



**Fig.S1.** Powder XRD patterns: COK-11 as-synthesised (a), leached (b), calcined at 573 K (c), calcined at 898 K (d), calcined at 898 K and stored 3 years at room temperature (e), calcined at 1273 K (f) and calcined at 898 K and hydrothermally treated for 24 h at 373 K (g). Signals originating from CTAB crystals are marked with an \*.

### Different models used to calculate the pore wall thickness of COK-11 and other mesoporous materials

In order to calculate the pore wall thickness of mesoporous materials several models have been used. While these models applied on the same sample yield slightly different values, results obtained by the same model can be used to compare different samples.

Generally the pore wall thickness ( $W_p$ ) is calculated using the relation of the lattice constant ( $LP$ ) obtained by X-ray diffraction to the pore diameter  $D_p$ .

$$W_p = LP - D_p \quad (1)$$

The pore diameter ( $D_p$ ) can be calculated using different approaches.

#### Models A and B:

From  $N_2$ -physorption different parameters can be obtained:

The BJH model will calculate a pore diameter. Pore diameters derived using BJH on the adsorption (**Model A**) or desorption (**Model B**) branch are different, both can be used.

#### Models C and D:

The BET surface area, the external surface area, the total pore volume and the mesopore volume can also be obtained using  $N_2$ -fysisorption measurements.

For cylindrical pores the pore diameter (**Model C**) can then be calculated using the following formula:

$$D_p = \frac{4V_p}{A_p} \quad (2)$$

$$\text{With } A_p = A_{BET} - A_{External} \quad (3)$$

Where  $D_p$  is the mesopore diameter and  $V_p$  the mesopore volume.  $A_{BET}$ ,  $A_{External}$ , and  $A_p$  are the BET surface area, the external surface area (calculated using t-plot method) and the mesopore surface area, respectively.

It can be shown mathematically that the same formula Eq. 2 is also valid for regular hexagonal pores (**Model D**). In this case  $D_p$  is equal to the diameter of the biggest cylinder that fits inside the hexagonal pore.

The pore wall thickness  $W_p$  is calculated using Eq. 1

**Models E and F:**

Another way to calculate the pore wall thickness takes into account the pore wall density<sup>1</sup>. In literature two different values are used for the pore wall density. A wall density ( $\rho_w$ ) of 2.2 g/cc –typical of amorphous silica- is assumed by some authors. A more generally accepted value is a pore wall density of 1.6 g/cc (**Model E**).

$$D_p = \left(\frac{8}{3^{1/2}\pi}\right)^{1/2} LP \left(\frac{\rho_w V_p}{1 + \rho_w V_p}\right)^{1/2} \quad (4)$$

A good estimation of the true pore wall density can be obtained from argon picnometry. Taking into account the mass of the sample and assuming all mesopores are filled, the wall density ( $\rho_w$ ) can be calculated through Eqs. 5-7. Using this measured density and formula (4) the pore wall thickness can be calculated (**Model F**).

$$P_1 * (V_1 - V_s) = P_2 * (V_1 + V_2 - V_s) \quad (5)$$

$$V_s = V_1 + \frac{V_2 * P_2}{P_2 - P_1} \quad (6)$$

$$\rho_w = \frac{M_s}{V_s} \quad (7)$$

Where  $V_1$  is the sample holder volume,  $V_2$  a known volume and  $V_s$  the volume taken by the sample,  $P_1$  and  $P_2$  are the initial and final argon pressure respectively.

**Model G:**

A more direct way to estimate the pore wall thickness is through HRTEM measurement. From the calibration of the microscope or from the known spacing of the mesopores the wall thickness can be measured on the TEM pictures (**Model G**). However, the result obtained this way has to be treated with caution as the apparent wall thickness changes with variation of the focus. Close to zero defocus the wall thickness can be measured.

Important to note is that none of the mentioned models provide a reliable way to calculate the true pore wall thickness. It is generally accepted that the BJH model underestimates the true pore diameter for mesoporous materials having pores below 4 nm. Consequently the obtained pore wall thicknesses are overestimated.

Also the BET surface area is known to be not completely accurate for mesoporous materials. The BET model is in principle only valid for flat surfaces, the curvature of COK-11 and other mesoporous materials like MCM-41 disturb the multilayer formation during the N<sub>2</sub>-fysisorption measurement. Since the BET model is based on this multilayer formation, the BET method is known to be not completely accurate.

The mesopore volume can be easily obtained from N<sub>2</sub>-fysisorption measurements. Care should be taken to exclude the measured pore volume originating from interparticle voids. The t-plot method can be used to obtain the true mesopore volume. When the mesopore is determined extra care should be taken for mesopore materials containing micropores. Depending on the method used to measure the pore wall density, the micropore volume should be included or excluded when Eq. 4 is applied to calculate the pore wall thickness.

When using picnometry to calculate the density of a material, the diameter of the probe should be small compared to the pore that is to be probed. The probe molecule also should not be chemisorped on the probed material. Argon picnometry at room temperature should give a reliable density of the pore walls.

Caution is advised when TEM micrographs are used to measure a pore wall thickness. Variation in focusing dept shows differently appearing wall thicknesses. Therefore only simulation of a defocusing series and comparison with measurements at different focus depths can give fully accurate results. The smallest error is obtained at zero defocus, where usually the obtained contrast is very low.

We have used all of these strategies to estimate the wall thickness of COK-11 (Table S1). A wall thickness of 0.8 nm is obtained according to HRTEM for COK-11 (**Model G**). **Models A-D** lead to thicker walls, while wall thickness obtained from the **Model E** and **Model F** are similar to **Model G**.

**Table S1: Pore wall thickness of COK-11 obtained using the different models is listed. Values in bold are measured values, values in *italic* are calculated using the above formulae.**

Model	A	B	C (and D*)	E	F	G
Method	BJH <sub>ADS</sub>	BJH <sub>DES</sub>	$D_p = V_p/A_p$	Wall density (from literature)	Wall density (from argon sorption)	HRTEM
Mesopore surface area ( $A_p$ ) (BET surface area- external surface area) (m <sup>2</sup> /g)			<b>1049</b>	<i>947</i> (994*)	<i>933</i> (980*)	
mesopore volume ( $V_p$ ) (Corrected using t-plot method) (CC/g)			<b>0.912</b>	<b>0.912</b>	<b>0.912</b>	
pore wall density ( $\rho_w$ ) (g/CC)	<i>0.44</i> (0.34*)	<i>0.66</i> (0.49*)	<i>1.03</i> (1.25*)	<b>1.6</b>	<b>1.72**</b>	
XRD lattice constant (LT) (nm)	<b>4.76</b>	<b>4.76</b>	<b>4.76</b>	<b>4.76</b>	<b>4.76</b>	<b>4.76</b>
Mesopore diameter ( $D_p$ ) (nm)	<b>2.67</b>	<b>3.06</b>	<i>3.4</i>	<i>3.86 nm</i>	<i>3.91</i>	
Wall thickness ( $\rho_w$ ) (nm)	<i>2.09</i>	<i>1.70</i>	<i>1.29</i> (1.29*)	<i>0.91</i> (1.09*)	<i>0.85</i> (1.04*)	<b>0.8</b>

\* Values calculated using a hexagonal pore model; \*\*According to argon picnometry.

The most popular model for the estimating of a pore wall thicknesses is model E assuming a wall density of 1.6 g/cc (Table S2 and S3). Some articles do not specify whether the total pore volume or the actual mesopore volume is reported. The pore diameter calculated using Eq. 4 will be overestimate and the wall thickness underestimated. In the modeling of COK-11 (Table S1) the actual mesopore volume was used. The walls of COK-11 are indeed unusually thin in view of its outstanding stability.

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Table S2. Literature data on approaches to improve thermal stability of hexagonally ordered mesoporous materials

Ref.	sample type	Modification of synthesis recipe/additive	Q <sup>4</sup> /Q <sup>3</sup> ratio in as synthesised material	pore wall thickness <sup>a</sup> (nm)	duration (h)	Calcination at 1273 K	
						XRD	Stability
							Loss of BET Surface Area (%)
<i>Maintaining pH constant</i>							
2	MCM-41	small amines	>1/1	1.07	<i>na</i>	Excellent stability until 1373K <sup>e</sup>	
<i>Alternative silica source</i>							
3	Si-MCM-41	TEOS	<i>na</i>	<i>na</i>	6	Almost total amorphisation	
3	Si-MCM-41	Fumed silica	<i>na</i>	1.31 <sup>b</sup>	6	Structural damage	
4	MCM-41	Fumed silica	1.4/1	0.98	4	Almost total amorphisation	90
5	MCM-41	Fumed silica	1.5/1	1.0 <sup>c</sup>	6	Strong structural damage	97
6	Si-MCM-41	Silica gel	<i>na</i>	<i>na</i>	12 <sup>f</sup>		65
7	MCM-41	Polymeric ethyl silicate	<i>na</i>	0.9 <sup>d</sup>	6 <sup>g</sup>	Strong structural damage	
8	MCM-41	71% Cab-O-Sil 29% soluble silicate	<i>na</i>	1.0	3 <sup>g</sup>		22
<i>Recrystallisation</i>							
4	MCM-41		3.4/1	1.2	4	Structural damage	
5	MCM-41		3.5-4.5/1	1.14 <sup>c</sup>	6	Limited structural damage	70
<i>Reduction of CTAB to Silica molar ratio</i>							
9	MCM-41	low CTAB to silica ratio	<i>na</i>	1.02 <sup>d</sup>	1	Structural damage and strong unit cell contraction	58
<i>Prolonged synthesis time</i>							
4	MCM-41		4.5/1	1.57	4	Structural damage	
4	MCM-41		4.5/1	1.57	4	Structural damage	
5	MCM-41	recrystallisation and long synthesis time	3.5-4.5/1	1.52 <sup>c</sup>	6	Limited structural damage	35
<i>Post synthesis hydrothermal restructuring</i>							
3	Si-MCM-41		<i>na</i>	1.36 <sup>b</sup>	6	Structural damage	

*na*, not available; <sup>a</sup> pore wall thickness of calcined material calculated using a geometrical model E assuming a pore wall density of 1.6 g/cm<sup>3</sup>; <sup>b</sup> pore wall thickness from article recalculated assuming a wall density of 1.6 g/cm<sup>3</sup> instead of 2.2g/cm<sup>3</sup>; <sup>c</sup> pore wall thickness calculated using the total pore volume at P/P<sup>o</sup>=0.99; <sup>d</sup> pore wall thickness calculated using the total pore volume; <sup>e</sup> no figure in article to prove the stability; <sup>f</sup> calcination at 1073 K; <sup>g</sup> calcination at 1123 K

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Table S3

Literature data on approaches to improve hydrothermal stability of hexagonally ordered mesoporous materials

Ref.	Sample type	Modification of synthesis recipe/additive	Q <sup>4</sup> /Q <sup>3</sup> ratio in as synthesised material	pore wall thickness <sup>a</sup> (nm)	Concentration. of mesoporous material (g/L)	duration (h)	Treatment in boiling water	
							XRD	Stability Loss of BET Surface Area (%)
<i>Standard Synthesis</i>								
10	Si-MCM-41		na	0.74 <sup>b</sup>		24		>80
10	Si-MCM-41		na	0.74 <sup>b</sup>		168	Total amorphisation	>90
<i>Salt addition</i>								
2	MCM-41	Na <sub>2</sub> O	<1/1	1.05	50	24 <sup>e</sup>	Total amorphisation	65
11	MCM-41	pH adjustment/acetic acid & NaCl	na	na	1	12	Limited structural damage	
11	MCM-41	pH adjustment/acetic acid & Na <sub>4</sub> EDTA	>>1/1	na	1	12	Limited structural damage	
<i>Maintaining constant Ph</i>								
2	MCM-41	small amines	>1/1	1.07	50	24 <sup>e</sup>	Limited structural damage	24
2	MCM-41	small amines & aluminium	na	1.24	50	72 <sup>e</sup>	Limited structural damage	
11	MCM-41	acetic acid & Na <sub>2</sub> O	~1/1	na	1	12	Total amorphisation	
11	MCM-41	acetic acid & Na <sub>2</sub> O	~1/1	na	1	1	30% reduction of intensity	
12	Si-MCM-41	NH <sub>4</sub> OH	~1/1	na	na	12 <sup>f</sup>	Strong structural damage	35
13	MCM-41	sulphuric acid & no alkali cations	~1/1	0.95 <sup>b</sup>	10	96	Strong structural damage	35
13	MCM-41	sulphuric acid & TPA	>>1/1	0.93 <sup>b</sup>	10	96	Limited structural damage	0
<i>Alternative silica source</i>								
3	Si-MCM-41	Fumed silica	na	1.31 <sup>d</sup>	na	6	Structural damage	
4	MCM-41	Fumed silica	1.4/1	0.98	1	24	Almost total amorphisation	80
14	MCM-41	Fumed silica	na	na	1	16	Total amorphisation	65
15	MCM-41	Fumed silica	1.5/1	1.00 <sup>c</sup>	1	24		75
16	MAS-5	Aluminosilicate zeolite precursors	na	0.78 <sup>b</sup>	na	300	Structural damage	
17	Beta/MCM-41	Beta aluminosilicate nanocluster	>>1	1.4 <sup>g</sup>	na	260/336	Limited structural damage	2
6	Si-MCM-41	pH adjustment Silica gel	na	na	50	2		40

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Table S3 (continued)

Ref.	Sample type	Modification of synthesis recipe/additive	Q <sup>4</sup> /Q <sup>3</sup> ratio in as synthesised material	pore wall thickness <sup>c</sup> (nm)	Concentration of mesoporous material (g/L)	duration (h)	Treatment in boiling water	Loss of BET Surface Area (%)
							Stability	
							XRD	
<i>Alternative silica source (continued)</i>								
18	ZSM-5/MCM-41	ZSM-5 and fumed silica/ pH adjustment	na	na	10	120	Limited structural damage	
19	Beta/MCM-41	Beta zeolite	na	na	na	24	Limited structural damage	
<i>Recrystallisation</i>								
4	MCM-41	Recrystallisation	3.4/1	1.2	1	24	Structural damage	Modest decrease
15	MCM-41	Recrystallisation	3.5-4.5/1	1.14 <sup>c</sup>	1	24		17
<i>Prolonged synthesis time</i>								
4	MCM-41		4.5/1	1.57	1	24	Structural damage	Modest decrease
<i>Addition of hetero elements</i>								
10	Si-Al-MCM-41	Aluminium	na	0.89 <sup>b</sup>		168	Structural damage	25
14	CAH5	Post synthesis aluminium grafting	na	1.29 <sup>b</sup>	1	150	Structural damage	
14	CAP10	Post synthesis aluminium grafting	na	1.06 <sup>b</sup>	1	150	Structural damage	
<i>Post synthesis hydrothermal restructuring</i>								
3	Si-MCM-41		na	1.36 <sup>d</sup>	na	6	Limited structural damage	

na not available; <sup>a</sup> pore wall thickness of the calcined materials calculated using a geometrical model E assuming a pore wall density of 1.6 gcm<sup>-3</sup>; <sup>b</sup> pore wall thickness calculated using the total pore volume; <sup>c</sup> pore wall thickness calculated using the total pore volume at P/P<sup>o</sup>=0.99; <sup>d</sup> pore wall thickness from article recalculated assuming a wall density of 1.6 g/cm<sup>3</sup> in stead of 2.2g/cm<sup>3</sup>; <sup>e</sup> hydrothermal stability test at 353 K; <sup>f</sup> stability in water at room temperature; <sup>g</sup> estimation of xrd lattice constant and mesopore volume from figure.

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**References**

- 1 M. Kruk, M. Jaroniec, A. Sayari, *J. Phys. Chem. B*, 1997, **101**, 583.
- 2 W. Lin, Q. Cai, W. Pang, Y. Yue, B. Zou, *Microporous and Mesoporous mater.*, 1999, **33**, 187.
- 3 L. Chen, T. Horiuchi, T. Mori, K. Maeda, *J. Phys. Chem. B*, 1999, **103**, 1216.
- 4 R. Mokaya, *J. Phys. Chem. B*, 1999, **103**, 10204.
- 5 R. Mokaya, *J. Mater. Chem.*, 2002, **12**, 3027.
- 6 X.Liu, H. Sun, Y. Yang, *J. Colloid Interface. Sci.*, 2008, **319**, 377.
- 7 T.R. Gaydhankar, V. Samuel, R.K. Jha, R. Kumar, P.N. Joshi, *Mater. Res. Bull.*, 2007, **42**, 1473.
- 8 P.B. Amama, S. Lim, D. Ciuparu, L. Pfefferle, G.L. Haller, *Microporous and mesoporous mater.*, 2005, **81**, 191.
- 9 J. Yu, J.-L. Shi, L.-Z. Wang, M.-L. Ruan, D.-S. Yan, *Materials Letters*, 2001, **48**, 112.
- 10 S.-C. Shen, S. Kawi, *J. phys. Chem. B*, 1999, **103**, 8870.
- 11 R. Ryoo, S. Jun, *J. Phys. Chem. B*, 1997, **101**, 317.
- 12 X.S. Zhao, F. Audsley, G.Q. Lu, *J. Phys. Chem. B*, 1998, **102**, 4143.
- 13 D. Das, C.-M. Tsai, S. Cheng, *Chem. Commun.*, 1999, 473.
- 14 R. Mokaya, *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 2930.
- 15 R. Mokaya, *Chem. Commun.*, 2001, 933.
- 16 Z. Zhang, Y. Han, F.-S. Xiao, S. Qiu, L. Zhu, R. Wang, Y. Yu, Z. Zhang, B. Zou, Y. Wang, H. Sun, D. Zhao, Y. Wei, *J. Am. Chem. Soc.*, 2001, **123**, 5014.
- 17 H. Xu, J. Guan, S. Wu, Q. Kan, *J. Colloid. Interface Sci.*, 2009, **329**, 346.
- 18 S. Habib, F. Launay, S. Laforge, J.-D. Comparot, A.-C. Faust, Y. Millot, T. Onfroy, V. Montouillout, P. Magnoux, J.-L. Paillaud, A. Gédéon, *Appl. Catal. A*, 2008, **344**, 61.
- 19 H. Zhang, Y. Li, *powder Technology*, 2008, **183**, 73.