Supplementary info

1. Small angle X-ray diffraction

The small angle X-ray diffraction patterns were obtained using a Philips X'Pert diffractometer (Philips Electronics NV, Eindhoven, Holland) with Bragg-Brentano geometry. The device operates at 20 kV and 20 mA and using the CuKα line at 0.15406 nm. Diffraction patterns are shown in Figure S1.

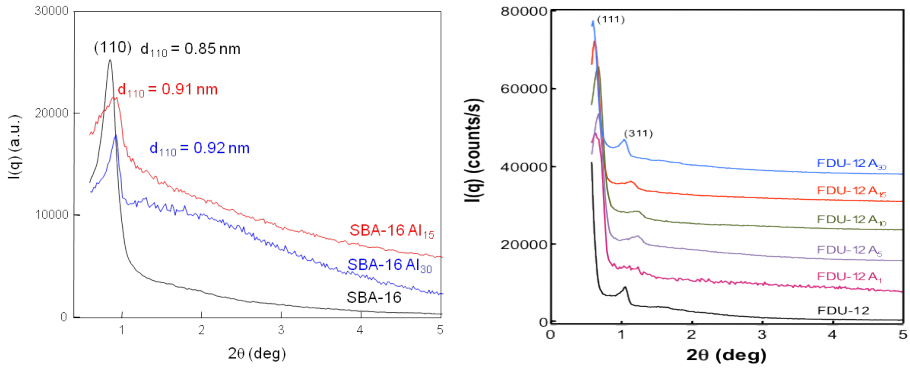

Figure S1. SA-XRD patterns of the SBA-16 and FDU-12 materials

2. Pore size and wall thickness determination from XRD and N_2 adsorption

The relative variations of pore sizes were corrected employing the Kruk-Jaroniec-Sayari (KJS) geometrical scheme[1] where $\mathbf{w_{KJS}}$ is the primary mesopore width calculated after the following expression:

$$w_{KJS} = a \cdot \left(\frac{6}{\nu\pi} \frac{\rho V_{mp}}{1 + \rho\left(V_{mp} + V_{micp}\right)} \right)^{\frac{1}{3}}$$

where **a** is the cubic unit cell parameter obtained from the SA-XRD patterns, **ν** is the number of spherical mesopores per unit cell (**ν** = 4 for F*m*3*m* and **ν** = 2 for I*m*3*m*), **ρ** is the density of the solid silica walls (assumed as 2.2 g/cm^3), $\mathbf{V_{mp}}$ is the mesopore volume and $\mathbf{V_{micp}}$ is the micropore volume. The values of $\mathbf{V_{mp}}$ were graphically calculated from the thickness-transformed isotherm at the top of the adsorption plateau (N_2 layer thicknesses over 15 nm). In Figure S2 are plotted the thickness-transformed isotherms used for calculating both $\mathbf{V_{mp}}$ and $\mathbf{V_{micp}}$ for SBA-16 and FDU-12.

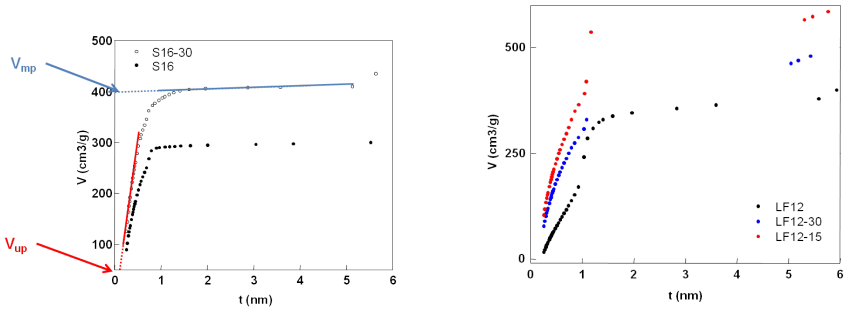

Figure S2. Thickness-transformed isotherms for SBA-16 and FDU-12 materials

The thickness of the silica wall between adjacent mesopores can be calculated after the values of w_{KJS} and the unit cell parameters. Since cubic structures show different pore wall thicknesses depending on the direction in which is measured, the shortest thickness is only considered here. The calculation in the case of SBA-16 structures, with pore ordering in the Im3m space group, the minimal distance between pores is found from the vertex to the centre of the cell, which is calculated using the following expression:

[1] M. Kruk, M. Jaroniec and A. Sayari, *Chem. Mater.,* 1999, **11**, 492.

$$t_P = \frac{\sqrt{3}}{2}a - w_{KJS}$$

For the FDU-12 structures with Fm3m, the minimal pore distance between adjacent mesopores is found from the vertex to the centre of the faces, and can be calculated as:

$$t_P = \frac{\sqrt{2}}{2}a - w_{KJS}$$

The average pore wall thickness in cubic structures is estimated using the Ravikovitch-Neimark expression[2]:

$$t_{AVG} = \left(\frac{2a^3}{\pi w_{KJS} v} - \frac{w_{KJS}}{3}\right)$$

The final values of the surface area calculations are shown in Table S1.

Table S1. Composition and texture data calculated from XRF, XRD and N_2 adsorption

Sample	Nom Si/Al	Exp Si/Al	S_{BET} (m^2/g)	V_T (cm^3/g)	V_{micp} (cm^3/g)	V_{mp} (cm^3/g)	ν	a (nm)	D_{BJH} (nm)	D_{DFT} (nm)	w_{KJS} (nm)	t_P (nm)	t_{avg} (nm)
SBA-16	∞	∞	670	0.467	0.032	0.416	2	14.7	6.0	7.10	11.2	1.53	4.38
SBA-16 A_{30}	30.0	→ ∞	933	0.631	0.039	0.583	2	11.4	5.0	6.10	9.11	0.76	2.59
SBA-16 A_{15}	15.0	$6.2 \cdot 10^3$	1094	0.765	0.053	0.694	2	12.5	6.0	8.48	10.2	0.63	2.51
FDU-12	∞	∞	520	0.680	0.015	0.665	4	31.5	13.0	13.0	20.6	1.67	4.86
FDU-12 A_{30}	30.0	→∞	599	0.716	0.010	0.716	4	24.7	12.0	14.4	16.4	1.06	3.48
FDU-12 A_{15}	15.0	$1.4 \cdot 10^3$	754	0.875	0.039	0.864	4	27.4	12.5	16.7	18.5	0.87	3.38
FDU-12 A_{10}	10.0	$3.0 \cdot 10^3$	562	0.597	0.007	0.559	4	22.2	10.0	12.6	14.2	1.50	3.88
FDU-12 A_5	5.0	$6.1 \cdot 10^3$	583	0.614	0.014	0.583	4	21.8	9.41	12.7	13.9	1.51	3.83
FDU-12 A_1	1.0	$2.8 \cdot 10^3$	631	0.648	0.049	0.610	4	23.6	9.21	12.1	14.9	1.79	4.49

3. Chemical analysis

For resolving the Al content in the processed materials, several analysis techniques were used. The initial scanning transmission electron microscopy (STEM) analysis allows the determination of the bulk atomic concentration in small fractions of materials that can be observed in HRTEM images. The STEM analysis was performed in the FEI Tecnai F30 electron microscope equipped with a STEM module with a high angle annular dark field (HAADF) to obtain images of this type. The surface chemical analysis was performed with an EDAX device with super ultra thin window. The powder samples were softly crushed in a mortar and mixed in ethanol, sonicated for 2 min. Then a drop of each sample was placed on lacey carbon film copper grids and then allowed to dry before TEM and STEM analysis. Details on the STEM technique are discussed elsewhere.

In Figure S3 are collected the STEM analysis spectra for the prepared materials, showing the high-angle annular dark field (HAADF) image of the material specimen, the energy dispersive X-ray (EDX) spectrum acquired in the red squared area and the corrected atom percent composition obtained from the EDX.

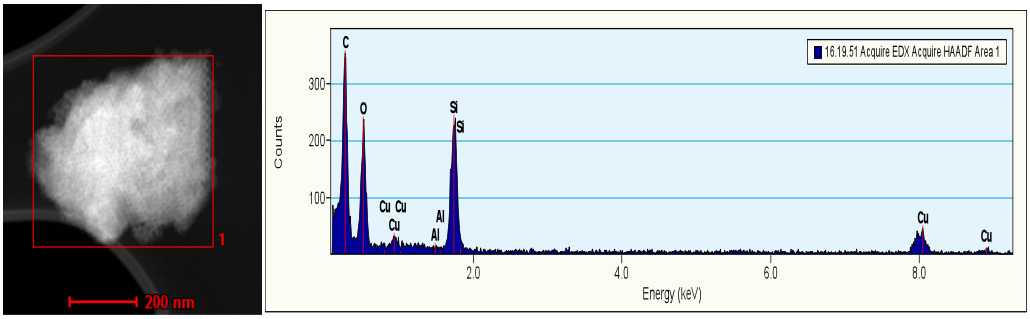

Figure S3. STEM analysis of FDU-12 Al_{15} mesoporous material

[2] P.I. Ravikovitch and A.V. Neimark, *Langmuir*, 2002, **18**, 1550

The eventual incorporation of Al in the mesoporous structures was determined using X-ray fluorescence (XRF) in a Bruker AXS S4 Pioneer spectrometer. This is an extremely sensitive technique for analyzing the total atomic composition in those elements from fluorine to uranium. In Table S1 is shown the percent silicon and aluminium concentration in every analyzed specimen.

Table S2. XRF spectrometry data

	%Si	%Al
SBA-16 Al_{30}	99.38	-
SBA-16 Al_{15}	99.58	0.0160
FDU-12 Al_{30}	99.35	-
FDU-12 Al_{15}	99.54	0.0698
FDU-12 Al_{10}	99.08	0.0334
FDU-12 Al_5	99.38	0.0162
FDU-12 Al_1	99.35	0.0354

4. ^{27}Al Nuclear Magnetic Resonance spectroscopy

The ^{27}Al NMR spectra in D_2O solution were obtained on a Bruker AV400 spectrometer operating at 104.26 MHz and using $[Al(OH_2)_6]^{3+}$ as reference. ^{27}Al NMR spectra of representative samples synthesized using D_2O as reagent are given in Figure S4.

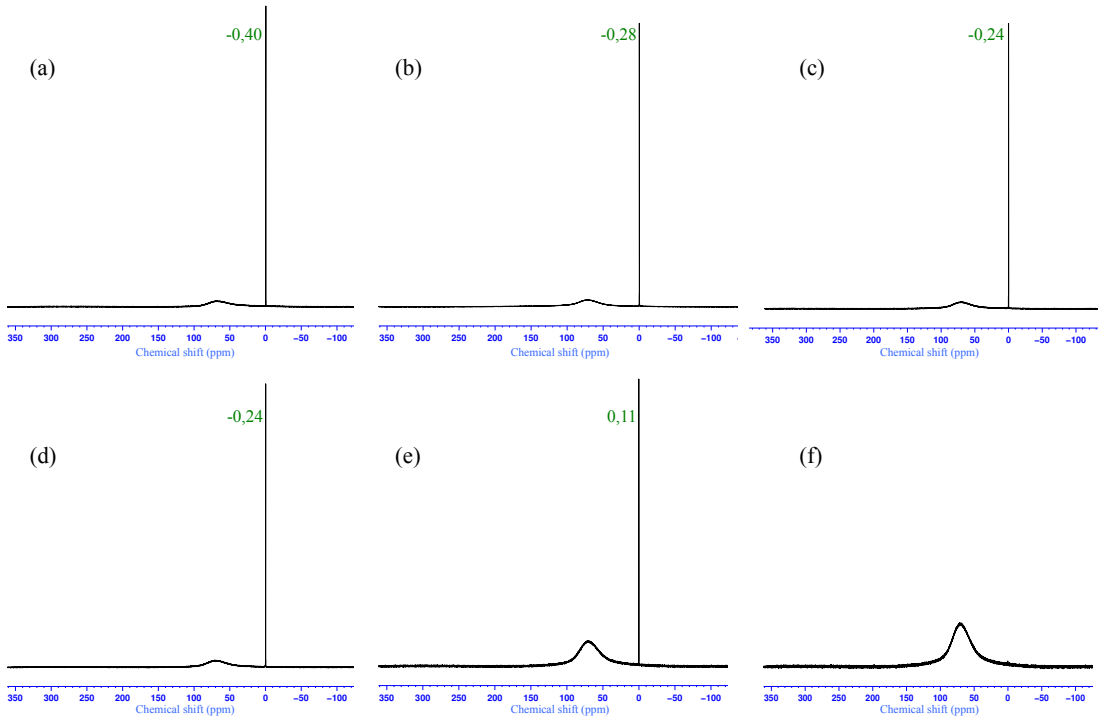

Figure S4. 27Al NMR spectra of $Al(OPr^i)_3$ in D_2O (a) and sample liquids obtained before (b) and after (c) hydrothermal treatment for the synthesis of FDU-12 Al_{15}, and the resulting waters obtained after filtering (d), washing for three times with D_2O (c) and the final rinse with EtOH (e) of the solid powder