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iGC SEA
Application
Note 223

Determination of Energy Parameters of Highly Microporous Activated Carbons by Inverse Gas Chromatography

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In the present paper the dispersive surface energy and specific energies of interaction for three microporous activated carbons have been calculated from IGC SEA measurements. The enhanced adsorption potential in the micropores requires a measurement temperature of at least 350 °C to achieve equilibrium conditions.

Introduction

Activated carbons are materials widely used for various applications. Their versatility is due to their high adsorption capacity and surface reactivity. Activated carbons are typically used as catalyst supports, adsorbents for air and water purification, decolorisation and as filler materials [1]. Therefore, these materials have been the subject of various studies in the past. However, most of these investigations were focused on the determination of the surface area and the porosity [2]. Only a few attempts to date have been made to gain a better understanding of their surface chemistry. The acid-base chemistry of activated carbons is of interest since many processes are affected by specific rather than dispersive interactions.

Dynamic sorption methods have been proven to be a very useful tool for the characterisation of these properties since they facilitate the work with organic vapours at process relevant temperatures [3]. Inverse Gas Chromatography (IGC SEA) is an especially useful tool for the determination of energetic parameters and is widely used for various materials [4].

However, a common challenge for all sorption methods is the characterisation of highly microporous materials. Micropores are, according to the UPAC-classification, smaller than 2 nm in diameter. This small pore diameter causes an enhanced adsorption potential due to the overlap of the potential fields of close adjacent pore walls. The enhanced adsorption potential can affect practical measurements significantly since the desorption out of the pores is a very slow, diffusion-controlled process [5]. Therefore, high temperatures are required to attain the activation energy for a fast desorption equilibrium.

This paper is dedicated to the study of the surface chemistry of highly microporous materials at elevated temperatures.

Theory

IGC SEA pulse experiments are carried out at infinite dilution. In this range the adsorption is independent of the surface coverage and only interaction with the highest energy sites occur. Therefore peaks are symmetrical and the retention volume can be calculated from the retention time at the peak maximum. The net retention volumes VN are computed using Equation 1.

$$V_N = j/m \cdot F \cdot (t_R - t_0) \cdot \frac{T}{273.15} \qquad (1),$$

where *T* is the column temperature, m the sample mass, F is the exit flow rate at 1 atm and 273.15K, t_R is the retention time for the adsorbing probe and t0 is the mobile phase hold-up time (dead time). *"j"* is the James-Martin correction, which corrects the retention time for the pressure drop in the column bed.

Two methods are described in literature to calculate γ_S^D which is the dispersive component of the solid surface energy. The method of Schultz et al [ ] is based on the Fowkes equation and uses a plot of RTlnV versus a $(\gamma_S^D)^{1/2}$ for a series of alkanes.

$$RT \ln V_R^0 = 2N_A \left(\gamma_S^D\right)^{1/2} a \left(\gamma_l^D\right)^{1/2} + const. \qquad (2).$$

This is the most commonly applied model for the determination of the dispersive surface energy and the free energy. One alternative method is based on an incremental system for a series of n-alkanes [1]. This leads to the expression:

$$\gamma_S^D = \frac{\left[RT \ln\left(\frac{V_{M(C_{n+1}H_{2n+4})}}{V_{M(C_nH_{2n+2})}}\right)\right]}{4N_A^2 a_{CH_2}^2 \gamma_{CH_2}} \qquad (3),$$

where a_{CH2} is the surface area of a CH_2 unit (6Å^2) and γ_{CH2} is its energy (35.6 mJ/m2).

Other methods provide an alternative determination of free energy values. In this case the expression RTlnV is plotted versus the boiling point of the probe molecule [8] or versus the logarithm of the saturation pressure [9]. A theoretically more settled approach for the determination of the free energy uses a plot of RTlnV versus the polarisation PD [10], which is calculated according to Equation 4:

$$P_D = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{M}{\varphi_{lq}} \qquad (4),$$

where n is the refraction index, M the molar mass and □lq the liquid density of the probe molecule.

Method

Three types of activated carbons have been investigated: a SA4 (Norit), a F400 (Chemviron) and a STA04 (Imperial College). Their properties are listed in Table 1.

Table 1. Properties of activated carbons used in this study.

Name	Manufacturer	S_{BET} (m^2/g)	Source
SA4	Norit	717.7	Peat
F400	Chemviron	1051.3	Coal
STA04/7	Imperial College	592.9	Contaminated soil

The BET surface areas have been determined by standard nitrogen adsorption at 77 K.

For all three samples the surface energy and free energies have been determined.

All sorption experiments were carried out on an SMS-*iGC* 2000. The materials were packed into standard columns (0.2 cm ID, 30 cm in length). SA4 and STA04 were diluted with glass beads (<106 um, ratio 1:10) to reduce the pressure drop across the column. Measurements were performed with various alkanes and polar probe molecules, all supplied by Aldrich. Prior to the measurements a pre-treatment was carried out for 2 h at 623 K to remove impurities adsorbed on the surface. After the pre-treatment procedure pulse injections were performed by a 0.25 ml gas loop at 623 K and a concentration of 0.01 p/po (injection pressure).

Results

Figure 1 shows the dispersive surface energies for all three samples. Surface energies were determined by an injection of a series of alkanes from hexane to nonane.

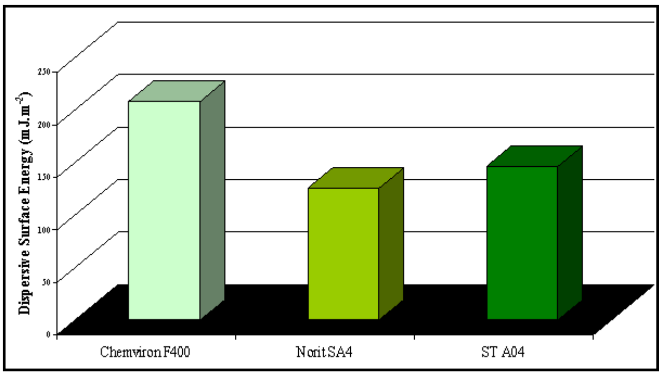

Figure 1. Dispersive surface energies of three different types of activated carbon.Measurements were carried out at 623 K by an injection of a series of alkanes from hexane to nonane. Measurements are analysed according to [6].

Chemviron F400 has the highest surface energy (208.20 mJ/m2 average) while STA04 and Norit SA4 are much lower (146.23 and 125.35 mJ/m2). The experiment-to-experiment reproducibility is <6%, which is a common value for carbon measurements. The column to column reproducibility is in the same range. The only exception is the STA sample where the column-to-column error reaches up to 16%. This could be explained with a more heterogeneous nature of the sample compared to the other two activated carbons.

The dispersive surface energies show a similar trend as the BET surface areas determined by nitrogen adsorption. Chemviron F400 has a significantly higher value than the other activated carbons (STA04 and Norit SA4). However, the sequence for the latter two is different from the BET values.

Initially, one would expect the trends in the surface energy and area to be the same since they are both based on dispersive interaction. This is the case for the Chemviron sample. The difference in the sequence for the two other samples could be due to the surface heterogeneity. The dispersive surface energy is measured at infinite dilution and indicates therefore the highest energy sites of the surface while the BET area reflects a finite dilution value, taking various different energy sites into account. Additionally it should be mentioned that the BET concept is, strictly speaking, not applicable to highly microporous materials since micropore filling does not represent a monolayer mechanism, which is assumed in the BET theory.
Besides from using the standard calculation method [6], dispersive energies have also been analysed according to the concept of Dorris and Gray [7]. The values showed the same trends but absolute numbers were in the range of 20 to 50 mJ/m2. These values seem to be unreasonably low for carboneous materials and were not considered for comparison. This huge difference could be due to a failure of the incremental system for very heterogeneous surfaces.
However, the goal of this study is the characterisation of specific interactions. For this purpose polar probe molecules have also been injected.

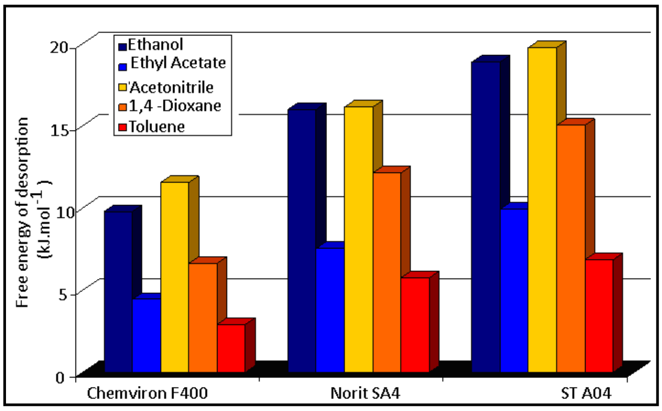

*Figure 2. Specific free energies of interaction for three different types of activated carbon, analysed according to the polarisation approach [**Error! Bookmark not defined.**]. Measurements were carried out at 623 K.*

Figure 2 shows the specific free energies (dG) for the three carbon samples, analysed according to the polarisation approach. The reproducibility was similar to that of the dispersive surface energy measurements.

It is very obvious that the trends in the dG-numbers are very different from those of the dispersive interactions. This is no surprise as specific interactions are determined by the (acid-base) chemistry of the surface rather than by the surface area of the materials. Chemviron F400 shows the lowest dG-numbers for all probe molecules considered while STA04 shows the highest. This means, in terms of practical applications, that STA04 is the best adsorbent for polar probe molecules of the three carbons considered.

The trends for the different probe molecules appear to be the same for all samples: acetonitrile and ethanol show the strongest interaction while ethyl acetate and toluene show the lowest. 1,4-dioxane seems to be intermediate. Ethanol has a slightly acidic character whereas acetonitrile and ethyl acetate are weak bases. There is no obvious explanation for the low interaction of ethyl acetate compared to acetonitrile since they are both basic and relatively hydrophilic. However, there could be group-specific as well as geometrical reasons for the difference in interaction.

Toluene and dioxane are rather hydrophobic and show a lower interaction. Dioxane is usually also a good indicator for hydrogen-bonding on the surface since interaction can take place through its O-atom. It should also be mentioned that toluene is sometimes considered as an indicator of the “aromacity” of a carbon system.

The differences in the specific interactions can be explained by the differences in origin and activation process of the carbon material.

Conclusion

The adsorption of organic vapours on activated carbon can be studied by IGC SEA. The interaction with non-polar probe molecules, expressed by the dispersive surface energy shows similar trends as the surface area. Polar probe molecules show a different trend. Chemviron F400 gives the strongest interaction with non-polar probe molecules while STA04 seems to be the best adsorbent for polar probe molecules. The surfaces of all three materials appear to be quite hydrophilic.

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