

Electronic Supporting Information

Polymer-Templated Mesoporous Hybrid Oxides of Al and Cu: Highly Porous Sorbents for Ammonia

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EXPERIMENTAL

Chemicals used. Aluminum isopropoxide and copper nitrate were purchased from Acros Organic (New Jersey). Pluronic F127 (EO₇₀PO₁₀₆EO₇₀) triblock copolymer was donated by BASF Corporation, Flortham Park, New Jersey. Anhydrous ethanol, HCl (37 %), and citric acid were purchased from Fisher Scientific, Pittsburgh, Pennsylvania. Deionized water (DW) was obtained using in house Ion pure Plus 150 Service Deionization Ion-Exchange purification system. All reagents were in analytical grade and used without further purification.

Measurements. High resolution thermogravimetric measurements were recorded on TGA Q-500 analyzer (TA Instruments, Inc., New Castle, DE). Thermogravimetric (TG) profiles were recorded from 25 to 800 °C in flowing nitrogen with a heating rate of 10 °C / min using a high resolution mode. The weight of each analyzed sample was typically in 5-20 mg range. The TG profiles were used to obtain information about the extent of the template removal.

Power X-ray diffraction (XRD) measurements were performed using an X'Pert Pro MPD multipurpose diffractometer (PANalytical, Inc.) with Cu K α radiation (0.15406 nm) at room temperature from 0.4° to 5.0° (small angle) and 20.0° to 80.0° (wide angle). Measurements were conducted using a voltage of 40 kV, a current setting of 40 mA, a step size of 0.02°, and count time of 20 s (small angle) and 4 s (wide angle). Microscope glass slides were used as sample supports for all samples.

The XPS data were taken on an AXIS Ultra instrument from Kratos Analytical. The data were converted into VAMAS file format and imported into CasaXPS software package for manipulation and curve-fitting.

Nitrogen adsorption isotherms were measured at -196 °C on ASAP 2010 and ASAP 2020 volumetric analyzers (Micromeritics, Inc., Norcross, GA). Prior to adsorption measurements, all samples were out gassed under vacuum at 200 °C for 2 hours.

NH₃ and CO₂ temperature programmed desorption (TPD) experiments were conducted using a Micromeritics Auto Chem II chemisorption Analyzer (Norcross, GA), which was equipped with a thermocouple detector (TCD) measurements. The experimental details are very similar as those reported in previous works.¹⁻³ For NH₃ TPD, approximately 50-100 mg of each sample were loaded in a quartz tube microreactor supported by quartz wool and subjected to pretreatment at 400 °C for 10 min before NH₃ adsorption, using a heating rate of 10 °C/min in flowing helium (at a rate of 50 cm³/min). Next, the sample was cooled to selected temperature (50 °C) using heating rate of 10 °C/min, exposed to pulse of 5 % NH₃-He (50 cm³/min) as a loop gas, kept for 3 minutes and allowed for return to the baseline. Recording was repeated until peaks are equal or 30 times. Recording was taken every 0.1 seconds and finally post NH₃ pulse purge was applied in flowing helium (50 cm³/min) for 30 min. In the TPD experiments, the samples were heated up to selected temperature (400, 550, 700 °C) using a heating rate of 5 °C/min and kept at this temperature for 120 min. The amounts of desorbed NH₃ were obtained by integration of the desorption profiles and referenced to the TCD signals calibrated for known volumes of analyzed gases. The TPD procedure for CO₂ was similar as that used for NH₃ TPD.^{1,2}

Calculations. The Brunauer-Emmett-Teller specific surface areas (S_{BET}) for the samples studied were determined on the basis of N₂ adsorption isotherms in the relative pressure range of 0.05-0.2. The total (single-point) pore volumes were evaluated from the volumes adsorbed at a relative pressure of ~ 0.98. The pore size distributions (PSD) were determined by the improved Kruk-Jaroniec-Sayari (KJS) method calibrated for cylindrical pores using adsorption branches of nitrogen adsorption-desorption isotherms.⁴ W_{max} refers to the pore width at the maximum of the PSD curve.

(1) C. Gunathilake and M. Jaroniec, *Appl. Mater. Interfaces*. 2014, **6**, 13069.

(2) C. Gunathilake and M. Jaroniec, *J. Mater. Chem. A*, 2015, **3**, 2707.

(3) W. Cai, J. Yu, C. Anand, A. Vinu and M. Jaroniec, *J. Mater. Chem.* 2011, **23**, 1147.

(4) M. Kruk, M. Jaroniec and A. Sayari, *Langmuir*.1997, **13**, 6267.

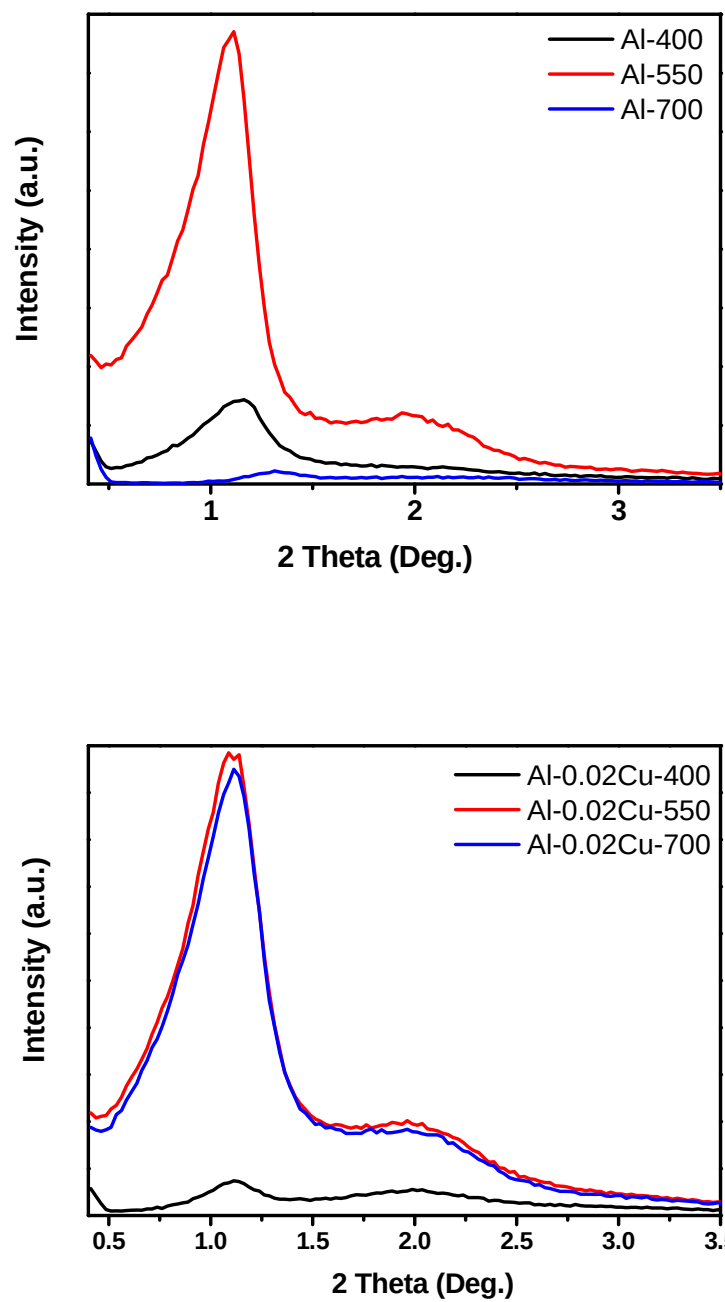


Figure S1. Small angle XRD patterns recorded for the Al-T (top panel) and Al-0.02Cu-T (bottom panel) samples.

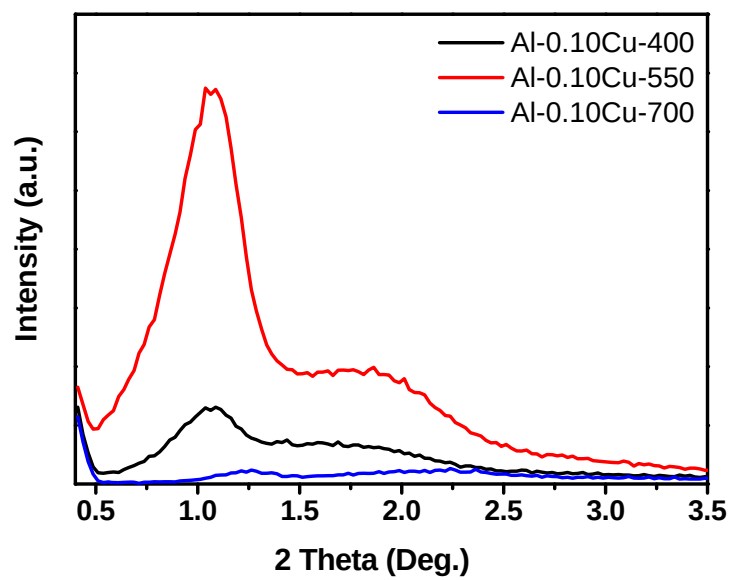


Figure S2.Small angle XRD patterns recorded for the Al-0.10Cu-T samples.

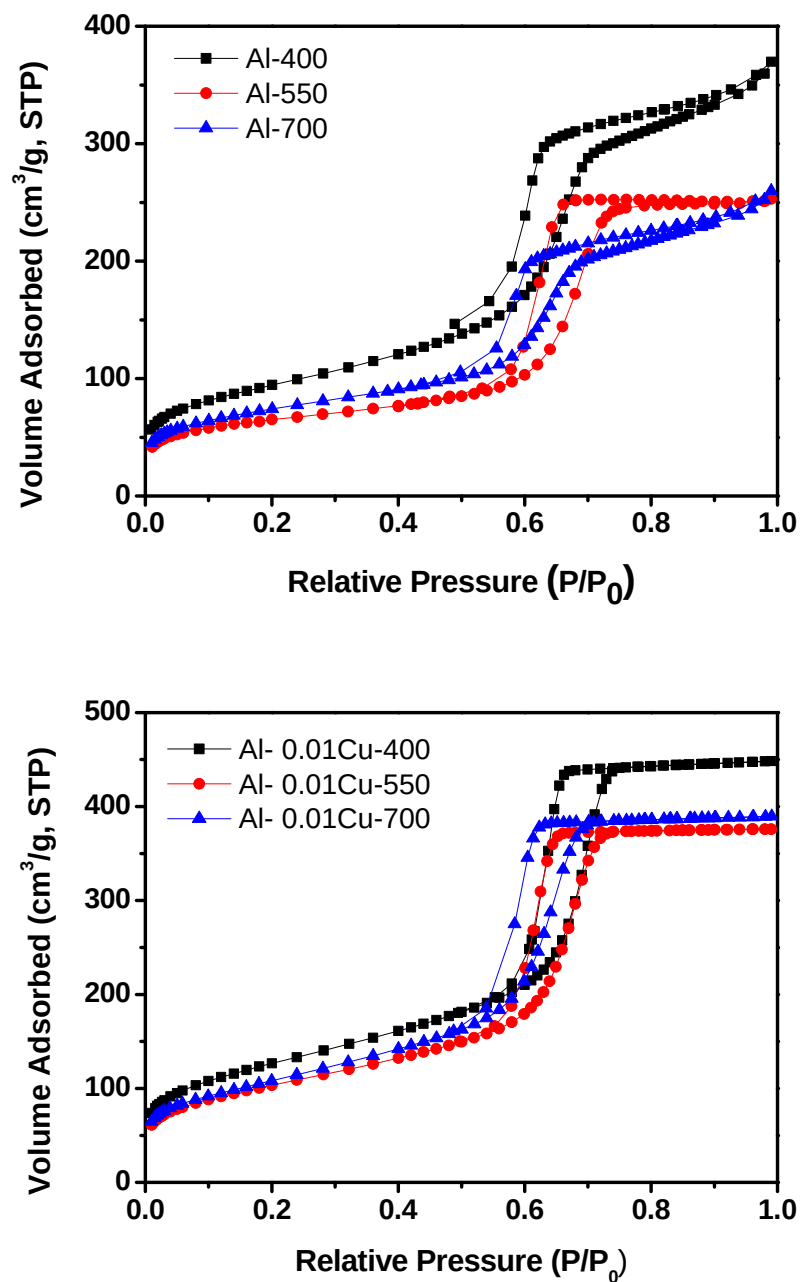


Figure S3. N_2 adsorption isotherms for the Al-T (top panel) and Al-0.01Cu-T (bottom panel) samples.

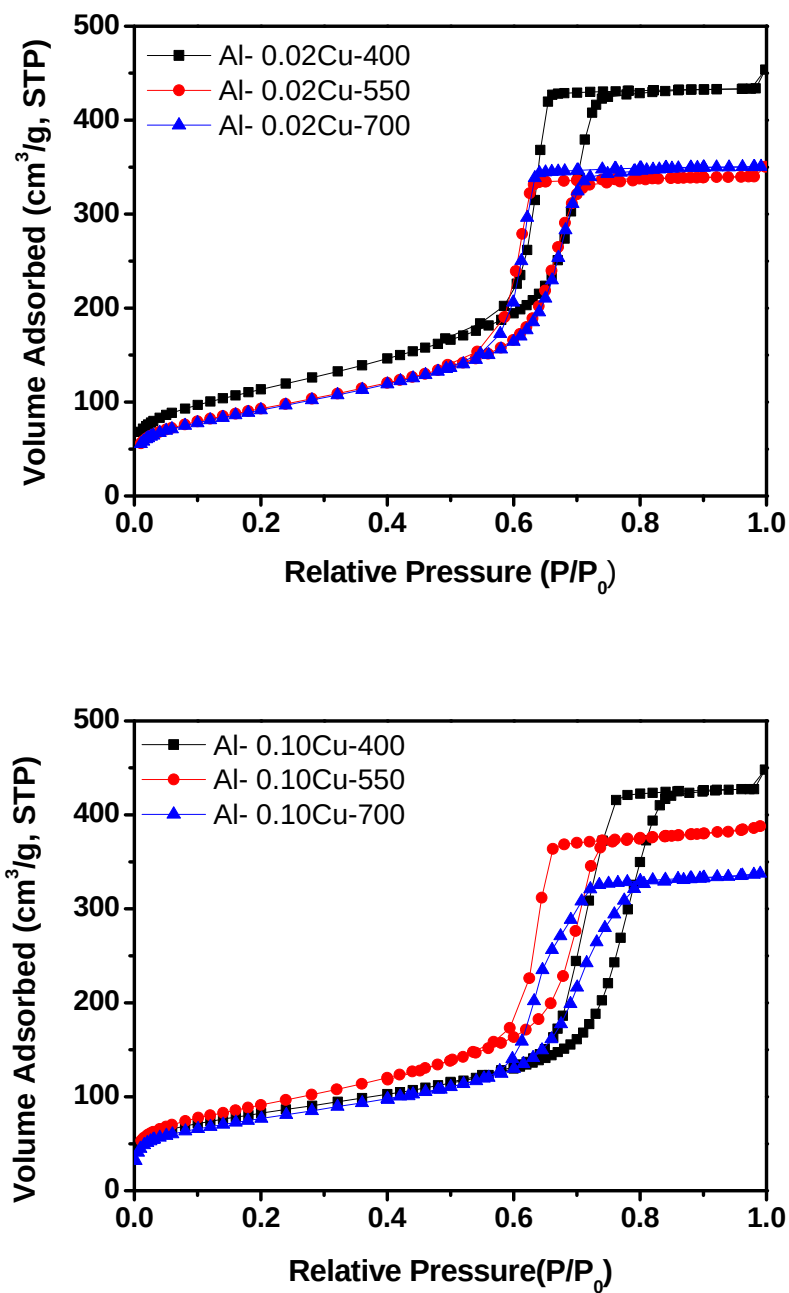


Figure S4. N₂ adsorption isotherms for the Al-0.02Cu-T (top panel) and Al-0.10Cu-T (bottom panel) samples.

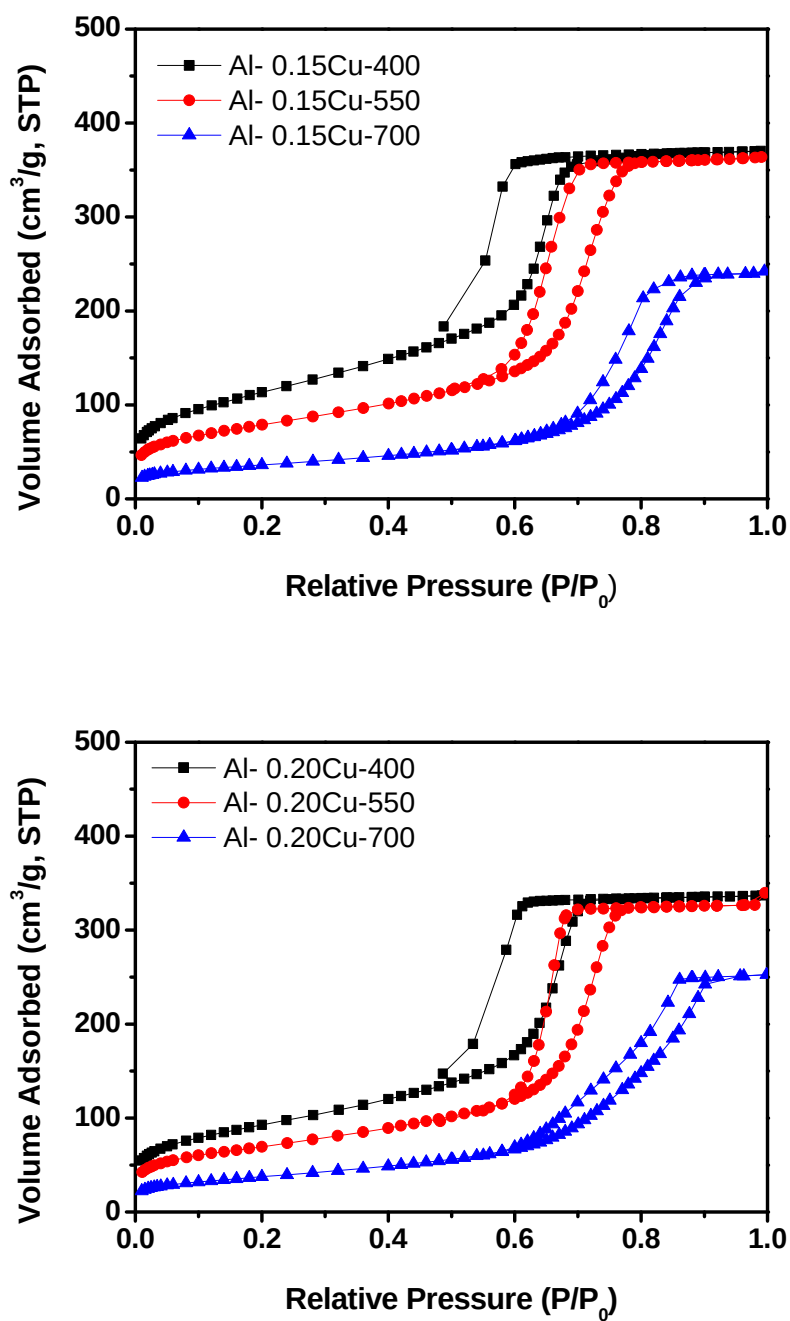


Figure S5. N₂ adsorption isotherms for the Al-0.15Cu-T (top panel) and Al-0.20Cu-T (bottom panel) samples.

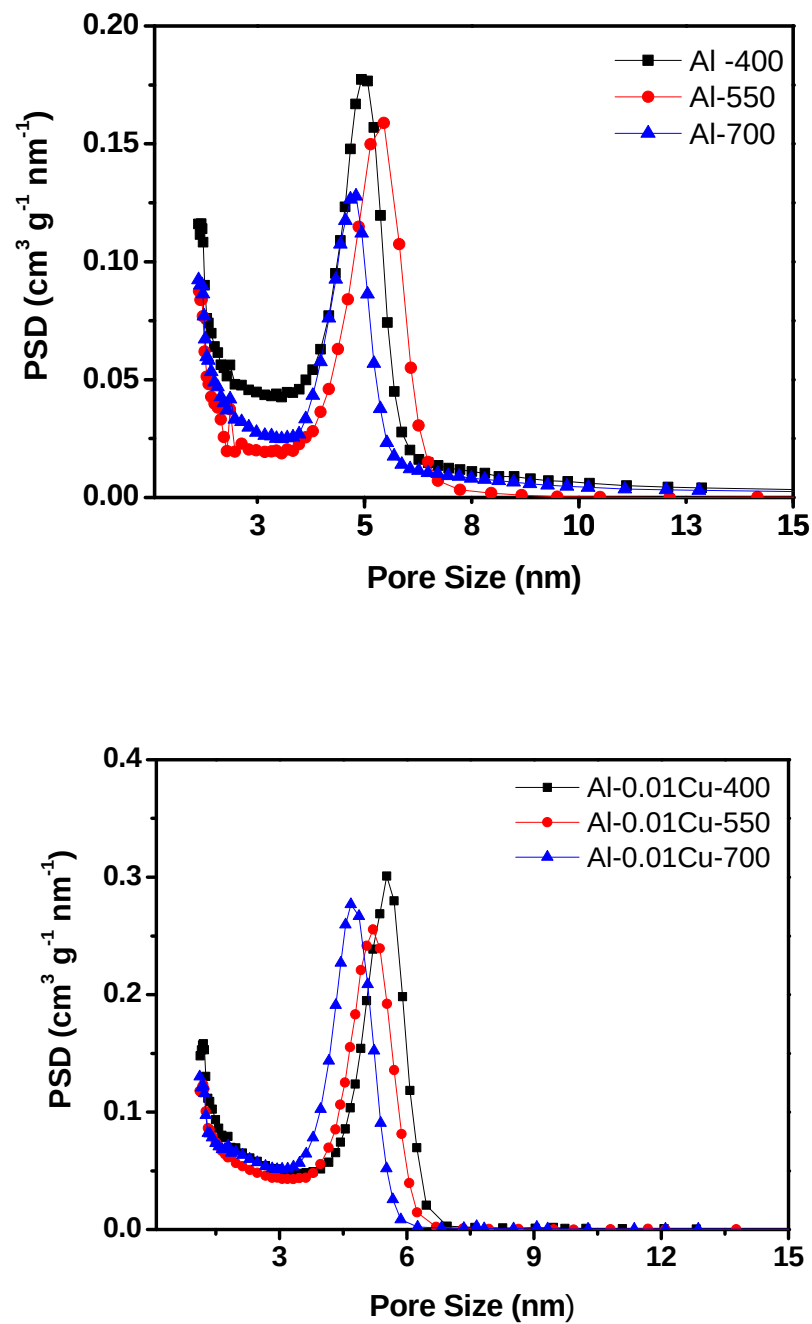


Figure S6. Pore size distribution (PSD) curves for the Al-T (top panel) and Al-0.01Cu-T (bottom panel) samples.

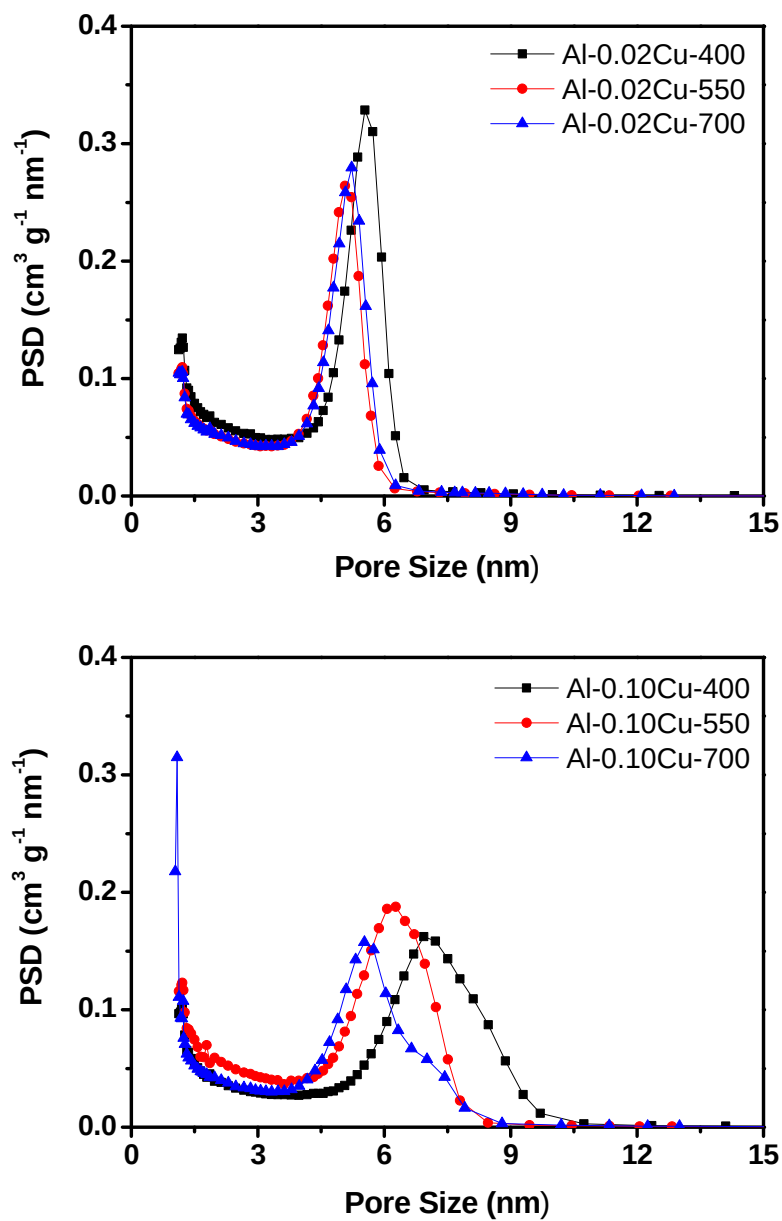


Figure S7. Pore size distribution (PSD) curves for the Al-0.02Cu-T (top panel) and Al-0.10Cu-T (bottom panel) samples.

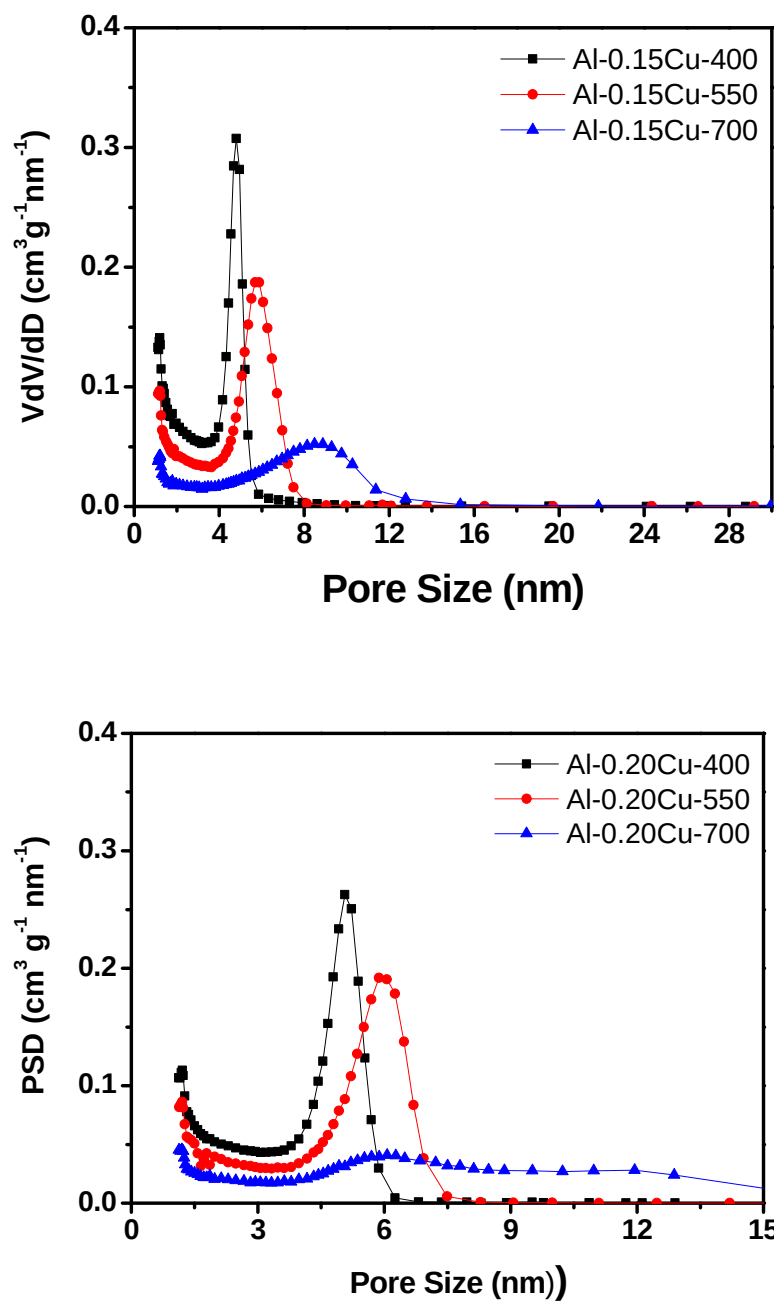
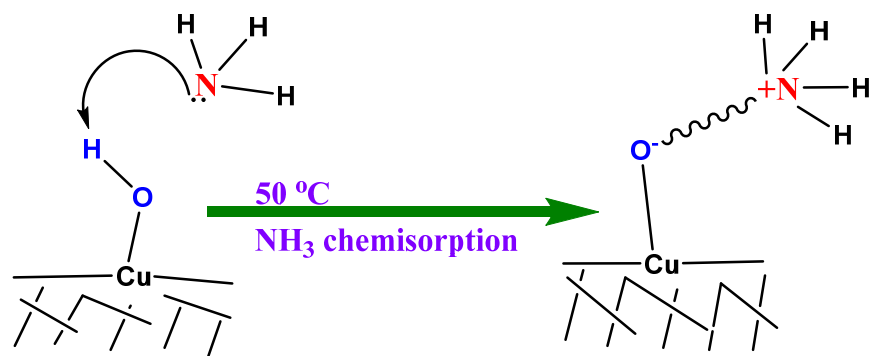
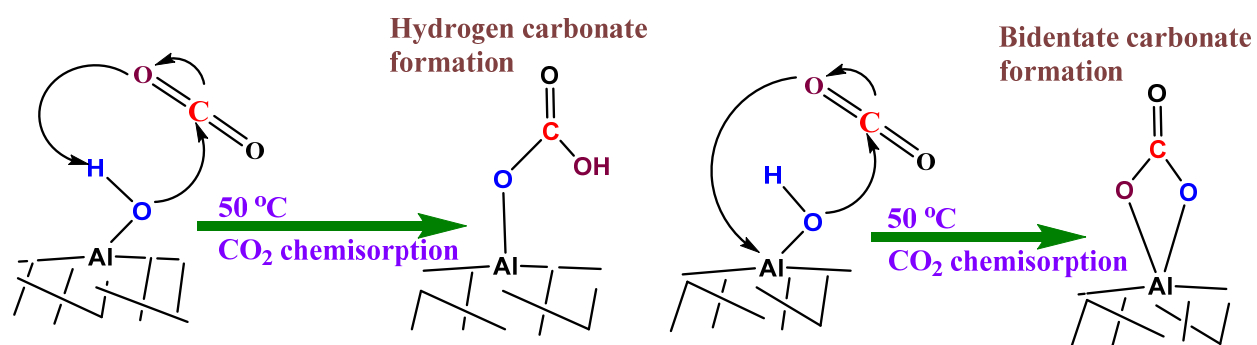


Figure S8. Pore size distribution (PSD) curves for the Al-0.15Cu-T (top panel) and Al-0.20Cu-T (bottom panel) samples.



Scheme S1: Systematic illustration of possible NH_3 binding via acid-base interactions.



Scheme S2: Systematic illustration of possible CO_2 binding models on the surface of alumina: (left) bicarbonate structures; (right) bi-dentate carbonate structures.