Frequency-Response Evidence for Parallel Diffusion Processes in the Bimodal Micropore System of an Activated Carbon

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The rates of mass transport of gases such as propane, carbon dioxide, and ammonia have been studied in an activated carbon sorbent. The frequency-response (FR) method was used to measure these rates. Small-angle X-ray scattering (SAXS) and nitrogen-adsorption isotherm at 77 K showed that the activated carbon contains small micropores with diameters around 0.64 and 0.92 nm, respectively. The FR-rate spectra distinguished two parallel diffusion processes with different time constants, suggesting that the smaller and the larger micropores were not interconnected.

Introduction. – The extensive use of porous carbons motivates research to understand and control the structure and surface properties of these materials. The structure of the activated carbons develops during the preparation involving carbonization of a selected carbon source material, followed by activation of the resultant product [1–5]. According to present knowledge, the activated carbons are built up of a more or less orderly stacking of graphite crystallites [1]. During activation, graphite layers are burnt out from the crystallites leaving behind slit-like micropores. As a consequence, the most frequent micropore sizes are integral multiples of 0.34–0.35 nm, the thickness of a single graphite layer. The macro- and mesoporous texture reflects the texture of the carbonaceous precursor. These large pores contribute little to the total gas-adsorption capacity at low relative pressures but act as transport pores.

Both the equilibrium and the dynamic properties of a sorption system are of decisive importance when determining the efficiency of a sorption process. The relationship between the equilibrium adsorption properties, such as capacity and selectivity, and the structure of the sorbent is quite well-established. However, the relation between the structural properties and mass-transport dynamics is less well-understood. The objective of this work is to correlate the pore structure determined by conventional methods with the mass-transport dynamics of gases diffusing in the pores.

Experimental. – *Materials.* The 0.85–1.7 mm size granules of a commercial charcoal adsorbent (*BDH Laboratory Supplies, Merck Ltd.*, UK) were ground and sieved into the following narrow size fractions: 1.00–0.71; 0.71–0.50; 0.50–0.25 and 0.25–0.1 mm. The sorbates CO_2 (99.998% purity) and NH_3 (99.96% purity) were obtained from *ARGO International*; the propane (C_3H_8; 99.95% purity) was from *Linde Gas*, UK, and the N_2 (99.995% purity) was produced by *Messer Hungarogáz Kft.*

Methods. The pore and matrix structures of the carbon adsorbent were characterized from the adsorption isotherms of N_2 at (77 K) and small-angle X-ray scattering (SAXS) [6–8]. The adsorption isotherms were determined by the gas-volumetric method in a conventional BET apparatus after pretreatment of the activated

carbon samples in a flowing N_2 stream overnight, followed by vacuum treatment for 1 h at 573 K. The N_2 isotherms for determining the pore-size distribution were recorded at 77 K. For other gases such as NH_3, CO_2, and C_3H_8, the adsorption isotherms were determined at 373 K. These latter temp. were also used in the FR measurements.

The *BDH* charcoal sample was studied by SAXS. A classical *Kratky* camera with slit geometry and proportional counter (*Anton Paar*, Graz, Austria) was used. The scattering of the Ni-filtered CuK_α radiation ($\lambda = 1.542$ Å) was recorded in the $6 \times 10^{-3} - 0.6$ Å^{-1} range of the scattering variable, defined as $h = (4\pi\sin\Theta)/\lambda$, where 2Θ and λ are the scattering angle and the wavelength, resp. A focused primary beam was used. The intensity curves were corrected for the geometry of the beam profile in order to obtain point-focused curves. Data were evaluated by the method based on the moments of the scattering-intensity function.

The pore-size distribution of the charcoal was determined also by Hg porosimetry. The porosimeter (*Micrometrics* model) operated in the 1 to 2000-bar pressure range. Thus, the distribution of the pore volume was calculated as a function of the pore radius in the $3 - 10000$ nm range. After recording volume *vs.* pressure curves, the cumulative pore size distribution was calculated by the cylindrical pore model. On the basis of the pore-size distribution, the specific surface area and the average pore radius was also determined.

A scanning electron microscope (*HITACHI SEM-570*) provided visual information on the structure of the carbons.

The mass-transport dynamics of gases was studied by the frequency-response (FR) method [9 – 12]. The frequency-response apparatus has been described in [13]. The sample was dispersed in a glass-wool plug in a FR chamber and outgassed at 573 K for 1 h. The sorbate was admitted into the chamber to the pretreated sample and allowed to come to adsorption equilibrium in the pressure range of $0.1 - 0.8$ kPa at 373 K. The volume of the chamber was then modulated with a $\pm 1\%$ square wave, and the generated pressure wave was recorded. The frequency window used in this study was $0.01 - 10$ Hz. Measurements were carried out in the presence and absence of sorbent samples to eliminate any influence of the apparatus. Frequency-response parameters such as phase lag and amplitude were derived from equivalent fundamental sine-wave perturbations by a *Fourier* transformation of the volume and pressure square waves. The phase lag, $\phi_{Z\text{-}B} = \phi_Z - \phi_B$, and the amplitude ratio, P_B/P_Z, were determined, where P is the pressure and the indices Z and B refer to the presence or the absence of sorbent, respectively.

The response wave functions,

in-phase $\quad (P_B/P_Z) \cos \phi_{Z\text{-}B} - 1 = K\delta_{in}$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (1)

out-of-phase $\quad (P_B/P_Z) \sin \phi_{Z\text{-}B} = K\delta_{out}$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (2)

were calculated, where δ_{in} and δ_{out} are the overall in-phase and out-of-phase characteristic functions, resp. The in-phase and the out-of-phase components plotted as a function of the modulation frequency gives the FR-rate spectra. *Yasuda* [9] calculated the theoretical FR spectra for various different rate-controlling processes such as rates of sorption on different sites, diffusion in micropores involving one or two independent intracrystalline diffusion processes, and transport through surface barriers.

Results and Discussion. – The adsorption isotherm of N_2 obtained for the *BDH* charcoal at 77 K was of Type I according to the BET classification. This type of isotherm is characteristic for microporous solids. The absence of hysteresis suggests the absence of mesopores. The specific surface area of the sorbent calculated by the BET method was 650 m^2 g^{-1}. The debate about the real significance of this important physical parameter for characterizing microporous materials has continued over a period of 30 years. However, BET surface areas are frequently used to characterize microporous materials. The SEM examination suggested that the sorbent was prepared from a coal precursor. The vegetal structure could be hardly recognized in the pictures, but large cavities and wide channels of 5 – 40-μm diameter could be seen. These pores would offer little mass-transport resistance. The pore-size distribution of these macropores was determined by Hg porosimetry. Macropores larger than 3 μm were, thus, measured. These pores clearly provided the way for rapid gas transport to the micropores. Very little porosity existed between the extremely wide macro- and the

very narrow micropores. Similar pore-size distributions were obtained by Hg porosimetry for the whole and the fragmented samples.

The N_2 adsorption data obtained at 77 K were used to determine the microporosity of the sample. The isotherm was analyzed according to the pore-filling model. Over the $0 < p/p_0 < 0.2$ range of the N_2 isotherm, the two-term *Dubinin-Radushkevich* equation substantiated the presence of two distinct sizes of micropores [14]. Characteristic adsorption energies of 20.8 ± 0.6 and 5.3 ± 0.3 kJ mol^{-1} were found to be suitable fitting parameters. The pore-size distribution, as well as the mean widths of the slit-like micropores, was calculated by the *Spitzer* equation [15]. A distribution curve was obtained with maxima at *ca.* 0.64 and 0.92 nm. These pore sizes correspond to the thickness of two and three graphite layers, respectively.

The pore and matrix structures of the carbons can also be studied by small-angle X-ray scattering (SAXS). The strong small-angle-scattering property of the active carbons is the consequence of the significant difference between the electron density of the matrix and that of the pores. The SAXS data were evaluated by the method based on the moments of the scattering-intensity function. The mean micropore width was 0.81 nm, which is in good agreement with the average of the widths determined from the N_2 adsorption isotherm. An important structural parameter generally obtained from SAXS data is the *Guinier* radius, which can be calculated from the initial part of the scattering curve. The average size of the microporous graphite particles, so obtained, was *ca.* 9 nm.

The FR spectra shown in the *Figure* demonstrate the different dynamics of sorption of the various gases over the activated carbon sample. When the characteristic time of periodic modulation approaches that of the transport process, resonance occurs, which is indicated by the appearance of a step and a peak in the δ_{in} and δ_{out} curves, respectively. Theoretical FR functions can be determined for isothermal transport in isotropic and uniform particles [9][10]. It was shown, when diffusion was rate-controlling, that the δ_{in} and δ_{out} curves approach each other asymptotically at higher frequencies. The best computer fits of these response functions recorded with C_3H_8, NH_3, and CO_2 described two independent diffusion-controlled processes (see *Fig.*, full lines). The intensity ratios of the deconvoluted component FR functions (see *Fig.*, dotted lines) were different for the various gases and changed with the equilibrium pressure. According to theory, the intensity of each of these response signals is determined by the sorption capacity associated with each of these two diffusion processes. The total FR intensity is proportional with the gradient of the adsorption isotherm at the equilibrium pressure of the measurement.

For spherical particles, the resonance frequency (time constant) can be given by D_c/r^2, where D_c and r are the transport diffusivity and the particle radius, respectively. The 0.85 – 1.7-mm particles of the parent charcoal sample were ground and sieved to different size fractions. The frequency of resonance was found not to change with the particle size, suggesting that the diffusion resistance of the macropores between the graphite crystallites was not controlling the rate of propane uptake. Thus, the resonance signals obtained at certain frequencies of modulation are controlled by the diffusion resistance of the various intracrystalline micropores. The resonance frequencies for the diffusion of propane were found to be virtually independent of the pressure over the pressure range covered (see *Fig.*). Theoretically, the *Fickian* and the surface
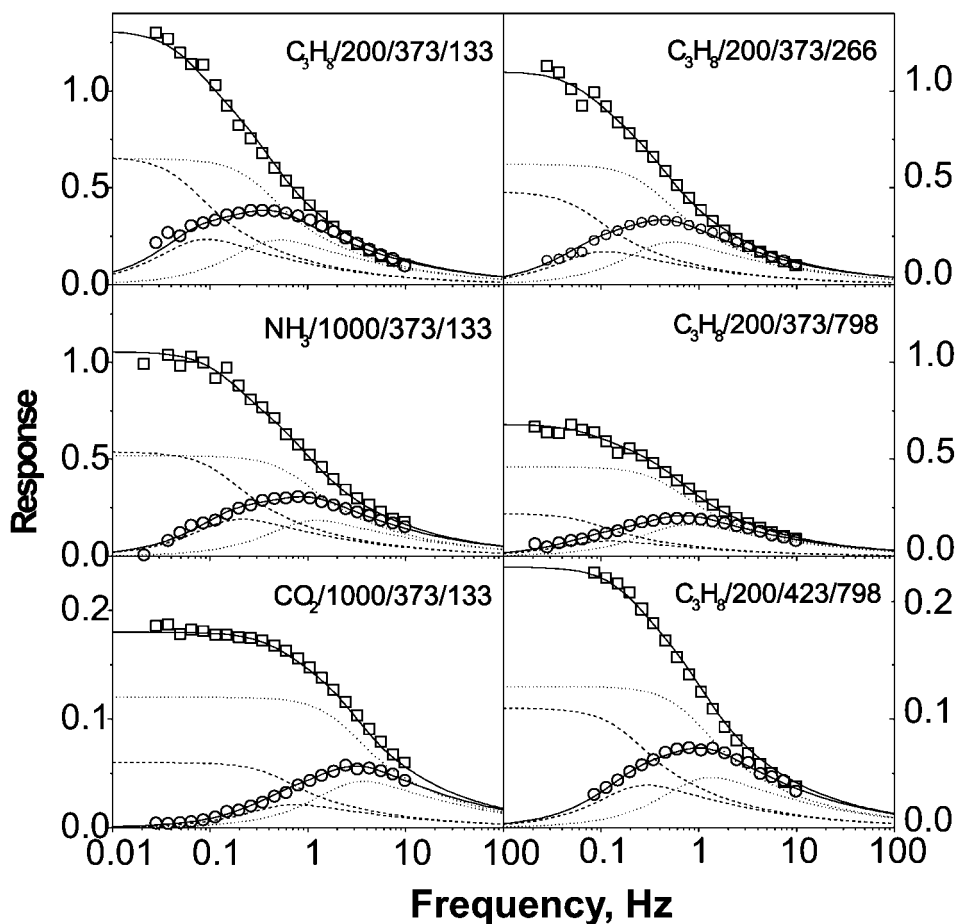
Figure. *Frequency-response spectra determined with the BDH activated carbon.* Symbols correspond to the in-phase (□) and out-of-phase components (○) of the experimental response functions. Full and dotted lines represent the best-fit characteristic curves and component curves, respectively, obtained with the model developed by *Yasuda* [9] for rate-controlling isothermal diffusion in isotropic, uniform, spherical particles with bimodal pore system. Measurement conditions, *i.e.*, such as the sorbate/the weight of the sorbent in milligrams/ the temperature in K/the pressure in Pa, respectively, are given in each spectrum.

diffusivities depend on the concentration of the adsorbed phase (q) and the pressure (p) of the measurement. The variation of these diffusivities with concentration is given by the equation $D_c(q) = D_0(q) \, [d(\ln p)/d(\ln q)]$, where $D_0(q)$ is the corrected, intrinsic, self-diffusivity, which can still, however, depend on q the surface loading.

The adsorption isotherms of the sorbate gases, determined at 373 K, could be properly represented by the *Freundlich* isotherm up to the pressures used in the FR measurements. Thus, the above $d(\ln p)/d(\ln q)$ factor is constant and is given by the reciprocal of the *Freundlich* exponent. The value so obtained was 2, 1.2, and 1.1 for C_3H_8, NH_3, and CO_2, respectively, suggesting that the apolar propane molecule is the most sensitive molecule for determining the energetical heterogeneity of the carbon

surface. The pressure invariance of the C_3H_8 D_c coefficient suggests that D_0 must also be independent of q under the quasi-equilibrium conditions of the FR measurement. If *Knudsen*-type diffusion controlled the transport rate, the same time constant would be expected for molecules of the same molecular weight, such as, C_3H_8 and CO_2. Obviously, this is not the case. It is conceivable that the transport is controlled by the mobility of the molecules in sorption equilibrium with the surface of the micropores.

If the wider micropores were transport pores feeding the smaller pores, the transport rate would be given by the process having the lower time constant. For example, the diffusion of small molecules, such as C_3H_8, in *Silicalite-1*, which has a channel system of interconnecting straight and sinusoidal micropores, is fitted with a single diffusion coefficient, which is the average of the two different diffusivities involved [10]. However, the transport of propane in the activated carbon under study resulted in a bimodal FR spectrum (see *Fig.*). Similar bimodal out-of-phase curves were obtained for the diffusion of larger molecules, such as butane in *Silicalite-1*. It has been shown that, for such larger molecules, which cannot change direction at the channel intersections, the straight and the sinusoidal channels behave as independent pore systems with two different diffusion resistances [10]. The bimodal size distribution of the micropores and the bimodal character of the FR spectra of intraparticle diffusion suggest, therefore, that the smaller and the larger micropores of the activated carbon are not interconnected.

For spherical particles of *ca.* 9-nm size (see [12]), the transport diffusivity of propane was estimated to be in the range of $10^{-17}-10^{-15}$ m^2 s^{-1} between 373 and 473 K. The activation energies for the slower and the faster propane diffusions in the narrower and the wider micropores were 34.7 and 28.5 kJ mol^{-1}, respectively. The order of the transport diffusivities is $C_3H_8 < NH_3 < CO_2$. The much higher diffusivity of CO_2 is in accordance with its weaker adsorption on the carbon surface.

The genesis of micropores was described as conversion of graphite layers of carbon particles to CO_2 during activation. It is not unreasonable to find that mainly non-interconnected micropores are generated at low conversions. The FR results provide experimental evidence for the formation of noninterconnected micropores in the crystallites of activated carbons.

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