NON-LINEAR KINETICS OF SORPTION OF OXYGEN AND NITROGEN MIXTURES IN CARBON MOLECULAR SIEVES

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INTRODUCTION

The non-cryogenic production of nitrogen by pressure swing adsorption (PSA) using kinetically selective carbon molecular sieves (CMS) is widely practiced in the chemical industry. Owing to the commercial interest in CMS, various researchers have investigated diffusion in these materials. Interestingly, reseachers have found that some CMS follow Fickian uptake behavior (1), while some CMS do not (2). Dominguez et al. showed that the Langmuir kinetic model more accurately described gas uptake in CMS than the linear driving force model (3). Srinivasan et al. noted that that none of their CMS uptake data could be described by a pore resistance model, some data were well described by a surface barrier model and a dual "shell' and "core" resistance model could describe all their uptake data (4). The purpose of this paper is to present an alternative theoretical approach based on a hopping mechanism to describe kinetics of sorption in two different types of CMS.

EXPERIMENTAL

A conventional volumetric adsorption apparatus was used for measurement of pure component isotherms and transient uptakes (5). In the experiments, the vacuum regenerated CMS was exposed to a dosing pressure of oxygen or nitrogen at time > 0. As adsorption proceeded, the decay in pressure as a function of time was measured. By mass balance, the amount adsorbed at ant time, t, could be calculated. When equilibrium was established, the final pressure was recorded and the equilibrium adsorption calculated. Transient uptake data here is reported only for small dosing pressures (150 torr or less) to ensure the uptake was as isothermal as possible.

The CMS material tested in our labs was an experimental CMS designated H-844. The material was supplied as 6 x 16 mesh pellets with a bulk density of 0.69 g/cc. The single component isotherms and uptakes for a CMS from Bergbau-Forshung (BF) were obtained from the literature (6). Binary uptakes from this reference were also used to test our mathematical model for binary gas uptake in CMS.

DATA ANALYSIS AND THEORICAL APPROACH

The equilibrium adsorption isotherms for both CMS samples was adequately described (± 3%) by the Langmuir isotherm:

$$n = mbP/1 + bP \qquad [1]$$

$$b = b_0 \exp(q/RT) \qquad [2]$$

where n is the amount adsorbed (mmoles/g), m is the saturation capacity (mmoles/g), q is the isosteric heat of adsorption (Kcal/mole), b is the Langmuir adsorption constant (atm^{-1}), b_0 is the value of b at infinite T, R is the gas constant and T is temperature. The Langmuir parameters for both CMS are given in Table 1.

Table 1

CMS	(mmole/g) m	(atm^{-1}) b_0 x 10^4	(Kcal/mole) q
BF/O$_2$	1.63	0.77	4.55
BF/N2	1.63	1.33	4.10
H-844/O$_2$	2.34	1.09	4.39
H-844/N$_2$	2.34	1.19	4.24

A mathematical model was developed to describe the kinetics of sorption in CMS. Molecular movement in the model is ascribed to jumps from one adsorption site to a free adsorption site. The probability of such a jump is dependent on the amount of free adsorption sites. The governing equations for flow in the CMS is as follows:

$$j_i = n_i \lambda \Psi_i \qquad [3]$$

where j is the flux of component i, n is the adsorbed concentration of component i, Ψ is the probability of a molecular jump and λ is the characteristic distance between adsorption sites. Given that the number of adsorption sites is limited and the probability of a jump decreases with increasing extent of adsorption, the probability of a jump can be given by:

$$\Psi_i = v_i [1 - \Sigma n/m] \exp[-E_i/RT] \qquad [4]$$

where v_i is a kinetic coefficient and E_i is the activation energy. For single component diffusion the equation for flow reduces to:

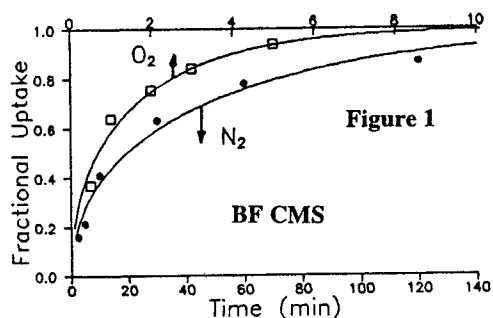$$j = -\lambda v_i \exp[-E_i/RT] \partial n/\partial r \qquad [5]$$

where $\lambda v_i \exp[-E_i/RT]$ corresponds to the diffusion coefficient of the pure component i. For binary diffusion, the governing equations are:

$$j_1 = -D_1[(1-n_2/m)\partial n_1/\partial r + (n_1/m)\partial n_2/\partial r] \quad [6]$$

$$j_2 = -D_2[(1-n_1/m)\partial n_2/\partial r + (n_2/m)\partial n_1/\partial r] \quad [7]$$

Boundary conditions at the pellet surface depend on the type of CMS. For Fickian diffusion, $n_1 = n_{1eq}$ and $n_2 = n_{2eq}$. For non-Fickian uptake, $n_1 = n_{1eq}$ and $r(\partial n_2/\partial r) = B(n_{2eq}-n_2)$. The subscript eq denotes the amount adsorbed at equilibrium.

Figure 1 shows the oxygen and nitrogen uptake curves on Bergbau CMS at 27°C. The solid lines in the plot correspond to the solution for Fickian diffusion (7) using the diffusion parameter (D/r^2) given in Table 2. The goodness of fit clearly shows that oxygen and nitrogen uptake in Bergbau CMS follows Fickian diffusion behavior, indicative of diffusional resistance throughout the CMS pellet. On the other hand, uptake

Figure 1

BF CMS

rates in the experimental CMS, H-844, could not be fitted to Fickian diffusion. Using the model described above, Figure 2 shows experimental uptake points at 30°C and the model fit (solid line) with the parameters given in Table 2. These results clearly show that CMS from different sources demonstrate different gas uptake behavior.
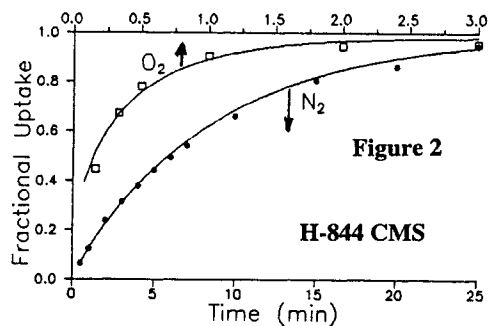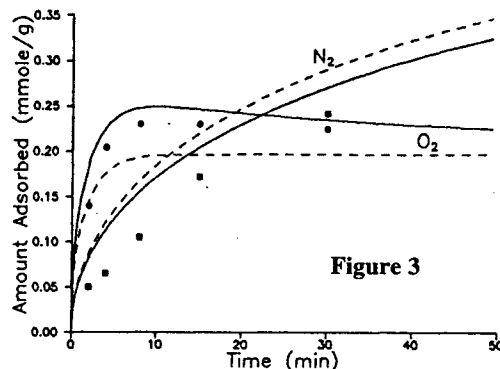

Figure 2

H-844 CMS

Table 2

CMS	(1/sec) D/r^2 for O_2	(1/sec) D/r^2 for N_2	B for N_2
BF	7.6×10^{-4}	2.6×10^{-5}	-
H-844	2.6×10^{-3}	4.5×10^{-4}	2

The model presented was further tested by comparing to the experimental results of Chen et al. (6). Figure 3 gives a comparison of the experimental adsorption results obtained by Chen et al. with Bergbau CMS. The material was exposed to 5 atm pressure of air at 27°C with 0.17 and 0.41 mmole/g initial loading of oxygen and nitrogen, respectively. Figure 3 shows the current model results in solid lines and Fickian diffusion results in dotted lines. Clearly, the current model more accurately predicts the experimental data than Fickian diffusion. It should be emphasized that the fit was obtained with parameters derived from pure component data (diffusion parameters and monolayer capacity as given in Tables 1 and 2). Another advantage of the current model is that the diffusion parameters are not concentration dependent.

Figure 3

SUMMARY AND CONCLUSION

Equilibrium and kinetics of oxygen and nitrogen sorption in two different CMS have been modelled. In both CMS materials, equilibrium characteristics are adequately described by the Langmuir model. However, for kinetics of sorption, one CMS followed classic Fickian diffusion, while the other sample did not. A model was developed which accurately describes both pure component as well as binary uptakes. Attractive aspects of the model include all parameters needed for binary uptake estimation are obtained from pure component data and diffusion coefficients are not concentration dependent.

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