Electronic Supplementary Information for

Temperature-Responsive Smart Molecule Gate in Metal-Organic Framework for Task-Specific Gas Separation

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Materials.

All of the solvents and reagents were commercially available and used without further purification.

Preparation of MOFs.

CAU-10-X were synthesized according to the reported method[1] with minor modifications.

CAU-10-OMe: A solution containing $Al_2(SO_4)_3 \cdot 18H_2O$ (2.04 g, 3.06 mmol), 5-methoxysiophthalic acid (1.20 g, 3.06 mmol), N, N'-dimethylformamide (DMF, 3 ml) and H_2O (12 ml) was transferred to the Teflon-line stainless steel autoclave. This reaction was heated at 130℃ for 12 h under autogenous pressure. After cooling down to room temperature, the product was filtered off. Subsequently, the obtained product was treated by sonication and stirring in water, until form a homogeneous mixture. The dispersion was filtered again and the obtained powder was washed with deionized water and fresh acetone for several times. After that, the obtained white crystals were heated at 150℃ under vacuum overnight.

CAU-10-H: $Al_2(SO4)_3 \cdot 18H_2O$ (1.20 mmol, 800 mg) and isophthalic acid (1.20 mmol, 200 mg) were dissolved in DMF (1 ml) and H_2O (4 ml) in a Teflon-line stainless steel autoclave. The mixture was heated at 135℃ for 12 h. Afterward, the product was cooled down to room temperature and collected by filtered. The obtained solid was stirred under sonication in water. Therefore, the mixture was filtered again and then washed with deionized water and acetone for several times. Finally, the white microcrystalline was dried at 150℃ for 12 h under vacuum.

CAU-10-NH_2: 2 M $AlCl_3 \cdot 6H_2O$ water solution (6.6mmol Al^{3+}, 3.3ml) and 5-aminoisophthalic acid (6.63 mmol, 1200mg) were dissolved in DMF (4 ml) and H_2O (12.7 ml) in a glass reactor with screw cap. The mixture was heated at 120℃ for 12 h. Afterward, the product was cooled down to room temperature and collected by filtered. The obtained solid was stirred under sonication in water. Therefore, the mixture was

filtered again and then washed with deionized water and acetone for several times. Finally, the white microcrystalline was dried at 150℃ for 12 h under vacuum.

CAU-10-NO_2: 2 M $AlCl_3 \cdot 6H_2O$ water solution (6.80 mmol Al^{3+}, 3.4 ml) and 5-nitroisophthalic acid (6.82 mmol, 1440 mg) were dissolved in DMF (4 ml) and H_2O(12.6 ml) in a glass reactor with screw up. The mixture was heated at 120℃ for 12 h. Afterward, the product was cooled down to room temperature and collected by filtered and the product was processed in the same way as CAU-10-NH_2.

CAU-10-F: 0.5 M $Al_2(SO4)_3 \cdot 18H_2O$ solution (6.88 mmol Al^{3+}, 6.88 ml) and 5-fluoroisophthalic acid (6.85 mmol, 1260 mg) were dissolved in DMF (4 ml) and H_2O (9.12 ml) in a Teflon-line stainless steel autoclave. The mixture was heated at 120℃ for 12 h. Afterward, the product was cooled down to room temperature and collected by filtered. The obtained solid was stirred under sonication in water. Therefore, the mixture was filtered again and then washed with deionized water and acetone for several times. Finally, the white microcrystalline was dried at 150℃ for 12 h under vacuum.

Characterization

The Fourier transform infrared (FT-IR) were measured on a Nicolet 6700 FTIR spectrophotometer. Power X-ray diffraction data (PXRD) were recorded on D8 Advanced X diffractometer with Cu Kα radiation (λ= 1.5406 Å) at RT. The 2θ was scanned ranging from 5^o to 50^o in 0.02^o steps with a scan rate of 5^o/min. Variable temperature powder X-ray diffraction (VT-PXRD) were recorded on a PANalytiacal X'PertPro. Fourier transform infrared (FTIR) measurements were recorded using a Thermo Nicolet iS50 FTIR (Thermo Fisher Scientific Co., MA, USA) spectrometer equipped with a single-bounce diamond crystal and a deuterated triglycine sulfate detector. Raman spectra were obtained using a Renishaw InVia Reflex spectrometer (Wotton-under-Edge, UK). The BET surface areas of the samples were done on a Micromeritics ASAP 2020 using N_2 adsorption data at 77 K.

Gas Adsorption Measurement

Gas adsorption measurements were performed on a Micromeritics ASAP 2020 surface area and pore size analyzer. The sample tube filled with about 300 mg sample. Before the adsorption/desorption, the adsorbent was degassed under vacuum at 423 K for 12 h by using the "automatic degas" function of the analyzer. Ultrahigh purity grade N_2, CH_4, C_2H_4, C_3H_6, C_3H_8 and i-C_4H_{10} were used for gas adsorption measurement. The temperatures at 87 K, 143 K, 175 K, 203 K, 213 K, 233 K, 273 K, 298 K, 323 K, 343 K were maintained with liquid argon bath, n-pentane-liquid nitrogen bath, methanol-liquid nitrogen bath, low temperature thermostat and thermostat, respectively.[2,3] To prevent condensation of CH_4 at 87 K, the pressure range was below 7.2 KPa. To prevent condensation of C_2H_4 and C_2H_6 at 143 K, the pressure range was below 15.8 KPa and 5.1 KPa. To prevent condensation of C_3H_6 at 213 K, the pressure range was below 73.4 KPa. For all adsorption isotherms, we choose a relative saturation pressure given by the Micromeritics ASAP 2020 surface area and pore size analyzer during the measurements: at 87 K, N_2 was 100 KPa and CH_4 was 6.6 KPa; at 143 K, CH_4 was 100 KPa, C_2H_4 was 14.5 KPa and C_2H_6 was 5 KPa; at 213 K, C_2H_4 was 100 KPa and C_3H_6 was 71.7 KPa; at other temperature, all gases of measurement were 100 KPa. However, in order to facilitate the observation of molecular sieving effect, the minimum relative pressure of the measurement gases as the highest pressure on the abscissa of the graph was selected at a certain temperature.

Ideal adsorption solution theory (IAST) calculations

The Dual-site Langmuir model was carried out by fitting adsorption isotherms of C_3H_6 and C_3H_8 in CAU-10-OMe at 298 K. The Dual-site Langmuir equation can be defined as,

$$q = q_A + q_B = q_{sat,A}\frac{b_A p}{1+b_A p} + q_{sat,B}\frac{b_B p}{1+b_B p}$$

Where, q is a molar loading of adsorbate; q_{sat} is a saturation loading; b is coefficient in the pure component Langmuir adsorption isotherm; A and B refer to two different

sites on the molecules. The adsorption selectivity for the C_3H_6:C_3H_8 (50:50 v/v %) can be defined by

$$s = \frac{q_1 p_2}{q_2 p_1}$$

Where, q_i is the quantity adsorbed of component *i*; p_i represents the partial pressure of the component *i*.

Density functional theory calculations

All quantum chemistry calculations were performed by using the plane wave density functional theory (DFT) implemented in the Vienna ab initio simulation package (VASP).[4-7] The projector augmented wave (PAW)[8] method was used to describe the nuclei and core electrons interactions. The electron exchange correlation energy was calculated within the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof formalism (PBE).[9] DFT-D2 method[10] is applied to account for van der Waals interactions. The energy cutoff for the plane-wave basis expansion was set to be 400 eV. Periodic boundary conditions were used for all simulations. The simulation cell dimension was about 21.36 Å × 21.36 Å × 10.57 Å. The energy and force convergence criteria were set to be 10^{-4} eV and 0.01eV/Å, respectively. The geometry of structure was optimized with conjugate gradient algorithm using the convergence criteria mentioned above. The optimized geometry was used to perform ab initio molecular dynamics (AIMD) simulations within the canonical ensemble (NVT) at different temperatures (87 K, 143 K, 213 K, 273 K, and 343 K). The temperature was controlled with the Nosé-Hoover thermostat.[11,12] For each temperature mentioned above, a 2.0 ps AIMD simulation with a time step of 1.0 fs was run and the initial 0.5 ps part was discarded for equilibration. Note: during AIMD simulations, the methoxy groups of optimized geometry were set to be flexible, whilst the rest of the

atoms were kept frozen.

Breakthrough Experiment.

The samples were filled with the column and heated at 423 K for 12h for activation before breakthrough test. The carried gas (He ≥ 99.99) was through the adsorption bed for 1 h with a flow rate of 5 ml min^{-1}. Then, a gas mixture of C_3H_6/C_3H_8 (50:50, V: V) was feed into the adsorption column. The gas mixture flow rate was 5ml min^{-1}, which controlled by a mass flow controller. In this work, breakthrough experiment was carried out at 298 K, 100 KPa. The composition of effluent from adsorption bed is monitored by a gas chromatography.

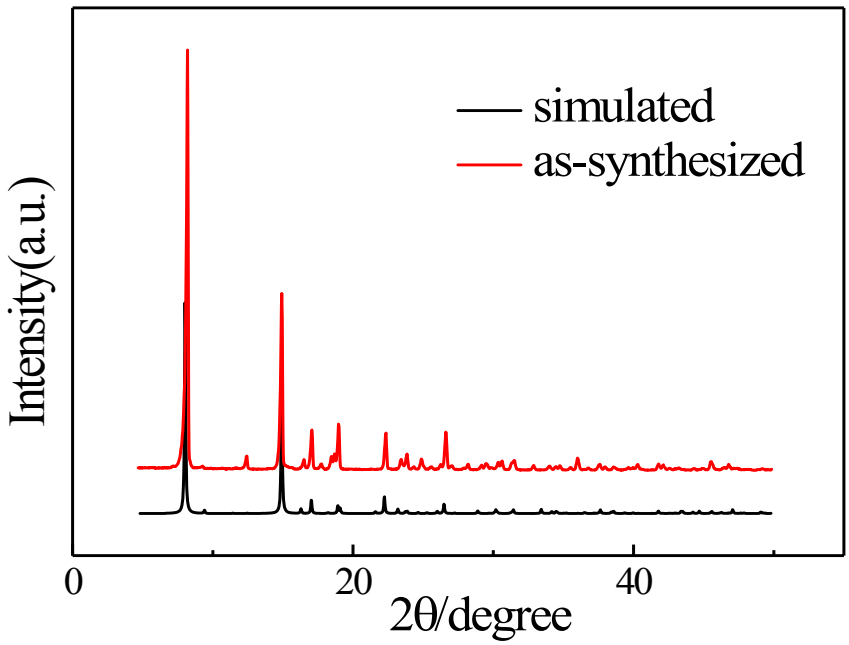

Fig. S1 PXRD patterns of CAU-10-OMe.

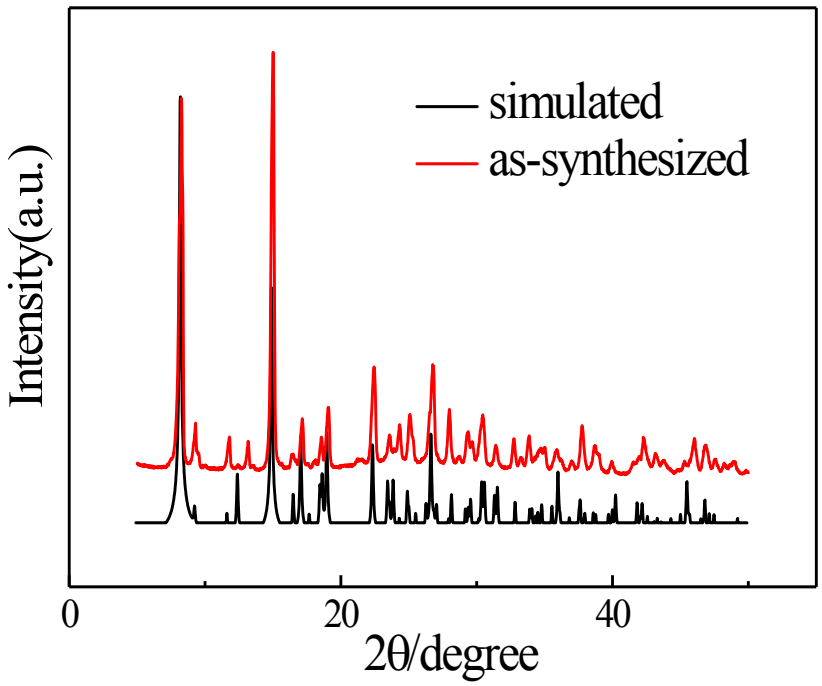

Fig. S2 PXRD patterns of CAU-10-H.

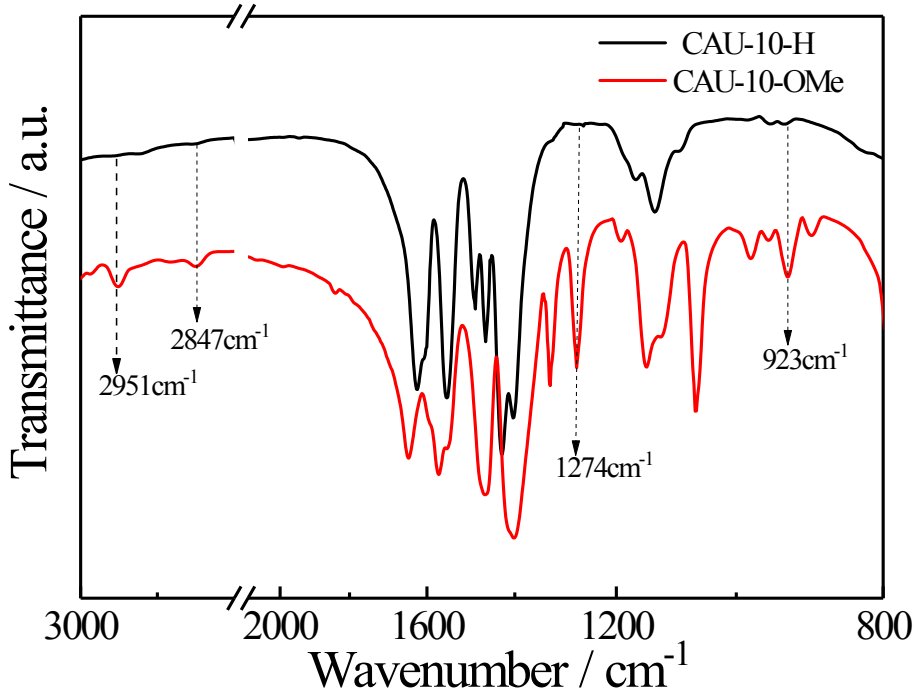

Fig. S3 FTIR spectra of CAU-10-H and CAU-10-OMe.

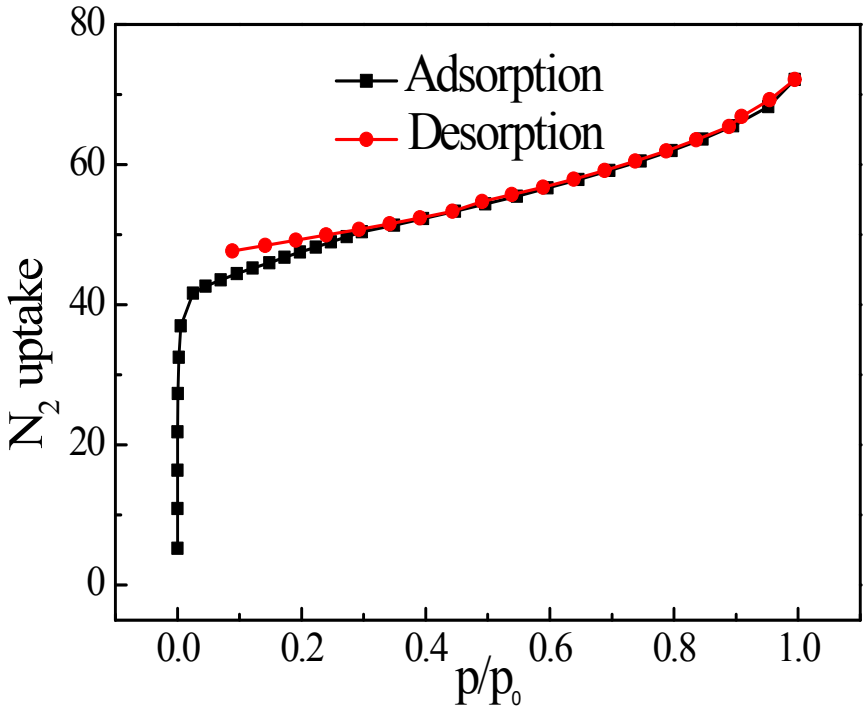

Fig. S4 N_2 adsorption-desorption isotherms at 77 K of CAU-10-OMe.

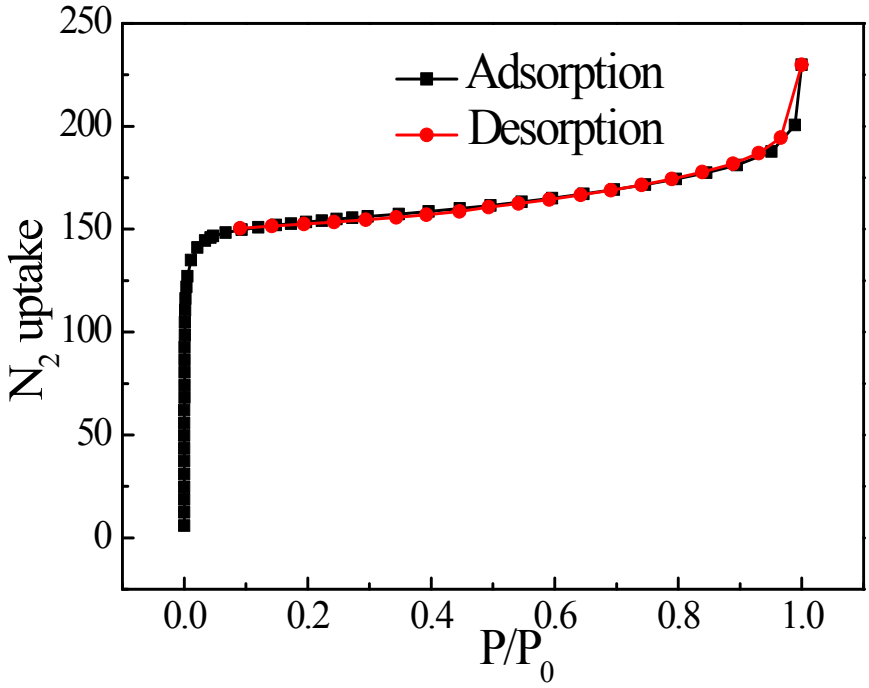

Fig. S5 N_2 adsorption-desorption isotherms at 77 K of CAU-10-H.

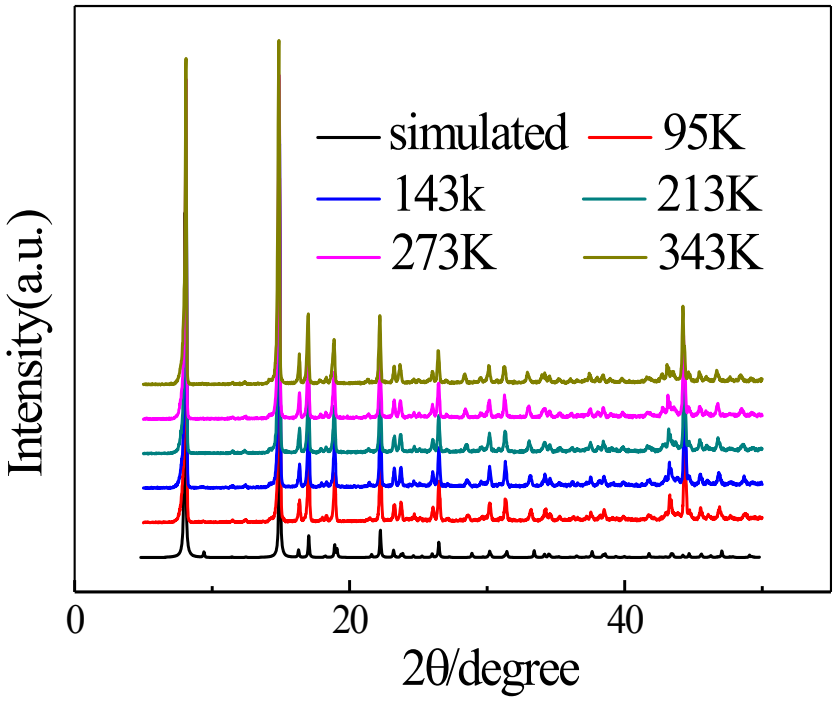

Fig. S6 Variable-temperature PXRD (VT-PXRD) patterns of CAU-10-OMe under air atmosphere.

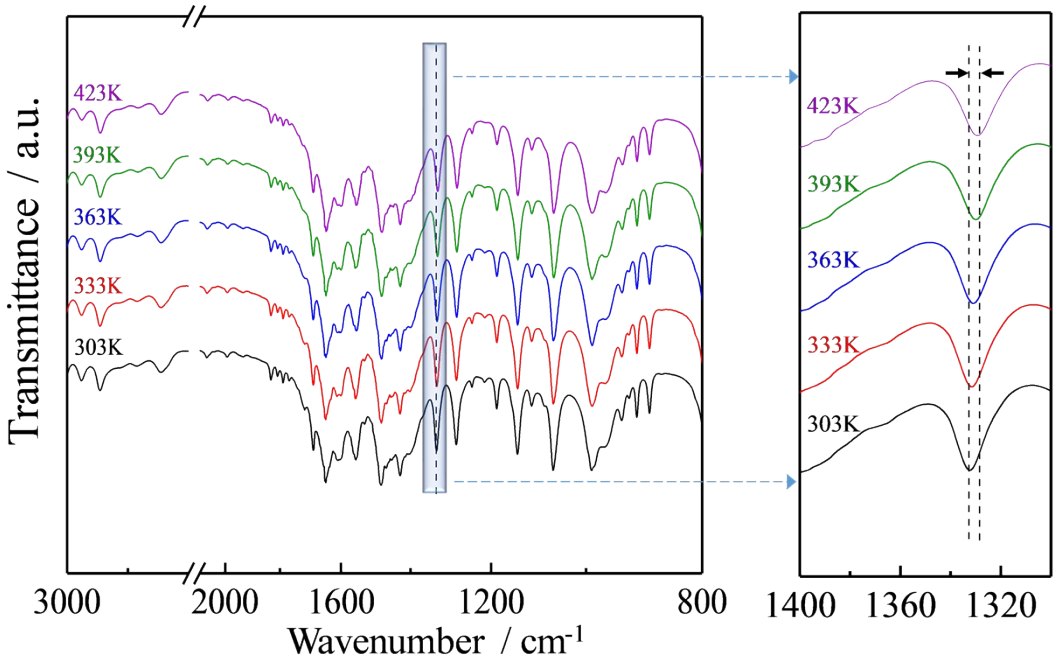

Fig. S7 Temperature dependence FTIR spectra of CAU-10-OMe.

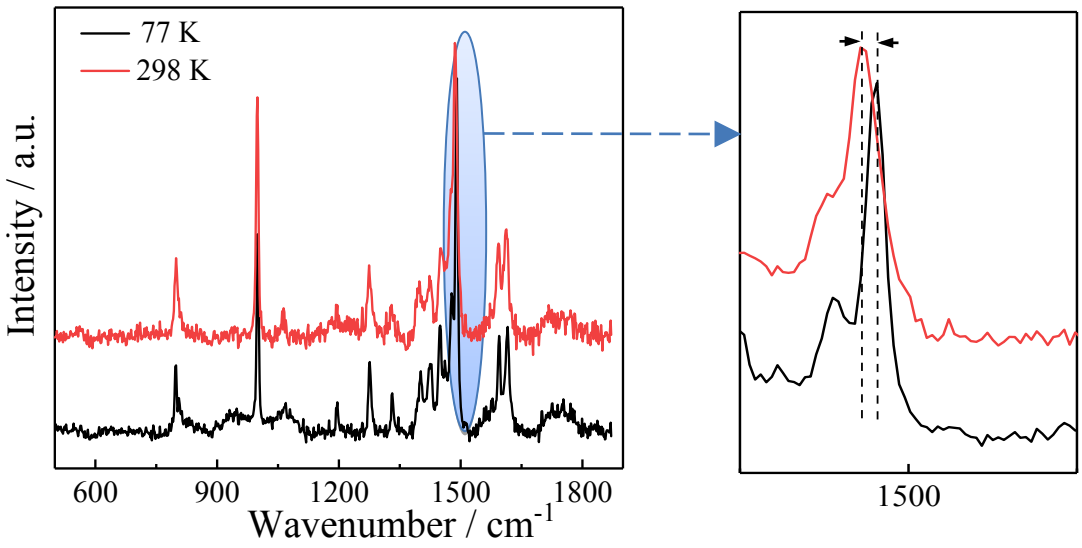

Fig. S8 Temperature dependence Raman spectra of CAU-10-OMe.

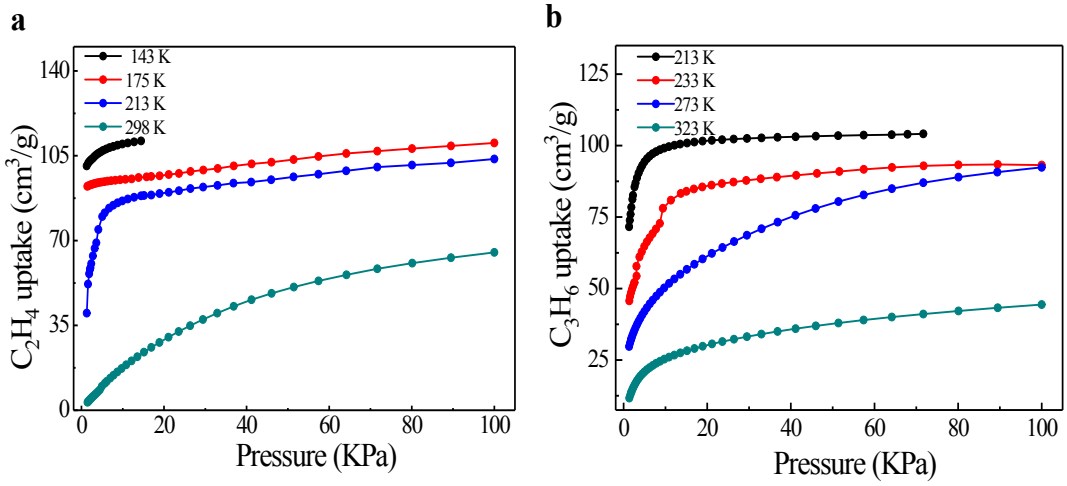

Fig. S9 The adsorption isotherms of C_2H_4 (a) and C_3H_6 (b) on CAU-10-H at 143 K - 323 K.

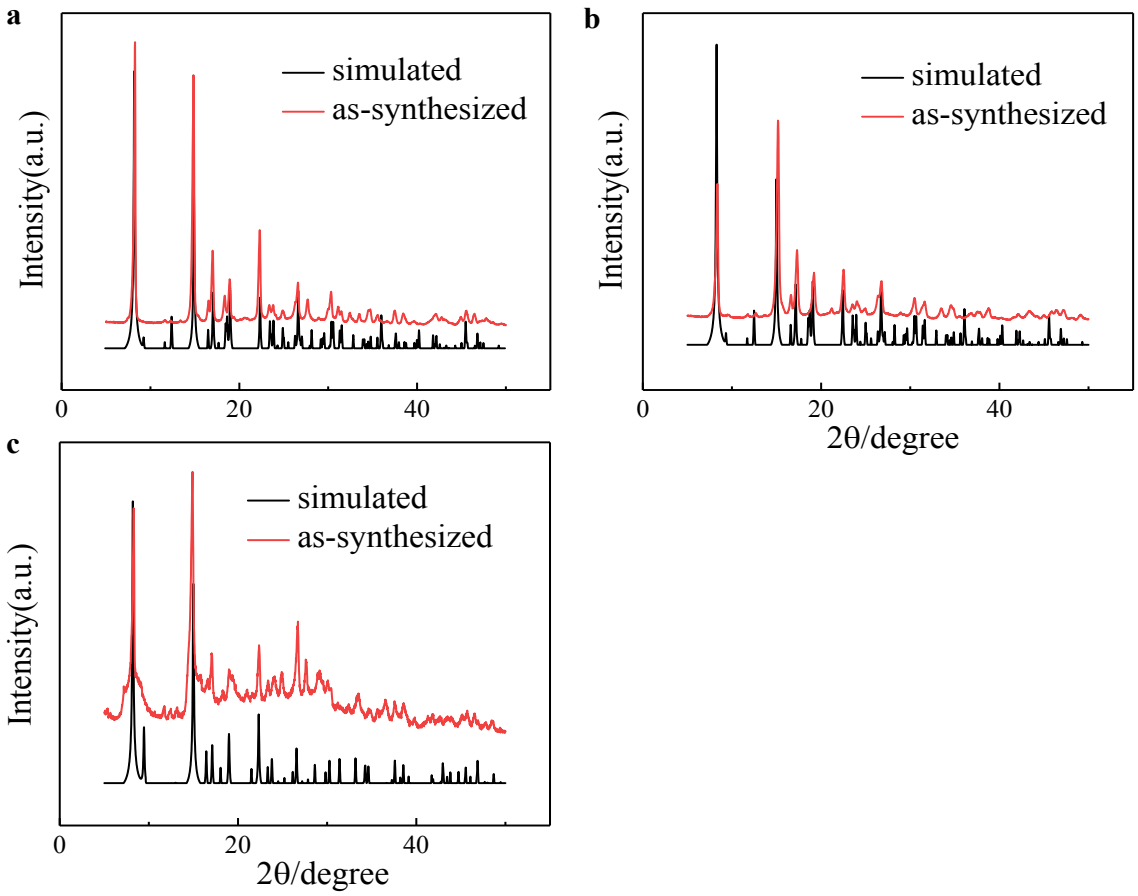

Fig. S10 PXRD patterns of CAU-10-NH_2 (a), CAU-10-NO_2 (b) and CAU-10-F (c).

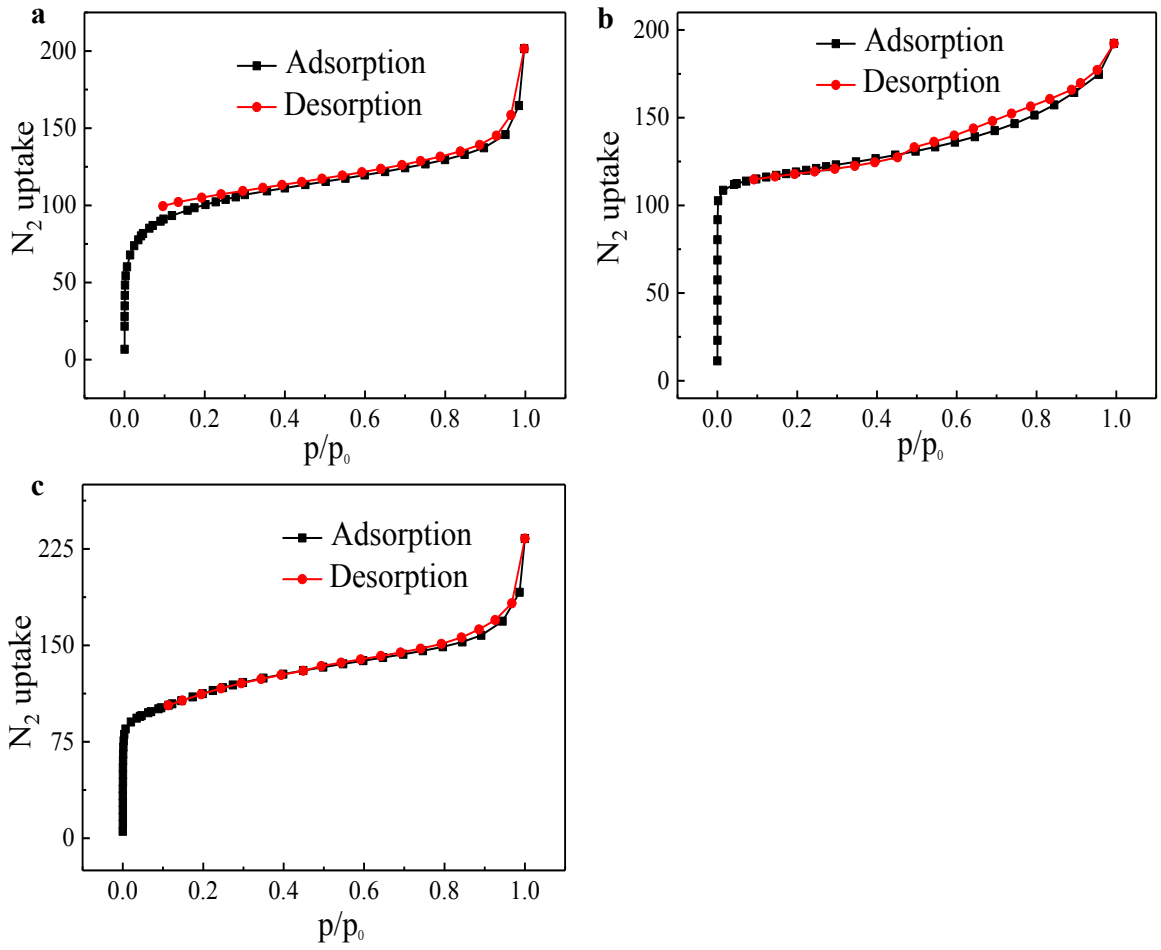

Fig. S11 N_2 adsorption-desorption isotherms at 77K of CAU-10-NH_2 (a), CAU-10-NO_2 (b) and CAU-10-F (c).

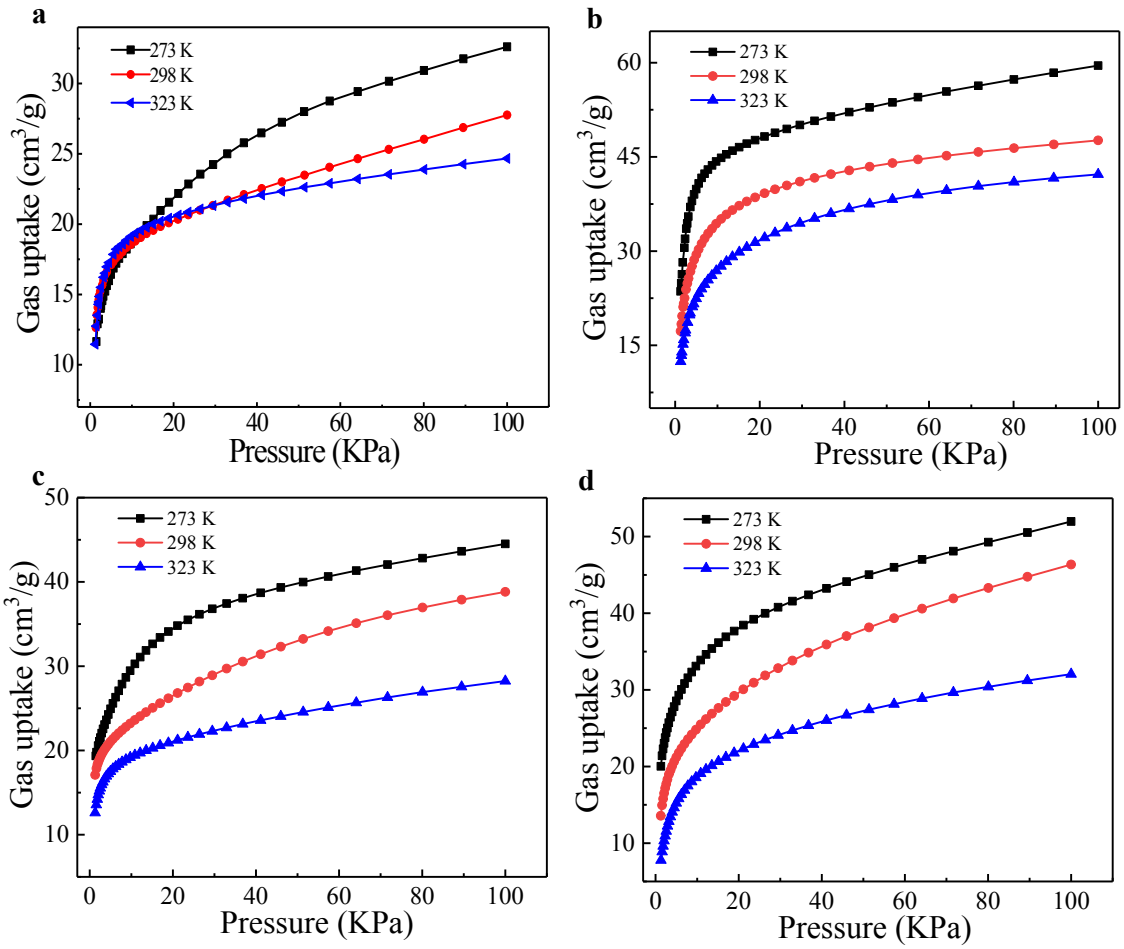

Fig. S12 The adsorption isotherms of C_3H_6 on CAU-10-OMe (a), CAU-10-NH_2 (b), CAU-10-NO_2 (c) and CAU-10-F (d) at 273 K-323 K.

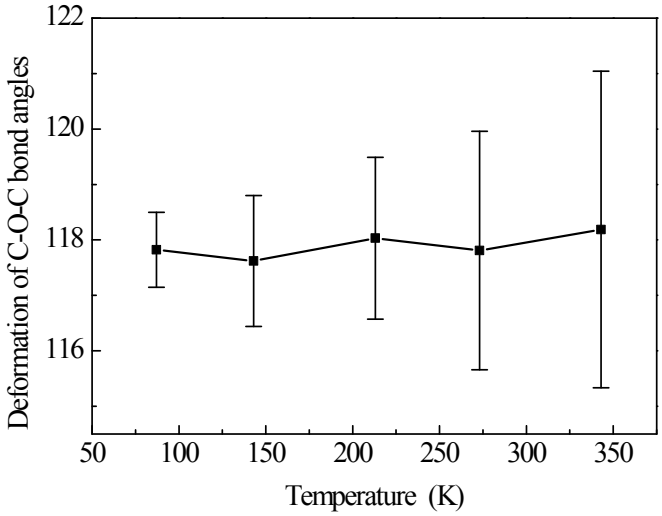

Fig. S13 AIMD simulated evolution of the C-O-C bond angles in the flexible methoxyl groups of CAU-10-OMe as a function of the temperature.

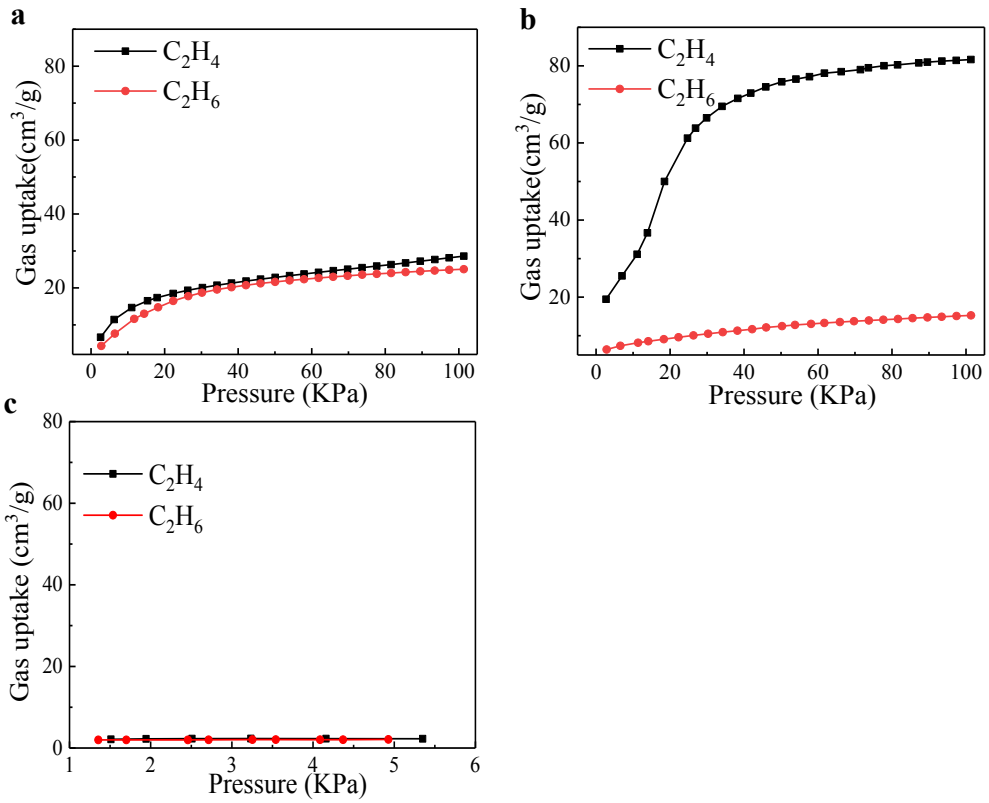

Fig. S14 The adsorption isotherms of C_2H_4 and C_2H_6 on CAU-10-OMe at 298 K (a), 203 K (b) and 143 K (c).

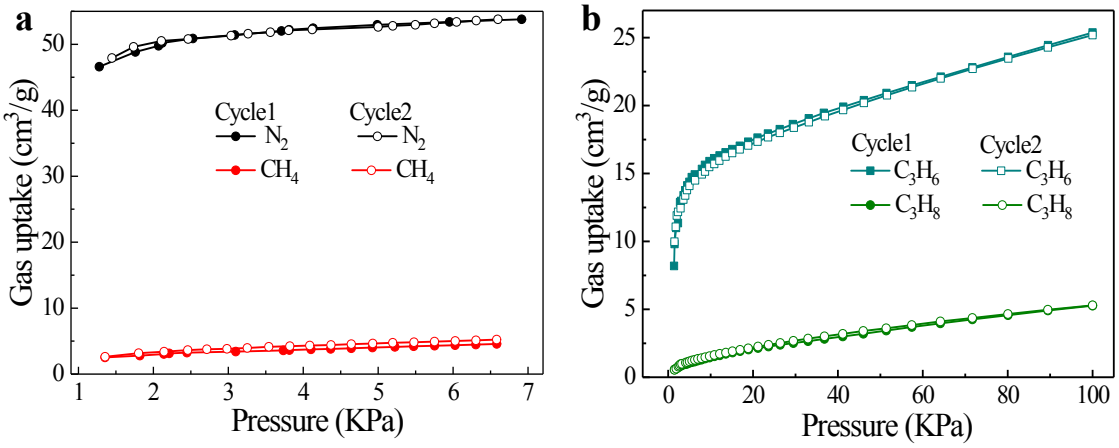

Fig. S15 Reversible adsorption of N_2/CH_4 at 87 K (a) and C_3H_6/C_3H_8 at 298 K (b) on CAU-10-OMe.

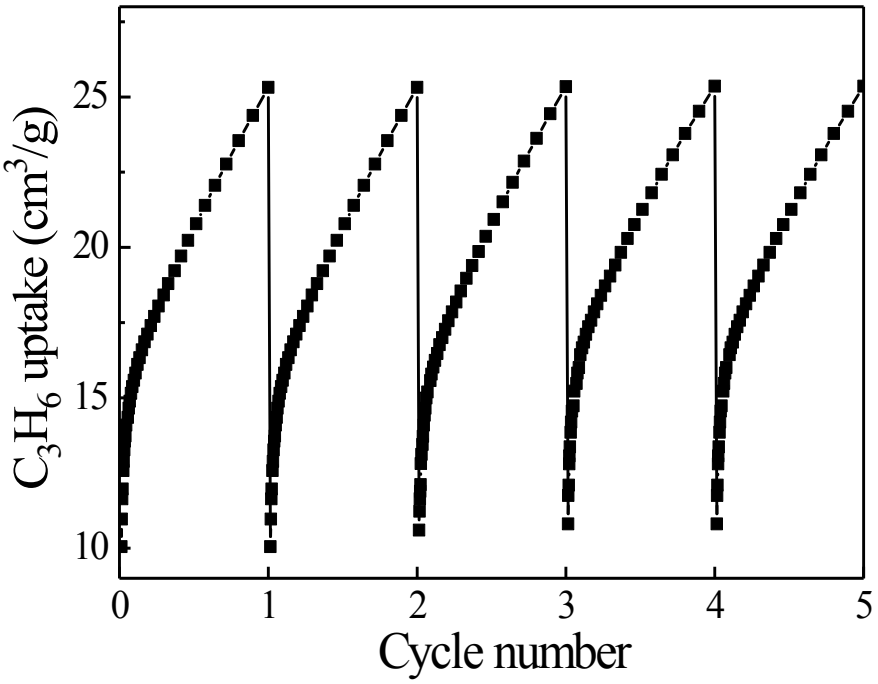

Fig. S16 Five cycles of C_3H_6 adsorption-desorption on the CAU-10-OMe at 298 K and 100 KPa for adsorption and under dynamic vacuum at 423 K for 12 hours for desorption.

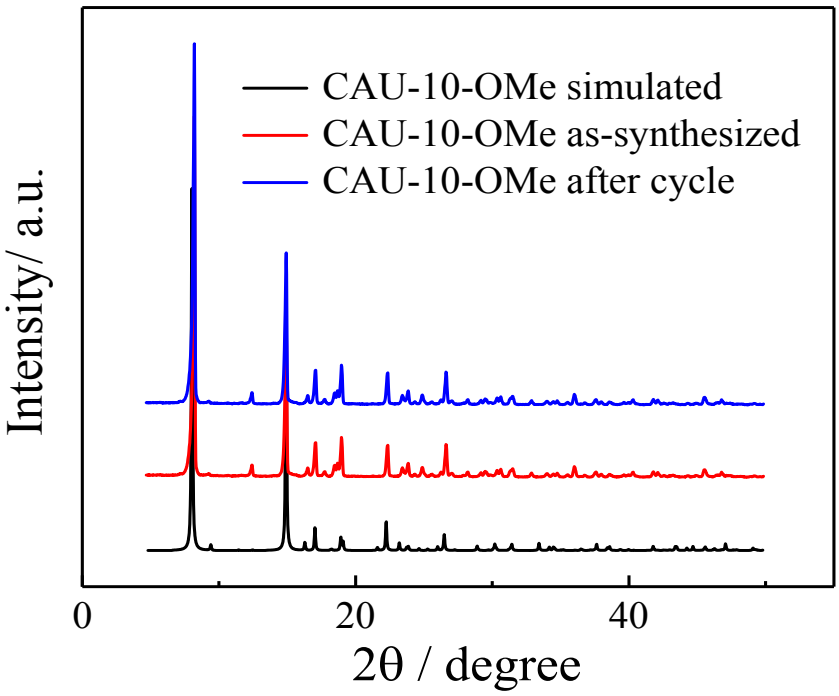

Fig. S17 PXRD result of CAU-10-OMe after cycle experimental.

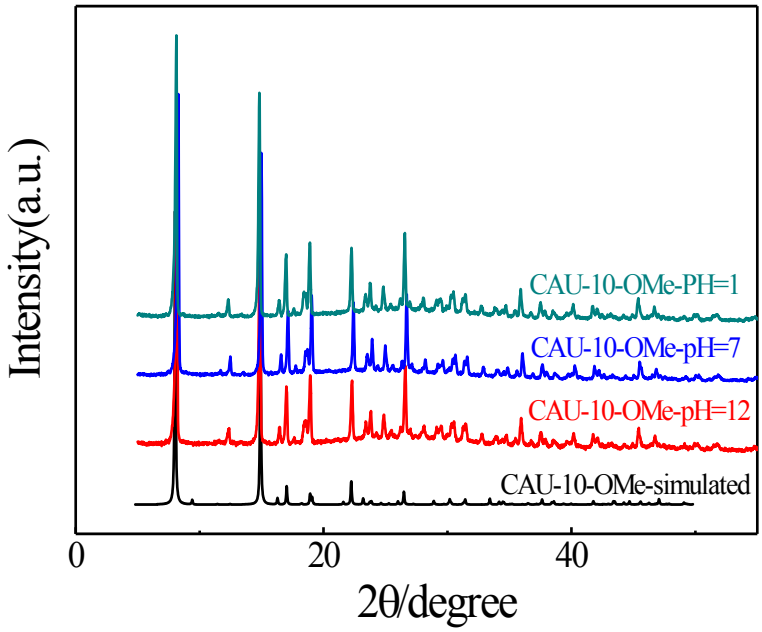

Fig. S18 Comparison of PXRD patterns of CAU-10-OMe after immersing water solution for 24h with different pH.

Reference

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