

Supplementary Information

Enhancing catalytic performance of Cu-SSZ-13 for NH₃-SCR reaction via *in situ* introduction of Fe³⁺ with diatomite

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Experimental section

Materials

Diatomite (Table S1, Tianjin Guangfu Chemical Reagents Co., Ltd, Tianjin, China), aluminum hydroxide ($\text{Al}(\text{OH})_3$, 99 wt.%, Tianjin Fuchen Chemical Reagents Company, Tianjin, China), aluminum hydroxide ($\text{Al}(\text{OH})_3$, 76.5 wt.%, Alfa Aesar, Heysham, UK), Ludox® HS-40 colloidal silica (40 wt.%, Sigma-Aldrich, Los Angeles; USA), copper (II) nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, purity above 99.5 wt.%, Tianjin Fuchen Chemical Reagents Company, Tianjin, China), sodium hydroxide (NaOH , 98 wt.%, Beijing Chemical Works, Beijing, China) and N,N,N-trimethyl-1-adamantane ammonium hydroxide (TMAdaOH, 25 wt.%, Beijing Innochem Chemical Reagent Co., Ltd, Beijing, China).

Synthesis of SSZ-13-D using diatomite as silicon source

SSZ-13-D zeolites with different silicon content or different crystallization time were synthesized via a hydrothermal method as described as below. Typically, 0.2 g NaOH and 3 g TMAdaOH were dissolved in 6.65 g deionized water. Thereafter, 0.156 g $\text{Al}(\text{OH})_3$ (99 wt.%) was added. After stirring for 1 h, 3 g diatomite was mixed with the final solution, followed by stirring for 3 h. The final composition of the typical synthesis mixture was 0.5 Al_2O_3 : 11 SiO_2 : 2.5 NaOH : 1.8 TMAdaOH: 250 H_2O . The mixture was transferred into a 20 mL autoclave and the hydrothermal synthesis was then carried out at 160 °C under static condition for different crystallization time (0-72 h). The obtained sample was centrifuged and washed several times with deionized (DI) water, then dried overnight at 80 °C, followed by calcination at 600 °C for 8 h. The as-synthesized SSZ-13 zeolite is denoted as SSZ-13-D, in which D stands for diatomite.

Synthesis of SSZ-13-S and Fe-SSZ-13 using silica sol as silicon source

SSZ-13-S zeolites with different crystallization time were synthesized via a hydrothermal method as described as below. Typically, 0.2 g NaOH and 3 g TMAdaOH were dissolved in 7.15 g deionized water. Thereafter, 0.1 g $\text{Al}(\text{OH})_3$ (76.5 wt.%) was added under stirring. Afterwards, 1.825 g silica sol was added to the mixture under

stirring. The molar ratio of the final mixture was 0.5 Al₂O₃: 12 SiO₂: 5 NaOH: 3.57 TMAOH: 522 H₂O. The mixture was transferred into a 20 mL autoclave and the hydrothermal synthesis was then carried out at 160 °C under static condition for different crystallization time (0-120 h). The obtained sample was centrifuged and washed several times with deionized (DI) water, then dried overnight at 80 °C, followed by calcination at 600 °C for 8 h. The as-synthesized SSZ-13 zeolite is denoted as SSZ-13-S, in which D stands for silica sol.

The control Fe-SSZ-13 crystallized from silica sol was synthesized according to the literature ¹. The synthesis procedure is the same to that of SSZ-13-S besides that 0.03 g Fe(NO₃)₃·9H₂O was added into the mixture before the addition of TMAOH and silica sol. The molar ratio of the final reaction mixture was 0.5 Al₂O₃: 12 SiO₂: 5 NaOH: 3.57 TMAOH: 0.07 Fe: 522 H₂O. Finally, the mixture was transferred into a 20 mL Teflon-lined stainless-steel autoclave heating in an oven at 160 °C under static conditions for different crystallization time (0-96 h). The as-synthesized SSZ-13 zeolite denoted as Fe-X h (X represents the different crystallization time) was centrifuged, and washed several times with water and ethanol, then dried overnight at 80 °C, followed by calcination at 600 °C for 8 h.

Preparation and high temperature hydrothermal ageing of Cu-SSZ-13 catalysts

Cu-SSZ-13 catalysts were prepared via an ion exchange method. The detail steps were listed in supplementary information. The SSZ-13 zeolites were ion-exchanged twice with 1 M NH₄NO₃ at 80 °C to mostly remove Na⁺ ions for getting NH₄-SSZ-13. Then, copper ions were introduced by the ion-exchange of NH₄-SSZ-13 with aqueous solution of 0.05 M Cu(NO₃)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 SSZ-13-S and SSZ-13-D exchanged with copper ions were denoted as Cu-SSZ-13-S and Cu-SSZ-13-D, respectively. To investigate the hydrothermal stability of the Cu-catalysts, Cu-SSZ-13-S and Cu-SSZ-13-D were hydrothermally aged in flowing air containing 10 vol.% H₂O at 750 °C for 16 h and denoted as Cu-SSZ-13-S_HTA and Cu-SSZ-13-D_HTA, respectively.

NH₃-SCR catalytic test

SCR activity measurements of the catalysts were performed in a fixed-bed quartz reactor with an inner diameter of 6 mm. The catalysts of 0.1 g with particle size of 40-60 mesh were placed in the tubular reactor. The reaction conditions were as follows: 500 ppm NO, 500 ppm NH₃, 5% O₂, 5% H₂O, N₂ as balance gas. The total flow rate was 500 mL/min and thus a normal gaseous hourly space velocity (GHSV) of ~200,000 h⁻¹ (0.1 g catalysts were used for evaluation). The inlet and outlet gas compositions were monitored by a FTIR spectrometer (MKS, MultiGas 2030HS). NO conversion was calculated as $\text{NO}\% = (1 - ([\text{NO}]_{\text{out}} + [\text{NO}_2]_{\text{out}}) / ([\text{NO}]_{\text{in}} + [\text{NO}_2]_{\text{in}})) \times 100\%$, N₂ selectivity was calculated as $\text{N}_2\% = (1 - ([\text{NO}_2]_{\text{out}} + 2[\text{N}_2\text{O}]_{\text{out}}) / ([\text{NO}]_{\text{in}} + [\text{NO}_2]_{\text{in}} + [\text{NH}_3]_{\text{in}})) \times 100\%$.

Characterization

The crystallinity and phase purity of the samples were characterized by power X-ray diffraction (XRD) on a Rigaku D-Max 2550 diffractometer (Rigaku Corporation, Tokyo, Japan) using Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$). The relative crystallinity was evaluated by comparing the sum of the peak areas ((at $2\theta = 9.7^\circ, 16.3^\circ, 20.9^\circ, 31.1^\circ$ and 31.6°) of the synthesized samples. Back-scattering scanning electron microscopy images and scanning electron microscopy (SEM) images were measured with JEOL JSM-7800F (JEOL Ltd., Tokyo, Japan). Transmission electron microscopy (TEM) images were recorded on a Tecnai G2 S-Twin F20 (FEI Company, Oregon, USA). Chemical composition was determined with inductively coupled plasma (ICP) analyses carried out on a Perkin-Elmer Optima 3300 DV ICP instrument (PerkinElmer, Inc., Waltham, Massachusetts, USA) and an X-ray fluorescence (XRF) spectrometer (PANalytical-AXIOS, Amsterdam, Netherlands). Nitrogen adsorption/desorption measurements were carried out on a Micromeritics 2020 analyzer (Micromeritics Instrument Corp., Norcross, Georgia, USA) at 77.35 K after the samples were degassed at 350 °C under vacuum. The temperature-programmed desorption of ammonia (NH₃-TPD) experiments were performed using a Micromeritics AutoChemII 2920 automated chemisorption analysis unit (Micromeritics Instrument Corp., Norcross, Georgia, USA)

with a thermal conductivity detector (TCD) under helium flow. Solid-state ^{29}Si NMR and ^{27}Al NMR experiments were performed on Bruker Avance Neo 600Mz WB spectrometer with BBO MAS probe operating at a magnetic field strength of 14.1 T (Bruker Company, Karlsruhe, Germany). Fourier Transform infrared spectroscopy (FTIR) spectrums were measured on a Bruker FTIR IFS-80V/S with KBr pellets (Bruker Company, Karlsruhe, Germany), and a baseline correction was applied after measurement. The electron paramagnetic resonance (EPR) spectrum was obtained with a JES-FA200 (JEOL Ltd., Tokyo, Japan) to investigate Fe species. The EPR signals of Cu^{2+} species were recorded at 150 K on an EMXPLUS10/12 ESR spectrometer. (Bruker Company, Karlsruhe, Germany) in the region of 2200–3800 G. The H_2 -TPR experiments were performed on an AutoChemII 2920 analyzer (Micromeritics Instrument Corp., Norcross, Georgia, USA). The sample was pretreated in air atmosphere at 500 °C for 1 h before TPR was conducted in 10% H_2/Ar at a flow rate of 50 ml/min. X-ray photoelectron spectroscopy (XPS) spectra were measured using a Thermo ESCALAB 250 spectrometer (Thermo Scientific, New York, USA) with monochromatized Al K_α excitation. Ultraviolet -Visible diffuse reflection spectrums (UV-Vis DRS) were obtained in the range of 200-800 nm on a λ Lambda 950 spectrometer (PerkinElmer, Massachusetts, USA) at the ambient temperature.

Figures

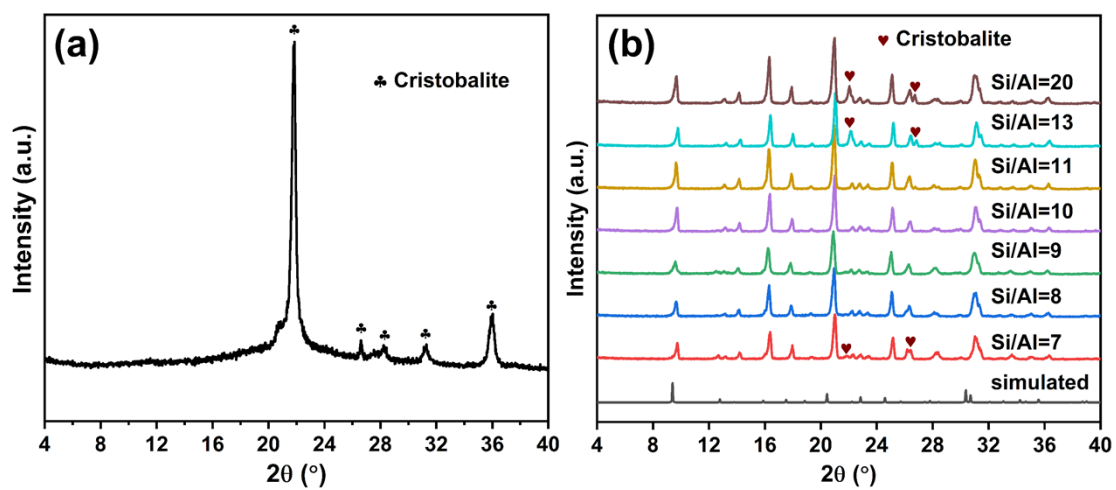


Fig. S1 XRD analysis of (a) raw diatomite and (b) as-synthesized samples using diatomite as silicon source.

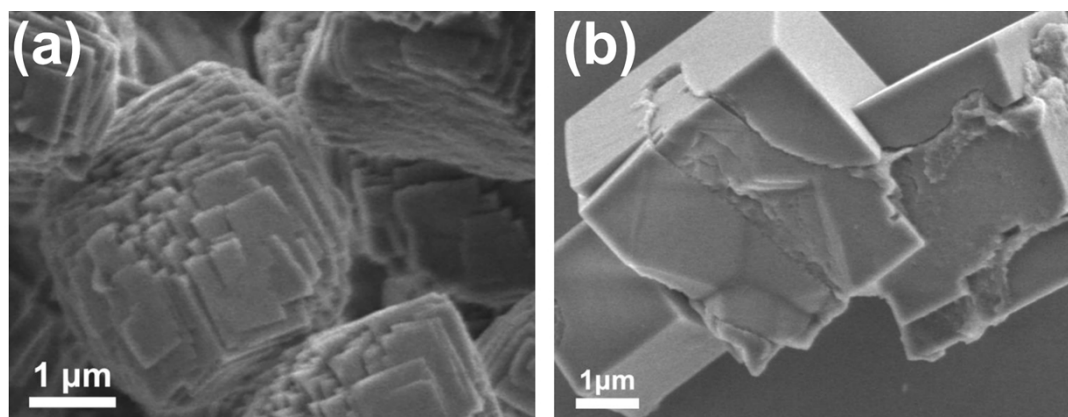


Fig. S2 The SEM images of SSZ-13-S crystallized at 120 h (a) and SSZ-13-D crystallized at 60 h (b).

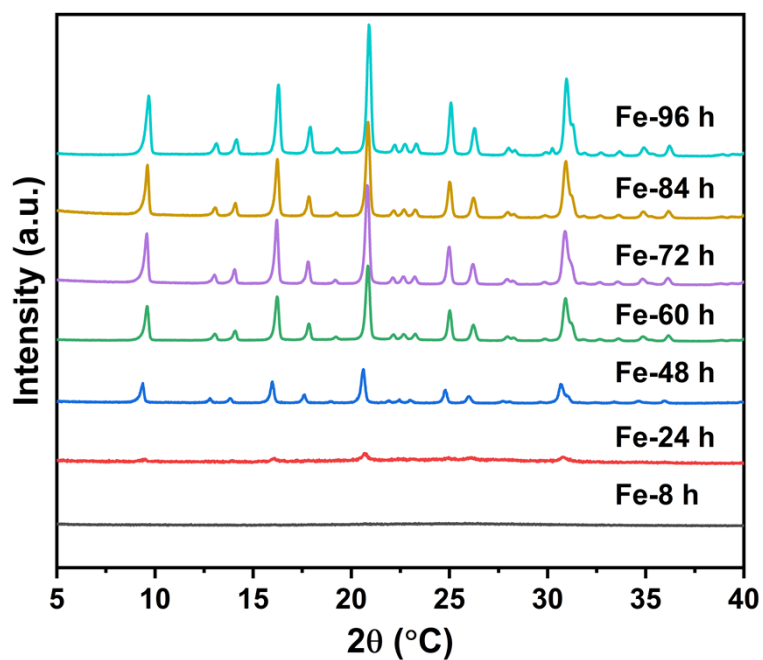


Fig. S3 Time-dependent XRD patterns of Fe-SSZ-13 obtained at varied period of crystallization times.

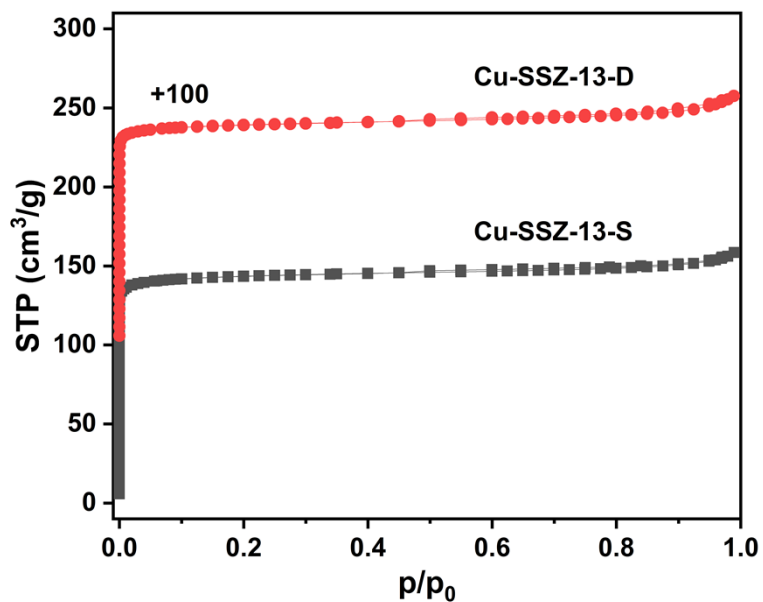


Fig. S4 Nitrogen adsorption-desorption isotherms of Cu-SSZ-13-S and Cu-SSZ-13-D catalysts.

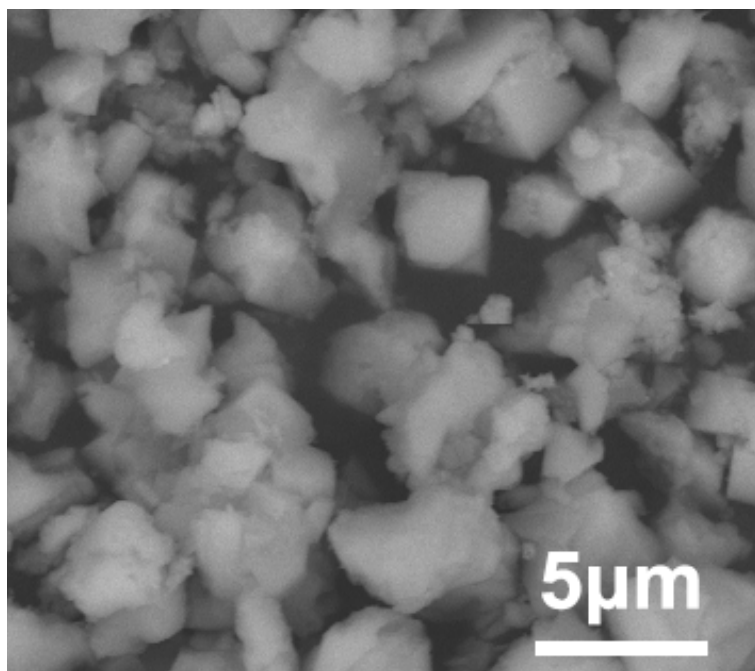


Fig. S5 Back-scattering SEM image of Cu-SSZ-13-D catalyst.

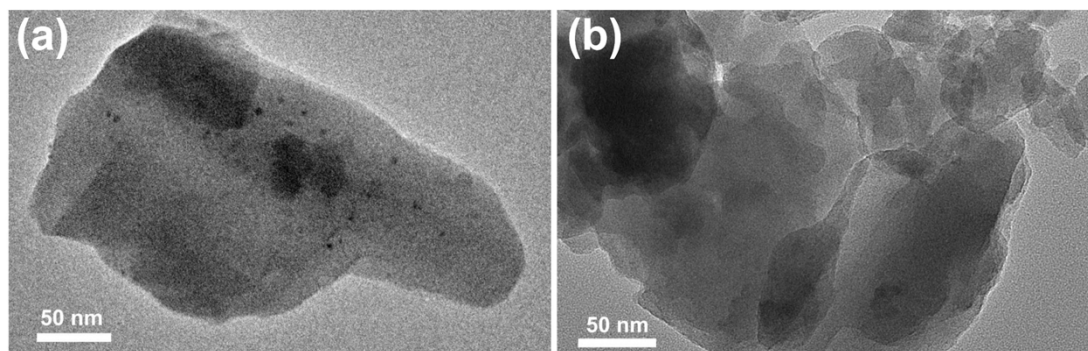


Fig. S6 TEM images of (a) Cu-SSZ-13-S catalyst and (b) Cu-SSZ-13-D catalyst.

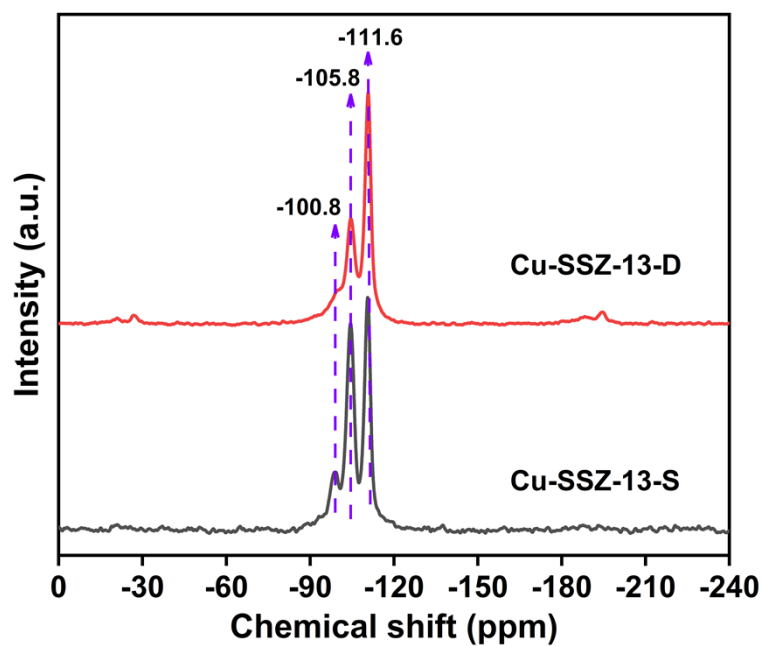


Fig. S7 ^{29}Si MAS NMR spectra of Cu-SSZ-13-S and Cu-SSZ-13-D catalysts.

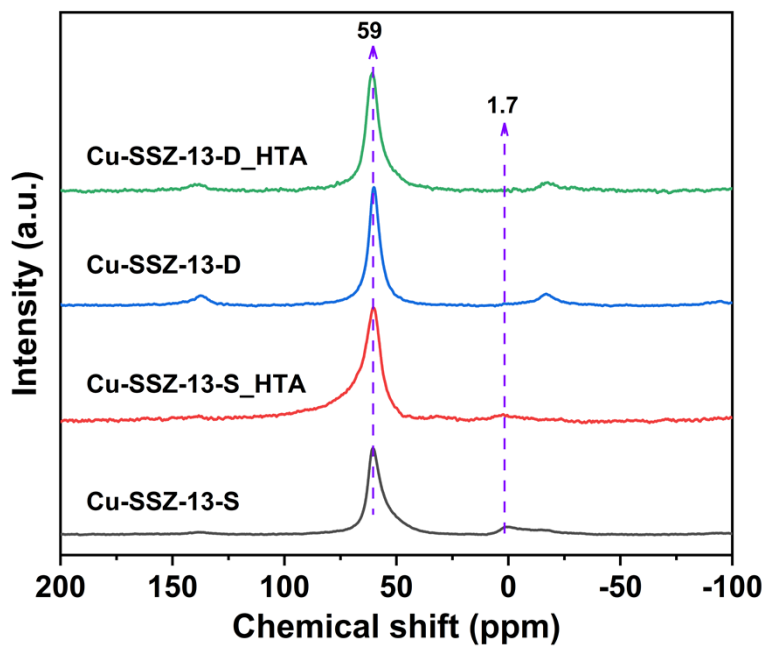


Fig. S8 ^{27}Al MAS NMR spectra of Cu-SSZ-13-S, Cu-SSZ-13-S_HTA, Cu-SSZ-13-D and Cu-SSZ-13-D_HTA catalysts.

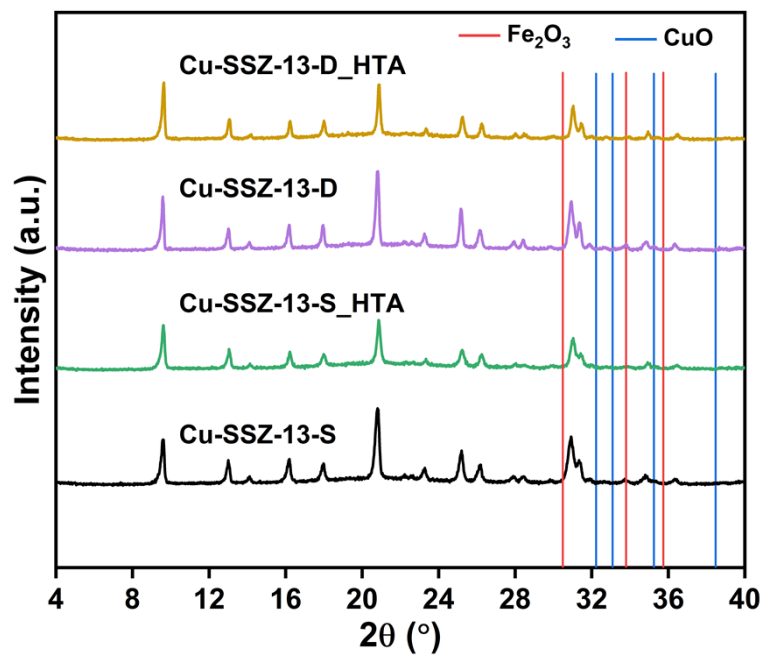


Fig. S9 The XRD patterns of fresh and aged Cu catalysts and the simulated XRD patterns of CuO and Fe_2O_3 .

Tables

Table S1. Chemical composition of diatomite determined by XRF.

Composition	Si	Al	Fe	Na	Ca	K	Ti	O
Wt. %	41.604	1.987	1.254	3.348	0.192	0.45	0.096	51.069

Table S2. The comparison of catalytic performance between Cu-SSZ-13-D and other CuFe-zeolites.

Sample	Si/Al, Cu wt %, Fe wt %	Test conditions	NO conversion ≥90 %	note
Fe-Cu-SSZ-13-1	3.73; 0.13; 0.089	1000 ppm NO, 1000 ppm NH ₃ , 3% O ₂ , GHSV=50,000 h ⁻¹	225–550 °C	Ref [2]
Fe _{0.53} /Cu _{1.55} -SSZ-13	5; 1.55; 0.53	500 ppm NO, 500 ppm NH ₃ , 5% O ₂ , GHSV=50,000 h ⁻¹	175–500 °C	Ref [3]
FeCu-SSZ-13M	/; 4.8; 0.5	500 ppm NO, 500 ppm NH ₃ , 5% O ₂ , GHSV=180,000 h ⁻¹	200–550 °C	Ref [4]
CuFe-SSZ-13	/; 2.71; 0.357	8.5% O ₂ , 8.0% CO ₂ , 7.25% H ₂ O, 250 ppm NO ₂ , 250 ppm NO, 500 ppm NH ₃ , GHSV= 50,000 h ⁻¹	200–450 °C	Ref [5]
Cu-SSZ-13-D	9.7; 2.3; 0.89	500 ppm NO, 500 ppm NH ₃ , 5% O ₂ , 5% H ₂ O, GHSV=200,000 h ⁻¹	200–550 °C	This work

References

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