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Electronic Supplementary Information

Turning periodic mesoporous organosilicas selective to CO_2/CH_4 separation: deposition of aluminum oxide by atomic layer deposition

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1. Experimental - characterization

Morphology and composition of the Al-PMO composites were further analyzed by scanning electron microscopy (SEM) and electron dispersive spectroscopy (EDS) using a SU-70 (Hitachi) microscope with a Bruker silicon drift detector. The sample for scanning transmission electron microscopy (STEM) measurements was prepared by deposition a drop of a diluted ethanol dispersion of the material (previously sonicated for a few seconds) on a holey carbon grid; the solvent was allowed to dry in air.

Powder X-ray diffraction (PXRD) data were recorded using a Phillips X'Pert MPD diffractometer with Cu-Kα radiation.

TEM images were recorded in transmission electron microscopy Jeol 2100 UHR equipped with analysis EDX Si(Li) and camera CCD Gatan ultrascan (2k x 2k). For preparation samples are included into a polymeric resin and cut by ultramicrotomy with a diamond knife to have a thickness between 50nm and 70nm. Cut sections are deposited on grids with holey carbon film.

Fourier transform infrared (FTIR) spectra were performed in a FTIR Bruker Tensor 27 instrument with a Golden Gate ATR (Attenuated Total Reflectance). The PMO powders were dehydrated during 24h at 100 ºC before FTIR analysis. The FTIR spectra were collected in absorbance mode.

Nitrogen adsorption-desorption isotherms were collected at -196 ºC by a Gemini V 2.00 instrument model 2380. All PMOs materials were dehydrated overnight at 150 ºC and 1024 mbar. Then the materials were cooled to room temperature before adsorption.

^{13}C, ^{29}Si and ^{27}Al spectra were recorded at 100.62, 79.49 and 100.62 MHz, respectively, using a Bruker Avance III 400 spectrometer operating at 9.4 T. The spectra were quoted in ppm from trimethylsilane. ^{13}C cross-polarization magic-angle spinning (CP MAS) NMR spectra were collected using a 4 μs ^{1}H 90º pulse, 1 ms contact time, a spinning rate of 15 kHz and 4 s recycle delay. ^{29}Si CP MAS NMR spectra were acquired with a 4 μs ^{1}H 90º pulse, 8 ms contact time, a spinning rate of 5 kHz and 5 s recycle delay. ^{27}Al MAS NMR spectra were recorded employing a 10º flip angle pulse; a spinning rate of 14 kHz and 1 s recycle delays.

Thermogravimetric analysis (TGA) was made on a Shimadzu TGA-50 instrument with a heating rate of 5 ºC min^{-1} in air.

2. Characterization PMO materials

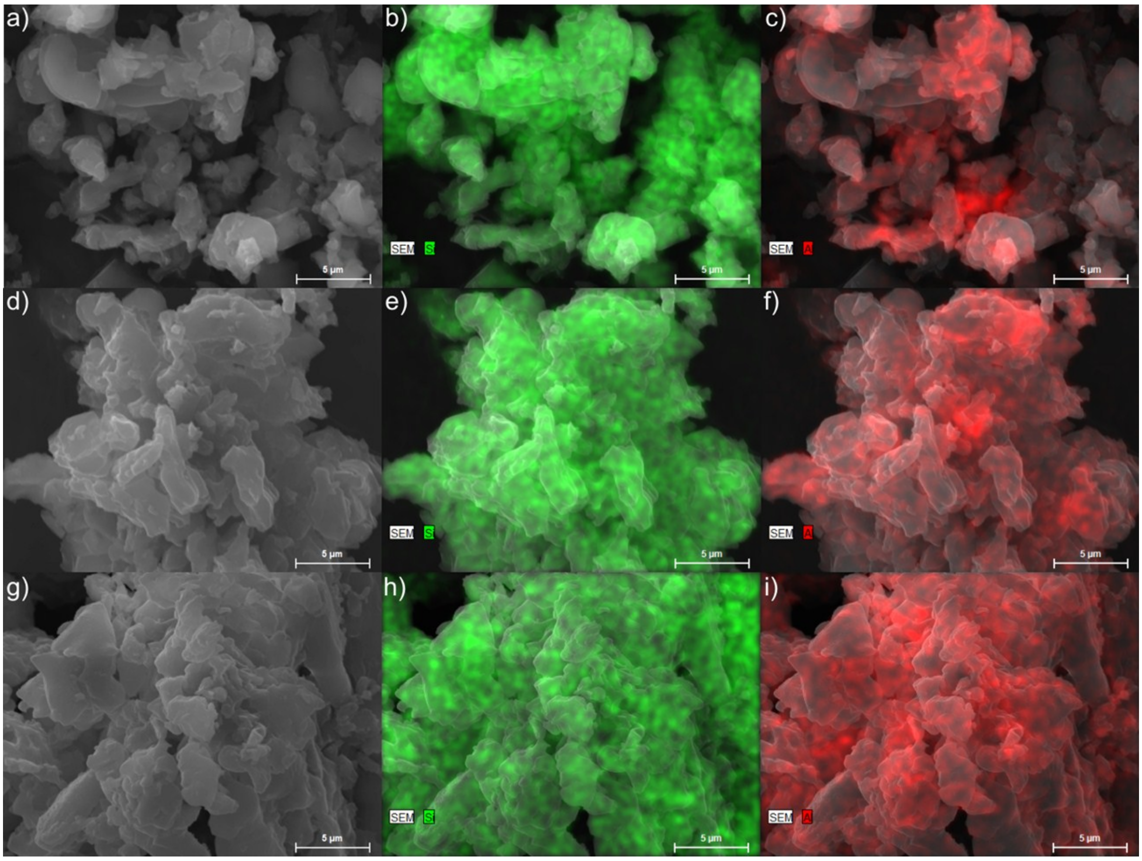


Figure S1. SEM and EDS mapping images of Al-PMO#10 (a), b), and c)), Al-PMO#20 (d), e), and f)) and Al-PMO#100 (g), h), and i)).

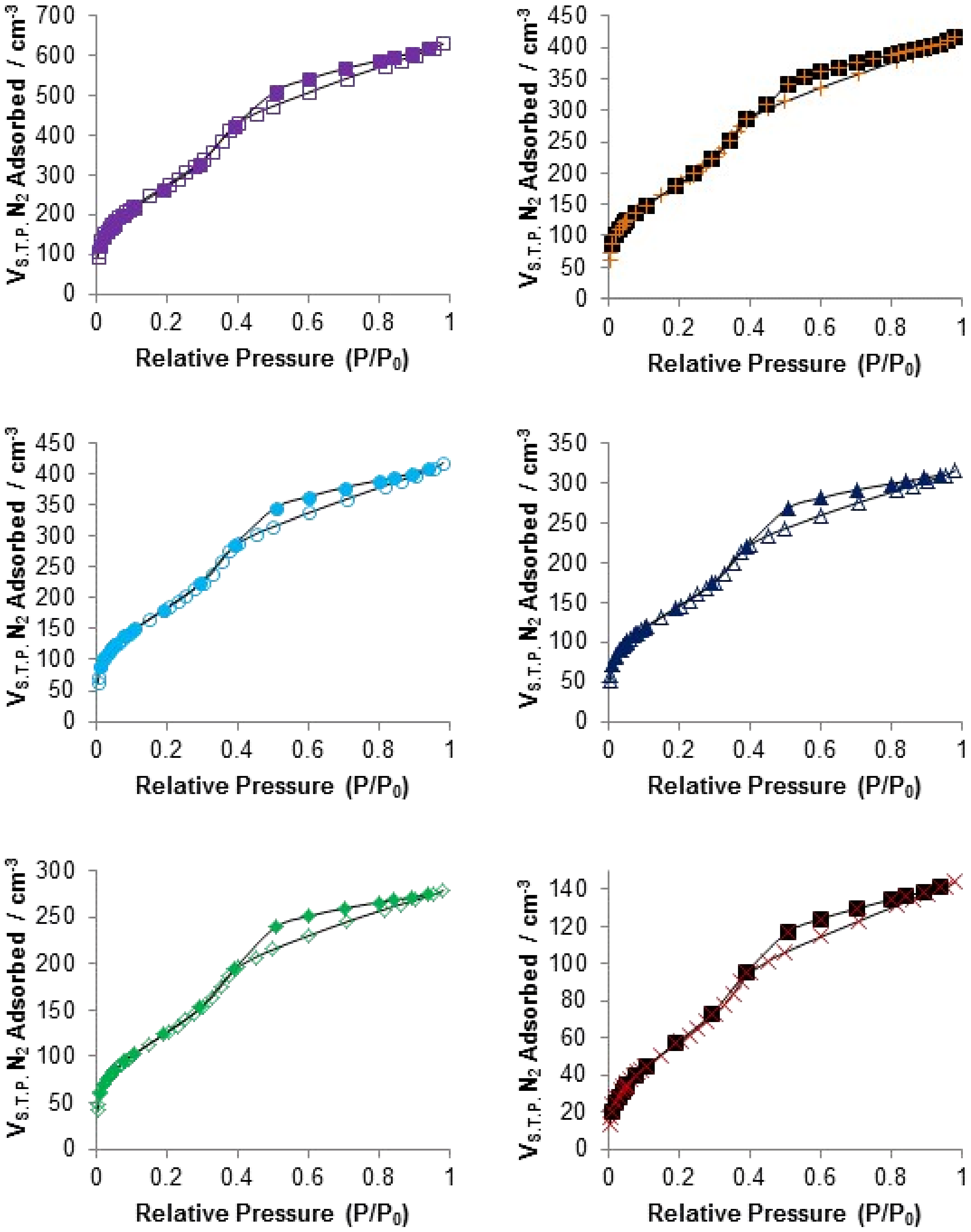
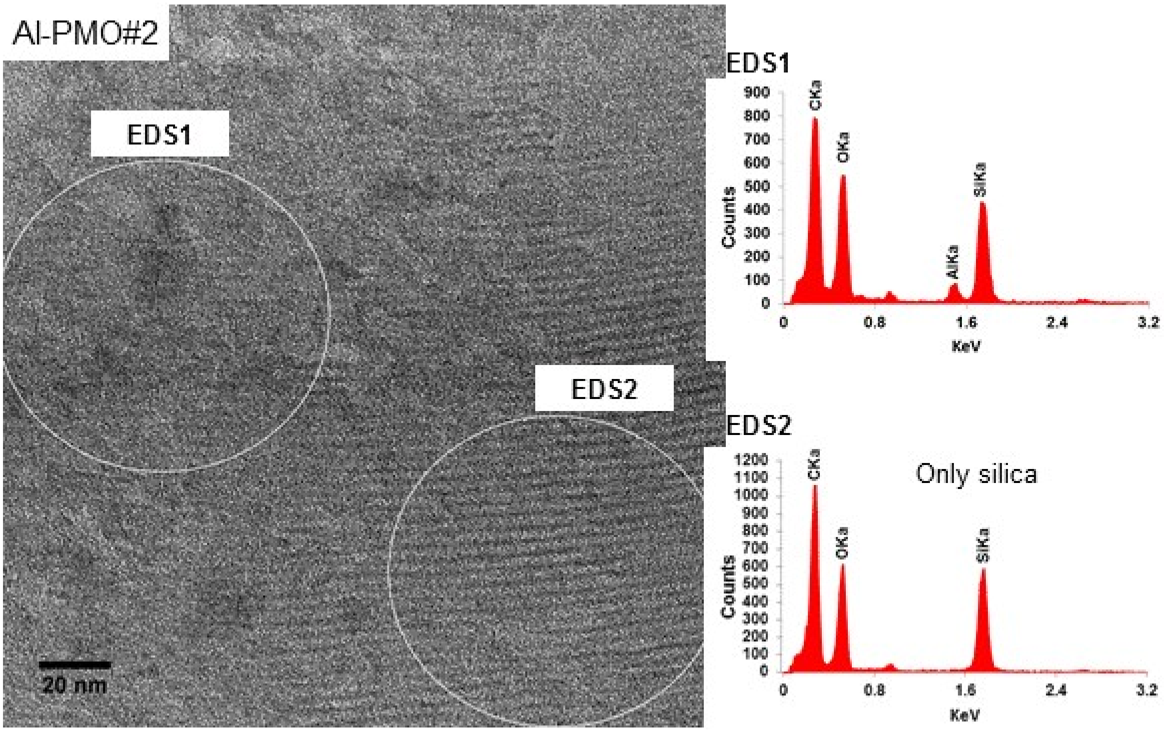
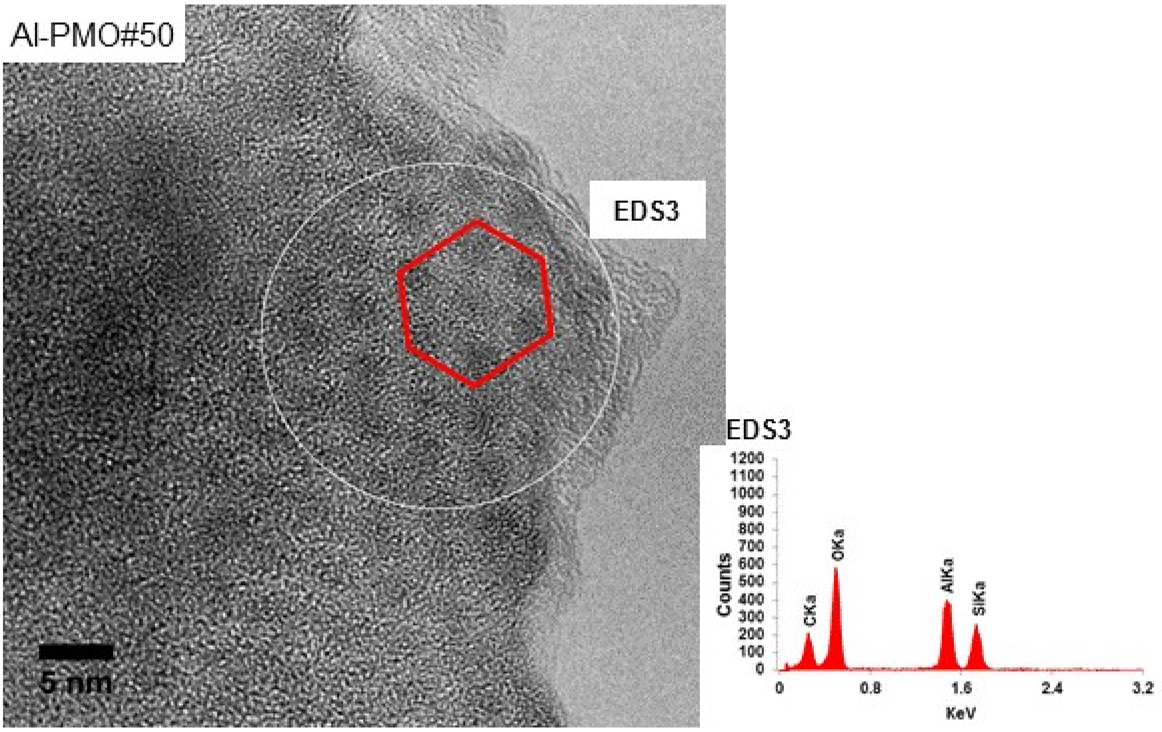


Figure S2. -196 ºC N_2 adsorption desorption isotherms of PMO (□), Al-PMO#2 (+), Al-PMO#10 (○), Al-PMO#20 (Δ), Al-PMO#50 (◊) and Al-PMO#100 (x). Empty symbols correspond to the adsorption and fully symbols correspond to the desorption.


Al-PMO#2
EDS1
EDS2
20 nm
EDS1
Counts
900
800
700
600
500
400
300
200
100
0
CKa
OKa
AlKa
SiKa
0
0.8
1.6
2.4
3.2
KeV
EDS2
Only silica
Counts
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
CKa
OKa
SiKa
0
0.8
1.6
2.4
3.2
KeV


Al-PMO#50
EDS3
5 nm
EDS3
Counts
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
CKa
OKa
AlKa
SiKa
0
0.8
1.6
2.4
3.2
KeV

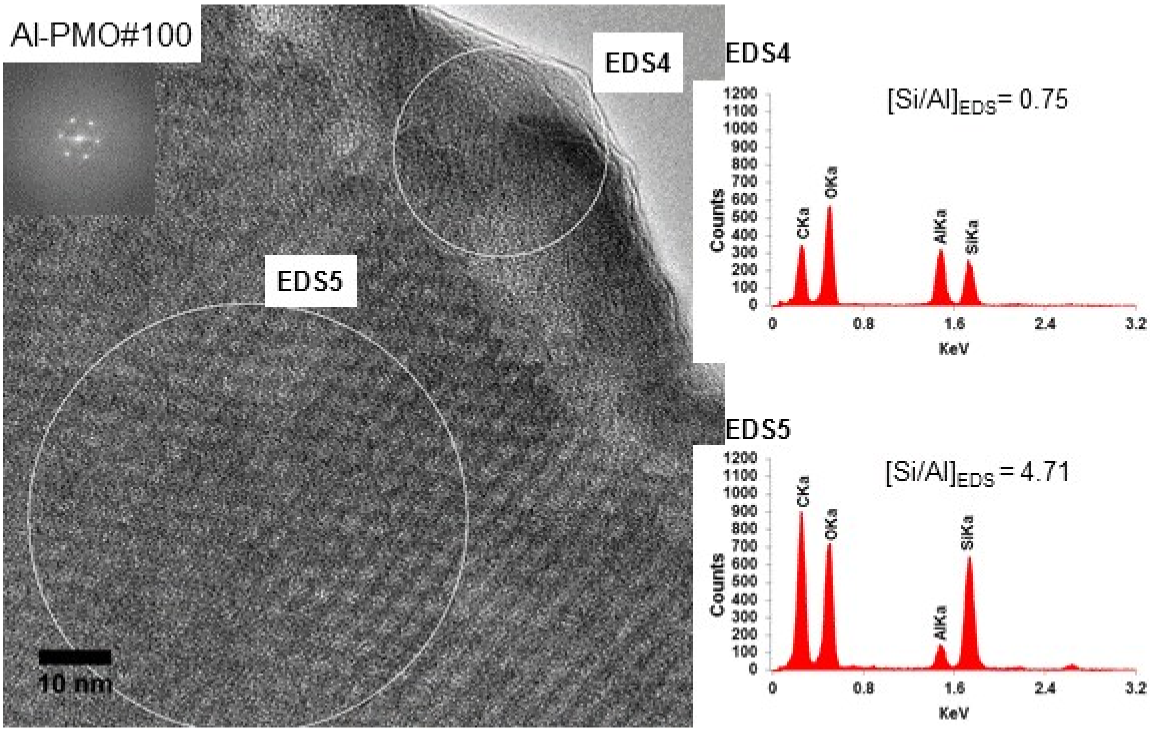
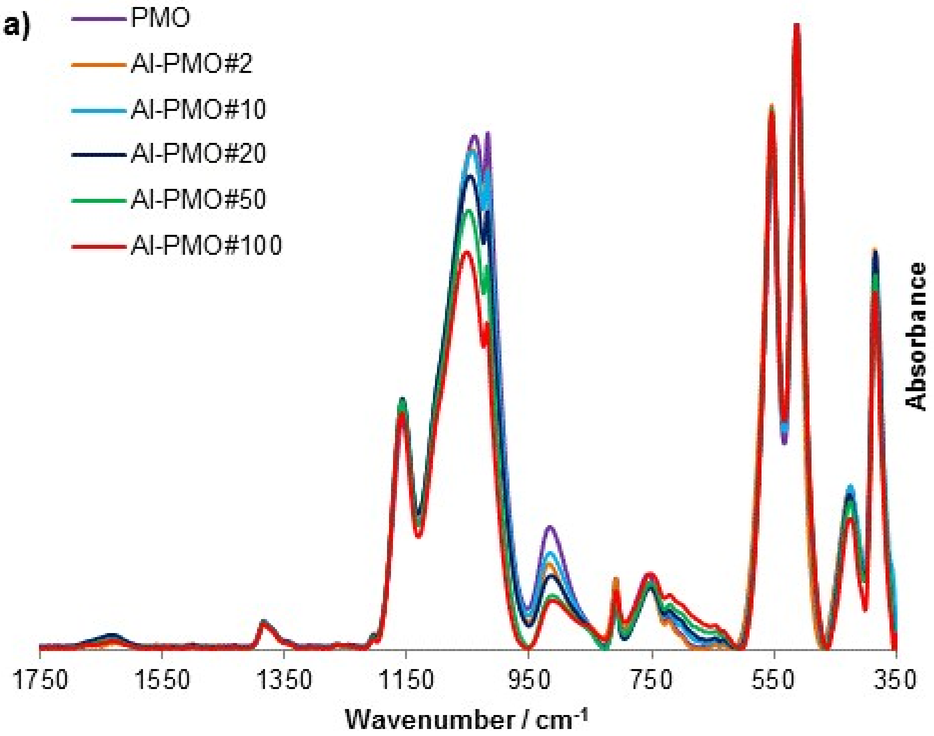


Figure S3. TEM images and EDS analyses of Al-PMO#2, Al-PMO#50 and Al-PMO#100 composites.



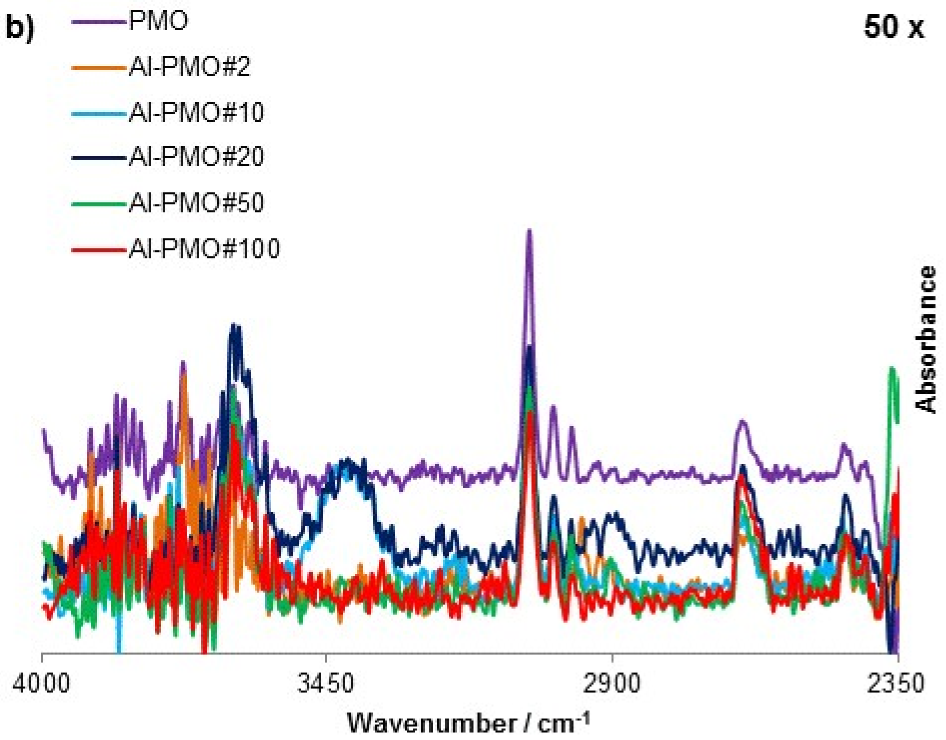


Figure S4. FTIR (ATR) spectra of PMO, Al-PMO#10, Al-PMO#20, Al-PMO#50 and Al-PMO#100 in the range of a) 350-1750 cm^{-1} b) 2350-4000 cm^{-1}.

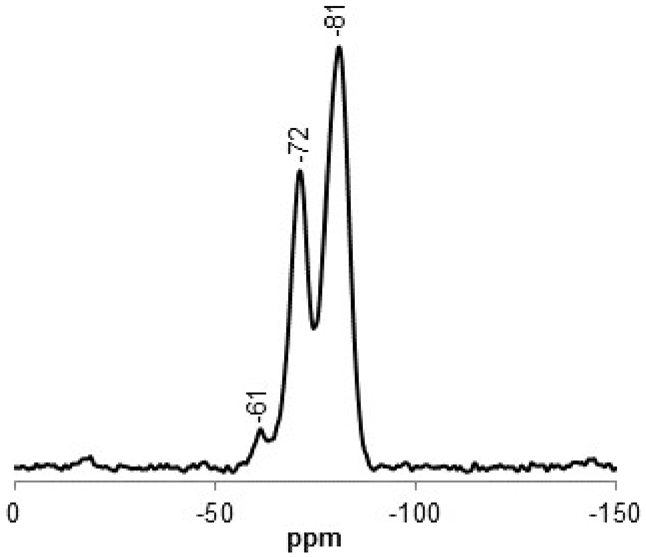


Figure S5. ^{29}Si CP MAS NMR spectra of Al-PMO#50.

Table S1. Percentage of T^m silanol species calculated from the fits of the ^{29}Si MAS NMR spectra.

PMO	% T^1	% T^2	% T^3
PMO	3.89	37.31	58.80
Al-PMO#50	3.38	33.10	63.52

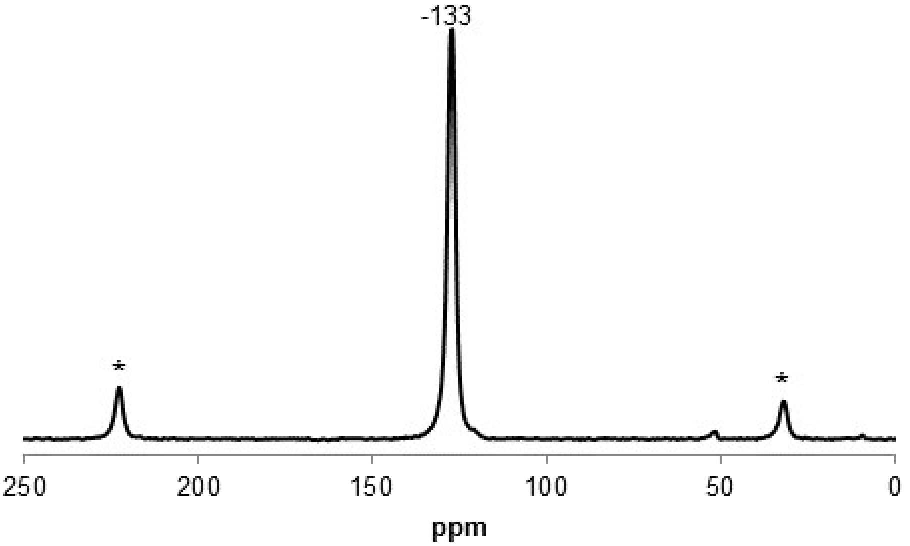


Figure S6. ^{13}C CP MAS NMR spectra of Al-PMO#50.

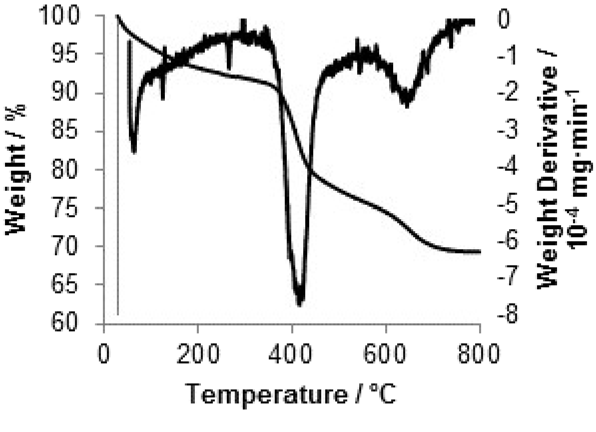


Figure S7. TGA of Al-PMO#50 composite.

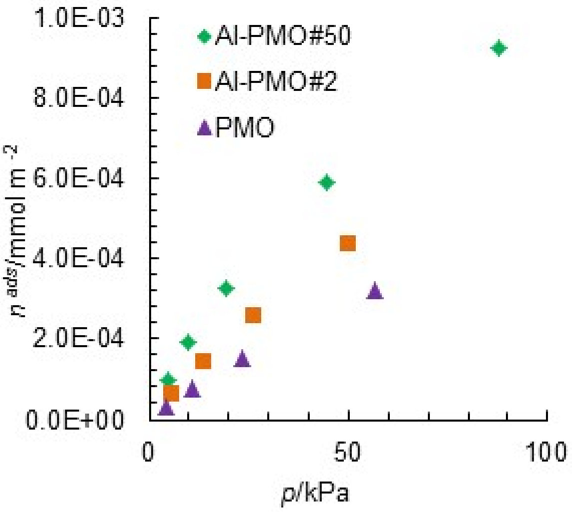


Figure S8. Carbon dioxide adsorption isotherms at 25ºC on the PMO, PMO#2 and PMO#50, expressed by surface area (A_{BET}) of the material.

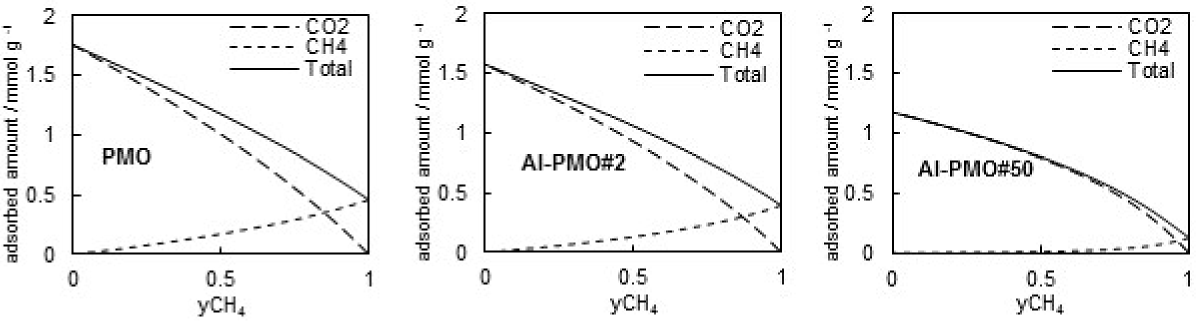


Figure S9. Adsorbed amounts of the CO_2/CH_4 mixture as a function of the CH_4 molar fraction in the gas phase, at 500 kPa and 25ºC, for PMO samples.

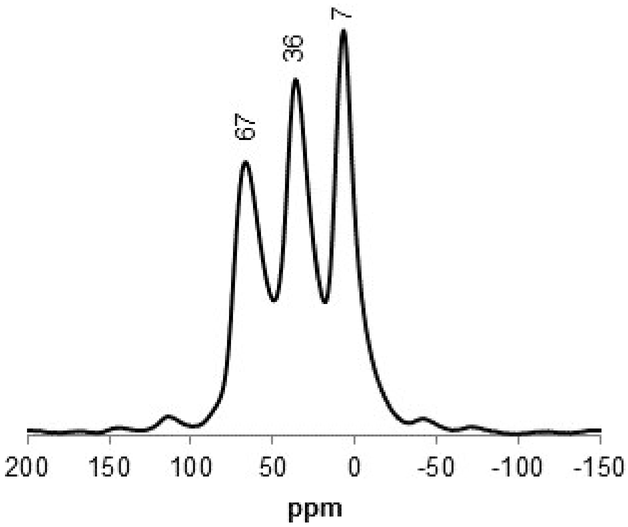
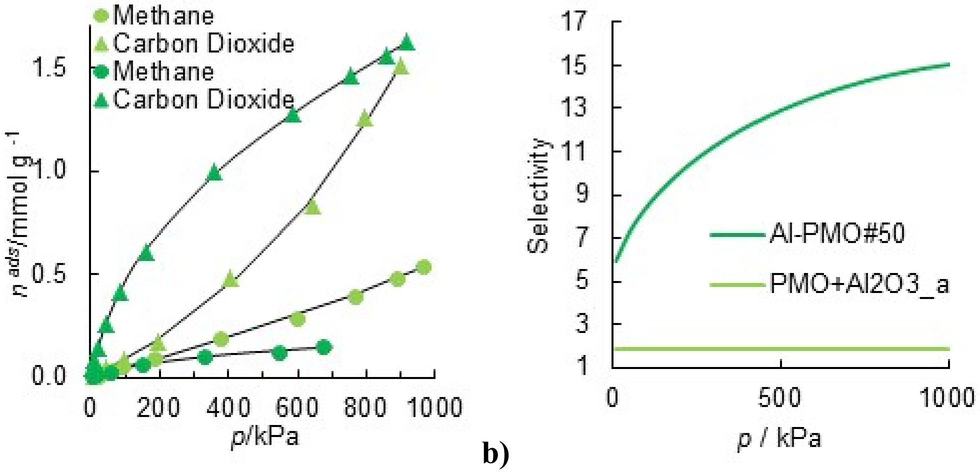


Figure S10. ^{27}Al MAS NMR spectrum of PMO+Al_2O_3_a material mixture.



a) **b)**

Figure S11. a) Carbon dioxide and methane adsorption isotherms at 25ºC on the Al-PMO#50 and PMO+Al_2O_3_a. The lines represent the fitting of the virial equation. b) Average selectivity for the CO_2/CH_4 separation on the Al-PMO#50 and PMO+Al_2O_3_a.

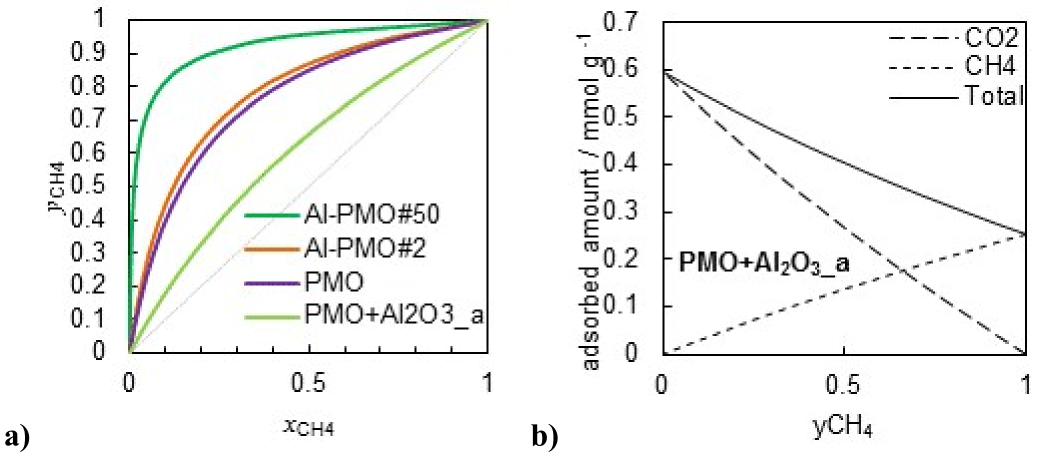


Figure S12. a) Isothermal (25ºC), isobaric (500 kPa) *xy* phase diagrams of the CO_2/CH_4 mixtures on the PMO+Al_2O_3_a. y_{CH4} is the molar faction of methane in the gas phase; x_{CH4} is the molar faction of methane in the adsorbed phase and b) adsorbed amounts of the CO_2/CH_4 mixture as a function of the CH_4 molar fraction in the gas phase, at 500 kPa and 25ºC, for PMO+Al_2O_3_a sample.