

## Supporting Information

### Copper-Exchanged SUZ-4 Zeolite Catalysts for Selective Catalytic Reduction of NO<sub>x</sub>

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## Materials

All chemicals and materials used in this study were obtained through commercially available routes and used directly without any further treatment and purification. Tetraethylammonium hydroxide (TEAOH, 25% in water, Beijing Innochem Chemical Reagent Co., Ltd, Beijing, China), aluminite powder (Al, 99.5% Alfa Aesar Chemical Co., Ltd, Heysham, UK), potassium hydroxide (KOH 85wt%, Tianjin Guangfu Science and Technology Development Co., Ltd, Tianjin, China), Ludox® AS-40 colloidal silica (40 wt%, Sigma-Aldrich Co., Ltd, Los Angeles, USA), copper nitrate trihydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , 99.5 wt%, Tianjin Fuchen Chemical Reagent Co., Ltd, Tianjin, China), commercial Cu-SSZ-13 catalyst (AOS Catalysts Co., Ltd, Dalian, China).

## Synthesis of SUZ-4

SUZ-4 zeolites with different silicon contents or different crystallization times were synthesized via a hydrothermal method as described as below. Typically, 0.586 g KOH and a certain amount of Al powder were dissolved in 6.356 g deionized water. Thereafter, 1.5316 g TEAOH was added. After stirring for 15 min, 3.180 g silica sol (AS-40) was mixed with the final solution, followed by stirring for 0.5 h. The final composition of the typical synthesis mixture was  $X \text{ Al}_2\text{O}_3 : 21 \text{ SiO}_2 : 9 \text{ KOH} : 2.6 \text{ TEAOH} : 520 \text{ H}_2\text{O}$  ( $X = 1.5, 1.3, 1.0, 0.7, 0.6, 0.5$  and  $0.42$ ). The mixture was transferred into a 25 mL autoclave and the hydrothermal synthesis was then carried out at 150 °C under rotate condition of 60 rpm for different crystallization time (0–96 h). The obtained sample was centrifuged and washed several times with deionized (DI) water, then dried overnight at 80 °C, followed by calcination at 550 °C for 6 h.

## Preparation and high temperature hydrothermal ageing of Cu-SUZ-4 catalysts

Cu-SUZ-4 catalysts were prepared via two-step ion-exchanged method. SUZ-4 zeolites were ion-exchanged twice with 1 M  $\text{NH}_4\text{NO}_3$  at 80 °C to mostly remove  $\text{K}^+$  ions for getting  $\text{NH}_4$ -SUZ-4. Then, copper ions were introduced by ion exchanging  $\text{NH}_4$ -SUZ-4 with aqueous solution of 0.02–0.1 M  $\text{Cu}(\text{NO}_3)_2$  at 80 °C for 1 h. Thereafter, the zeolite slurries were filtered, washed with DI water and dried at 80 °C

overnight. Subsequently, the samples were calcined in a muffle oven at 550 °C for 5 h. The obtained Cu-SUZ-4 catalysts with different contents of copper were denoted as Cu-SUZ-4-1, Cu-SUZ-4-2 and Cu-SUZ-4-3, respectively. To investigate the hydrothermal stability of the Cu-SUZ-4 catalysts, Cu-SUZ-4-1, Cu-SUZ-4-2 and Cu-SUZ-4-3 were hydrothermally aged in flowing air containing 10 vol.% H<sub>2</sub>O at 600 °C for 16 h and denoted as Cu-SUZ-4-1-HTA, Cu-SUZ-4-2-HTA and Cu-SUZ-4-3-HTA, respectively.

### **Characterization**

The crystallinity and phase purity of the samples were characterized by X-ray diffraction (XRD) using Cu  $K_{\alpha}$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) on a Rigaku D-Max 2550 diffractometer (Rigaku Co., Tokyo, Japan). The relative crystallinity was evaluated by comparing the sum of peak areas ( $2\theta = 7.8^{\circ}$ ,  $11.79^{\circ}$ ,  $15.5^{\circ}$ ,  $19.38^{\circ}$ ,  $22.18^{\circ}$ ,  $22.51^{\circ}$ ,  $25.03^{\circ}$ ,  $25.56^{\circ}$  and  $28.45^{\circ}$ ). Scanning electron microscopy (SEM) images were obtained by a JEOL JSM-7800F scanning electron microscope (JEOL Co., Tokyo, Japan). Transmission electron microscopy (TEM) images were recorded on a Tecnai G2 S-Twin F20 (FEI Company, Oregon, USA). The chemical composition of the samples was analyzed by inductively coupled plasma (ICP) on a Perkin-Elmer Optima 3300 DV ICP instrument (PerkinElmer, Inc., Waltham, Massachusetts, USA). Nitrogen adsorption/desorption characterization of samples was performed at 77.35 K after degassing at 350 °C under vacuum using a Micromeritics 2020 analyzer (Micromeritics Instrument Co., Norcross, Georgia, USA). Ammonia temperature-programmed desorption (NH<sub>3</sub>-TPD) testing of samples was performed using a Micromeritics AutoChemII 2920 automated chemical adsorption analysis unit (Micromeritics Instrument Co., Norcross, Georgia, USA) under helium flow using a thermal conductivity detector (TCD). The hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR) tests were performed on an AutoChemII 2920 analyzer (Micromeritics Instrument Co., Norcross, Georgia, USA). Samples were pretreated at 500°C for 1 h in an air atmosphere and then TPR tests were performed in 10% H<sub>2</sub> / Ar at a flow rate of 50 ml/min. X-ray photoelectron spectroscopy (XPS) spectra were

tested using a Thermo ESCALAB 250 spectrometer (Thermo Scientific Co., New York, USA) under monochromatic Al  $K_{\alpha}$  excitation. Ultraviolet-visible diffuse reflectance spectra (UV-Vis DRS) of the samples in the 200-800 nm range were obtained on a  $\lambda$  Lambda 950 spectrometer (PerkinElmer, Massachusetts Co., USA) at room temperature.  $^{27}\text{Al}$  NMR tests were performed on Bruker Avance Neo 600Mz WB spectrometer with BBO MAS probe operating at a magnetic field strength of 14.1 T (Bruker Co., Karlsruhe, Germany).

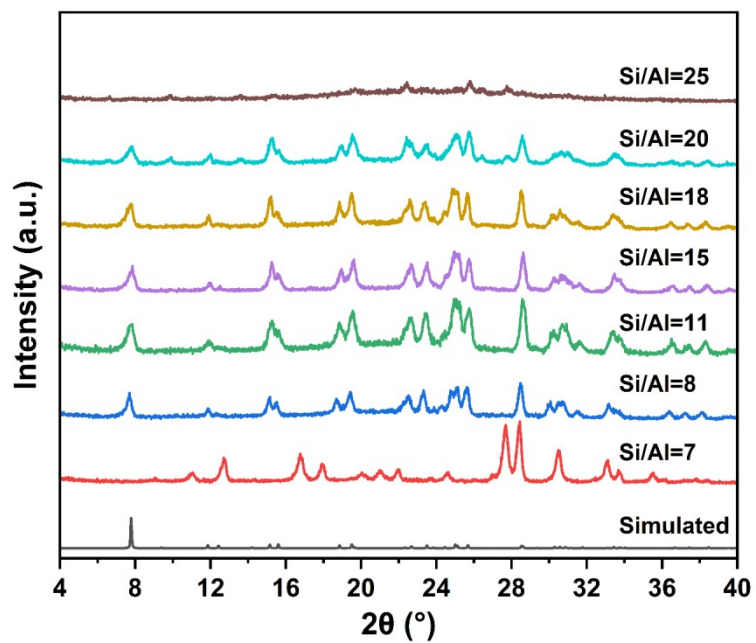
### Catalytic test

SCR activity testing of the catalysts was conducted in a quartz reactor with a fixed bed inner diameter of 6 mm. 0.1 g of the 40–60 mesh catalyst was placed in the tube reactor. The test reaction conditions were as follows.

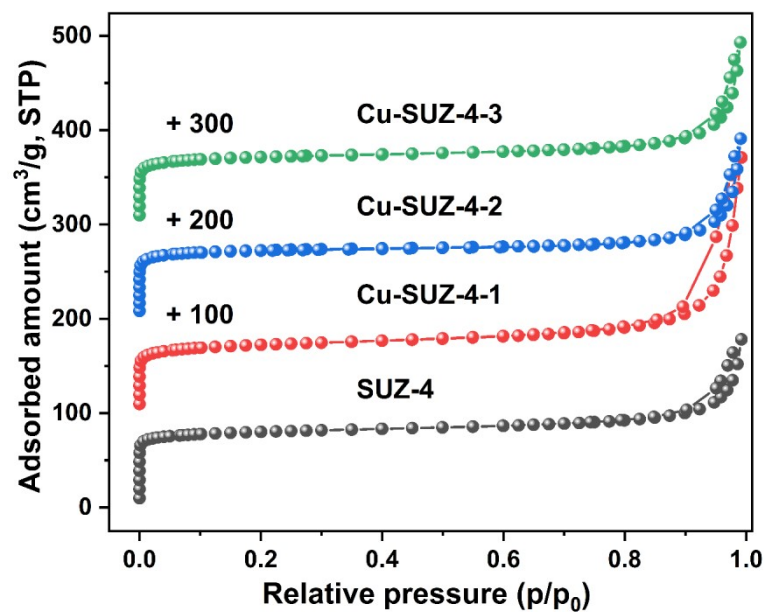
500 ppm NO, 500 ppm  $\text{NH}_3$ , 5%  $\text{O}_2$ , 5%  $\text{H}_2\text{O}$ , and  $\text{N}_2$  were used as the balance gas. The total flow rate was 500 mL/min and the gaseous hourly space velocity (GHSV) was about 200,000  $\text{h}^{-1}$ . The inlet and outlet gas compositions were monitored in real time by FTIR spectrometer (MKS, MultiGas 2030HS), the NO conversion was calculated as follows:

$$\text{NO conversion} = \left( 1 - \frac{2[\text{NO}]_{out} + [\text{NO}_2]_{out}}{[\text{NO}]_{in} + [\text{NO}_2]_{in}} \right) \times 100\%$$

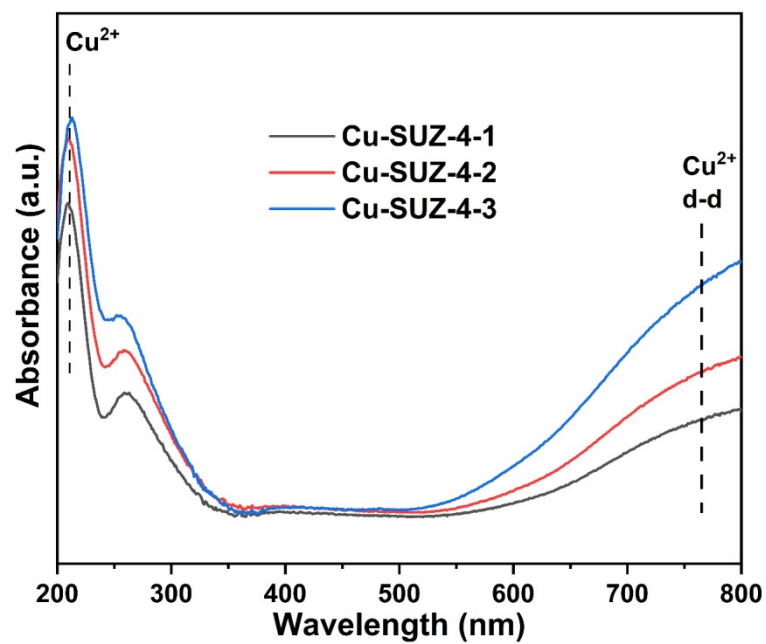
## Figures



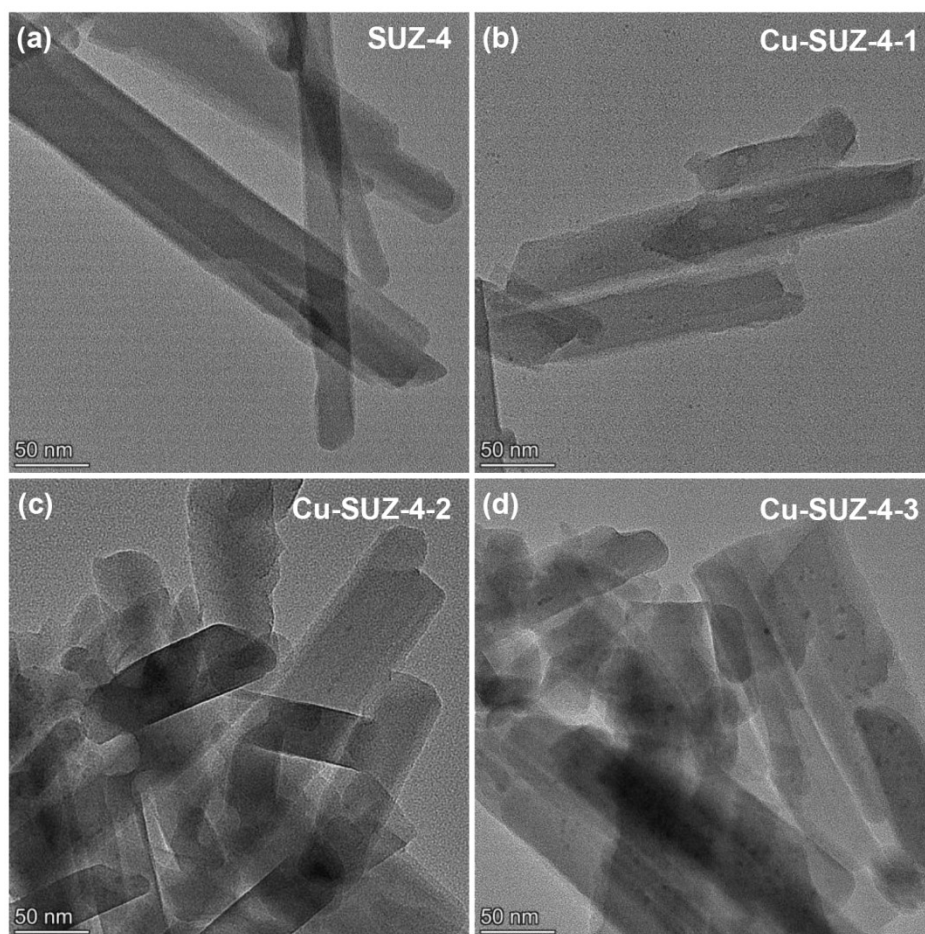
**Fig. S1** XRD patterns of as-synthesized SUZ-4 zeolites with different Si/Al ratios.



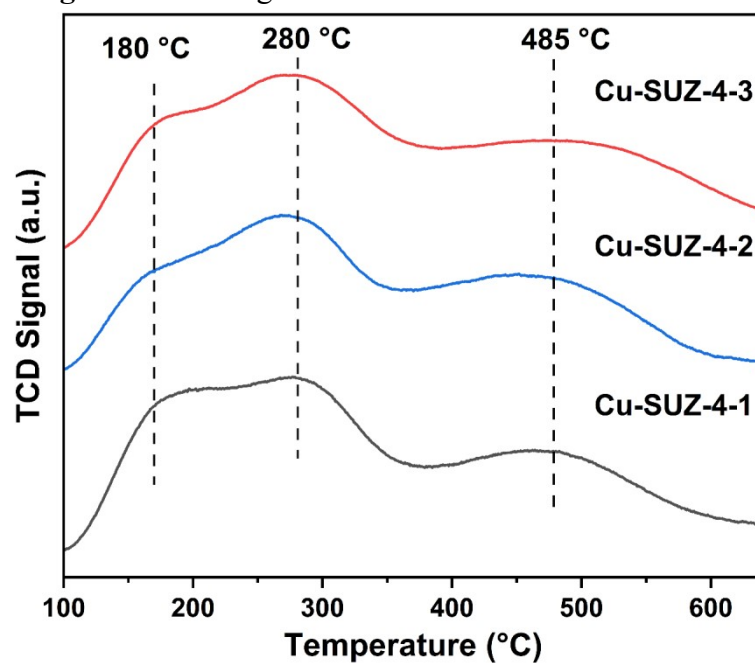
**Fig. S2** Nitrogen adsorption-desorption isotherms of SUZ-4 and Cu-SUZ-4 samples.



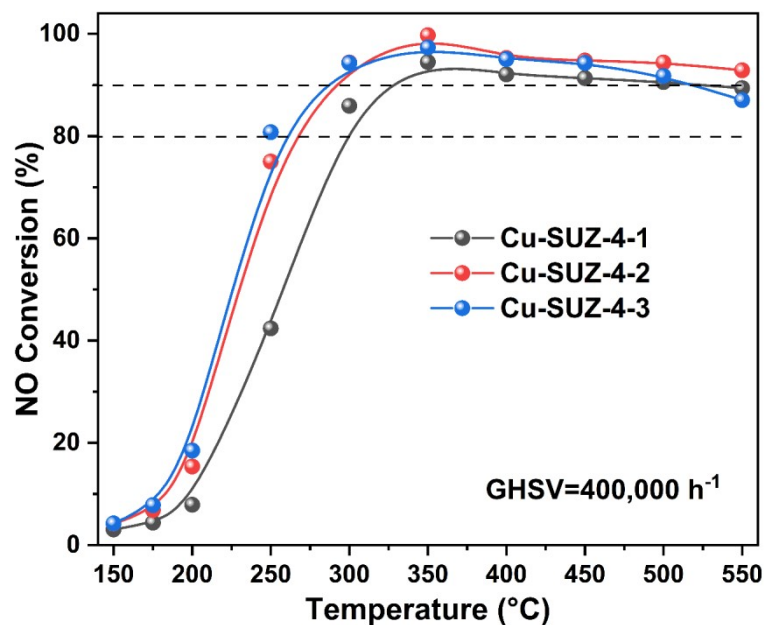
**Fig. S3** UV-Vis DRS spectra of Cu-SUZ-4 samples.



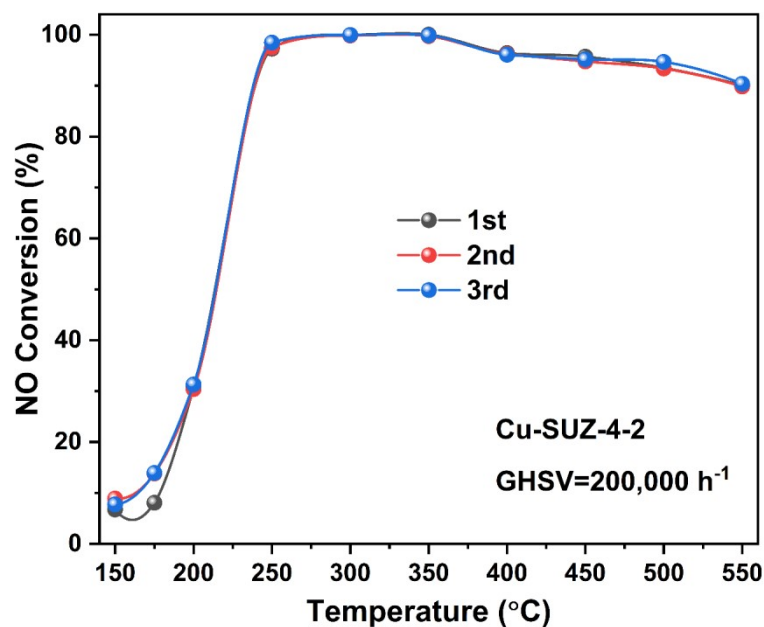
**Fig. S4** TEM images of SUZ-4 and Cu-SUZ-4 zeolites.



**Fig. S5** NH<sub>3</sub>-TPD profiles of Cu-SUZ-4 zeolites.

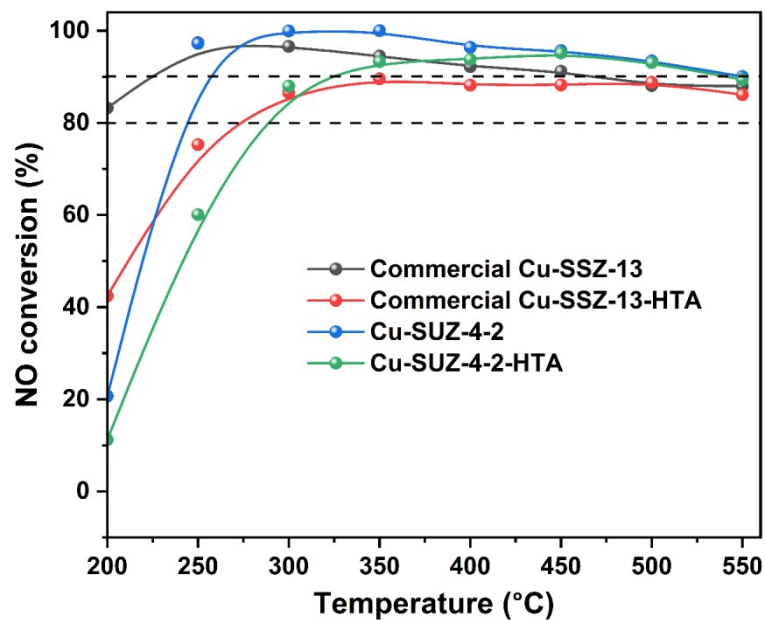


**Fig. S6** NO conversion as a function of temperature on fresh Cu-SUZ-4 samples. Reaction conditions: 500 ppm NO, 500 ppm NH<sub>3</sub>, 5% O<sub>2</sub>, and 5% H<sub>2</sub>O, balanced with N<sub>2</sub> at a GHSV of 400,000 h<sup>-1</sup>.

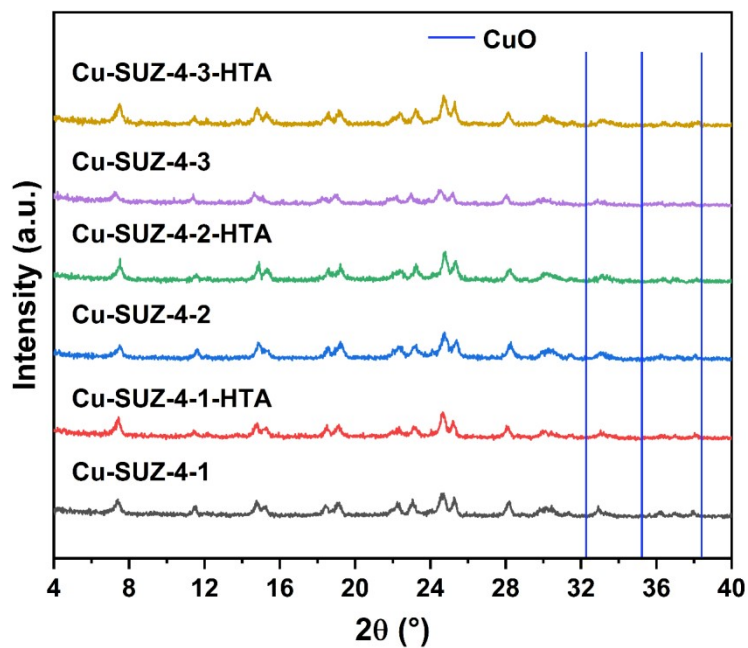


**Fig. S7** Cycling stability of Cu-SUZ-4-2 zeolite. Reaction condition: 500 ppm NO, 500 ppm NH<sub>3</sub>, 5% O<sub>2</sub>, and 5% H<sub>2</sub>O, balanced with N<sub>2</sub> at a GHSV of 200,000 h<sup>-1</sup>.





**Fig. S8** NO conversion as a function of temperature on commercial Cu-SSZ-13 and Cu-SUZ-4 samples. Reaction condition: 500 ppm NO, 500 ppm NH<sub>3</sub>, 5% O<sub>2</sub>, and 5% H<sub>2</sub>O, balanced with N<sub>2</sub> at a GHSV of 200,000 h<sup>-1</sup>.



**Fig. S9** XRD patterns of Cu-SUZ-4 zeolites before and after hydrothermal ageing. No CuO<sub>x</sub> diffraction peaks as indicated by the blue lines are observed in each sample.

## Tables

**Table S1.** The synthesized products influenced by the composition of the initial gel.

Sample	Si/Al (gel)	Si/Al (product)	Yield (%)
1	8	5.78	84
2	11	6.62	66
3	15	9.33	59
4	18	10.37	56
5	20	11.13	56

**Table S2.** Texture property and chemical composition of SUZ-4 and Cu-SUZ-4.

Samples	Si/Al <sup>a</sup>	Cu wt% <sup>a</sup>	Cu/Al <sup>a</sup>	S <sub>BET</sub> (m <sup>2</sup> / g) <sup>b</sup>	V <sub>micro</sub> (cm <sup>3</sup> /g) <sup>c</sup>
SUZ-4	6.62	/	/	236	0.10
Cu-SUZ-4-1	6.46	1.43	0.12	219	0.08

Cu-SUZ-4-2	6.55	1.89	0.16	215	0.09
Cu-SUZ-4-3	6.35	2.21	0.19	214	0.09

<sup>a</sup> Measured by inductively coupled plasma (ICP). <sup>b</sup>  $S_{\text{BET}}$  (total surface area) calculated by applying the BET equation in the 0–1.0 partial pressure range. <sup>c</sup>  $V_{\text{micro}}$  (micropore area) calculated using the  $t$ -plot method in the 0–1.0 partial pressure range.

**Table S3.** The comparison of catalytic performance between Cu-SUZ-4-2 catalyst and other similar zeolite catalysts for  $\text{NH}_3$ -SCR.

Sample	Zeolite topology	Si/Al	Cu wt%	Reaction conditions	$T_{90}$ window	note
Cu-SUZ-4-2	<b>SZR</b> , 10-ring channel system	6.15	1.89	500 ppm NO, 500 ppm $\text{NH}_3$ , 5% $\text{O}_2$ , 5% $\text{H}_2\text{O}$ , GHSV = 200,000 $\text{h}^{-1}$ .	250-550 °C	this work
SZR	<b>SZR</b> , 10-ring channel system	7.0	3.5	500 ppm NO, 450 ppm $\text{NH}_3$ , 5% $\text{O}_2$ , 2% $\text{CO}_2$ , 2.2% $\text{H}_2\text{O}$ , GHSV = 30,000 $\text{h}^{-1}$ .	200-250 °C	ref [24]
MOZ	<b>MOZ</b> , 12-ring channel system	3.6	2.6	500 ppm NO, 450 ppm $\text{NH}_3$ , 5% $\text{O}_2$ , 2% $\text{CO}_2$ , 2.2% $\text{H}_2\text{O}$ , GHSV = 30,000 $\text{h}^{-1}$ .	175-300 °C	ref [24]
Cu-UZM-35	<b>MSE</b> , 12 and 10-ring channel system	8.9	3.3	500 ppm NO, 500 ppm $\text{NH}_3$ , 5% $\text{O}_2$ , 10% $\text{H}_2\text{O}$ , GHSV = 100,000 $\text{h}^{-1}$ .	200-525 °C	ref [49]
Cu-FER	<b>FER</b> , 10-ring channel system	10	2.8	500 ppm NO, 450 ppm $\text{NH}_3$ , 10% $\text{O}_2$ , 10% $\text{CO}_2$ , 9% $\text{H}_2\text{O}$ , GHSV = 200,000 $\text{h}^{-1}$ .	275-475 °C	ref [50]
Cu-SSZ-52	<b>SFW</b> , 8-ring channel system	4.7	2.4	500 ppm NO, 500 ppm $\text{NH}_3$ , 5% $\text{O}_2$ , 5% $\text{H}_2\text{O}$ , GHSV = 80,000 $\text{h}^{-1}$ .	250-550 °C	ref [51]
Cu-ZSM-5	<b>MFI</b> , 10-ring channel system	14	3.0	500 ppm NO, 500 ppm $\text{NH}_3$ , 5% $\text{O}_2$ , 10% $\text{H}_2\text{O}$ , GHSV = 100,000 $\text{h}^{-1}$ .	200-400 °C	ref [49]