Electronic Suporting Information

1. Synthesis of PE-SBA-15

The synthesis of PE-SBA-15 material was carried out in acidic medium at 17 ºC using TEOS (tetraethyl-orthosilicate) as a silica source and Pluronic P123 as a structure directing agent. 1, 3, 5-trisopropylbenzene (TIPB) was used as a swelling agent and NH₄F as a solubility enhancer, following the procedure described by Cao et al.¹ A P123:TIPB ratio of 2.4:1 was employed in order to preserve mesoscopic structure at the same time that pore diameter is increased. Also, a hydrolisis temperature of 17 ºC was used. The surfactant was removed from the mesostructured support by ethanol-extraction for 24 h and obtained material was named PE-SBA-15.

2. Functionalization of PE-SBA-15

Three different procedures were used to incorporate amino functionalities into PE-SBA-15:

2.1. Grafting

Grafted materials were obtained by refluxing 1 g of PE-SBA-15 silica in 100 mL toluene with selected quantities of 3-aminopropyl-trimethoxysilane, (NH₂-(CH₂)₃-Si(OCH₃)₃), and N-(3-Trimethoxysilylpropyl)diethylenetriamine, (H₂N-(CH₂)₂-NH-(CH₂)₂-NH-(CH₂)₃-Si(OCH₃)₃), denoted aminopopyl, AP, and diethylenetriamine, DT, respectively.

Organosilane incorporated amounts were calculated assuming a superficial silanol concentration of 6 SiOH/nm² and considering that the stoichiometry of the reaction between organosilane molecules and silanol groups is 1:1.
Obtained samples were dried at room temperature for 24 h, as a previous work shown that amino groups undergo a degradation reaction when dried at mild temperatures (such as 110 °C) under air atmosphere. Obtained samples were named as PE-SBA-AP and PE-SBA-DT.

2.2. Impregnation

Mesostructured silica PE-SBA-15 were impregnated with tetraethylenepentamine (TEPA) and an organic polymer, polyethyleneimine (PEI), both of them containing a high amount of amine groups in their structure. The impregnation procedure was carried out by dispersing 1 g PE-SBA-15 material into a methanol solution of PEI or TEPA, following the original method of Song and coworkers. After stirring for 30 minutes, the solvent was removed by drying at room temperature for 24 °C. The support was impregnated by adding different quantities of the organic compounds to obtain 30 and 50 % weight ratios in the final product. Resulting solids were named PE-SBA-PEI-(x) or PE-SBA-TEPA-(x), where x corresponds to the organic percentage in the adsorbent material.

2.3. Double functionalization by grafting-impregnation

This is the original procedure described in this work. An impregnation method analogous to the above-described (section 2.2) has been followed to incorporate TEPA or PEI over previously grafted materials (section 2.1). Thus, PE-SBA-AP-PEI (30), PE-SBA-AP-TEPA (30), PE-SBA-DT-TEPA (30), and PE-SBA-DT-TEPA (50) adsorbents were synthesised.

3. Characterization

3.1. Physical-chemical characterization
Textural properties were determined from N$_2$ adsorption-desorption isotherms at 77 K measured in a Micromeritics Tristar 3000 sorptometer. Surface area was calculated by using the B.E.T. equation (P/P$_0$ from 0.05 to 0.20) and the pore size distribution was obtained from the adsorption branch by means of the B.J.H. model assuming a cylindrical geometry of the pores. The nitrogen content, corresponding to incorporated amino groups, was measured by elemental microanalysis on a CHNOS model Vario EL III of Elemental Analyses System GMHB.

Figure 1 displays nitrogen adsorption-desorption isotherms at 77 K and pore size distributions of PE-SBA-15 materials and adsorbents functionalized by grafting with AP and DT. As seen, siliceous PE-SBA-15 presents a Type IV isotherm, showing the contribution of both micro and mesopores, as typical in SBA-15 materials. Also, the adsorption branch of the isotherm presents a steep slope, characteristic of materials with an homogeneous pore size. In Figure 1b it is confirmed the narrow pore size distribution of PE-SBA-15, centered around 15 nm. The functionalization by grafting of this material leads to a decrease in textural properties due to pore filling. AP and DT seem to yield adsorbents with very similar textural properties. Mesoscopic structure is maintained after grafting process.

**Fig. 1** a) N$_2$ adsorption-desorption isotherms at 77 K and b) pore size distributions of PE-SBA-15 siliceous support and adsorbents grafted with AP and DT
Figure 2 shows nitrogen adsorption-desorption isotherms for impregnated PE-SBA-15 with PEI and TEPA. Now, as the whole pore volume of this pore-expanded support can be occupied by TEPA or PEI, a further reduction of textural properties is achieved when obtaining 50% loaded adsorbents. If PEI polymer is used, the observed reduction is more marked in comparison with the use of TEPA. This is because TEPA molecules are distributed occupying the inner pores, whereas PEI lays in the outer surface of PE-SBA-15 particles, blocking pore entrances. Even when a 50% organic content is incorporated over the siliceous support, its structure is preserved.

Finally, Figure 3, already described in the main text, presents nitrogen adsorption-desorption isotherms at 77 K for double functionalized samples. As seen, a higher extent of pore filling is achieved by this original procedure, while mesostructure is maintained for all samples.
Fig. 3 $\text{N}_2$ adsorption-desorption isotherms at 77 K and pore size distributions of PE-SBA-15 siliceous support and double-functionalized adsorbents by grafting-impregnation with a), b) AP and PEI or TEPA and c), d) DT and TEPA

3.2. Adsorption of CO$_2$

Pure CO$_2$ adsorption-desorption isotherms were carried out at 45 ºC from 0 to 6 bar at 45 ºC in a Scientific Instruments HVPA-100 equipment, VTI. Samples were previously outgassed at 110 ºC under vacuum ($5 \times 10^{-3}$ mbar) for 2 h. Sievert method was used to measure free volume with helium prior to every measurement and to acquire isotherm points and two equilibrium criteria were considered for every point: a pressure drop below 0.2 mbar/3 min or a maximum equilibration time of 60 min.

A fix bed reactor (PID Eng & Tech Microactivity-Reference) coupled to a mass spectrometer (Pfeiffer Vacuum QMG220) was used to perform cyclic adsorption measurements with a CO$_2$ diluted stream at 45 ºC (80 % N$_2$, 15 % CO$_2$, 5 % O$_2$, dry basis) with around 5 % H$_2$O. Samples were pre-treated before each adsorption cycle.
by heating up to 110 °C under 100 mL/min Ar for 2 h to remove moisture and adsorbed gases. After that, the temperature was decreased to 45 °C and subsequently, the gas mix was introduced. Breakthrough curves representing the variation of CO$_2$ concentration after the fix bed with the time were integrated to calculate CO$_2$ adsorbed volume.

Kinetic experiments were carried out in a DSC-TGA thermobalance model SDT Simultaneous 2960 from TA instruments. A degassification step at 110 °C for 2 h was carried out prior to each analysis. An inlet pure CO$_2$ flow of 100 mL/min was used in all cases. Adsorption rates were obtained by differentiating the CO$_2$ uptake with respect to the time.

References

1 L. Cao, T. Man, M. Kruk, Chem. Mater., 2009, 21, 1144

