SUPPLEMENTARY INFORMATION

A simple liquid state ^{1}H NMR measurement to directly determine the surface hydroxyl density of porous silica

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S1. NMR Acquisition Parameters

^{1}H NMR spectra were collected using a Magritek Spinsolve 43 MHz NMR benchtop spectrometer. The following parameters were used: 90° pulse duration was 7 µs, pulse amplitude was 0 dB, receiver gain was 40, number of points on FID collected was 16384, dwell time was 100 µs, number of scans was 8 and recycle time was 120 s.

The recycle time is calculated on the basis that T$_1$ of ^{1}H for magnetically diluted systems like this one are much longer. T$_1$ were recorded for 10, 5 and 0 µL of H$_2$O in 1 mL of D$_2$O, as 10.26 ± 0.04 s, 10.41 ± 0.04 s and 9.00 ± 0.20 s respectively. Hence 120 s ensures that the acquired data is free from relaxation artefacts.

S2. Error Analysis

There are several sources of experimental error that need to be accounted for when producing the calibration plot in Figure 1. The error in the integral of ^{1}H intensity relates to the precision of the NMR spectrometer and was determined by calculating the uncertainty from three independent repeat ^{1}H NMR measurements of the same flame sealed 1 mL D$_2$O + 10 µL H$_2$O sample across multiple days. The uncertainty in the integral of intensity from these measurements came to ± 0.9 %. Figure 1 represents this uncertainty in y-axis error bars.

The error associated with the mass concentration δ_{OH} is derived from the standard error of prediction[1] in determining [H atoms]. A modified standard error of prediction is provided using the following equation (Eq.2):

$$s_{[H\ atoms]} = \frac{s(r)}{m}\sqrt{\frac{1}{n} + \frac{\left(I_{sample} - \bar{I}_{calibration}\right)^2}{m^2\sum_{i=1}^{n}\left([H\ atoms]_i - [H\ \bar{a}toms]\right)^2}} \quad (2)$$

where

$$s(r) = \sqrt{\frac{\sum_{i=1}^{n}\left(I_{calibration} - \hat{I}_{calibration}\right)^2}{n-2}}$$

here s(r) is the residual standard deviation, m is the gradient of the calibration plot, n is the number of calibration points taken ([H atoms], $I_{calibration}$) and I_{sample} is the integral of intensity for the silica sample measured. The bars over parameters represent mean values and $I_{calibration}$ with the hat is the integral value as predicted by the line of best fit $I_{calibration} = m[H\ atoms]$.

The standard error of prediction was modified to remove the term that would have concerned N number of ^{1}H NMR repeat measurements on the same silica sample. As the uncertainty from repeat measurements on the same flame sealed sample were small, it should be fair to use this modification. The unmodified version penalises systems where the uncertainty between N repeat measurements could be much larger than it is here. The maximum standard error prediction for all samples except the 800 °C dehydroxylation, was calculated to be ± 4.2 %. The samples dehydroxylated at 800 °C had a maximum standard error prediction of ± 11.6 % instead.

The total uncertainty for α_{OH} is derived from the error propagation of instrument precisions, the standard error of prediction and uncertainty from (n =3) replicated silica samples. For the full breakdown of individual errors check S4.

S3. BET N_2 Surface Area Method Details

Brunauer–Emmett–Teller BET N_2 analysis was performed on a Micromeritics 3Flex. Experiments were conducted at 77 K and degassing conditions of 300 °C for 4 hours under N_2 purge. The silica samples were measured as received, and after any dehydroxylation or rehydroxylation treatment. These measurements were used to obtain the BET specific surface areas.

S4. Expanded Table on As Received CARiACT Q Series Hydroxyl Densities

The expanded Table S4 shows the full results of the as received CARiACT Q series silicas it includes the values for each replicated sample (n = 3) as well as the BET surface areas and background corrected integral of ^{1}H intensity. The error in the background correction is linked to the purity of the D_2O used, therefore the highest purity D_2O should be used to minimise the overall error associated with the final α_{OH} calculation. With this expanded table it should be easier working left to right using Eq.1 to work the surface hydroxyl density α_{OH}. Also, the table provides the errors associated with each of measurements and also the uncertainty from replicated samples can be

calculated. Therefore, the total uncertainty can be worked out by error propagation of the uncertainty from replications (n = 3) and the uncertainty from the sum of errors from the mass of beads to the BET surface area which comes to ± 7.15 %.

Table S4: Expanded table of hydroxyl densities of CARiACT Q Series silica with full list of parameters to calculate the surface hydroxyl density.

Sample	Batch	Mass of silica beads / g ± 0.05 %	Background Corrected Integral of ^1H intensity ± 0.9 %	Mass concentration δ_{OH} / mmol/g ± 4.2 %	Surface area / m^2/g ± 2.0 %^{2}	Surface hydroxyl density α_{OH} / OH/nm^2	Average α_{OH} / OH/nm^2
Q6	1	0.1543	1.9984e+04	0.97	407	1.44	1.51 ± 0.13
	2	0.1798	2.5366e+04	1.06		1.57	
	3	0.1974	2.6813e+04	1.02		1.51	
Q10	1	0.1333	1.3017e+04	0.73	312	1.41	1.29 ± 0.17
	2	0.1350	1.0582e+04	0.59		1.14	
	3	0.1678	1.5789e+04	0.68		1.31	
Q15	1	0.1006	2.0289e+04	1.51	207	4.39	4.52 ± 0.36
	2	0.1161	2.3642e+04	1.53		4.45	
	3	0.1397	3.0255e+04	1.62		4.71	
Q30	1	0.1699	2.1390e+04	0.94	107	5.29	5.35 ± 0.81
	2	0.1583	1.7578e+04	0.83		4.67	
	3	0.1779	2.5512e+04	1.08		6.08	
Q50	1	0.1640	1.4301e+04	0.65	70	5.59	5.16 ± 0.70
	2	0.1719	1.1584e+04	0.51		4.39	
	3	0.1756	1.5031e+04	0.64		5.51	

S5. Silica Left at Different Durations in D_2O Solution and its Effects on the Surface Hydroxyl Density

The CARiACT Q6 and Q15 beads were left in D_2O solution for both 3 hours as described in step (4) in the main text, and alternatively the same procedure was carried out, but the beads were left for 24 hours. It is important to note that the background integral mentioned in step (7) in the main text was retaken as well with a 24 hour duration and is used in subsequent calculations for the surface hydroxyl densities α_{OH} provided in Figure S5.
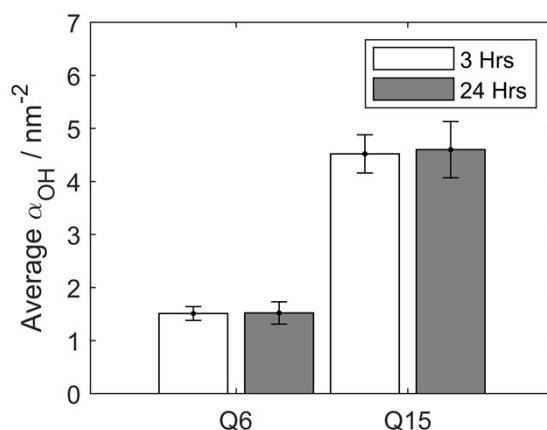

Figure S5: The average surface hydroxyl densities α_{OH} of CARiACT Q6 and Q15 silicas when left for 3 hours (white) and 24 hours (grey) in D_2O solution. The error bars are derived from the uncertainty of n = 3 batches.

S6. Active region of RF coil

In order to asess the "active region" of the RF coil for different solvent column heights we ran three different ^1H NMR experiments of three separate 5 mm nmr tubes filled to heights/volumes of solvent of stock solution: (i) 30.0 mm/ 400 µl; (ii) 46.0 mm/ 600 µl; (iii) 78.0 mm / 1000 µl. The stock solution was 5 mL of D_2O with 10 µL of H_2O so it was representative of samples used during a OH density measurement involving silica. Note all our sample volumes from actual experiments described in the main manuscript were > 500 µl (> 38.0 mm solvent column height)

The ^1H spectra were run under identical acquisition parameters to those of the experiments and figure 1 below shows the results of the integration of the ^1H signal and indicates that there is no systematic change in ^1H integral with solvent column height (data in Table 2).

Table 2. Results of ^1H integrals for three different solvent heights

Sample	^1H integral
30 mm Height/0.4 mL	6.9504 +/- 0.0177e+04
46 mm Height/0.6 mL	7.1938 +/- 0.0421e+04
78 mm height/1.0 mL	6.9857 +/- 0.0369e+04
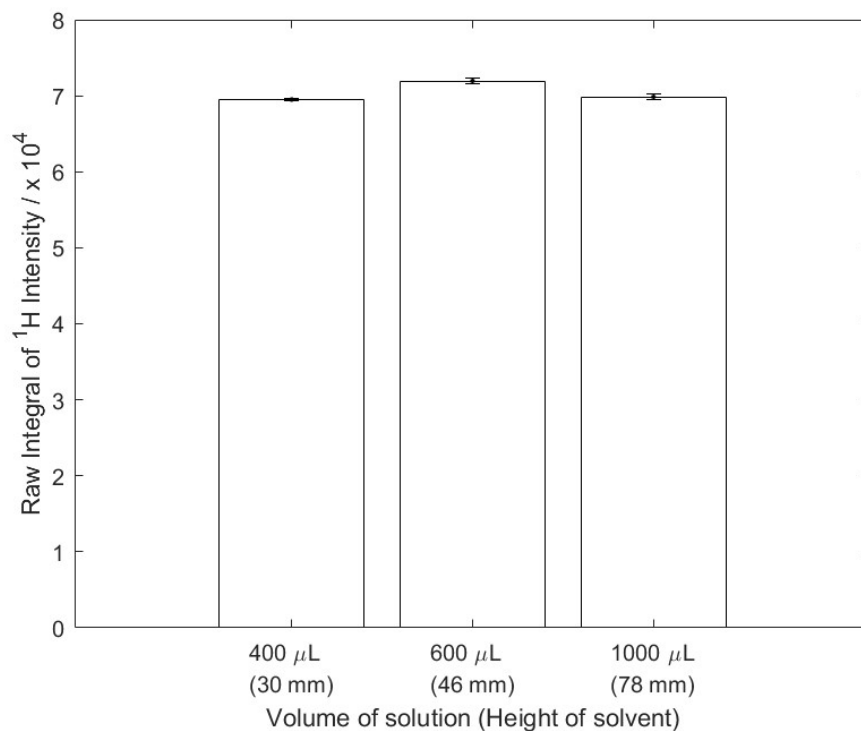
The error bars on the figure above represent the standard deviation of 3 independent repeats for each sample. The difference between the absolute integrals is less than 0.5 % which is negligible.

References

1 L. Prichard and V. Barwick, *Preparation of Calibration Curves A Guide to Best Practice*, 2003.
2 V. A. Hackley and A. B. Stefaniak, *J Nanopart Res*, 2013, **15**, 1742.