Supplementary Information for

Judicious design of Cu-SSZ-39@ZSM-5 core-shell architectural catalyst for elevated hydrothermal stability in NH3-SCR reaction

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Experimental Section

Materials

The 3,5-dimethylpiperidine, methanol (CH_3OH), Methyl iodide (CH_3I), $KHCO_3$, chloroform, ether, triethylene tetramine (TETA), $Cu(NO_3)_2 \cdot 3H_2O$ were all procured from Shanghai Titan Technology Co., LTD, China. The $(NH_4)_2SO_4$; Tetrapropylammonium hydroxide solution (TPAOH); Tetraethyl orthosilicaite (TEOS); Poly(diallyldimethylammonium chloride) solution (PDDA) were all procured from Meryer (Shanghai) Chemical Technology Co., LTD, China. The silica sol and sodium silicate were purchased from Zhejiang Yuda Chemical Co., LTD, China. The aluminum source was purchased from Shandong Hefa Environmental Protection Technology Co., LTD, China. All chemicals were of analytical grade and used without further purification. De-ionized water (H_2O) was obtained by reversed osmosis followed by ion-exchange and filtration.

Synthesis of $DMDMP^+$ template

In a typical preparation, 10 g 3,5-dimethylpiperidine and 20 g $KHCO_3$ were dissolved in 150 mL CH_3OH. Then, 60 mL CH_3I were added, and this mixture was kept with magnetic stirring for 0.5 h. After this period, the mixture was transferred to a Teflon-lined stainless steel autoclave at 338 K for 120 h. The mixture was filtered to remove solid, and the iodide salt was precipitated with ether after washing several times with chloroform. The iodide salt was converted into hydroxide salt after treatment with hydroxyl anion-exchange resin. The hydroxide salt was dissolved in H_2O to form a 20% solution, and was denoted as $DMDMP^+$ template.

Synthesis of Cu-SSZ-39

The Cu-SSZ-39 catalyst was synthesized by a dual-template-assisted in situ Cu-loading method. The detailed synthesis procedure was as follows: First, an aqueous solution of triethylenetetramine (TETA) was added to a $Cu(NO_3)_2 \cdot 3H_2O$ solution and thoroughly mixed to form a stable Cu-amine complex (Cu-TETA) solution.

Subsequently, the Cu-TETA solution was added to a mixed system containing silica sol, sodium silicate, an aluminum source, $DMDMP^+$ as the template, and deionized water, with a molar ratio of n(Cu-TETA) : n(SiO_2) : n(Na_2O) : n($DMDMP^+$) : n(H_2O) : n(Al_2O_3) = 1.6 : 50 : 12 : 8 : 2160 : 1. The resulting suspension was transferred into a Teflon-lined stainless-steel autoclave and crystallized at 180 ℃ for 96 h. The obtained solid was ion-exchanged twice with 1 mol/L $(NH_4)_2SO_4$ solution (liquid-to-solid ratio 8 : 1) at 80 ℃, followed by calcination at 500 ℃ for 7 h to remove organic species, yielding the Cu-SSZ-39 catalyst.

For comparison, the H-SSZ-39 catalyst was prepared by a conventional solvent-free hydrothermal method. The chemical composition of the reaction mixture was 96.66 SiO_2 : 1 Al_2O_3 : 12.99 Na_2O : 1348.44 H_2O : 31 $DMDMP^+$. Initially, predetermined amounts of Na_2SiO_3, $DMDMP^+$, silica sol, aluminum source, and seed crystals were sequentially added and stirred at room temperature for 5 h to obtain a homogeneous gel. Subsequently, the resulting gel was transferred into a 250 mL Teflon-lined stainless-steel autoclave and crystallized at 160 ℃ for 24 h. The obtained solid product was washed with deionized water and centrifuged until neutral, followed by drying at 90 ℃ and calcination at 600 ℃ for 13 h to yield Na-SSZ-39. The as-prepared Na-SSZ-39 was ion-exchanged with ammonium ions to obtain H-SSZ-39.

Synthesis of Core-shell catalyst

The Cu-SSZ-39@ZSM-5 catalysts with different ZSM-5 shell thicknesses were prepared via a self-assembly method, and the detailed procedure is as follows. 1 g Cu-SSZ-39 zeolite was added to 100 mL of PDDA solution (7 g/L) for cationic modification, stirred at 70 ℃ for 20 min, and the resulting functionalized particles were centrifuged, washed twice with deionized water, and dried overnight at 80 ℃. Subsequently, 1 g of the surface-functionalized core particles was dispersed in an aqueous 25 wt.% Tetrapropylammonium hydroxide (TPAOH) solution and stirred for 5 h, followed by the addition of Tetraethyl orthosilicate (TEOS) and further stirring for 2 h. The molar ratios of the synthesis components were x TPAOH : y TEOS : 2230 H_2O, where x = 1.5, 3, or 4.5 and y = 12.5, 25, or 37.5 for Cu39@Z5-1, Cu39@Z5-2,

and Cu39@Z5-3, respectively. As an example, the precursor solution for the Cu39@Z5-1 shell consisted of 0.61 g TPAOH, 5.19 g TEOS, and 80 g deionized water. The resulting sol was then transferred into a Teflon-lined stainless-steel autoclave and crystallized at 200 ℃ for 2 h. Finally, the obtained particles were collected by centrifugation, washed with deionized water, dried in air at 90 ℃, and calcined at 550 ℃ for 6 h to obtain Cu39@Z5-1, Cu39@Z5-2, and Cu39@Z5-3 catalysts.

Synthesis of $DMDMP^+$ template, H-SSZ-39, Cu-SSZ-39, and Silicalite-1 is listed in the supplementary information.

Synthesis of silicalite-1

Silicalite-1 zeolite was synthesized under the same synthesis conditions. TEOS, TPAOH, and H_2O were mixed at a molar ratio of 3 SiO_2 : 25 TPAOH : 230 H_2O, stirred for 1 h, and then transferred into a Teflon-lined stainless-steel autoclave for crystallization at 200 ℃ for 1 h. The obtained product was centrifuged, washed with distilled water, and calcined at 550 ℃ for 6 h.

Catalysts characterization

X-ray diffraction (XRD) patterns were performed on a Bruker D8X diffractometer equipped with Cu Kα radiation at a scanning rate of 10°/min over the 2θ range of 5~60° to confirm zeolite crystallinity. The obtained diffraction patterns were compared with JCPDS cards to identify the zeolite topology and crystalline phases.

Surface morphology and elemental distribution were examined by a dual-beam focused ion beam scanning electron microscope (FIB-SEM, Crossbeam 350). All samples were sputter-coated with a thin layer of gold prior to FIB-SEM analysis.

High-resolution transmission electron microscopy (HRTEM) observations were carried out on a Thermo Fisher Talos F200X, and energy-dispersive X-ray spectroscopy (EDS) was used to analyze surface elemental composition. Prior to HRTEM/EDS measurements, all samples were sonicated in ethanol for 1 h.

The chemical composition was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using an Agilent 5800 spectrometer.

Specific surface areas were measured at liquid-nitrogen temperature by the Brunauer-Emmett-Teller (BET) method on a Micromeritics ASAP 2020 analyzer. Pore-size distributions, surface areas, and pore volumes were calculated by the BJH, BET, and t-plot methods, respectively (measurement conditions: 77 K N_2 adsorption; random slit pore model). All zeolite samples were degassed under vacuum at 200 ℃ for 6 h prior to analysis to remove moisture and adsorbed impurities.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific K-Alpha spectrometer under ultra-high vacuum (UHV) using a monochromated Al Kα source; Binding energies were calibrated using the C 1s peak (C-C) at 284.8 eV arising from adventitious carbon on the sample surface.

Diffuse reflectance UV-Vis spectra (UV-Vis DRS) were recorded on a Shimadzu UV-3600 UV-Vis spectrophotometer. Spectra were collected in the 200~800 nm range with $BaSO_4$ as the reflectance standard.

Hydrogen temperature-programmed reduction (H_2-TPR) was performed on an automated chemisorption analyzer (Micromeritics ChemiSorb). In a typical experiment, 150 mg of catalyst was placed in a quartz reactor and pretreated in an Ar flow at 300 ℃ for 1 h. After cooling to room temperature under Ar, the gas was switched to a 10% H_2/Ar mixture, and the sample was heated from room temperature to 800 ℃ at a rate of 10 ℃/min. Hydrogen consumption during reduction was continuously monitored using a thermal conductivity detector (TCD).

Temperature-programmed desorption of NH_3 (NH_3-TPD) was conducted on the same analyzer using 150 mg of sample. The catalyst was first pretreated in Ar at 200 ℃ for 0.5 h, then cooled to 50 ℃ for NH_3 adsorption for 1 h. After saturation, the sample was purged with Ar for 0.5 h to remove physisorbed NH_3. Finally, the desorption was carried out by heating from 50 ℃ to 800 ℃ at 10 ℃/min under Ar flow, and the desorption profile was recorded.

Electron paramagnetic resonance (EPR) spectra were collected on a Bruker EMXplus-9.5/12 spectrometer operating in the X-band at 100 K. For dehydration, 15 mg of fresh sample was placed in a quartz tube and pretreated under dry N_2 at 550 ℃ for 3 h, followed by sealing for measurement. The low measurement temperature (100

K) was chosen to minimize signal broadening and loss caused by dipolar coupling between Cu ions.

Thermogravimetric analysis (TGA) was performed on a STA 449 F5 thermal analyzer under flowing N_2 from 30 to 800 ℃ at a heating rate of 10 ℃/min.

Catalyst activity evaluation

The catalytic performance for the NH_3-SCR reaction was evaluated in a fixed-bed reactor equipped with a programmable temperature controller. For each test, 550 mg of catalyst (20-40 mesh) was loaded into the reactor, and the total gas flow rate was maintained at 1 L/min. The feed gas composition was 500 ppm NO, 500 ppm NH_3, 10% H_2O, 5% O_2, and balance N_2, corresponding to a gas hourly space velocity (GHSV) of 60,000 h^{-1}. This GHSV was deliberately selected as a representative laboratory-scale condition that is widely adopted in the literature for Cu-based zeolite SCR catalysts.

During the reaction, the temperature was increased from 100 ℃ to 600 ℃, and at each target temperature, the reaction was maintained for at least 45 min to ensure steady-state conditions. Water vapor in the outlet stream was condensed using a GC 8003 condenser (compression cooling principle). The concentrations of NO in the inlet and outlet gases were measured using an S-ANALYZER 200V 5.0 gas analyzer (SIGAS, Jiangsu, China).

The NO conversion was calculated according to the following equation:

$$NO\ conversion\ (\%) = \frac{NO_{inlet} - NO_{outlet}}{NO_{inlet}} \times 100\% \qquad (2\text{-}1)$$

Hydrothermal aging was also performed in the fixed-bed reactor. Fresh samples were treated at 850 ℃ for 12 h in a flow of N_2 containing 10% H_2O. The aged samples were denoted as Cu-SSZ-39-HTA and Cu39@Z5-HTA.

Supplementary Figures

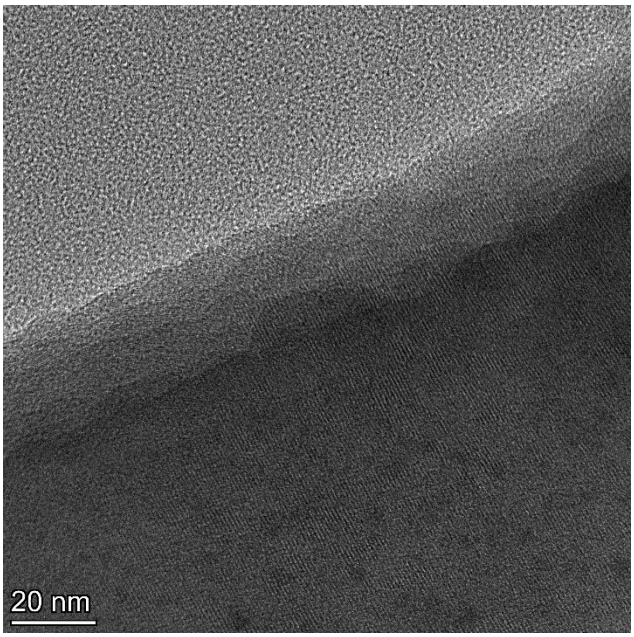

Fig.S1. HR-TEM images of Cu39@Z5-1.

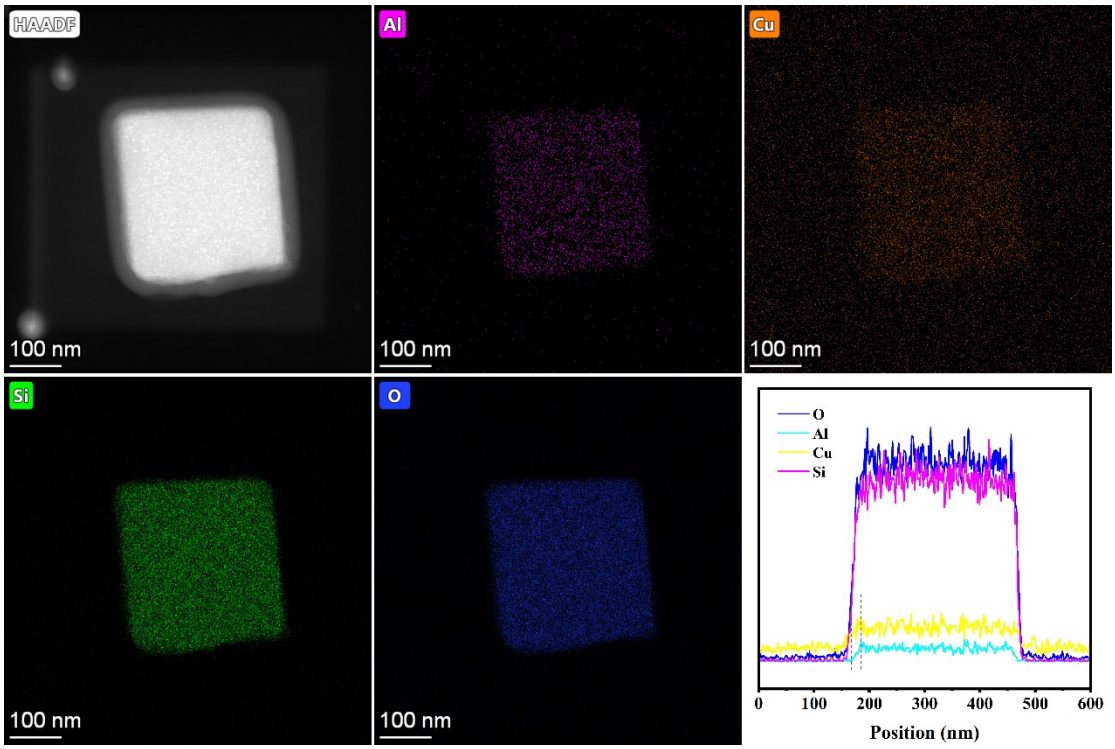

Fig.S2. HAADF, elementary line-scan spectra and HAADF-STEM element distribute on mapping of Cu-SSZ-39@ZSM-5-1.

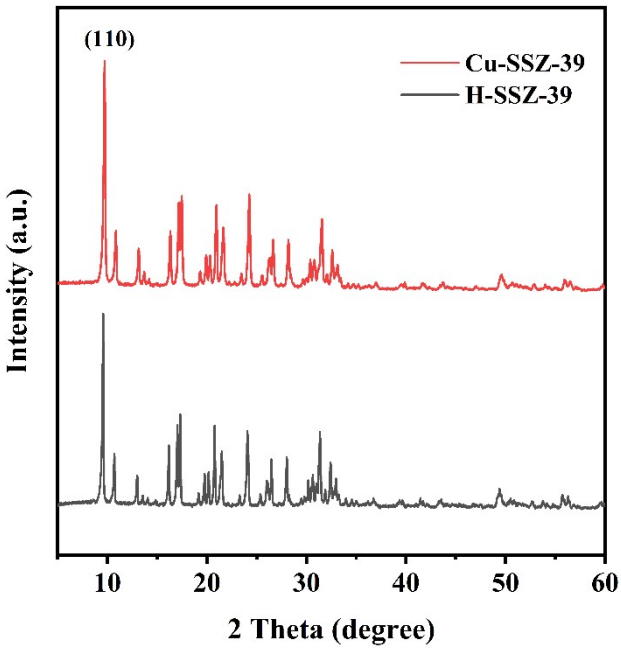

Fig.S3. XRD patterns of Cu-SSZ-39 catalyst and solvent-free hydrothermal H-SSZ-39 zeolite.

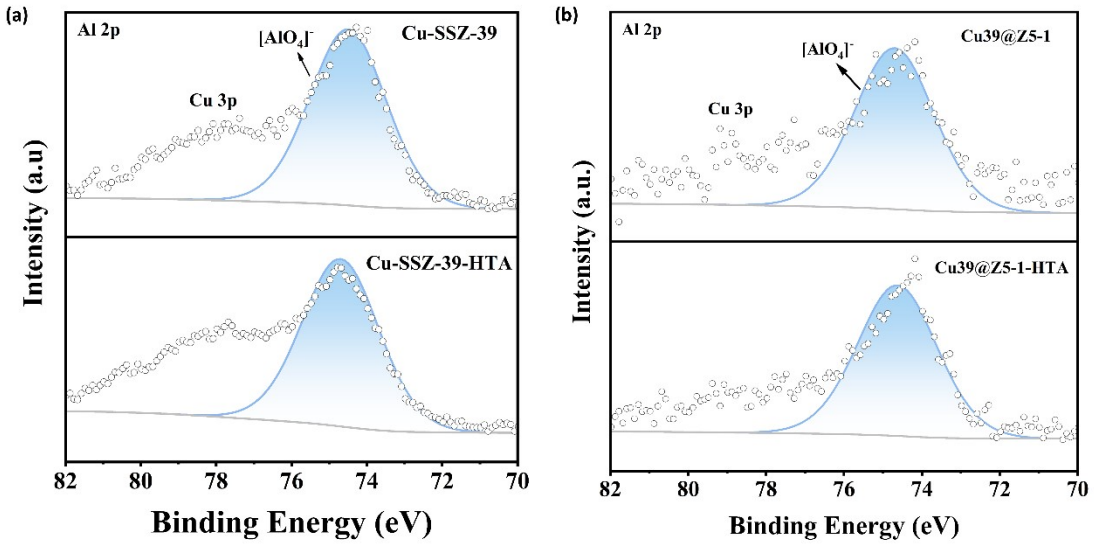

Fig.S4. XPS spectra of Al 2p (a) and Si 2p (b) for Cu-SSZ-39 and Cu39@Z5-1.

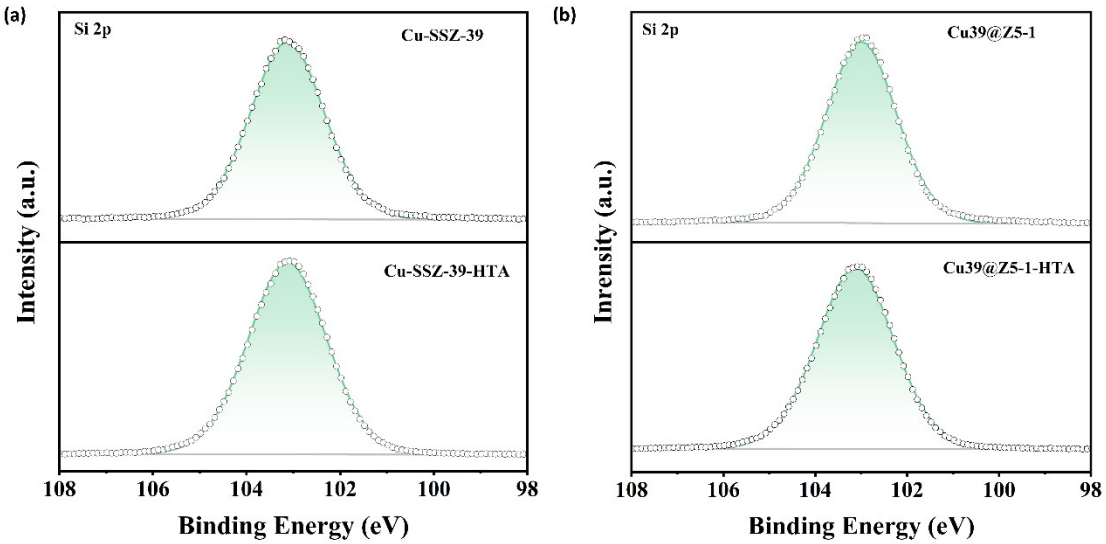

Fig.S5. XPS spectra of Si 2p (a) and Si 2p (b) for Cu-SSZ-39 and Cu39@Z5-1.

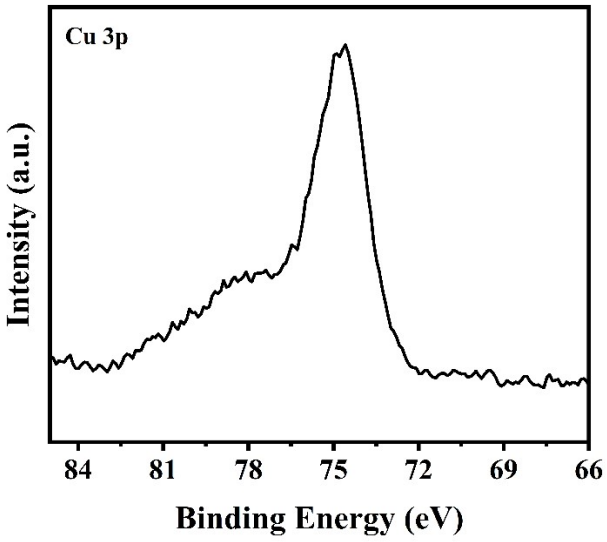

Fig.S6. XPS spectra of Cu 3p of Cu-SSZ-39.

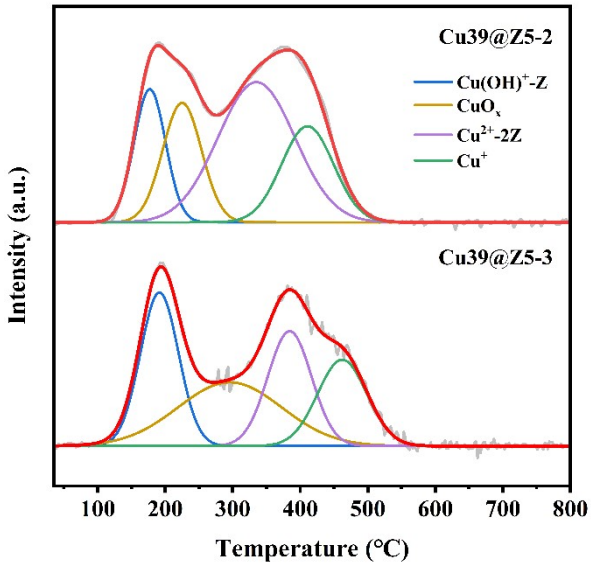

Fig. S7. H_2-TPR profiles of Cu39@Z5-2 and Cu39@Z5-3.

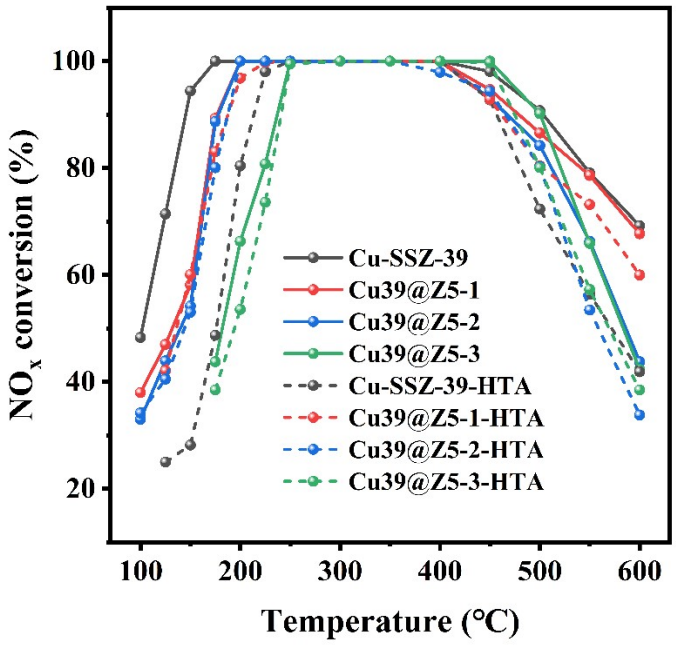

Fig. S8. NO_x conversion of different samples before and after hydrothermal aging.

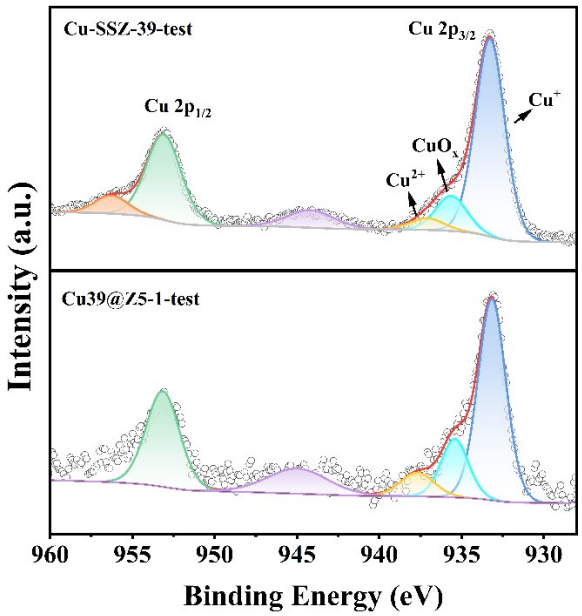

Fig. S9. Cu 2p XPS of Cu-SSZ-39 and Cu39@Z5-1 after test.

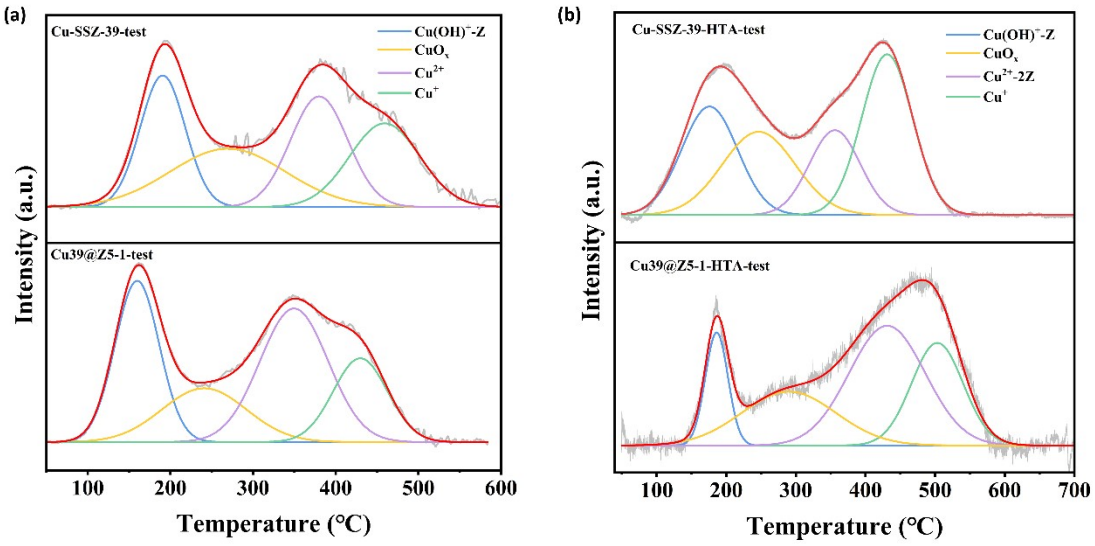

Fig. S10. H_2-TPR of Cu-SSZ-39 and Cu39@Z5-1 (a) before and (b) after test.

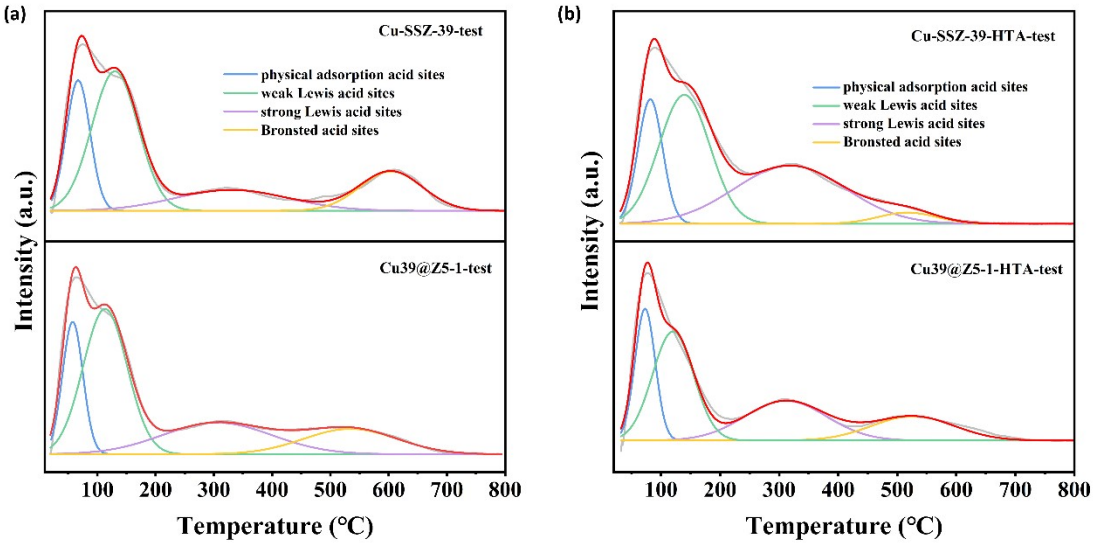

Fig. S11. NH_3-TPD of Cu-SSZ-39 and Cu39@Z5-1 (a) before and (b) after test.

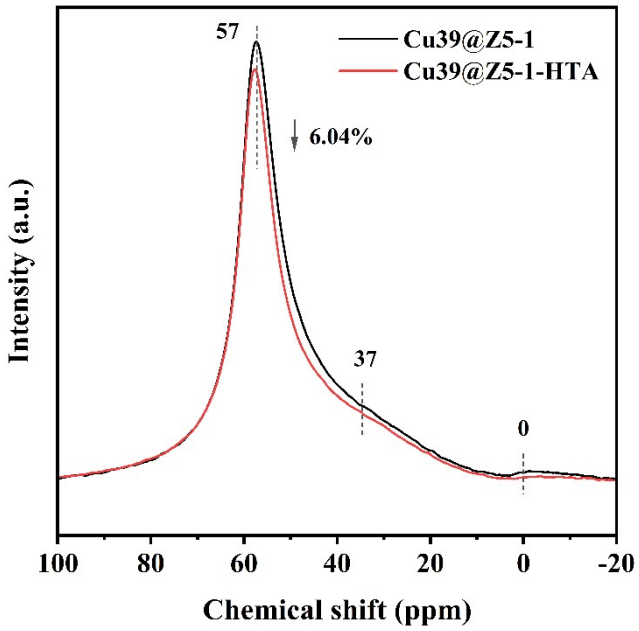

Fig. S12. ^{27}Al MAS NMR spectra of Cu39@Z5-1 (a) before and (b) after test.

Table S1 Atomic percentage (%) of different samples obtained by XPS analysis.

Sample	Si (%)	Al (%)	Cu (%)	Si/Al
Cu-SSZ-39	88.14	9.22	2.64	9.55
Cu39@Z5-1	92.9	5.53	1.57	16.80

Cu39@Z5-2	94.4	4.55	1.05	20.74
Cu39@Z5-3	96.04	3.53	0.43	27.02

Table. S2 The integrated area of the $[AlO_4]^-$ corresponding peak in the Al 2p XPS spectrum.

Sample	Area (P) CPS (eV)
Cu-SSZ-39	11131.53
Cu-SSZ-39-HTA	9121.63
Cu39@Z5-1	1618.19
Cu39@Z5-1-HTA	1537.73

Table. S3 The integrated area of the SiO_4 corresponding peak in the Si 2p XPS spectrum.

Sample	Area (P) CPS (eV)
Cu-SSZ-39	15279.10
Cu-SSZ-39-HTA	142558.47
Cu39@Z5-1	69983.69
Cu39@Z5-1-HTA	69521.44