Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

New insight in UTSA-16

Alessio Masala[a], Jenny G. Vitillo[a], Francesca Bonino[a], Maela Manzoli[a], Carlos A. Grande[b] and Silvia Bordiga*[a]

[a]Chemistry Department, NIS and INSTM reference Centres, University of Torino, Via Quarello 15/A, 10135 Torino, Italy. [b]SINTEF Materials and Chemistry, P.O. Box 124 Blindern, N0314 Oslo, Norway

List of contents

Supporting tables and figures

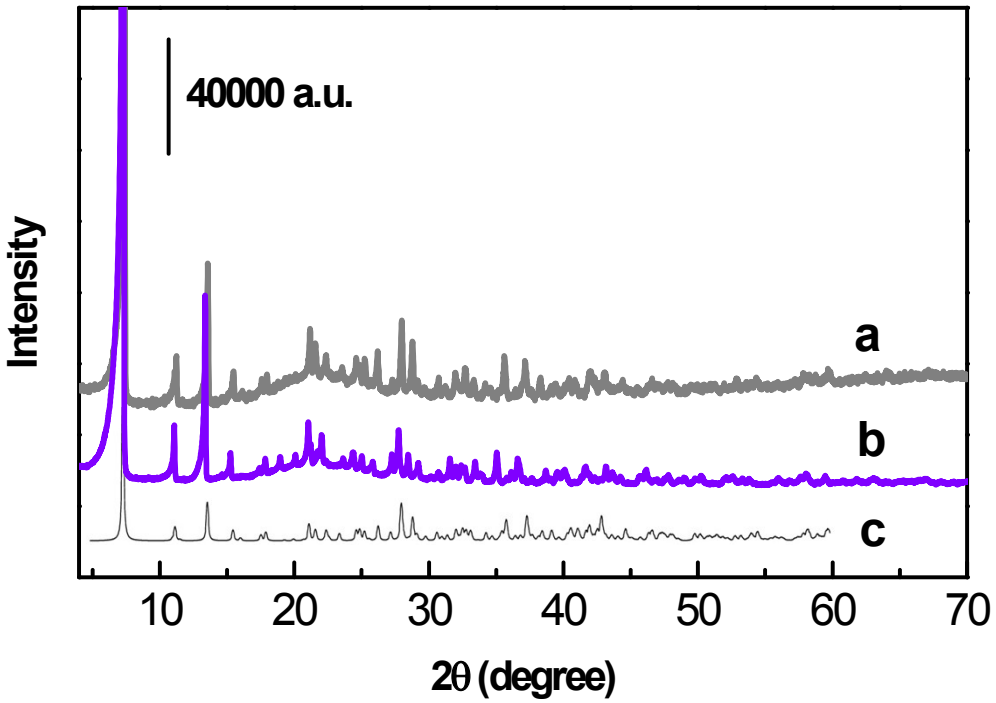

Fig. S1 Powder X-ray diffraction patterns of UTSA-16**.** Experimental powder diffraction pattern of **a**) as-synthesized UTSA-16 sample (grey line) and **b**) after activation over night at 363 K. (violet line). **c**) Simulated powder diffraction pattern obtained from the structure reported in Ref.[1].

Tab. S1 UTSA-16 elemental analysis by means of energy dispersive X-ray spectroscopy (EDX).

Analysis parameters:

Magnification: 30000 X
Accelerating voltage (kV): 300.00
Tilt (deg): 0.0
Elevation (deg): 17.8
Azimuth (deg): 0.0

Specimen	K ato.%	Co ato.%	K:Co ato. ratio
1	5.51	7.61	1.38
2	5.44	7.5	1.38
3	4.04	5.19	1.28
4	6.6	8.78	1.33
5	6.28	8.68	1.38

6	5.41	7.24	1.34
7	3.83	5.3	1.38
8	4.05	5.52	1.36
9	3.82	5.09	1.33
10	4.71	6.37	1.35
11	4.92	5.74	1.17
12	4.22	5.58	1.32
13	4.38	6.05	1.38
14	3.24	4.3	1.33
15	5.53	7.1	1.28
16	3.23	4.23	1.31
17	4.35	5.8	1.33
18	4.09	5.55	1.36
19	5.37	7.28	1.36
20	4.49	5.86	1.31
21	5.85	8.8	1.5

The average value of K:Co found in 21 UTSA-16 particles is **1:1.34**.

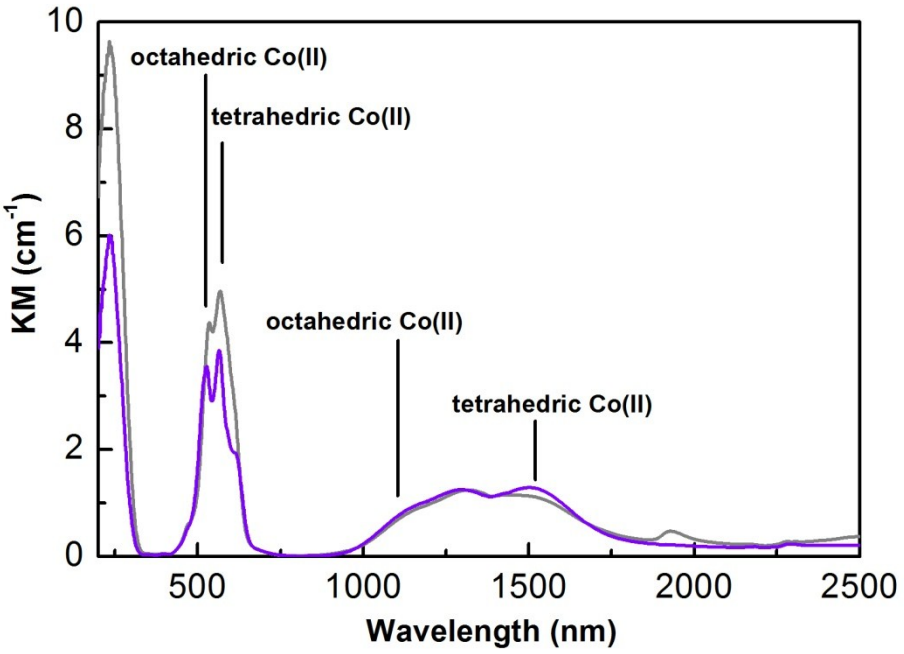

Fig. S2 DR-UV-VIS spectra of as-synthesized and activated UTSA-16 (grey and violet lines respectively).

Tab. S2 Review of CO_2 uptakes by some relevant MOFs at the typical CO_2 partial pressure in post-combustion CCS.

Adsorbent	CO_2 uptake at 0.15 bar (wt %)	Temperature (K)	Reference
Ni-CPO-27	16.9	298	[2,3]
HKUST-1	11.6	293	[4]
UTSA-16	11.1	298	Present work
mmen-Cu-BTTri	9.5	298	[5]
MIL-47	1.1	298	[3]
ZIF-100	1.0	298	[6]
IRMOF-3	0.6	298	[3,7]

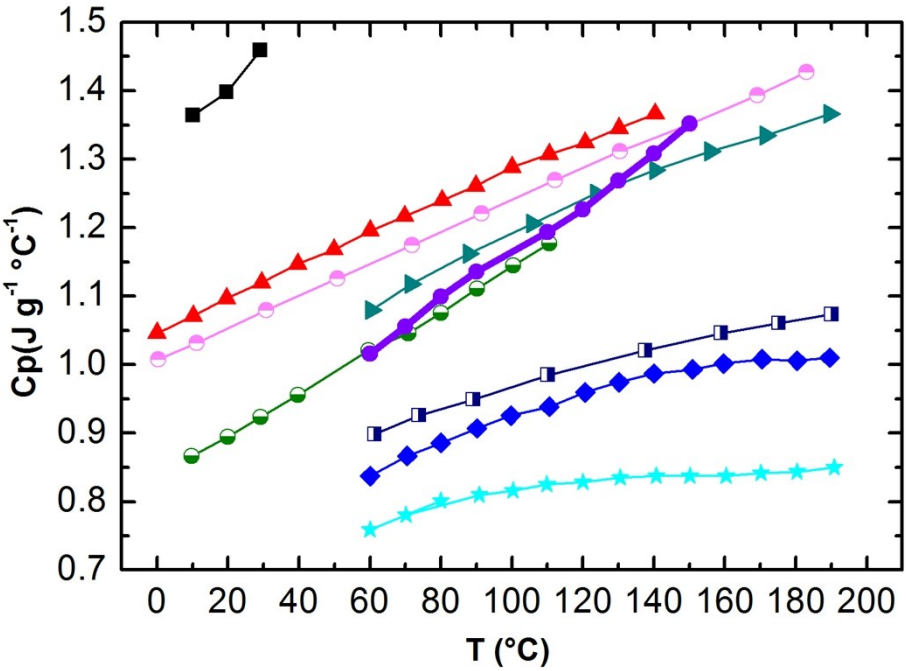

Fig. S3 Comparison of specific heat capacity of UTSA-16 with other MOFs. From top to bottom, Mg-BTC (■ black)[8], Co-BTC (▲ red)[9], DWCNT (◓ magenta)[10], Ni-BTB (▶ dark cyan)[11], UTSA-16 (● violet, bold line), Mn-BDC (◒ olive)[9], LaBTB (◨ navy)[11], MOF-177 (◆ blue)[11], IRMOF-1 (★ cyan)[11]. It is evident as UTSA-16 shows suitable Cp for CCS applications.

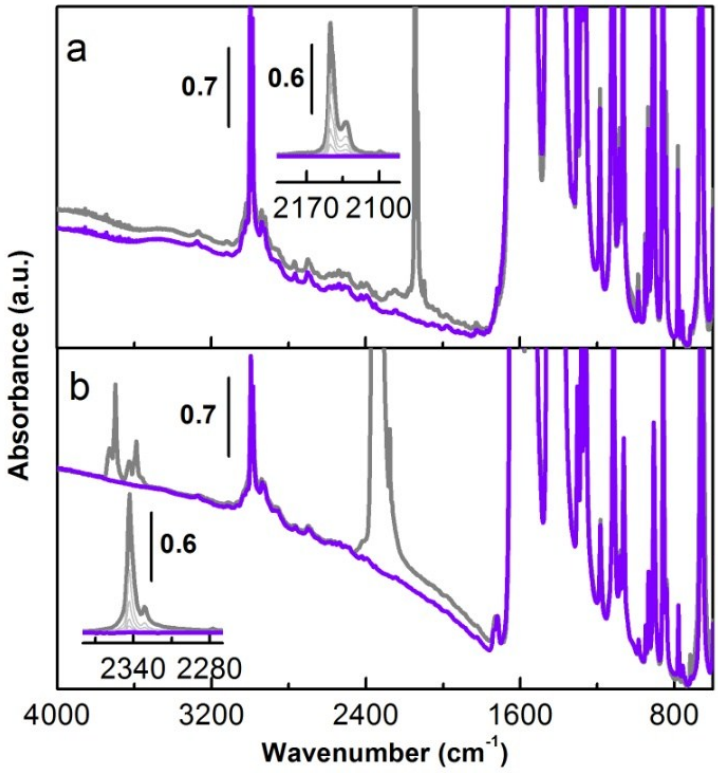

Fig. S4. FTIR spectra of activated UTSA-16 probed by CO and CO_2. a) Spectrum recorded in presence of 20 mbar of carbon monoxide (grey line). The inset shows the effect of progressive ougassing in the ν(CO) region. b) Effect of 10 mbar of CO_2 (grey line). The inset reports the effect of progressive ougassing in the $\nu_3(CO_2)$ region. Spectra reported in the insets are background subtracted. In both (a) and (b) parts, the IR spectrum of activated UTSA-16 is reported (violet line).

Tab. S3 Dual-site Langmuir model fit parameters for CO_2 adsorption isotherms of UTSA-16 at 273, 298 and 313 K and 1 bar

T = 273 K:
$q \equiv q_A + q_B = \frac{q_{sat,A} b_A p}{1 + b_A p} + \frac{q_{sat,B} b_B p}{1 + b_B p}$
$q_{sat,A} = 5.005\ mmol\ g^{-1}$
$q_{sat,B} = 0.05\ mmol\ g^{-1}$
$b_A = 2.094554 * 10^{-4} Pa^{-1}$
$b_B = 3.5 * 10^{-4} Pa^{-1}$
T = 298 K:
$q \equiv q_A + q_B = \frac{q_{sat,A} b_A p}{1 + b_A p} + \frac{q_{sat,B} b_B p}{1 + b_B p}$
$q_{sat,A} = 5.015\ mmol\ g^{-1}$

$q_{sat,B} = 0.5\ mmol\ g^{-1}$

$b_A = 6.29836 * 10^{-5} Pa^{-1}$

$b_B = 1.81628 * 10^{-7} Pa^{-1}$

T = 313 K:

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

$q_{sat,A} = 5.401714\ mmol\ g^{-1}$

$q_{sat,B} = 0.05424\ mmol\ g^{-1}$

$b_A = 2.28 * 10^{-5} Pa^{-1}$

$b_B = 2.19 * 10^{-5} Pa^{-1}$

Variables index:

$q_{A(B)}$ = adsorbed quantity of CO_2 by site A (B) at pressure p.
$q_{sat,A(B)}$ = maximum adsorbed quantity of CO_2 by site A (B) at saturation pressure.
$b_{A(B)}$ = Langmuir constant for the site A (B).

Tab. S4 Zero-coverage heat of CO_2 adsorption on some selected MOFs. All Q_{st} values were originally determined by a fitting to the published adsorption isotherms.

Adsorbent	$-Q_{st}$ (kJ/mol)	Technique	Reference
Ni-CPO-27	42	Clausius-Clapeyron	12
UTSA-16	39.7	Clausius-Clapeyron	Present work
HKUST-1	35	Clausius-Clapeyron	13
IRMOF-1	34	Clausius-Clapeyron	14

Reference

1 Xiang, S., Wu, X., Zhang, J., Fu, R., Hu, S and Zhang, X., *J. Am. Chem. Soc.*, 2005, **127**, 16352–16353.

2 P. D. C. Dietzel, V. Besikiotis and R. Blom, *J. Mater. Chem.*, 2009, **19**, 7362–7370.

3 A. Ö. Yazaydın, R. Q. Snurr, T.-H. Park, K. Koh, J. Liu, M. D. LeVan, A. I. Benin, P. Jakubczak, M. Lanuza, D. B. Galloway, J. J. Low and R. R. Willis, *J. Am. Chem. Soc.*, 2009, **131**, 18198–18199.

4 P. Aprea, D. Caputo, N. Gargiulo, F. Iucolano and F. Pepe, *J. Chem. Eng. Data*, 2010, **55**, 3655–3661.

5 T. M. McDonald, D. D'Alessandro, R. Krishna and J. R. Long, *Chem. Sci.*, 2011, **2**, 2022–2028.

6 B. Wang, A. P. Côté, H. Furukawa, M. O'Keeffe and O. M. Yaghi, *Nature*, 2008, **453**, 207–211.
7 A. R. Millward and O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 17998–17999.
8 L.-F. Song, C.-H. Jiang, J. Zhang, L.-X. Sun, F. Xu, Y.-Q. Tian, W.-S. You, Z. Cao, L. Zhang and D.-W. Yang, *J. Therm. Anal. Calorim.*, 2009, **101**, 365–370.
9 C.-H. Jiang, L.-F. Song, J. Zhang, L.-X. Sun, F. Xu, F. Li, Q.-Z. Jiao, Z.-G. Sun, Y.-H. Xing, Y. Du, J.-L. Zeng and Z. Cao, *J. Therm. Anal. Calorim.*, 2010, **102**, 1087–1093.
10 G. G. Silva, A. W. Musumeci, A. P. Gomes, J.-W. Liu, E. R. Waclawik, G. A. George, R. L. Frost and M. A. Pimenta, *J. Mater. Sci.*, 2009, **44**, 3498–3503.
11 B. Mu and K. S. Walton, *J. Phys. Chem. C*, 2011, **115**, 22748–22754.
12 P. D. C. Dietzel, R. E. Johnsen, H. Fjellvåg, S. Bordiga, E. Groppo, S. Chavan and R. Blom, *Chem. Commun.*, 2008, 5125–5127.
13 D. S. Qing Min Wang, *Microporous Mesoporous Mater.*, 2002, 217–230.
14 Z. Zhao, Z. Li and Y. S. Lin, *Ind. Eng. Chem. Res.*, 2009, **48**, 10015–10020.