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Accessible Catalyst Pore Volumes, for Water and Organic Liquids, as probed by NMR Cryoporometry.

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Abstract

Chemical reaction speed is frequently enhanced at a surface, particularly when materials like platinum are present. It is well known that porous materials such as sol-gel silicas, controlled pore glasses, templated porous materials such as SBA-15, MCM-41, MCM-48, and zeolites, offer large surface areas. This in turn makes them ideal for catalysing chemical reactions. Thus an important use for porous materials is as a substrate and media to promote chemical reactions. However small pores are not always easily accessed by some of the organic liquids in which these catalytic reactions ideally take place. Cryoporometric techniques offer the possibility of directly probing the fraction of a pore that is actually accessible to a probe liquid. This fractional volume has significant impact on the catalytic efficacy of a particular solvent that is used to promote a reaction in the pores. Pore size, pore geometry, pore throat, pore surface material (hydrophilic/hydrophobic) and choice of probe liquid all influence the accessible fraction. By performing an NMR cryoporometric measurement using a particular liquid of interest, it is possible to directly access this information, which is of prime importance for catalysis, and financially very significant on an industrial scale. Results are reported here for a set of liquids, some simple alkanes (dodecane, tetradecane and hexadecane) plus water and cyclohexane, accessing pores in sol-gel silicas of nominal pore diameters 60Å, 100Å, 200Å, 500Å. The key conclusions were that for the alkanes, the dimension of chain length was not relevant to the filling fraction, however for the cyclohexane a molecular diameter of 3.8 Å fitted the data well.

Keywords

catalysis, confined geometry, NMR cryoporometry, porosimetry, pore volume.

1. Introduction

1.1 Nano-metric structural measurement techniques

It is well known that porous materials such as sol-gel silicas, controlled pore glasses, templated porous materials such as SBA-15, MCM-41 and MCM-48, and zeolites offer large surface areas. This in turn makes them ideal for catalysing chemical reactions. To probe the dimensions of these pores there are a range of techniques. The scattering techniques (using neutrons or X-rays) [1] and thermodynamic techniques using gas adsorption (constant temperature) or NMR/neutron cryoporometry (constant pressure) [2,3,4,5] offer complementary methods of determining pore structure information such as pore-size distribution, surface area and pore volume.

1.2 Porous Materials as Catalysts

Chemical reaction speed is frequently enhanced at a surface, particularly when materials like platinum are present. Thus an important use for porous materials is as a substrate and media to promote chemical reactions [6,7,8].

Small pore materials such as zeolites have vast surface areas per gram. On an industrial scale, these chemical reactions frequently take place in organic liquid solvents. This study uses NMR Cryoporometry to probe the extent to which water and various organic liquids can enter into porous media, due to both the geometric size limiting effect of the porous media, and surface interactions with the probe liquid. This reduction in accessible pore volume is clearly an important parameter that limits the increase in reaction rate that is obtainable by going to smaller pore size.

1.3 Accessible pore fraction

Of the above nano-metric measurement techniques, it is only the cryoporometric techniques that offer the possibility of directly probing the fraction of a pore that is actually accessible to a probe liquid. This fractional volume has significant impact on the catalytic efficacy of a particular solvent that is used to promote a reaction in the pores. Pore size, pore geometry, pore throat, pore surface material (hydrophilic/hydrophobic) and choice of probe liquid all influence the accessible fraction.

This change in accessible pore volume for different liquids has been known for some time, to practitioners of NMR cryoporometry [3], as well as subject to theoretical studies, but to our knowledge there have not to date been detailed systematic experimental studies using a range of porous materials and probe liquids. We have begun such a study, in part as an industrial study, using sol-gel silicas, controlled pore glasses, templated porous materials such as SBA-15 and MCM-48, and zeolites, with both water and a range of organic liquids particularly relevant to catalysis work. Here we report on work using a limited range of sol-gel silicas as porous media, and dodecane, water, tetradecane, cyclohexane, and hexadecane as probe liquids. Further data will be published later.

2. Methods

2.1 Bulk Nano-Metrology of porous structure

There are a range of techniques to probe the dimensions of pores. Lab-Tools has been developing scattering techniques using neutrons for nano-metrology since 1995 [1], has being developing NMR cryoporometry [2,4] since 1992, and neutron diffraction cryoporometry [5] since 2003. These offer complementary methods of determining the pore structure information pore-size distribution, surface area and pore volume.

2.2 NMR Cryoporometry

Neutron scattering [1] and NMR Cryoporometry (NMRC) [2,3,4,9,10,11,12] are now important methods for determining pore sizes in porous media. It is here shown that NMRC can also be used to probe the fraction of the geometric pore volume that can be directly accessed by a given liquid.

Josiah Willward Gibbs and three different Thomsons [2,3] applied thermodynamics, generalised dynamics and experiment to produce an equation that well describes the phase-change behaviour of liquids in confined geometry. At MRPM6 a development of the Gibbs-Thomson equation was discussed [11], that relates these phase changes so that the pore area a_p and volume v_p are related to the melting point depression {K} :

$$\Delta T_m = T_m - T_m(x) \approx \frac{a_p}{v_p}\frac{\sigma_{sl} T_m \cos(\varphi)}{\Delta H_f \rho_s} \approx \frac{k_d \sigma_{sl} T_m}{x \Delta H_f \rho_s}, \tag{1}$$

where for pore diameter x, kd is the geometry term, and equals to four for a spherical liquid-crystalline interface (conventionally assumed for cylindrical pores). T_m is the bulk melting point and the other terms are thermodynamic and density terms.

For many purposes this may be simplified [4] to a melting point depression {K} equals to

$$\Delta T_m = \frac{k_{GT}}{x}, \tag{2}$$

where we are grouping all the thermodynamic terms into a single constant, k_{GT} {K.Å} - the Gibbs-Thomson coefficient - usually established by experiment. In Figure 5, the Gibbs-Thomson Coefficients k_{GT} are calculated from the slopes of the plotted lines of melting point depression vs inverse nominal pore diameter. The calibration as in this case is usually based on nominal pore diameter x from gas-adsorption measurements, however we now have a nano-calibration program in hand, to base them on neutron scattering data [1].

Cryoporometry can also be used to show the relative pore volumes occupied by two liquids simultaneously as one liquid displaces another from the pores [13], a process that is very relevant to oil recovery.

3. Experimental

3.1 NMR Cryoporometry Protocol

The protocol of an NMR Cryoporometry experiment involves absorbing a liquid into pores; freezing the liquid, and then warming the sample. The NMR signal amplitude is monitored, so as to determine the amount of liquid that has melted as a function of temperature. This gives a measure of the pore volume vs. melting temperature, and hence, via the Gibbs-Thomson equation, the pore size distribution. Figure 1 shows data from an example warming curve.

3.2 Apparatus

The NMR cryoporometric instrumentation uses an NMR spectrometer that has been specifically designed to have unusually precise and wide range temperature control.

3.21 NMR Spectrometer

The NMR spectrometer is a solid-state NMR spectrometer, originally designed and implemented from about 1972 to 1990, at the University of Kent [3]. This design has a digital-switching transmitter with an unusually fast recovery (active quench plus active damping). This provides an approximately 3μs π/2 pulse for protons with a 5mm diameter tube sample (B_1 ~6mT). The receiver employs sub-nano-Volt dual-gate FETs at the front-end for low noise, and can be used in hardware phase-lock loop mode. A number of copies were sold nationally and internationally, up six being used simultaneously at Kent by research students over a number of decades. Built-in electrical control of a number of parameters is now used for both manual and software computer control such as fine tuning, frequency locking and sample locking.

3.22 Temperature control and Measurement

NMR Cryoporometry ideally needs very well controlled wide-range temperature ramps (typically up to ~100K to ~350K). The temperature measurement needs to reflect as true a temperature measurement of the sample as possible, and this apparatus is currently believed to give a precision better than 10mK. The design of the NMR Cryoporometric probe has evolved over two decades, since the origin of NMR Cryoporometry [4]. Cooling methods employed have included direct injection of liquid nitrogen droplets (Lindacot Cooling [14]), liquid nitrogen gas evaporating from a Dewar, highly dried air bubbled through a liquid nitrogen Dewar, and injected liquid CO_2. Currently while all these methods are still available, the main cooling method now used is Peltier (thermoelectric) cooling. This has the advantage of negligible running costs, superb computer controllability, no cryogenic gasses, and the ability to do daily 24 hour measurements, sometimes back-to back over a number of days, for multi-ramp protocols [12], or over weeks for gas-hydrate measurements at pressure [15].

3.3 Samples

The samples used in this particular study were all porous sol-gel silicas. The nominal 60Å, 100Å, 200Å, 500Å pore diameter samples were prepared by Dr. D. Ward of Unilever, the nominal 100Å pore diameter sample supplied by Sigma Aldrich. Gas adsorption pore diameter calibration measurements have been made on them using three different instruments. However the scatter in those measurements is considerably higher than the scatter now obtained by NMR cryoporometry using the current apparatus. The samples were prepared in the measurement tubes, and dried over night at 120C, before liquid being added and being flame sealed [3].

The cryoporometric probe liquids used in this particular study were: dodecane, water, tetradecane, cyclohexane, and hexadecane, with significantly different overall size, and melting points ranging from nearly -10C to +20C.

The sample were prepared in standard 3mm economy NMR tubes (~2.5 mm ID) to a length of about 12 mm, to ensure that all the sample was inside the NMR receiver coil. To ensure that liquid did not condense elsewhere in the tube due to temperature gradients, and thus fail to contribute to the measurement, the sample tubes were cut to a length of 35mm, so as to be all inside the isothermal probe cap.

The following weightings were performed so as to obtain fully mass-calibrated Cryoporometric data : Empty tube + cap; Silica + tube + cap; Liquid + silica + tube + cap. The samples were then flame-sealed [3], and weighed again, acting both as additional identification and for long-term stability monitoring.

4. Results

4.1 A typical measurement.

See figure 1, for Hexadecane in100 Å nominal pore-diameter sol-gel silica. The melting event in the pores at about +10 C can be seen, followed by a plateau that gives the effective pore volume for hexadecane in the pores, followed by a further melting event as the bulk liquid outside the grains melts at +18 C.

Experiments have been performed using a range of liquids particularly relevant to catalysis work, in a number of porous materials. However some of this is still privileged data, so this set of experiments were performed for publication using common liquids and sol-gel silicas :

Table.1. Bulk Melting Points for water and 4 organic liquids.

	Dodecane	**Water**	**Tetradecane**	**Cyclohexane**	**Hexadecane**
Bulk Melting Point C°	-9.6	0	5.69	6.5	18.05

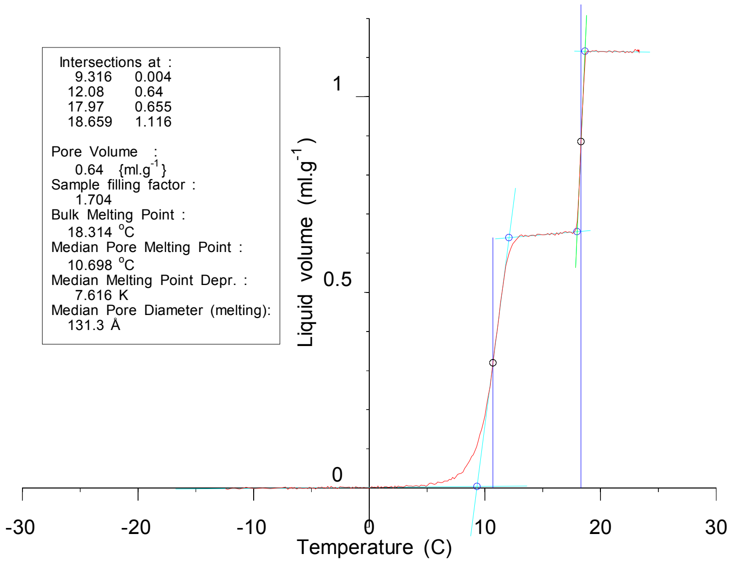

Fig.1. Melting curve for Hexadecane in sol-gel silica with a nominal pore diameter of 100 Å.

4.2 Calibration of the Gibbs-Thomson Coefficient

The most straight forward method of determining the Gibbs-Thomson coefficient for a liquid is to measure the melting point depression experienced by the liquid in a series of mono-modal porous materials of differing pore diameter. This calibration has been performed in the past for water and cyclohexane [2,3,9,10,12], using up to 10 different porous silicas ranging from 25Å to 500Å pore diameter. This data and recent even more precise experiments have resulted in a situation where the scatter in the data from a set of cryoporometric experiments using these Gibbs-Thomson coefficients for water and cyclohexane is far smaller than the scatter from the original gas adsorption data. Thus best-fit pore diameters for a set of five sol-gel silicas have been derived :

Table.2. Pore diameters for a set of 5 sol-gel silicas.

Nominal (Å)	Best-Fit (Å)
500	464.9
200	150.9
100	89.1
60	57

A set of calibration experiments are shown in figure 2, where melting curves can be seen for the alkane dodecane in sol-gel silicas with nominal pore diameter of 60 Å (red), 100 Å (green), 200 Å (blue) & 500Å (cyan).

Repeating these experiments for the other liquids in table 1 gives figure 3 and table 3 :

Table.3. Bulk Melting Points and Gibbs-Thomson Coefficients k_{GT} for water and four organic liquids.

	Dodecane	Water	Tetradecane	Cyclohexane	Hexadecane
Bulk Melting Point (C°)	-9.6	0.00	5.69	6.5	18.05
$\mathbf{k_{GT}}$ (K.Å)	805	580	781	1592	652

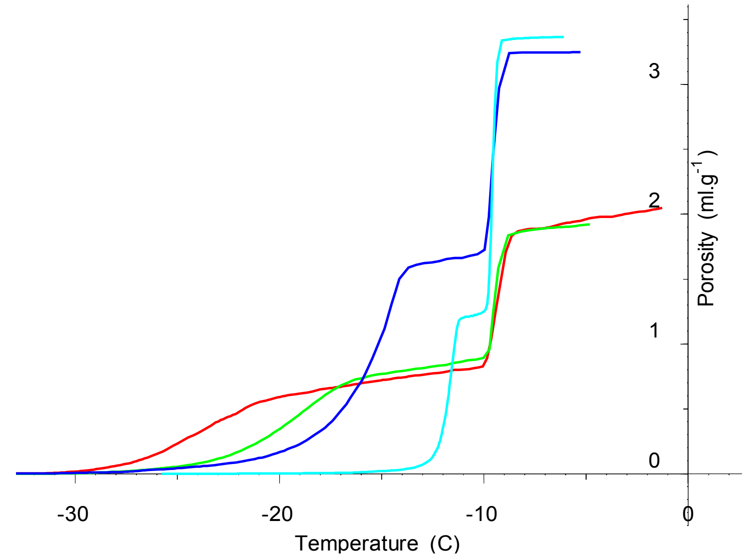

Fig.2. Melting curves for Dodecane in sol-gel silicas with nominal pore diameters of about 60 Å (red), 100 Å (green), 200 Å (blue) & 500Å (cyan).

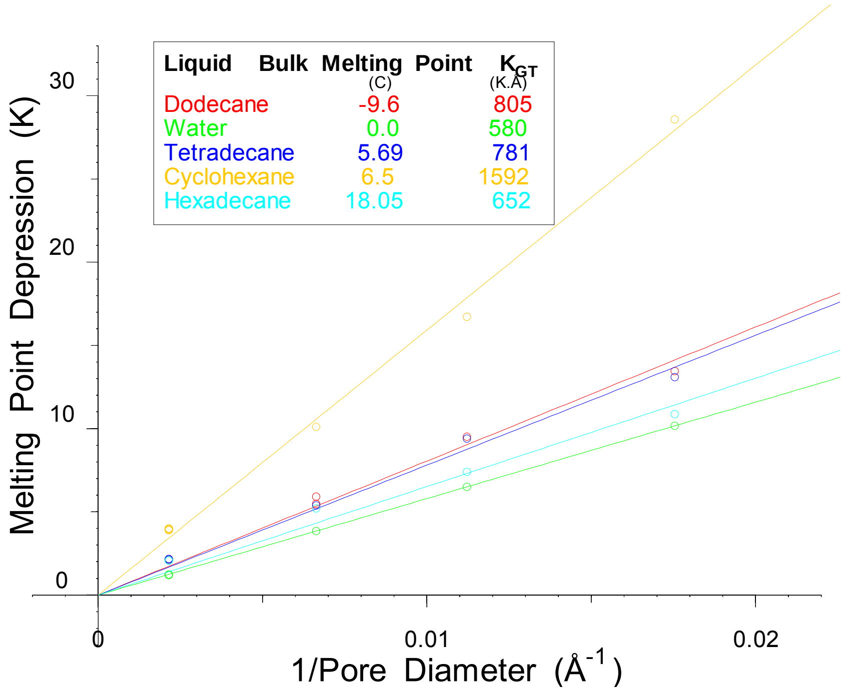

Fig.3. Melting Point Depressions for 5 liquids in 4 sol-gel silicas, with Gibbs-Thomson Coefficients k_{GT} calculated from the slopes.

4.3 Measurement of Pore Volumes and Filling Factors.

For each liquid, as per for Figure 2, fitting the segments of the measured data set for all the above sol-gel silicas and liquids, as demonstrated for one case in Figure 1, allows both the observed pore volumes and the normalised reduction in pore volume to be obtained.

The Peltier cooler was used for all these measurements, for its high controllability with some additional liquid CO_2 cooling used to reach lower temperatures for some of the measurements, and this returned data over the needed range 233K to 296K. Prior measurements using both sol-gels and zeolites for the porous media, as well as both some of the above liquids plus probe liquids particularly relevant to catalysis work, used both Peltier and Lindacot cooling, down to 100K.

5. Discussion

It is the cryoporometric techniques that offer the possibility of directly probing the fraction of a pore that is actually accessible to a probe liquid. This fractional volume has significant impact on the catalytic efficacy of a particular solvent that is used to promote a reaction in the pores. Pore size, pore geometry, pore throat, pore surface material (hydrophilic/hydrophobic) and choice of probe liquid all influence the accessible fraction. By performing a NMR cryoporometric measurement using a particular liquid of interest it is possible to directly access this information, which is of prime importance for catalysis, and financially very significant on an industrial scale.

Figure 2 shows that the pore-plateau volumes (extrapolated to the bulk melting point, as per figure 1) serve as a good measure of the porous pore volume that is accessed by the Dodecane. It can be seen that pore volumes are very different for the different sol-gel silicas. For small pores, such as were explored in the preliminary (industrially funded) measurements, it can be seen there are very significant difference in the accessed pore volumes for different liquids in the same porous material, to the extent that some liquids failed to access the smaller pore sized porous solids..

The differences for most of these liquids in these larger pore sol-gel silicas is much less marked, for all the liquids bar the cyclohexane, and with the exception of the data for the 100 Å pore diameter silica. The 100 Å silica is from a different manufacturer than the other silicas, with different surface properties, as discussed in a prior paper [16]. The water-normalised data for cyclohexane is shown in figure 4, which shows the data for the relative pore volumes accessed by cyclohexane, normalised to the pore volumes accessed by water, is dependent on the pore size. The change is consistent with the cyclohexane having a characteristic diameter of 3.8Å.

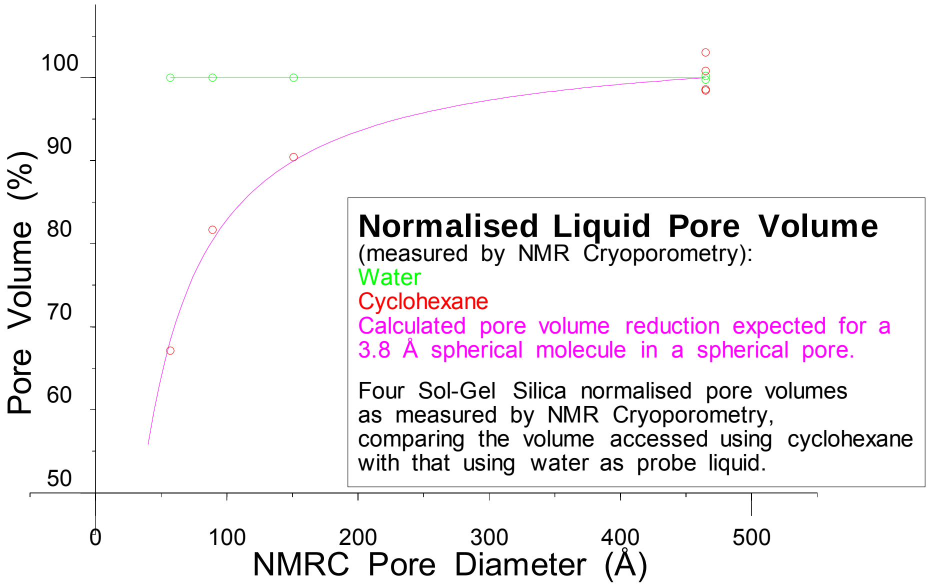

Fig.4. Pore Volume accessed by Cyclohexane, normalised to Water.

6. Conclusions

The main conclusions seem to be that for these relatively large pore size sol-gel silicas, the relevant dimension for the alkanes is their cross-sectional diameter, not their chain length – they appear to be fitting end-wise into the pores, with little effective restriction on accessing the pores.

The cyclohexane seems to be behaving like a spherical molecule, as is well known from prior NMR work. This work indicates that the accessed pore volume appears to be reduced as per a 3.8 Å sphere.

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