Supplementary information

Experimental details

Synthesis and functionalization

MCM-41 MSN was prepared by using cetyltrimethylammonium bromide (CTAB) as structure directing agent (SDA) according to a slightly modified literature procedure.\textsuperscript{1,2} CTAB (1 g, 2.74 mmol) was dissolved in 480 ml of deionized water under stirring and heating. At the stable temperature of 80°C, a NaOH solution (2.0 M, 3.5 ml) was slowly added to the mixture. Tetraethyl orthosilicate (TEOS) (5 ml, 22.4 mmol) was then added drop-wise over 10 min under vigorous stirring. After 2 hours of stirring at 80°C the milky reaction mixture was cooled to room temperature (RT) and the white precipitate was filtered off and washed with abundant water and methanol. The SDA was removed from the as-synthesized material by calcination at 550°C, heating to the desired temperature under N\textsubscript{2} flow and switching to O\textsubscript{2} for 7 hours isotherm.

Carboxy-MSN sample was prepared by post-synthesis grafting by a modified literature procedure.\textsuperscript{3,4} 1 g of MSNs were dried at 100°C overnight to remove adsorbed water and suspended in 100 ml of methanol with gentle mixing; then 2 ml of carboxyethylsilanetriol sodium salt were added to the particles suspension and the mixture was stirred at room temperature for 4 h. The obtained carboxy-MSN sample was filtered off, washed with methanol and successively dried at 80°C overnight.

Amino-MSN was prepared by post-synthesis grafting with a procedure modified from the literature.\textsuperscript{5} 1 g of MSN (overnight dried at 100°C) were suspended in 30 ml of anhydrous toluene. The particle suspension was heated at 130 °C under stirring. Next, 0.6 ml of 3-aminopropyl triethoxysilane (APTS) were added drop-wise and the mixture was allowed to reflux for 17 h. The modified amino-MSN was filtered off and washed with toluene, ethanol, deionized water and then methanol. Subsequently the sample was dried at 110°C for 3 h to favor the curing\textsuperscript{6} and at 80°C overnight.
**Characterization**

Water adsorption microcalorimetric measurements on sample Sipernat 320 were carried out on a Tian-Calvet microcalorimeter (Setaram, Lyon, France) equipped with a gas-volumetric apparatus. The measurements were carried out by dosing small amounts of water at 30 °C on the sample previously outgassed at 30 °C.

**Additional Figures**

![Figure S1](image.png)

**Figure S1** Powder XRD patterns of MSNs (full curve), amino-MSNs (dotted) and carboxy-MSNs (dashed).
**Figure S2** Nitrogen gas-volumetric adsorption and desorption isotherms of (a) MSN, (b) amino-MSN and (c) carboxy-MSN
Figure S3 Experimental data about reference sample Sipernat 320: (a) TGA profile; (b) Infrared spectrum in the high frequency range of RT dehydrated sample; (c) nitrogen gas-volumetric adsorption and desorption isotherms and (d) microcalorimetric data (heat of adsorption vs coverage) relative to water vapour adsorbed at 30 °C on the sample outgassed at 30 °C.
Figure S4 Comparison of primary and secondary water desorption microgravimetric curves on (from top to bottom): MSN, amino- and carboxy-MSN samples at three temperatures. Symbols for primary curves are in the figure, while the secondary corresponding ones are reported as cross symbols.
**Figure S5** Water desorption microgravimetric isotherms measured on samples amino- and carboxy-MSN (top and bottom, respectively). The experimental data were fitted with cubic spline functions. Horizontal lines represent the constant water coverage employed for the estimation of $q_{st}$. 
Figure S6 Water desorption microgravimetric isotherms measured on Sipernat 320 (top). The experimental data were fitted with cubic spline functions. Horizontal lines represent the constant water coverage employed for the estimation of $q_{st}$, which are reported in the bottom panel as a function of the adsorbed quantity.
Figure S7 Comparison of the isotherms measured on the three samples at 35°C, expressed as μmol/m²
Figure S8 Additional water desorption microgravimetric isotherms measured on samples MSN, amino- and carboxy-MSN (from top and bottom, respectively). Horizontal lines represent the constant water coverage employed for the estimation of \( q_{st} \).
References


