Electronic Supplementary Information

Microwave assisted N-alkylation of amine functionalized crystal-like mesoporous phenylene-silica

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1. Experimental - characterization

Transmission electron microscopy (TEM) images were recorded by a 200 kV Hitachi H8100 Instrument and by a 200 kV High Resolution (HR) and energy-filtered (EF) TEM JEOL 2200FS Instrument.

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

Nitrogen adsorption-desorption isotherms were recorded at -196 ºC using a Gemini V 2.00 instrument model 2380. Functionalized PMO materials were dehydrated overnight at 150 ºC to an ultimate pressure of 1024 mbar and then cooled to room temperature prior to adsorption.

$^{13}$C, $^{29}$Si and $^{15}$N NMR spectra were recorded using a double resonance MAS probe on a Bruker Avance III 400 spectrometer operating at 9.4 T. $^{13}$C cross-polarization magic-angle spinning (CP MAS) NMR spectra were collected using the following parameters: 4 $\mu$s $^1$H 90º pulse; contact time (CT): 1 ms; $v_{1H}^\text{H}$: 70 kHz and $v_{1C}^\text{C}$: 78 kHz for CT pulses; MAS rate ($v_R$): 8 kHz and recycle delay (RD): 4 s. TPPM decoupling during the acquisition of the $^{13}$C signal was employed using a pulse length of 4.5 $\mu$s (ca. 165º pulses) for the basic unit block. $^{29}$Si MAS NMR spectra were collected employing a 40º flip angle pulse; $v_R$: 5 kHz; RD: 60 s. $^{29}$Si CP MAS NMR spectra were acquired with a 4 $\mu$s $^1$H 90º pulse; CT: 8 ms, $v_R$: 5 kHz; RD: 5 s. $^{15}$N CP MAS NMR spectra were recorded using a 4 $\mu$s $^1$H 90º flip angle pulse; $v_{1H}^\text{H}$: 57.7 kHz and $v_{1N}^\text{N}$: 62.5 kHz for CT pulses; CT: 8 ms; $v_R$: 5 kHz and RD: 5 s. In both $^{29}$Si and $^{15}$N NMR experiments a CW decoupling rf field strength of 53 kHz was applied during the acquisition time. In all the CPMAS experiments, the $^1$H rf field strengths used during the CT pulse were ramped from 50% to 100% to improve CP stability.

The $^{13}$C and $^{29}$Si NMR spectra were quoted in ppm from trimethylsilane, while $^{15}$N NMR spectra were referenced against a solid sample of natural abundance L-glycine, a secondary reference standard with respect to nitromethane.

Thermogravimetric analysis (TGA) was carried out on a Shimadzu TGA-50 instrument with a program rate of 5 ºC min$^{-1}$ in air.
Fourier transform infrared (FTIR) was done in a FTIR Bruker Tensor 27 instrument with a Golden Gate ATR (Attenuated Total Reflectance). Mesoporous powders were dehydrated at 100 °C for 24 h before FTIR analysis. The FTIR spectra were recorded in transmittance mode. Elemental analysis was carried out in C.A.C.T.I. in the Vigo University.

2. Characterization PMO materials

Figure S1. X-ray diffraction patterns of PMO, NH$_2$-PMO, Alk-NH-PMO1 and Alk-NH-PMO2. The inset displays the magnified patterns in the 2θ region from 2.5 to 5.5°.
Table S1. Physical properties of PMO, NH₂-PMO, Alk-NH-PMO1 and Alk-NH-PMO2.

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<th>Sample</th>
<th>(d_{100}/\text{nm})</th>
<th>(S_{BET}/\text{m}^2\text{ g}^{-1})</th>
<th>(V_P/\text{cm}^3\text{ g}^{-1})</th>
<th>(d_P/\text{nm})</th>
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*aPore width obtained from the maximum on the BJH pore size distribution calculated on the basis of adsorption data. *bPore wall thickness calculated as \((2d_{100}/\sqrt{3} - d_P)\), where the first term is the unit cell parameter.

Figure S2. TEM micrographs of: a) PMO, b) NH₂-PMO, c) Alk-NH-PMO1 and d) Alk-NH-PMO2 (the inset displays a micrograph where the hexagonal arrangement of pores can be seen).
Figure S3. -196 °C N\textsubscript{2} isotherms of PMO (□ adsorption; ■ desorption), NH\textsubscript{2}-PMO (○ adsorption; ● desorption), Alk-NH-PMO1 (△ adsorption; ▲ desorption) and Alk-NH-PMO2 (◊ adsorption; desorption ♦).
Figure S4. $^{29}$Si MAS (left) and CP-MAS (right) NMR spectra of PMO, NH$_2$-PMO, Alk-NH-PMO1 and Alk-NH-PMO2.
Figure S5. FTIR (ATR) spectra of PMO, NH$_2$-PMO, Alk-NH-PMO1 and Alk-NH-PMO2 in the range of 1200 - 4000 cm$^{-1}$ (C$_{ar}$ and C$_{al}$ despite for aromatic and aliphatic carbons, respectively).
Figure S6. TGA of PMO, NH₂-PMO, Alk-NH-PMO1 and Alk-NH-PMO2.

Table S2. Elemental analyses of PMO, NH₂-PMO, Alk-NH-PMO1 and Alk-NH-PMO2.

<table>
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<th>Sample</th>
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<th>% H</th>
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