Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Unprecedented activation and CO_2 capture properties of an elastic single-molecule trap

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Low-pressure gas adsorption measurements

Gas adsorption isotherms for pressures in the range 0-1.1 bar were measured by a volumetric method using a Micromeritics ASAP2020 surface area and pore analyzer. A pre-weighed analysis tube was charged with a sample of PCN-200-syn, capped with a transeal and evacuated by heating at 30 °C under dynamic vacuum for 5 minutes. The evacuated analysis tube containing the activated sample was then carefully transferred to an electronic balance and weighed to determine the mass of sample (287.6 mg). The tube was then transferred to the analysis port of the gas adsorption instrument. For all isotherms, warm and cold free space correction measurements were performed using ultra-high purity He gas (UHP grade 5.0, 99.999% purity). All gases used are UHP grade (99.999% purity). N2 and Ar isotherms at 77 K were measured in liquid nitrogen, isotherms at 87 K were measured using liquid argon, isotherms at 195 K were measured using a dry ice/acetone bath, isotherms at 273 K were measured using ice water and isotherms at 283 K and 296 K were measured using water baths. All temperatures and fill levels were monitored periodically throughout the measurement. Oil-free vacuum pumps and oil-free pressure regulators were used for all measurements to prevent contamination of the samples during the evacuation process or of the feed gases during the isotherm measurements.

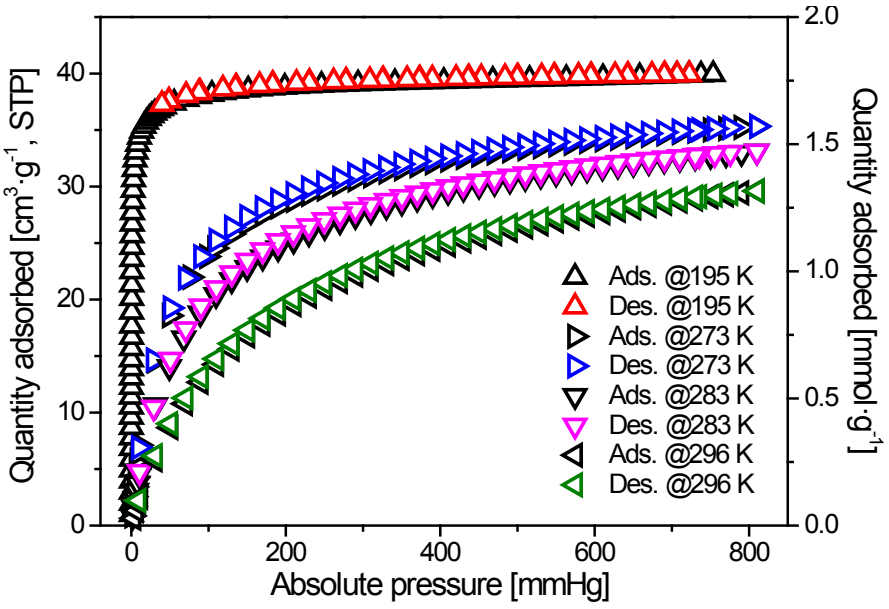

Fig. S1. Carbon dioxide adsorption isotherms collected at different temperatures.

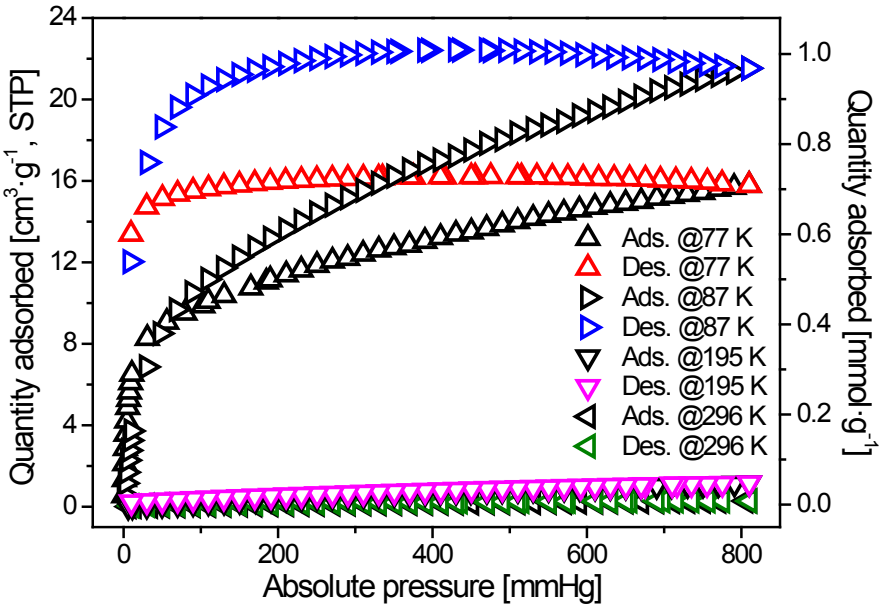

Fig. S2. Hydrogen adsorption isotherms collected at different temperatures.

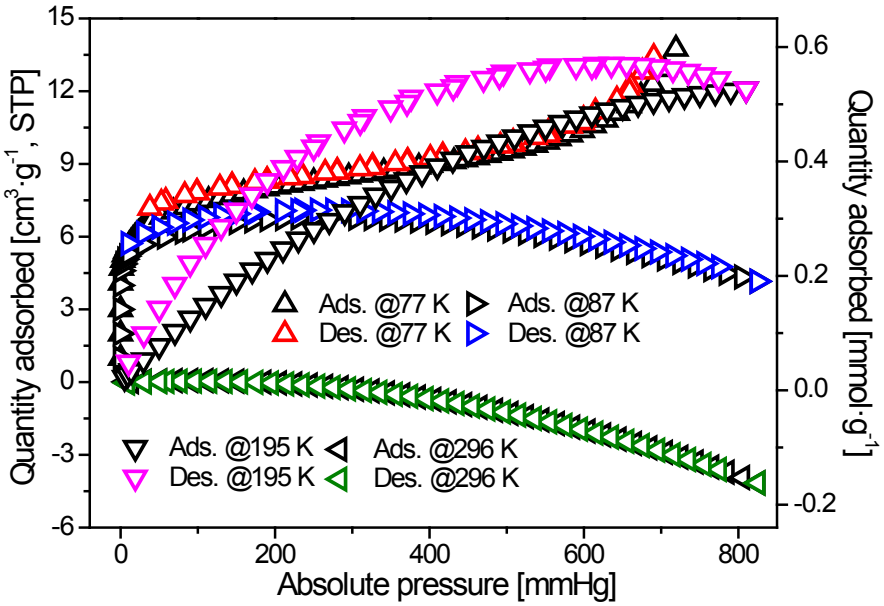

Fig. S3. Nitrogen adsorption isotherms collected at different temperatures.

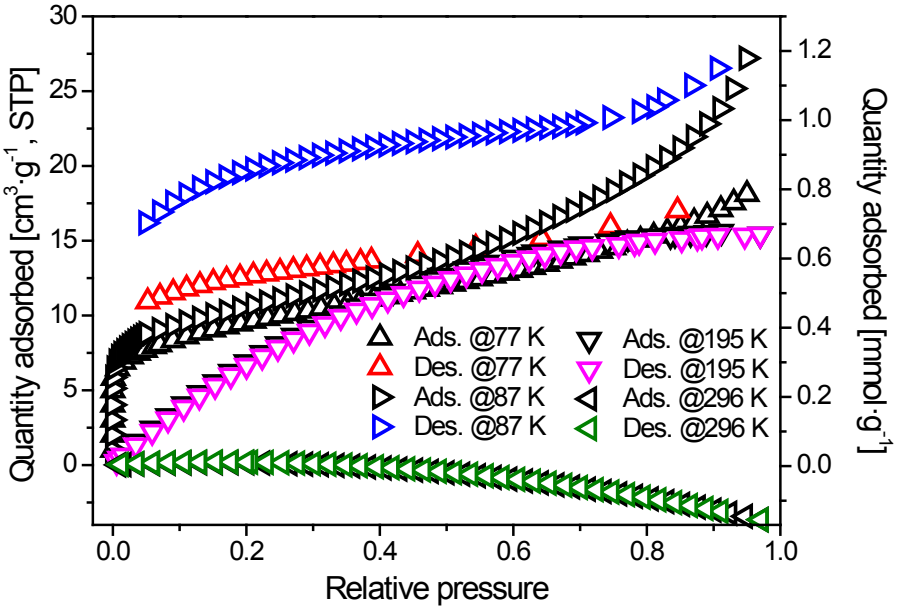

Fig. S4. Oxygen adsorption isotherms collected at different temperatures.

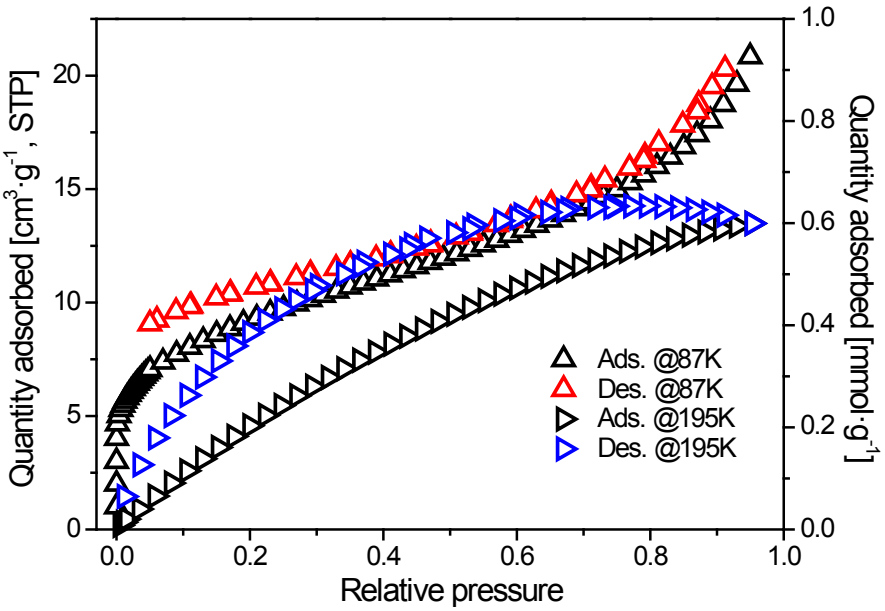

Fig. S5. Argon adsorption isotherms collected at different temperatures.

Breakthrough method for mixed gas adsorption measurements

Two gas inputs can be chosen where each of them can be connected to different gas storages (Fig. S6). The gas flow can be conducted either through the bypass or through the adsorption column. The adsorption column with an upstream connected heat coil can be temperated in an oil or water bath. The gas flow over the column can be either conducted through a manual flow measurement device or as exhaust gas analyzed by a mass spectrometer.

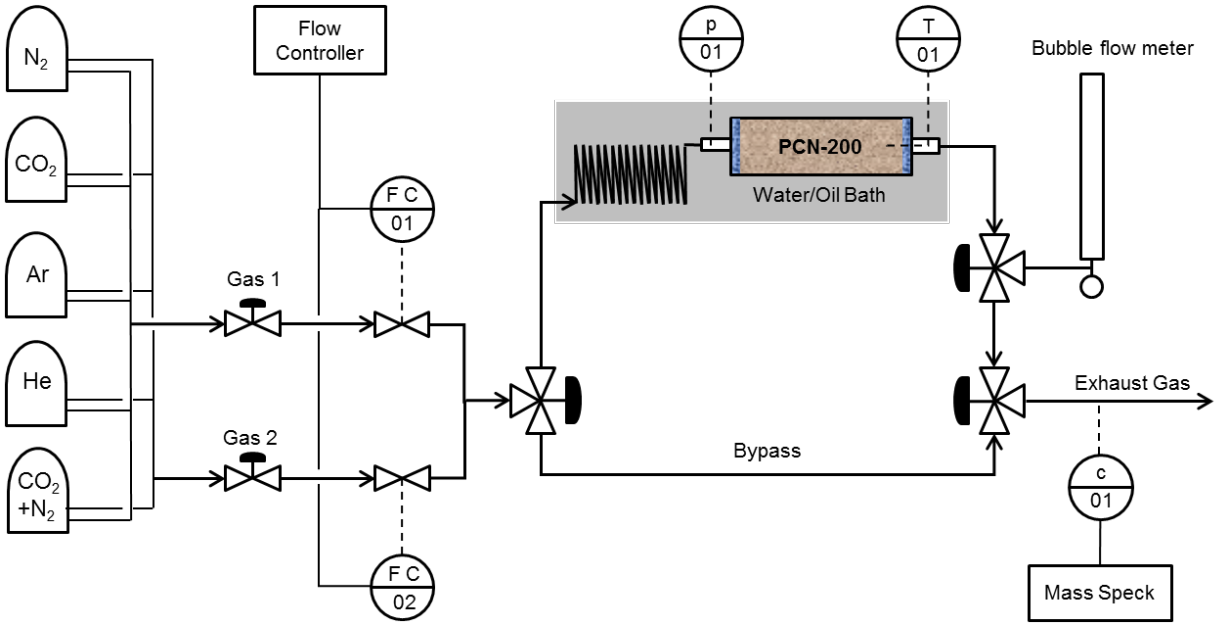

Fig. S6. Flow sheet of the breakthrough setup.

Before every measurement the material is activated by heating the packed column in inert gas stream and the whole system is flushed with inert gas. To begin of the measurement the mixed gas stream of test gas is first conducted through the bypass until the concentrations measured by the mass spectrometer are constant. At that point the test gas stream is changed to the packed column by sudden and synchronic turn of the two bypass vents. The pressure in front of the bed

is measured in relation to the surrounding environmental pressure to consider the pressure drop over the packed bed. In addition the temperature of the test gas is measured *in situ* in the end of the packed bed. At the end of each measurement the real gas flow is measured by the bubble flow meter.

For the experiments with PCN-200 we have used test gas volume flows of around 10 mL/min. The column had a diameter of 8 mm and a length of 40 mm. First measurements have been carried out with 556 mg of material (the 23 °C measurements). Because of a high pressure drop of up to 100 mbar we repacked the column for the 40 °C measurements with only 488 mg and reduced pressure drops to less than 10 mbar.

Fig. S7 shows the outlet concentration analysis of an exemplary breakthrough measurement. At 120 s the flow is changed from bypass through the column (after all concentrations were constant). The test gas mixture is 15% CO_2 in N_2. Starting at time = 120 s pure helium can be observed in the outlet of the system. This helium is purged by the test gas flow. Because CO_2 is adsorbing into the material a pure N_2 breakthrough can be detected from t = 230 s. After the material is fully saturated with CO_2 the breakthrough of CO_2 can be observed at t = 300 s. The system gains equilibrium conditions and the gas concentration is equal to the inlet concentration after around 650 s. The amount of CO_2 that remains in the system can be calculated by the integration of the outlet concentration subtracted by the inlet concentration (the red colored area). Part of this volume fills the empty space of the system (tubing etc.). The empty volume is measured by a breakthrough measurement using two inert gases that have shown no adsorption characteristic towards PCN-200 (Argon and Helium). By integration of those breakthrough curves the result is idealistic the pure empty volume of the system. Next to the concentration curve we have established continues temperature measurement. We can clearly observe a temperature raise at the end of each CO_2 breakthrough which is related to the heat of adsorption of the material. More important we can show that the temperature is fast enough reduced back to surrounding water temperature that at the end of each breakthrough we reach back the equilibrium temperature of the measurement. This is important because we compare the results to isotherms of one specific temperature and the temperature has a high influence on the adsorption capacity.

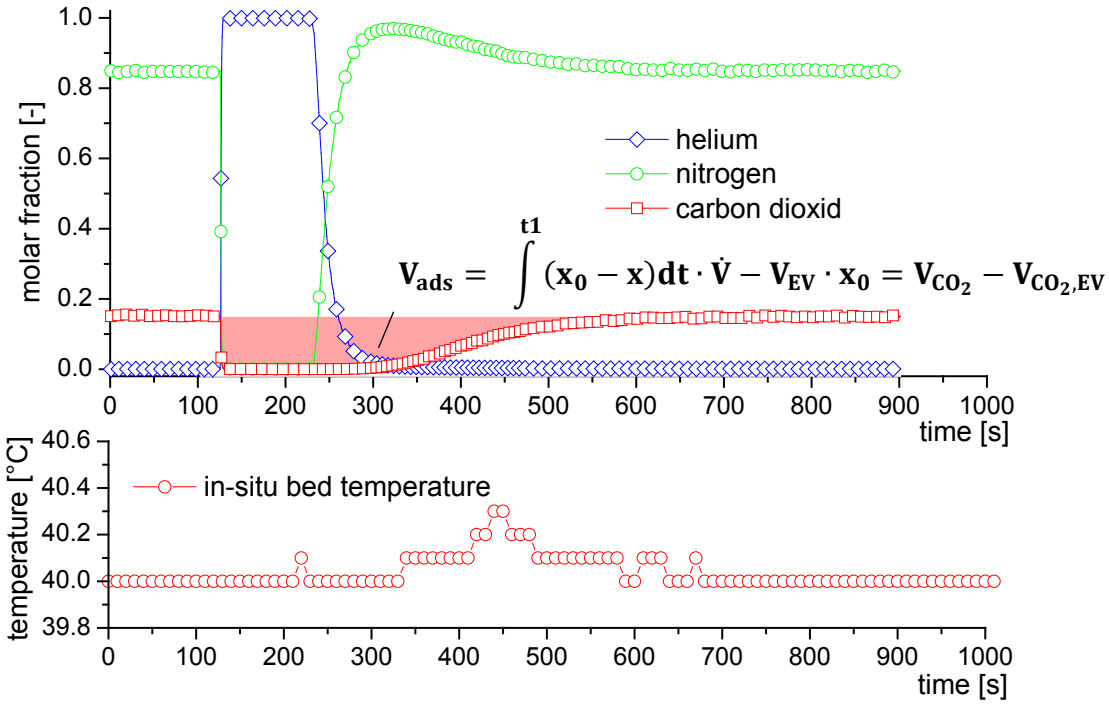

Fig. S7. Example of a breakthrough curve. PCN-200 at one bar and 40 °C.

Results of breakthrough:

We have measured the breakthrough for three different test gas compositions (15% CO_2 / 85% N_2, 50% CO_2 / 50% N_2, 100% CO_2) and two different temperatures (40 °C and 23 °C). Each measurement we have repeated at least two times.

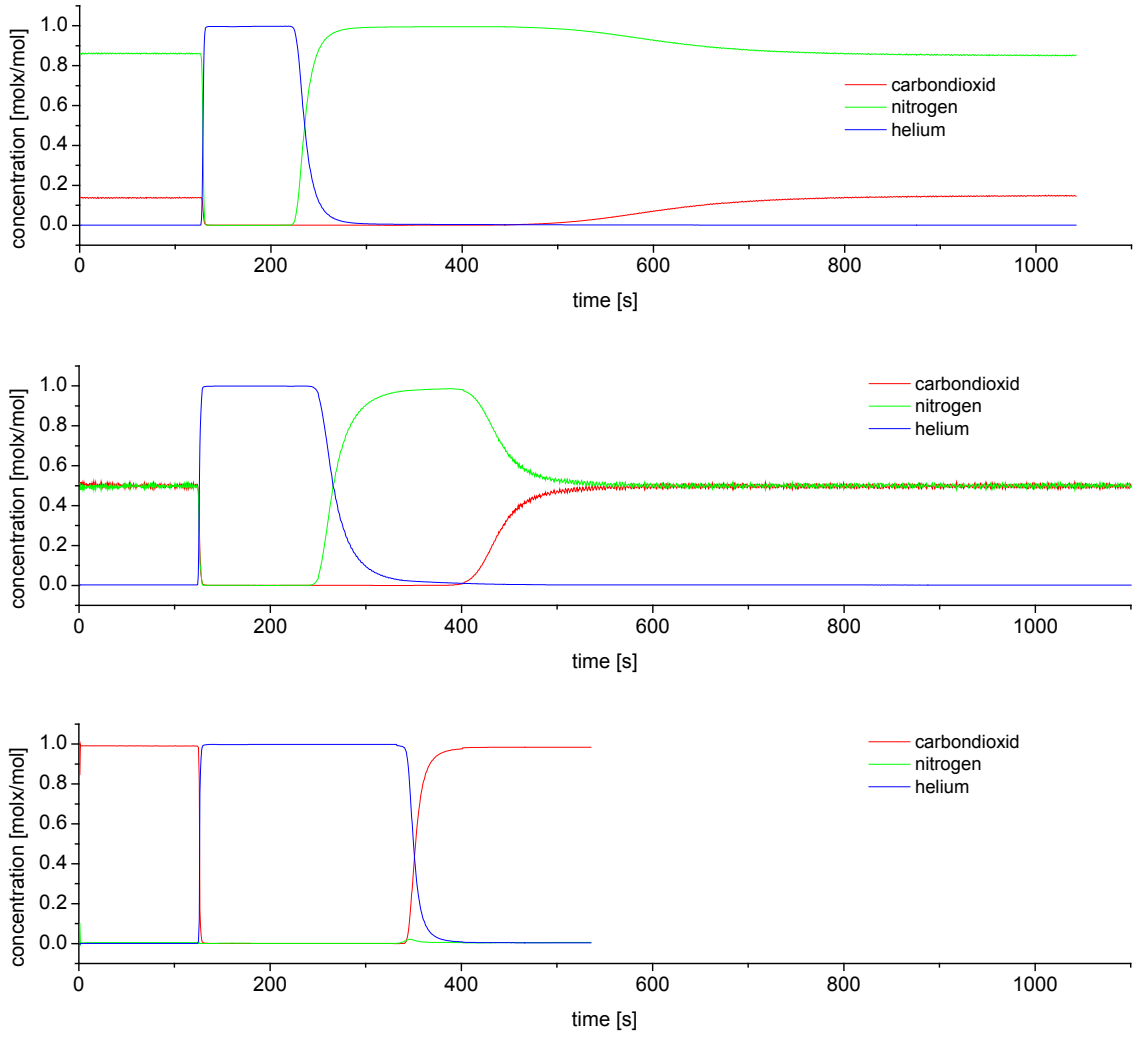

Fig. S8. Breakthrough at 295 K: Top: 15% CO_2 / 85% N_2 mixture, volume flow = 12.44 ccm/min. Middle: 50% CO_2 /50% N_2 mixture, volume flow = 11.49 ccm/min. Bottom: 100% CO_2, volume flow = 11.71 ccm/min.

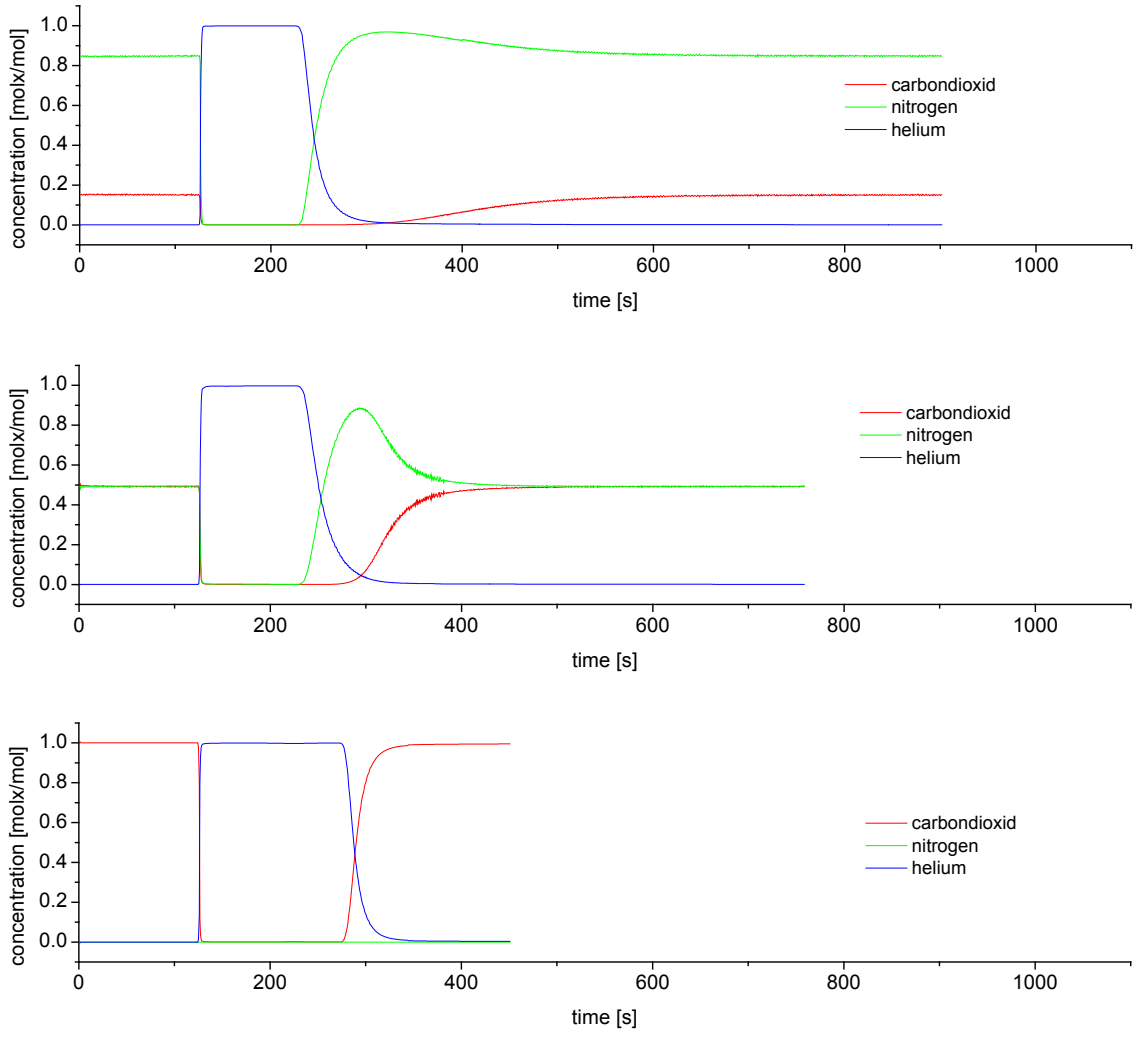

Fig. S9. Breakthrough at 313 K: Top: 15% CO2 / 85% N2 mixture, volume flow = 10.27 ccm/min. Middle: 50% CO2 / 50% N2 mixture, volume flow = 11.45 ccm/min. Bottom: 100% CO2, volume flow = 11.92 ccm/min.

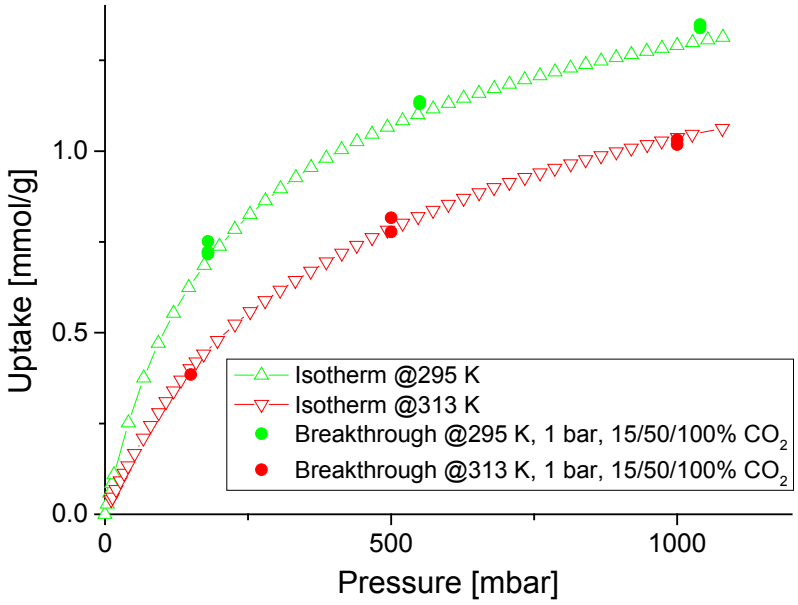

Fig. S10. CO_2 adsorption isotherms of PCN-200 from volumetric measurements at 313/295 K in comparison with adsorption values obtained from mixed gas breakthrough measurements at 313/295 K and 1 bar with 15, 50% CO_2 in N_2, and 100% CO_2.

Results of integration

Pressure [mbar] (*)	**Integrated uptake** [mmol/g] breakthrough @295 K	**Pressure** [mbar] (*)	**Integrated uptake** [mmol/g] breakthrough @313 K
178	0.7515	153	0.385
184	0.7166	-	-
182	0.7227	-	-
551	1.1302	502	0.8163
550	1.1367	502	0.7775
1038	1.3389	1004	1.0313
1040	1.3486	1008	1.0181

(*) as adsorption pressure we used a middle value between the environmental pressure and the elevated pressure in front of the packed bed to compare the uptake with the pure gas isotherms.

Gas-purge activation measurements

In situ synchrotron-based powder diffraction experiments were performed at the 1-BM beamline of the Advance Photon Source in Argonne National Laboratory (Argonne, IL, USA) from a sample contained in a 0.9 mm diameter polyimide capillary using a flow-cell setup (for details see Chupas *et al.*[1]). The incident X-ray wavelength was 0.6057 Å. Data were collected using a Perkin-Elmer flat panel area detector (XRD 1621 CN3-EHS) over the angular range 1-25° 2-Theta at room tempearture. The raw images were processed within Fit-2D,[2] refining the sample-to-detector distance and tilt of the detector relative to the beam based on the data obtained for a LaB_6 standard.

Nitrogen, Helium, carbon dioxide and air were purged through a capillary packed with PCN-200. All experiments result in the activation on PCN-200 as indicated by the abrupt phase transition (Fig S11).

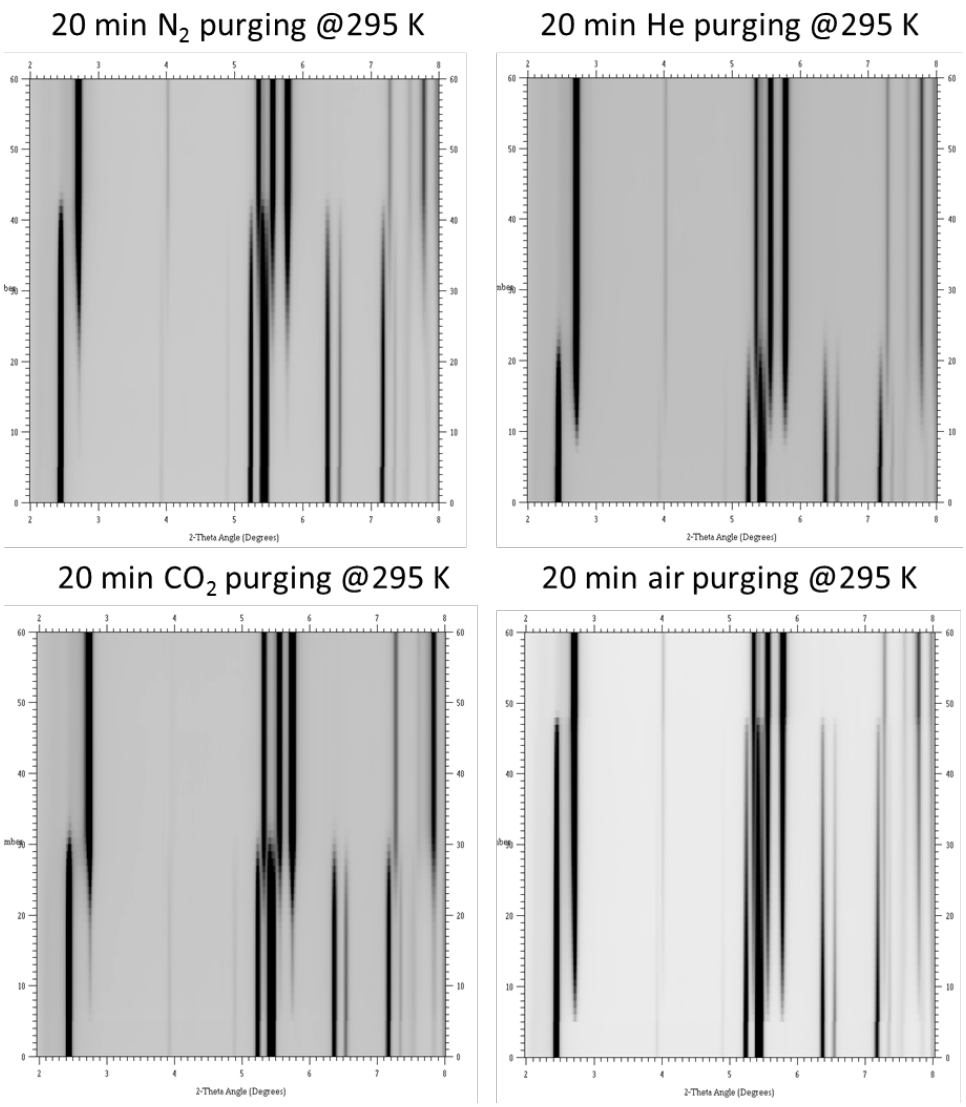

Fig. S11. Gas-purge activation of PCN-200 monitored by *in situ* synchrotron-based powder diffraction at 295 K using different purge gases.

References

1. P. J. Chupas, K. W. Chapman, C. Kurtz, J. C. Hanson, P. L. Lee and C. P. Grey, *J. Appl. Phys.*, 2008, **41**, 822.
2. A. P. Hammersley, S. O. Svensson, M. Hanfland, A. N. Fitch and D. Hausermann, *High Pressure Research*, 1996, **14**, 235.