

An investigation on textural properties of mesostructured silica-based adsorbents for predicting CO₂ adsorption capacity

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SUPPORTING INFORMATION

1. Preparation of Supports

All the adsorbents used in this work were synthesized following the procedures described below, except Silica Gel (SG), purchased from Merk (Silica Gel 60 F₂₅₄).

1.1. Conventional and modified SBA-15

The original procedure developed by Stucky and coworkers¹ was scaled up to obtain 40 g of SBA-15. The experimental procedure consisted in the dissolution of Pluronic P123 (PEO₂₀-PPO₇₀-PEO₂₀, Mn~5800, Sigma-Aldrich), used as a structure directing agent, in 1.9 M HCl aqueous solution. After that, TEOS (tetraethyl orthosilicate, 98 %, Sigma-Aldrich), the silica source, was added to the previous mixture. A hydrolysis step at 40°C for 20 h was carried out and, finally, an ageing step at 110°C for 24 h was performed to complete the formation of the SBA-15 hexagonal mesostructure. The solid product was recovered by filtration and the surfactant was removed either by calcination in air at 550°C for 5 h (SBA-15) or by ethanol extraction (SBA-15e).

Also, several Al-SBA-15 supports were prepared with different aluminum contents in order to evaluate the influence of this metal in the surface chemistry. The synthesis followed is similar to that of the conventional SBA-15 silica.² First of all, 9 mL of a mixture of TEOS and IPA (aluminum isopropoxide, 98 %, Sigma-Aldrich) were jointly added to a 10 mL HCl aqueous solution. The TEOS/IPA ratio was set considering the desired Si/Al ratio in the final material. In this work, Si/Al ratios of 10, 30 and 60 were

used. After that, a hydrolysis step at 40°C was carried out for 20 h, followed by an ageing step at 100°C for 48 h. Mesoporous solids were recovered by filtration and the surfactant was removed by calcination in air at 550°C for 5 h. Obtained materials were named Al-SBA (x), where x is the Si/Al theoretical ratio.

Pore expanded SBA-15 materials were obtained following the method reported by Kruk et al.³ The experimental procedure consisted of the dissolution of P-123 and NH₄F (used as a co-solvent, Sigma-Aldrich) in a 1.3 M HCl aqueous solution at the desired temperature (here 12 and 17 °C have been used). A mixture of TEOS and TIPB, the swelling agent (1,3,5-triisopropylbenzene, 96 %, Sigma-Aldrich) was added to the previous media under vigorous stirring and a hydrolysis step at 12°C (or 17°C) was performed during 24 h. Finally, an ageing step was carried out at 100 °C during 48 h. The product was similarly recovered and calcined or extracted in order to remove the surfactant. Calcined samples were named SBA-PE- T_c , while ethanol-extracted samples were referred as SBA-PE- T_e , with T being the temperature of dissolution and hydrolysis in both cases.

1.2. Hexagonal Mesoporous Supports (HMS)

HMS silica supports were synthesized according to the procedure described by Tanev and Pinnavaia.⁴ A primary alkylamine was used as a structure directing agent, commonly dodecylamine (99.5 %, Fluka). The appropriate amount of this compound was dissolved in a mixture of ethanol and water, where TEOS was also added. The so-obtained medium was aged at room temperature for 18 h and then filtered to obtain the solid product. The surfactant was removed by calcination at 450°C for 5h or else by ethanol extraction, obtaining products HMS-12c or HMS-12e depending on the method

used for the removal of the surfactant. Alternatively, other alkylamines with longer and shorter hydrocarbon chains were employed in order to obtain materials with slightly different pore diameters. The use of octylamine (99 %, Sigma-Aldrich), decylamine (98 %, Fluka), hexadecylamine (98 %, Sigma-Aldrich) and octadecylamine (99 %, Sigma-Aldrich) gave as a result samples named HMS-8c, HMS-10c, HMS-16c and HMS-18c.

1.3. Conventional and pore-expanded MCM-41

The synthesis route uses an aqueous solution of dimethylamine (40 % in water, Sigma-Aldrich) and hexadecyltrimethylammonium bromide (98 %, Sigma-Aldrich), stirred at 18°C for 24 h.⁵ After that, TEOS was added drop by drop and a hydrolysis step was performed at 18°C for 4h. After that, a hydrothermal ageing was carried out at 100 °C for 48 h. The solid product obtained was recovered by filtration and calcination at 550°C for 6 h or either ethanol extraction. Obtained samples were named MCM-41 and MCM-41e.

A pore expansion process was applied to the MCM-41 support as made, i.e., not calcined. With this aim, a certain amount of *as made* MCM-41 was dispersed into a dimethyldecylamine aqueous solution (90 %, Sigma-Aldrich) and autoclaved at 120°C for 72 h. After that, the resulting product was filtered and calcined at 550°C for 6 h,⁶ being named MCM-PEc.

2. Modification of SBA-15

2.1. Co-condensation

SBA-15 materials co-condensed with amino groups were prepared in a single-step synthesis.⁷ A short pre-hydrolysis step of 45 min was allowed for the TEOS-HCl (aq) mixture, followed by the addition of the desired organosilane, e.g. aminopropyl-trimethoxysilane (AP, 97 %, Sigma-Aldrich), ethylenediamine-trimethoxysilane (ED, 97 %, Sigma-Aldrich), and diethylenetriamine-trimethoxysilane (DT, technical grade, Sigma-Aldrich). After that, a hydrolysis step at 40°C for 20 h and an ageing process at 100°C for 24 h were performed. Co-condensed materials were recovered by filtration and ethanol extraction. The obtained solids were named SBA-C-AP, SBA-C-ED and SBA-C-DT.

2.2. Grafting

SBA-15 silica was grafted with organosilanes by refluxing 1 g of the support in 250 mL toluene with the desired organosilane for 24 h. In all cases, 6.89 mmol of each organic compound was added, an amount enough to react with a 1:1 stoichiometry for a typical SBA-15 material that presents a surface silanol concentration of 6 SiOH/nm². All the materials were washed with ethanol, recovered by vacuum filtration and dried at room temperature for 24 h. Drying at higher temperatures was avoided, since it was previously demonstrated that the air-drying of amino-containing solids at mild temperatures (110 °C) gave as a result an undesired oxidation of the amino groups.⁸

Several kinds of organosilanes were used: butyl-trimethoxysilane (BT, 97 %, ABCR), isobutyl-trimethoxysilane (IB, 97 %, ABCR) and octyl-trimethoxysilane (OC, 97 %, ABCR), without amino groups in their structures; (N,N-dimethylaminopropyl)trimethoxysilane (DM, 96 %, Sigma-Aldrich), (N,N-diethylaminopropyl)trimethoxysilane (DE, 98 %, Sigma-Aldrich) and N-hydroxyethyl-

N-methylaminopropyl-trimethoxysilane (HE, 75 % in methanol, ABCR), with tertiary amino groups; and finally, AP, ED and DT, with primary and secondary amino groups. Grafted materials were named SBA-*Org*, where *Org* refers to the organosilane compound used.

3. Physico-chemical characterization of supports

Complementing the physico-chemical properties displayed in Table 1 and the N₂ adsorption-desorption isotherms shown in Figure 1, the complete set of N₂ isotherms for the synthesized supports are presented here in Figures SI 1 to SI 3.

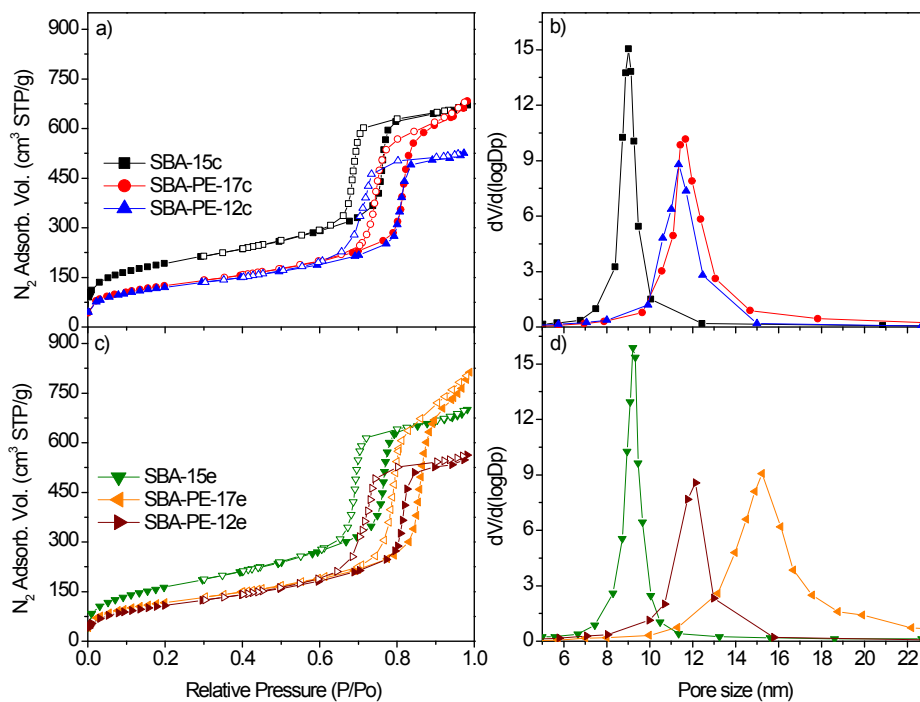


Figure SI 1. Characterization of SBA-15 and SBA-PE series of materials: a), c) N₂ adsorption-desorption isotherms at 77 K and b), d) BJH pore size distributions.

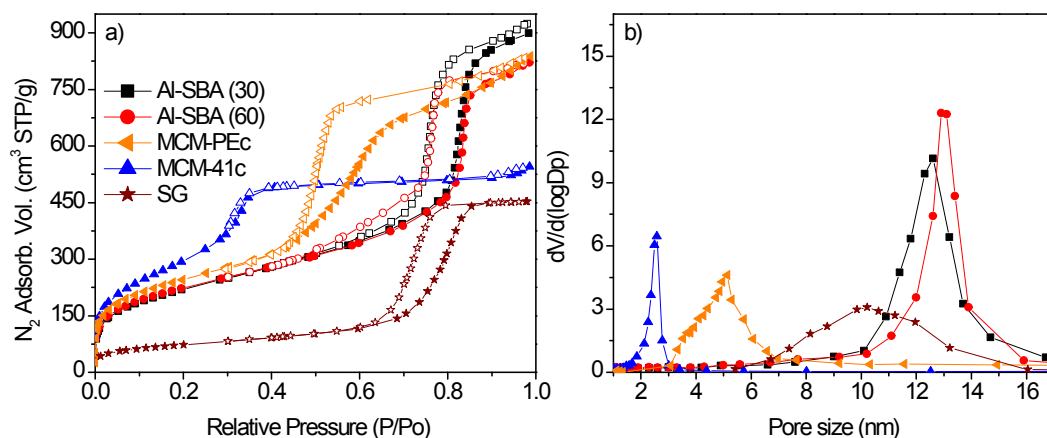


Figure SI 2. Characterization of Al-SBA-15, MCM-41 and SG series of materials: a) N_2 adsorption-desorption isotherms at 77 K and b) BJH pore size distributions.

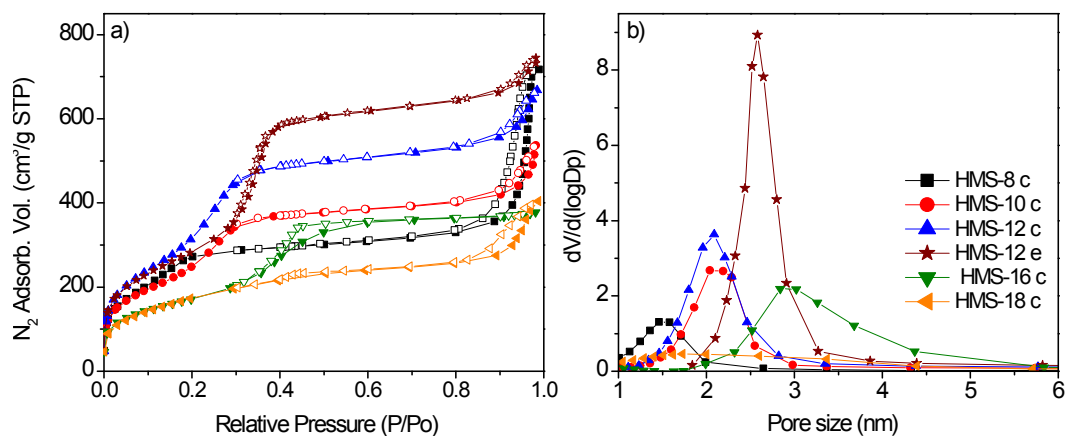


Figure SI 3. Characterization of HMS series of materials: a) N_2 adsorption-desorption isotherms at 77 K and b) BJH pore size distributions.

4. CO_2 adsorption analyses

Pure CO_2 isotherms were acquired at 45 °C, obtaining the results shown in Figures SI 4 to SI 6 for unmodified supports, and in Figure SI 7 for functionalized samples.

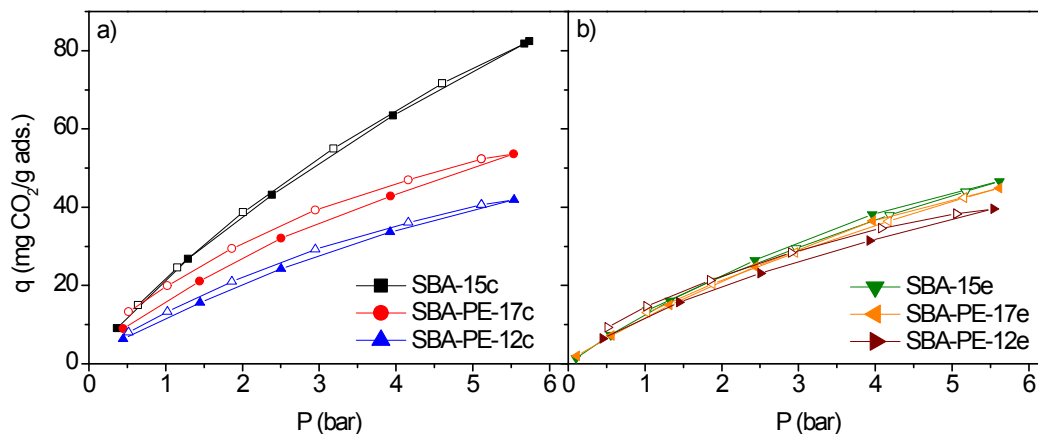


Figure SI 4. Pure CO₂ adsorption-desorption isotherms at 45 °C for SBA-15 and SBA-PE series of materials a) calcined and b) ethanol-extracted.

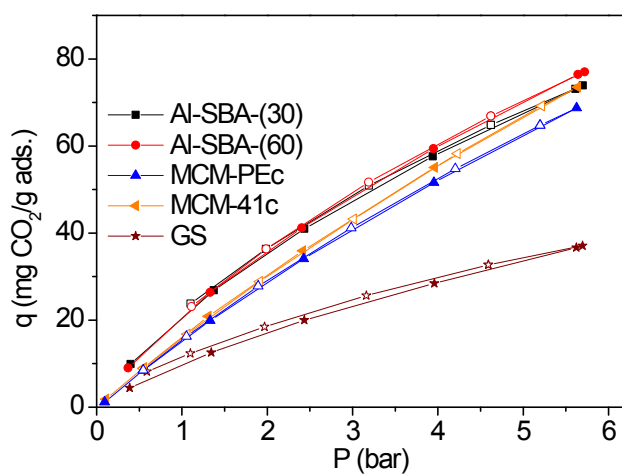


Figure SI 5. Pure CO₂ adsorption-desorption isotherms at 45 °C for Al-SBA-15, MCM-41 and SG series of materials.

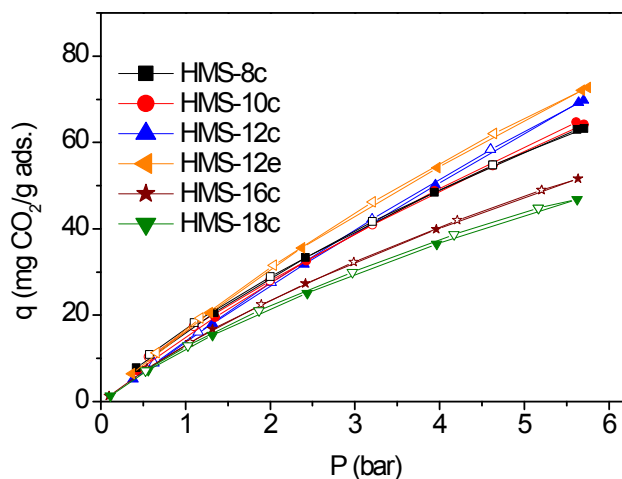


Figure SI 6. Pure CO₂ adsorption-desorption isotherms at 45 °C for HMS series of materials.

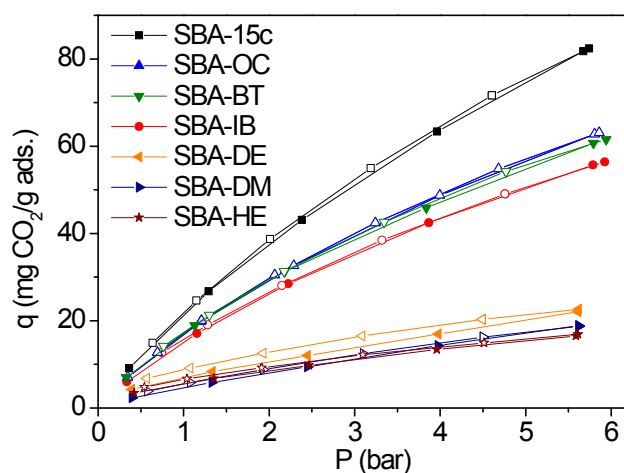


Figure SI 7. Pure CO₂ adsorption-desorption isotherms at 45 °C for SBA-15 silica functionalized with organosilanes without amino groups (OC, BT, IB) or containing tertiary amino groups (DE, DM, HE).

5. Determination of isosteric heat of adsorption

CO₂ isotherms for SBA-15 and SBA-C-ED were acquired at 35, 45, 55 and 65 °C.

Figure 4 in the main text shows experimental equilibrium points for each isotherm as well as the Sips isotherm model fit. Sips parameters are shown in Table S1.

For given CO₂ uptakes, the corresponding pressure was calculated by interpolation using the modeled isotherms. The Clausius-Clapeyron equation was used to determine the isosteric heat of adsorption from the slope of the best linear fit of $\ln(P)$ versus $(1/T)$ at each CO₂ uptake (Figure SI 8).

Isosteric heat of adsorption for SBA-15 and SBA-C-ED is shown and discussed in the manuscript.

Table SI 1 Sips parameters of the temperature-dependent isotherm form for CO₂ adsorption on SBA-15 and SBA-C-ED.

Adsorbent	Temp. (°C)	n _s (mg CO ₂ /g ads)	b (bar ⁻¹)	t	R ²
SBA-15	35	315.42	0.0612	1.22	0.9997
	45	181.44	0.115	1.10	0.9997
	55	167.40	0.0983	1.08	0.9998
	65	108.08	0.144	0.99	0.9998
SBA-C-ED	35	103.54	0.103	1.16	0.9987
	45	81.71	0.129	1.01	0.9990
	55	41.61	0.236	0.92	0.9993
	65	36.40	0.204	0.89	0.9986

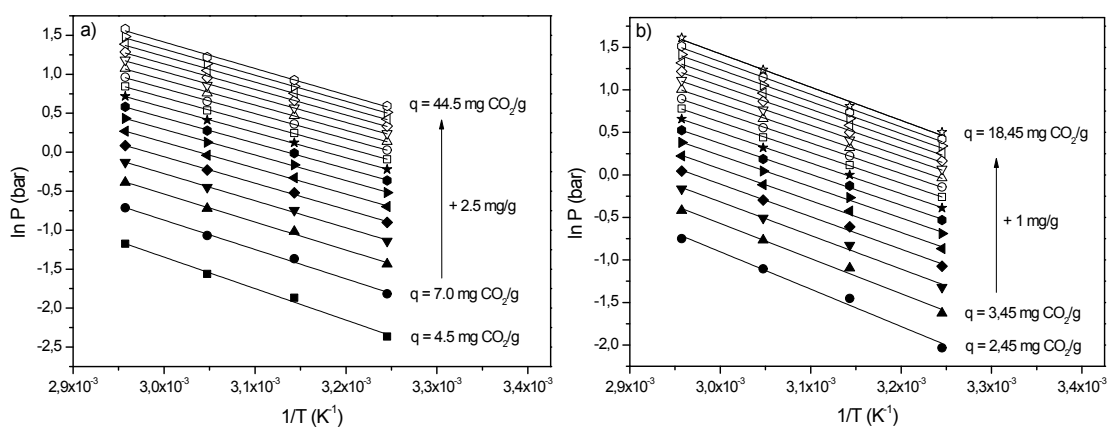


Figure SI 8. Dependence of pressure with temperature for given CO₂ uptake values in samples of a) SBA-15 silica and b) co-condensed SBA-C-ED.

6. References

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