Characterisation of Microporous Materials by Finite Concentration Inverse Gas Chromatography

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Finite concentration IGC SEA is a useful tool for the investigation of surface and pore properties. A novel combination of finite concentration IGC SEA and thermal desorption provides the possibility to separate micropore adsorption from surface and mesopore adsorption. This allows the calculation of BET values with physical relevance for highly microporous materials and the consideration of molecular sieve effects.

Introduction

The most versatile surface characterisation methods are based on gas or vapour sorption and these techniques can provide physico-chemical information such as enthalpies, surface energies and diffusion constants but also surface area and pore size distributions.

Vapour and gas sorption measurements can be performed with static or dynamic methods, either of which can provide information on equilibrium behaviour. Furthermore, the measurements can be performed using gravimetric or volumetric based instrumentation. The most common flow methods are inverse gas chromatography (IGC SEA) [1] for volumetric studies and dynamic gravimetric instrumentation [2].

The difference between IGC SEA and conventional analytical gas-solid chromatography is the adsorption of a *known* vapour phase on an *unknown* adsorbent stationary phase (solid state sample). Depending on experiment setup, IGC SEA can be used at finite or infinite dilution concentrations of the vapour (adsorptive). Infinite dilution conditions allow for a high sensitivity in the determination of surface energetics and heat of sorption of particulate materials [3]. With IGC SEA at finite dilution, it is possible to measure sorption isotherms for the determination of surface area and porosity [4]. The benefits of using dynamic techniques are faster equilibrium times at ambient temperatures.

Despite the advantages described above, there is a common problem of both static and dynamic methods in the analysis of highly microporous materials. The adsorption process in the micropores is completely different to the adsorption in the mesopores and on the outer surface area. Whereas the latter can be described by a monolayer mechanism according to the BET equation [5] the adsorption in smaller micropores takes place as a so-called volume filling process [6]. This means an immediate condensation of the vapour due to an enhanced adsorption potential caused by an overlap of potential fields of close adjacent pore walls.

This means that BET values calculated from isotherms of highly microporous materials have no physical meaning because the assumed sorption mechanism is inappropriate. In such cases a separate consideration of the mono and multilayer sorption and the micropore contribution becomes necessary.

Method

Calculation of the isotherm can be performed by the method of Cremer and Huber [7] for pulse measurements or by the approach of James and Phillips [8] for frontal analysis.

The separation of micropore and mesopores plus outer surface area was done by a combination of elution and flash thermodesorption [9]. The latter allows for a seperate consideration of the micropore contribution in the sorption process since micropore desorption requires a higher activation energy because of the above mentioned effects. After injection of an organic vapour, adsorption takes place on the sample in the column. In the following desorption the adsorbate is eluted by the carrier gas and the the elution peak recorded.

As soon as the detector signal retuns to the baseline, the sample is heated to 473 K with a ramp rate of ca. 50 K/min. The obtained thermodesorption peak has the same shape as the elution peak and can be analysed using the same calculation methods.

Results

The results will be illustrated by three examples. The first example shows an alumina (Degussa, type C) that is non-porous and shown in Figure 1.
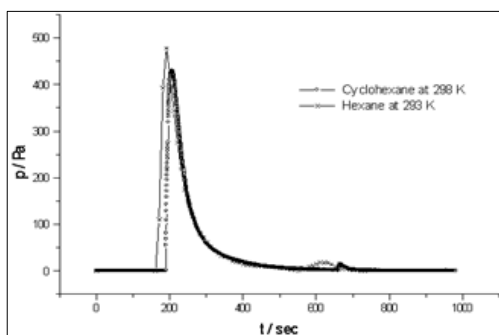

Figure 1. Chromatograms of cyclohexane adsorption on alumina.

The very small thermodesorption peak near 600 sec. supports this assumption.

For this reason the isotherm obtained from the first peak should be very similar to the one that results from a static gravimetric measurement. This is shown in Figure 2 .
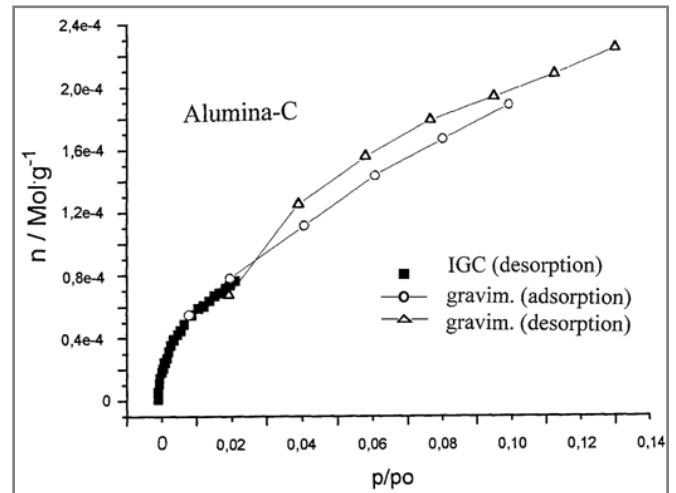

Figure 2. Comparison of grav.-static measured isotherms and IGC SEA elution isotherm for alumina.

The second example is the measurement of two zeolites of different pore size and illustrates the other extreme of adsorption behaviour - a material that has a negligible surface adsorption but a strong micropore contribution.

In Figure 3 two experiments with a 3A and a 13X zeolite are shown. Cyclohexane was used as a probe molecule. In both cases the temperature ramp started after 600 sec.
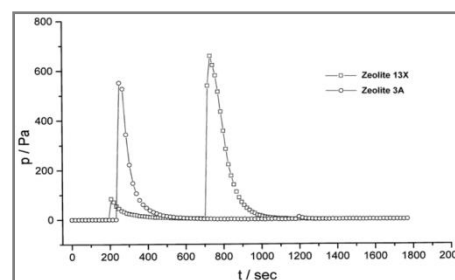

Figure 3. Chromatograms of cyclohexane adsorption on zeolite 3A and 13X.

The 13X shows a strong thermodesorption peak whilst the 3A shows none. This is due to the size of the cyclohexane which has a critical diameter of 6 Å. Therefore it has access to the pores of the 13X with 10 Å diameter whilst there is no access to the pores of the 3A with a diameter of 3 Å. In this case the thermodesorption isotherm should be similar to the isotherm obtained by a static gravimetric experiment, as shown in Figure 4.
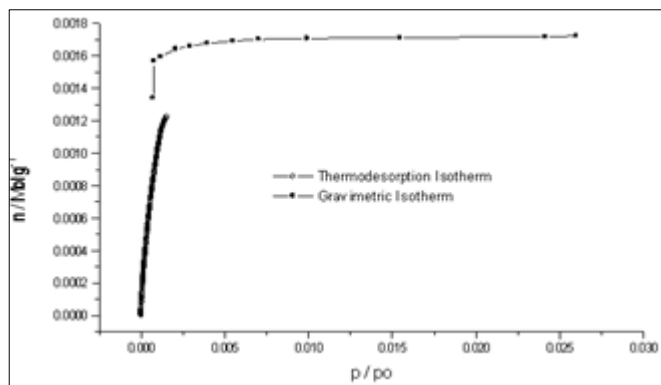
Figure 4. Comparison of static-grav. measured isotherm and IGC SEA thermodesorption isother for zeolite 13X.

The example demonstrates that this method is also as a useful tool to display the molecular sieve effect in a simple way.

Another application is the measurement of activated carbon. Two different types of carbon were used for this investigation. One standard carbon with a rather low surface area of 75 m²/g (manufacturer's data) and one typical porous carbon supplied by Norit (GAC) with a surface area of 1100 m²/g (manufacturer's data).
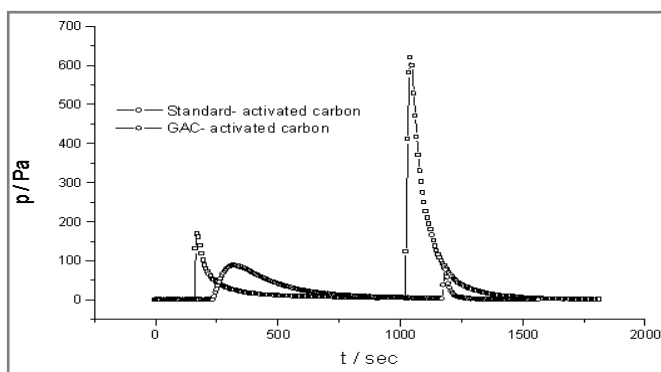

Figure 5. Pulse chromatograms for cyclohexane sorption on activated carbon.

Figure 5 shows the chromatograms of both carbons in the case of a pulse measurement with cyclohexane.

It is easy to recognize that the thermodesorption behaviour for both samples is completely different. This suggests a difference in micropore structure, which is confirmed by a comparison of the micropore size distributions (Figure 6) calculated from the isotherm of the second peak.
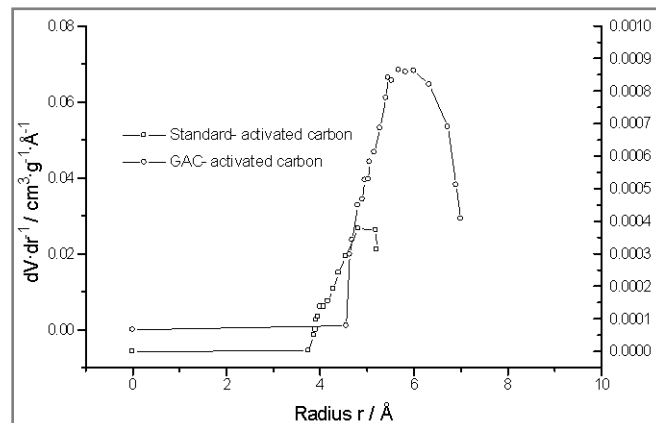

Figure 6. Pore size distributions for different activated carbon materials (left scale GAC, right scale standard material).

The micropore size distributions have been calculated by the method of Horvath and Kawazoe [10]. The maxima are located at 5.0 Å for the standard material and 5.8 Å for the GAC carbon. The area under the peak, which is related to the pore volume, is much bigger in the case of GAC. The DR equation [6] yields a micropore volume of 0.591 ml/g in the case of GAC and 0.005 ml/g in the case of the standard material.

The sorption isotherms of the first peak were used to calculate the BET surface area [5] of both samples. The results of this calculation and of comparison measurements with a static volumetric device are shown in Table 1.

Table 1: Values for S_{BET} (m^2/g).

Material	Manufacturer	IGC SEA	Static-vol.
Standard Activated Carbon	75	71.36	74.77
Norit GAC	1100	57.74	1114.44

It can be seen that surface areas obtained from static measurements are very similar to the manufacturer's values whereas the surface areas from the IGC SEA measurements show only a good coincidence with this data for the standard carbon. The GAC sample, however, gives a very different results for the surface area in case of an IGC SEA experiment.

This is easy to explain because values derived from the elution partial isotherm only pay regard to the amount adsorbed in the mesopores and the outer surface area. By contrast, the static method is not able to distinguish between these contributions and the micropore part of adsorption. The results for the standard carbon are very similar to the static values. This means that there are almost no micropores and the sorption processes take place in the mesopores and on the outer surface, while the adsorption on the GAC carbon is dominated by its high microporosity. This is confirmed by the huge difference in the thermodesorption peak of both material.

Conclusion

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

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