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Investigation of Surface Energy of Porous Adsorbents

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Abstract: Surface energy of adsorbent materials is one of the critical parameters which can be used to understand the insight of the adsorption phenomenon. In this work, a comparative study on surface energies at infinite delusion is presented for activated carbon, silica gel, and carbon fiber. Additionally, ethanol and hexane adsorptions are studied with 0.1 coverage to determine the influence of high energy sites at the adsorption process. The study explicitly explains the possible influence of surface energy on gas adsorption with experimental findings.

Keywords: Adsorption; Surface energy; Inverse gas chromatography; Porous Adsorbent.

1. INTRODUCTION

The sorption phenomenon of porous adsorbents plays a vital role in various applications in industrial and environmental sectors. One of the conventional ways of understanding this adsorption phenomenon is by measuring adsorption isotherms [1,2]. These adsorption isotherms are the state diagram influenced by adsorbent’s pore size distribution, surface energy, site energy distribution, and adsorbate properties. Recently the International Union of Pure and Applied Chemistry (IUPAC) has introduced six types of isotherms with two subcategories [3]. Different models have been addressed for each of the isotherm types, however no universal model yet been proposed. Ng *et al.*, [4] found that if the site energy distribution with their prospective probability function is considered for modeling, then a universal isotherm model can be developed. This finding revealed that surface energy might be the key to understanding the adsorption phenomenon. However, there is a lack of experimental findings which can relate the adsorption phenomenon with the surface energy.

Therefore, in this work, ethanol and hexane adsorption on three different types of adsorbents are studied. To find a connection between the surface energy with the adsorption phenomenon, dispersive and specific surface energies of the mentioned adsorbents were measured using inverse gas chromatography (IGC).

2. EXPERIMENTAL

2.1 Materials

Highly porous activated carbons and silica gel were studied in this work to measure surface energy. Maxsorb III and activated carbon fiber (ACF) are the porous carbons having a very high surface area. On the other hand, porous silica gel, like RD silica gel, contains a moderate surface area. Porous properties of the samples are presented in Table 1.

Table 1. Porous properties of samples [5,6]

Parameter	Maxsorb III	ACF A-20	RD silica gel
Surface area [m ² /g]	3045	1900	798
Pore volume [cm ³ /g]	1.7	1.028	0.415
Pore size [nm]	1.12	2.16	2.28

2.2 Apparatus and Procedure

The experiments were conducted with an inverse gas chromatography equipment (SEA-iGC, Surface measurement systems, UK). Here samples/adsorbents were placed in a narrow column of 30 cm length and 3 mm in diameter. Each sample was packed with glass wools. Polar (ethanol, dichloromethane, ethyl acetate, acetone, acetonitrile) and non-polar (hexane, heptane, octane) gases were sent to the column for adsorption; helium was used as a carrier gas. For desorption, helium was flowed through the column with a flow rate of 30 sccm. The schematic of IGC equipment is shown in Fig. 1. Desorbed gases then detected using a flame ionization detector (FID).

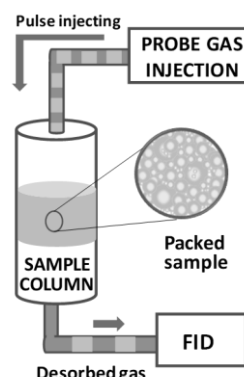


Fig. 1. Schematic of IGC

through the column with a flow rate of 30 sccm. The schematic of IGC equipment is shown in Fig. 1. Desorbed gases then detected using a flame ionization detector (FID).

3. RESULTS AND DISCUSSION

Typically, one IGC experiment provides the information of two retention times, one is for probe molecule (t_R), and another one is for inter gas (t_0). The amount of carrier gas required to remove the adsorbed gas from the adsorbents is termed as retention volume (V_g), which can be obtained by multiplying the net retention time ($t_R - t_0$). The higher value of retention volume means higher interaction between the probe molecules and adsorbents. In this work, the flow rates were kept constant. Therefore, the higher value of net retention time indicates higher interaction. The relation between these parameters can be presented in equation 1 [7].

$$V_g^0 = \frac{j}{m_s} F_c (t_R - t_0) \frac{273.15}{T} \dots\dots\dots(1)$$

The position of the peaks showed in Fig. 2(a) indicates there is a strong interaction between hexane with the porous carbon samples because this non-polar probe elutes later from the surface of these samples. Furthermore, asymmetric peaks are found for the porous

carbons due to the stronger attraction. On the other hand, polar probe ethanol shows higher affinity with RD silica gel samples (Fig 2(b)). The peak for silica gel is generated significantly later than that for porous carbons. There is a high possibility that the hydroxylated surface of RD silica gel has an additional attraction to the hydroxyl part of ethanol. Carbon samples show very low affinity towards ethanol.

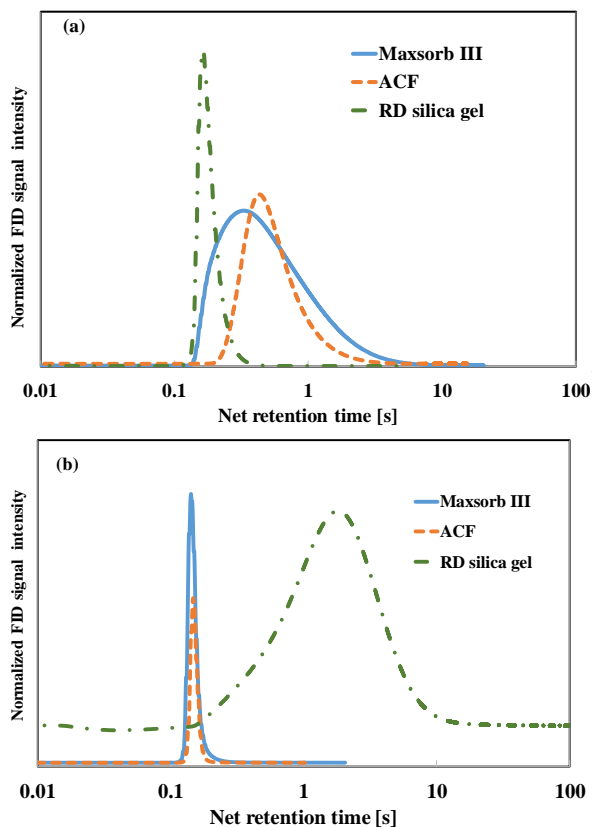


Fig. 2. Experimental chromatograph on different samples at 0.01 surface coverage a) non-polar probe hexane and b) polar probe ethanol.

The total surface energy for each sample was measured using eight different probe materials. It has two components: (i) dispersive and (ii) specific. The source of dispersive surface energy is the weak van der Waals force between surface atoms. Moreover, the specific surface energy is influenced by acid-base interaction, magnetic force etc. The surface energies of the samples are presented in Fig. 3. Dispersive component of surface energy is found higher in the carbon materials. According to this experiment, no direct relationship is found between the surface area and surface energy. For instance, Maxsorb III has a higher surface area, however, it has lower dispersive surface energy than ACF.

The specific component of silica gel is significantly higher than porous carbons. For 0.01 surface coverage, specific surface energy silica gel is $19.87 \text{ m}^2/\text{g}$, whereas carbon materials have below $1.5 \text{ m}^2/\text{g}$. The low specific surface energy measured with the polar probe indicates these carbon materials have high hydrophobic surfaces.

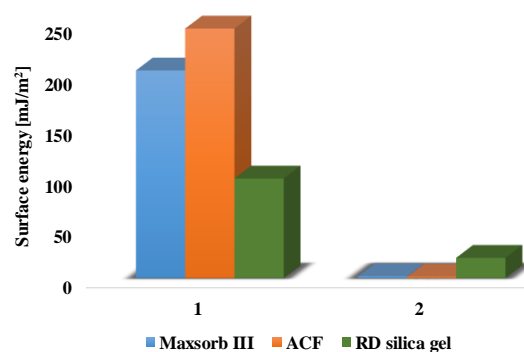


Fig. 3. Surface energy comparison of different samples at infinite dilution.

4. CONCLUSION

The interaction between hexane probe and porous carbon is found more intense than the silica gel surface. However, RD silica gel shows a stronger affinity for ethanol. The total surface energy of ACF is higher than the other samples. Nevertheless, ACF has a lower surface area than Maxsorb III. Surface energy is heavily influenced by the surface of the adsorbents, and the types of adsorbate are used rather than the surface area and pore size distribution.

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