Supporting Information

Selective Catalytic Reduction over Cu-exchanged X zeolite catalyst: In situ DRIFTS and DFT studies of NH_3-SCR mechanism

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Text S1: preparation procedure

Zeolite X was prepared from blast furnace slag by hydrothermal reaction as described in our previous study.[1] The Cu-exchanged zeolite was prepared by impregnation method. In detail, a certain amount (2.95-11.82 g) of $Cu(NO_3)_2 \cdot 6\ H_2O$ was dissolved in 100 mL deionized water. Then 2 g zeolite X was impregnated in the precursor solution at 50 °C for 3 h. The sample was dried at 110 °C for 12 h, and calcined at 450 °C for 3 h. The obtained catalyst was denoted as γ-Cu-X (Different Cu content ion exchange X zeolite), where γ represented the Cu/Al mass ratios (wt.%). The γ value was calculated by ICP.

Text S2: Catalytic activity test conditions

The catalytic performance of Cu-X catalyst with different Cu exchanged amounts was investigated by measuring the NO conversion. SCR performance measurements were conducted with 0.3 g (40-60 mesh) catalyst under the following reactant gas conditions:1000 ppm NO, 1000 ppm NH_3, 11% O_2 with N_2 as balance gas at a total flow rate of 200 mL/min and GHSV 40000 h^{-1}. The concentrations of NH_3, NO, NO_2 and SO_2 in flue gas were measured by Thermo Scientific, Antaris IGS flue gas analyzer. The NO conversion and N_2 selectivity were calculated as follows:

$$NO\ conversion(\%) = \left(1 - \frac{[NO]_{out}}{[NO]_{in}}\right) \quad \text{（S1）}$$

$$N_2\ selectivity(\%) = \left(1 - \frac{[NO_2] + 2[N_2O]_{Out}}{[NO]_{In} + [NH_3]_{In} - [NO]_{out} - [NH_3]_{out}}\right) \quad \text{（S2）}$$

where $[NO]_{in}$ and $[NO]_{out}$ represent the inlet and outlet concentration of NO. $[NO_2]_{out}$ and $[N_2O]_{out}$ stand for the outlet concentration of NO_2 and N_2O, respectively.

Text S3: Catalytic characterization

Rigaku D/max-2500 PC diffractometer was used to record X-ray diffractometer (XRD) patterns with Cu-Kα radiation operating at 40 kV and 40 mA over a 2θ range of 5-80° with 0.02° interval at a scanning rate of 10°/min.

The specific surface area and average pore size of the catalysts were measured on the American MicrometriticsASAP2020 surface area analyzer. The specific surface areas were determined by the Brunauer-Emmett-Teller (BET) method by nitrogen adsorption at 77 K.

The morphology and microstruture of the prepared specimens were examined by scanning electron microscopy (SEM, ZEISS Sigma 300) at an accelerating voltage of 15 kV.

NH_3 temperature-programmed desorption (NH_3-TPD) and NO temperature-programmed desorption (NO-TPD) was performed on the SCR reactor system to test adsorption capacity of catalysts. In detail, 0.3 g sample was firstly saturated with adsorption in 30 °C, and the purged with nitrogen followed by temperature programmed to 600 °C in 57 minutes. The concentration of desorbed gases can be determined by the flue gas analyzer.

In situ diffuse reflectance infrared Fourier transform spectra (in situ DRIFTS) were collected from 1000 to 4000 cm^{-1} with scanning numbers of 64 times at a spectral resolution of 8 cm^{-1} on a Nicolet iS50 FTIR spectrometer. The samples were firstly pretreated at 300 °C for 1 h in N_2 flow and cooled to each target temperature. Then the background spectrum was collected during the cooling process and automatically subtracted from the sample spectrum.

The computation works were completed by Density functional theory (DFT) as implemented modeling CASTEP in Material Studio 2020 (Accelrys, USA). The chemical model was provided by the standard FAU model derived from the Material Studio (MS) package, which was selected to describe the structural units of X zeolite. The Cu-X original model for SCR reaction mechanism was the X zeolite (1 1 1) with 78 atoms loaded on a Cu atom. A vacuum layer of 15 Å in the vertical direction was used to minimize the interaction between neighboring slab surfaces. Geometry Optimization was conducted with GGA-PBE as the exchange-correlation function. The SCF tolerance was set 2.0×10^{-6} eV and the max SCF cycle was 150. The adsorption energy, Eads (eV) was defined by the following Eq. (S1), where Eadsorbate/substrate, Eadsorbate and Esubstrate are the total energies of the surface with the adsorbate present, the corresponding free adsorbate gas and the free surface, respectively.

$$Eads = Eadsorbate/surface - Eadsorbate - Esurface \quad (S1)$$

Table S1. BET surface area and pore parameters of Cu-exchanged zeolite X

Sample	BET surface area (m^2/g)	Pore size (nm)
X-zeolite	721	1.90
1.32-Cu-X	310	3.33
1.41-Cu-X	224	3.70
1.50-Cu-X	115	4.83
1.76-Cu-X	97	4.19

Table S2. Energy change of NH_3-SCR reaction.

Sample	Cu^{n+}	Cu^{n+}-NH_3	$Cu^{(n-1)+}$-NH_2+H^+	$Cu^{(n-1)+}$-NH_2+NH_4^+	$Cu^{(n-1)+}$-NH_2NO+NH_4	$Cu^{(n-1)+}$+NH_4^+	$Cu^{(n-1)+}$-NO+NH_4^+	Cu^{n+}-NO_3^- +NH_4^+	Cu^{n+}-NO_2^- +NH_4^+	Cu^{n+}

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Energy change (eV)	0	-1.75	+0.41	-1.20	-0.51	-1.99	-0.66	-1.77	+0.65	-2.08
Total energy (eV)	0	-1.75	-1.34	-2.54	-3.05	-5.04	-5.70	-7.47	-6.75	-8.83

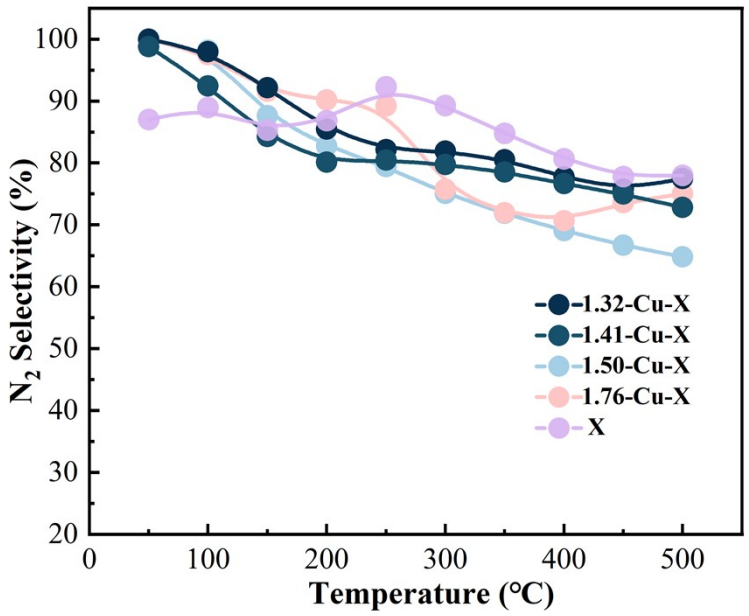

Fig. S1. N_2 selectivity of catalysts as a function of reaction temperature.

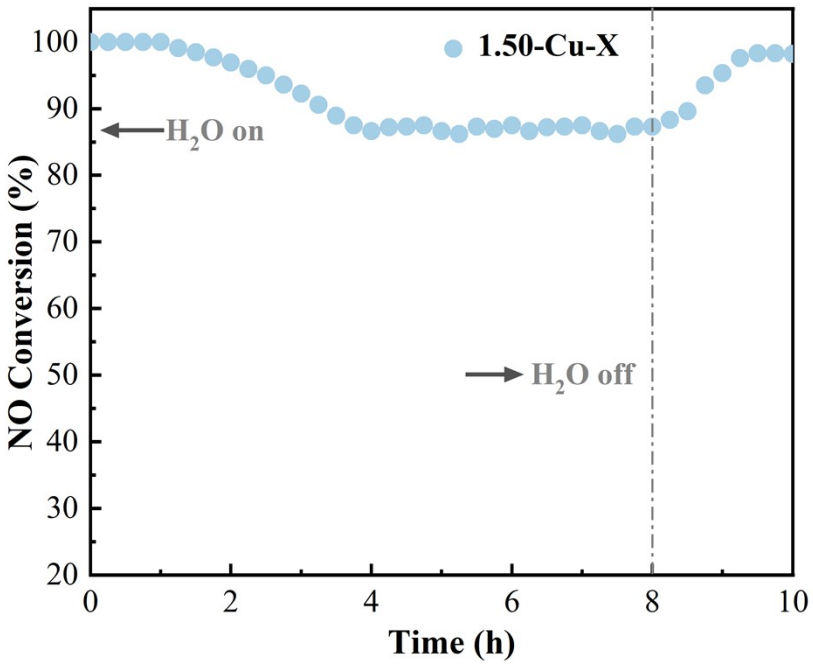

Fig. S2. NO conversion of 1.50-Cu-X catalyst as a function of reaction temperature in the presence of H_2O.

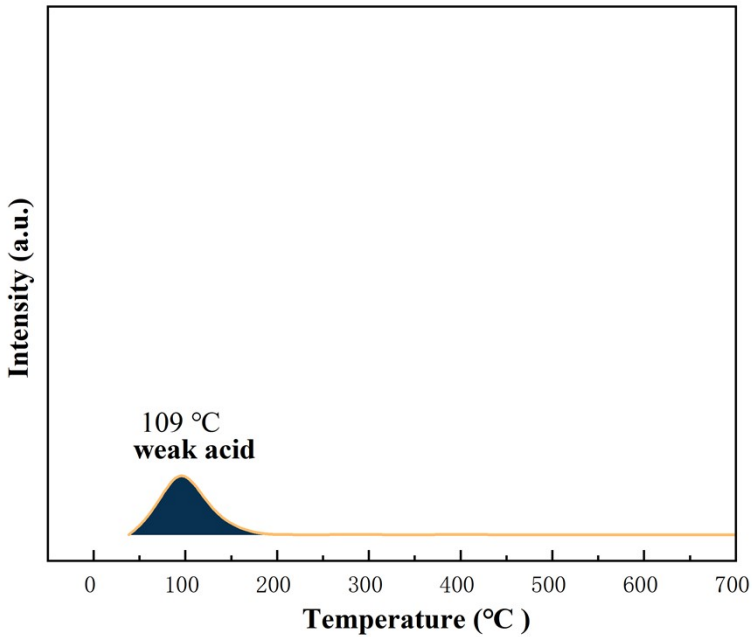

Fig. S3. NH_3-TPD profile of X zeolite.

Notes and references

1. G. Hu, S. Rohani, X. Jiang, J. Li, Q. Liu and W. Liu, ACS Sustainable Chem. Eng., 2021, **9**, 13963-13971.