



## The influence of Si/Al ratio on the catalytic property and hydrothermal stability of Cu-SSZ-13 catalysts for NH<sub>3</sub>-SCR

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### ABSTRACT

Cu-SSZ-13 catalysts with three Si/Al ratios of 6, 15 and 30 were synthesized by a one-pot method. The catalytic property and hydrothermal stability of as-prepared catalysts were studied to understand the influence of Si/Al ratio on the NH<sub>3</sub>-SCR performance over Cu-SSZ-13 catalysts. Although the three catalysts contain equivalent Cu loading, they perform different catalytic activities for NO reduction. The EPR and H<sub>2</sub>-TPR results clearly show that the Si/Al ratio not only has influence on the nature of Cu species but also on the Cu species distribution. With increasing the Si/Al ratio, the amount of CuO increases while the number of highly stable Cu<sup>+</sup> ions decreases. Such a phenomenon could be attributed to the less Al content in high-Si/Al-ratio catalysts. Besides, the acidity is also found to be affected by the Si/Al ratio. The NH<sub>3</sub>-TPD results demonstrate that the total number of acid sites decreases with increasing the Si/Al ratio. Lacking sufficient acidity is also responsible for the inferior NO reduction activity of Cu-SSZ-13 with Si/Al = 30. Meanwhile, kinetic analysis over fresh catalysts was conducted and the conclusion correlated well with the NH<sub>3</sub>-SCR performance. Additionally, three catalysts exhibit distinct resistances to hydrothermal treatment. The XRD, N<sub>2</sub> physisorption and NH<sub>3</sub>-SCR performance results consistently indicate the Cu-SSZ-13 with Si/Al = 15 is much more resistant to hydrothermal aging than another two catalysts probably due to its considerably stability of zeolite structure and Cu ions.

### 1. Introduction

Selective reduction of NO<sub>x</sub> by ammonia (NH<sub>3</sub>-SCR) over effective catalysts is considered as an efficient technology for the elimination of NO<sub>x</sub> in the diesel vehicle emissions [1,2]. In particular, copper containing zeolite catalysts have been reported as the most promising candidates as SCR catalysts for diesel exhaust purification due to the superior deNO<sub>x</sub> activity, improved hydrothermal stability and alkali metal resistance [1–4]. At present, small-pore (3.8 Å) copper containing catalysts with the CHA structure (i.e., Cu-SSZ-13 and Cu-SAPO-34) are shown to exhibit outstanding hydrothermal durability and N<sub>2</sub> selectivity among Cu-based zeolite catalysts, and have attracted extensive research interests [2–9]. Until now, the researches mainly concentrate on the activity and hydrothermal stability of Cu-CHA catalysts [3,10,11].

It has been revealed that the nature of Cu species and the acidity of the zeolite play decisive roles in the NH<sub>3</sub>-SCR process for zeolite type

catalysts [10–16]. Although the location of the Cu species is still widely debated [7,11], the isolated Cu<sup>2+</sup> ions are proved as catalytic centers, in contrast, the CuO decreases the catalytic activity at high temperatures seriously due to the oxidation of NH<sub>3</sub> and destroys the zeolite structure during the hydrothermal process [2,11,17,18]. Generally, the nature and location of copper species are influenced by two aspects: the Si/Al ratio and the synthesis method [9,14,19–22]. Meanwhile, the Si/Al ratio has also been found to influence the number of acid sites in catalysts, which further significantly affects the deNO<sub>x</sub> performance [14,19,20]. Peden et al. [19] discussed the nature of the multiple Cu species with varying Si/Al ratios and found the Cu<sup>2+</sup> ions locations and redox properties could be systemically tuned by Si/Al and Cu/Al ratios of the Cu/SSZ-13 catalysts. Besides, Li et al. [14] investigated the effect of Si content on the NO selective catalytic reduction over the Cu/SAPO-34 catalyst and found the numbers of isolated Cu<sup>2+</sup> ions and acid sites vary with different Si contents. More recently, Shen et al. [20] prepared the Cu/SAPO-34 catalysts with various acid contents and

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equivalent Cu loading, and it is concluded that the acidity of SAPO-34 can be adjusted by altering the Si content. Moreover, the high content of Si could increase the acidity of catalyst and thus improve the NO conversions.

Additionally, with respect to the influence of preparation methods on the status of Cu species in catalysts, Shen et al. [10] studied effect of different synthesis methods on Cu species over Cu/SAPO-34, and found external surface CuO, isolated Cu<sup>2+</sup> ions and Cu<sup>+</sup> ions at the exchange sites exist in all catalysts but the distributions of Cu species are varied by different synthesis methods. The dominant Cu species is isolated Cu<sup>2+</sup> ions for the ion-exchange catalyst, while both CuO and isolated Cu<sup>2+</sup> ions co-exist in comparable amount for the one-pot catalyst.

Currently, the zeolites catalysts are usually synthesized by an ion-exchange or a one-pot method [10,22,23]. The one-pot method is regarded as more cost-effective than ion-exchange method due to the simpler synthetic process and shorter production period simultaneously. However, the influences of Si/Al ratio on the Cu species and the acidity of one-pot synthetic Cu-SSZ-13 catalyst are seldom reported. In this work, three Cu-SSZ-13 catalysts with different Si/Al ratios and equivalent Cu loading are synthesized by a one-pot method. The catalytic activity and hydrothermal stability of Cu-SSZ-13 catalysts are evaluated to obtain the correlation between the Si/Al ratio and NH<sub>3</sub>-SCR performance. In addition, XRD, H<sub>2</sub>-TPR, EPR, NMR and NH<sub>3</sub>-TPD are used to explore the discrepancies in the structure, Cu species and acidity among prepared catalysts. The different deNO<sub>x</sub> performances and resistances to hydrothermal aging over Cu-SSZ-13 catalysts are also investigated.

## 2. Experimental

### 2.1. Catalyst preparation

Cu-SSZ-13 catalysts with different Si/Al ratios were synthesized by a one-pot method reported by Corma [22]. The composition of the gel is shown as follows: 2Cu-TEPA: 10TMAdaOH: 10NaOH: xAl<sub>2</sub>O<sub>3</sub>: 100SiO<sub>2</sub>: 220H<sub>2</sub>O, where x varies to prepare catalysts with different Si/Al ratios. In a typical synthesis procedure, NaOH, SiO<sub>2</sub> and NaAlO<sub>2</sub> were mixed with H<sub>2</sub>O, and the mixture was stirred for 3 h. Then Cu-TEPA and TMAdaOH were added into the homogeneous gel and blended for another 3 h. The final gel was sealed into a 100 ml Teflon-lined stainless steel autoclave and heated at 150 °C for 120 h. The product was filtered and washed with deionized water for 3 times, and dried at 80 °C overnight. Since the Cu content in the initial sample was relatively high, which may be detrimental for the NO reduction at high temperatures, an ion-exchange method using NH<sub>4</sub>NO<sub>3</sub> solution was conducted to reduce the Cu content in the final product [24]. Besides, to avoid the interference of different Cu content on the NH<sub>3</sub>-SCR performance, the Cu content was precisely controlled. In a typical ion-exchange method, the initial product was ion-exchanged at 70 °C for 6 h once. The equivalent Cu-loading was obtained by tuning the concentrations of NH<sub>4</sub>NO<sub>3</sub> solution for different samples with various Si/Al ratios. Following which, the sample was calcined at 600 °C for 5 h to remove the occluded organic species. The Cu loading and sodium content was measured by AAS and ICP, respectively, and the results are shown in Table 1. The Si and Al weight content and the composition of the initial samples are shown in Supporting Information (Table-S1). The corresponding catalyst was denoted as “Si/Al-x”, where “x” indicates the Si/Al ratio.

### 2.2. Hydrothermal aging treatment

The hydrothermal aging was performed in a simulated diesel engine exhaust gas composed of 10% H<sub>2</sub>O in air with a flow rate of 1000 cm<sup>3</sup>/min for 12 h at 800 °C and 850 °C, respectively. The corresponding hydrothermal aged catalysts were labeled as “Si/Al-x-800” and “Si/Al-x-850”, where “x” refers to the Si/Al ratio.

**Table 1**  
Cu loading, Na<sup>+</sup> content and N<sub>2</sub> physisorption results for the catalysts.

Sample	Cu loading <sup>a</sup> (wt.%)	Na <sup>+</sup> content <sup>b</sup> (wt.%)	SBET (m <sup>2</sup> /g)	Vmicro (cm <sup>3</sup> g <sup>-1</sup> )
Si/Al-6	2.90	2.35	761	0.22
Si/Al-6-800	2.82	–	620	0.14
Si/Al-6-850	2.81	–	423	0.08
Si/Al-15	2.82	1.49	788	0.26
Si/Al-15-800	2.79	–	720	0.20
Si/Al-15-850	2.80	–	607	0.16
Si/Al-30	2.88	1.32	689	0.22
Si/Al-30-800	2.80	–	462	0.12
Si/Al-30-850	2.90	–	410	0.10

<sup>a</sup> Data were obtained by the AAS technique.

<sup>b</sup> Data were obtained by the ICP technique.

### 2.3. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were performed on PANalytical X'Pert Pro diffractometer with a Cu K $\alpha$  detector, and the diffraction angle ranged from 5 to 50° at a scanning speed of 5°/min. The surface area and N<sub>2</sub> physisorption isotherm (77.3 K) of the catalyst were measured using Micrometrics ASAP 2020 M surface area and porosity analyzer. The temperature programmed desorption of ammonia (NH<sub>3</sub>-TPD) was conducted on Micrometrics AutoChem 2920II chemisorption analyzer. 50 mg of the sample was first pretreated in Ar at 550 °C for 1 h to remove the impurities, and then cooled down to 100 °C. The sample was saturated with 3000 ppm NH<sub>3</sub>/Ar at 100 °C for 45 min. After that, the sample was purged with Ar for 1 h to remove the physical adsorbed NH<sub>3</sub> and then heated in Ar from 100 to 600 °C at ramp rate of 10 °C/min. The outlet NH<sub>3</sub> was monitored by the thermal conductivity detector. H<sub>2</sub>-TPR analysis was also carried out on Micrometrics AutoChem 2920II chemisorption analyzer. After pretreated in Ar at 550 °C for 1 h, the sample was cooled down to 40 °C. Finally, the sample was heated to 1000 °C in a flow of 10% H<sub>2</sub>/Ar at a ramp rate of 10 °C/min. The liquid nitrogen cold trap was used to remove the interference of H<sub>2</sub>O. The electron paramagnetic resonance (EPR) spectra were recorded on a Bruker A 300 spectrometer. 10 mg of powder sample was put into the OD quartz tubes and sealed with rubber septa. In order to decrease the mobility of Cu<sup>2+</sup> ions, the EPR measurements were performed at 150 K. The X-band frequency was 9.43 GHz and a time constant of 20 ms was used. The field was swept from 2400 to 3800 Gauss in 84 s and modulated at 100 kHz with 5 G amplitude. Solid-state <sup>29</sup>Si and <sup>27</sup>Al MAS NMR spectra were collected on an Agilent 600 MHz solid state NMR spectrometer. <sup>29</sup>Si MAS NMR was acquired at the spectral frequency of 79.52 MHz and a relaxation delay of 10 s for Si was applied to collect single pulse spectra. And tetramethylsilane (TMS) was used as an external reference. <sup>27</sup>Al MAS NMR spectra were acquired at 130.2 MHz and chemical shifts were referenced to 1% AlCl<sub>3</sub> aqueous solution.

### 2.4. Catalyst testing

The monolithic SCR catalyst was used to evaluate the catalytic activity. In a typical coating process, the cordierites were the same size and weight. To deposit the catalyst powder on the cordierite, a certain amount of powder was added into deionized water to form slurry firstly. And then, the cordierite was put in the as-prepared slurry until the channel was filled with liquid. The wet cordierite was dried in an oven at 100 °C for 2 h to remove the water drastically so that the catalyst powder could uniformly coat on the cordierite support. In order to deposit a similar amount of catalyst powder on each cordierite, the immersion times and the concentration of slurry were controlled strictly. Finally, the coated cordierite was weighed to ensure a same

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