

Electronic supplementary information (ESI)

Bio-inspired zinc finger analogue anchored in 2D hexagonal mesoporous silica for room temperature CO₂ activation via a hydrogenocarbonate route

H. Doghri,^{a,c} Elena Baranova,^b B. Albela,^c M. Saïd Zina^a and L. Bonneviot^{*c}

^aLaboratoire de Chimie des Matériaux et Catalyse, Faculté des Sciences de Tunis, Université Tunis El Manar, Campus Universitaire, Tunis 2092, Tunisia.

^bDepartment of Chemical and Biological Engineering, Centre for Catalysis Research and Innovation (CCRI), University of Ottawa, 161 Louis-Pasteur Ottawa ON K1N 6N5 Canada

^cLaboratoire de Chimie, Ecole Normale Supérieure de Lyon, UMR-CNRS 5182, Université de Lyon, 69364 Lyon, France.

1. Synthesis

Microwave assisted synthesis of the MCM-41 like LUS.²

Ludox (15.5 g, 0.26 mol) was added to sodium hydroxide (2 g, 50 mmol) in 50 mL of distilled water, and then stirred at 40°C until clear (\approx 24 h). A second solution of cetyltrimethylammonium *p*-toluenesulfonate (CTATos, Tos = *p*-toluenesulfonate, tosylate) (1.96 g, 4.3 mmol) in distilled water (71 mL) was stirred at 60°C for 1 h. In the meantime, the first solution (49 mL) was also stirred at 60°C for 1 h. Then the second solution was slowly added to the first one affording a gel molar composition: 1SiO₂/0.05CTATos/0.5NaOH/79H₂O. The resulting mixture was transferred to Teflon autoclaves and heated at 180°C using a Berghof Speedswave oven which provides a microwave irradiation at 2450 MHz with a power of 1450 W. Then, the autoclave was transferred to a cooling water bath (\approx 0°C) for half an hour. Afterward, the solution was filtered and the resulting solid was washed with distilled water before drying overnight at 80°C. *Elemental analysis (wt%): MS: Si: 23.61, C: 30.88, H: 6.56, N: 1.80, S: 0.39.*

References

- 1 J. M. Berg, J. L. Tymoczko, L. Stryer, J. M. Berg, J. L. Tymoczko and L. Stryer, *Biochemistry*, W H Freeman, 5th edn., 2002.
- 2 J. Chaignon, Y. Bouizi, L. Davin, N. Calin, B. Albela and L. Bonneviot, *Green Chem.*, 2015, **17**, 3130–3140.

2. Figures

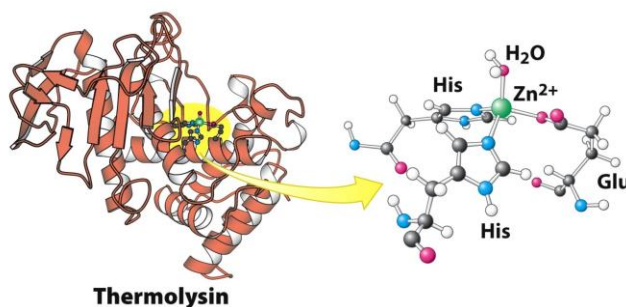


Fig. S1: Active center of thermolysin an equivalent of the human carbonic anhydrase II.¹

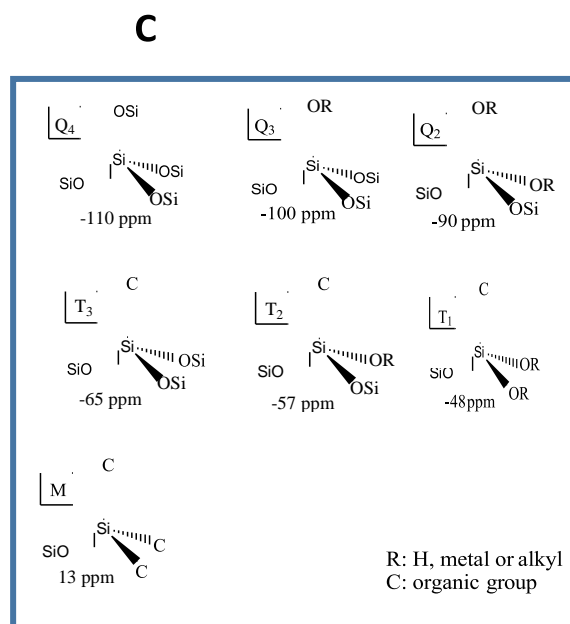
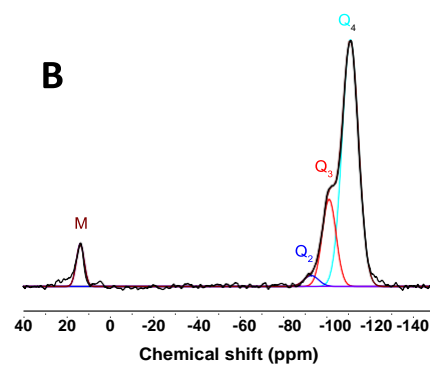
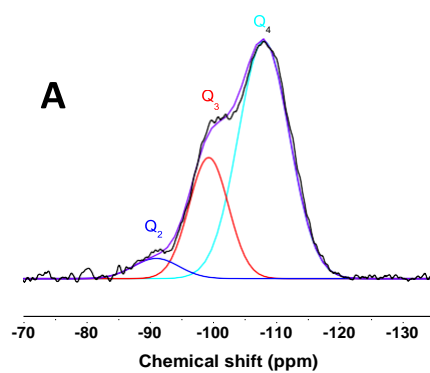


Fig. S2: Solid state MAS ^{29}Si -NMR at 298 K of A) material MS-C , B) Solid state MAS ^{29}Si -NMR at 298 K of material MS-S and C) corresponding M, Q_n and T_n species.

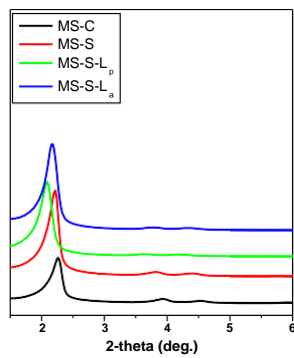


Fig. S3: X-ray diffraction patterns (powder) of materials; MS-C, MS-S, MS-L_p and MS-L_a.

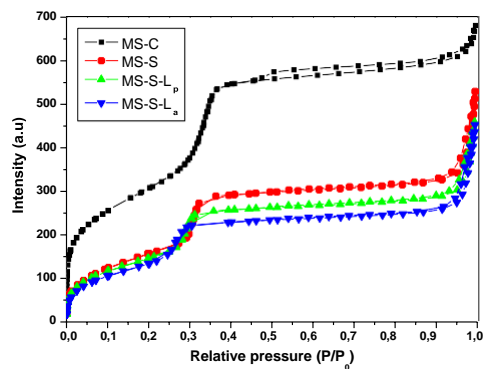


Fig.S4: N₂ adsorption/desorption isotherms at 77 K on materials MS-C, MS-S, MS-S-L_p and MS-S-L_a.

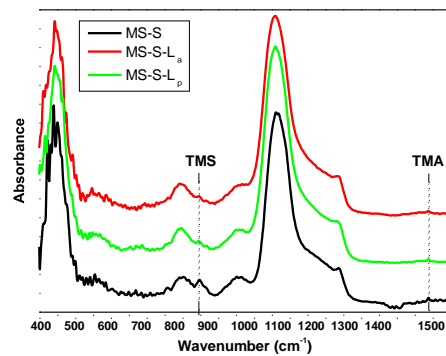


Fig. S5: Normalized FT-IR spectra in the range 400-1550 cm⁻¹ of calcined silica MS-C, after silylation (MS-S) and after DETA anchoring in isopropanol and cyclohexane in MS-S-L_p and in MS-S-L_a, respectively; normalization using the band at 450 cm⁻¹ as a reference.

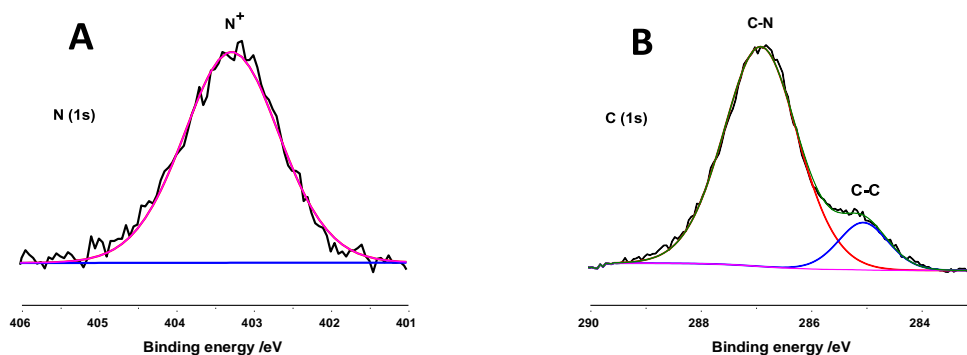


Fig. S6: XPS spectra of material A) MS-A100%; N (1s) and B) C (1s) (bottom) with deconvoluted.; In this material, the surfactant was exchanged for TMA⁺ using a solution of TMABr (3 times). The N 1s spectrum is characterized by a single contribution arising at 403.3 eV that clearly evidences where positively charged nitrogen should arise. Some minor deviation is expected from the binding energy of the nitrogen element in protonated amines of the DETA moieties as it is not rigorously the same environment. The C 1s spectrum of MS-A100% (Fig.S9, bottom) is characterized by two contributions pointing at 285 eV (12.6%) and 286.8 eV (87.4%), which are assigned to traces of surfactant left behind the extraction and the carbon linked to nitrogen in TMA⁺, respectively. It shows that at this stage of synthesis about 5% of CTA⁺ resists to extraction. Carboneous pollution during the XPS measurement could also contribute to the peak assigned to carbon in alkyl chains though it has not been interpreted like that in the text.

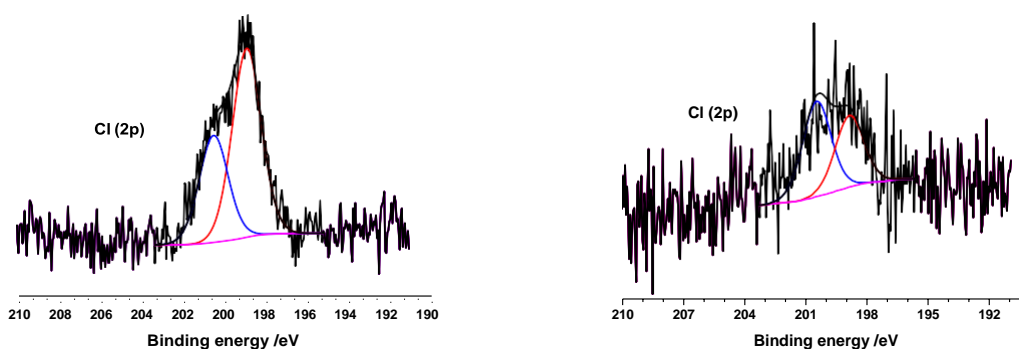


Figure S7: Cl 2p_{3/2} and 2p_{1/2} XPS experimental and deconvoluted lines of the material MS-S-L_p-ZnCl₂.t (left) and MS-S-L_p-Zn(NO₃)₂-3x (right) arise at 198.9 and 200.5 eV. These XPS signals left by chlorine atoms after metallation by ZnCl₂ are well characterized and found still present, though marginal, after metallation repeated three times. This evidences the difficulty to fully remove the chloride anions even after repeated contacts with a nitrate containing solution.

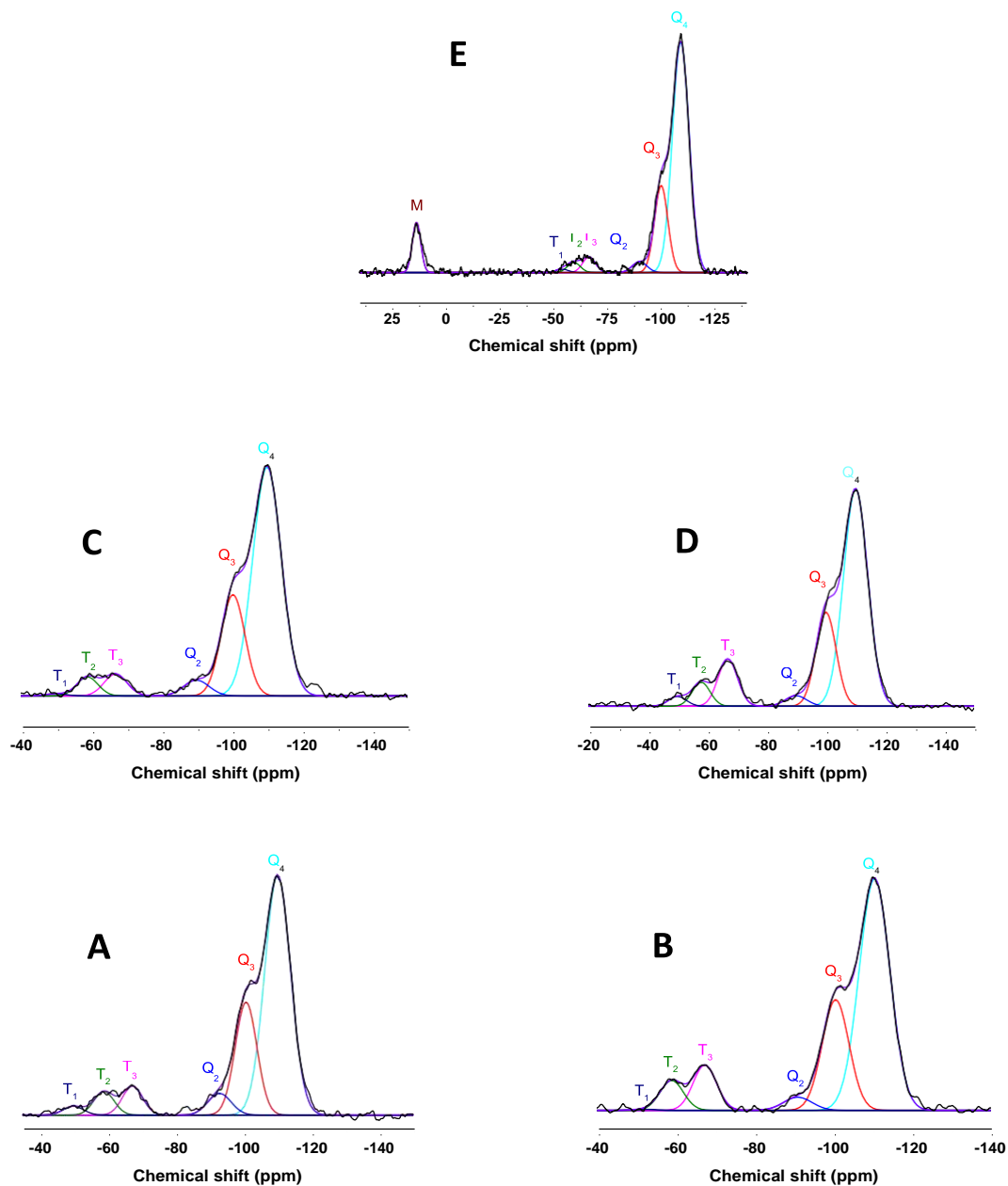


Fig. S8: Solid state MAS ^{29}Si -NMR at 298 K of DETA ligands grafted in TMS free material (no pre-capping using MSP as for the other materials) A) MS-L_p, B) MS-L_a, C) MS-L_p-Zn, D) MS-L_a-Zn, E) MS-L_a-S.

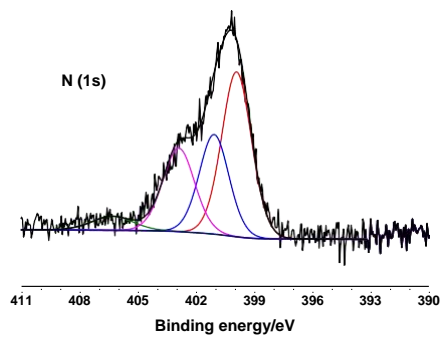


Fig. S9: XPS spectra of material MS-S-L_p-ZnCl₂.

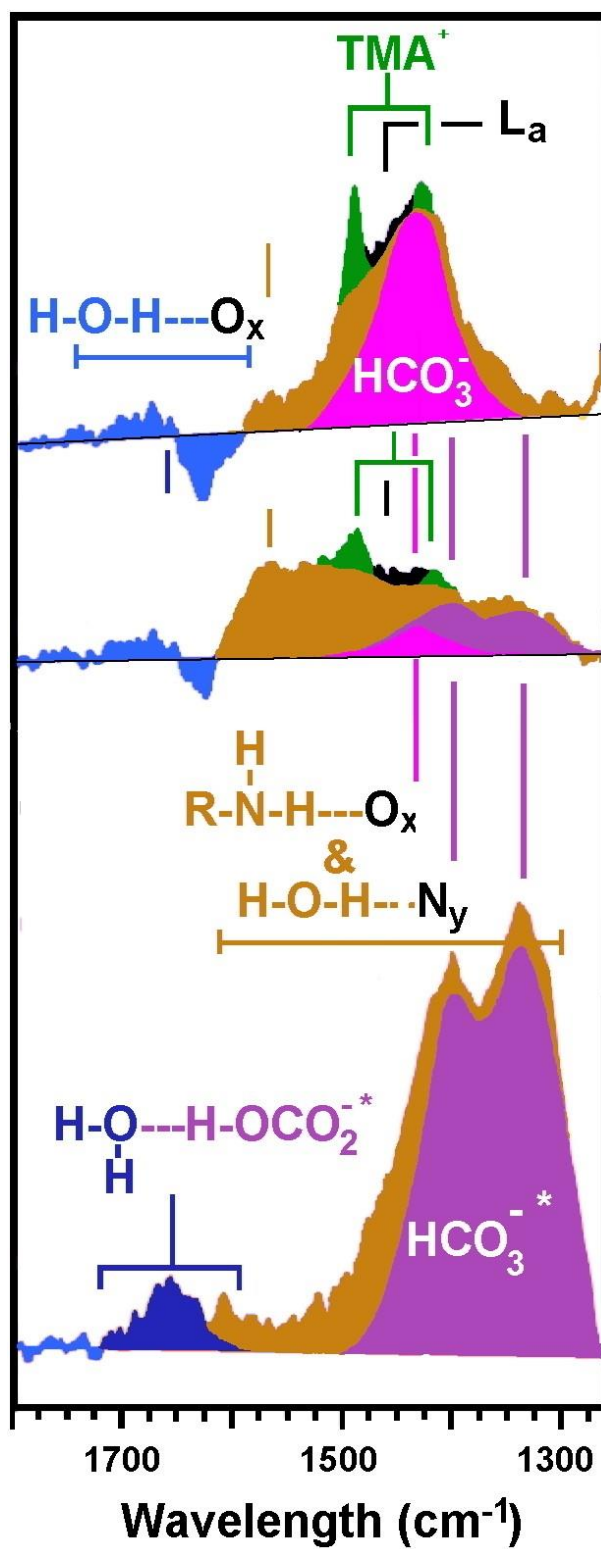


Fig. 10: FT-IR difference-spectra at RT in the range 1260-1800 cm^{-1} of (top line) MS-La-NaHCO₃, (middle line) MS-La-Ca(NO₃)₂, and (bottom) MS-La-Zn(NO₃)₂; same color codes as in Figs. 6 and 7.

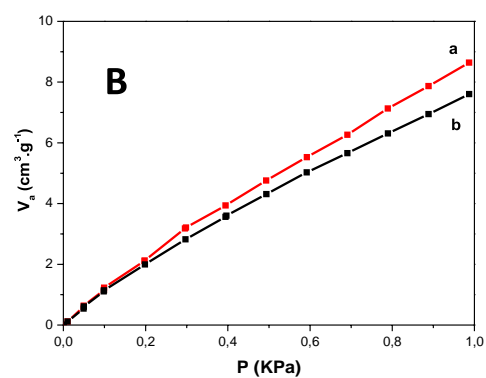
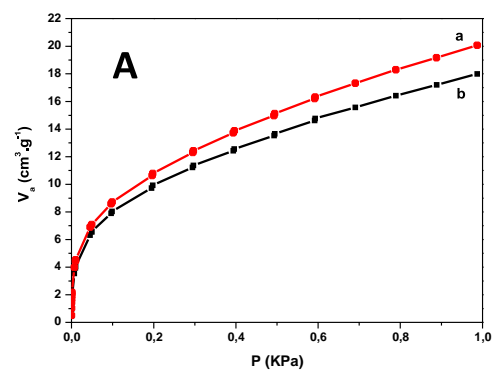


Fig. S11: CO₂ adsorption isotherms at 298 K A) for the anchoring ligand (MS-S-L_x) and B) for the zinc complexed ligand (MS-S-L_x-Zn) for anchoring in a) isopropanol, x = p or in b) in cyclohexane, x = a.