

Supplementary Information

“Hidden” CO₂ in Amine-modified Porous Silicas Enables Full Quantitative NMR Identification of Physi- and Chemisorbed CO₂ Species

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Table S1 Elemental analysis data from each of the three replicas for each material.

	as-synthesized SBA-15			calcined SBA-15			APTES@SBA-15		
mass /mg	0.853	0.781	0.893	0.923	1.061	1.238	1.501	1.217	1.315
C %	11.123	10.145	10.023	0.16	0.242	0.118	5.117	4.910	4.999
H %	2.79	2.425	2.5	0.743	0.479	0.83	1.979	1.833	1.978
N %	0.000	0.000	0.000	0.000	0.000	0.000	1.857	1.805	1.816
S %	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

- **Chemical Shift Anisotropy (CSA) Tensor Convention**

The fitted CSA parameters shown in **Tables S3** and **S4** follow the *Haeberlen* convention. This implies that principal values of the CSA tensor (δ_{11} , δ_{22} and δ_{33}) are ordered as follows: $|\delta_{33} - \delta_{\text{iso}}| \geq |\delta_{11} - \delta_{\text{iso}}| \geq |\delta_{22} - \delta_{\text{iso}}|$. The isotropic value δ_{iso} is defined as:

$$\delta_{\text{iso}} = (\delta_{11} + \delta_{22} + \delta_{33})/3$$

Reduced anisotropy d is the largest separation from the isotropic value and is defined as:

$$d = \delta_{33} - \delta_{\text{iso}}$$

The CSA asymmetry parameter can be written as:

$$\eta = (\delta_{22} - \delta_{11})/(\delta_{33} - \delta_{\text{iso}})$$

Table S2 Fitting parameters obtained from the CSA analysis for APTES@SBA-15.

Component	fraction (%)	δ_{iso} /ppm	δ /ppm	η
E+F	47(1)	125.2(2)	-	-
D	8.0(2)	125.1(2)	-100(3)	0.8(1)
A	2.0(1)	154.0(2)	-	-
B	16.0(5)	161.5(2)	55(2)	0.3(1)
C	27.0(8)	164.6(2)	-51(2)	0.6(1)

Table S3 Fitting parameters obtained from the CSA analysis for the calcined SBA-15.

Component	Fraction (%)	δ_{iso} /ppm	δ /ppm	η
E+F	97(2)	125.3(2)	-	-
D	3.0(8)	125.4(2)	-57(6)	0*

* Value fixed at 0 due to the low amount of visible spinning sidebands.

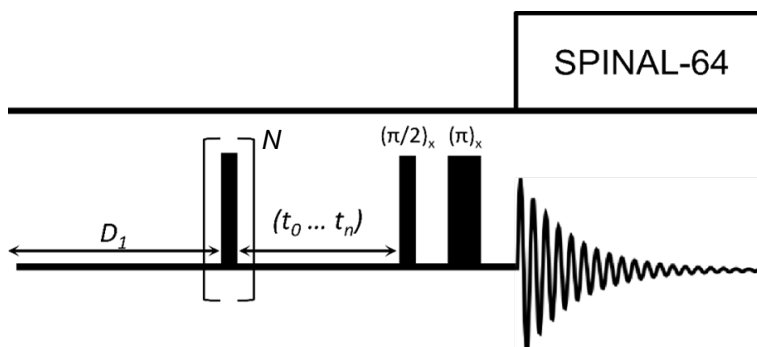


Figure S4 Saturation-recovery pulse sequence used to measure T_1 of physisorbed species **D**, **E**, and **F**. After a recycling delay (D_1) to restore the thermal equilibrium magnetization along z-axis, a train of N $\pi/2$ -pulses are applied to pre-saturate the spin states. Next, the magnetization is recovered along the z-axis for a period t which is incremented according to the values shown in **Table S5**. Before acquisition, a Hahn echo block is employed to read the magnetization while removing the interfering inhomogeneous background signals.

Table S5 Magnetization recovery times (in seconds) used to measure T_1 for each of the three different materials.

<i>t</i> /s	
5×10^{-7}	0.75
1×10^{-6}	1
1×10^{-5}	1.25
1×10^{-4}	1.5
5×10^{-4}	1.75
1×10^{-3}	2
1.5×10^{-3}	2.25
2×10^{-3}	2.5
3×10^{-3}	3
4×10^{-3}	4
1×10^{-2}	5
2.5×10^{-2}	6
4×10^{-2}	7
5×10^{-2}	8
7.5×10^{-2}	9
0.1	10
0.15	12
0.2	15
0.25	18
0.3	20
0.35	23
0.4	27
0.5	30

Table S6 Transverse magnetization recovery times (in milliseconds) used to measure T_2^* for each of the three different materials.

t /ms
1×10^{-3}
2×10^{-3}
5×10^{-3}
1×10^{-2}
5×10^{-2}
0.1
0.5
1
2
5
7.5
10
20
50
100
200

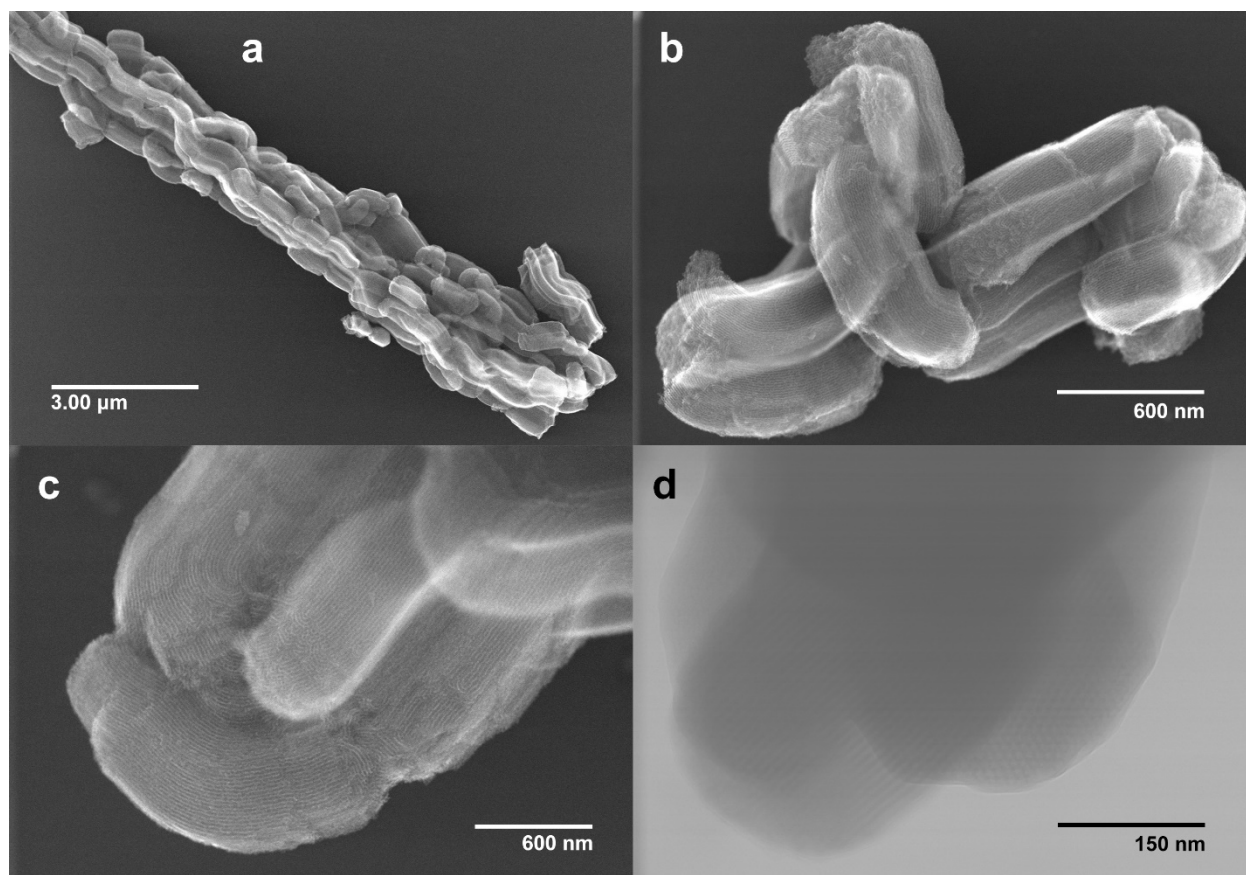


Figure S7 Representative electron micrographs of the calcined SBA-15 at different scales: a, b, and c: transmission mode, d: scanning mode.

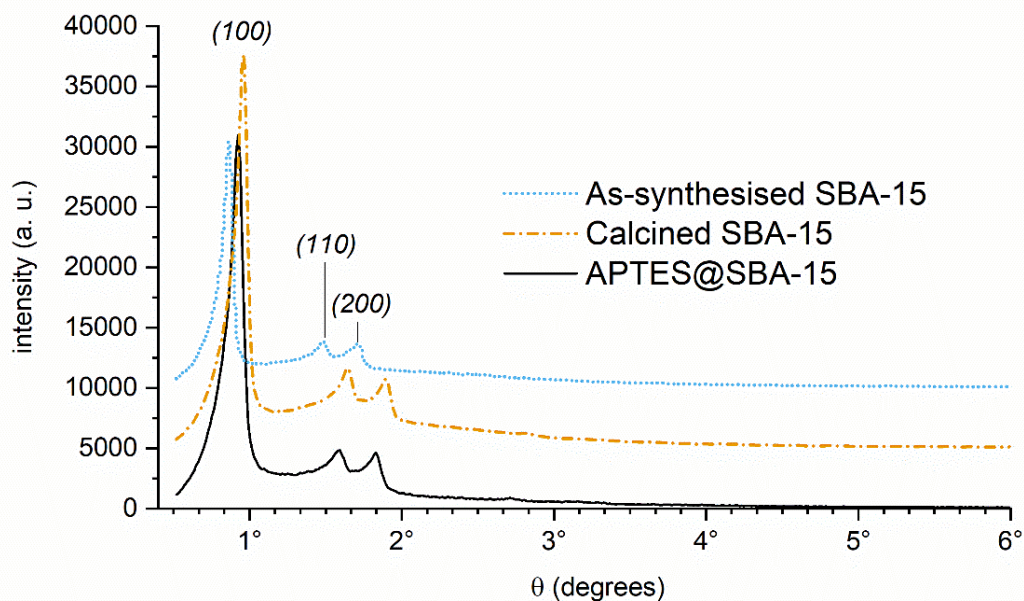


Figure S8 Stacked plot of the powder X-ray diffractograms (intensity vs 2θ angle)—each plot offset by 5000 units on the vertical axis. The peaks are labelled with the corresponding pore lattice indices. Through the equation $d = \sqrt{3a^2/4}$ and Bragg's Law, the peak (100) yields the hexagonal cell parameter corresponding to inter-pore distance.

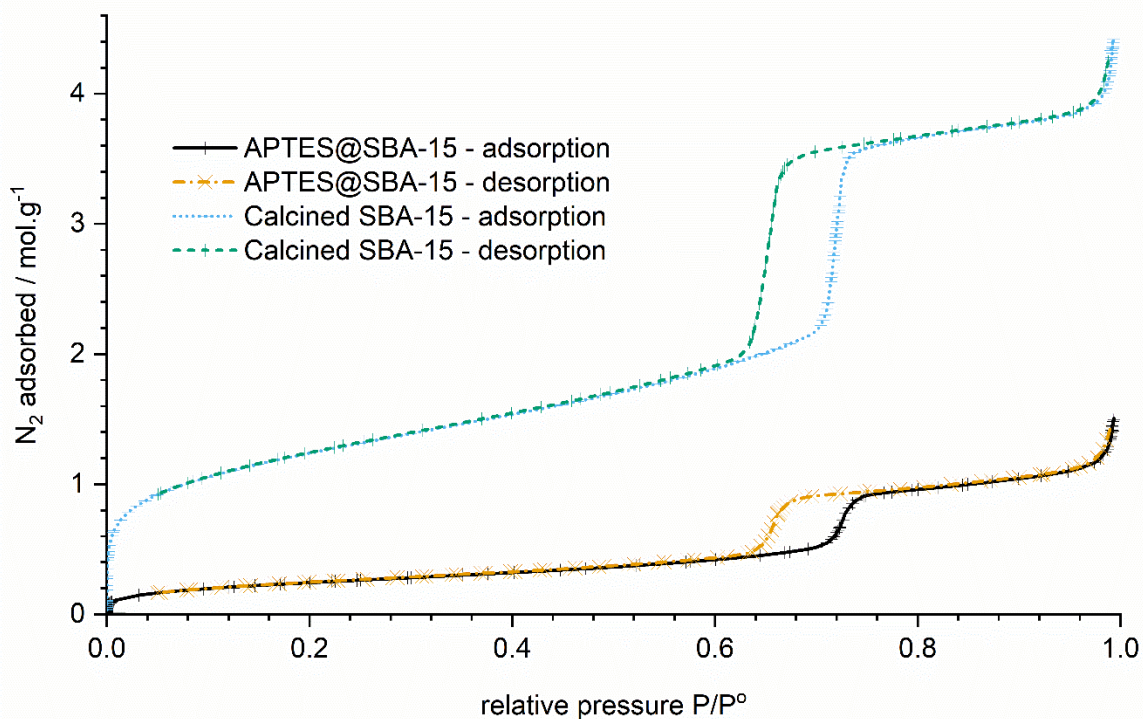


Figure S9 Plot of the calcined SBA-15 and APTES@SBA-15 N_2 sorption isotherms (at 77 K) as adsorbed molar quantity per sample mass vs relative pressure.

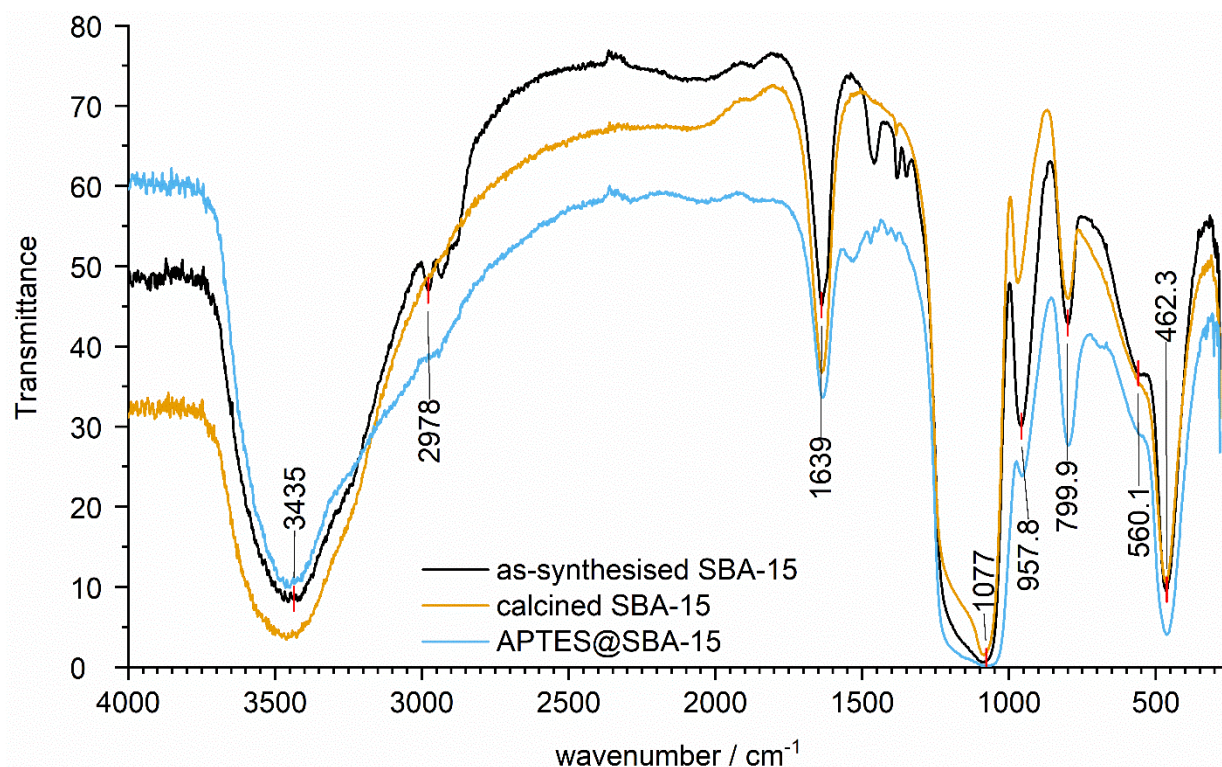


Figure S10 Stacked FTIR transmission spectra of the as-synthesized, calcined, and functionalized SBA-15 (no baseline correction was applied). Broad band peaking around 3450 cm^{-1} : stretching of OH of surface silanols and adsorbed water; bands around 2940 cm^{-1} : CH_2 stretching (from APTES or from OSDA molecules); 1639 cm^{-1} : deformation of adsorbed water; bands at 1525–1380 cm^{-1} : NH_2 deformation modes in APTES and ether bridge deformation in template; 1077 cm^{-1} : SiO_2 asymmetric stretching; 958 cm^{-1} : Si-OH group stretching; 800 cm^{-1} : SiO_2 bond bending; 460 cm^{-1} : SiO_2 bond rocking.

Table S11 ^{13}C T_1 relaxation times of the chemisorbed CO_2 species obtained from the *Torchia* method.^{1,2} This experiment measures the ^{13}C T_1 using the advantages of cross-polarization (reduced recycle delay) for the long ^{13}C T_1 values of chemisorbed species **A-C**.

Component	T_1/s
A	57.0(4.2)
B	7.1(1.4)
C	12.8(4×10^{-15})
D*	3.0(0.7)

* T_1 of **D** species (the only detected physisorbed CO_2 species using CP) was also measured. Note that the T_1 value obtained by this method is close to the one shown in **Table S2**.

Table S12 ^{13}C T_1 curve fitting parameters for physisorbed CO_2 species obtained from the saturation-recovery analysis.

	$M_{0,D}$	$T_{1,D}/s$	$M_{0,E}$	$T_{1,E}/s$	$M_{0,F}$	$T_{1,F}/s$
Calcined SBA-15	-	-	0.95(0.02)	0.296(0.017)	0.05(0.01)	$<5.00 \times 10^{-4}$
APTES@SBA-15	0.15(0.01)	2.4(0.3)	0.70(0.01)	0.090(0.003)	0.15(0.02)	$<5.00 \times 10^{-4}$
As-synthesized SBA-15	-	-	1(0.01)	0.072(0.005)	-	-
CO_2 gas	-	-	-	-	1	$<5.00 \times 10^{-4}$

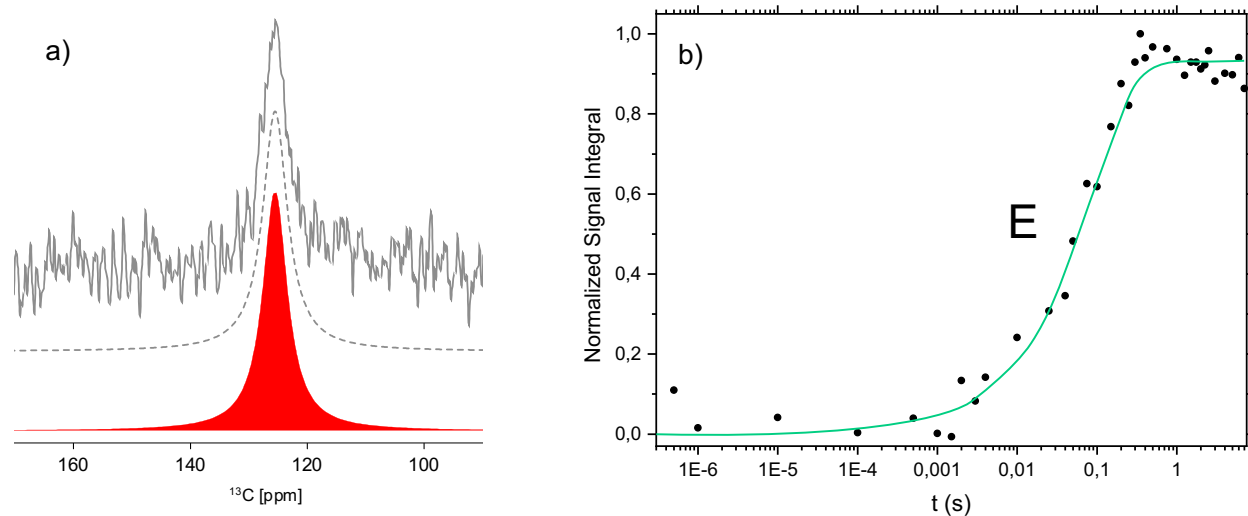


Figure S13 a) ^{13}C Single pulse MAS NMR spectrum of as-synthesized SBA-15, solid gray line is the experimental spectrum, dashed line is the fitting. Red represents physisorbed CO_2 species **E**. **b)** Plot of the normalized ^{13}C signal intensity vs magnetization recovery times (t). Green line is the fitted curve described in the text. Only one component is observed in b) assigned to CO_2 species **E**.

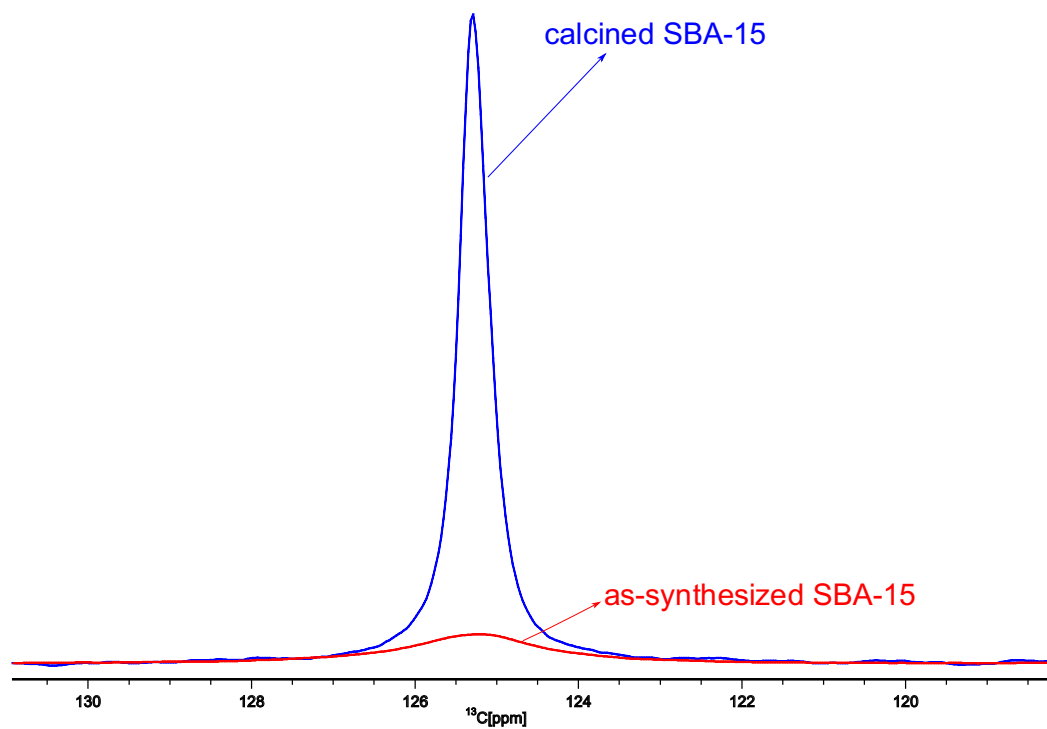


Figure S14 Comparison of ^{13}C MAS NMR spectra of SBA-15 samples with and without OSDA after exposure to $^{13}\text{CO}_2$ ($P = 770$ Torr). Same acquisition conditions were used in both spectra.

Table S15 Full width at half maximum (FWHM), estimated T_2 and measured T_2^* relaxation times for each observed physisorbed CO_2 species in the SBA-15 materials studied. The FWHM of species **D** was obtained from CSA fitted parameters. **E** and **F** FWHM were obtained by fitting the spectra at saturation recovery times: $t = 1 \times 10^{-4}$ s for **F** in calcined and APTES@SBA-15 samples, $t = 24$ s for **E** in calcined and as-synthesized samples, and $t = 0.15$ s for **E** in for the APTES@SBA-15 sample. T_2^* refocused transverse dephasing time were measured using a spin-echo pulse sequence.

Sample	F			E			D		
	FWHM/Hz	T_2 /ms	T_2^* /ms	FWHM/Hz	T_2 /ms	T_2^* /ms	FWHM/Hz	T_2 /ms	T_2^* /ms
APTES@SBA-15	109(2)	2.9	13.4(7)	106(2)	3.0	1.7(0.5)	108(2)	3.0	2.8(0.5)
Calcined SBA-15	28(1)	11.4	51.9(6)	42(1)	7.6	14.3(1)	50(1)	6.3	5.6(2)
As-synthesized SBA-15	-	-	-	187(1)	1.7	0.8(0.1)	-	-	-

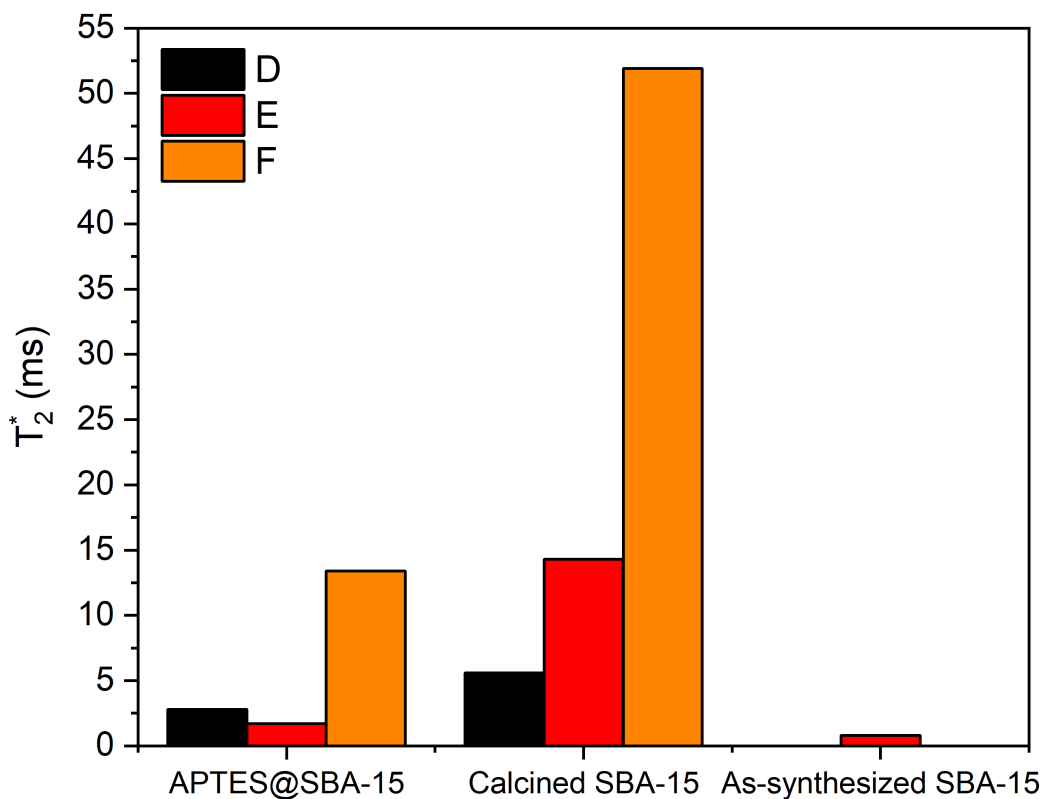


Figure S16 Graphical presentation of the T_2^* obtained for each observed ^{13}C resonance associated to the CO_2 species **D-F** in the different SBA-15 materials studied.

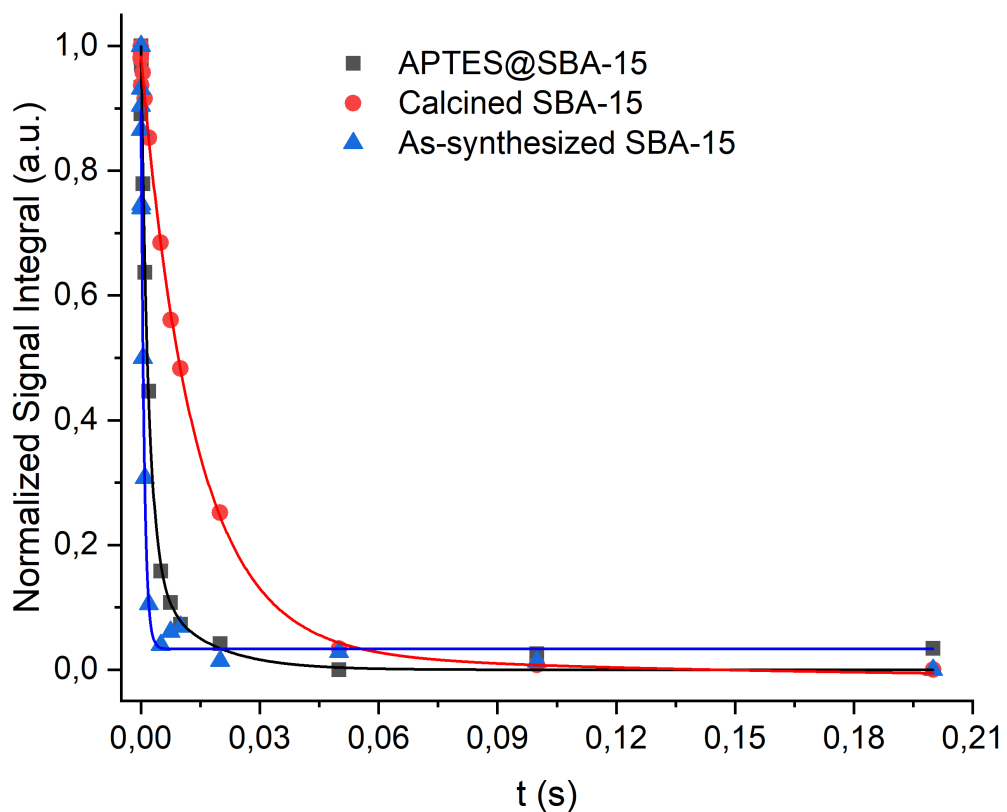


Figure S17 Plot of the normalized ^{13}C signal intensity vs magnetization transverse dephasing time (t) for the peak containing the NMR resonances of the physisorbed species **D**, **E**, **F** in the SBA-15 materials studied. The lines are the best-fitted curve using the equation: $M_{xy}(t) = M_{xy,i}^0 e^{-t/T_{2,i}^*}$ described in **section 2.4** of the main text.

Table S18 ^{13}C T_2^* curve fitting parameters for physisorbed CO_2 species obtained from the spin-echo analysis.

Sample	F		E		D	
	$M_{0,xy}$	T_2^*/ms	$M_{0,xy}$	T_2^*/ms	$M_{0,xy}$	T_2^*/ms
APTES@SBA-15	0.13(0.04)	13.4(7)	0.53(0.17)	1.7(0.5)	0.3(0.2)	2.8(0.5)
Calcined SBA-15	0.03(0.01)	51.9(6)	0.93(0.06)	14.3(1)	0.04(0.01)	5.6(2)
As-synthesized SBA-15	-	-	0.9(0.02)	0.8(0.1)	-	-

References

- (1) Torchia, D. A. The Measurement of Proton-Enhanced Carbon-13 T_1 Values by a Method Which Suppresses Artifacts. *J. Magn. Reson.* **1978**, 30, 613–616.
- (2) Ohgo, K.; Kumashiro, K. K. Efficient and Accurate Determination of ^{13}C T_1 and $T_{1\rho}$ Relaxation Time Constants of High-Mobility Polymers from Limited-Resolution Spectra with Optimized Pulse Sequences and Data Fitting. *J. Magn. Reson.* **2018**, 297, 161–171.