catalysts.

3.5. MAS-NMR spectroscopy

^{27}Al MAS-NMR spectroscopy was used to study the coordination state of the aluminum in the Cu-SAPO-34 and H-Cu-SAPO-34 catalysts. The three main peaks centered at $\delta = 38$, 10.3 and -11.5 are assigned to tetrahedrally, pentahedrally and octahedrally coordinated Al, respectively (Fig. 5) [21–23]. A weak shoulder peak at $\delta = \sim 67$ is likely the result of Al with distorted tetrahedral coordination [13]. The formation of pentahedrally and octahedrally coordinated Al features is caused

by reversible SAPO-34 hydrolysis and these features are lost upon dehydration [8,24].

Fig. 4. XRD patterns of Cu-SAPO-34 samples. (1) Cu-SAPO-34; (2) H-Cu-SAPO-34-5; (3) H-Cu-SAPO-34-10; (4) H-Cu-SAPO-34-20; (5) H-Cu-SAPO-34-40.

Fig. 5. ^{27}Al NMR spectra of Cu-SAPO-34 samples. (1) Cu-SAPO-34; (2) H-Cu-SAPO-34-5; (3) H-Cu-SAPO-34-10; (4) H-Cu-SAPO-34-20; (5) H-Cu-SAPO-34-40.

Table 1

Physicochemical properties of Cu-SAPO-34 and H-Cu-SAPO-34 catalysts.

Sample	$A_{\text{BET}}^a/(\text{m}^2/\text{g})$	$V_t^b/(\text{mL}/\text{g})$	$A_{\text{mic}}^a/(\text{m}^2/\text{g})$
Cu-SAPO-34	426	0.04	419
H-Cu-SAPO-34-5	180	0.20	146
H-Cu-SAPO-34-10	282	0.25	234
H-Cu-SAPO-34-20	370	0.24	313
H-Cu-SAPO-34-40	361	0.19	320

^a Calculated by BET method.

^b Calculated by t -plot method.

Fig. 6. UV-Vis DRS of Cu-SAPO-34 samples. (1) Cu/SAPO-34; (2) H-Cu-SAPO-34-5; (3) H-Cu-SAPO-34-10; (4) H-Cu-SAPO-34-20; (5) H-Cu-SAPO-34-40.

3.6. UV-Vis DRS analysis

UV-Vis DRS was performed to better understand the local environment and nuclearity of the Cu species in the Cu/SAPO-34 and H-Cu-SAPO-34 catalysts. There are two main characteristic absorption bands for all of the samples (Fig. 6); the absorption band centered at ~230 nm is attributed to charge transfer lattice $O^{2-} \rightarrow Cu^{2+}$ [6,25,26], and the other centered at 750 nm is ascribed to $d-d$ Cu^{2+} transition in disperse CuO particles [27]. The shoulder peak adsorbed at 650 nm is related to bulk CuO [28], which was also detected by TEM. Liu *et al.* [26] attributed a peak at 450 nm to dimeric copper $[(Cu-O-Cu)^{2+}]$ species, which result from the dehydration of hydroxyl-bridged dimers. Gang *et al.* [29] suggested that $CuAl_2O_4$ species display absorption bands at 740 nm. These bands were not detected in our results, suggesting that $CuAl_2O_4$ species are not present, which is consistent with the XRD results. UV-Vis DRS shows the presence of highly dispersed CuO clusters and bulk CuO, which were not detected by XRD because of their small size.

3.7. XPS analysis

XPS and ICP experiments were carried out to characterize the atomic distribution and composition of Cu/SAPO-34 and H-Cu-SAPO-34 catalysts (Table 2). All of the Cu-SAPO-34 samples possess similar element contents (P, Si, Al and Cu). Im-

Fig. 7. Cu 2p XPS spectra of Cu-SAPO-34 samples. (1) Cu/SAPO-34; (2) H-Cu-SAPO-34-5; (3) H-Cu-SAPO-34-10; (4) H-Cu-SAPO-34-20; (5) H-Cu-SAPO-34-40.

portantly, the surface Cu/Al ratio is much lower than that in the bulk, indicating that the Cu ions are predominantly at the exchanged sites inside the SAPO-34 pores. Increasing the molar ratio of DIPEA to Cu-TEPA used in the gel synthesis gradually decreases, then dramatically increases, the Si/Al molar ratio on the surface of the H-Cu-SAPO-34 catalysts. Thus, the ratio of DIPEA to Cu-TEPA can be used to effectively control the location of Si species and the performance of H-Cu-SAPO-34 catalysts.

The binding energy of the Cu 2p transition peaks provides information on the state of Cu species. The binding energies of the catalysts determined by XPS are shown in Fig. 7. Cu species from CuO result in two shake-up satellite peaks centered at 942.2 and 962.5 eV. The main Cu $2p_{3/2}$ transition peak is located at 932.6 (with a shoulder peak at 935) eV and the Cu $2p_{1/2}$ transition peak is at 952.8 eV [30]. These satellites are not observed for Cu^+ and Cu^0 species and this feature can be used to distinguish between Cu^{2+} and Cu^+ or Cu^0 species [31]. The shakeup satellites observed for the Cu/SAPO-34 and H-Cu-SAPO-34 samples are attributed to the existence of CuO on the surface of the catalysts. The peak attributed to Cu^{2+} for the H-Cu-SAPO-34-20 catalyst is bigger than that for the other H-Cu-SAPO-34 samples, which may contribute to the improved NH_3 -SCR performance of this catalyst (see below).

3.8. H_2 -TPR results

H_2 -TPR was used to investigate the reducibility of Cu species

Table 2

Chemical composition of H-Cu-SAPO-34 catalysts obtained by ICP and XPS.

Sample	Concentration ^a (wt.%)				Molar ratio			
	Al	P	Si	Cu	Cu/Al ^a	Si/Al ^a	Cu/Al ^b	Si/Al ^b
Cu/SAPO-34	19.8	9.8	6.1	4.5	0.094	0.30	0.032	0.14
H-Cu-SAPO-34-5	19.2	9.4	5.6	4.2	0.093	0.27	0.025	0.24
H-Cu-SAPO-34-10	19.7	9.7	5.1	4.5	0.096	0.25	0.025	0.16
H-Cu-SAPO-34-20	19.6	9.9	5.4	4.4	0.095	0.26	0.032	0.12
H-Cu-SAPO-34-40	19.7	9.8	5.1	4.3	0.093	0.25	0.024	0.49

^a Obtained by ICP.

^b Obtained by XPS.

Fig. 8. H₂-TPR profiles of Cu-SAPO-34 samples. (1) Cu/SAPO-34; (2) H-Cu-SAPO-34-5; (3) H-Cu-SAPO-34-10; (4) H-Cu-SAPO-34-20; (5) H-Cu-SAPO-34-40.

and to identify their locations and chemical states. The H₂-TPR curves of the catalysts are displayed in Fig. 8. H-Cu-SAPO-34-5 has three H₂ consumption peaks in the range of 100–700 °C. The peak centered at 230 °C is assigned to the reduction of isolated Cu²⁺ ions (Cu²⁺→Cu⁺) [13,32]. The peak located at 303 °C is ascribed to the reduction of highly dispersed nanosized CuO (Cu²⁺→Cu⁺ and Cu⁺→Cu⁰) [33,34]. Finally, the peak at ~520 °C is a result of the reduction of Cu⁺ to Cu⁰ [32]. Increasing the molar ratio of DIPEA to Cu-TEPA shifted the reduction peaks assigned to isolated Cu species from 230 to 223 °C and then to 228 °C. Increasing the DIPEA/Cu-TEPA ratio from 5 to 20 increased H₂ consumption by isolated Cu species, with a further increase to 40 resulting in decreased H₂ consumption (Table 3). The maximum H₂ consumption of H-Cu-SAPO-34-20 can be explained by this sample having the greatest proportion of Cu²⁺, as shown by the XPS results. The differences in the reduction ability of the H-Cu-SAPO-34 catalysts may affect their NH₃-SCR performance. The H₂/Cu values of H-Cu-SAPO-34-5 and H-Cu-SAPO-34-10 are much lower than those of H-Cu-SAPO-34-20 and H-Cu-SAPO-34-40 (Table 3), indicating that the former samples have a higher content of Cu⁺ than the latter ones. There are three types of Cu species in all the samples: highly dispersed CuO clusters both internally and on the external surface, and isolated Cu²⁺ and Cu⁺ ions located at the exchange sites. The isolated Cu²⁺ and Cu⁺ ions are the active

centers for NH₃-SCR. The lower temperature required for reduction and greater number of active centers of H-Cu-SAPO-34-20 improved its NH₃-SCR performance. However, the high content of CuO in this catalyst may result in poor high-temperature reduction performance.

3.9. EPR spectroscopy

Only isolated Cu²⁺ ions (3d⁹, 2d_{5/2}) are EPR active; all other Cu species ([Cu(II)-O-Cu(II)]²⁺ or Cu⁺ ions) are EPR silent [35]. Therefore, EPR is an excellent technique to qualitatively and quantitatively identify the amount of isolated Cu²⁺ ions and probe the structure and coordination environment of paramagnetic isolated Cu²⁺ ions in the catalysts. The framework of chabazite is formed from units of two six-membered rings of aluminum-oxygen and silicon-oxygen tetrahedra, bound face to face to form a hexagonal prism. Eight-membered rings form at the pore openings on the particle surface. There are four types of cationic sites in the chabazite framework: Site I is displaced from a six-membered-ring into the ellipsoidal cavity; Site II is located near the face of the ellipsoidal cavity; Site III is located in the center of the hexagonal prism; and Site IV is located near the eight-membered-ring at the pore [36]. Fig. 9 shows the EPR spectra of Cu/SAPO-34 and the H-Cu-SAPO-34 samples. Xiao's group [19] reported an EPR signal of $g_{//} = 2.378$ with $A = 140$ G for Cu²⁺ in site I for a hydrated sample. Similar EPR signals, such as $g_{//} = 2.39$ with $A = 111$ G [13] and $g_{//} = 2.394$ with $A = 131$ G [36], for Cu-CHA catalysts with site I Cu²⁺ species have been reported. The Cu²⁺ species of the SAPO-34 samples prepared show the same coordination environment, with $g_{//} = 2.384$ and $A = 132$ G, indicating an identical location for the Cu²⁺ irrespective of the DIPEA/Cu-TEPA ratio. This result, combined with the results of UV-Vis DRS and H₂-TPR, indicates that the isolated Cu²⁺ ions are located in site I. The total isolated Cu²⁺ content was quantified by the signal area integrations and the H-Cu-SAPO-34-20 sample possesses the highest content of isolated Cu²⁺ ions (Table 3). These results are consistent with the findings of the H₂-TPR and XPS analyses and NH₃-SCR performance.

Fig. 9. EPR spectra of Cu-SAPO-34 samples measured at -183 °C. (1) Cu/SAPO-34; (2) H-Cu-SAPO-34-5; (3) H-Cu-SAPO-34-10; (4) H-Cu-SAPO-34-20; (5) H-Cu-SAPO-34-40.

Table 3

Reduction behavior of H-Cu-SAPO-34 catalysts.

Sample	H ₂ consumption ^a			H ₂ /Cu ^b (mol/mol)
	Peak 1 (~230 °C)	Peak 2 (~300 °C)	Peak 3 (~500 °C)	
Cu/SAPO-34	21.3	214.0	113.4	0.84
H-Cu-SAPO-34-5	99.6	51.9	77.0	0.66
H-Cu-SAPO-34-10	129.8	58.9	39.4	0.69
H-Cu-SAPO-34-20	148.9	209.6	44.0	0.88
H-Cu-SAPO-34-40	120.0	253.0	68.6	0.91

^aHydrogen consumption determined from TPR results.

^bHydrogen consumption content vs. Cu loading amount.

Fig. 10. NO conversions over H-Cu-SAPO-34 and conventional Cu/SAPO-34 catalysts as a function of reaction temperature. Reaction conditions: 0.1% NO, 0.1% NH₃, 3% O₂, balanced with N₂; GHSV = 50000 h⁻¹.

3.10. NH₃-SCR performance

NO conversion as a function of reaction temperature between 100 and 550 °C was measured for conventional Cu/SAPO-34 and H-Cu-SAPO-34 catalysts (Fig. 10). The low-temperature (100–250 °C) NO conversion increased from H-Cu-SAPO-34-5 to a maximum at H-Cu-SAPO-34-20 and then decreased for H-Cu-SAPO-34-40. The H-Cu-SAPO-34-20 catalyst exhibited the best performance because this sample has the highest isolated Cu²⁺ content (XPS and H₂-TPR) and more readily reduced active Cu species. The conventional Cu/SAPO-34 catalyst exhibited the lowest low-temperature performance. Consequently, we conclude that the mesopores in the H-Cu-SAPO-34 catalysts facilitate physical transport of NO and improve accessibility of reactants to catalytic active sites.

NH₃-SCR reactions were carried out with various GHSVs over the H-Cu-SAPO-34-20 sample (Fig. 11(a)). Increasing the GHSV from 50000 to 400000 h⁻¹ resulted in a decrease in NH₃-SCR performance at low temperatures. High-temperature SCR performance was unaffected by varying the GHSV. SCR

Fig. 11. (a) NO conversions over H-Cu-SAPO-34-20 catalyst under different GHSV; (b) NO conversion ratios with respect to that at GHSV = 800000 h⁻¹ as a function of reaction temperature, using data from (a).

Fig. 12. NO conversion versus reaction temperature for standard NH₃-SCR over H-Cu-SAPO-34 samples. The differential regime (NO conversion ≤ 15%) is marked grey. Reaction mixtures contain 0.1% NO, 0.1% NH₃, 3% O₂; GHSV = 800000 h⁻¹. (1) H-Cu-SAPO-34-5; (2) H-Cu-SAPO-34-10; (3) H-Cu-SAPO-34-20; (4) H-Cu-SAPO-34-40.

reactions were conducted to establish kinetically benign (*i.e.*, mass-transfer limitation free) regimes. Fig. 11(b) presents NO conversion ratios compared with that at GHSV = 800000 h⁻¹ as a function of reaction temperature using data from the GHSV experiments with H-Cu-SAPO-34-20. NO conversion is expected to increase *n*-fold as the space velocity decreases *n*-fold in the absence of interparticle mass transfer limitations. We found that interparticle mass transfer was more than 99% free of limitation using conditions of GHSV ≥ 400000 h⁻¹ and temperature ≤ 200 °C. (NO conversions ≤ 15%; data points below the dashed horizontal line in Fig. 12).

The apparent activation energy for NO oxidation over H-Cu-SAPO-34 catalysts (Fig. 13) was calculated using reaction data (Fig. 12). The linearity indicates the NO oxidation at 100–200 °C is first order with respect to NO over Cu-SAPO-34; like other SCR catalysts. The rate constants estimated from these plots show apparent activation energy of approximately 98 kJ/mol and similar *E_a* values for NO conversion for all four H-Cu-SAPO-34 samples, suggesting an identical reaction rate-limiting mechanism. This rate is somewhat higher than

Fig. 13. Arrhenius plots of NO conversion (TOF) over H-Cu-SAPO-34 catalysts. TOFs were calculated using reaction data shown in Fig. 12. Reaction mixtures contain 0.1% NO, 0.1% NH₃, 3% O₂, N₂ balanced, at GHSV = 800000 h⁻¹.

those reported previously for conventional CHA-based SCR catalysts (*e.g.*, 62–89 kJ/mol) [13,32,37], indicating that the formation of mesopores in H-Cu-SAPO-34 catalysts lowers the pore diffusion limitations and improves the accessibility of reactants to the catalytically active sites. The formation of mesopores greatly improves NH₃-SCR performance [38].

4. Conclusions

A series of H-Cu-SAPO-34 catalysts with full mesopores have been synthesized with varying ratios of DIPEA to organometallic Cu complex in the synthesis gel. The mesopores in

H-Cu-SAPO-34 catalysts remarkably lower the diffusion limitation of reactant molecules. These catalysts exhibit excellent catalytic NH₃-SCR reaction performance at low temperature. The best catalytic performance was obtained over the H-Cu-SAPO-34-20 sample, for which the ratio of DIPEA to Cu-TEPA was 20, and NO conversion reached 94% at 150 °C. The main active sites for the NH₃-SCR reaction are the isolated Cu²⁺ ions in site I, displaced from the six-membered ring into the ellipsoidal cavity.

References

- [1] M. G. Schultz, T. Diehl, G. P. Brasseur, W. Zittel, *Science*, **2003**, 302, 624–627.
- [2] K. Skalska, J. S. Miller, S. Ledakowicz, *Sci. Total Environ.*, **2010**, 408, 3976–3989.
- [3] R. J. Farrauto, R. M. Heck, *Catal. Today*, **1999**, 51, 351–360.
- [4] J. Dedecek, O. Bortnovsky, A. Vondrova, B. Wichterlova, *J. Catal.*, **2001**, 200, 160–170.
- [5] L. Xu, C. Shi, Z. S. Zhang, H. Gies, F. S. Xiao, D. De Vos, T. Yokoi, X. H. Bao, M. Feyen, S. Maurer, B. Yilmaz, U. Müller, W. P. Zhang, *Microporous Mesoporous Mater.*, **2014**, 200, 304–310.
- [6] N. Wilken, R. Nedyalkova, K. Kamasamudram, J. H. Li, N. W. Currier, R. Vedaiyan, A. Yezerets, L. Olsson, *Top. Catal.*, **2013**, 56, 317–322.
- [7] Y. P. Chen, D. G. Cheng, F. Q. Chen, X. L. Zhan, *Progr. Chem.*, **2014**, 26, 248–258.
- [8] P. N. R. Vennestrom, T. V. W. Janssens, A. Kustov, M. Grill, A. Puig-Molina, L. F. Lundegaard, R. R. Tiruvalam, P. Concepcion, A. Corma, *J. Catal.*, **2014**, 309, 477–490.
- [9] L. J. Xie, F. D. Liu, X. Shi, F. S. Xiao, H. He, *Appl. Catal. B*, **2016**, 179, 206–212.
- [10] D. W. Fickel, E. D'Addio, J. A. Lauterbach, R. F. Lobo, *Appl. Catal. B*, **2011**, 102, 441–448.

Graphical Abstract

Chin. J. Catal., 2016, 37: 750–759 doi: 10.1016/S1872-2067(15)61072-5

Synthesis of a chabazite-supported copper catalyst with full mesopores for selective catalytic reduction of nitrogen oxides at low temperature

Jixing Liu, Jian Liu*, Zhen Zhao, Weiyu Song, Yuechang Wei, Aijun Duan, Guiyuan Jiang
China University of Petroleum-Beijing

H-Cu-SAPO-34 catalysts with full mesopores and excellent performance in low-temperature NH₃-SCR of NO have been controllably synthesized via a one-pot hydrothermal crystallization method. Importantly, the formation of micro-mesopores in the Cu-SAPO-34 catalysts decreases diffusion resistance and greatly improves the accessibility of reactants to the catalytic active sites.

- [11] B. Z. Zhan, E. Iglesia, *Angew. Chem. Int. Ed.*, **2007**, 46, 3697–3700.
- [12] R. Martínez-Franco, M. Moliner, C. Franch, A. Kustov, A. Corma, *Appl. Catal. B*, **2012**, 127, 273–280.
- [13] F. Gao, E. D. Walter, N. M. Washton, J. Szanyi, C. H. F. Peden, *ACS Catal.*, **2013**, 3, 2083–2093.
- [14] L. Ma, Y. S. Cheng, G. Cavataio, R. W. McCabe, L. X. Fu, J. H. Li, *Chem. Eng. J.*, **2013**, 225, 323–330.
- [15] J. C. Groen, L. A. A. Peffer, J. Pérez-Ramírez, *Microporous Mesoporous Mater.*, **2003**, 60, 1–17.
- [16] N. N. Gao, S. J. Xie, S. L. Liu, W. J. Xin, Y. Gao, X. J. Li, H. Wei, H. Liu, L. Y. Xu, *Microporous Mesoporous Mater.*, **2015**, 212, 1–7.
- [17] H. J. Wei, S. J. Xie, N. N. Gao, K. F. Liu, X. H. Liu, W. J. Xin, X. J. Li, S. L. Liu, L. Y. Xu, *Appl. Catal. A*, **2015**, 495, 152–161.
- [18] Y. Cao, S. Zou, L. Lan, Z. Z. Yang, H. D. Xu, T. Lin, M. C. Gong, Y. Q. Chen, *J. Mol. Catal. A*, **2015**, 398, 304–311.
- [19] L. J. Xie, F. D. Liu, L. M. Ren, X. Y. Shi, F. S. Xiao, H. He, *Environ. Sci. Technol.*, **2014**, 48, 566–572.
- [20] B. K. Kwak, D. S. Park, Y. S. Yun, J. Yi, *Catal. Commun.*, **2012**, 24, 90–95.
- [21] M. Briend, R. Vomscheid, M. J. Peltre, P. P. Man, D. Barthomeuf, *J. Phys. Chem.*, **1995**, 99, 8270–8276.
- [22] T. Fjermestad, S. Svelle, O. Swang, *J. Phys. Chem. C*, **2013**, 117, 13442–13451.
- [23] X. X. Wang, W. Zhang, S. Q. Guo, L. F. Zhao, H. W. Xiang, *J. Brazil. Chem. Soc.*, **2013**, 24, 1180–1187.
- [24] J. H. Kwak, D. Tran, S. D. Burton, J. Szanyi, J. H. Lee, C. H. F. Peden, *J. Catal.*, **2012**, 287, 203–209.
- [25] S. F. Kang, Z. Jiang, Z. P. Hao, *Acta Phys.-Chim. Sin.*, **2005**, 21, 278–282.
- [26] Z. Liu, M. D. Amiridis, Y. Chen, *J. Phys. Chem. B*, **2005**, 109, 1251–1255.
- [27] M. Zabilskiy, P. Djinić, B. Erjavec, G. Dražić, A. Pintar, *Appl. Catal. B*, **2015**, 163, 113–122.
- [28] H. Pralaud, S. Mikhailenko, Z. Chajar, M. Primet, *Appl. Catal. B*, **1998**, 16, 359–374.
- [29] L. Gang, J. van Grondelle, B. G. Anderson, R. A. van Santen, *J. Catal.*, **1999**, 186, 100–109.
- [30] R. P. Vasquez, *Surf. Sci. Spectra*, **1998**, 5, 262–266.
- [31] C. Z. Sun, J. Zhu, Y. Y. Lü, L. Qi, B. Liu, F. Gao, K. Q. Sun, L. Dong, Y. Chen, *Appl. Catal. B*, **2011**, 103, 206–220.
- [32] F. Gao, E. D. Walter, N. M. Washton, J. Szanyi, C. H. F. Peden, *Appl. Catal. B*, **2015**, 162, 501–514.
- [33] R. Martínez-Franco, M. Moliner, P. Concepcion, J. R. Thøgersen, A. Corma, *J. Catal.*, **2014**, 314, 73–82.
- [34] S. K. Fan, J. J. Xue, T. Yu, D. Q. Fan, T. Hao, M. Q. Shen, W. Li, *Catal. Sci. Technol.*, **2013**, 3, 2357–2364.
- [35] M. Zamadics, X. H. Chen, L. Kevan, *J. Phys. Chem.*, **1992**, 96, 2652–2657.
- [36] J. J. Xue, X. Q. Wang, G. S. Qi, J. Wang, M. Q. Shen, W. Li, *J. Catal.*, **2013**, 297, 56–64.
- [37] T. Yu, T. H. Hao, D. Q. Fan, J. Wang, M. Q. Shen, W. Li, *J. Phys. Chem. C*, **2014**, 118, 6565–6575.
- [38] C. H. Christensen, K. Johannsen, E. Tornqvist, I. Schmidt, H. Topsøe, C. H. Christensen, *Catal. Today*, **2007**, 128, 117–122.

具有丰富介孔 Cu-SAPO-34 催化剂制备及其低温氨气选择性催化还原反应

刘计省, 刘 坚*, 赵 震, 宋卫余, 韦岳长, 段爱军, 姜桂元

中国石油大学(北京), 重质油国家重点实验室和油气污染防治北京市重点实验室, 北京102249

摘要: 氮氧化物(NO_x)是主要的大气污染物之一,与光化学烟雾、全球气候变暖等环境问题密切相关.随着汽车产业的高速发展,柴油车排放尾气中的 NO_x 脱除成为国内外尾气催化净化领域最突出的难点之一.其中氨气选择性催化还原技术($\text{NH}_3\text{-SCR}$)由于其高效率、低成本的特征已成为主要的移动源脱硝技术.目前,实际应用中最广泛的是 $\text{V}_2\text{O}_5\text{-WO}_3(\text{MoO}_3)/\text{TiO}_2$ 催化剂,然而一些不可避免的因素仍然存在,比如V具有较强的毒性,较高的操作温度,较窄的活性温度窗口以及易将 SO_2 氧化为 SO_3 导致催化剂表面会有大量的硫酸盐沉积而失活等.因此很有必要开发一种无钒SCR催化剂.

近年来,分子筛负载过渡金属作为催化剂引起了研究者的广泛兴趣,其中Cu-CHA分子筛催化剂因其高SCR活性,高 N_2 选择性,较宽的温度窗口以及优异的稳定性引起研究者的广泛关注.就Cu-SAPO-34而言,传统的制备方法是利用离子交换法将Cu离子引入到SAPO-34微孔孔道中,然而由于微孔会限制Cu离子的分布,导致绝大多数Cu优先分布在分子筛外表面,从而限制了其活性发挥. Martínez-Franco课题组利用双模板一步法成功制备了Cu-SAPO-34催化剂,提高了分子筛中活性Cu离子数目. Peden课题组发现在 NO_x 的 $\text{NH}_3\text{-SCR}$ 反应中Cu-SAPO-34催化剂存在低温动力学限制.因此开发一种具有丰富介孔的多级孔Cu-SAPO-34催化剂势在必行.

我们利用一步水热晶化法成功制备了一系列具有丰富介孔的Cu-SAPO-34催化剂.采用扫描电子显微镜(SEM)、透射电子显微镜(TEM)、氮气吸附-脱附、X射线衍射(XRD)、 ^{27}Al 核磁共振(Al-NMR)、紫外可见漫反射光谱(UV-Vis DRS)、电感耦合等离子体-原子发射光谱(ICP-AES)、X射线光电子能谱(XPS)、氢气程序升温还原($\text{H}_2\text{-TPR}$)和电子顺磁共振(EPR)等表征手段研究了Cu-SAPO-34多级孔催化剂的物理化学性质.

XRD测试结果证实,H-Cu-SAPO-34催化剂具有典型的CHA结构. TEM和 N_2 吸附-脱附测试结果表明,H-Cu-SAPO-34催化剂具有丰富的介孔结构. Al-NMR 测试结果表明,多种配位的Al物种存在于H-Cu-SAPO-34中. UV-Vis DRS测试结果证实了孤立 Cu^{2+} 和高分散的CuO的存在,没有观察到 $(\text{Cu-O-Cu})^{2+}$ 和 CuAl_2O_4 物种的存在. ICP-AES和XPS测试结果表明,H-Cu-SAPO-34催化剂具有相似的Cu含量,并且H-Cu-SAPO-34-20催化剂具有最高的 Cu^{2+} 含量. $\text{H}_2\text{-TPR}$ 测试结果表明,H-Cu-SAPO-34-20催化剂具有最低的孤立 Cu^{2+} 还原温度以及最高的孤立 Cu^{2+} 含量. 这

可能有利于其 $\text{NH}_3\text{-SCR}$ 活性提高. 同时 $\text{H}_2\text{-TPR}$ 还表明, H-Cu-SAPO-34 催化剂中存在含量不等的孤立 Cu^+ , 并且孤立 Cu^{2+} 是 $\text{NH}_3\text{-SCR}$ 反应的主要活性中心. EPR 测试结果进一步表明, 位于 SAPO-34 椭球腔内 (Site (I)) 的孤立 Cu^{2+} 是该反应的主要活性位.

由 NO 的 $\text{NH}_3\text{-SCR}$ 反应测试结果来看, 相比于普通的 Cu/SAPO-34 催化剂, 具有丰富介孔结构的 H-Cu-SAPO-34 催化剂呈现出更高的低温催化活性, 同时 H-Cu-SAPO-34-20 催化剂具有最高的低温 $\text{NH}_3\text{-SCR}$ 催化活性, 这与其较高的活性 Cu^{2+} 含量以及较低的孤立 Cu^{2+} 还原温度密切相关. 动力学测试结果表明, 所合成的 H-Cu-SAPO-34 多级孔催化剂具有相似的活化能 ($E_a = 98 \text{ kJ/mol}$), 并且该值远大于普通 CHA 基 SCR 催化剂, 这意味着介孔的存在确实大大降低了反应物分子在 H-Cu-SAPO-34 孔道内的扩散阻力, 提高了反应物分子与活性位的接触概率, 从而提高了其低温 $\text{NH}_3\text{-SCR}$ 催化性能.

关键词: 一步合成; 介微孔 Cu-SAPO-34 ; 低温; 选择性催化还原; 氮氧化物

收稿日期: 2016-01-10. 接受日期: 2016-02-22. 出版日期: 2016-05-05.

*通讯联系人. 电话: (010)89732326; 传真: (010)69724721; 电子信箱: liujian@cup.edu.cn

基金来源: 国家自然科学基金 (21376261, 21173270); 国家高技术研究发展计划 (863 计划, 2015AA034603); 北京市自然科学基金 (2142027); 中国石油大学 (北京) 基金 (20130007110007, 2462015QZDX04).

本文的英文电子版由 Elsevier 出版社在 ScienceDirect 上出版 (<http://www.sciencedirect.com/science/journal/18722067>).