

Supporting Information

Insights into Molecular Accessibility in Catalyst and Sorbent Materials using NMR Porosity Measurements

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Materials and Methods

Three alumina and five titania samples were provided by Shell Global Solutions International B.V. as trilobe extrudates (typically 2 mm diameter and 8 mm length). Al-I, Al-II, and Al-III were alumina catalyst carriers, Ti-I, Ti-II and Ti-III were titania carriers, and Ti-IV and Ti-V were titania carriers loaded with 1 wt.% MnO₂. Spherical pellets of zeolite 3A and 4A were purchased from Alfa Aesar, with a diameter of 2-5 mm. The zeolites were crushed and sieved to a size class of 20-30 mesh prior to measurement to mitigate against pellet-to-pellet variations in the porosity. Deionised water was produced in-house using a Elga Purelab DV25 purification system. All other liquids were purchased from Alfa Aesar at a purity of >98% and used without further purification.

Bulk and skeletal densities were measured using mercury porosimetry on a Micromeritics Autopore V. The mercury pressure versus intrusion data were analysed using the Washburn equation with a contact angle of 140°. For zeolites 3A and 4A and Al-I, helium pycnometry measurements were performed using a Micromeritics AccuPyc II 1340 pycnometer. The pore size distributions of the materials were measured by a combination of mercury porosimetry and Ar physisorption (Micromeritics 3Flex adsorption analyser) to ensure that both the meso/macro and microporosities were well-described.

NMR experiments were carried out on either a Bruker AV400 NMR spectrometer operating at a ¹H frequency of 400.23 MHz equipped with a Diff30 probe and a 5 mm ¹H/¹³C coil or a Bruker DMX300 NMR spectrometer operating at a ¹H frequency of 300.23 MHz equipped with a Diff30 probe and an 8 mm ¹H coil. Experiments were primarily performed on the AV400 spectrometer, and the experiments shown in S4 and S5 were performed on the DMX300. The linear response region of the radiofrequency (RF) coil was approximately 1 cm, which was measured from a 1D profile of a bulk liquid sample that extended beyond both ends of the coil. ¹H spectra were acquired using a standard pulse-acquire sequence with a dead time of 4.5 μs, a dwell time of 20 μs, and 32,768 points in the FID to ensure that both samples of bulk liquids and liquid in porous media could be measured using the same parameters. For the latter, zero filling was applied after the signal had decayed fully to limit the amount of noise introduced into the spectra. All spectra were then manually phased and a polynomial baseline correction was applied prior to integration in Matlab. 1D ¹H NMR z-profiles were recorded parallel to the B_0 field before each measurement to ensure that the sample had not moved during the experiments, as changes in the sample position may alter the value of K_S in eq. 2 and result in erroneous values of porosity. A one-off calibration of the RF coil (detailed below) was carried out prior to the porosity measurements to ensure that the samples were placed into a linear region of signal response.

Porosity Measurement Method

Alumina and titania samples were dried at 200 °C overnight prior to spontaneous imbibition of the probe liquid. For zeolite samples, drying was carried out at 300 °C under reduced pressure for 2 h. When water was used as the probe molecule the drying step was omitted. Following imbibition, the excess fluid was removed by thoroughly drying the sample on filter paper. 1-3 imbibed extrudates were used for each measurement of the liquid in the pore space, denoted S_1 in Figure S1. Excess liquid was then added to NMR tube and the measurement was repeated, as shown by S_2 in Figure S1. Finally, the pellets were removed and only the bulk liquid spectrum was recorded, as shown by S_3 in Figure S1. Before each measurement a delay of 5 minutes was used to ensure that the sample had reached thermal equilibrium. Longer thermal equilibration delays did not affect the results at room

temperature, but may be required for elevated or reduced temperatures. Each measurement was repeated in triplicate and the average value is quoted along with the standard error from the 3 measurements.

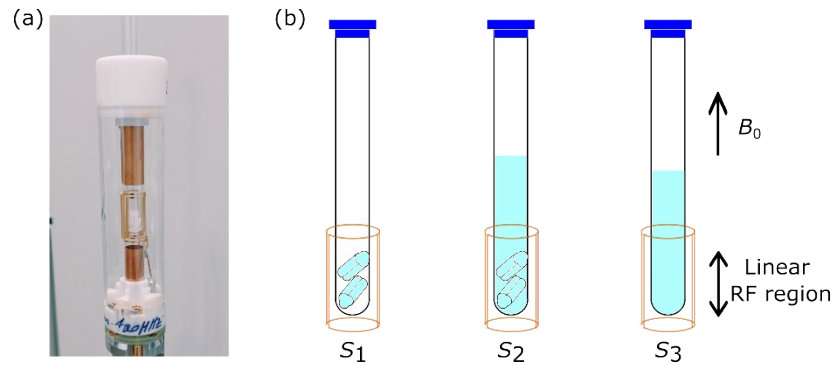


Figure S1: The (a) sample placement within the RF coil and (b) schematic diagram of the three NMR measurements required for the NMR porosity method. The region of RF signal response that is approximately linear is denoted.

In the absence of NMR relaxation effects the porosity, ε , is simply:

$$\varepsilon = \frac{S_1}{S_1 + S_3 - S_2}. \quad (\text{S1})$$

However, T_2^* relaxation during the dead time can distort the quantitative nature of Eq. S1 by reducing the size of the spectral integrals. If this signal loss is large and not uniform for each sample, then the measured porosity value will be unreliable. Relaxation effects are particularly significant for confined liquids, such as those within zeolite pores or liquids in proximity to paramagnetic species, and small for bulk liquids. The difference in relaxation behaviour between samples means that it is necessary to consider the relaxation losses in each experiment. The signal losses due to T_2^* relaxation were assumed to follow an exponential decay such that:

$$S_i = S_{i,0} \exp\left(\frac{-(t_{de} + t)}{T_{2,i}^*}\right) \text{ where } i = 1, 2, 3. \quad (\text{S2})$$

S_i is the observed signal, $S_{i,0}$ is the signal unaffected by relaxation losses, t_{de} is the dead time of the experiment and t is the time point of the signal acquisition. Eq. S2 was fitted to the first 10 points of the FID to estimate T_2^* for each sample. The relaxation effects on the peak integrals occurring during the dead time were then removed according to:

$$S_{i,0} = S_i / \exp(-t_{de}/T_{2,i}^*), \quad (\text{S3})$$

and the values of $S_{i,0}$ were substituted into Eq. S1 to calculate the corrected porosity. The correction was applied to all integrals for each fluid (i.e. signals S_1 , S_2 , and S_3 as outlined above). The effect of T_2^* relaxation on porosity was explored for the 5 titania extrudates with water as the imbibed fluid. Ti-I, Ti-II, and Ti-III were anatase titania with no additives and Ti-IV and Ti-V contained 1 wt.% of paramagnetic MnO_2 . The inclusion of MnO_2 allowed the NMR porosity method to be tested on samples with low values of T_2^* . Figure S2a shows that increasing the dead-time resulted in an underestimate of the porosity, with errors of approximately 30% observed for Ti-IV and Ti-V when a

75 μs dead-time was used. Dead-times were minimised for all further experiments and Figure S2b shows the relaxation effects on the porosity measurement for a dead-time of 4.5 μs (the minimum dead-time due to hardware limitations). For the Ti-I, Ti-II, and Ti-III, which relaxed slowly, the relaxation correction was shown to have minimal effects on the porosity measurement. For Ti-IV and Ti-V, the presence of MnO_2 shortened the T_2^* relaxation time constants and the relaxation correction increased the measured porosities by 4.9% and 3.2% respectively. Minimising the dead-time of the experiment and applying the relaxation correction ensures that absolute quantitation can be achieved even for samples that show very rapid NMR relaxation and are incompatible with many other NMR techniques.

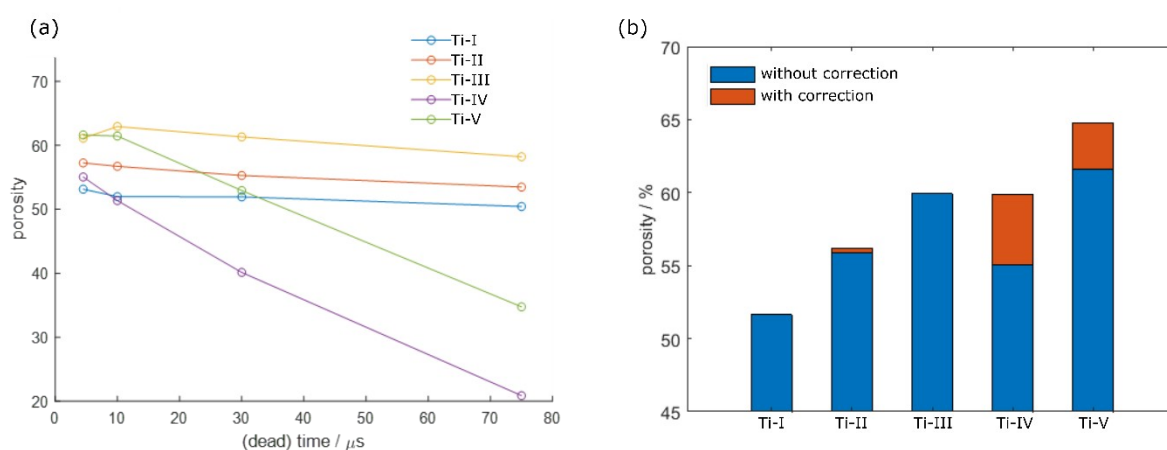


Figure S2: The porosity of the titanias measured with water as a probe molecule. The porosities were measured as (a) a function of the dead-time of the ^1H NMR spectra and (b) at the shortest dead-time with and without the relaxation correction applied.

A final consideration when carrying out the NMR porosity measurements relates to the positioning of samples within the coil. Four steps must be followed to ensure that Eq. S1 is quantitative:

- 1) The sample base must be located within the linear signal response region of the RF coil.
- 2) The height of the pellets must not extend beyond the linear signal response region of the RF coil.
- 3) The liquid level of samples S_2 and S_3 must extend beyond the limit of the coil so that the non-uniform signal response at the top of the coil can be removed when taking the difference $S_3 - S_2$.
- 4) The sample must not change position within the magnet between each measurement.

Figure S3 shows the 1D profiles of each sample measured parallel to the applied field. These profiles were used to confirm that the above criteria were fulfilled. The slight curvature in the shape of the profile at $z=1.2$ cm is ascribed to the curvature of the base of the NMR tube rather than signal inhomogeneity. If any of the above criteria are not fulfilled, then the measured signal intensities will not be directly proportional to the number of spins (and hence molecules) in the coil region. In such a limit the porosity measurement will not provide reliable and quantitative results.

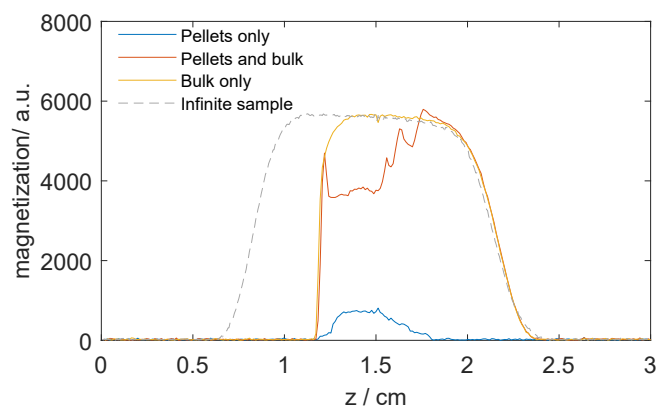


Figure S3: The 1D profiles of each sample depicted in Figure S1. Recycle delays were set to $1xT_1$ to minimise acquisition times, therefore the absolute integrals of the profiles are not quantitative and used only to demonstrate the positioning requirements outlined above. An infinite bulk sample (extending beyond both ends of the RF coil) is shown for comparison.

Drying of Porous Materials

To ensure that the drying conditions used within this study were sufficient to remove water from the porous materials, samples of titania and zeolite 3A were dried and measured as outlined in the experimental section. The same sample was then imbibed with water before the extra pellet fluid was removed and the sample was remeasured. Figure S4 shows the comparison of ^1H spectra recorded for the dried and imbibed samples. In each case, the signal from the dried pellet was $<4\%$ of the signal from the imbibed pellet.

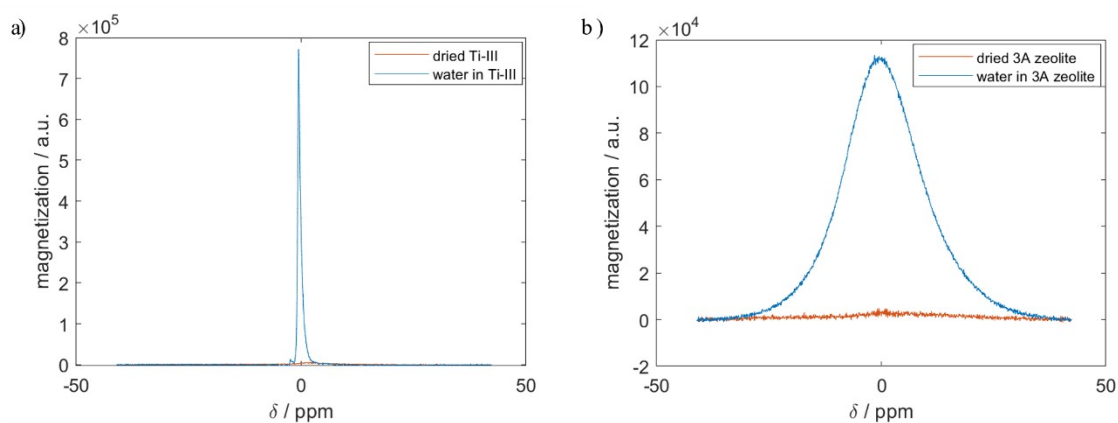


Figure S4: A comparison between the spectra obtained from dried and water imbibed pellets for (a) Ti-III and (b) zeolite 3A. Measurements were recorded at 300 MHz.