Surface Measurement Systems
World Leader in Sorption Science

GenRH Application Note 504

Water Vapor Induced Mesoporous Structure Collapse Observed by GenRH with Mcell and FT-IR

Surface Measurement Systems Ltd.

This application note illustrates how the GenRH and Mcell can be combined with FT-IR microscopy to investigate moisture-induced changes in a serious of mesoporous silicas. Combined with Dynamic Vapor Sorption results, these experiments can further elucidate the mechanisms of water sorption and any induced structural changes.

Introduction

Mesoporous silicas have found much interest since they were first synthesized by the Mobil scientists in 1991 [1]; using the inherent behavior of surfactants to self-assemble into rod-like, lamellar or spherical micelles as a template around which the silica can be formed. These materials have considerable potential for use as catalysts, as such their interactions with, and stability to, a variety of vapors, including water, is of considerable interest.

The GenRH is a novel line of humidity generation products. When combined with an environmental control cell (Mcell), designed to fit under a microscope, samples can be observed by FT-IR, Raman or optical microscopic techniques, under controlled humidity conditions. The GenRH-A instrument is an ambient temperature humidity generator that can deliver a steady stream of air over a wide range of flow rates and humidities.

In this paper we describe this technique, demonstrate the correlation of absorbance of spectral bands versus relative humidity plots to adsorption isotherms and follow in situ, by FT-IR spectroscopy, the interactions of the mesoporous silicas with water vapor. In particular, this study will investigate the minimum RH required to induce structural collapse of the silica structure within the mesoporous silicates, and the effect of different surfactants on the stability to atmospheric humidity.

Method

The GenRH-A consists of; a programmable digital controller with full time closed-loop control, temperature monitoring display, temperature and humidity probe, and a rotameter to control flow volume. A picture of the GenRH-A is shown in Figure 1.

Figure 1. Surface Measurement Systems GenRH-A humidity generator.

To use the GenRH-A efficiently with a microscope, Surface Measurement Systems has developed the Mcell. The sample is mounted into the Mcell, which is fixed to the microscope stage as shown in Figure 2. This stage has double-glazed top and bottom windows, allowing both transmission and reflection illumination of the sample while minimizing heat loss through the windows when being used under non-ambient conditions.

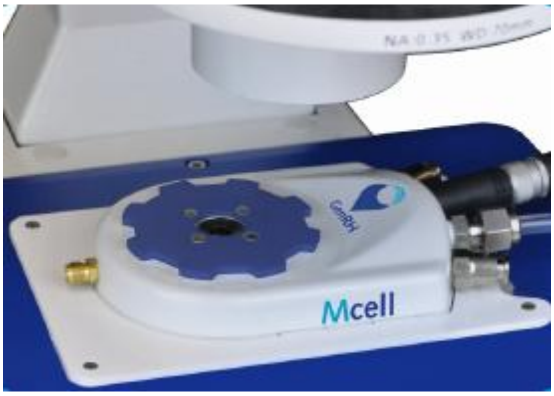


Figure 2. SMS Mcell microscope accessory for the GenRH line of products.

Small amounts of each of the three samples used for the study were placed on a slide within the cell. The automatic xy locator stage of the microscope was employed first to choose appropriate particles providing sufficiently good spectra, and secondly to allow multisampling within the cell. The samples were equilibrated at the appropriate RH for 20 min., the co-ordinates of each particle entered and the spectra collected in turn, enabling all spectral data presented herein to be collected within two, five-hour sessions.

The materials chosen for the study were based on the mesoporous (pore diameter within the range 2-10 nm) silicas, which are prepared by a template-assisted route, in which a silica source, a structure-directing surfactant and water are all present. The surfactant is dissolved in water forming a hexagonal H_1 phase and the silicate gel formed around the micellar array via a sol-gel condensation of $Si(OMe)_4$. The subsequent calcination step serves to remove the organic part of the surfactant, calcine the silica and oxidize the metal complex, leaving a catalytic species on the surface of the pore walls.

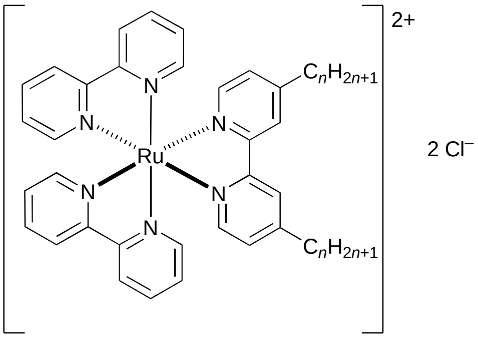


Figure 3. Templating surfactant, n = 19, Ru(bipy)$_2$(4,4’-di nonadecylbipy)]Cl$_2$.

Samples chosen for this study were MCM-41 prepared via a low-concentration route as described by Mobil, [1] a Ru-containing silicate (sample C)prepared as described above using true liquid crystal templating [1-3] and a similar sample from which the Ru surfactant has been removed by washing (sample W). Details of the three samples are given in Table 1.

Table 1. Sample properties.

Samples	BET Surface Area [m^2/g]	BET Pore Diameter [Å]
MCM-41	1301	26.6
Sample C	823	27.7
Sample W	1030	27.3

In order to establish appropriate humidity windows for study, DVS water vapor sorption/desorption isotherms were collected on each of the three mesoporous materials at 25 °C.

For the GenRH study, increasing RH steps of 5 or 10 % RH were chosen, dependent on the gradient obtained from the water isotherm measurements using the gravimetric Dynamic Vapor Sorption instrument (DVS). For MCM-41, data from only one particle were collected. For sample W, data from two particles were collected one ’thick’, one ‘thin’ (thus designated by visual assessment of the particles). For sample C, data were collected from two samples, one particle (’particle’) and a film (‘film’) formed via compression of the powder sample.

IR spectra were measured at Imperial College London using IFS66/S FT-IR spectrometer combined with IR microscope IRscopeII (Bruker Optics) with MCT detector. Spectra were measured with a spectral resolution of 2 cm^{-1} and 50 scans co-addition.

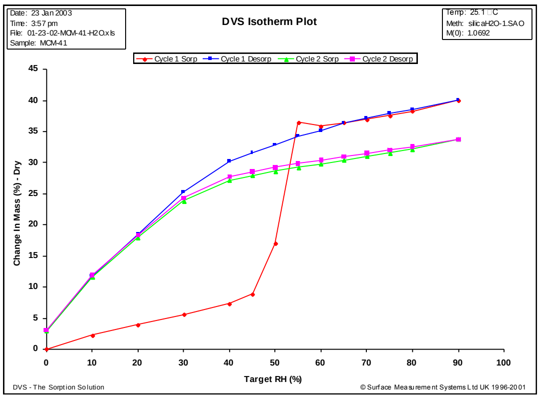
Results

DVS Data

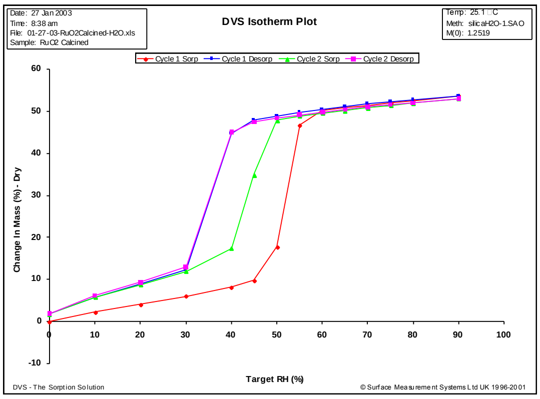
The DVS data are presented in detail in Figure 4, where it clearly shows that each of the three mesoporous samples behave differently. MCM-41 has three notable features, the first of which is the irreversible transition that occurs on the first adsorption cycle at approximately 55 %RH. The second is a lower adsorption of water vapor on the second cycle, whilst the third is the change in isotherm type, induced by the irreversible transition. The approximate shape of the initial section of the isotherm, on the first adsorption isotherm is Type IV (mesoporous), whilst the corresponding de-sorption run and subsequent ad- and de-sorption cycle could better be described by a Type I isotherm (microporous). This combined with the irreversible transition that occurs on the 1st adsorption cycle implies that adsorption of water vapor induces a collapse of the mesoporous structure in this material.

Sample C in contrast shows a reversible Type IV isotherm on both sorption cycles, with a greater hysteresis on the first cycle. The main point of note in this case is that some of the water sorbed in the first cycle remains within the pores, and is not removed even after extensive drying is not removed.

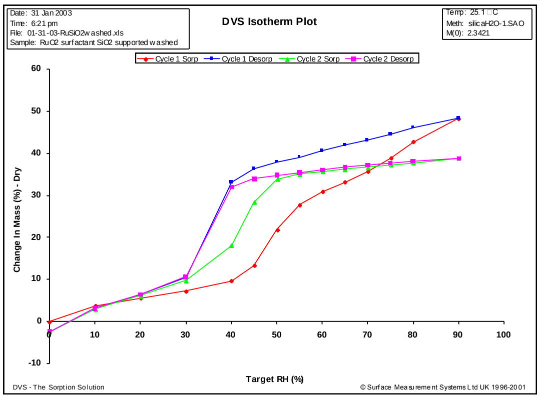
Sample W also behaves uniquely, the first adsorption run shows two regions of high water uptake, at approximately 50% and again, to a slightly lesser extent at approximately 75%. This first cycle shows considerable hysteresis, whilst on the second cycle the hysteresis is both reduced and the isotherm shape changes to a more typical Type IV isotherm. The second noteworthy point is the decrease in the maximum amount adsorbed in each cycle.



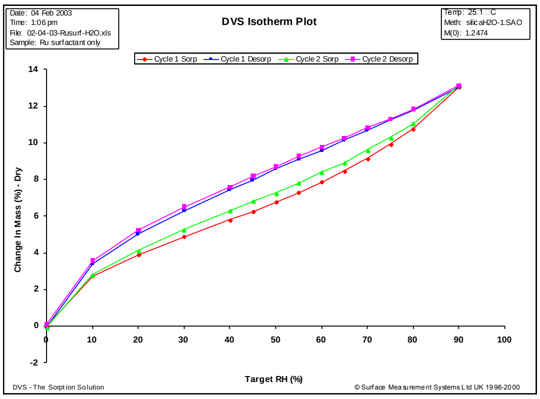
(a.)



(b.)



(c.)



(d.)

Figure 4. DVS Sorption data; MCM-41 (a.), Sample C (b.) Sample W (c.), and surfactant, [Ru(bipy)$_2$(4,4'-dinonadecylbipy)]Cl$_2$ (d.). In each case red=1st adsorption, blue=1st desorption, green=2nd adsorption, pink=2nd desorption.

Spectral Data

MCM-41

Based on the DVS data, spectra were collected within the range of most rapid increase in water uptake, and with the humidity steps as labeled in Figure 5 at 40%, 50%, 55%, 60%, 65%, 70% and 80% RH on the (increasing RH side), while decreasing RH measurements were taken at 60% and 0% RH. The principal spectral absorbance bands can be assigned as the following: at 3723 cm^{-1} - the non- hydrogen-bonded Si-OH, the region 3500 – 3300 cm^{-1} is comprised of the anti-symmetric stretching band of water (ν_3) and symmetric stretching band (ν_1). These bands broaden due to the effect of H-bonding of water molecules either with other water molecules or other basic or acidic sites in the sample. There is also a strong coupling between ν_3 and ν_1 modes. The band at 1631 cm-1 corresponds to the water bending mode (□2), the region 1241–1075 cm^{-1} to the bulk Si-O-Si modes, at 956 cm-1 the Si-O stretch of Si-OH, and at 788 cm^{-1} the O-Si-O stretching mode.

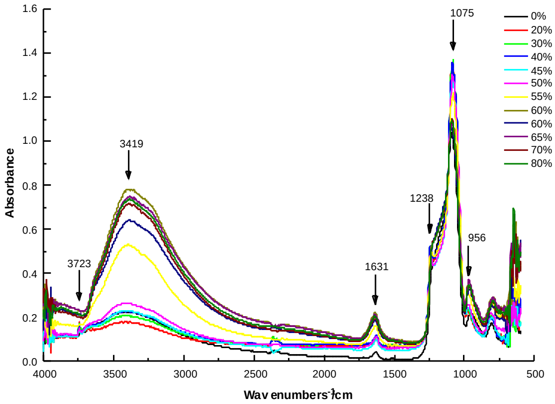


Figure 5. IR spectra of MCM-41 adsorption of water vapor, first exposure to water vapor, note change in peak shape at 1075 and 1241 wave numbers.

A simple examination of Figure 5 shows a number of changes occurring as RH is varied; specifically the loss of the band at 3723 cm^{-1}, the absorbance increase in the region 3500 – 3300 cm^{-1} and the change in both absorbance and band shape in the region 1240 – 1090 cm^{-1}.

The decrease and gradual disappearance by 55% RH of the band at 3723 cm^{-1} which corresponds to the non-hydrogen bonded Si-OH stretch, and suggests that before a sufficiently high RH level to induce high water adsorption is reached, there is an appreciable coverage of water molecules on the surface. This band reappears again after desorption at 0% RH, suggesting both that these surface silanols exist even after the collapse of the mesoporous structure. The second spectral feature is the increase in absorbance within the water O–H stretching region at 3500 – 3300 cm^{-1}. The peak of greatest absorbance remains centered at 3419 cm^{-1}, and a plot of absorbance versus RH at this wave number (Figure 6 - this these data had have been corrected relative to the absorbance at 1348 cm^{-1}) follows the shape of the DVS sorption isotherm, but is shifted to approximately 5% greater RH relative to the DVS isotherm. The similarity between Figure 6 and the DVS isotherm includes even the sudden decrease at around 60% RH. This decrease corresponds to the loss of water from the system, and can be used as a means of correlating the data available in other regions of the spectra to the information available within the DVS isotherm. This suggests that this kind of plot can be used to provide a quick, qualitative guide to the vapor isotherm shape, as this complete data set was collected in one afternoon.

A more subtle change in this region is that between the spectra at 0% RH and those at higher RH values, where there is a slight red-shift in the wave number of greatest peak intensity for the water O–H stretching region. This feature reflects the nature of the different water species present. These species include those molecules trapped within the amorphous bulk SiO_2 (at low RH), and those adsorbed onto the pore surface, either as monomeric water species, or as extended hydrogen-bonded extended networks of water molecules (at intermediate and high RH levels, respectively). Whilst it is possible to model the data to obtain precise information on the ice/liquid nature of the water molecules on the surface of the pores, it is sufficient for the purposes of this study to say that it is likely that both monomeric water molecules and trimers/tetramers exist at the pore surface at higher RH levels.

The third region to be considered is that of 1290 - 1090 cm^{-1}, corresponding to the bulk Si-O modes. At low RH there are two distinct bands at 1240 and 1090 cm^{-1}, which start to lose their distinct identity at 50% RH. They broaden, decrease in absorbance and the band at 1240 cm^{-1} develops into a shoulder of the band at 1090 cm^{-1}. This coalescence and slight broadening of these bands indicates an increase in the amorphous nature of the bonding, most likely arising from a partial collapse of the mesoporous structure of the material, as MCM-type materials are known to be relatively unstable. This in turn is consistent with a reduction in the absorbance of the O–H stretching band corresponding to the stretching modes of water at 3500 – 3300 cm-1, a reduction in the surface area available for sorption, and the change in the DVS sorption isotherm shape.

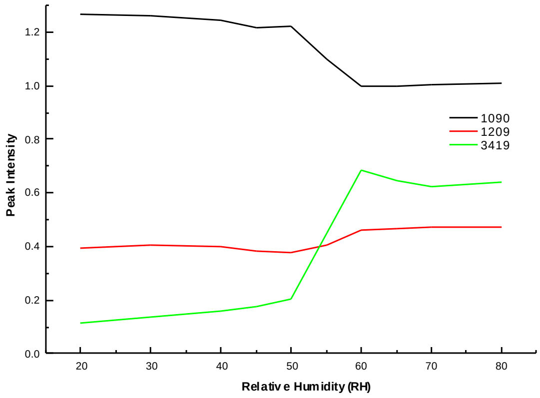
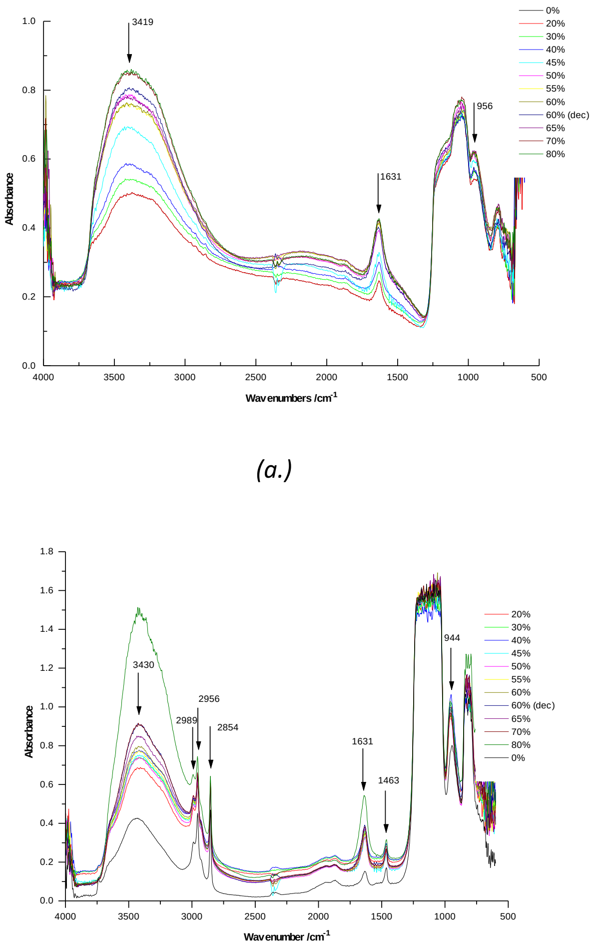


Figure 6. Absorbance/RH plot for 3419, 1090 and 1209 cm^{-1} (obtained from Figure 5), corrected relative to absorbance of the sample at 1348 cm^{-1}.

Sample W

Two sets of spectra were collected for the washed material from particles of two different thicknesses, one from a 'Thin' (Figure 7a) and one from a relatively 'Thick' particle (Figure 7b). The 'Thin' particle gave bands at 3400 cm^{-1}, 1623 cm^{-1}, the region 1250 – 1040 cm^{-1} and at 943 cm^{-1}, which can be assigned to the stretching modes of water the, bending mode of water, the bulk Si-O bulk modes and as Si-OH stretches, respectively. In addition to these modes the 'Thick' particle also gives bands at 2958, 2852, 1914, 1845 and 1459 cm^{-1}, of which the bands at 2958, 2852 and 1459 cm^{-1} can be assigned to the C-H and C-OH stretches of ethanol (used to wash the material), whilst the bands at 1914 and 1845. cm^{-1} can be assigned to the templating agent. This difference between the two spectra can be attributed to the difficulty of removing ethanol from pores deep within the larger particles.

Notable by its absence in both sets of spectra is the non-hydrogen bonded Si-OH stretch at 3745 cm^{-1}, implying that in this washed material all surface silanols are hydrogen bonded to surface water (or ethanol in the case of the 'Thick' particle).



(a.)

(b.)

Figure 7. IR spectra, adsorption of water vapor for washed thin (a.) and thick (b.) samples.

As discussed for MCM-41 above, the region of greatest variation with RH is the water O–H stretch region. The absorbance/RH plot of the above data of both particles for the absorbance at 3419 cm^{-1} is shown in Figure 8, The thin particle has a steep adsorption increase at 50% whilst for the thick particle this occurs at 75% RH, although individually neither of these curves accurately reflect the DVS isotherm (Figure 3), by simple observation and comparison of the data, it is obvious that a weighted sum of the two curves would give the DVS isotherm. Such a weighting parameter would therefore provide a measure of the relative amounts of the two types of particles within the bulk, and provide detailed information on how bulk measurements correspond to the real situation on the molecular level.

There are no obvious changes in either set of spectra corresponding to the Si-O stretching bands, indicating that there are no significant changes within the silica structure induced by water vapor adsorption.

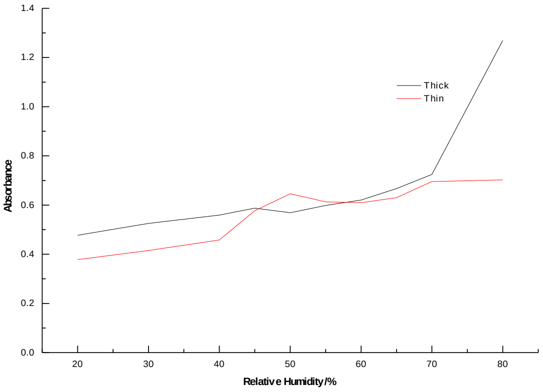
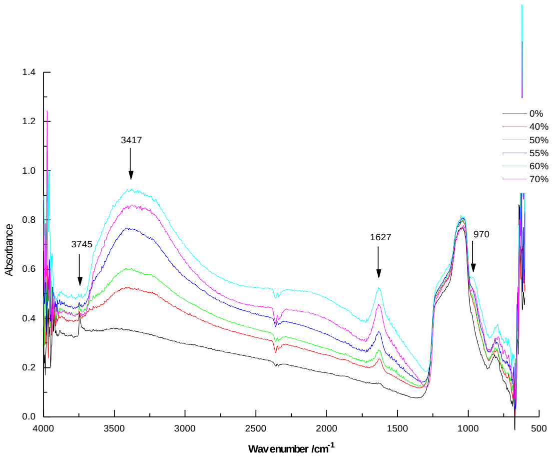


Figure 8. Comparison of absorbance of the band at 3419 cm^{-1} for thick and thin samples of sample W, washed mesoporous silicas.

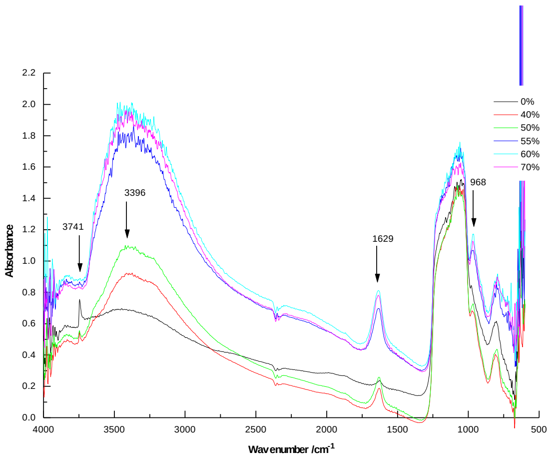
Sample C

The DVS data for this material (Figure 3) shows a type IV isotherm with the region of greatest adsorption being within the range 30 - 60 % RH. Spectral data were collected for both a single particle, and a film formed by compressing the powdered material, to investigate any changes this might cause. Spectra were recorded for both adsorption (Figures 9a and 9b) and desorption (Figures 9c and 9d) at the RH values stated. As can be observed, there is little difference between the spectra of the particle and film, with peak assignments the same as already discussed for MCM-41. The overall intensity of the peaks is greater for the film than the particle as is expected when observing transmission spectra through a thicker sample. Again as with MCM-41 the principal change induced by increasing RH is an increase in the intensity of the water absorption band at around 3400 cm^{-1}, corresponding to water adsorbed onto the surface of the material.

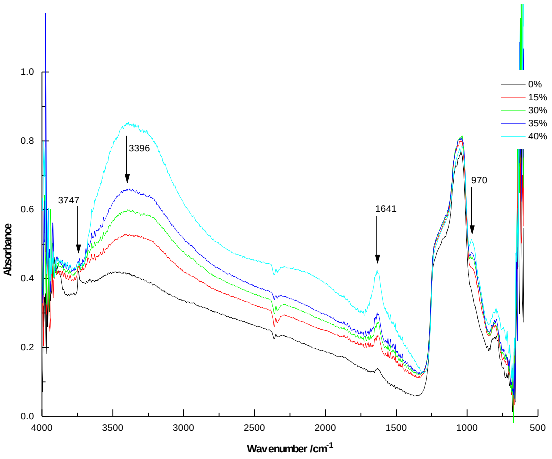
As with the MCM-41 sample the peak due to hydrogen-bonded surface silanols (3741 cm^{-1}) decreased as soon as the water vapor started to adsorb appreciably, whilst the Si-OH band increases increased in intensity as water vapor adsorbed.



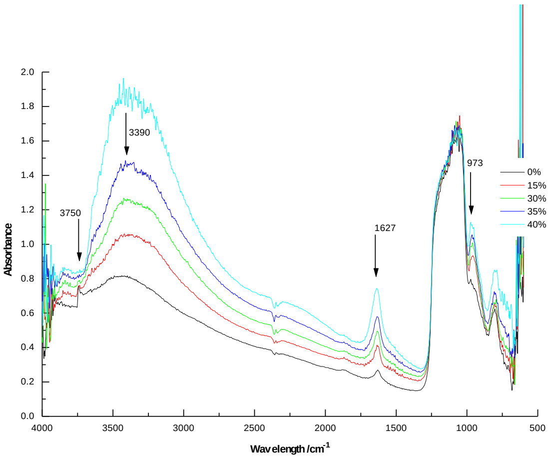
(a.)



(b.)



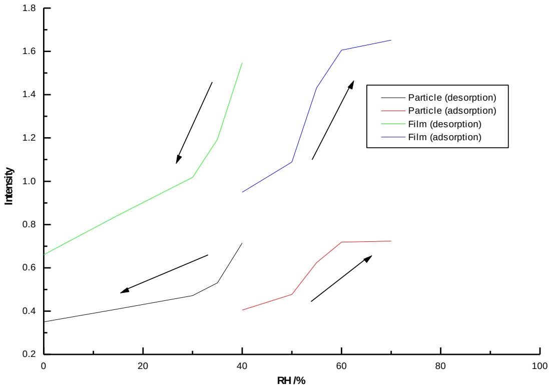
(c.)



(d.)

Figure 9. IR spectra, adsorption of water Sample C particle (a.) and film (b.) samples. IR spectra, desorption of water Sample C particle (c.) and film (d.) samples.

The plot of absorbance versus RH for both samples is shown in Figure 10, and shows two isotherms closely resembling the DVS data. The regions of greatest gradient occur at the same RH values and the hysteresis is the same in both samples.



(d.)

Figure 10. Comparison of Absorbance/RH plots for water absorption band at 3417 wave numbers for Sample C as a particle (red and black) and a film (blue and green).

Conclusion

This study indicates how the GenRH and Mcell can be combined with IR spectroscopy to identify changes occurring within the solid and also demonstrates the observation of different states of individual particles, giving an indication of the variety of states present and their approximate populations rather than a bulk averaging of all states present. Also demonstrated is the application of the GenRH to quickly generate qualitative sorption isotherms and their correlation to those obtained by DVS.

Acknowledgement:

The Authors would like to thank Duncan Bruce and Nicola King at University of Exeter, School of Chemistry for the generous supply of the three silica samples. Also, special thanks to H. Jervis formerly with SMS and S. Kazarian and A. Chan from Imperial College London for their contributions and supplying the experimental data.

References

[1] C. T. Kresge, M. E., Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, Nature (London), 359 (1992) 710.

[2] T. Lopez, L. Herrera, J. Mendez-Vivar, P. Bosch, R. Gomez, R. D. Gonzalez, J. Non-Cryst. Solids, 147&148, (1992) 773.

[3] N. Igarashi, K. A. Koyano, Y. Tanaka, S. Nakata, K. Hashimoto, T. Tatsumi, Micropor. Mesopor. Mater., 2003 59, 43-52.