# **Supporting information**

## **Experimental section:**

- **Synthesis of mesoporous silica materials:**
- SBA-1

Surfactant preparation: Hexadecyltrimethylammonium bromide (HTEABr) was synthesized as reported by Kim *et al.*[1]. 6.3 g of 1-bromohexadecane was dissolved in 50 mL of absolute ethanol. 2.8 mL of triethylamine was combined with the ethanol solution at room temperature. The resultant mixture was heated while being stirred for 20 h under reflux conditions. The solvent was evaporated until a brown viscous liquid was obtained, using a rotary evaporator at 80 °C. The brown liquid turned to a solid upon cooling to room temperature. A minimum amount of dichloromethane was added to dissolve the solid. To this solution was added ethyl acetate slowly while the mixture stirred until the precipitation of the HTEABr reached a maximum. The mixture was cooled in a refrigerator for 20 h in order to increase precipitation. The resultant precipitate was filtered, and dried under vacuum at room temperature.

Synthesis of SBA-1 silica: 1.2 g of HTEABr was mixed with 42.8 mL of water and 18.2 mL of 6 M hydrochloric acid. To this solution 5.2 g of tetraethyl orthosilicate (TEOS) was added at room temperature and stirred for 1h. The mixture was then placed in an oven at 100 °C for 20 h. The solid product was recovered by filtration on a Buchner funnel and dried in air at room temperature. Then, an acetone soxhlet extraction procedure was used to surface-clean the powder for 24 h. Finally, SBA-1 was calcined at 450 °C in air for 4 h.

SBA-3

SBA-3 was prepared as reported by Anunziata *et al.* [2]. 2 g of cetyltrimethylammonium bromide (CTAB) and 40 mL of HCl (37%) were dissolved in 100 mL of water. 10 mL of TEOS were added dropping to the acidic solution of CTAB with vigorous stirring at 30 °C. After 2 h, the white precipitated was aged for 12 h. The sample was filtered and dried for 12 h at 80 °C. SBA-3 was immersed in ethanol reflux for 8 h. Then, the sample was filtered and washed with distilled water. After drying it, SBA-3 was calcined at 550 °C in air for 8 h (heating rate: 2 °C/min).

SBA-15

SBA-15 silica was synthesized as reported by Zhao *et al.* [3] using Pluronic P123 triblock copolymer ( $PEO_{20}PPO_{70}PEO_{20}$ ). A 10 g sample of Pluronic P123 was dissolved in 100 mL of water and 40 mL of 12 M HCl solution. Then, 22.5 mL of TEOS was added, and the resulting mixture was stirred for 30 min and then kept at 40 °C for 20 h without stirring. Then, the mixture is dried in an oven at 100 °C for 48 h. The solid product was filtered, washed with water or ethanol. To completely remove the surfactant, the as-synthesized product was calcined in air at 550 °C for 5 h.

## MCM-41

MCM-41 material was synthesized as reported by Kumar *et al.* [4]. 2.4 g of cetyltrimethylammonium bromide (CTAB) was dissolved in 120 g of deionised water and stirring until the solution was homogeneous and clear. After adding 8 mL of ammonium

hydroxide, the mixture was stirred for 5 min after which 10 mL of TEOS were added. The reaction was stirred overnight after which the solution was filtered and washed consecutively with deionised water and ethanol. Calcination was performed at 550  $^{\circ}$ C for 5 h.

## MCM-48

Cubic MCM-48 was prepared by following Xu *et al.* [5] procedure. 10 mL of TEOS was added to an aqueous solution containing 88 g of CTAB solution (10 wt %) and 10 mL of 2 M NaOH. After being stirred for 30 min, the resulting homogeneous mixture was crystallized under static hydrothermal conditions at 100 °C in a Teflon bottle for 72 h. The product was filtered out, washed with deionized water and air-dried overnight. As-synthesized samples were calcined at 550 °C first in flowing nitrogen for 2 h and then in flowing oxygen for 5 h to remove CTAB.

## **Results and discussion:**

Stability of SBA-3 and SBA-15 silicas in different acid media:



Figure S1. N<sub>2</sub> adsorption-isotherms for SBA-3 before and after being mixed with the different acids



Figure S2. N<sub>2</sub> adsorption-isotherms for SBA-15 before and after being mixed with the different acids

Samples	S <sub>BET</sub> (m²/g)	V <sub>p</sub> (cm³/g)	D (nm)	d₀ (nm)	a (nm)	t* (nm)	DP (%)
SBA1-0h	950	0.229	2.1	3.7	7.4	8.6	93
SBA1-24h	870	0.223	2.0	3.7	7.4	8.6	93
SBA3-0h	1390	0,691	2.2	3.1	3.6	1.4	91
SBA3-24h	600	0,091	2.4	3.1	3.6	1.2	79
SBA15-0h	780	1,070	6.9	10.1	11.6	4.9	92
SBA15-24h	610	0,960	7.0	9.8	11.3	4.3	92
MCM41-0h	1460	1,060	2.9	3.8	4.4	1.5	94
MCM41-24h	880	0,681	2.9	3.8	4.4	1.5	89
MCM48-0h	690	1.836	2.5	3.2	8.1	1.4	93
MCM48-24h	340	0.474	2.1	3.3	7.7	1.4	89

Stability of several mesoporous silicas under phosphoric acid (5M) medium:

\*Wall thickness calculation details:

Samples	Structure	Wall thickness (Å)
SBA-3, SBA-15, MCM-41	Hexagonal P6mm	$t = a_0 - D_p$
MCM-48	Cubic Ia3d	$t = \frac{a_0}{3.0919} - \frac{D_p}{2}$
SBA-1	Cubic Pm3n	$t = \frac{a_0}{0.764} - \frac{D_p}{2}$



Figure S3. Pore size distribution obtained by BJH method. (Values below or equal to 20 Å are difficult to collect accurately, e.g. SBA-1)

### SBA-1 data:



Figure S4. Nitrogen adsorption-desorption isotherms of SBA-1 before and after acid attack



Figure S5. XRS spectra of SBA-1 (black dot) with 3D-cubic bicontinuous cage-type structure (Pm3n space group) displays the following peaks:  $q_0$ ,  $\sqrt{(5/4)}q_0$  and  $\sqrt{(6/4)}q_0$  for both unexposed sample and after acid exposure (red dot). A slight shift towards high angle is observed under acid exposure.



Figure S6. <sup>29</sup>Si NMR spectra for SBA-1 before and after phosphoric acid attack

SBA-3 data:



Figure S7. Nitrogen adsorption-desorption for SBA-3 before and after acid



Figure S8. SAXS spectra of SBA-3 (black dot) with 2D-hexagonal structure (P6mm space group) displaying the following Bragg peaks:  $q_0$ ,  $\sqrt{3}q_0$ ,  $\sqrt{4}q_0$ ,  $\sqrt{7}q_0$ . SBA3 \_24h (red square) after acid exposure exhibits only the two first and broader  $q_0$  and  $\sqrt{3} q_0$  peaks



Figure S9. <sup>29</sup>Si NMR spectra for SBA-3 before and after phosphoric acid attack

### SBA-15 data:



Figure S10. Nitrogen adsorption-desorption for SBA-15



Figure S11. SAXS spectra of SBA-15 (black dot) with 2D-hexagonal structure (P6mm space group) displaying five distinguishable Bragg peaks:  $q_0$ ,  $\sqrt{3}q_0$ ,  $\sqrt{4}q_0$ ,  $\sqrt{7}q_0$  and  $\sqrt{q_0}$ . SBA15\_24h (red square) seems unaffected by exhibiting the same serie and quit same intensity level magnitude order



Figure S12. <sup>29</sup>Si NMR spectra for SBA-15 before and after phosphoric acid attack

### MCM-41 data:



Figure S13. Nitrogen adsorption-desorption for MCM-41



Figure S14. SAXS spectra of MCM-41 (black dot) with 2D-hexagonal structure (P6mm space group) displays typical indexation:  $q_0$ ,  $\sqrt{3}q_0$ ,  $\sqrt{4}q_0$ ,  $\sqrt{7}q_0$  and  $3q_0$ . MCM41\_24h (red square) exhibits the same pattern as initial MCM-41



Figure S15. <sup>29</sup>Si NMR spectra for MCM-41 before and after phosphoric acid attack

### MCM-48 data:



Figure S16. Nitrogen adsorption-desorption for MCM-48



Figure S17. SAXS spectra of MCM-48 (black dot) with 3D-cubic bicontinuous structure (Ia3d space group) displays the following peaks:  $q_0$ ,  $\sqrt{(4/3)}q_0$ ,  $\sqrt{(7/3)}q_0$ ,  $\sqrt{(8/3)}q_0$ ,  $\sqrt{(10/3)}q_0$  and  $\sqrt{(12/3)}q_0$ . MCM48\_24h (red square) after acid exposure exhibits only three peaks  $q_0 \sqrt{(4/3)}q_0$  and  $\sqrt{(12/3)}q_0$ 



Figure S18. <sup>29</sup>Si NMR for MCM-48 before and after phosphoric acid attack

- [1] Kim M.J. et al., *Synthesis and pore size control of cubic mesoporous silica sba-1*. Chemistry of Materials, 1999. **11**(2): p. 487-491.
- [2] Anunziata O.A. et al., Synthesis and characterization of sba-3, sba-15, and sba-1 nanostructured catalytic materials. Journal of Colloid and Interface Science, 2007. 315(1): p. 184-190.
- [3] Zhao D.Y. et al., *Triblock copolymer syntheses of mesoporous silica with periodic 50* to 300 angstrom pores. Science, 1998. **279**(5350): p. 548-552.
- [4] Kumar D. et al., *Mcm-41*, *mcm-48* and related mesoporous adsorbents: Their synthesis and characterisation. Colloids and Surfaces a-Physicochemical and Engineering Aspects, 2001. **187**: p. 109-116.
- [5] Xu J. et al., *A reliable synthesis of cubic mesoporous mcm-48 molecular sieve*. Chemistry of Materials, 1998. **10**(11): p. 3690-3698.