

Electronic Supplementary Information

Correlations of acidity-basicity of solvent treated layered double hydroxides/oxides and their CO₂ capture performance

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1. Characterisation techniques

Powder X-ray diffraction patterns (XRDs) were carried out on a PANalytical X'Pert Pro Diffractometer in scanning mode using Cu K α radiation ($\lambda = 1.542 \text{ \AA}$), between 5 to 70°.

Surface area analysis was carried out using the BET method on a Micromeritics Tristar II plus. Nitrogen adsorption and desorption isotherms were collected at 77 k and ~ 100 mg of samples were degassed at 110 °C overnight prior to analysis.

For Brønsted basicity titrations, 50 mg of the sample was then dispersed in 30 mL methanol and 0.5 mL of a 0.1% solution chosen indicator (bromothymol blue (pKa = 7.1), phenolphthalein (pKa = 9.3) and clayton yellow (pKa = 12.7)) in methanol was also added. The solution was then titrated against benzoic acid (0.1 M) using a syringe pump with a drop rate of 50 mL h⁻¹ and stirred at 375 rpm. For LDOs, the procedure was performed under N₂ atmosphere using a Schlenk line and samples were dispersed in anhydrous methanol that was further dried over molecular sieves. The values obtained from this method are less accurate when compared to TPD due to the limitations of the usage of Hammett indicators in a heterogeneous system.¹ As a result, the number of basic sites obtained in this fashion will be less than the actual value. Hence it can only be taken in a qualitative way and be used to observe relative trends between samples.

In situ Fourier transform infrared (FTIR) spectra were taken on a Bruker VERTEX 80 on a Specac High Temperature High Pressure cell with an Ar and CO₂ gas supply. The spectrometer was set to record 64 scans between 600 and 4000 cm⁻¹ with a resolution of 4 cm⁻¹. 5 mg of sample was ground together with 300 mg KBr and pressed into a pellet. The pellet was then loaded into the cell and heated to the desired pre-treatment temperature (200 °C for LDHs and 450 °C for LDOs) for 1 h under Ar flow (0.8 cm³ min⁻¹). The sample was then cooled to 100 °C and a spectrum was recorded. Afterwards CO₂ was flown through the cell for 1 h to fully saturate all the basic sites. Ar was then flown through the cell to remove any excess and physisorbed CO₂ for 1 h. Finally, a spectrum was recorded after 1 hour of gas flow.

CO₂ TPD traces were recorded on a Micromeritics AutoChem II 2920 Chemisorption Analyser equipped with a thermal conductivity detector (TCD). The sample (100 mg) was loaded in a quartz U-tube and first purged in a flow of He (50 cm³ min⁻¹) at room temperature for 10 min to remove impurities. The temperature was then raised to 450 °C at a ramp rate of 10 °C min⁻¹ and held at this temperature for 1 h to remove water and any other impurities. The temperature was then reduced to 100 °C. For basicity tests, the gas changed to CO₂ in He (30 cm³ min⁻¹ CO₂, 50 cm³ min⁻¹ He) and flown over the sample for 1 h. For acidity test, a 10% NH₃ in He gas flow was used instead. Physically adsorbed CO₂/NH₃ was then removed by changing the gas flow to He (50 cm³ min⁻¹) for 1 h. For the desorption step, the sample was heated from 100 to 450 °C under He flow (50 cm³ min⁻¹) and a sampling rate of 1 measurement per second.

CO₂ capture readings were carried out on a Micromeritics 3Flex with a chemisorption attachment. LDO samples were first calcined *ex situ*. 100 mg of sample was placed in the machine for a further calcination at 450 °C at a ramp of 5 °C min⁻¹ for 1 h. The sample was cooled to 40 °C at a ramp of 30 °C min⁻¹ and left to evacuate to a vacuum at 40 °C for 3 h. the CO₂ measurements were then carried out twice at 40 °C. The first value provides the total adsorption value, the second physisorption. The difference between the two values provides the chemisorption value.

2. Characterisation data for LDHs

Table S1. Summary of elemental composition

Sample	Mg:Al	Mg(%)	Al(%)	C(%)	H(%)	Composition
LDH-W	2.57	22.07	8.58	2.25	1.98	[Mg _{0.72} Al _{0.28} (OH) ₂](CO ₃) _{0.14} ·H ₂ O _{0.66}
LDH-E	2.50	18.63	7.46	2.93	1.84	[Mg _{0.71} Al _{0.29} (OH) ₂](CO ₃) _{0.15} (H ₂ O) _{1.08} (E) _{0.038}
LDH-A	2.57	22.07	8.58	2.85	3.00	[Mg _{0.72} Al _{0.28} (OH) ₂](CO ₃) _{0.14} (H ₂ O) _{0.61} (A) _{0.016}
LDH-IPA	2.57	22.07	8.58	2.86	2.91	[Mg _{0.72} Al _{0.28} (OH) ₂](CO ₃) _{0.14} (H ₂ O) _{0.61} (IPA) _{0.016}
LDH-EA	2.57	22.07	8.58	2.68	2.53	[Mg _{0.72} Al _{0.28} (OH) ₂](CO ₃) _{0.14} ·(H ₂ O) _{0.61} (EA) _{0.009}
LDH-1H	2.50	18.63	7.46	16.00	4.82	[Mg _{0.71} Al _{0.29} (OH) ₂](CO ₃) _{0.15} ·(H ₂ O) _{0.38} (1H) _{0.181}

W = H₂O; E = ethanol (C₂H₅OH); A = acetone ((CH₃)₂CO); IPA = isopropanol ((CH₃)₂CHOH); EA = ethyl acetate (CH₃COOC₂H₆); 1H = hexan-1-ol (C₆H₁₃OH)

Table S2. Summary of XRD data

Sample	Lattice Parameters		
	a/b (Å)	c (Å)	interlayer-spacing (Å)
LDH-W	3.06	23.34	7.78
LDH-E	3.06	23.43	7.81
LDH-A	3.06	23.49	7.83
LDH-IPA	3.06	23.49	7.83
LDH-EA	3.06	23.64	7.88
LDH-1H	3.06	23.34	7.78

Indexed on rhombohedral symmetry a = b ≠ c.

Table S3 – Composition and surface properties properties of LDH samples

Sample	Surface area (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)
LDH-W	91.6	0.54
LDH-E	196	0.70
LDH-A	173	0.82
LDH-IPA	184	0.81
LDH-EA	175	0.83
LDH-1H	166	0.61

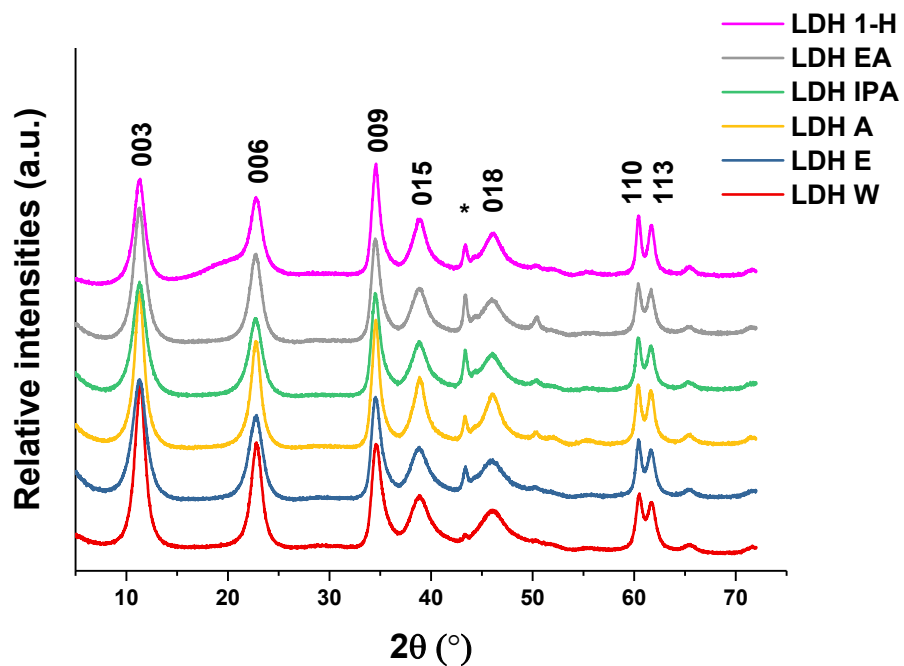


Fig. S1 – XRD patterns of various LDH samples.

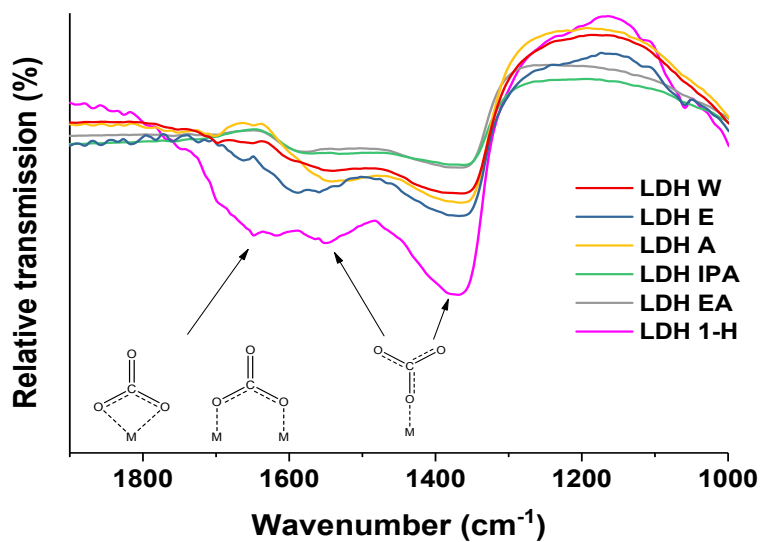
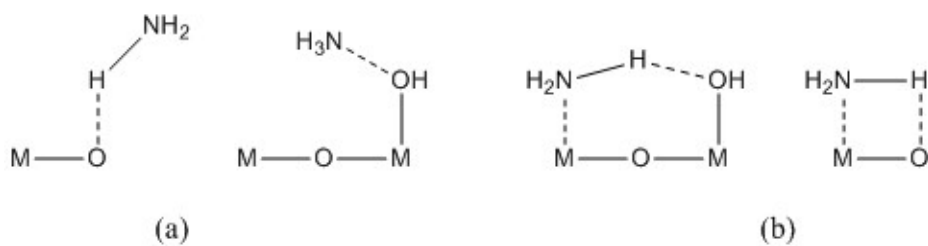


Fig. S2 *In situ* CO₂ FTIR spectra of LDH samples at 100 °C.

3. Bonding mode of NH₃ on solid surface



Scheme S1 - NH₃ bonding modes on an LDO surface according to Prinetto *et al.*²

4. Relationship between acid/base ratio and surface area of LDO

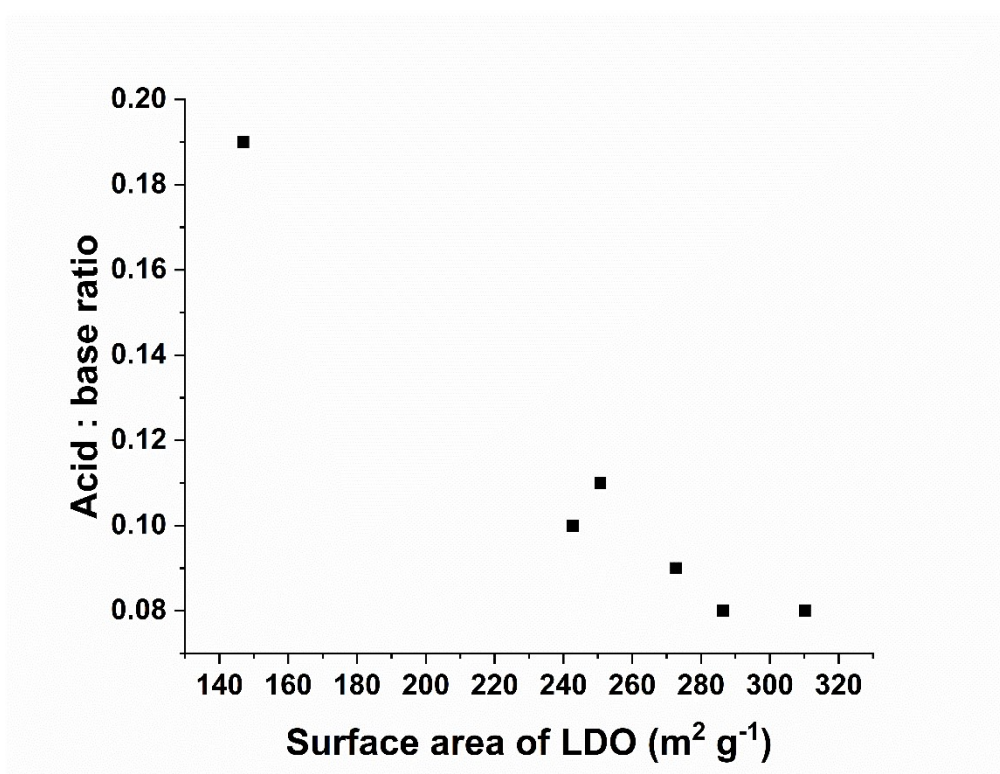


Fig. S3 Surface area of LDO as a function of acid/base ratio.

5. CO₂ adsorption curves

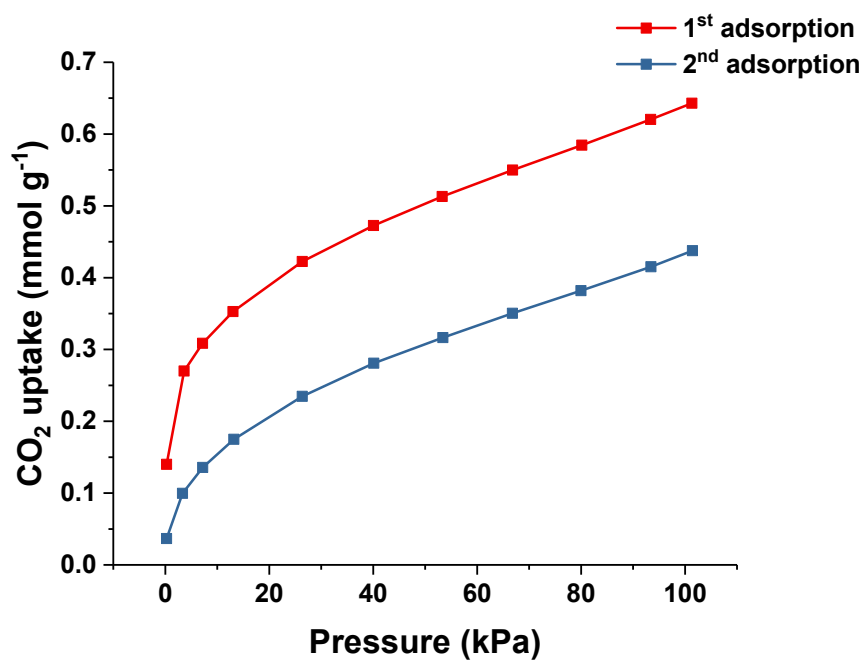


Fig. S4 – 1st and 2nd CO₂ adsorption profiles of LDO W.

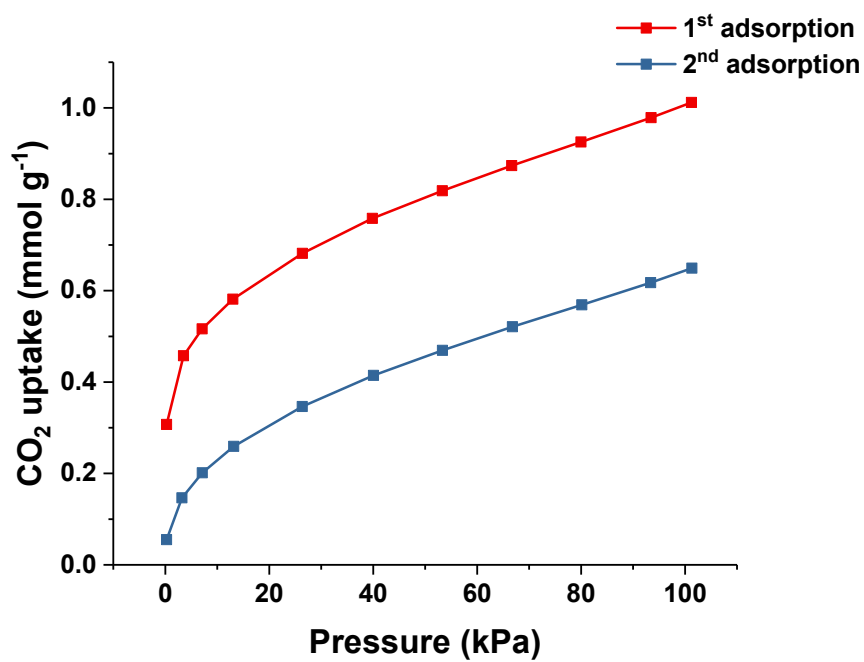


Fig. S5 – 1st and 2nd CO₂ adsorption profiles of LDO E.

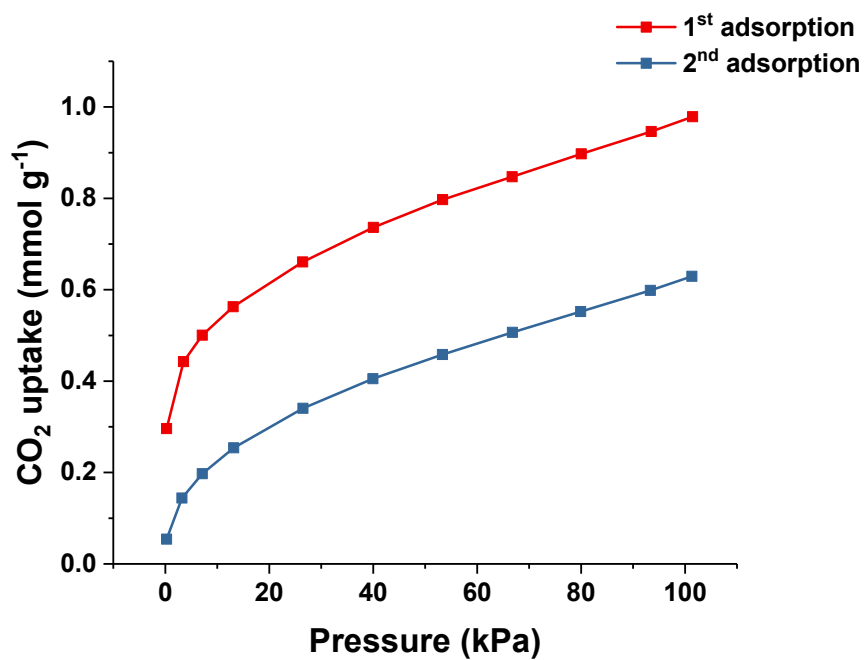


Fig. S6 – 1st and 2nd CO₂ adsorption profiles of LDO A.

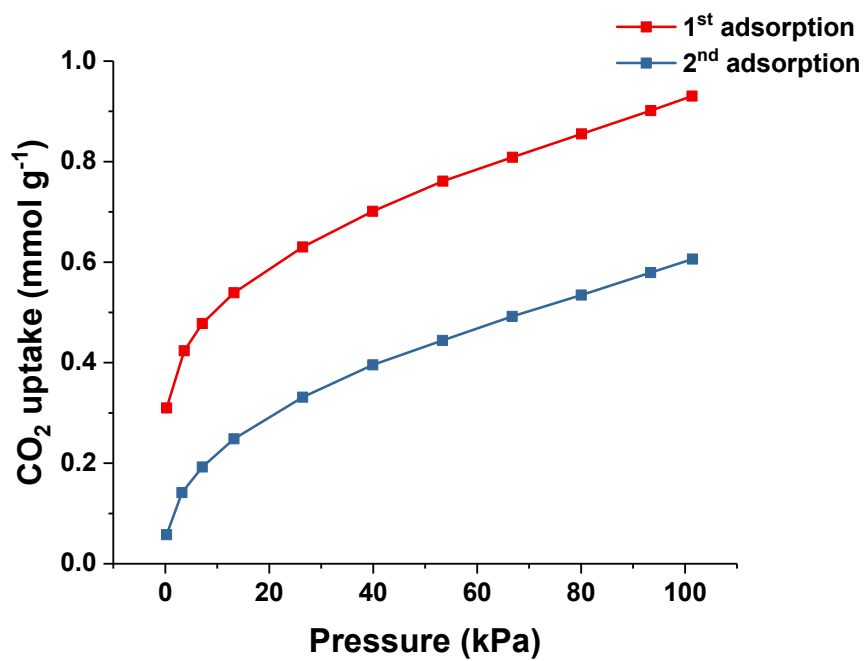


Fig. S7 – 1st and 2nd CO₂ adsorption profiles of LDO IPA.

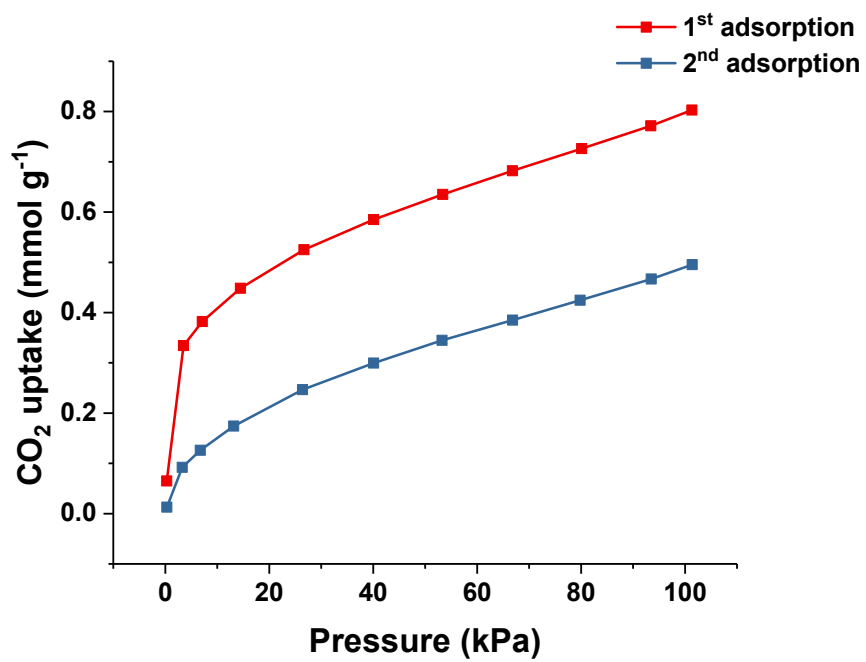


Fig. S8 – 1st and 2nd CO₂ adsorption profiles of LDO EA.

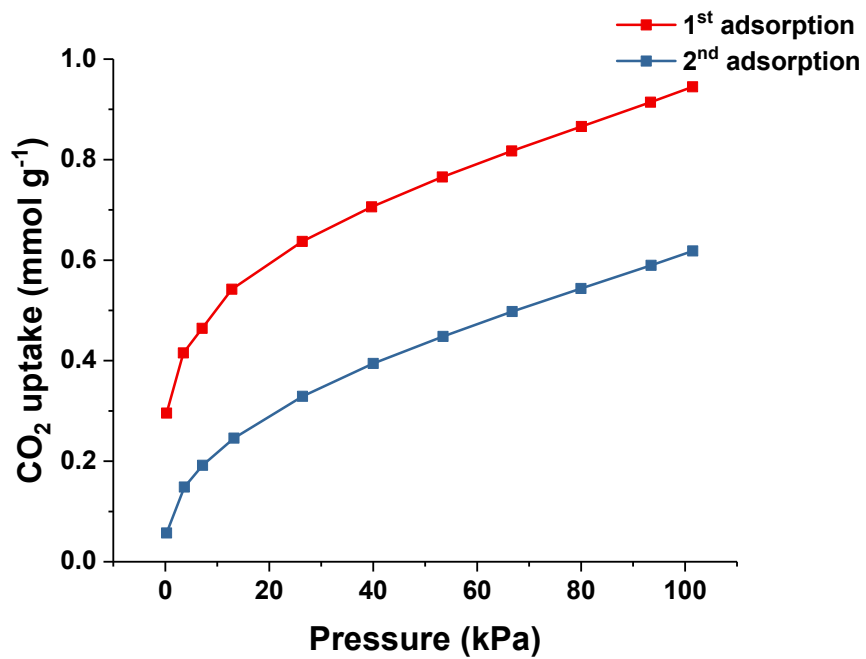


Fig. S9 – 1st and 2nd CO₂ adsorption profiles of LDO 1-H.

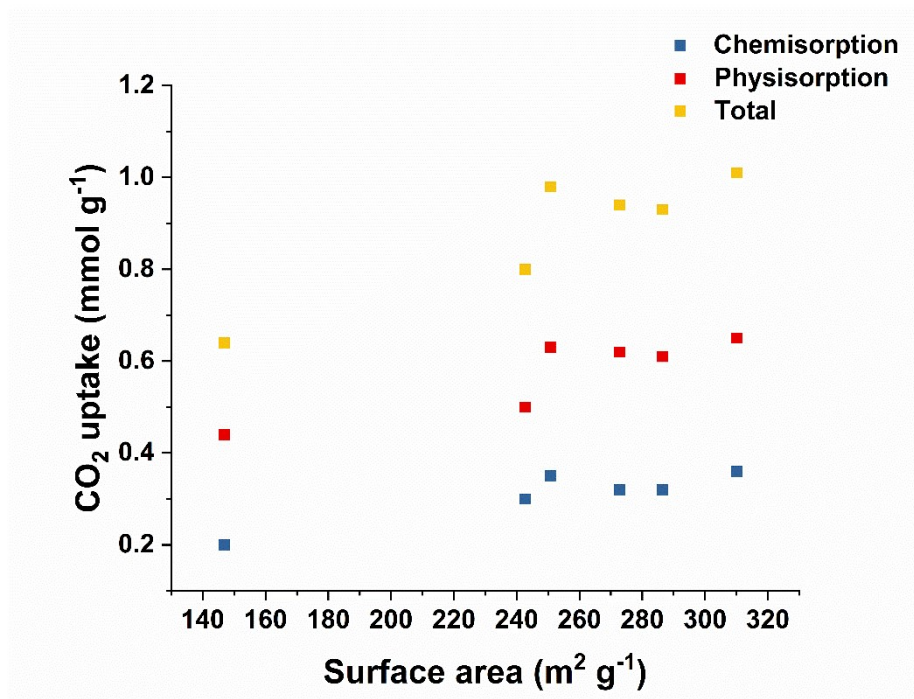


Fig. S10 – Molar CO₂ adsorption as a function of surface area for all ST-LDOs.

6. References

- 1 A. Navajas, I. Campo, G. Arzamendi, W. Y. Hernández, L. F. Bobadilla, M. A. Centeno, J. A. Odriozola and L. M. Gandía, *Appl. Catal. B Environ.*, 2010, **100**, 299–309.
- 2 F. Prinetto, G. Ghiotti, R. Durand and D. Tichit, *J. Phys. Chem. B*, 2000, **104**, 11117–11126.