

## Supporting Information

# Mesoporous alumina with amidoxime groups for CO<sub>2</sub> sorption at ambient and elevated temperatures

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## EXPERIMENTAL

### Materials

Boehmite (Catapal A) was donated from Sasol, Johannesburg, South Africa. Pluronic P123 (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>) triblock copolymer was donated by BASF Corporation, Flortham Park, New Jersey. (3-cyanopropyl)triethoxysilane (CPTS) was purchased from Alfa Aesar, Johnson Matthey Company, Ward Hill, Massachusetts. Hydroxylamine hydrochloride (NH<sub>2</sub>OH.HCl) was purchased from Sigma Aldrich. 200 proof ethanol was purchased from Fisher Scientific, Pittsburgh, Pennsylvania. 95 % ethanol, 36 % HCl, 69.1 % HNO<sub>3</sub>, and NaOH were also 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.

### Characterization

Experimental details related to the instruments used such as adsorption analyzers, thermogravimetry, elemental analyzer, NMR instrument and transmission electron microscope are similar to those provided in previous publications.<sup>1-4</sup> Nitrogen adsorption isotherms were measured at -196 °C on an ASAP 2010 volumetric analyzer (Micromeritics, Inc., Norcross, GA). Prior to adsorption measurements, all samples were out gassed under vacuum at 110 °C for 2 h. 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 720 °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 5-15 mg range. Elemental CHNS analysis was performed on a LECO model CHNS-932 elemental analyzer (St. Joseph, MI).

<sup>1</sup>H-<sup>13</sup>C cross polarization (CP) MAS NMR spectra were recorded using Bruker Avance (III) 400WB NMR spectrometer (Bruker Biospin Corporation, Billerica, MA, USA) with MAS triple resonance probe head using zirconia rotors 4 mm in diameter. <sup>1</sup>H-<sup>13</sup>C CP-MAS NMR spectra were acquired at 400.13 MHz for <sup>1</sup>H and 100.63 MHz for <sup>13</sup>C. The MAS rate was 5 KHz. <sup>1</sup>H  $\pi/2$  pulse length was 3.5  $\mu$ s and pulse delay 2.0 s. TPPM20 <sup>1</sup>H decoupling sequence was used during acquisition. The <sup>13</sup>C chemical shifts were referenced to p-dioxane 66.6 ppm. <sup>27</sup>Al magic-angle-spinning (MAS)-NMR spectra were acquired at 104.24 MHz using a single

pulse sequence with pulse shorter than  $\pi/4$  (1  $\mu\text{s}$  pulse length) and a MAS rate of 10 KHz, 400-1000 scans were acquired with recycle delay of 1s. The position of the  $^{27}\text{Al}$  resonance was referenced to 1M  $\text{Al}(\text{NO}_3)_3$  (0 ppm).  $^1\text{H}$ - $^{29}\text{Si}$  cross polarization (CP) MAS NMR spectra were recorded at 79.49 MHz for  $^{29}\text{Si}$  and 400.13 MHz ( $^1\text{H}$ ). The MAS rate was 5 KHz.  $^1\text{H}$   $\pi/2$  pulse length was 4.5  $\mu\text{s}$  and pulse delay 3.0 s. Two pulse phase modulated TPPM15 decoupling sequence was used during acquisition. The  $^{29}\text{Si}$  chemical shifts were referenced to TMS (0 ppm).

Transmission electron microscopy (TEM) images were obtained on a FEI Tecnai G2 F20 microscope. Prior to TEM analysis, the sample powders were dispersed in ethanol by moderate sonication at concentrations of ~5-10 wt. %. A Lacy carbon coated, 200-mesh, copper TEM grid was dipped into the sample suspension and then dried under vacuum at 80  $^\circ\text{C}$  for 20 h. Field emission scanning electron microscopy (FE-SEM) images of the selected samples were observed using Hitachi S-4700 FE-SEM. Resolution of 1.5 nm at 15 kV can be achieved at 12 mm working distance and 2.5 nm at low kV (2 kV), at a working distance of 3 mm.

### **Room temperature $\text{CO}_2$ adsorption measurements**

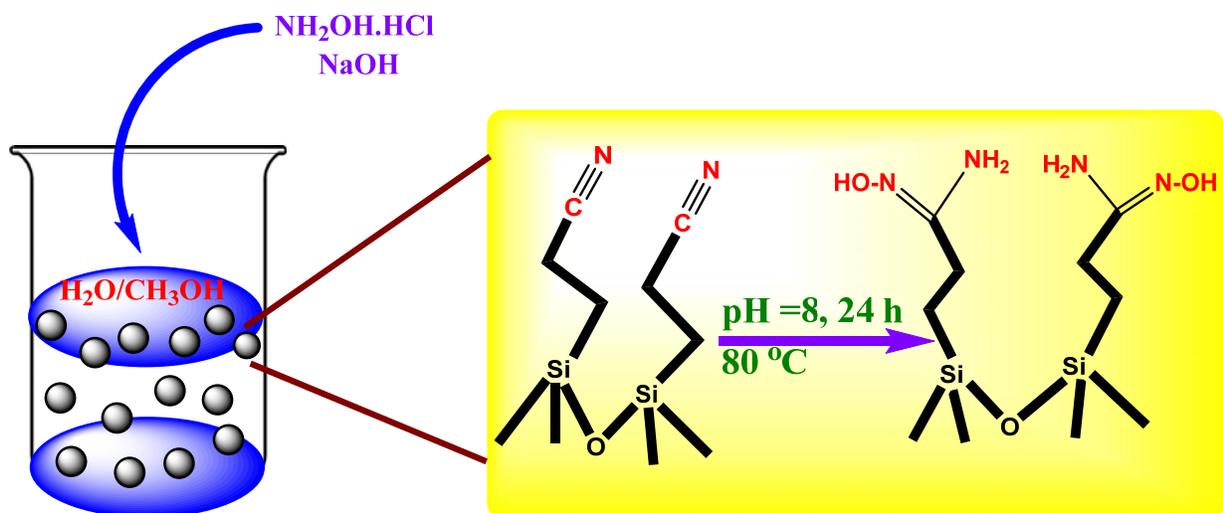
$\text{CO}_2$  adsorption on the selected samples studied was measured in the pressure range up to 1.2 atm on ASAP 2020 volumetric adsorption analyzer (Micromeritics, Inc., GA) at 25  $^\circ\text{C}$  using ultrahigh purity (99.99 %) gaseous  $\text{CO}_2$ . Prior to adsorption analysis each sample was outgassed at 110  $^\circ\text{C}$  for 2 h under vacuum.

### **$\text{CO}_2$ chemisorption and TPD measurements**

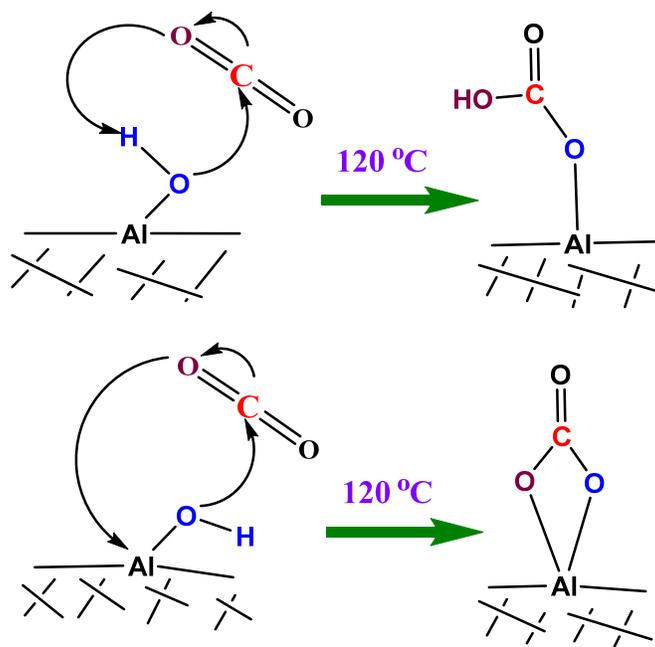
$\text{CO}_2$  chemisorption and TPD experiments were conducted using a Micromeritics Auto Chem II Chemisorption Analyzer (Micromeritics, Inc., GA) equipped with a thermocouple detector (TCD). Approximately 20-100 mg of each sample were loaded in a quartz tube microreactor supported by quartz wool and subjected to pretreatment at 370  $^\circ\text{C}$  for 10 min before  $\text{CO}_2$  adsorption, using a heating rate of 10  $^\circ\text{C}/\text{min}$  in flowing helium (at a rate of 50  $\text{cm}^3/\text{min}$ ). Next, the sample was cooled to selected temperature (120  $^\circ\text{C}$ ) using heating rate of 10  $^\circ\text{C}/\text{min}$ , exposed to pulse of 5 %  $\text{CO}_2$ -He (50  $\text{cm}^3/\text{min}$ ) as a loop gas, kept for 3 min and allowed for return to baseline. Recording was repeated until peaks are equal or 30 times. Recording was taken every 0.1 seconds and finally post  $\text{CO}_2$  pulse purge was applied in flowing helium (50  $\text{cm}^3/\text{min}$ ) for 30 min. In the TPD experiments, the samples were heated up to 370  $^\circ\text{C}$  using a heating rate of 5  $^\circ\text{C}/\text{min}$  and kept at this temperature for 90 min. The amounts of desorbed  $\text{CO}_2$  were obtained by integration of the desorption profiles and referenced to the TCD signals calibrated for known volumes of analyzed gases.<sup>1-3</sup>

### **Calculations**

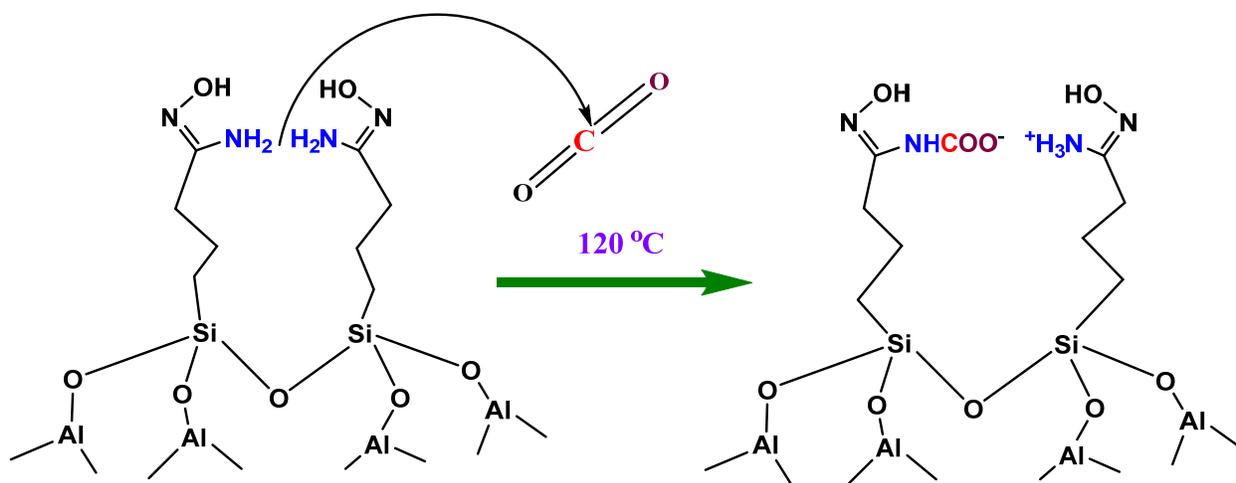
The Brunauer-Emmett-Teller specific surface areas ( $S_{\text{BET}}$ ) were calculated from  $\text{N}_2$  adsorption isotherms in the relative pressure range of 0.05-0.2 using a cross sectional area of 0.162  $\text{nm}^2$  per nitrogen molecule. The single-point pore volume ( $V_{\text{sp}}$ ) was estimated from the amount adsorbed at a relative pressure of ~ 0.98. The pore size distributions (PSD) were calculated using adsorption branches of nitrogen adsorption-desorption isotherms by the improved KJS method calibrated for cylindrical pores.<sup>5</sup> The volume of fine pores (micropores and small mesopores below 3 nm)  $V_{\text{mic}}$  was calculated by integration of the PSD curve up to 3 nm. The pore width ( $W_{\text{max}}$ ) was obtained at the maximum of the PSD curve.



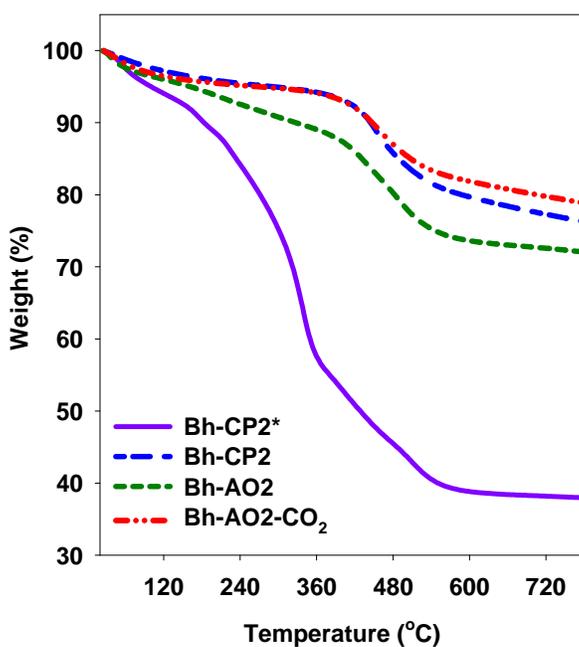
**Scheme S1.** Illustration of the conversion of cyano groups to amidoxime groups using hydroxylamine hydrochloride. Adapted from Ref. [1] by permission from the American Chemical Society.



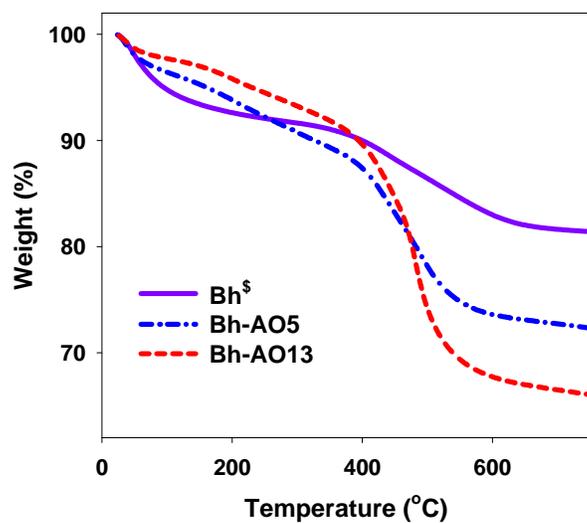
**Scheme S2.** Illustration of possible hydrogen carbonate (top) and bidentate carbonate (bottom) formation upon CO<sub>2</sub> chemisorption on the Bh<sup>s</sup>, Bh-CPX, and Bh-AOX samples; Adapted from Ref. [3] by permission from the Royal Society of Chemical.



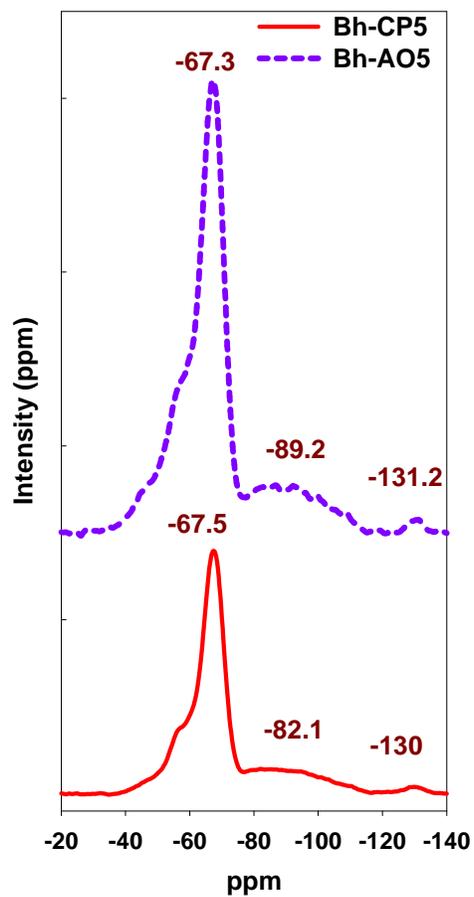
**Scheme S3.** Illustration of CO<sub>2</sub> binding on the Bh-AOX samples at 120 °C. Adapted from Ref. [1] by permission from the American Chemical Society.



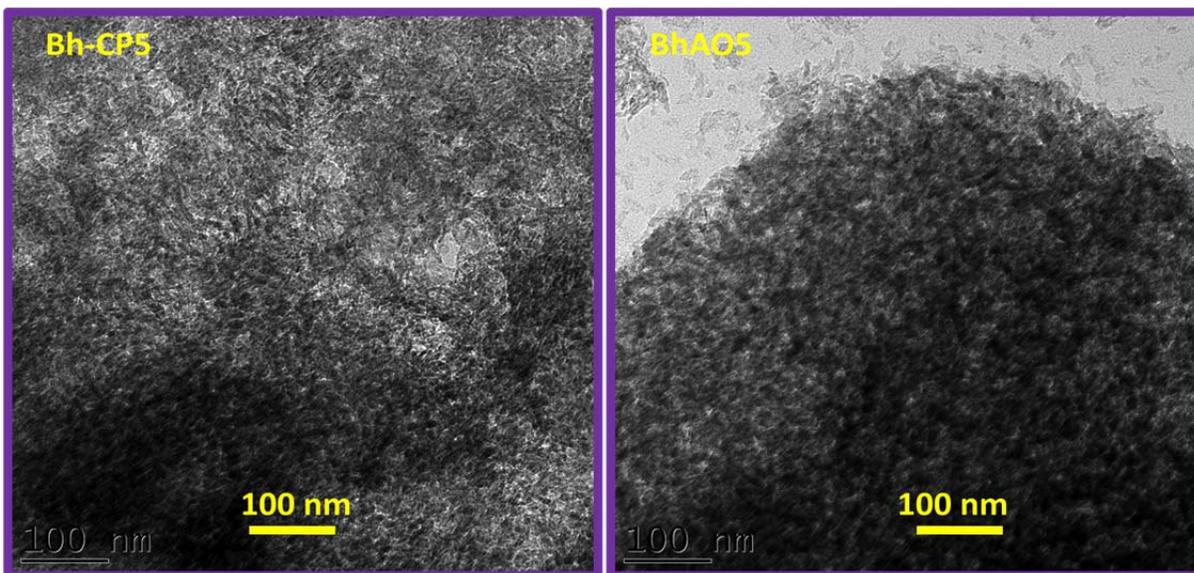
**Figure S1.** TG curves for the as-synthesized (Bh-CP2\*) and calcined cyanopropyl-containing (Bh-CP2) samples, and amidoxime-containing samples without (Bh-AO2) and with (Bh-AO2-CO<sub>2</sub>) chemisorbed CO<sub>2</sub>.



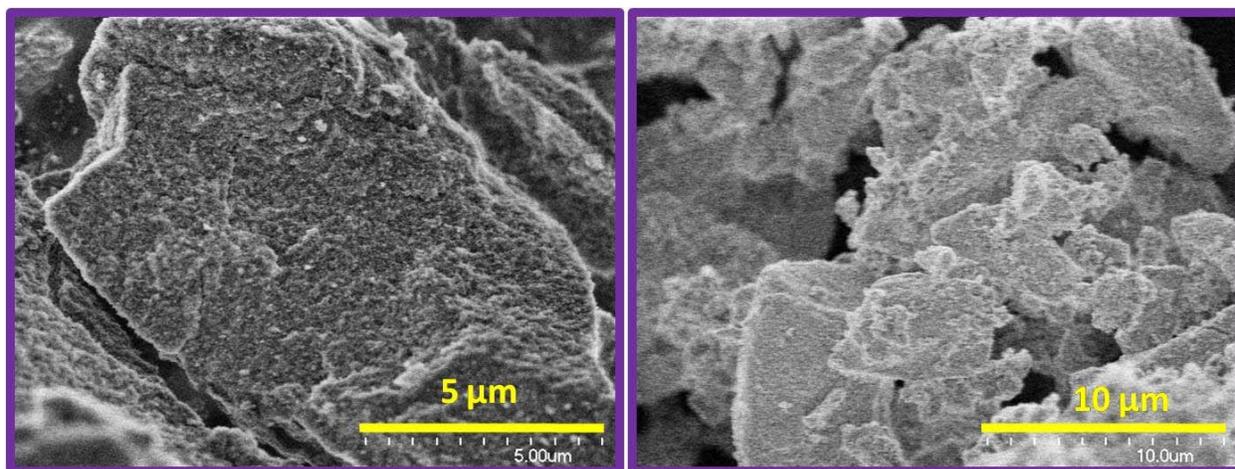
**Figure S2.** TG curves for the Bh<sup>S</sup> and Bh-AOX (X=5, 13) samples studied.



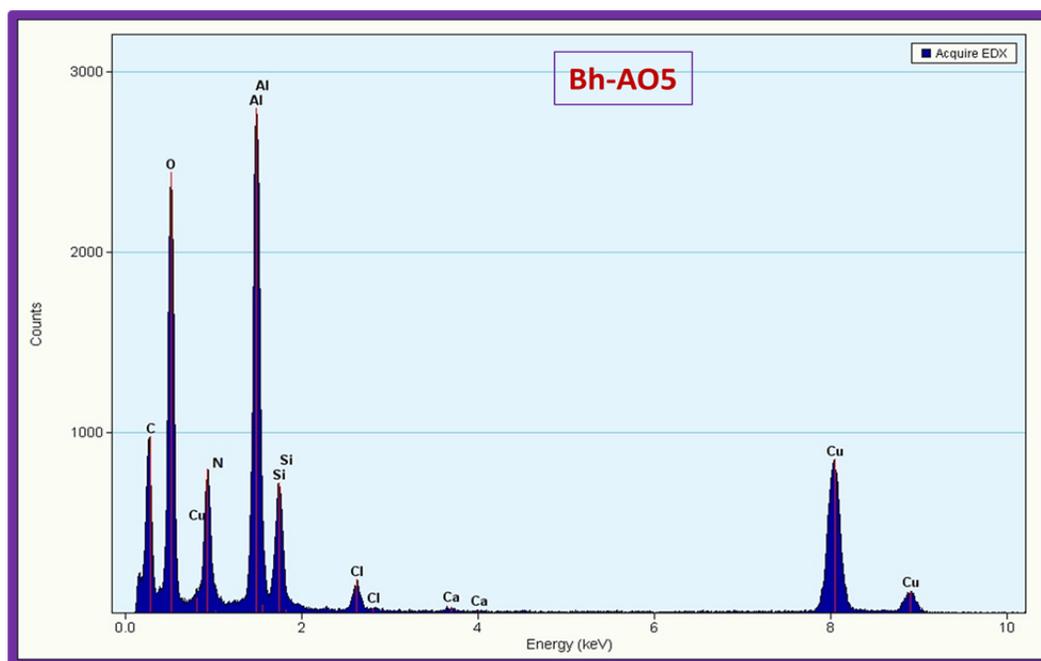
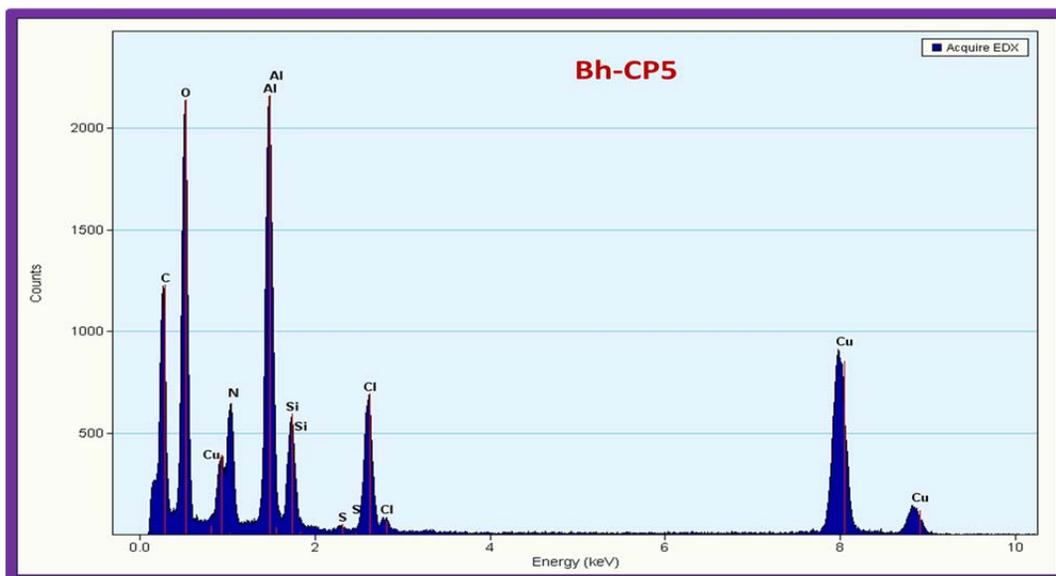
**Figure S3.** <sup>29</sup>Si MAS NMR spectra obtained for the Bh-CP5 and Bh-AO5 samples.



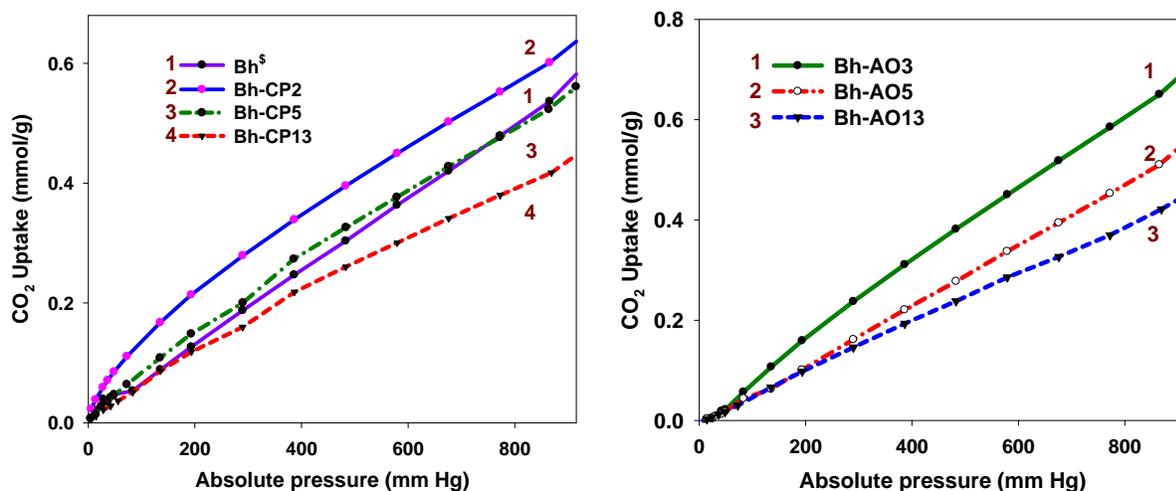
**Figure S4.** TEM images of the Bh-CP5 (left panel) and Bh-AO5 (right panel) samples.



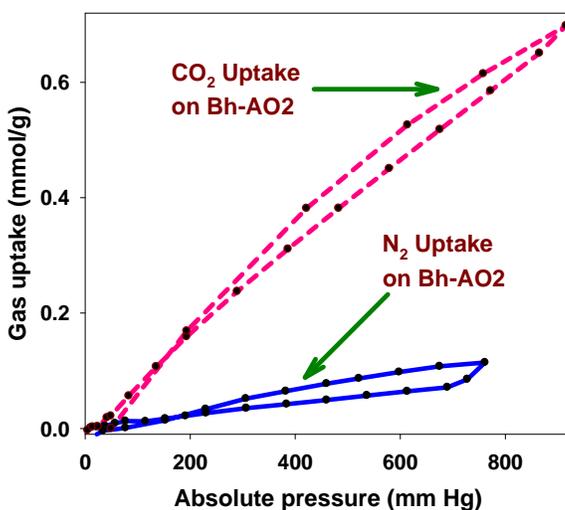
**Figure S5.** SEM images of the Bh-CP5 (left panel) and Bh-AO5 (right panel) samples.



**Figure S6.** EDX spectra obtained for the Bh-CP5 (top panel) and Bh-AO5 (bottom panel) samples.



**Figure S7.** CO<sub>2</sub> adsorption isotherms at 25 °C obtained for the Bh<sup>s</sup> and Bh-CPX (left panel) and Bh-AOX (right panel) samples.



**Figure S8.** CO<sub>2</sub> and N<sub>2</sub> adsorption-desorption isotherms at 25 °C measured on the Bh-AO2 sample studied.

## References

- 1) Gunathilake, C.; Jaroniec, M. *Appl. Mater. Interfaces*. **2014**, 6, 13069–13078.
- 2) Gunathilake, C.; Gorka, J.; Dai, S.; Jaroniec, M. *J. Mater. Chem. A*, **2015**, 3, 11650-11659.
- 3) Gunathilake, C.; Jaroniec, M. *J. Mater. Chem. A*. **2015**, 3, 2707-2716.
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- 5) Kruk, M.; Jaroniec, M.; Sayari, A. *Langmuir*. **1997**, 13, 6267-6273.