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ELECTRONIC SUPPLEMENTARY INFORMATION

Separation of CO_2 from CH_4 and CO_2 capture in the presence of water vapour in NOTT-400

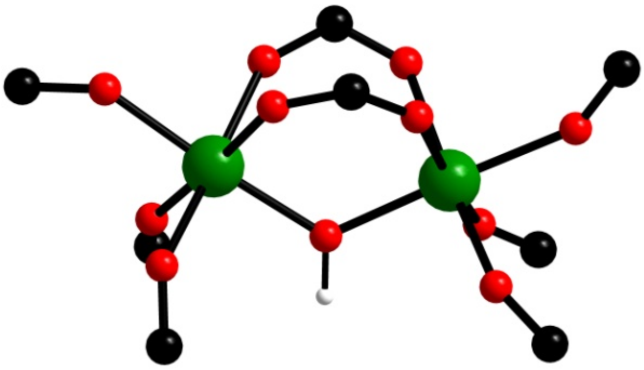
Maximiliano R. Gonzalez,[a] Juan H. González-Estefan,[b] Hugo A. Lara-García,[b] Pedro Sánchez-Camacho,[b] Elena I. Basaldella,[a,c] Heriberto Pfeiffer[b] and Ilich A. Ibarra*[,b]

[a] *Centro de Investigación y Desarrollo en Ciencias Aplicadas Dr. J.J. Ronco (CINDECA), (CONICET-CIC-UNLP) 47 No. 257, (B1900 AJK) La Plata, Argentina.*

[b] *Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior s/n, CU, Del. Coyoacán, 04510, México D. F., Mexico.*
E-mail: argel@unam.mx

[c] *CITEMA, Universidad Tecnológica Nacional, 60 y 124, (1900) La Plata, Argentina.*

1. Scheme of the binuclear $[M_2(\mu_2\text{-OH})]$ building block



Scheme S1: Binuclear building block of two metal ions oxygen octahedra bridged by a μ_2-hydroxo group. Green, red, black and white spheres represent M (metal ion such as In(III) or Sc(III)), O, C and H atoms, respectively.

2. Materials and Measurements

All reagents and solvents were used as received from commercial suppliers without further purification. Powder X-ray diffraction (PXRD) data were collected under ambient conditions on a Bruker AXD D8 Advance diffractometer operated at 160 W (40 kV, 40 mA) for Cu $K\alpha_1$ (λ= 1.5406 Å). Thermal gravimetric analysis (TGA) was performed under N_2 at a scan rate of 2 °C/min using a TA Instruments Q500HR analyser. N_2 adsorption was carried out in a conventional volumetric technique by a Micromeritics ASAP 2020 sorptometer. The surface area was calculated using the BET method based on adsorption data in the partial pressure (p/p_0) range 0.01 to 0.04. Dynamic and isothermal experiments were performed using a humidity-controlled thermobalance (TA Instruments, model Q5000SA) at 30 ^{o}C and a relative humidity (RH) of 40%. A catalytic reactor system (BEL-REA, BEL Japan) coupled to a Bruker TENSER 27 FTIR was employed to measure the gas selectivity.

3. Experimental

Crystalline samples of NOTT-400 were synthesised in gram quantities by a low temperature (75 °C) solvothermal reaction of $Sc(SO_3CF_3)_3$ and H_4BPTC (biphenyl-3,3',5,5'-tetracarboxylic acid) in a slightly acidified mixture of DMF/THF/H_2O.[1] The uncoordinated solvent molecules in the pores of the as-synthesised NOTT-400 was exchanged for acetone and this promotes accessibility to the desolvated framework after activation by heating. Thus, thermogravimetric analysis (TGA; Fig. S1, ESI) and bulk powder x-ray diffraction patterns (PXRD; Fig. S2, ESI) of as-synthesised and desolvated NOTT-400 confirmed that the material consistently retains its structural integrity upon solvent removal. N_2 adsorption isotherms for activated NOTT-400[1] at 77 K were used to calculate the BET surface area ($0.01<p/p_o<0.04$) of 1355 m^2 g^{-1}.

Thermoblance

By using a thermobalance, we performed kinetic uptake experiments at different temperatures with a constant CO_2 flow. Then, acetone-exchanged samples of NOTT-400 were placed into the thermobalance and activated by heating from room temperature to 150 °C for 2h and under a flow of N_2 gas. After the activated sample was cooled down, the desired temperature was set and a constant CO_2 flow (60 mL min^{-1}) was started.

4. TGA plots

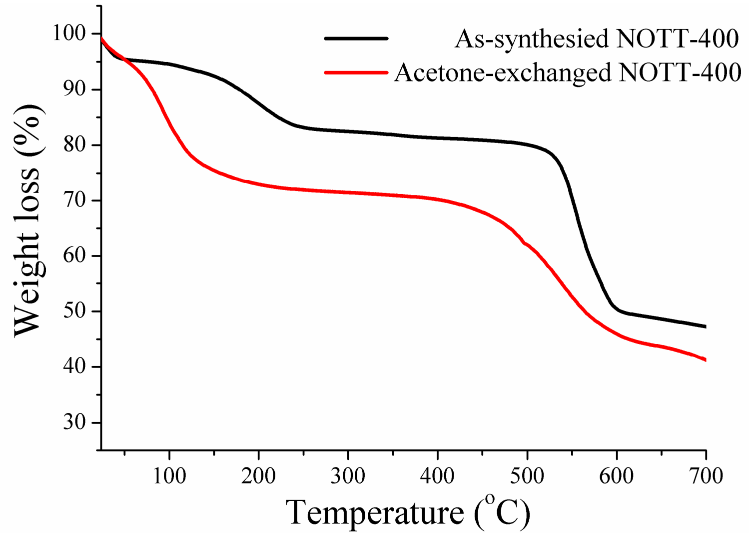


Fig. S1: TGA analyses of as-synthesised NOTT-400 (black line) and acetone-exchanged NOTT-400 (red line).

5. Powder X-ray Diffraction Patterns

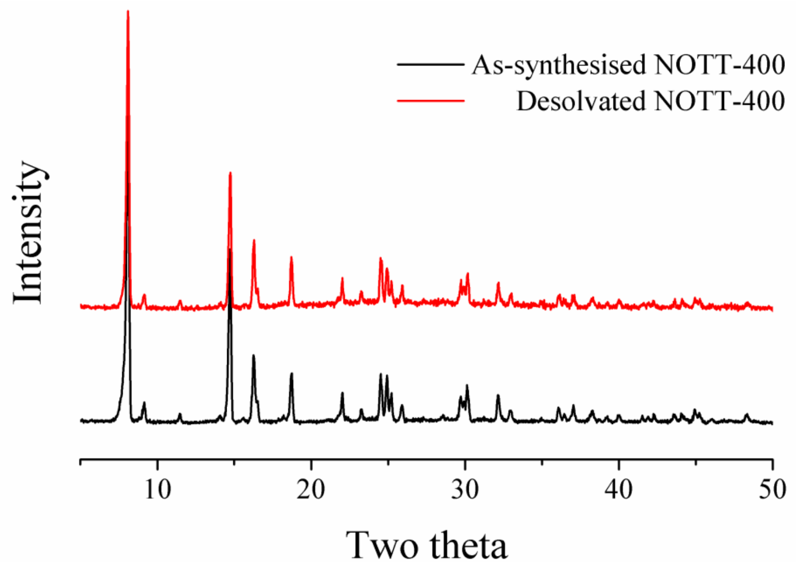


Fig. S2: PXRD patters of as-synthesised (black) and desolvated (red) NOTT-400.

6. Catalytic Reactor System (BEL-REA) for the Gas CO_2 and CH_4 Selectivity Experiments

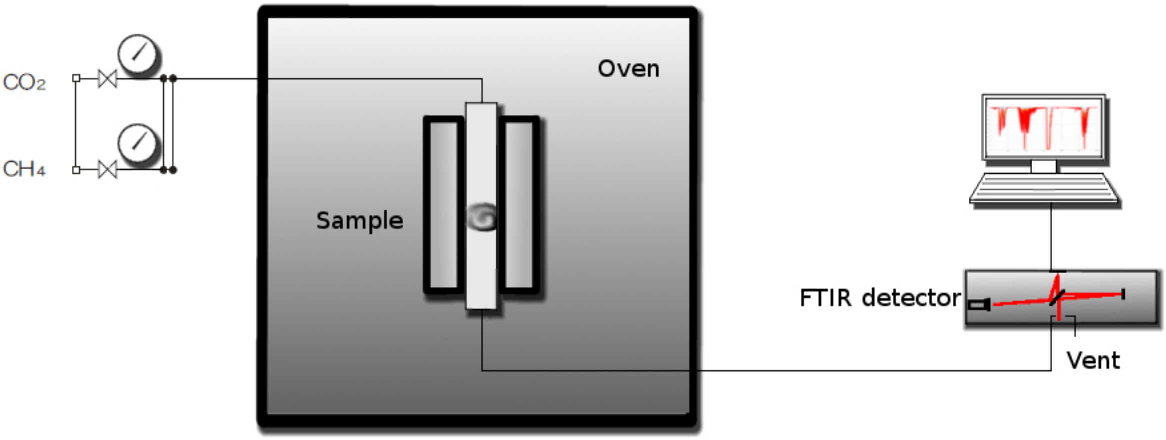


Fig. S3: Catalytic reactor system (BEL-REA) system.

7. FTIR Spectra

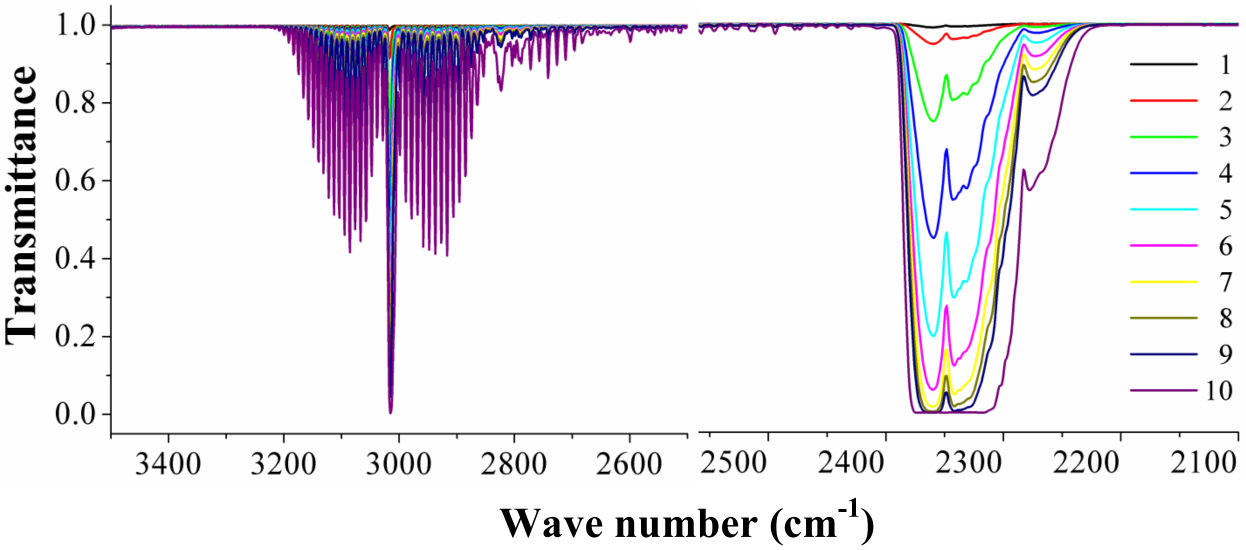


Fig S4: FTIR spectra of the resulting binary equimolar (0.13 mmol min^{-1}) gas-mixture flow (that passed through the activated NOTT-400 sample).

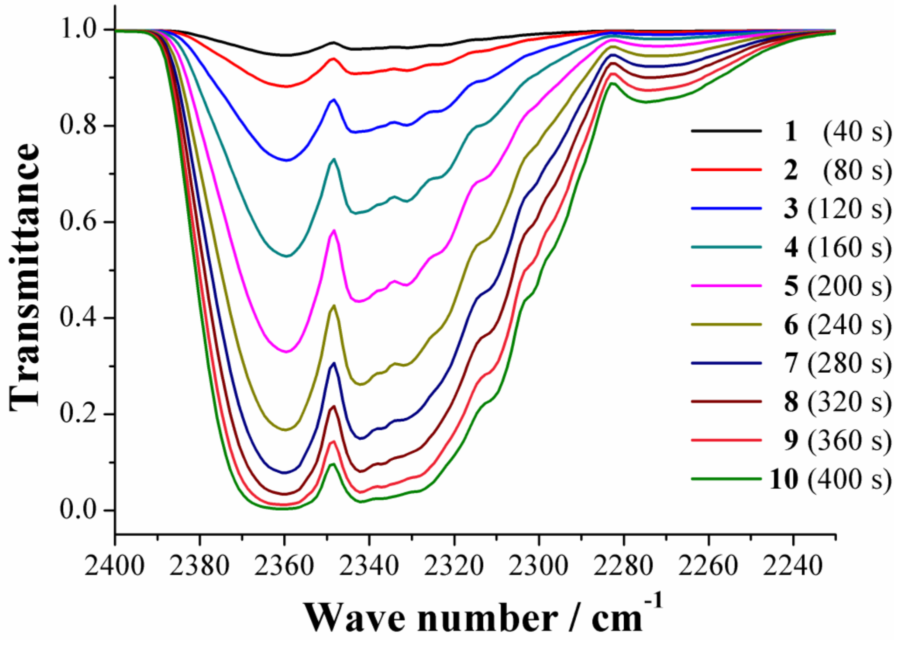


Fig S5: FTIR spectra of the resulting flow of only CO_2 gas (0.13 mmol min^{-1}) that passed through the activated NOTT-400 sample.

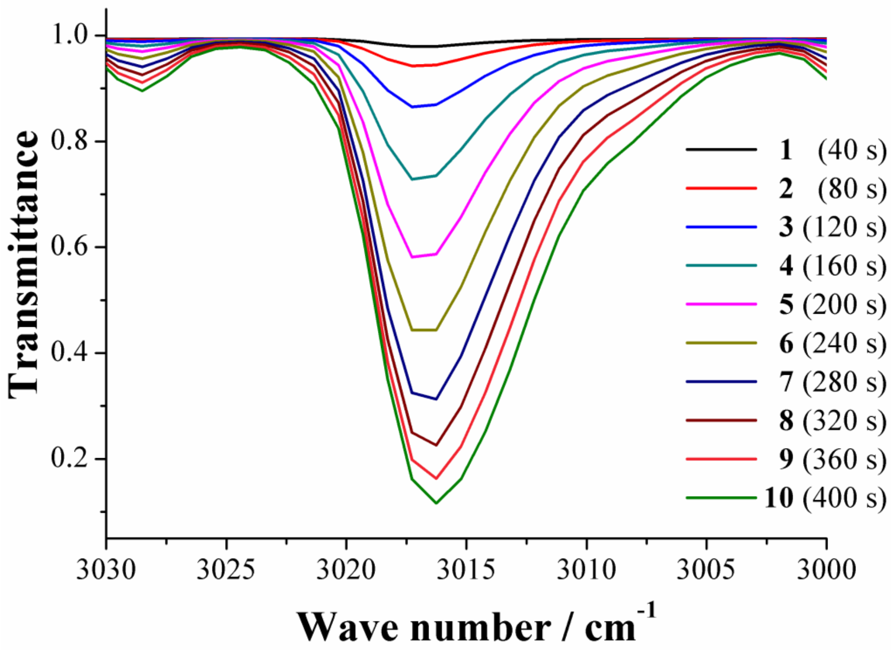


Fig S6: FTIR spectra of the resulting flow of only CH_4 gas (0.13 mmol min^{-1}) that passed through the activated NOTT-400 sample.

8. Polynomial Regressions

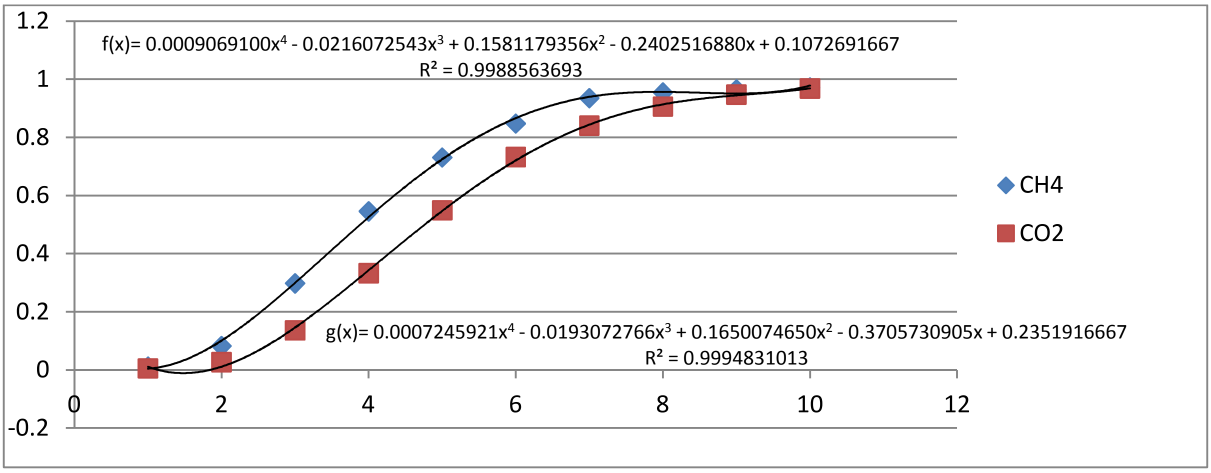


Fig S7: Polynomial regressions of the normalised intensities on Fig. 2 left.

By taking the derivative of both functions:

$f(x) = 0.0009069100x^4 - 0.0216072543x^3 + 0.1581179356x^2 - 0.2402516880x + 0.1072691667$

$g(x) = 0.0007245921x^4 - 0.0193072766x^3 + 0.1650074650x^2 - 0.3705730905x + 0.2351916667$

it is possible to plot both derivative functions ($df(x)/dx$ and $dg(x)/dx$) and find the maximum of both derivates. The difference of these derivates is equal to 0.70 scan which corresponds to ~ 28.19 s.

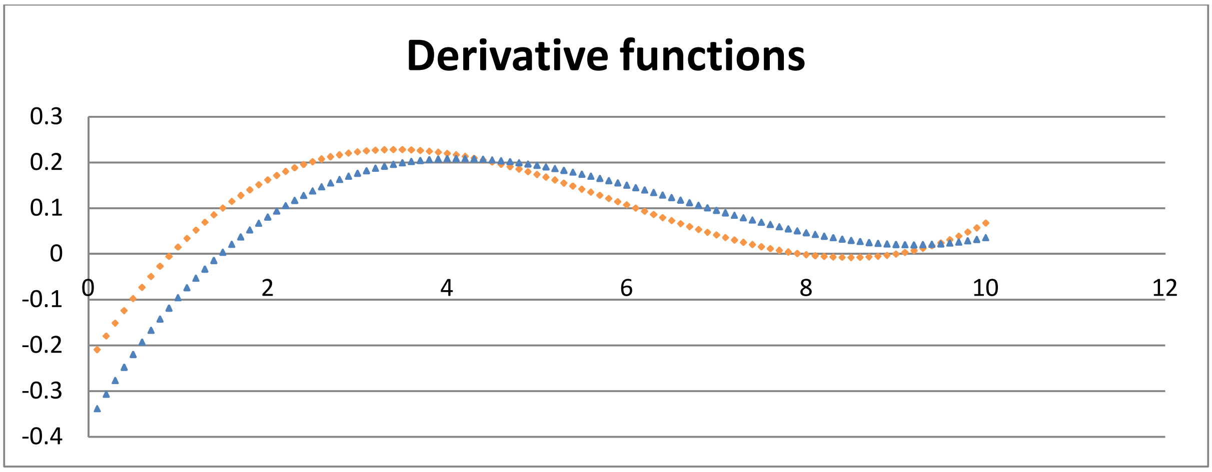


Fig. S8: Derivate functions ($df(x)/dx$ and $dg(x)/dx$) coming from polynomial regressions of the normalised intensities on Fig. 2 left. Methane in red and carbon dioxide in blue.

9. Normalised characteristic FTIR intensities of CO_2 and CH_4 as a function of the number of scans

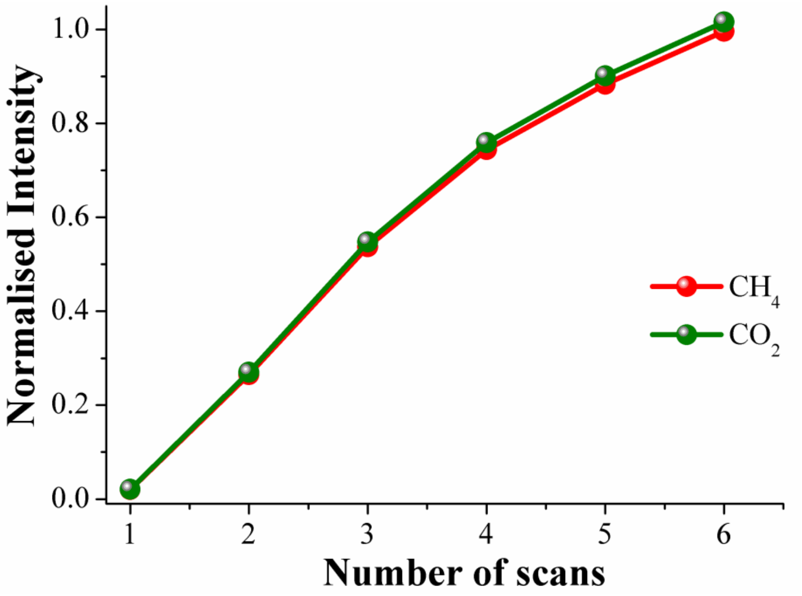


Fig. S9: Normalised characteristic FTIR intensities of CO_2 and CH_4 as a function of the number of scans from a resulting exit exhaust of the binary equimolar (0.13 mmol min^{-1}) gas-mixture of CO_2 and CH_4.

10.Kinetic Isotherms and PXRD

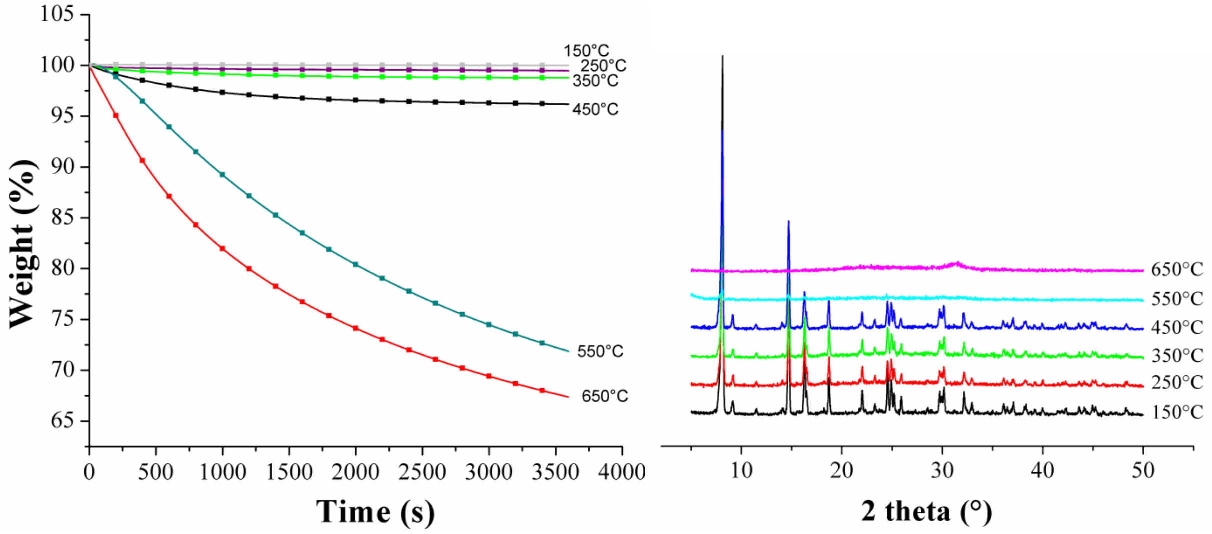


Fig. S10: (left) Kinetic uptake experiments performed at different temperatures (150, 250, 350, 450, 550, y 650 ^{o}C) with a CO_2 flow of 60 mL/min. Each curve shows the experimental data and the symbols were used to differentiate them; (right) PXRD patterns of each NOTT-400 samples after the kinetic CO_2 isotherms were carried out at different temperatures.

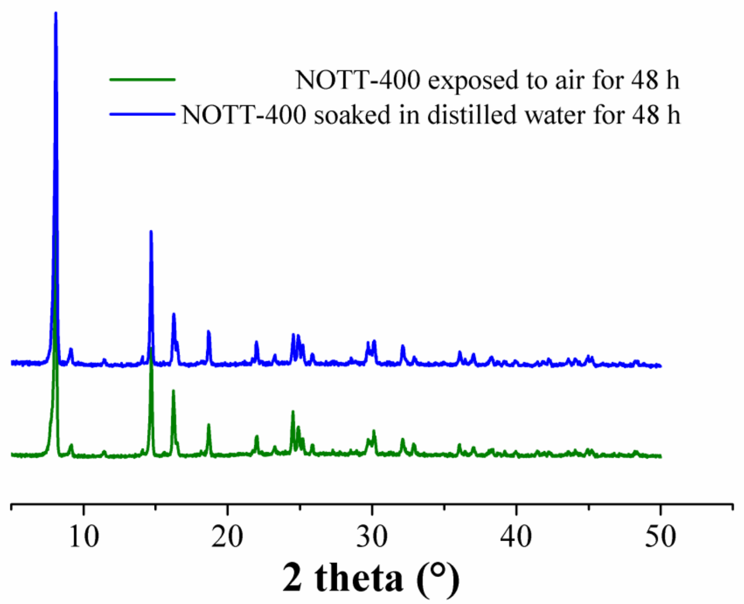


Fig. S11: Powder X-ray diffractions patterns of NOTT-400 after being exposed to air (green) and soaked in distilled water (blue) for 48 h.

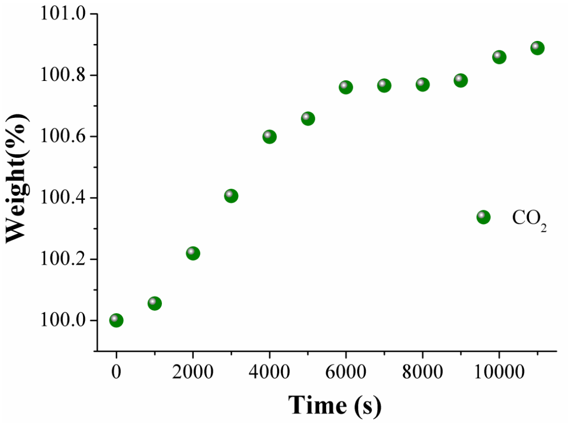


Fig. S12: Kinetic isotherms carried out at 30 °C and 40% RH with a CO_2 flow of 60 mL/min in PCM-14.

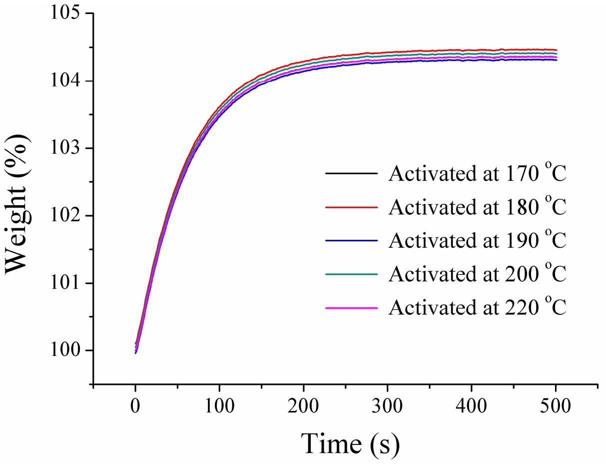


Fig. S13: Kinetic uptake experiments with a CO_2 flow of 60 mL/min. Each curve represents an acetone-exchanged sample of NOTT-400 activated under dynamic vacuum at different temperatures.

References

1. I. A. Ibarra, S. Yang, X. Lin, A. J. Blake, P. J. Rizkallan, Harriot Nowell, D. R. Allan, N. R. Champness, P. Hubberstey and M. Schröder, *Chem. Commun.,* 2011, **47**, 8304.