

Supporting Information

On the Adsorption of Toluene on Amorphous Mesoporous Silicas with Tunable Sorption Characteristics

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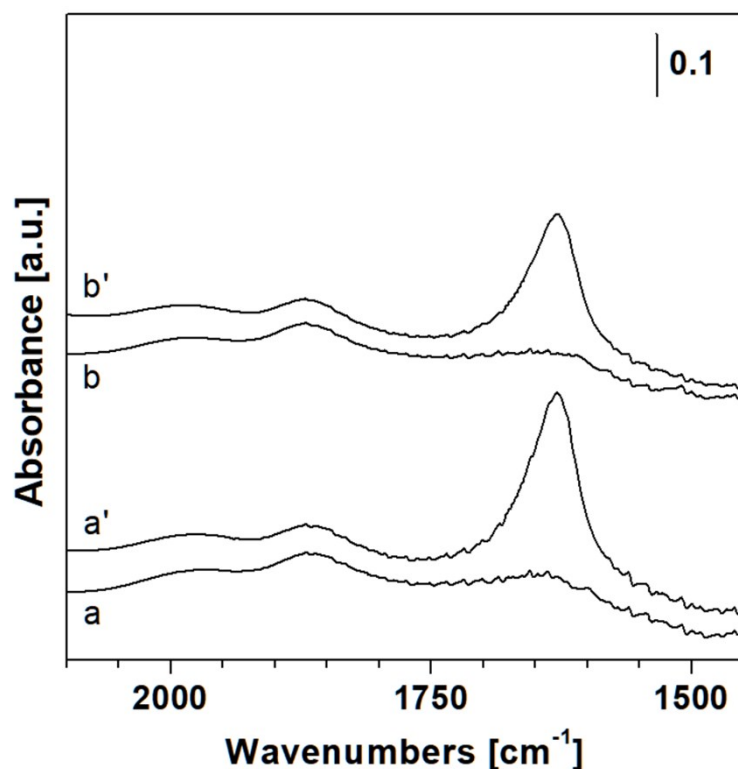


Figure S1: IR spectra of AMS-HAS (a, a') and AMS-LSA (b, b') before and after outgassing treatment at rt for 30 minutes.

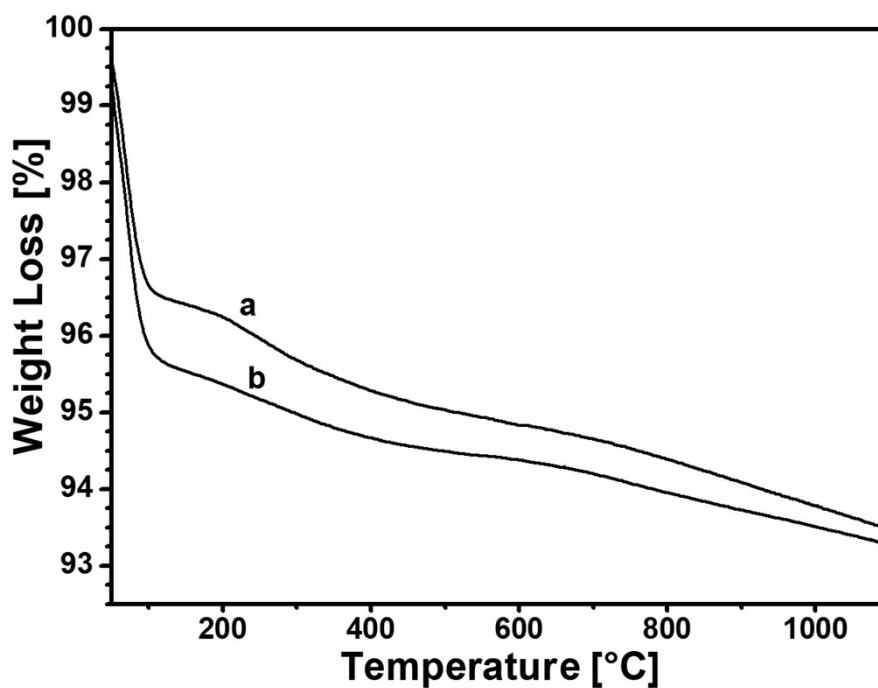


Figure S2: TGA analysis were performed at heating rate of 5 °C/min under oxygen flow (100 mL/min) of AMS-HSA (curve a), and AMS-LSA (curve b).

Table S1. Main Textural Properties of HSZ-Y and HSZ-Y-36h before and after treatment 36 h in water at 50°C.

Sample	SSA_{BET}^a (m^2g^{-1})	VP^b ($mL g^{-1}$)	$V<50 \text{ \AA}^c$ $mL g^{-1}$	$V 50-300 \text{ \AA}^d$ $mL g^{-1}$
HSZ-Y	991	0.68	0.37	0.20
HSZ-Y-36h	613	0.57	0.24	0.17

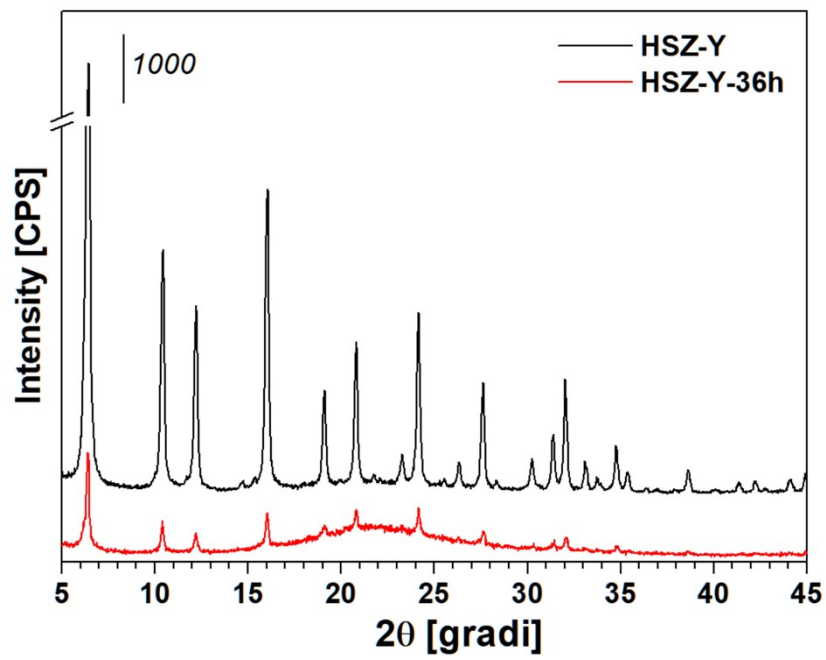


Figure S3: XRPD pattern of HSZ-Y samples before and after treatment in water at 50 °C
for 36h

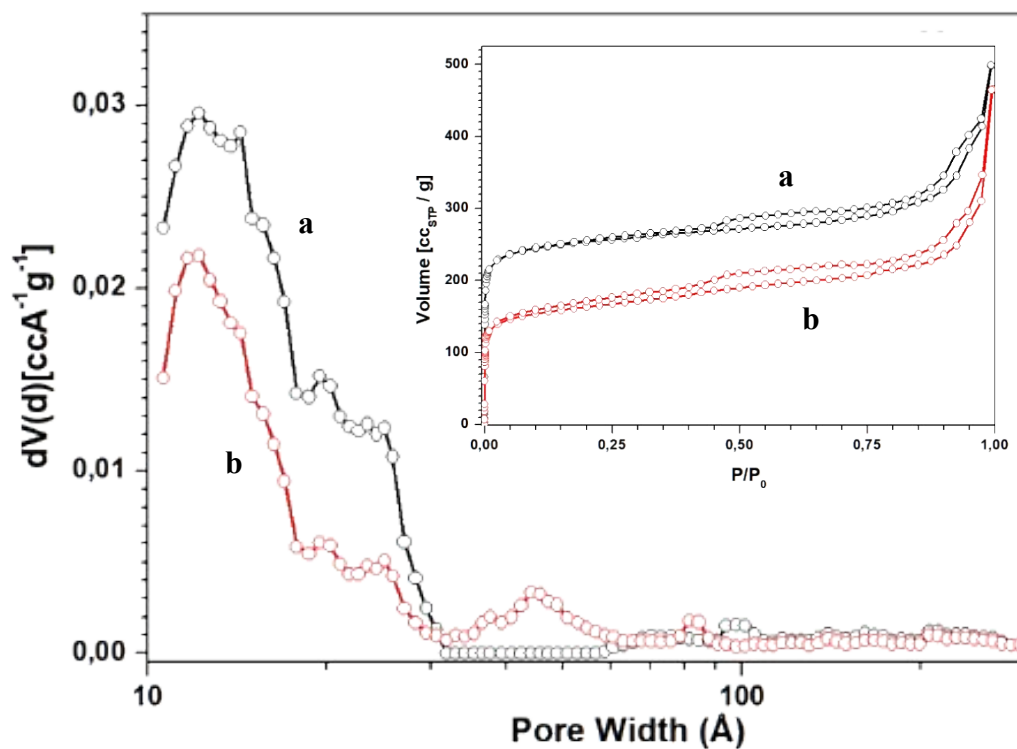


Figure S4: N_2 adsorption/desorption isotherms at -196°C (inset) and pore size distribution (main frame) of HSZ-Y before (a) and after treatment at 50°C for 36 h (curve b).

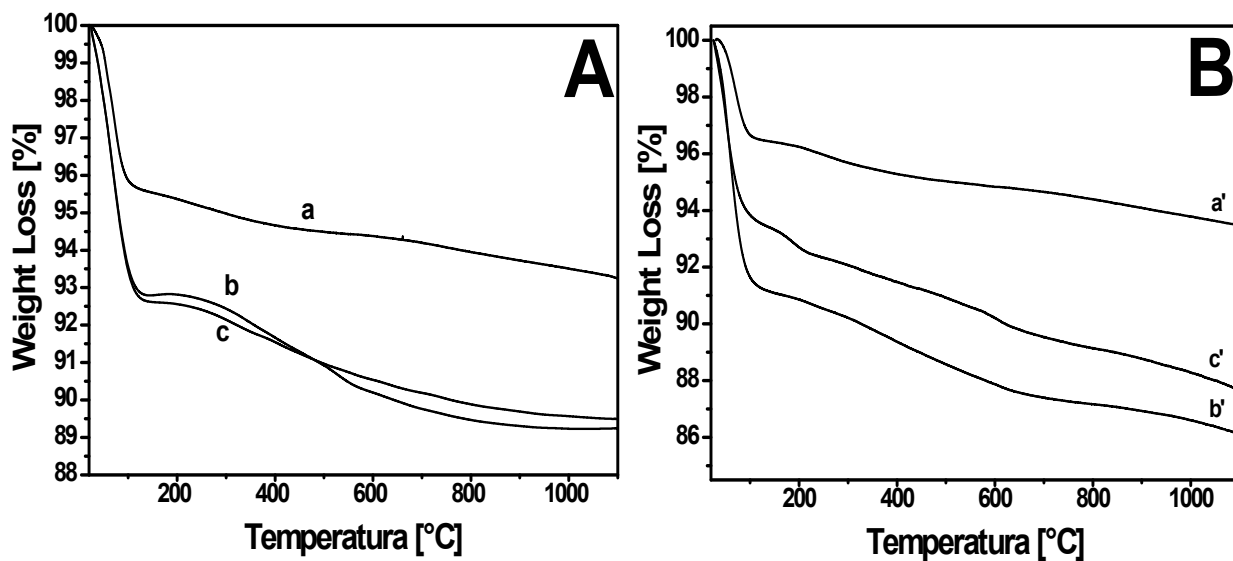
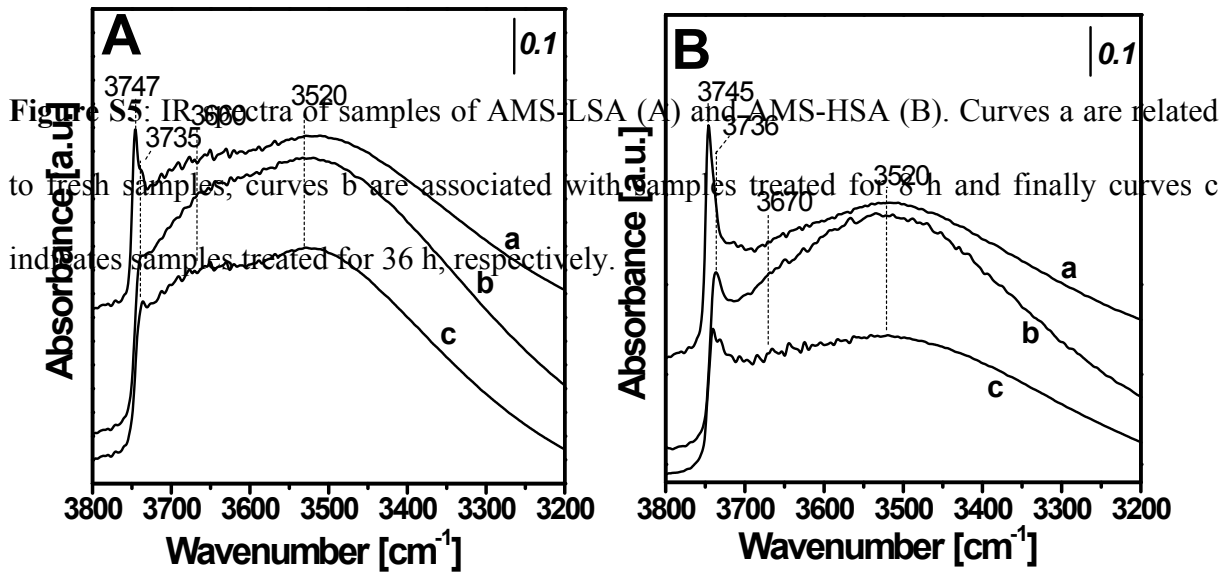


Figure S6. A: TGA for of AMS-LSA and AMS-HAS panel A and B respectively; before (curve a, a'), after hydrothermal treatment for 8 h (curve b, b') and for 36 h (curve c, c')

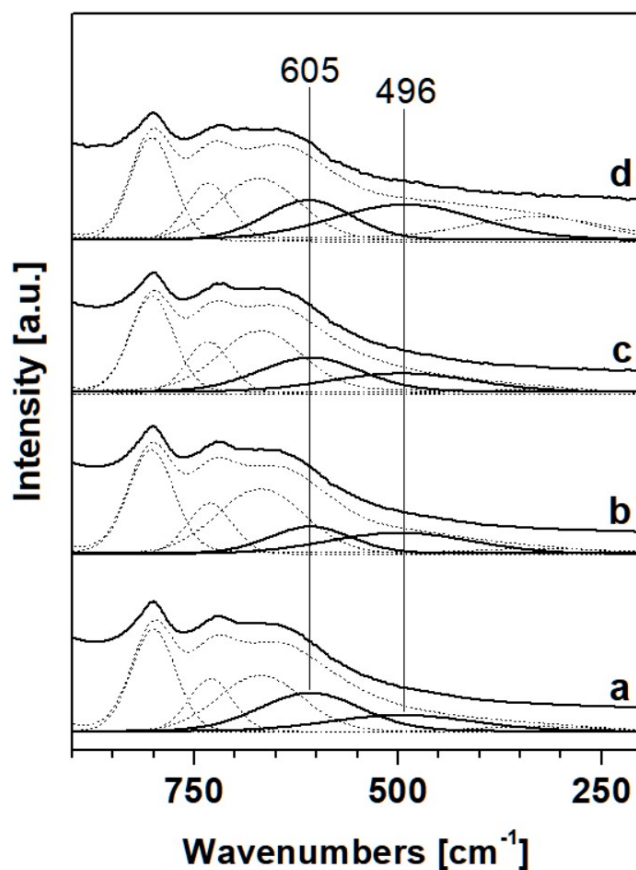


Figure S7: Raman spectra of MSA-HSA sample before (a) and after (b) treatment in water at 50°C for 36h, MSA-LSA sample before (c) and after (d) treatment in water at 50°C for 36h.

Sample	3-member ring (cm ⁻¹) (band at 496 cm ⁻¹)	4-member ring (cm ⁻¹) (band at 605 cm ⁻¹)	4MR/3MR*
MSA-HSA	35.6	21.4	0.6

MSA-LSA	31.6	24.4	0.8
MSA-HSA after 36h in H ₂ O at 50°C	20.0	28.2	1.4
MSA-LSA after 36h in H ₂ O at 50°C	31.5	46.1	1.5

Table S2: Data derived from the fitting of the Raman spectra of the MSA-HSA and MSA-LSA sample before and after contact with water for 36h.

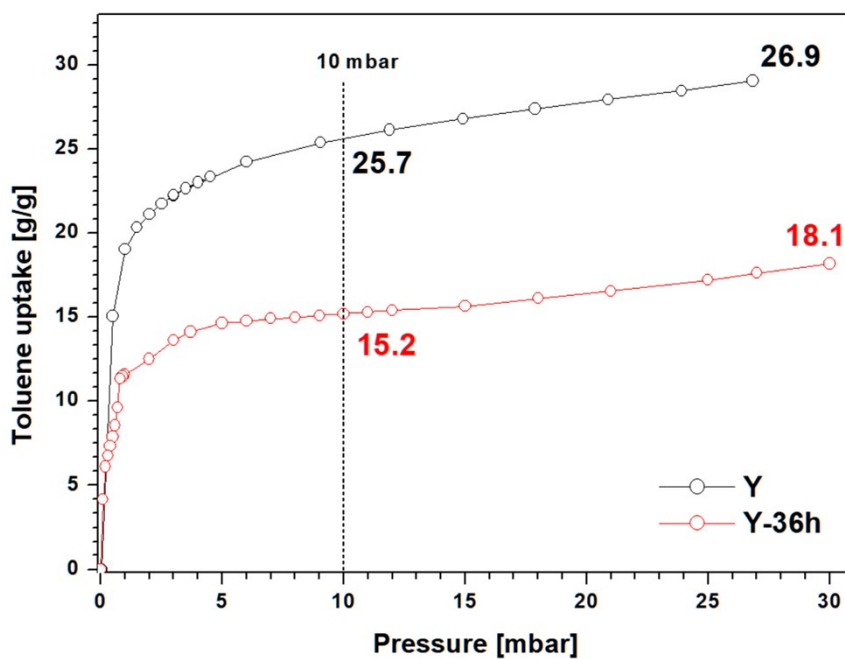


Figure S8: Gravimetric isotherms (Q% uptake vs pressure) for toluene adsorbed on HSZ-Y zeolite before and after treatment in water at 50°C.

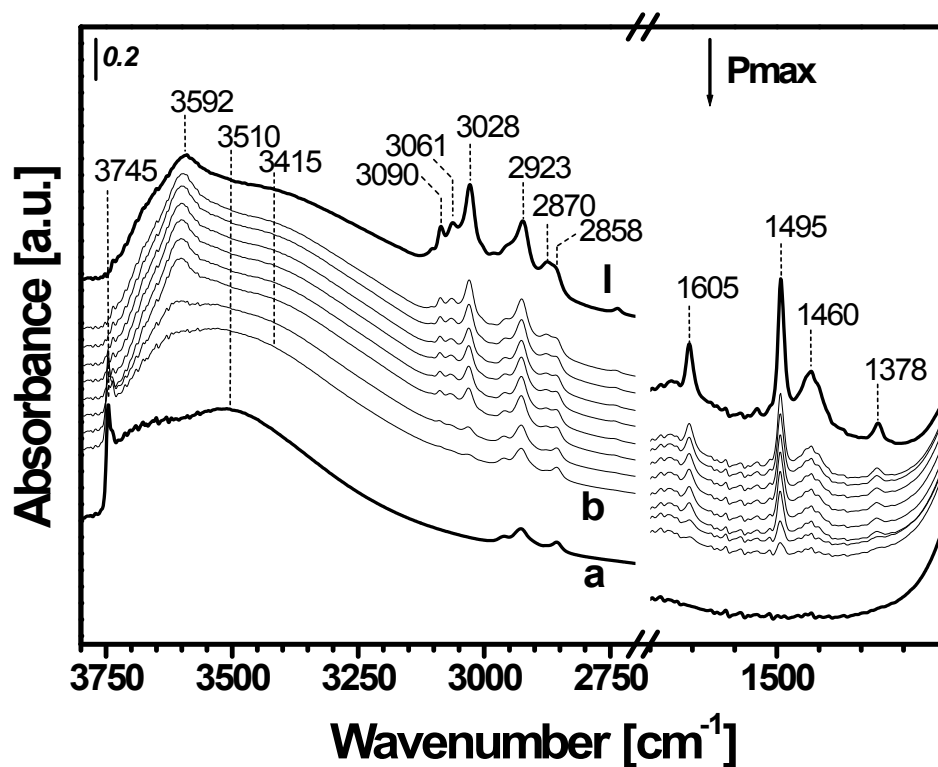


Figure S9: FTIR spectra at different doses of toluene adsorbed at room temperature on AMS-LSA preventively outgassed at room temperature for 30'. Spectra a were recorded after outgassing the samples for 60 minutes at beam temperature before toluene adsorption; spectra b to l were collected upon dosage of 0.1 to 30 mbar toluene.

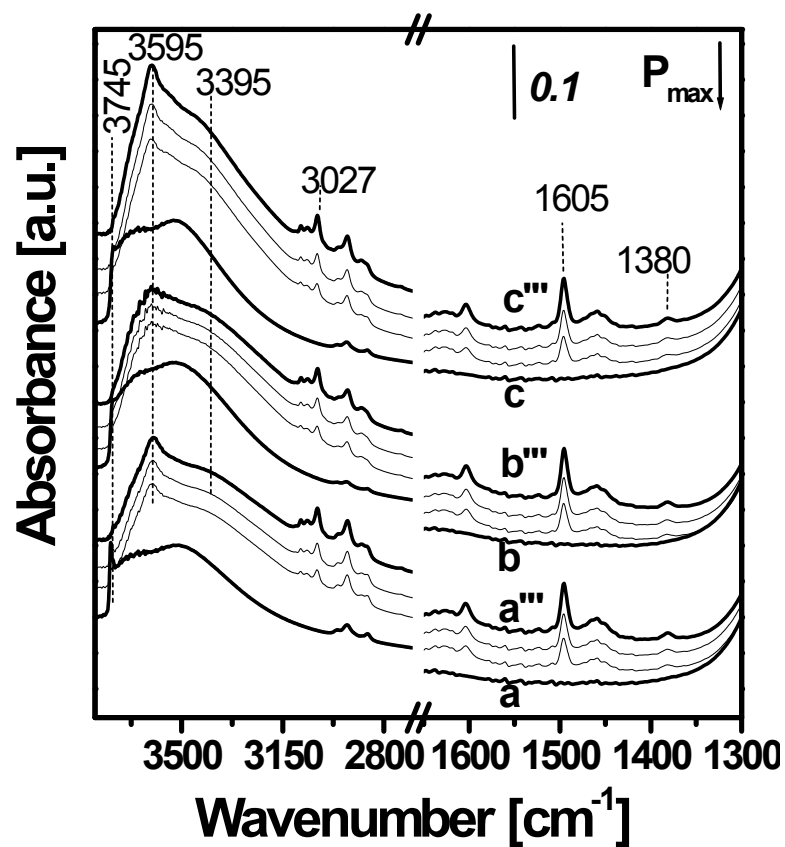


Figure S10: IR Spectra of AMS-LSA samples: before and after treatment in water for 8 h, for 36 h at 50°C and outgassed at r.t. for 1 h (curves a, b and c respectively); spectra collected after dosage of toluene at pressure of 1 mbar on the same supports (curves a'- c'); 5 mbar (curves a'' - c'') and 15 mbar (curves a''' - c''').

Determination of the optical isotherms of toluene adsorbed on AMS-LSA sample

Optical adsorption isotherms of toluene adsorbed on the AMS-LSA sample were derived from gas adsorption followed by FTIR spectroscopy. Specifically, the spectroscopic data related to the adsorption of pollutant on AMS-LSA at controlled pressures of the gas have been used to quantify the toluene uptake. The estimation of concentration of toluene on AMS-LSA was calculated using the molar absorption coefficient (ϵ) of the 1605 cm^{-1} band related to the C=C stretching mode of the toluene ring.

The molar absorption coefficient (ϵ) of the bands at 1605 of toluene singularly adsorbed on AMS with high specific surface area (AMS-HSA) was determined by combining FTIR and microgravimetric data.

The molar absorption coefficient of toluene adsorbed on AMS-HAS sample was determined following our previous work¹ related to the determination of the molar absorption coefficient of *n*-hexane adsorbed on different zeolites. In particular, it was obtained adapting the Beer-Lambert Law to adsorbent/substrate systems:

$$\epsilon [\text{mmol}^{-1} \text{ cm}] = \frac{A [\text{cm}^{-1}]}{N [\text{mmol g}^{-1}] \rho [\text{g cm}^{-2}]} \quad (1)$$

Where ϵ [$\text{mmol}^{-1} \text{ cm}$] is the molar absorption coefficient of the adsorbed species and A [cm^{-1}] is the integral absorption of the IR band at 1605 cm^{-1} and was calculated by the OPUS 5.5.4 software.

For the determination of A , from the IR spectra of samples after toluene adsorption was subtracted the spectrum of the bare AMS-HSA outgassed at room temperature (RT) in order to remove the absorption contribution of the solid. N [mmol g^{-1}] is the concentration of the adsorbed molecules (vide infra, equations 3) and ρ [g cm^{-2}] is the density of the pellet of the adsorbent. The pellet was weighed to know its density using the following formula:

$$\rho = \frac{\omega [g]}{S [cm^2]} \quad (2)$$

where ω [g] is the weight and S [cm²] is the pellet surface.

S was calculated using a specific image processing software (ImageJ), which calculates the area of each pellet correlating the number of pixels of their photographs to another photograph with pixels of known dimensions. The IR analysis was repeated 5 times, every time on a different pellet, in order to reduce the experimental errors.

The microgravimetric experiments allowed the determination of the uptake of toluene for each value of vapor pressure and from this the number of adsorbed molecules, N [mmol g⁻¹], was calculated using the formula:

$$N [mmol g^{-1}] = \frac{Q\%}{MW [g mol^{-1}]} * 1000 \quad (3)$$

Where, Uptake $Q\%$ is the weight percentage obtained from each microgravimetric adsorption isotherm and MW [g mol⁻¹] is the molecular weight of toluene (92.14 g mol⁻¹).

The average values of the ϵ_i of the band at 1605 cm⁻¹ calculated applying the equation (1) in the selected range of pressure where the integrated absorbance of 1605 cm⁻¹ band (A_i) and the amount of adsorbed molecules [mmol g⁻¹] has a linear trend. The average value of the molar absorption coefficient is $\epsilon_{1605} = 0.292 \pm 0.059 \text{ cm } \mu\text{mol}^{-1}$.

The concentration of adsorbed toluene (C_{toluene}) on AMS-LSA defined as $\mu\text{mol g}^{-1}$ was obtained by using the formula:

$$C_{\text{toluene}} = \frac{A_{MSA-LSA (1605)}}{\epsilon_{MSA-HSA-toluene} \rho} \quad (4)$$

where $A_{\text{AMS-LSA}(1605)}$ is the integral absorption of the IR band at 1605 cm^{-1} of toluene adsorbed on AMS-LSA, $\epsilon_{\text{AMS-HSA-toluene}}$ is the molar extinction coefficient ($\text{cm } \mu\text{mol}^{-1}$) of toluene adsorbed on AMS-HSA and ρ (g cm^{-2}).

From this calculation, the optical isotherms of toluene adsorbed on AMS-LSA samples, also hydrothermally treated, have been derived.

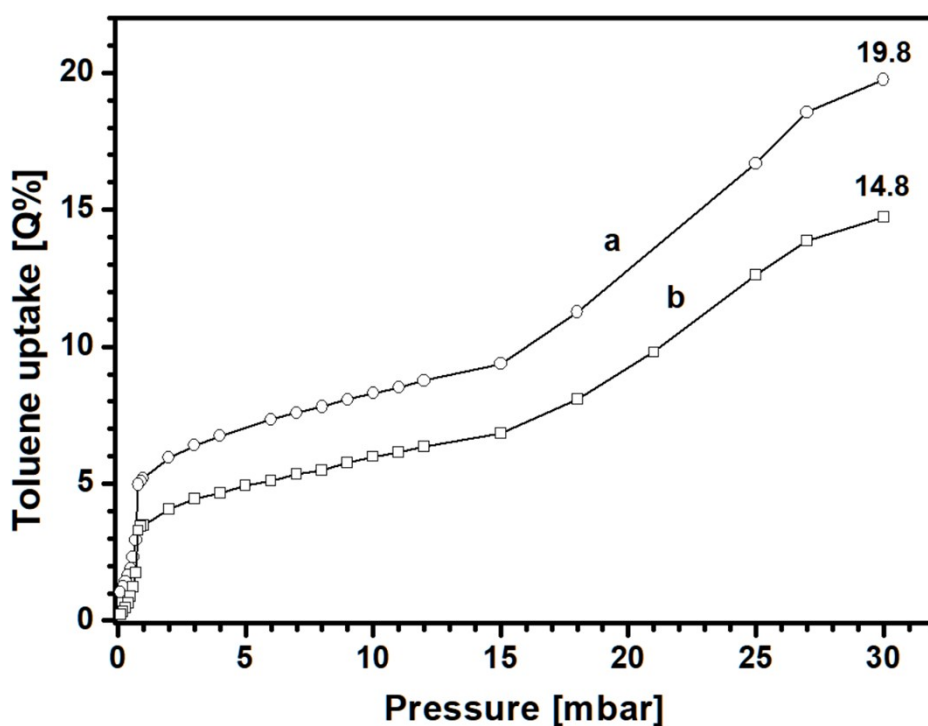


Figure S11: Optical isotherms (uptake vs pressure) for toluene derived from the 1605 cm^{-1} IR band formed upon adsorption of toluene from vapor phase on AMS-LSA samples before (curve a) and after treatment in water at 50°C for 36 h (curve b).

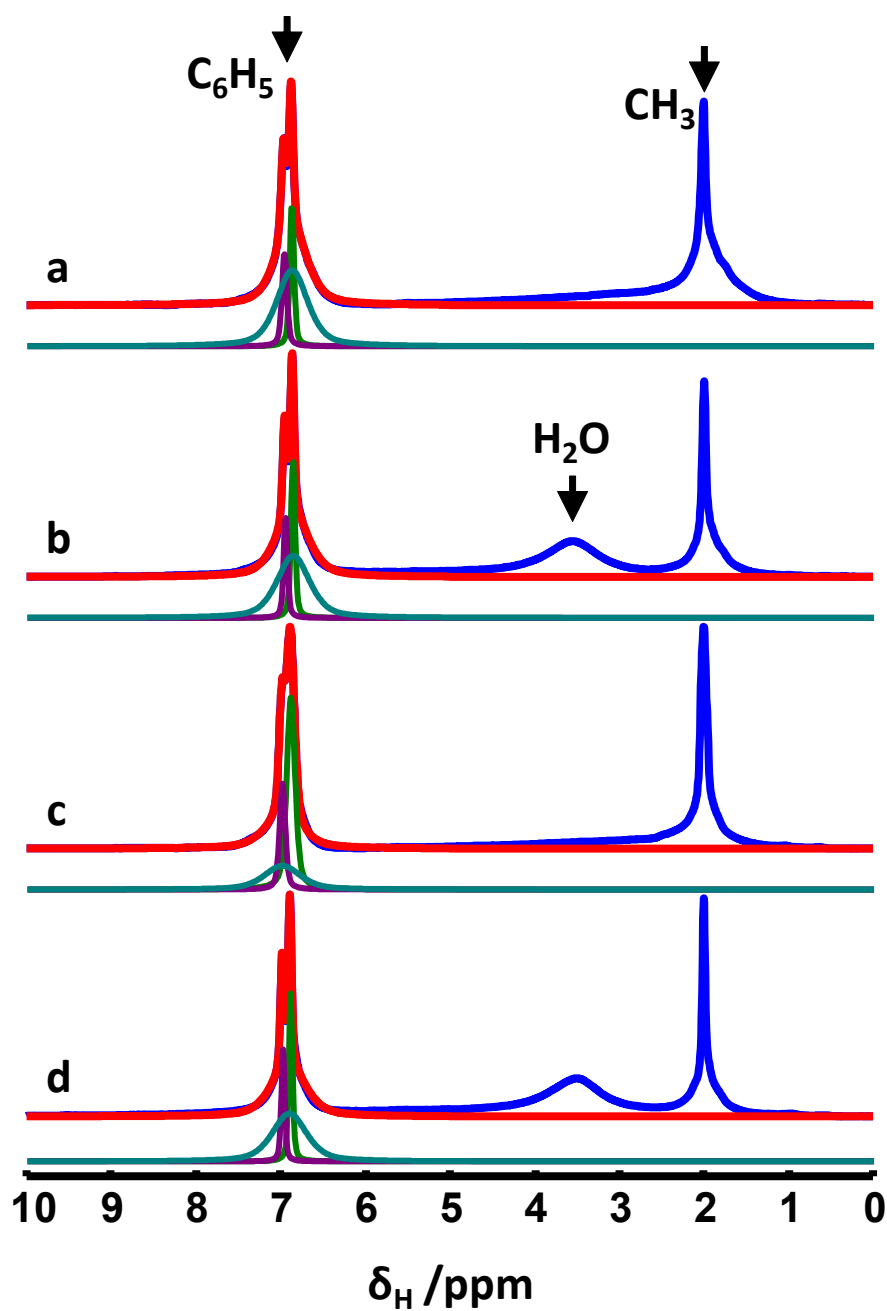


Figure S12: ^1H MAS NMR spectra of toluene adsorbed on AMS-LSA in the absence (a, c) and presence (b, d) of water, before (a, b) and after (c, d) treatment in water at 50°C for 36 h. Each spectrum includes experimental and corresponding selectively fitted (aromatic region only) spectra with individual contribution from each type of ^1H site.

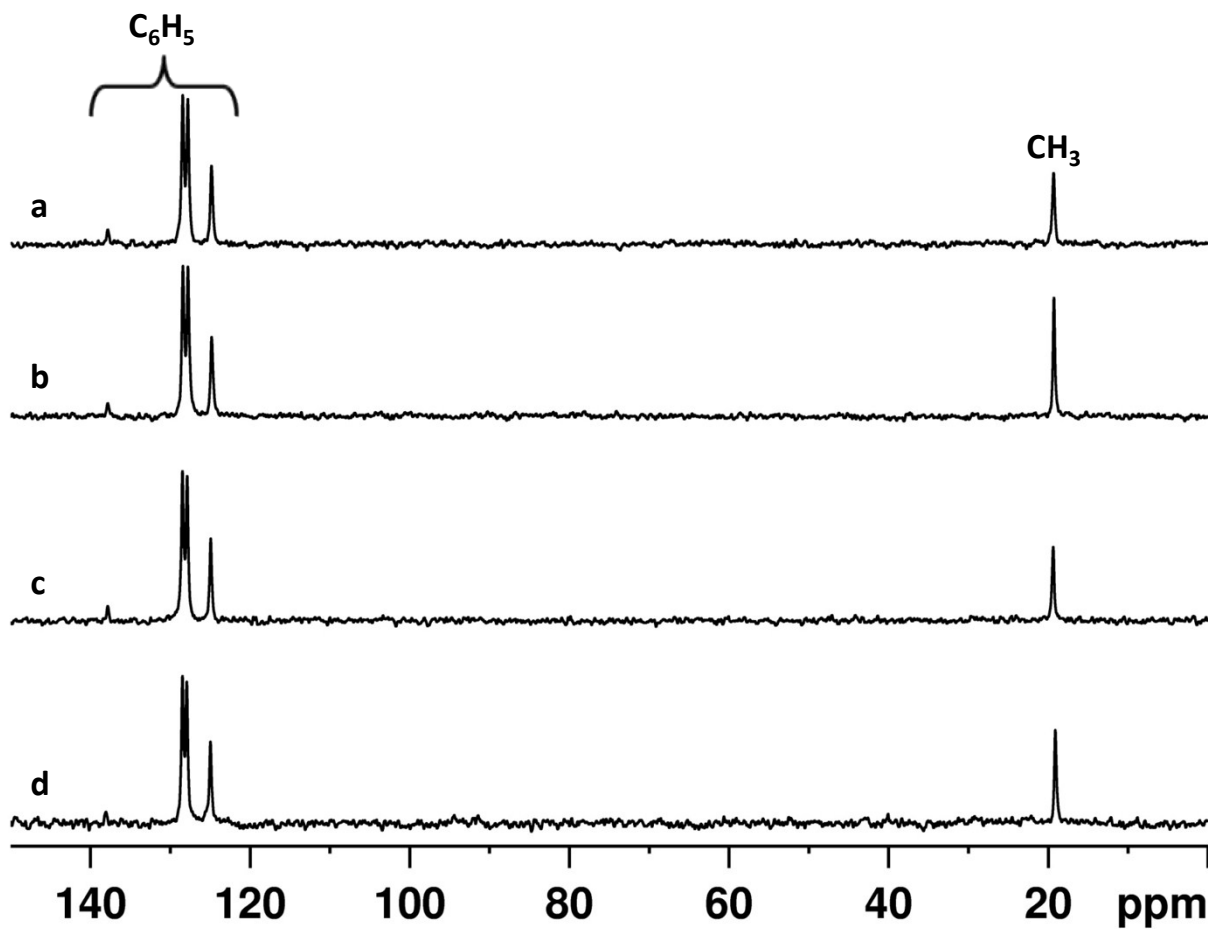


Figure S13: ^{13}C CPMAS NMR spectra of toluene adsorbed on AMS-LSA in the absence (a, c) and presence (b, d) of water before (a, b) and after (c, d) treatment in water at 50°C for 36 h. A MAS rate of 10 kHz and cross polarization contact time of 40 ms was used.

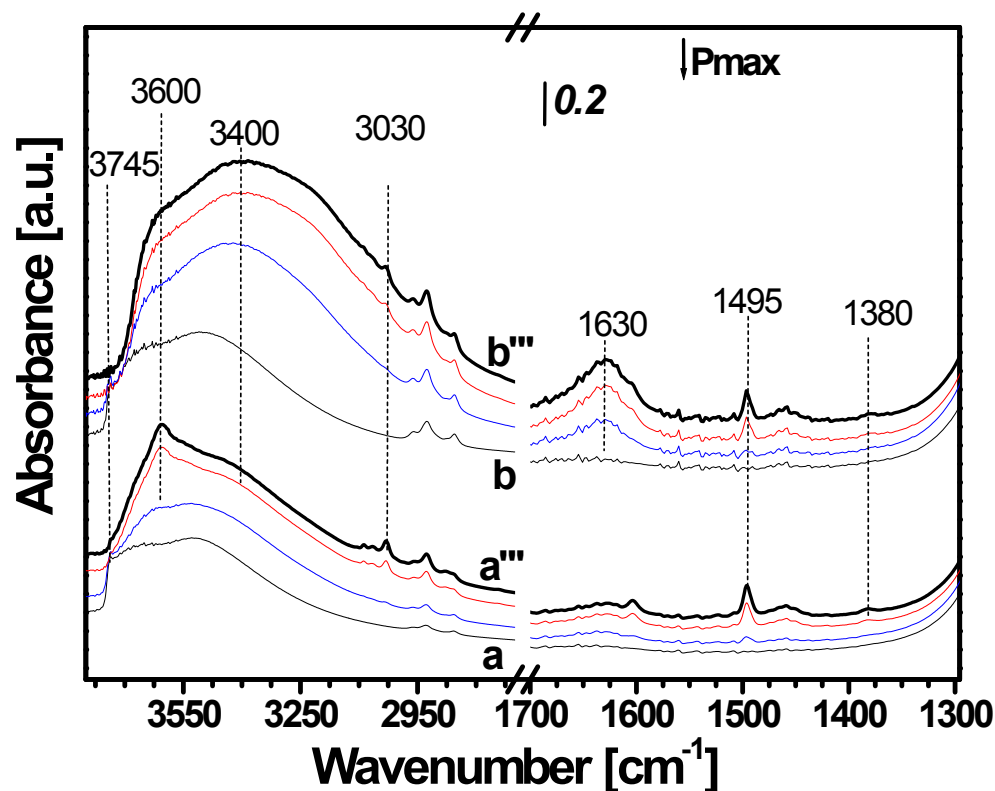


Figure S14: IR Spectra of AMS-LSA-36H sample after dosage of pure toluene (curves a' - a''') at partial pressures of 0.5 mbar (curves a'); 2.5 mbar (curves a'') and 7.5 mbar (curves a''') and after adsorption of the equimolar mixture of toluene and H₂O (curves b' - b''') at total pressures of 1 mbar (curves b'); 5 mbar (curves b'') and 15 mbar (curves b'''). Before the adsorption, the sample was preventively outgassed at room temperature for 30'.(curves a and b).

References

1: Giorgio Gatti, Diana F .Olivas Olivera, Vittoria Sacchetto, Maurizio Cossi, Ilaria Braschi, Leonardo Marchese and Chiara Bisio, “*Experimental Determination of the Molar Absorption Coefficient of n-Hexane Adsorbed on High-Silica Zeolites*” ChemPhysChem 2017, 18, 2374 – 2380.