

ENERGETICS OF METHANE ADSORPTION ON MICROPOROUS ACTIVATED CARBONS

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Abstract

The influence of microporous carbon surface oxidation on energetics of methane adsorption at 308 K is discussed. Obtained adsorption heats and integral molar entropies of the adsorbate show that microporous carbon surface oxidation changes the methane adsorption process. This is probably resulted by the existence of an endothermic effect during adsorption in oxidized carbon micropores.

Keywords: activated carbon, adsorption, adsorption calorimetry, methane

Introduction

Methane is widely used as an adsorbate because it has small dimension and does not possess any electric moments. It was applied for the theoretical description of potential energy of interaction between simple nonpolar molecules and different solids, for example: graphite [1-3], graphitized carbon blacks [4] or NaCl [5]. Methane adsorption heat, especially at low coverages, where fluid - fluid interactions can be neglected, may also be used for determination of an adsorbent heterogeneity [6]. The investigation of methane adsorption plays also an important role in the determination of mechanisms of some catalytic processes [7]. Because of methane properties, mentioned above, this hydrocarbon can be adequately represented as a simple spherical molecule as is done for monoatomic gases; therefore, it is used in virial analysis of adsorption and adsorption mechanism on zeolites [8-12]. This hydrocarbon is widely used in computer simulations of adsorption and this provides microscopic information about the arrangement of molecules in adsorbate micropores [13-17]. The latter may help to predict the behaviour of an adsorbent with regard for other adsorbates. Methane adsorption in microporous materials has been widely investigated because of the problem of its storage and transport [18, 19]. Cracknell, Gordon and Gubbins [18, 20] showed, by computer simulations, that an optimal porous carbon is a more suitable material for adsorptive storage of

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methane than an optimal zeolite. An optimal porous carbon should possess suitable both porosity and chemical nature of its surface. That is why Aukett and co-workers [21], using the same method, computed adsorption heats for slit-like carbons with different pore diameters. Despite the wide use of computer simulations for description of methane adsorption in carbon micropores, one should remember that those methods provide only approximate results. This is caused by the assumption of pore structural homogeneity, slit-like geometry, and by the negligence of pore connectivity, heteroatoms and defects (the last two contribute to energetic heterogeneity). All this is a crude approximation. On the other hand, there is still a lack of experimental results which would present methane adsorption heats on carbons with defined porous structure and chemical surface nature.

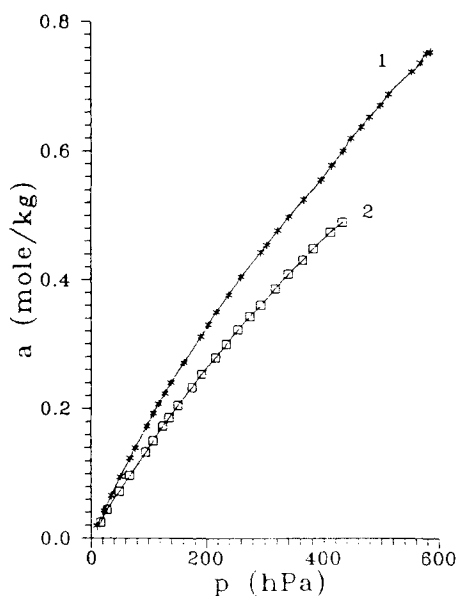


Fig. 1 Methane adsorption isotherms at 308 K on carbon A (1) and B (2)

Presented paper shows the experimental results concerning the energetics of methane adsorption on two types of microporous carbon with different chemical surface nature. The influence of carbon surface oxidation on methane adsorption is discussed by the use of adsorption calorimetry and thermodynamics.

Experimental

The adsorption of methane on two types of ashless microporous activated carbons obtained from poly(furfuryl) alcohol was investigated. The initial carbon (A) with negligibly small concentration of oxygen functionalities was oxi-

dized using nitric acid (carbon B). The detailed procedure of carbon preparation and carbon characteristics were given previously [22]. Adsorption isotherms (Fig. 1) were determined volumetrically. Differential heats of methane adsorption were measured with the accuracy of $\pm 1.5\%$ at 308 K, using a Tian–Calvet microcalorimeter.

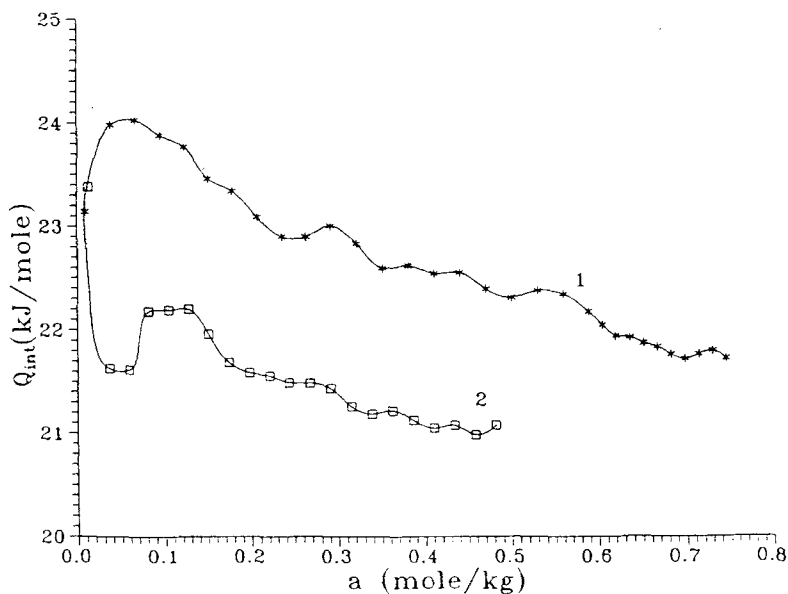


Fig. 2 Integral molar heats of methane adsorption at 308 K on carbon A (1) and B (2)

Results and discussion

The integral molar heats of adsorption (Q_{int} , Fig. 2) were calculated numerically according to:

$$Q_{\text{int}} = 1/n_{\alpha} \int q_{\text{diff}} \, dn_{\alpha} \quad (1)$$

where: q_{diff} the differential heat and n_{α} number of adsorbed molecules.

The integral molar entropy (S_{a} , Fig. 3) of adsorbed molecules was calculated on the basis of the relation:

$$S_{\text{a}} = 1/n_{\alpha} \int S_{\text{diff}} \, dn_{\alpha} \quad (2)$$

where S_{diff} is the differential molar entropy:

$$S_{\text{diff}} = S_g - q_{\text{diff}}/T + R - R \ln p/p_o \quad (3)$$

and: S_g the molar entropy of gaseous adsorbate at the standard pressure, T temperature, p equilibrium pressure, p_o pressure of the gas in the standard state (1 atm), R – gas constant.

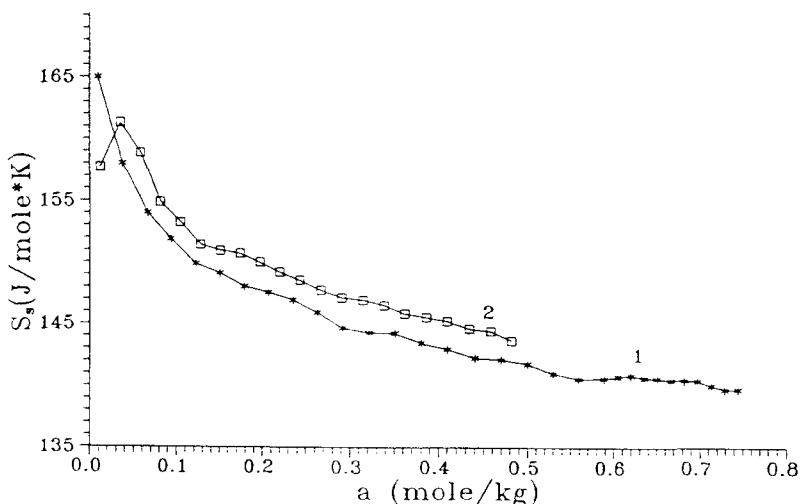


Fig. 3 The comparison of integral molar entropy of methane adsorbed at 308 K on carbon A (1) and B (2)

Figures 2 and 3 show higher methane adsorption heat on A type carbon than on carbon B, whilst integral molar entropies of the adsorbate are nearly the same in micropores of both carbons. The entropy of adsorbed methane falls down to the value of 140 J/mole·K, which suggests adsorbate – adsorbate interactions and the loss of one translational degree of freedom as compared with gaseous methane. Such enthalpy and entropy changes result that oxidized carbon (B) is worse adsorbent than unoxidized one (A) (Fig. 1). Because methane does not possess dipole and quadrupole moments and has relatively low polarizability, this effect cannot be resulted by the specific adsorbate – adsorbent interactions. The lower methane adsorption heat on oxidized carbon can be explained as the existence of a potential energy barrier resulted from the blocking of the narrowest pore entrances by the surface functionalities. The existence of the barrier causes the appearance of an endothermic effect, which contributes to the total adsorption enthalpy. Similar effect was observed during carbon tetrachloride adsorption on investigated carbons [22]. Presented results show that carbon surface modification influences the adsorption process in the investigated system even for such an adsorbate as methane that does not possess the ability for specific interactions.

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Zusammenfassung — Vorliegend wird der Einfluß der Oberflächenoxidation von mikroporösem Kohlenstoff auf die Energetik der Methanadsorption bei 308 K diskutiert. Die erhaltenen Adsorptionswärmen und integralen molaren Entropien des Adsorbates zeigen, daß die Oberflächenoxidation von mikroporösem Kohlenstoff den Vorgang der Methanadsorption verändert. Dies ist wahrscheinlich das Ergebnis der Existenz eines endothermen Effektes bei der Adsorption in oxidierten Kohlenstoff-Mikroporen.