Electronic Supplementary Information

Turning periodic mesoporous organosilicas selective to CO₂/CH₄ 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 °C 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 °C N₂ 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.
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.

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<thead>
<tr>
<th></th>
<th>% $T^1$</th>
<th>% $T^2$</th>
<th>% $T^3$</th>
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<tbody>
<tr>
<td>PMO</td>
<td>3.89</td>
<td>37.31</td>
<td>58.80</td>
</tr>
<tr>
<td>Al-PMO#50</td>
<td>3.38</td>
<td>33.10</td>
<td>63.52</td>
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</tbody>
</table>

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 25°C 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 25°C, for PMO samples.
Figure S10. $^{27}$Al MAS NMR spectrum of PMO+Al$_2$O$_3$-a material mixture.

Figure S11. a) Carbon dioxide and methane adsorption isotherms at 25ºC on the Al-PMO#50 and PMO+Al$_2$O$_3$-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$_2$O$_3$-a.
Figure S12. a) Isothermal (25°C), isobaric (500 kPa) $x_y$ phase diagrams of the CO$_2$/CH$_4$ mixtures on the PMO+Al$_2$O$_3$. $y_{CH_4}$ is the molar faction of methane in the gas phase; $x_{CH_4}$ 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 25°C, for PMO+Al$_2$O$_3$ a sample.