Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

One-pot synthesis of Na^+-free Cu-SSZ-13 and its application in the NH_3-SCR reaction

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Experimental Section

Materials

The chemical regents used for zeolite synthesis: *N,N,N*-trimethyl-l-adamant ammonium hydroxide (TMAdaOH, 25wt%), tetramethylammonium hydroxide (TMAOH, 25wt%); diethylamine (DEA, 99%), ethylenediamine (EDA, 99%), butylamine (BA, 99.5%), piprazine hexahydrate (PIP, 98%), tetraethylenepentamine (TEPA, 90%), pseudoboehmite (Al_2O_3, 66.5wt%), silica gel (99 wt%), $CuSO_4{\cdot}5H_2O$ (99%), aqueous NH_3 (25wt%).

Synthesis of Na^+-free SSZ-13 in the presence of TMAdaOH and TMAOH (named SSZ-13_{TMAOH})

The molar composition of the synthesis gel was 30 SiO_2:1 Al_2O_3:3 TMAOH:600 H_2O:1.5 TMAdaOH. The synthesis procedure was as follows. Pseudoboehmite was added to an aqueous solution containing TMAdaOH, TMAOH and deionized water under stirring. After a clear solution is obtained (about 10 minutes), silica gel and seeds (commercial SSZ-13 in protonated form, Figure S1) were further added and stirred for 12 hours. The final gel was transferred to a Teflon-lined stainless steel autoclave and crystallized at 175 °C for a desired time. The product was collected by filtration, washed three times with deionized water, and dried at 100 °C for 24 hours. The as-synthesized sample was calcined in air at 600 °C for 5 h to obtain the H-SSZ-13.

Synthesis of Na^+-free SSZ-13 in the presence of TMAdaOH and DEA (named SSZ-13_{DEA})

The synthesis procedure was the same as above, except DEA in place of TMAOH. Moreover, calcined Na^+-free SSZ-13_{TMAOH} was used as the seeds. The final gel composition was 30 SiO_2:1 Al_2O_3:4 DEA:600 H_2O:1.5 TMAdaOH

Synthesis of Na^+-free SSZ-13 in the presence of TMAdaOH and EDA (named SSZ-13_{EDA})

The synthesis procedure was the same as that of SSZ-13_{DEA}, except EDA in place of DEA. The final gel composition was 30 SiO_2:1 Al_2O_3:4 EDA:600 H_2O:1.5 TMAdaOH.

Synthesis of Na^+-free SSZ-13 in the presence of TMAdaOH and BA (named SSZ-13_{BA})

The synthesis procedure was the same as that of SSZ-13_{DEA}, except BA in place of DEA. The final gel composition was 30 SiO_2:1 Al_2O_3:4 BA: 600 H_2O:1.5 TMAdaOH.

Synthesis of Na^+-free SSZ-13 in the presence of TMAdaOH and PIP (named SSZ-13$_{PIP}$)

The synthesis procedure was the same as that of SSZ-13$_{DEA}$, except PIP in place of DEA. The final gel composition was 30 SiO_2:1 Al_2O_3:5 PIP: 600 H_2O:1.5 TMAdaOH.

Synthesis of Na^+-free SSZ-13 in the presence of TMAdaOH and NH_3 (aq) (named SSZ-13$_{NH_3}$)

The synthesis procedure was the same as that of SSZ-13$_{DEA}$, except NH_3 (aq) in place of DEA. The final gel composition was 30 SiO_2:1 Al_2O_3:5 NH_3: 600 H_2O:1.5 TMAdaOH.

Synthesis of Na^+-free CuSSZ-13 zeolites

Pseudoboehmite was added to an aqueous solution containing TMAdaOH, TMAOH and deionized water under stirring. After a clear solution was obtained (about 10 minutes), silica gel and seeds (commercial SSZ-13 in calcined form) were added and stirred for 2 hours. Subsequently, aqueous solution of Cu-TEPA complex, which was prepared by mixing a 20 wt% aqueous solution of $CuSO_4·5H_2O$ with the required amount of TEPA, was added into the gel. After being stirred for 12 hours, the final gel was transferred to a Teflon-lined stainless steel autoclave and crystallized at 175 °C for a desired time. The product was collected by filtration, washed three times with deionized water, and dried at 100 °C for 24 hours. The as-synthesized sample was calcined in air at 600 °C for 5 h to remove the organics.

Characterization

The powder X-ray diffraction (PXRD) data used for the phase identification were collected on a PANalytical X'Pert PRO X-ray diffract meter using the Cu Kα radiation ($\lambda = 1.54059$ Å), operating at 40 kV and 40 mA. The inorganic elemental compositions of the solid samples were measured with Philips Magix-601 X-ray fluorescence (XRF) spectrometer. The crystal morphology was observed using a scanning electron microscope (Hitachi SU8020). The textural properties of the calcined samples were measured by N_2 sorption at -196 °C on a Micromeritics ASAP2020 volumetric adsorption analyzer. Prior to the measurement, the sample was degassed at 350 °C under vacuum for 4 h. The total surface area was evaluated based on the BET equation. The micropore surface area and micropore volume were calculated using the t-plot method.

Thermal gravimetric analyses (TG-DSC) were carried out on NETZSCH ATS 449 F3 analyzer from room temperature to 1000 °C with a heating rate of 10 °C min^{-1} in an air flow of 20 mL min^{-1}.

All the solid state NMR experiments were performed using a Varian Infinity-plus 400 spectrometer equipped with a 9.4 T wide-bore magnet. Chemical shifts of ^{29}Si and ^{27}Al were referenced to kaolinite at -91.5 ppm and $(NH_4)Al(SO_4)_2·2H_2O$ at -0.4 ppm respectively. The spinning rate is 10 kHz. The liquid ^{13}C NMR analysis was performed on Bruker Avance III 400 using D_2O as deuterated reagent. Before NMR analysis, the as-synthesized sample was dissolved by 40 wt% HF acid (solid/liquid ≈ 0.1g/1mL), and the liquids were analyzed as they were.

NH_3-TPD experiments were carried out in Micromeritics Autochem II 2920 device. In the tests, 100 mg of calcined sample particles (40-60 mesh) were loaded into a U-shaped quartz tube and pretreated in He flow (30 mL/min) at 650 °C for 1 h to remove any impurities. Then, the mixture of 2% NH_3 and 98 % He was treated with a flow rate of 30 mL/min at 120 °C, and the adsorbed NH_3 (60 min) was used. Subsequently, He

(30 mL/min) was purified by a filter for 30 min to remove weakly adsorbed NH_3 molecules. NH_3 desorption measurement was conducted at 100-600 °C (10°C /min) under He flow (30 mL/min).

EPR measurements were performed on a Bruker A200 spectrometer. The samples were sealed in a nuclear magnetic tube and then purged with dry N_2 at ambient temperature for 1 h. During the spectral collection, the microwave power was 2 mW, and the frequency was 9.2 GHz. The sweep width was 2000 G, and the sweep time was 84 s, modulated at 100 kHz with a 2 G amplitude. A time constant of 41 ms was used. The spectra were collected at 102 K. For the quantification of isolated Cu^{2+} species, copper sulfate solution was used as a standard (at 102 K).

Temperature-programmed reduction by hydrogen (H_2-TPR) was performed on an AUTOCHEM II instrument from Micromeritics. In the TPR experiments, 150 mg calcined sample particles (40-60 mesh) were pretreated in Ar flow (30 mL/ min) at 80 °C for 1h to remove impurities. The H_2-TPR experiments were carried out at a 10% H_2 and 90% Ar flow (30 mL/min) from 80 °C to 900 °C at a heating rate of 10 °C/min, and the consumption of H_2 was determined by thermal conductivity detector (TCD).

Catalytic experiments

NH_3-SCR reaction was carried out in a fixed-bed quartz reactor. For each test, 0.30 g of Cu-SSZ-13 and 0.24 g of quartz beads (60-80 mesh) were blended and put into the reactor. The catalyst was activated in N_2 at 550 °C for 2 h prior to activity test. The feed gas contained NO (500 ppm), NH_3 (500 ppm), H_2O (6.4%), O_2 (6.4%) and N_2. The gas hourly space velocity (GHSV) was controlled as 100,000 h^{-1}. The gas compositions (NO, NO_2 and N_2O) were continually monitored by an FTIR spectrometer (Bruker). The FTIR spectra were collected after the reaction reaching a steady state (about 40 min). The formula shown below was used to determine the NOx conversion:

$$\text{NO conversion (\%)}=\frac{\left([NO]_{in}-[NO]_{out}-[NO_2]_{out}-2[N_2O]_{out}\right)}{[NO]_{in}}\times 100\%$$

High-temperature hydrothermal aging (HTA) treatment

HTA was performed at 750 °C for 16 h in the presence of 12.5% H_2O in air. The GHSV was controlled as 90,000 h^{-1}.

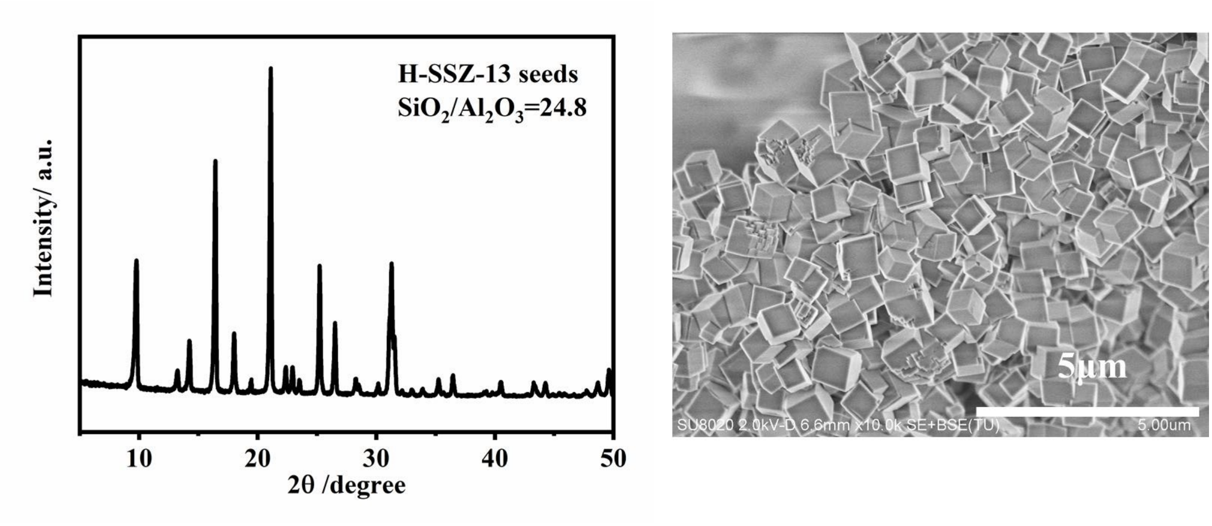

Figure S1 The XRD pattern and SEM image of the H-SSZ-13 seeds (commercial sample)

Table S1 Starting gel compositions, crystallization time and product SiO_2/Al_2O_3 ratios of Na^+-free SSZ-13

Sample [a]	**m SR**		**Time (h)**	**SiO_2/Al_2O_3**
SSZ-13$_{TMAOH}$	m=3	SR: TMAOH	9	24.8
SSZ-13$_{EDA}$	m=4	SR: EDA	108	27.3
SSZ-13$_{BA}$	m=4	SR: BA	72	24.8
SSZ-13$_{DEA}$	m=4	SR: DEA	108	24.0
SSZ-13$_{PIP}$	m=5	SR: PIP	108	25.1
SSZ-13$_{NH3}$	m=5	SR: NH_3 (aq)	72	26

[a] All samples were synthesized with the initial gel of 30 SiO_2:1 Al_2O_3:m SR:600 H_2O:1.5 TMAdaOH (10 wt% seeds addition) at 175 °C.

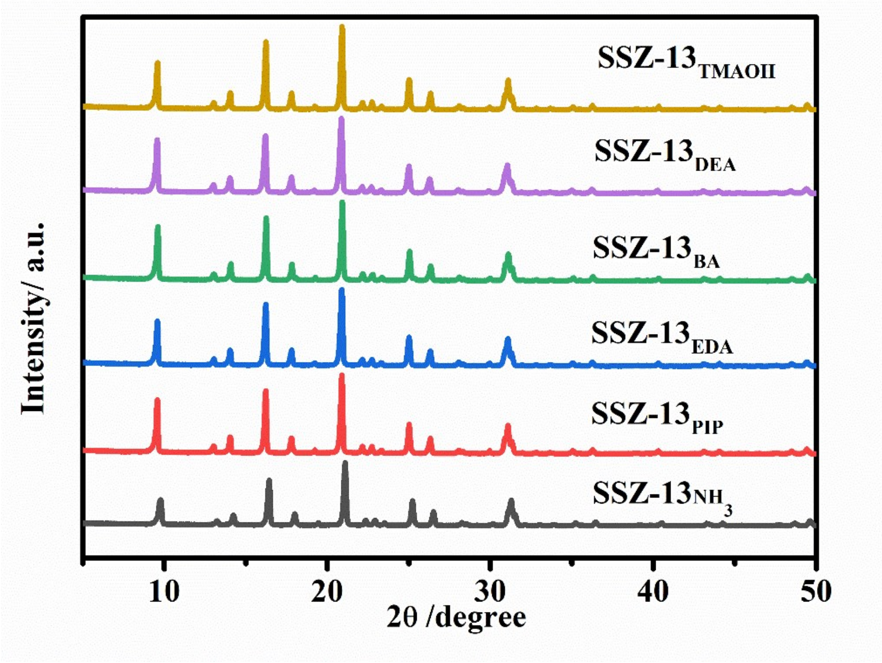

Figure S2 XRD patterns of the as-synthesized Na^+-free SSZ-13.

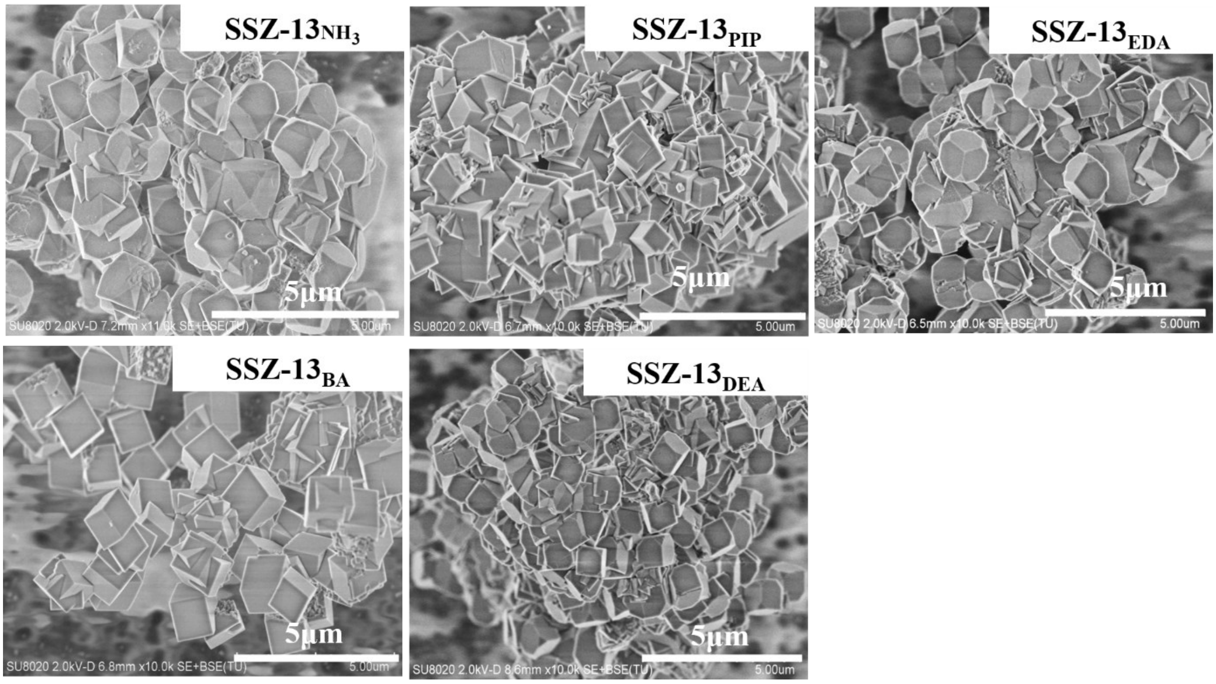

Figure S3 SEM images of the as-synthesized Na^+-free SSZ-13 zeolites.

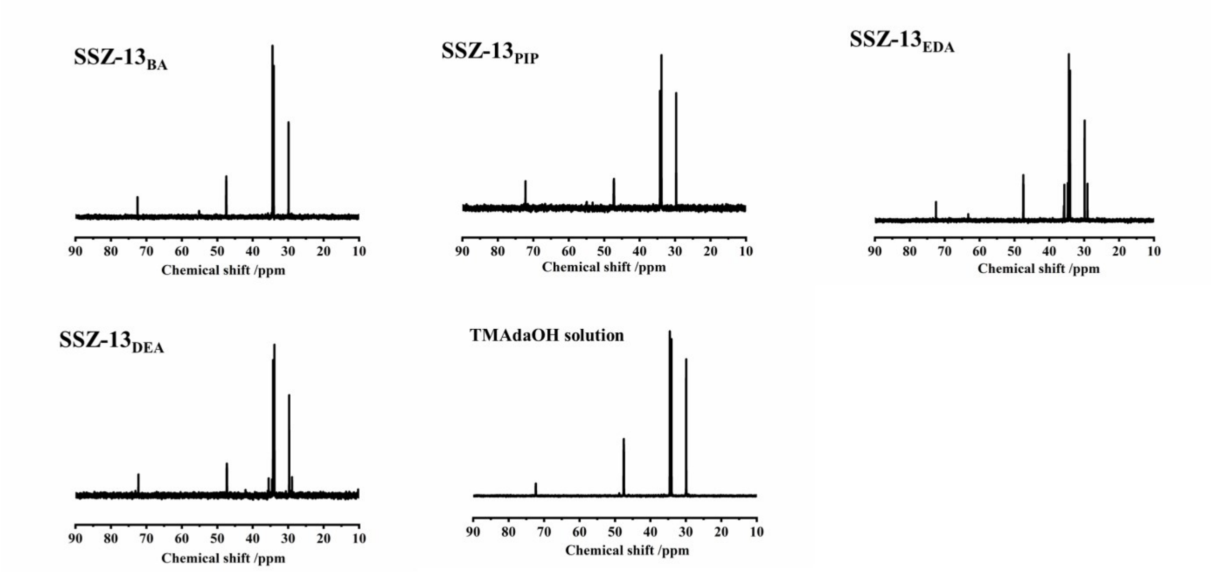

Figure S4 Liquid ^{13}C NMR spectra of the as-synthesized samples dissolved in HF solution.

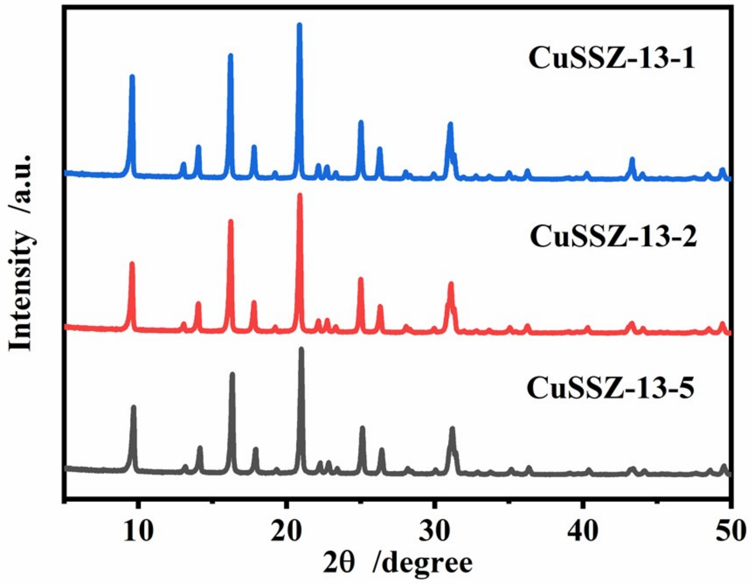

Figure S5 XRD patterns of the as-synthesized Na$^+$-free CuSSZ-13.

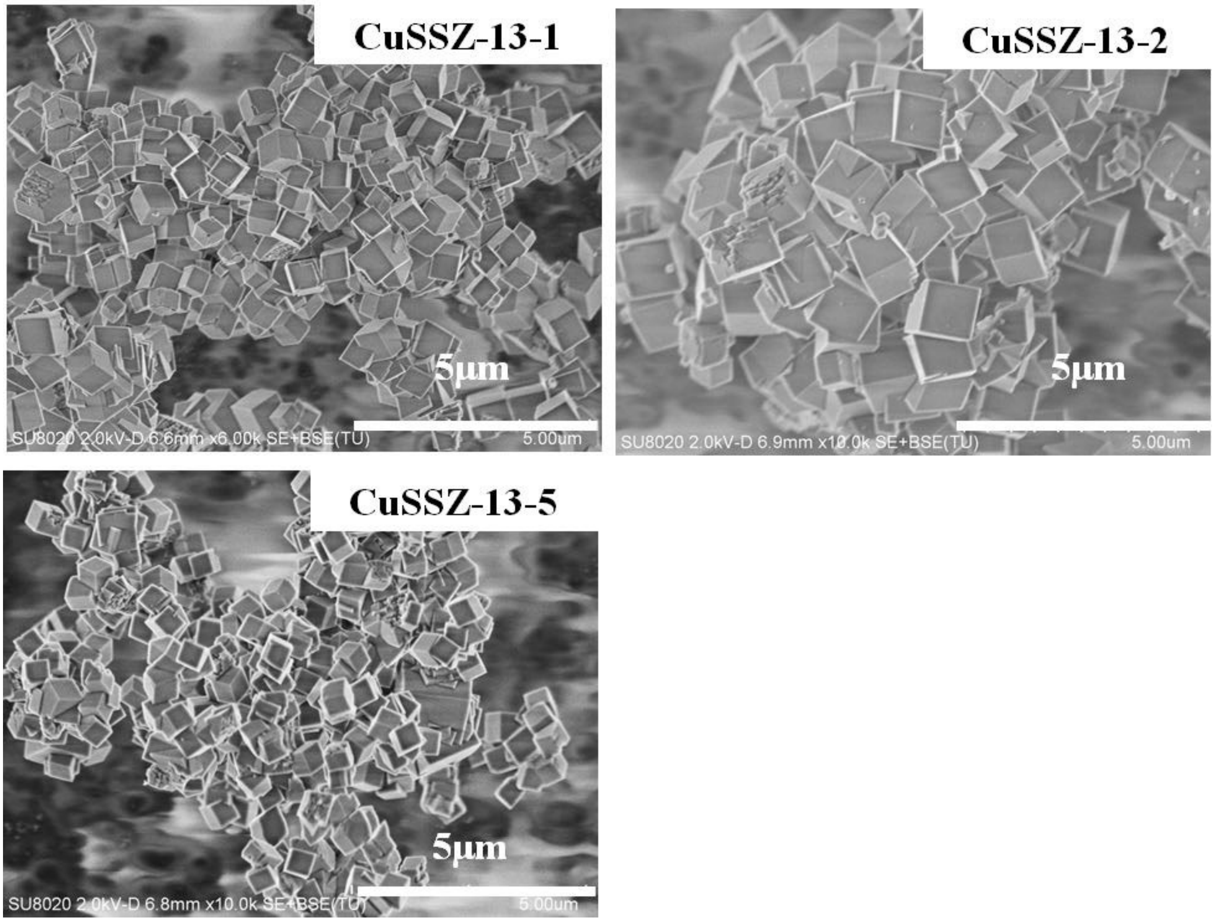

Figure S6 SEM images of the as-synthesized Na$^+$-free CuSSZ-13.

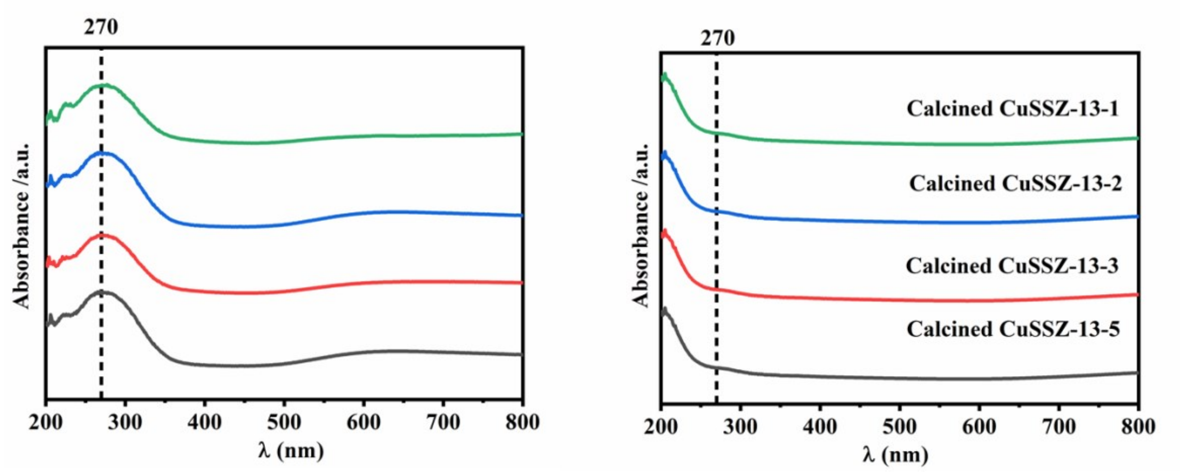

Figure S7 UV/Vis spectra of Na^+-free CuSSZ-13 before (left) and after calcination (right).

Table S2. Textural properties of Na^+-free CuSSZ-13-4

Sample	**Pore volume^a (cm^3 g^{-1})^a**			**Surface area^b (m^2 g^{-1})^b**		
	V_{total}	V_{micro}	V_{meso}	S_{total}	S_{micro}	S_{ext}
CuSSZ-13-4	0.29	0.27	0.02	603	583	20

a. V_{total} is evaluated at P/P_0=0.97; V_{micro} = t-plot micropore volume; V_{meso}= V_{total} - $V_{micro.}$

b. S_{total} : BET surface area; S_{micro}: t-plot micropore surface area; S_{ext} = S_{total} - S_{micro}.

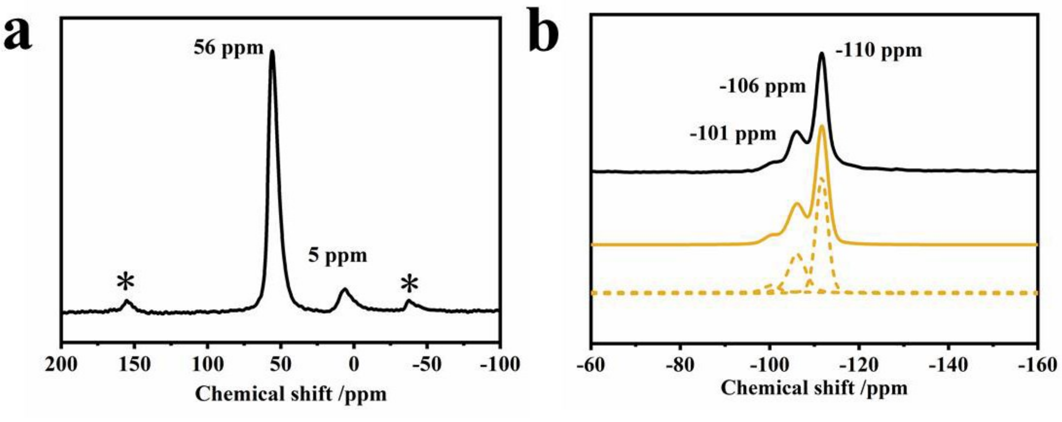

Figure S8 (a) ^{27}Al and (b) ^{29}Si MAS NMR spectra of the as-synthesized CuSSZ-13-4. * denotes spinning side band.

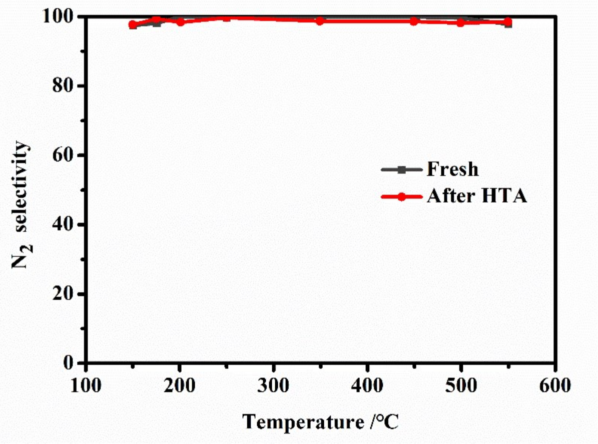

Figure S9 The N_2 selectivity over the CuSSZ-13-4 before and after hydrothermal aging treatment.

The N_2 selectivity was calculated according to the formula below:

$$N_2\,Selectivity = \left(1 - \frac{2[N_2O]}{[NO_X]in - [NO_X]out + [NH_3]in - [NH_3]out}\right) \times 100\%$$

Since NH_3 has not been monitored in real-time, the amount of NH_3 is considered equal to NO.

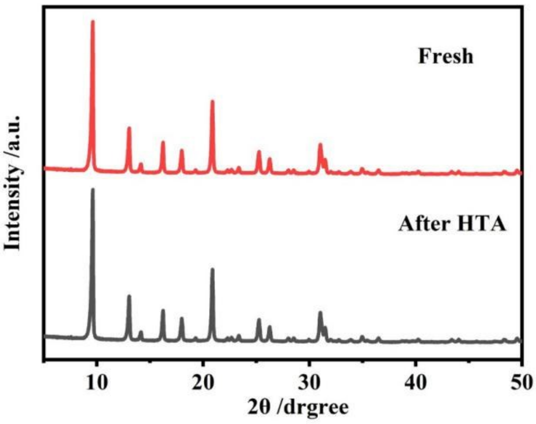

Figure S10 XRD patterns of calcined CuSSZ-13-4 before and after hydrothermal aging treatment.

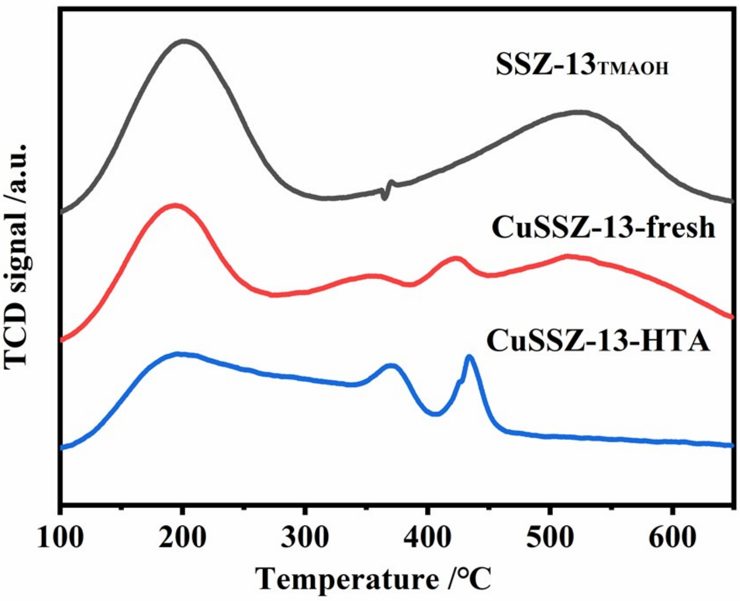

Figure S11 NH_3-TPD curves of calcined SSZ-13_{TMAOH} and CuSSZ-13-4 before and after hydrothermal aging treatment.

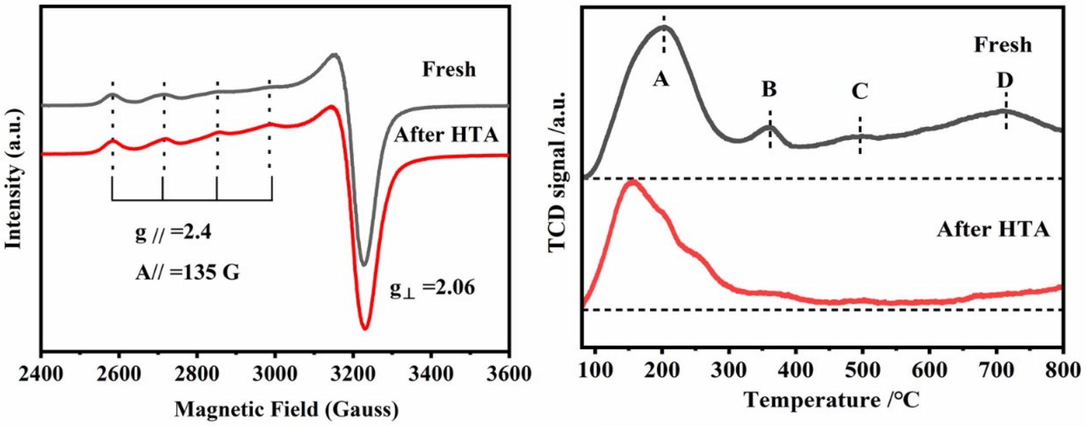

Figure S12 EPR spectra (left) and H_2-TPR profiles (right) of the calcined CuSSZ-13-4 before and after hydrothermal aging treatment.

Table S3. Isolated Cu^{2+} content of the samples by EPR analyses

Sample	Fresh (wt%)	After hydrothermal aging (wt%)
CuSSZ-13-4	2.11	2.11