Determination of Mesopore Size Distribution by Organic Vapour Sorption

Dan Burnett and Frank Thielmann, Surface Measurement Systems Ltd.

Alumina samples have been investigated by organic vapour sorption. Mesoporous structures were studied and pore size distributions have been calculated based on octane adsorption experiments at ambient conditions. The results were in good agreement with standard low temperature nitrogen adsorption measurements.

Introduction

Surface area and porosity are important parameters regarding industrial applications and performance of many materials [1]. According to the IUPAC classification one can distinguish three different types of pores: micro-, meso- and macropores [2]. They can be classified by pore diameter as shown in Table 1.

Table 1: Pore classification according to IUPAC

Type	Diameter
Micropores	< 2.0 nm
Mesopores	2.0 - 50 nm
Macropores	> 50 nm

In order to gain a better understanding of how different pores can affect product properties a knowledge of the pore size distribution is required. A standard method for the determination of micro- and mesopores size distributions is volumetric nitrogen adsorption measurements at 77 K [2]. Macroporosity is not measurable by gas sorption and is usually obtained from mercury porosimetry [3] or Inverse Size Exclusion Chromatography [4]. An alternative to nitrogen adsorption at 77 K is dynamic sorption at ambient conditions using non-polar organic vapours. This approach has several benefits, especially for organic solids such as pharmaceutical and food materials: organic solids are usually non-rigid meaning that they can change their surface properties when exposed to vacuum. Moreover, experiments at ambient temperature are closer to real world temperatures while materials at 77 K might behave differently. This paper describes the use of non-polar organic solvents for the determination of the mesopores size distribution. Mesoporous alumina has been chosen as a test material.

Theory

Classical mesopores size distribution calculations are based on the analysis of the desorption branch of a type IV isotherm. The most common methods utilise the BJH theory (Barrett, Joyner and Helanda, 1951) [5]. It assumes a mono-/multilayer formation in the mesopores and subsequent capillary condensation. This mechanism is illustrated below in Figure 1.
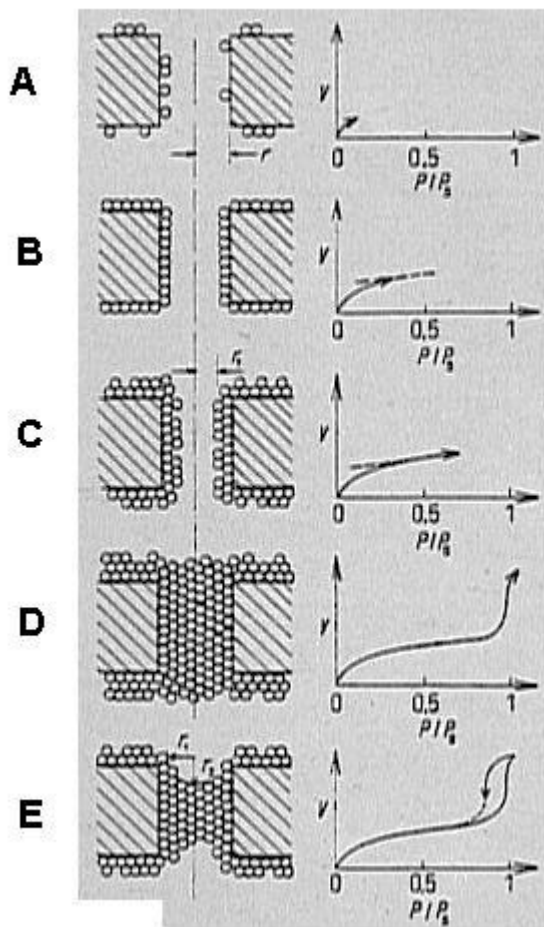
Figure 1. Capillary condensation and course of adsorption and desorption isotherms depending on the partial pressure (from [6]).

The capillary condensation process can be described by the Kelvin equation. This equation relates the shape of the pore structure and the partial pressure where condensation/evaporation of vapour occurs.

$$\ln(p/po) = \frac{-2\gamma V \cos\Theta}{RTr_k} \qquad (1)$$

In equation 1 γ is the surface tension of the vapour, V the molecular volume of the condensed phase, Θ the contact angle between adsorbed and solid phase, R the gas constant, T the absolute temperature and r_k the mean radius of the liquid meniscus. Assuming a cylindrical pore shape the pore volume V_P can be calculated if the thickness t of an adsorbed layer is known, as shown below:

$$V_P = V_K \left(\frac{r_k + t}{r_k}\right)^2 \qquad (2)$$

where V_K the volume of the condensed probe. The thickness of the adsorbed layer is related to the partial pressure by the t-Plot [2]. The t-plot compares the probe molecule uptake on a the surface under investigation with a standard, non-porous surface. If the measured material is non-porous a straight line is obtained in the t-plot, while for a mesoporous solid a positive deviation (upward from linear) is expected.

There is a wide variety of different approaches based on the equations above. In this paper the method described in ASTM 4641-88 was applied and modified for the use with organic vapours.

Method

Dynamic vapour sorption (DVS) is a well-established method for the determination of vapour sorption isotherms. The DVS instrument used for these studies measures the uptake and loss of vapour gravimetrically using a SMS Ultrabalance with a mass resolution of ±0.1 µg. The high mass resolution and excellent baseline stability allow the instrument to measure the adsorption and desorption of very small amounts of probe molecule. The vapour partial pressure around the sample is controlled by mixing saturated and dry carrier gas streams using electronic mass flow controllers. The temperature is maintained constant ±0.1 °C, by enclosing the entire system in a temperature-controlled incubator.

Two alumina samples have been used in this study. The non-porous reference sample was Alumina C, a flame-hydrolysed γ-alumina, supplied by Degussa, Germany. The mesoporous sample was obtained by agglomeration in water. For this purpose a 100 ml glass bottle was filled with Alumina C up to the 100 ml marker and then topped with deionised water. The bottle was then closed with a screw cap and shaken until a homogeneous suspension was obtained. The cap was removed and the bottle placed into a 60 C

warm incubator. After the evaporation of water the remaining cake was ground.

Octane (HPLC Grade), supplied by Aldrich was used as a non-polar organic vapour.

For the DVS experiments, 6 mg of an alumina sample was placed into a DVS sample pan and dried under a stream of dry nitrogen at 25 °C. Then, the octane concentration was increased in 1% steps up to 10% p/po and in 10% steps to 90% p/po. A final increase was made from 90% to 95% p/po. The octane concentration was decreased in a similar fashion for the desorption phase. The pore size distribution has been calculated using the SMS Isotherm Software v1.1.

Results

When Alumina C is suspended in water and then dried agglomeration occurs and the voids between primary particles can form a mesoporous system. To prove this octane sorption measurements have been carried out on Alumina C and the agglomerated form. Sorption isotherms are shown in Figure 2 (for Alumina C) and Figure 3 (for the agglomerate).
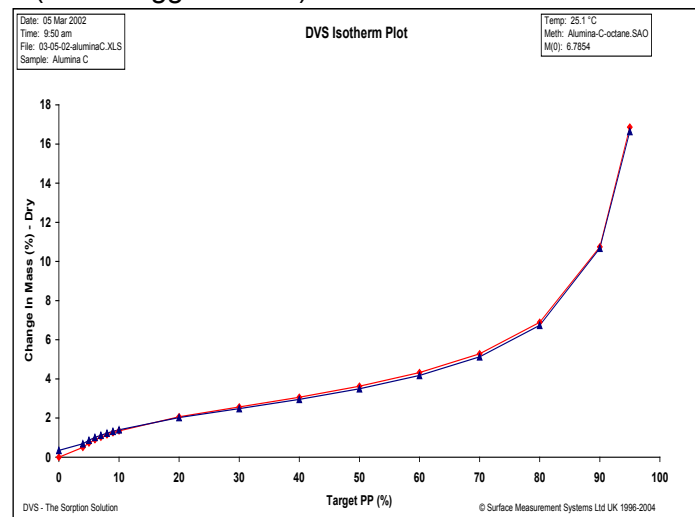

Figure 2. Adsorption and desorption isotherms of octane on non-porous Alumina C (adsorption in red and desorption in blue) at 25 °C.
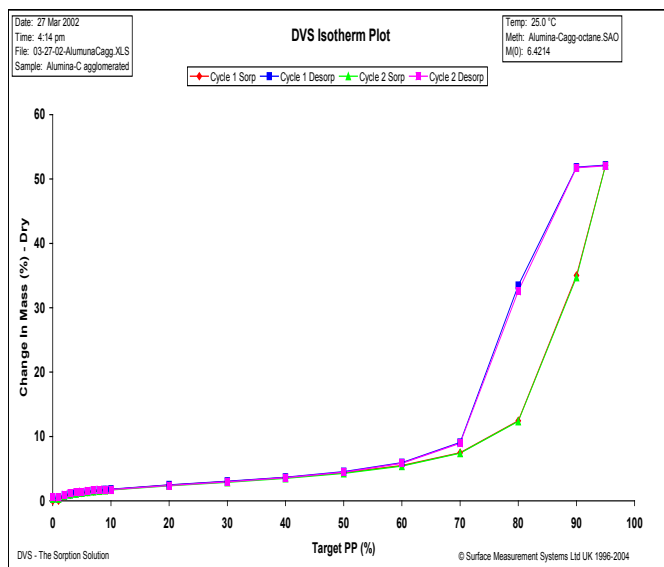

Figure 3. Adsorption and desorption isotherms of octane on agglomerated alumina (first cycle in red and blue, second cycle in green and pink at 25 °C).

As expected the isotherm shape is type II for the Alumina C and type IV for the agglomerate. For a detailed discussion of isotherm shapes and mechanisms see Application Notes 26 and 37. Figure 4 shows the resulting t-Plot of the agglomerate. A clear positive deviation from linearity can be seen which confirms the mesoporous structure of the agglomerate sample.
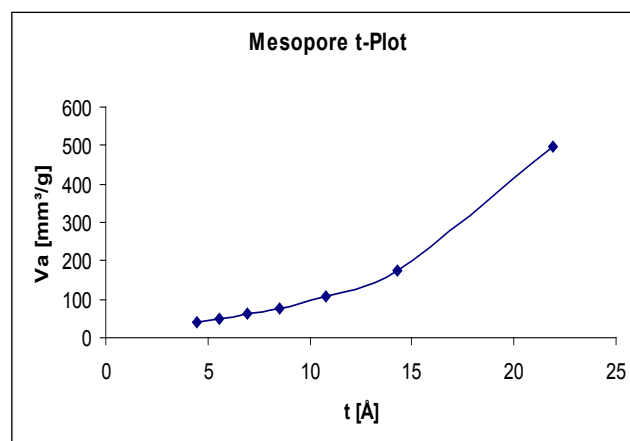

Figure 4. t-Plot for the agglomerated alumina sample.

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Based on the calculation described above the mesopores size distribution for the agglomerate has been calculated taking non-porous Alumina C as a reference. Figure 5 shows the resulting mesopores size distribution (by radius).
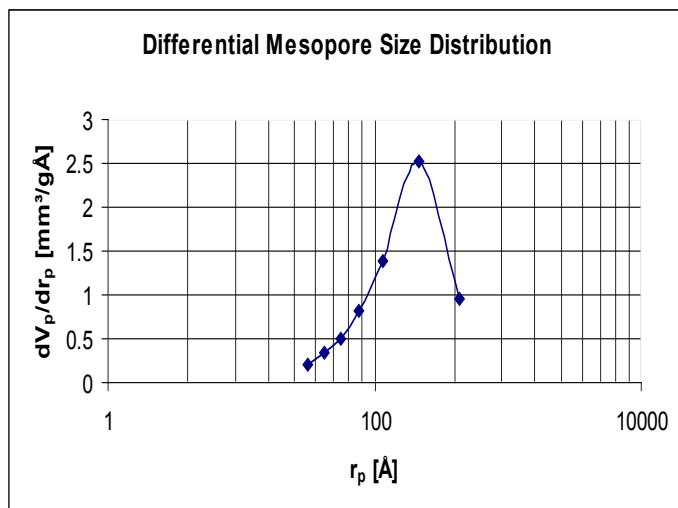
Differential Mesopore Size Distribution

Figure 5. Mesopore size distribution of agglomerated alumina obtained with octane at 25 °C.

The maximum is located at 21 nm (210 Å). This is in good agreement with the value of 18 nm obtained from nitrogen adsorption at 77 K, given the dissimilar measurement conditions and slightly different calculation procedures.

Conclusion

This method provides reliable, accurate and independent validation of RH generation and measurement in DVS water sorption instrumentation.

References

[1]Brunauer, S, Deming, L., Deming, W. and Teller, E., J. Amer. Chem. Soc. 62 (1940), 1732.
[2]Gregg, S. and Sing, K., Adsorption, Surface Area and Porosity, 2nd edition, Academic Press, NY (1982).
[3]Joyner, L. et al, J. Amer. Chem. Soc. 73 (1951), 3155
[4]Al-Bokari, M. Et al, J. Chromatogr. A 975 (2002), 275
[5]Barrett, E. et al, J. Amer. Chem. Soc. 73 (1951), 373
[6]Orr, C., Chem. Ing. Techn. 48 (1976), 680