

Supporting Information (SI)

Improved SO₂ tolerance of Cu-SAPO-18 by Ce-doping in the selective catalytic reduction of NO with NH₃

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Catalyst Preparation

The SAPO-18 zeolite was synthesized using *N,N*-diisopropylethylamine ($C_8H_{19}N$, DIPEA) as structure-directing agent (SDA) ²³. The molar ratio composition of Al_2O_3 : P_2O_5 : SiO_2 : DIPEA : H_2O was 1.0 : 0.9 : 0.3 : 2.0 : 50.0. The gel was sealed in a Teflon-lined stainless steel autoclave and heated at 175 °C for 5 days. After being filtered under vacuum, the obtained product was washed several times with deionized water and dried at 120 °C overnight. Then, the dried powders were calcined at 550 °C in air to remove the occluded organic species, obtaining the SAPO-18 zeolite.

Afterwards, 1.0 g of NH_4 /SAPO-18 was ion-exchanged by simultaneously adding 29 mL of $Cu(NO_3)_2$ aqueous solution (0.05 mol/L) and 29 mL of $Ce(NO_3)_3$ aqueous solution (0.005, 0.0075 or 0.01 mol/L) at 60 °C for 4 h under stirring. Then, the obtained product was filtered, washed with deionized water several times, dried in an oven at 120 °C for 12 h, and calcined in an air flow of 40 mL/min at 500 °C for 6 h, thus obtaining the Ce-Cu-SAPO-18 samples with different Ce contents.

Catalyst characterization

The crystal structures of the samples were determined on an X-ray diffractometer (XRD, X'Pert-Pro MPD, Philips, Netherlands) using $Cu\ K\alpha$ radiation, and the diffraction angle ranged from 5° to 45° at a scanning speed of 5°/min. The Cu and Ce

contents in the samples were analysed using an XRF spectrometer (XRF-1800, Shimadzu). X-ray photoelectron spectroscopy (XPS) was used to determine the Cu, and S surface compositions and binding energies of Cu 2p, and S 2s on the surface of the samples on an ESCALAB 250Xi spectrometer (Thermo Fisher, U.S.) using an Al $K\alpha$ radiation source ($h\nu = 1486.5$ eV). H_2 temperature-programmed reduction (H_2 -TPR) of the samples was carried out on the Builder PCA-1200 analyzer. Prior to H_2 -TPR experiment, 200 mg of the sample was pretreated in a 5 vol% O_2/N_2 mixture flow of 30 mL/min at 500 °C for 1 h, and subsequently cooled to room temperature (RT). The sample was then reduced in a 5 vol% H_2/N_2 mixture flow of 30 mL/min at a ramp of 10 °C/min from RT to 1000 °C. Surface morphologies of the samples were investigated by a scanning electron microscopic (SEM) equipment (SU-4800, HITACHI, Japan). Chemical compositions of the crystal phases were determined by an EDS coupled to the SEM. The in situ DRIFTS experiment was carried out on a Bruker TENSOR II spectrometer equipped with a smart collector and an MCT detector, which was cooled by liquid nitrogen. For each of the in situ DRIFTS experiments, the sample (60 mg) was placed in the sample cup of the reaction chamber that could withstand high temperatures (Harrick Praying Mantis). Prior to each experiment, the catalyst was pretreated in 14 vol% O_2/N_2 at 500 °C for 0.5 h and then cooled down to 150 °C. For the NH_3 , NO or SO_2 adsorption experiments, the sample was exposed to a 500 ppm NO + 14% vol% $O_2 + N_2$ (balance) flow of 100 mL/min, or a 500 ppm $NH_3 + N_2$ (balance) flow of 100 mL/min, or 100 ppm $SO_2 + 14\%$ vol% $O_2 + N_2$ (balance). The adsorption spectrum of each sample was obtained by

subtracting the background spectrum that was recorded by exposing the sample to a pure N₂ flow of 100 mL/min. All of the spectra were recorded by accumulating 100 scans with a resolution of 4 cm⁻¹. Thermo gravimetric and differential thermal analysis (TG-DSC) of the samples were carried out on a Netzsch thermoanalyzer STA F449 with a heating rate of 5 °C/min in an air flow of 30 mL/min.

Catalytic activity measurement

Catalytic activity of the samples was evaluated using a quartz tubular fixed-bed microreactor (i. d. = 8 mm). The NH₃-SCR reactions were carried out in the microreactor by mixing 150 mg of the catalyst with 150 mg of quartz sand. The simulated exhaust gas was composed of 500 ppm NO + 500 ppm NH₃ + 100 ppm SO₂ (when used) + 14 vol% O₂ + 5 vol% H₂O + N₂ (balance). The total gas flow rate was 300 mL/min and the gas hourly space velocity (GHSV) was about 130,000 h⁻¹. The concentration of NO was measured by a Thermo Model 42i-HL analyser.

The NO conversion was calculated according to their concentrations before and after the catalyst bed at a steady state, as shown below:

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

$$\text{N}_2 = \frac{[\text{NO}]_{\text{in}} + [\text{NH}_3]_{\text{in}} - [\text{NO}_2]_{\text{out}} - 2[\text{N}_2\text{O}]_{\text{out}}}{[\text{NO}]_{\text{in}} + [\text{NH}_3]_{\text{in}}} \times 100\%$$

Physical property

To further explain the mechanism of sulfur tolerance improvement, we measured crystal and textural properties of the fresh and sulfated samples using the XRD and BET techniques. XRD patterns of the fresh and sulfated samples are shown in Fig. S4.

The XRD peaks of all of the samples were consistent with the characteristic peaks of an AEI zeolite (JCPDS PDF# 45-0118), and no characteristic peaks of impurity phases appeared, declaring that the Cu and Ce species were well distributed in the zeolitic structure. No diffraction peaks of the sulfate species were observed in the sulfated samples, indicating that the sulfate species were mainly present in an amorphous state on the sample surface. For the Cu-SAPO-18-S sample, intensity of the XRD peaks was greatly reduced although the AEI structure was not remarkably changed, as compared with that of the fresh counterpart. The results indicate that Ce introduction played a protective role in the sulfur treatment process of the Ce-Cu-SAPO-18 sample. The BET results of the fresh and sulfated samples are listed in Table 1. Surface areas and pore volumes of the Cu-SAPO-18-S and Ce-Cu-SAPO-18-S samples decreased (as compared with those of the fresh counterparts), which were due to the fact that sulfation could cause partial blocking of some pores in the samples.

Table S1. Chemical compositions and textural properties of the Cu-SAPO-18, Ce-Cu-SAPO-18- samples.

Sample	Cu (wt%)	Ce (wt%)	Al (wt%)	P (wt%)	Si (wt%)	O (wt%)	BET surface area (m ² /g)	Micropore volume (V _{mic} , cm ³ /g)
Ce-SAPO-18	—	1.31	14.64	26.82	5.12	52.11	588	0.236
Cu-SAPO-18	1.76	—	15.40	25.95	5.19	51.70	597	0.237
Cu-SAPO-18-S ^a	-	—	-	-	-	-	567	0.209
Ce-Cu-SAPO-18	1.71	1.24	14.42	26.27	5.14	51.22	576	0.228
Ce-Cu-SAPO-18-S ^b	-	-	-	-	-	-	570	0.224

^a:The Cu-SAPO-18-S is derived from Cu-SAPO-18 treated with SO₂; ^b The Ce-Cu-SAPO-18-S is derived from Ce-Cu-SAPO-18 treated with SO₂.

Table S2. Surface element compositions of the samples obtained from the XPS spectra.

Sample	Cu 2p	S 2P
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	Isolated (mmol/g)	Cu ²⁺ (mmol/g)	CuO (mmol/g)	Cu _{surf} (mmol/g)	Cu ²⁺ /Cu molar ratio	Peak area
Cu-SAPO-18	0.025		0.182	0.207	0.121	-
Cu-SAPO-18-S	0.016		0.196	0.212	0.088	973.7
Ce-Cu-SAPO-18	0.084		0.166	0.250	0.336	-
Ce-Cu-SAPO-18-S	0.041		0.203	0.244	0.201	389.3

Table S3. H₂ consumption of the samples obtained from the H₂-TPR profiles.

Sample	H ₂ consumption (≤ 500 °C) (mmol/g)
Cu-SAPO-18	0.249
Cu-SAPO-18-S	0.155
Ce-Cu-SAPO-18	0.198
Ce-Cu-SAPO-18-S	0.175

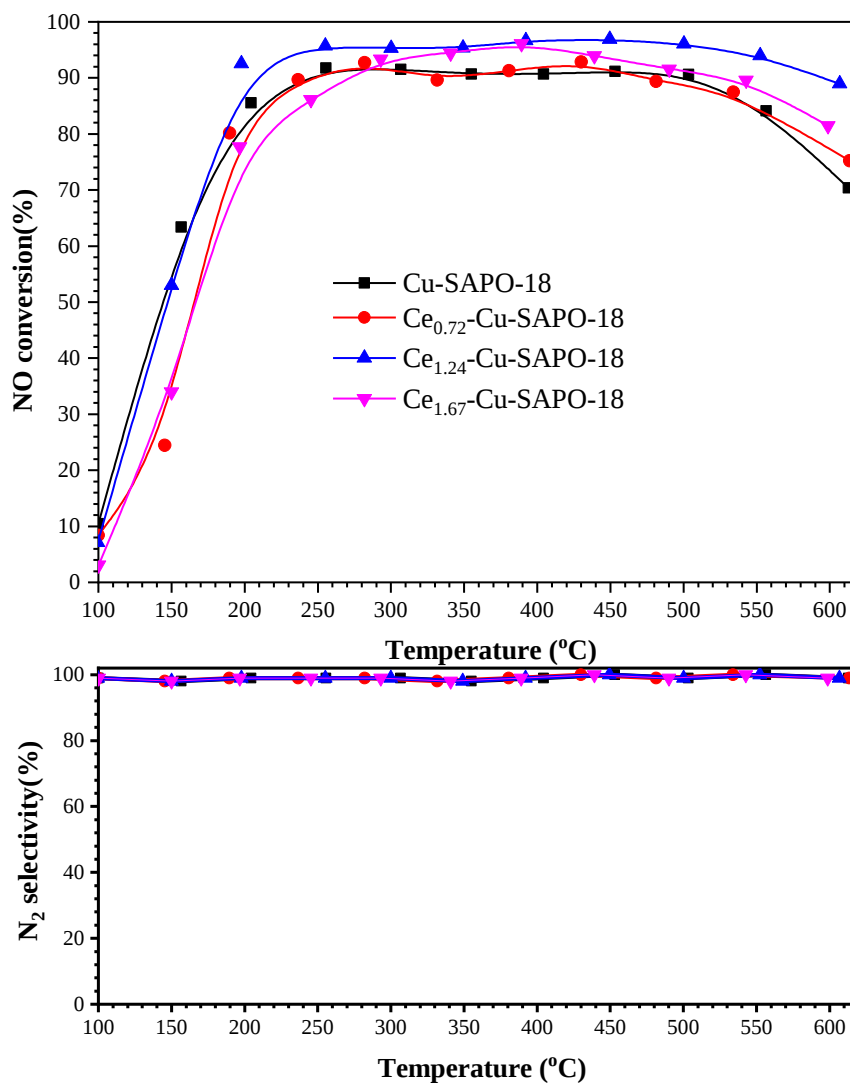


Figure S1. NO conversion and N₂ selectivity as a function of temperature for the NH₃-SCR

reaction over the Ce-Cu-SAPO-18 samples with different Ce contents at a GHSV of 130,000 h^{-1} . The reactant feed composition: 500 ppm NO, 500 ppm NH_3 , 14 vol% O_2 , 5 vol% H_2O , and N_2 (balance).

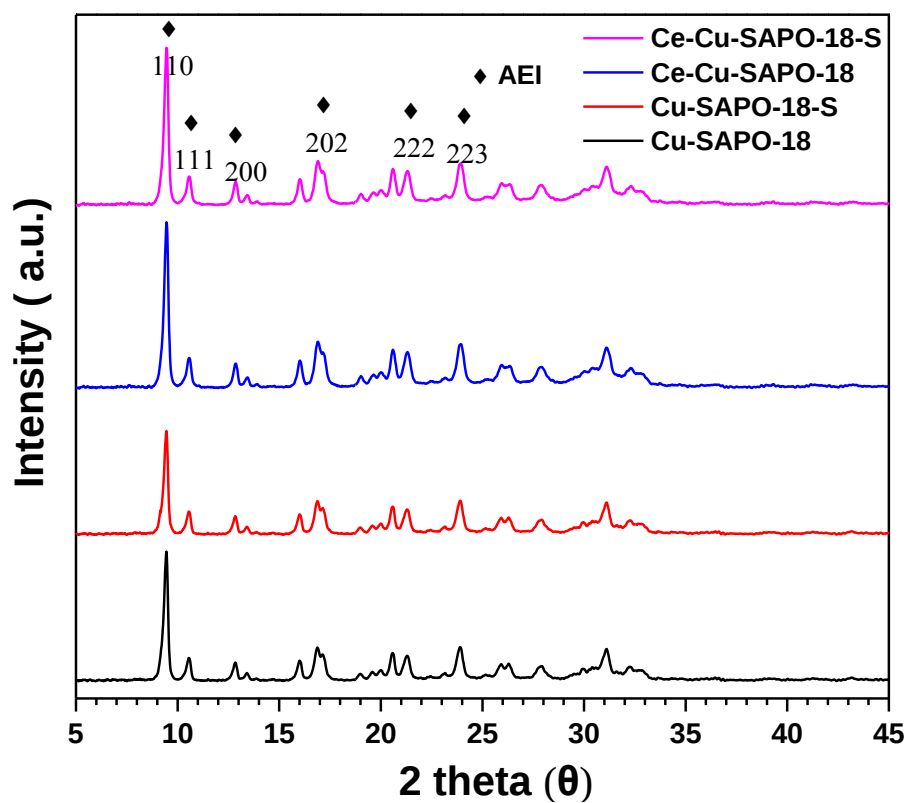


Figure S2. XRD patterns of the Cu-SAPO-18, Cu-SAPO-18-S, Ce-Cu-SAPO-18, and Ce-Cu-SAPO-18-S samples.

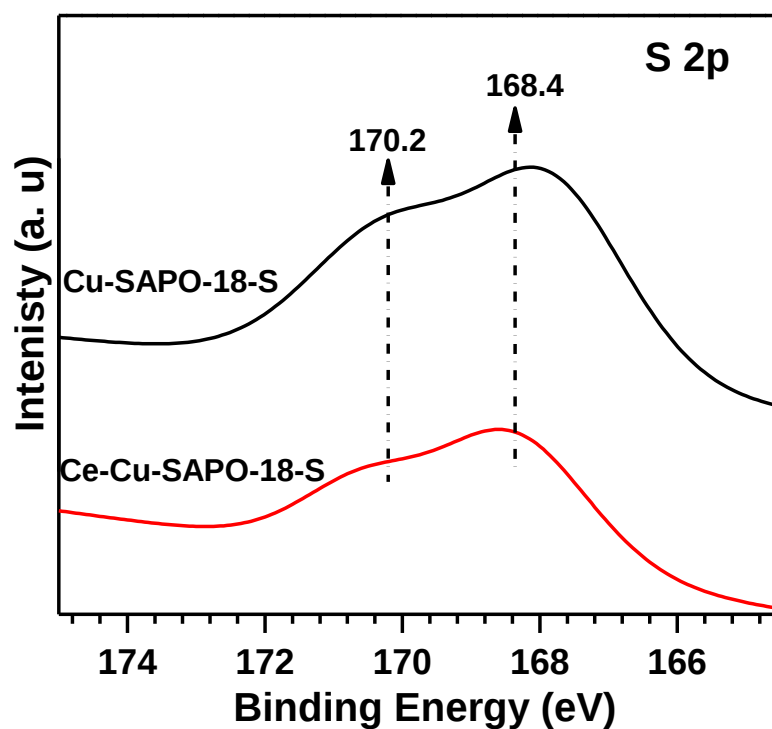


Figure S3. S2p XPS spectra of the sulfated samples.

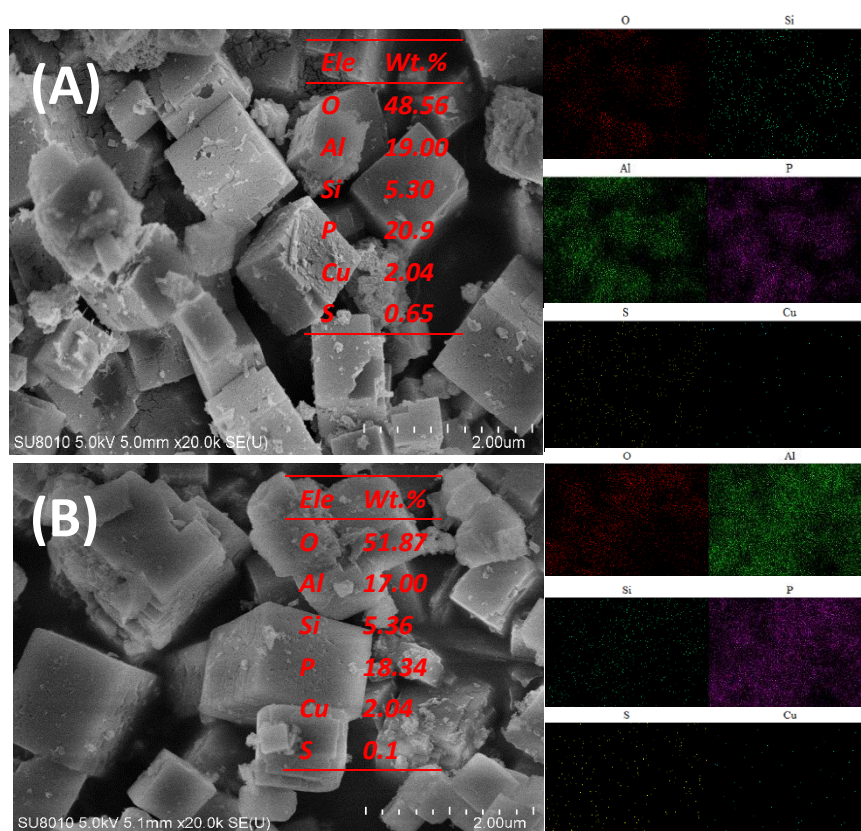


Figure S4. SEM images and EDS mappings of (A) Cu-SAPO-18-S and (B) Cu-SAPO-18-S-650.

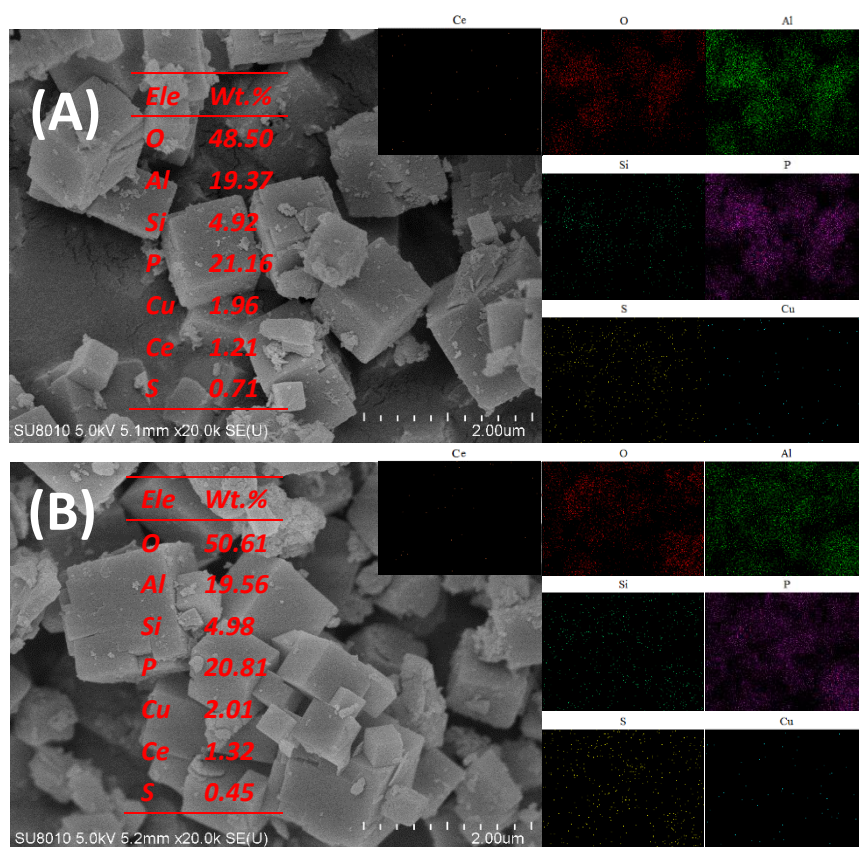


Figure S5. SEM images and EDS mappings of (A) Ce-Cu-SAPO-18-S and (B) Ce-Cu-SAPO-18-S-650.

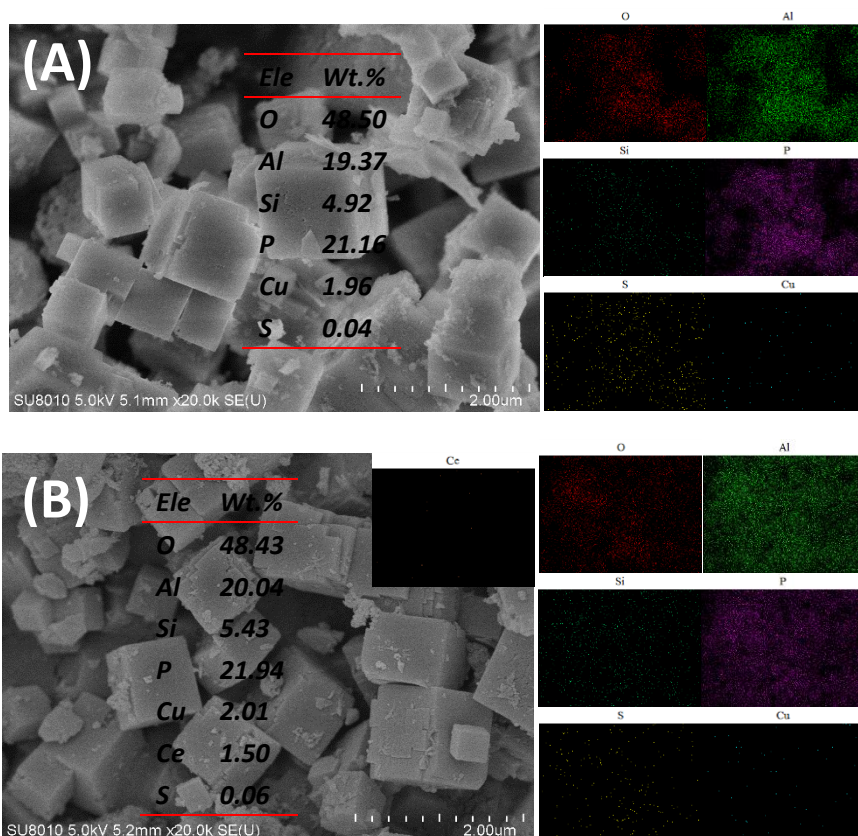
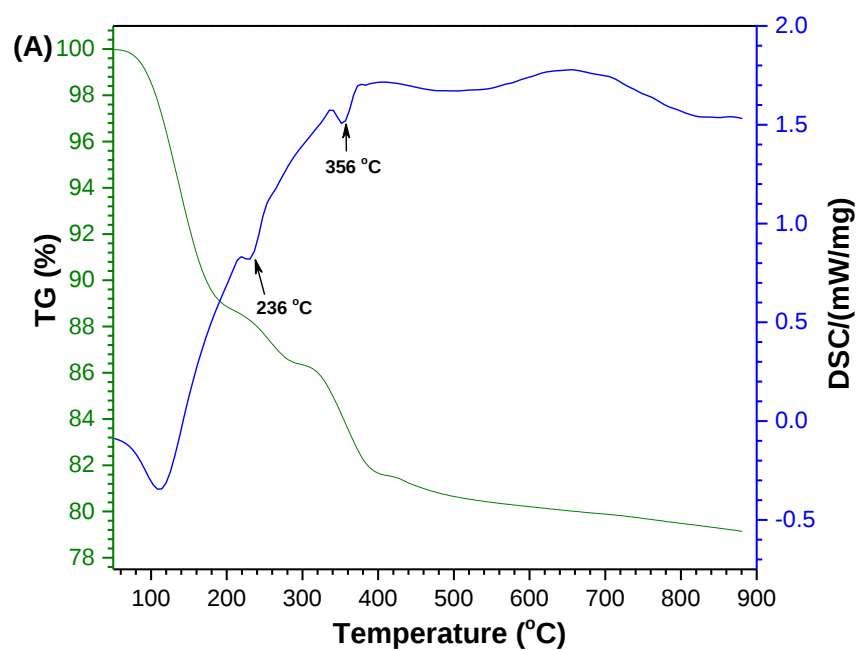


Figure S6. SEM images and EDS mappings of (A) Cu-SAPO-18-S-950 and (B) Ce-Cu-SAPO-18-S-950.



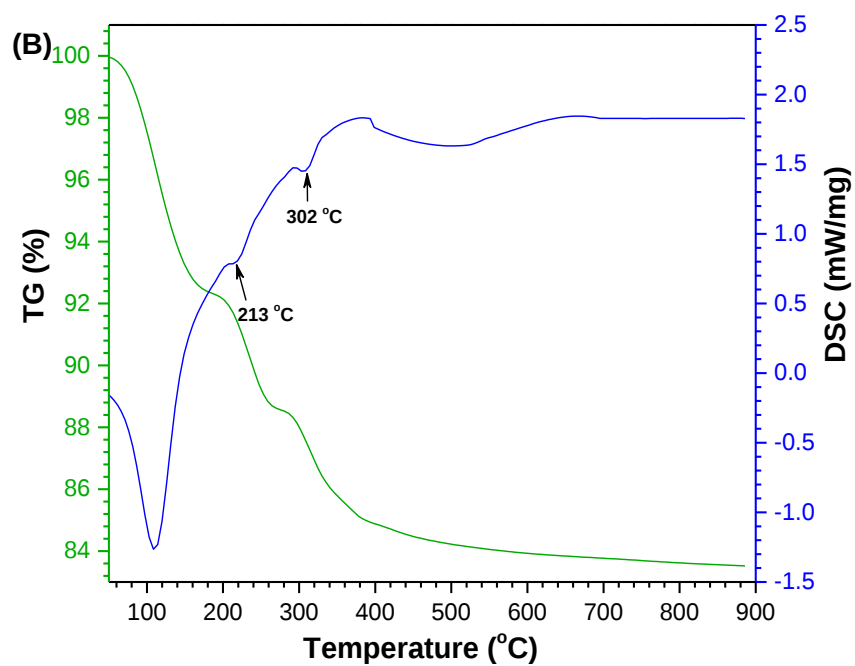


Figure S7. TG and DSC curves of NH_4HSO_4 deposited on (A) Cu-SAPO-18-SN and (B) Ce-Cu-SAPO-18-SN.