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Adsorption on Kureha Activated Carbon: Isotherms and Kinetics

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Abstract. Adsorption equilibria and kinetics of butane isomers in Kureha activated carbon were investigated using a volumetric method and the tapered element oscillating microbalance (TEOM). The isotherm data measured by the TEOM technique are in good agreement with those determined by the volumetric method. The Tóth model appropriately describes the equilibrium data. The model used to describe the desorption profiles determined with the TEOM is based on the overall transport kinetics controlled by both micropore diffusion and mass transfer across the gas film around the adsorbent particles. The conventional Darken relation fails to capture the concentration-dependent diffusion in Kureha carbon. Alternatively, the structural model proposed by Do (1996) well describes this stronger concentration-dependent micropore diffusion.

Keywords: activated carbon, TEOM, Tóth isotherm, micropore diffusion, modelling

Introduction

This paper presents experimental results for the equilibrium and kinetic adsorption of butane isomers in the activated carbon commercialised by Kureha Chemical Industry, Japan. The aim of the present study is twofold. In previous work, a novel technique, the so-called tapered element microbalance (TEOM), has been used to measure adsorption isotherms on zeolites (Zhu et al., 1998, 2000a, 2000b, 2001a). Although the isotherms of light alkanes on silicalite-1 determined by the TEOM are in remarkable agreement with those obtained by employing either a volumetric or a gravimetric method in the literature (Zhu et al., 2000c), a comparison study of in-house measurements for the same system has not been reported. In the present study, the isotherms of butane isomers on Kureha carbon are measured by both volumetric and TEOM techniques.

The second objective is to characterize the activated carbon by means of the probe molecules *n*-butane and isobutane. Butane isomers are chosen because they have very similar physical properties but a significant difference in the molecular diameter. This paper provides an explanation for the difference in the adsorption and diffusion behaviour for these two adsorptives.

Experimental

Adsorbent

The commercial sample, spherical bead activated carbon, was supplied by Kureha Chemical Industry. This activated carbon is referred to as Kureha carbon. Kureha carbon particles in this study were of spherical shape and had an average diameter of 0.34 mm.

Porous texture analysis of Kureha carbon was carried out by the adsorption of N_2 at 77 K. The grain density of the adsorbent particles was measured by He pycnometry. The textural properties of Kureha carbon are presented in Table 1. The pore size distribution was evaluated in terms of the simulation of the density functional theory (DFT) using the isotherm data of nitrogen adsorption at 77 K and relative pressures up to 0.2. Only micropores contribute to the total pore volume and surface area. This was further confirmed by mercury intrusion porosimetry, no significantly additional

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Table 1. Textural properties of Kureha carbon.

Micropore volume (cm^3/g)	BET surface area (m^2/g)	He grain density (kg/m^3)	Particle density (kg/m^3)
0.56	1300	1860	1098

porosity was observed in the pore size range from 2 nm to 100 μm.

Volumetric Method

A Micromeritics ASAP 2010 gas adsorption analyser (stainless steel version) was used to measure the adsorption isotherms of butane isomers on Kureha carbon in the pressure range from 0.002 to 120 kPa. The instrument was equipped with a turbomolecular vacuum pump and three different pressure transducers (0.13, 1.33, and 133 kPa, respectively) to enhance the sensitivity in different pressure ranges. The static-volumetric technique was used to determine the volume of the gas adsorbed at different partial pressures.

The sample cell was loaded with 155.7 mg of Kureha carbon particles. Prior to the adsorption measurements the adsorbent particles were outgassed *in situ* in vacuum at 623 K for 16 h to remove any adsorbed impurities. The obtained dry sample weight was used in the calculation of isotherm data. Adsorption measurements were subsequently done at five different temperatures from 298 to 393 K. The temperature was controlled within ±0.3 K by means of a circulating oil bath.

TEOM Technique

A Rupprecht & Patashnick TEOM 1500 mass analyser (100 mg sample volume) was used for measurements of equilibrium, transient adsorption, and desorption in porous materials. A detailed description of the TEOM operating principles is given elsewhere (Zhu et al., 1998). A sample of 13.5 mg of the adsorbent particles was used in the TEOM experiments. The isotherms were obtained by a stepwise increase of the partial pressure of the feed gas at fixed temperatures. The partial pressure of the feed gas was determined by its fraction of the total molar-feed-flow rate through the sample bed and the total pressure. A mixture of helium, which was obtained as an ultra-high purity gas (>99.999%), and the sample gas (>99.95%) was used to establish the partial pressure.

An adsorption run was initiated by replacing the helium stream by a predetermined mixture of helium and the sample gas. The feed was maintained until the sample was equilibrated as indicated by constant mass change. Desorption was then carried out by changing the helium-feed gas mixture to pure helium and running until the sample mass change returned to its initial value. Nearly constant total flows were maintained during the uptake and desorption experiments. This essentially minimized the experimental errors that could be caused by a system pressure change. In the present study, the total flow rate through the sample bed was 200 cm^3 (NTP)/min (NTP: 298 K and 101.325 kPa). The detailed experimental procedures for transient measurements are given elsewhere (Zhu et al., 2001b).

Results and Discussion

Isotherms

The isotherms of butane isomers on Kureha carbon, measured by the volumetric method, are given in Figs. 1 and 2. Figure 3 shows a comparison of the isotherm data of butane isomers at 373 K measured by the volumetric method and the TEOM technique. The isotherms of butane isomers were reversible over the complete pressure and temperature range investigated. For the sake of clarity, the desorption data are omitted. Under the same conditions, the amount adsorbed for n-butane is slightly higher than for isobutane. The experimental data from the TEOM measurements are in good agreement with those from the volumetric measurements. These in-house observations verify the agreement between TEOM and volumetric techniques for the same

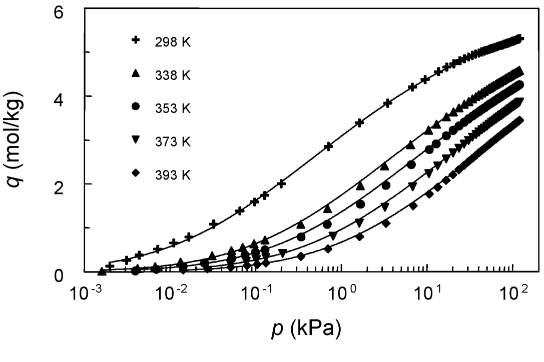

Figure 1. Isotherms of n-butane on Kureha carbon. Lines are the Tóth model fits.

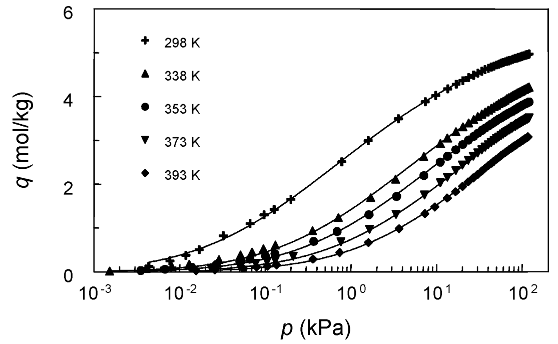

Figure 2. Isotherms of isobutane on Kureha carbon. Lines are the Tóth model fits.

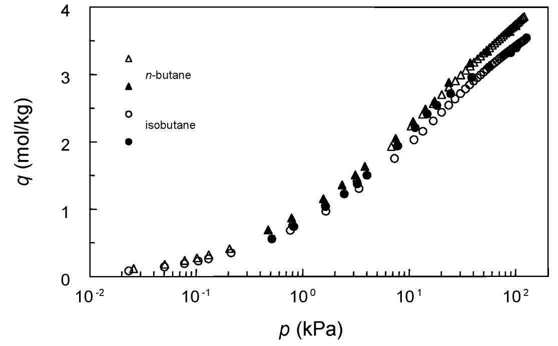

Figure 3. Comparison of the isotherm data of butane isomers on Kureha carbon at 373 K measured by the TEOM (closed symbols) and volumetric (open symbols) techniques.

system. This also implies the quality of the measured isotherm data.

Although Kureha carbon is a purely microporous material, the pore size distribution is wide and its range covers from 0.4 to 1.9 nm. Kureha carbon is, therefore, considered as a heterogeneous adsorbent. For adsorption on heterogeneous adsorbents, the Tóth model is often used to correlate isotherm data (Do, 1998)

$$q = q^{\mathrm{sat}} \frac{Kp}{[1 + (Kp)^m]^{1/m}} \tag{1}$$

where q is the amount adsorbed, q^{sat} is the saturation amount adsorbed, K is the equilibrium constant, p is the pressure, and m is the parameter that characterizes the system heterogeneity. The parameters K and m are temperature dependent, with the parameter K taking the usual form of the adsorption affinity and the parameter m having the empirical form (Do, 1998)

$$K = K_0 \exp\left[\frac{Q}{R_g T_0}\left(\frac{T_0}{T} - 1\right)\right] \quad \text{and}$$
$$m = m_0 + \alpha\left(1 - \frac{T_0}{T}\right) \tag{2}$$

where K_0 is the equilibrium constant at a reference temperature of T_0, Q is a measure of the heat of adsorption, R_g is the universal gas constant, m_0 is the Tóth parameter at T_0, and α is a constant parameter. In combination with temperature-dependent equation (2), the Tóth equation is used to simultaneously fit the isotherm data at five different temperatures, also shown in Figs. 1 and 2. The extracted values of the fitting parameters are listed in Table 2. The extracted saturation capacity for n-butane is higher than for isobutane. The kinetic diameter of n-butane (0.43 nm) is smaller than that of isobutane (0.50 nm). In Kureha carbon part of the micropores are smaller than 0.5 nm, and n-butane molecules can access these micropores while isobutane cannot. This probably gives an explanation on the difference in the saturation capacity between n-butane and isobutane.

The parameter m in the Tóth model reflects a degree of the system heterogeneity (Do, 1998). The larger the deviation from unity, the system is said to be more heterogeneous. The extracted values of m are 0.333 and 0.362 for n-butane and isobutane, respectively. This implies a strong degree of heterogeneity for the adsorption of butane isomers on Kureha carbon. In addition, for n-butane the adsorbent appears to be slightly more heterogeneous than for isobutane in terms of the m value.

The derived Q values are also presented in Table 2. The heat of adsorption for n-butane is somewhat higher than that for isobutane. It indicates that there is a stronger interaction between adsorptive and adsorbent for n-butane on Kureha carbon. Linders et al. (2001) used a novel low-pressure-pulse-response technique (similar to a Temporal Analysis of Products technique) to measure the heat of adsorption for

Table 2. Optimal values of adsorption parameters in the Tóth isotherm.

Adsorptive	T_0 (K)	q^{sat} (mol/kg)	K_0 (kPa^{-1})	m_0	α	Q (kJ/mol)
n-butane	298	6.19	56.6	0.333	0	44.0
Isobutane	298	5.78	23.8	0.362	0	42.5

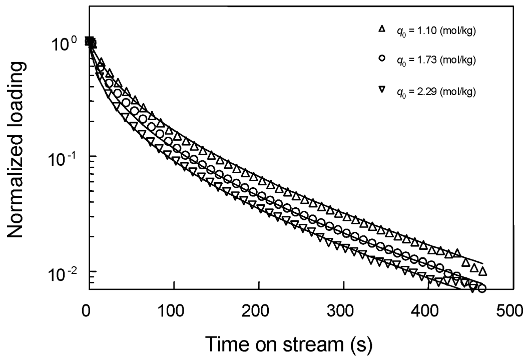

Figure 4. Normalized desorption profiles of isobutane in Kureha carbon at 338 K and different initial loadings. Lines are the model fits.

n-butane on Kureha carbon. The reported value is 45.2 kJ/mol, which is comparable with the current result, 44.0 kJ/mol for n-butane.

Kinetics

The desorption curves of butane isomers in Kureha carbon were measured with the TEOM at multiple temperatures and different initial loadings. Figure 4 represents the normalized desorption curves of isobutane at 338 K and different initial loadings.

A model, based on the non-linear Tóth isotherm and the overall rate of desorption controlled by both mass transfer across the gas film surrounding each particle and micropore diffusion, is considered. In addition, it is assumed that diffusion in the microporous carbon is described by Fick's law with a concentration-dependent diffusivity. The mass balance equation describing the concentration distribution of the adsorbed species in a spherical particle takes the following form

$$\frac{\partial q}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 D_0 \Gamma \frac{\partial q}{\partial r}\right) = D_0\left(\frac{2\Gamma}{r}\frac{\partial q}{\partial r} + \frac{\partial \Gamma}{\partial r}\frac{\partial q}{\partial r} + \Gamma\frac{\partial^2 q}{\partial r^2}\right) \quad (3)$$

where r is the radial coordinate of a particle, D_0 is the micropore diffusivity at zero coverage, and Γ is the thermodynamic correction factor.

$$D = D_0 \frac{d \ln p}{d \ln q} = D_0 \Gamma \quad \text{with} \quad \Gamma = \frac{1}{1-\theta^m} \quad \text{for the Tóth isotherm} \quad (4)$$

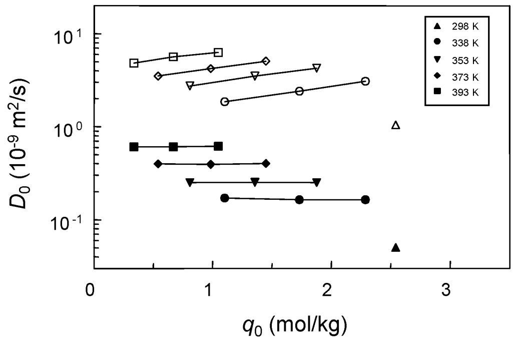

Figure 5. Extracted diffusivity D_0 by the model with the Darken relation (open symbols) and with the structural approach (closed symbols) for isobutane in Kureha carbon.

One of the generally used models for describing surface and micropore diffusion is based on the gradient of chemical potential as a driving force for the diffusion. This leads to a relation in which the Fickian diffusivity can be represented by a diffusivity at zero coverage, D_0, the so-called corrected diffusivity, times a thermodynamic correction factor Γ, the Darken correction, i.e. Eq. (4). Usually, D_0 is assumed to be concentration independent. However, the estimated diffusivity D_0 is strongly dependent on the adsorbed concentration and its value significantly increases with initial loading, as shown in Fig. 5. Apparently, the Darken relation fails also to capture the concentration-dependent diffusion in Kureha carbon.

Alternatively, Do (1996) proposed a model for activated carbon that addressed the effect of structure on the transport surface diffusivity. The dependence of diffusivity D on fractional loading takes the following form

$$D = D_0 \frac{dp}{dq} = D_0 \Gamma \quad \text{with} \quad \Gamma = \frac{1}{(1-\theta^m)^{1/m+1}} \quad \text{for the Tóth isotherm} \quad (5)$$

In the model with the concentration dependence described by the structural approach, i.e. Eq. (5), the extracted values of the fitting parameter D_0 at the same temperature are independent of initial loading (Fig. 5). The model appropriately describes the desorption curves, as shown in Fig. 4. The dependence of the apparent diffusivity D on loading predicted by the structural approach model is far stronger than that exhibited by the Darken relation.

Plotting D_0 versus the inverse of the absolute temperature, a straight line is observed, as indicated in Fig. 6.

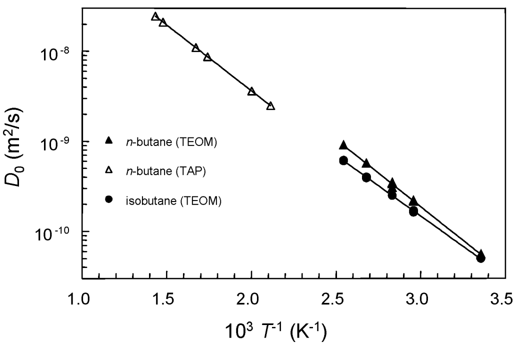

Figure 6. Corrected diffusivity D_0 as a function of 1/T for butane isomers in Kureha carbon.

Although the diffusivities of n-butane are slightly larger than those of isobutane under similar conditions, the derived diffusivity activation energy E_a for n-butane is also somewhat higher than for isobutane. The magnitude of E_a reflects the energy barrier during diffusion, which is related to the interactions between diffusing species and adsorbent. The heat of adsorption for n-butane is higher than that for isobutane. This is also the case for the derived diffusivity activation energy at zero coverage. The penetration of n-butane molecules into smaller micropores, in which there are stronger interactions between n-butane and adsorbent, results in a stronger temperature dependence for diffusion. The reported literature data for n-butane in Kureha carbon are also included in Fig. 6. The current results are in good agreement with those from Linders et al. (2001) who used the TAP technique to measure the diffusivities of n-butane at very low loadings. This further confirms the current approach.

Conclusions

The adsorption isotherms of butane isomers on Kureha carbon have been accurately measured over a temperature between 298 and 393 K and pressures up to 120 kPa. The isotherms measured by both TEOM and volumetric methods show good agreement. This further verifies the TEOM technique as applied to adsorption on porous materials. The Tóth model gives a good description of the adsorption isotherms. The conventional Darken relation fails to capture the concentration-dependent diffusion in Kureha carbon. Alternatively, the structural model proposed by Do (1996) appropriately describes this stronger concentration-dependent micropore diffusion.

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