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Quantification of silanol sites for the most common mesoporous ordered silicas and organosilicas: total versus accessible silanols.

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Supplementary Information:

Table S1: The number of Si atoms was estimated from a static Si-O-Si bond length model. The percentage of surface silicon atoms was calculated from this number, taking into account that per chain for SBA-15, MCM-41, MCM-41 (SD) and Ethene PMO [1] one surface silicon atom can be found. Wheareas for SBA-16 and MCM-48 two surface silicon atoms are present, due to the definition of the wall thickness for these pore structures.

	Wall thickness (nm)	# Si atoms in the wall (based on static Si-O-Si bond lengths)	% surface silicon atoms (to total silicons in the material)
SBA-15	4.2	21	5
SBA-16	6.4	32	6*
MCM-41	1.1	5.5	22
MCM-48	1.0	5	50*
MCM-41 (SD)	1.2	6	20
Ethene PMO	3.1	15.5	7

** For these two cubic structures, the silanols are available at both sides of the wall, whereas all other materials have the P6/m honeycomb structure, and these walls are only accessible from one side. This has been taken into account in the calculation of the "% surface silicon atoms".*

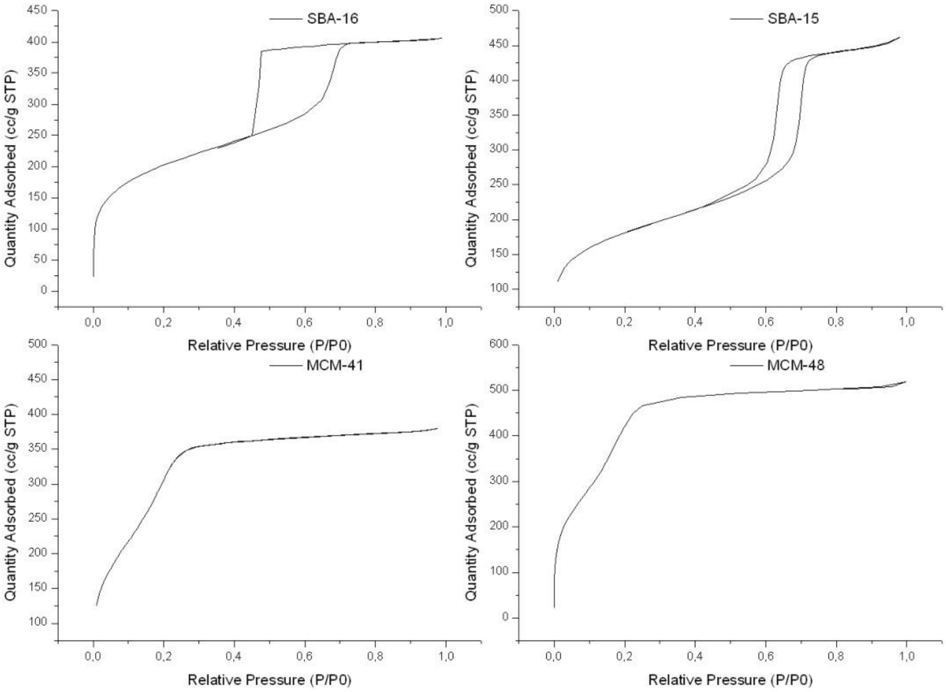

Figure S1: The N_2 adsorption/desorption isotherms of SBA-16, SBA-15, MCM-41 and MCM-48.

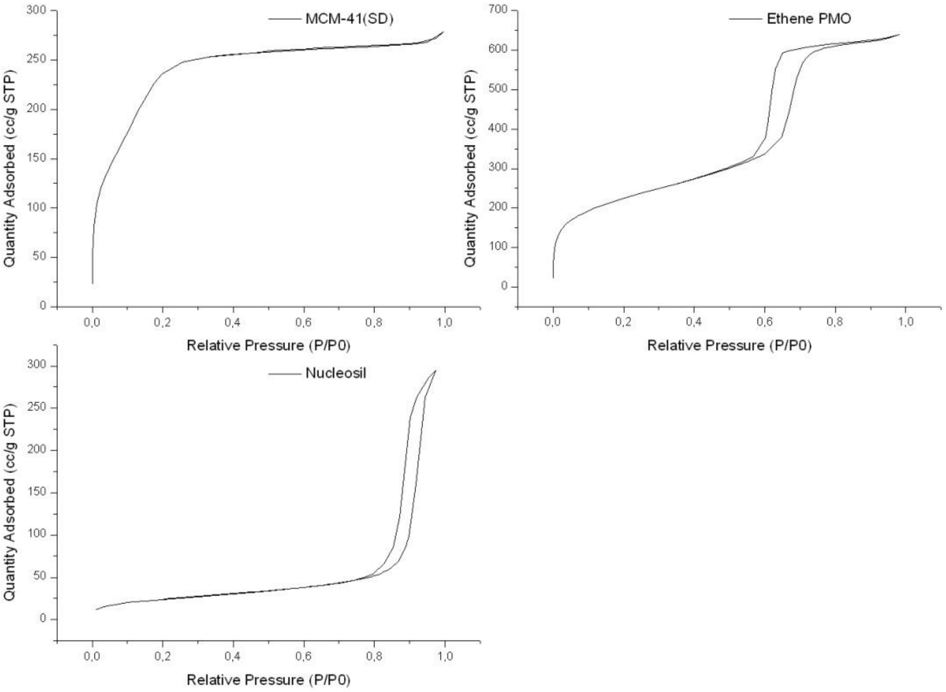

Figure S2: The N2-adsorption/desorption isotherms of MCM-41 SD, Ethene PMO and Nucleosil.

SYNTHESIS OF MCM-41

MCM-41 (Mobil Composition of Matter No 41. – space group P6mm hexagonal): Ordered mesoporous silica with tetraethyl orthosilicate (TEOS) as a silica source.

The first step in this synthesis is the preparation of a solution in which 1.64 g CTAB (surfactant), 8.97 mL NH_4OH, 50.77 mL EtOH and 38.9 mL H_2O are mixed. When a homogeneous solution is obtained (stirring for 1h at 25 °C), 3.35 mL TEOS (precursor) is added and the solution is stirred for another hour under reflux conditions. Finally the solution is filtrated and the resulting powder is calcined under air at a heating rate of 1.5°C per minute from room temperature to 550°C and kept at this temperature for 6h.

SYNTHESIS OF MCM-41-SD

MCM-41 (Mobil Composition of Matter No 41. – space group P6mm hexagonal): Ordered mesoporous silica with tetraethyl orthosilicate (TEOS) as a silica source.

The first step in this synthesis is the preparation of a solution in which 0.3996 g CTAB (surfactant), 112.25 mL H_2O, 4.13 mL BuOH and 1.89 mL HCl are present. After obtaining a homogeneous solution (stir vigorously at room temperature until all CTAB is dissolved), 1 mL of TEOS (precursor) is added and the solution is left stirring for 30min at room temperature.

The solution is fed to a Buchi B290 spray dryer with a two-fluid nebulizer connected to pressurized air. The heater inlet temperature was held constant at 220°C and the outlet temperature stayed constant at 133°C. The aspirator ran at a maximum air velocity of 40 m^3/h. The nozzle gas flow was held constant at 8 L/min and the feeding speed was 2.9 mL/min. After 40 minutes a white/yellow powder is collected from the cyclone and calcined under air at a heating rate of 1.5°C per minute from room temperature to 550°C and kept at this temperature for 6h.

SYNTHESIS OF MCM-48

MCM-48 (Mobil Composition of Matter No 48. – space group Ia3d cubical): Ordered mesoporous silica with fumed silica as a silica-source and Gemini 16-12-16 as structure directing agent.

A solution of 0.3346 g NaOH and 2.89 g Gemini 16-12-16 surfactant (synthesized according to a previous reported procedure [1]) in 62 mL water is stirred in an autoclave. When all is dissolved 2 g fumed silica is added and the mixture is stirred for 0.5h. Subsequently the autoclave is placed in an oven at 115 °C for 3 days. Hereafter the white precipitate is filtrated and washed with 30 mL water, placed back in the autoclave and put back in the oven at 115 °C for 24 hours. This is repeated one more time and then a white powder is filtrated and dried at ambient conditions for 24h before it is calcined under air at a heating rate of 1.5°C per minute from room temperature to 550°C and kept at this temperature for 6h.

SYNTHESIS OF SBA-15

SBA-15 (Santa Barbara No 15. – space group P6/mm hexagonal): Ordered mesoporous silica with tetraethylorthosilicate (TEOS) as a silica source and pluronic P123 as structure directing agent.

For this 4 g of pluronic P123 is dissolved into 120 mL HCl (2M) and 30 mL water. The solution is stirred vigorously and refluxed at 45 °C until all surfactant is dissolved after which 9.1 mL TEOS is added. The solution is stirred at 45°C for 5h and then the solution is aged for 18h at 90°C.The solution is filtrated and washed 3 times with 10 mL water. Finally the white powder is calcined under air at a heating rate of 1.5°C per minute from room temperature to 550°C and kept at this temperature for 6h.

SYNTHESIS OF SBA-16

SBA-16 (Santa Barbara No 16. – space group Im3m cubic): Ordered mesoporous silica with tetraethylorthosilicate (TEOS) as a silica source and pluronic F127 as structure directing agent. BuOH functions as a co-solvent.

For this 4g of F127 is dissolved in 120 mL HCl (2M), 30 mL H_2O and 15 ml BuOH. The solution is stirred vigorously and refluxed at 45 °C until all surfactant is dissolved after which 12 mL TEOS is added. The solution is stirred at 45°C for 20h and then the solution is aged for 24h at 90°C.The solution is filtrated and washed 3 times with 10 mL water. Finally the white powder is calcined under air at a heating rate of 1.5°C per minute from room temperature to 550°C and kept at this temperature for 6h.

SYNTHESIS OF ETHENE BRIDGED PMO

The PMO material is synthesized according to a recipe reported by our research group [2]. A total amount of 1 g P123 is weighed and diluted in 47.80 ml destilled water, 3.42 concentrated HCl and 2.45 ml BuOH. The mixture is vigorously stirred at room temperature during 1.5 hours. Next, the home made pure trans 1,2-bis(triethoxysilyl)ethene[2] is added and the temperature is raised to 35°C for 4 hours. Afterwards, the mixture is aged at a temperature of 90°C. After 16 hours, the mixture is allowed to cool down and subsequently a filtration is performed where the collected solids are washed three times with destilled water and acetone. Finally, the surfactant is removed by using a Soxhlet extraction with acetone during 5 hours. The PMO materials is then vacuum dried at 120°C overnight.

[1] Huo, Q.; Margolese, D.; Stucky, G.; Chem. Mater.,**1996**, *8*, 1147.

[2] Vercaemst, C.; Ide, M.; Allaert, B.;Ledoux, N.; Verpoort, F.; Van Der Voort, P.; Chem. Commun., **2007**, 2261.