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New Developments in Flow-Through Apparatus for Measurement of Adsorption Mass-Transfer Rates by Frequency Response Method

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Abstract. A new flow-through frequency response method based on a sinusoidal modulation of pressure is developed to measure gas adsorption equilibria and kinetics simultaneously. The transfer phenomena of pure N_2 and O_2 gases in carbon molecular sieve are investigated for different pressures and particle sizes by this method. Also, this apparatus has been extended to measure data for mixtures at different compositions at atmospheric pressure and room temperature. This is the first application of the flow FR system for a mixture. A negative cross-term diffusivity is reported. It shows that for co-diffusion, the fast diffusing molecule O_2 is decelerated by the slow diffusing molecule N_2, and the slower moving molecule N_2 is sped up by the faster moving O_2. The main-term diffusivities agree with the pure component diffusivities.

Keywords: frequency response, mass transfer, adsorption rates, carbon molecular sieve

Introduction

Knowledge of adsorption dynamics is important for the design of adsorption processes. Mass transfer in adsorbents can be a complex phenomenon as it is strongly influenced by the structure of the solid, the system, and the precise process conditions. The frequency response method has the potential for discriminating between different rate-limiting mechanisms, and it has been widely used to investigate the kinetic behavior of gas-solid systems.

Most theoretical and experimental aspects have been studied for a batch system in which the gas pressure is changed by a forced periodic volume fluctuation (Yasuda, 1994; Jordi et al., 1993; Reyes and Iglesia, 1994; Sun et al., 1994). A few applications are reported in flow systems involving flow rate (Boniface and Ruthven, 1985), concentration (Li et al., 1989; Harkness et al., 2003), or temperature variations. Flow systems have the advantages of maintaining isothermal conditions and decreasing nonlinear behavior compared to batch systems (Petkovska and Do, 1998). Even though the FR technique has been shown to be very powerful in measurement of pure component kinetics, it has very few applications in multicomponent systems (Yasuda et al., 1988; Yasuda and Matsumoto, 1989; Shen and Rees, 1995) and the related analysis is scarce (Sun et al., 1994; Park et al., 2000).

As the studies on pure gases alone are not enough to provide accurate information for process design and performance, the experimental data and models for mixture diffusion are essential in practical adsorption technology. A variety of models and techniques have been used to describe the multicomponent diffusion including Fick's law (Kärger and Ruthven, 1992; Ruthven et al., 1994), the Maxwell-Stefan (MS) formulation (Krishna and Wesselingh, 1997), and Onsager's formulation derived from irreversible thermodynamics (Sundaram and Yang, 2000; Kärger and Bülow, 1975). Fick's law has the advantage of the simplest appearance, and it is often possible to derive analytical expressions for describing the mass-transfer behavior, so it has been widely used to describe transport behavior.

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In this paper, a new flow-through frequency response method is reported, which builds on earlier work (Sward and LeVan, 2003). This apparatus has the ability to measure diffusivities of pure components or mixtures. The diffusion of pure nitrogen and oxygen and their mixtures in carbon molecular sieve (CMS) are examined by this method. The transfer phenomena of pure gases are investigated for different pressures and particle sizes, and the binary N_2 and O_2 system is studied at different compositions. We consider a simple model in which the entire system volume is at a time-varying but spatially-uniform concentration, and diffusivities are treated as constants.

Theory

Consider flow through an adsorption bed subjected to a sinusoidal pressure perturbation of frequency ω and amplitude ΔP. The flow-rate response in the periodic state is also a sinusoidal wave with the same frequency but a different amplitude ΔF. The amplitude ratio ($\Delta F/\Delta P$) and phase shift (ϕ) of the response wave relative to the input are used to extract mass-transfer rates from models. The system is justifiably assumed to be isothermal (Wang et al., 2003). Perturbations in pressure are kept small (<5%) to ensure that the system is appropriately linearized.

A schematic diagram of the apparatus is shown in Fig. 1. The material balance for component i is

$$M_b \frac{dn_i}{dt} + \frac{V}{RT}\frac{dP_i}{dt} = F_{i,\text{in}} - F_{i,\text{out}} \tag{1}$$

where V is the volume of the pressure-controlled region, M_b is the amount of adsorbent, F_{in} is the constant gas mass flow rate into the system as set by the mass flow controller, and F_{out}, the flow rate through the mass flow meter, is the response variable for pressure perturbation. The total material balance for the system is similar.

Using deviation variables to simplify the material balance equation and taking the Laplace transform gives the transfer function of the system

$$G(s) = \frac{\overline{F_T}}{\overline{P_T}} = -M_b G_n s - \frac{V}{RT}s \tag{2}$$

where G_n is the transfer function for the adsorbed-phase. The form of the adsorbed-phase transfer function G_n depends on the mass-transfer mechanism within the particle. For pure components, four different models have been used to obtain the best description of the transport mechanism. These models include micropore diffusion, surface barrier described by a LDF, distribution of LDF transfer rates, and a combined resistance model, which considers a surface barrier to exist at the opening of micropores and surface diffusion to occur inside the micropores. Details have been published in a previous paper (Wang et al., 2003) on pure-component systems. Based on the information from the pure system, N_2 and O_2 on CMS, the combined resistance model provides an excellent fit and is used to describe the mixture behavior.

For multicomponent adsorption systems, a general form of Fick's law is adopted here to represent the adsorption process of component i in an m-component system. The material balance describes the concentration distribution inside a porous particle

$$\frac{\partial n_i}{\partial t} = \sum_{1}^{m} \nabla \cdot (D_{ij} \nabla n_j) \tag{3}$$

where D_{ij} are the diffusivities. In fact, the D_{ij} are dependent on concentration, but they can be assumed constant for a small range of concentration. In this

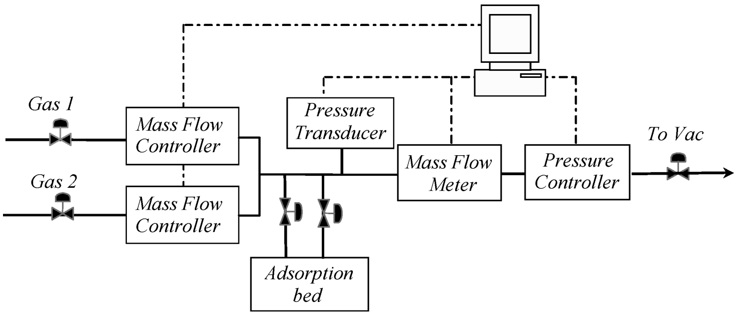

Figure 1. Schematic of experimental apparatus.

paper, to simplify the analysis, we will assume that the D_{ij} are constant over the entire experimental concentration range.

Equation (3) can be linearized to give

$$\frac{\partial n_i}{\partial t} = \sum_{1}^{m} \frac{D_{ij}}{r^2} \frac{\partial}{\partial r}\left[r^2 \frac{\partial n_j}{\partial r} \right] \tag{4}$$

where the D_{ij} are constants. D_{ii} are the main-term diffusivities and D_{ij} $(i \neq j)$ are the cross-term diffusivities.

The saturation loading for pure N_2 and O_2 are similar, and the mixture equilibrium can be described by the multicomponent Langmuir isotherm.

Experiment

Adsorption rate measurements were carried out in the continuous-flow system shown in Fig. 1. The main improvement of this apparatus over that of Sward and LeVan (2003) is to reduce system pressure drop, which makes the technique capable of measuring moderately fast diffusion (Yu and LeVan, 2003). Another change is that two mass flow controllers were used to extend the system capability to mixture measurement. After blending, the procedure for mixture measurement is the same as that for the pure system. The system pressure was modulated via a pressure controller. The response of the total mass flow rate was recorded. System control and data acquisition were accomplished using LabVIEW 6i. The amplitude ratio and phase angle are extracted directly with the software.

The adsorbent used in this study is Takeda MSC-3 K type 161. It is in the form of cylindrical pellets 1.18–2.80 mm in diameter (also reported as 7 × 14 mesh). The adsorbent was regenerated at 150°C for 24 h with helium flowing at 200 mL/min. N_2 (99.5%) and O_2 (99.6%) were obtained from J&M Cylinder Gases. Helium (99.995%) was supplied by Air Liquide.

The measurements were carried out at 298 K and 1 atm with a constant flow rate of 1 sccm. The pressure was perturbed in a sinusoidal wave over the range of 5×10^{-5} to 0.2 Hz. The transfer phenomena were investigated for pure nitrogen and oxygen and their mixtures at different molar compositions: 80% N_2 + 20% O_2, 50% N_2 + 50% O_2, and 20% N_2 + 80% O_2.

Results and Discussion

The apparatus is designed to obtain the information on transport kinetics, but it can also provide information on equilibrium at very low frequencies, where the system is close to equilibrium. The response functions contain a mass-transfer coefficient (D or k) and a capacity term (K), which can be obtained from experimental measurements. In our previous paper, the transfer phenomena of pure N_2 and O_2 gases on Takeda carbon molecular sieve were investigated for different pressures and particle sizes by this method (Wang et al., 2003). The mass-transfer mechanism for N_2 can be best explained by a surface barrier using a modified linear driving force model, but that for O_2 requires a combination of a surface barrier and micropore diffusion using a combined resistance model.

As the combined resistance model can describe transport of both gases, it was used in the binary gas experiments to extract the mixture diffusivities. To confirm our previous results, we used this modified apparatus to rerun the pure N_2 and O_2 experiments at room temperature and 1 atm. The results, which are shown in Table 1, are in excellent agreement with the previous paper (Wang et al., 2003). The parameter $\beta(\equiv r_p k_B/(D/r_p^2))$ is defined as the ratio of the micropore diffusion time scale to the surface barrier time scale. The applicability of this model suggests that a barrier resistance exists at the surface of CMS, followed by micropore diffusion within the CMS. The relative contribution of each resistance can be determined from the parameter β. Following Jordi (2001), the system is considered to be controlled only by micropore diffusion if β is greater than 10^2, only by the surface barrier if β is less that 10°, and by the mixed micropore diffusion and surface barrier for intermediate values of β. To minimize the unknown parameters for the mixture, the pure component βs are used in the mixture model. These values of pure component β are the low and high limits of those for the mixture; pure O_2 will have the highest β and pure N_2 will have the lowest.

Table 1. Diffusivities results for pure O_2 and N_2 in CMS1: O_2, 2: N_2.

	N_2		O_2	
	D/r_p^2 (s^{-1})	β	D/r_p^2 (s^{-1})	β
Previous work (Wang et al., 2003)	8.8×10^{-5}	3.0	1.4×10^{-3}	16.0
This work	9.4×10^{-5}	3.1	1.3×10^{-3}	24.9

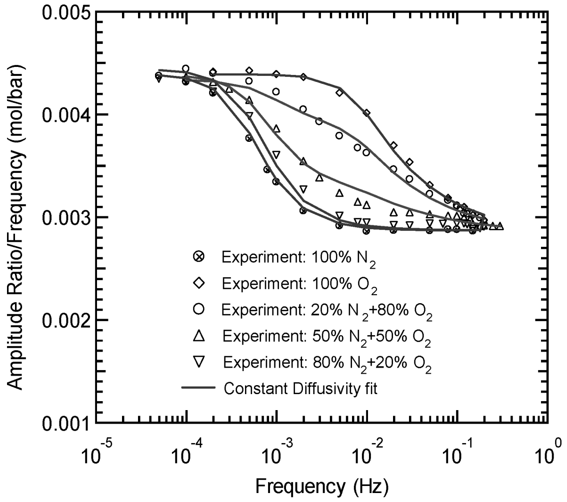

Figure 2. Frequency response curves of experiments and Fickian model.

Based on the Fickian model, the values of main and cross diffusion coefficients for a binary N_2 and O_2 mixture on CMS have been calculated for a constant diffusion matrix. The experimental data and model results are shown in Fig. 2. It is shown that Fick's model has excellent agreement with the experimental data. The diffusivities are listed in Table 2. The sign of the cross-term diffusivity can be negative or positive. A negative D_{12} indicates that the flux of component 1 will decrease if the composition gradient of component 2 is of the same sign; on the contrary, a positive D_{12} means that the flux of component 2 will be enhanced by component 1 in a co-diffusion situation. Our results show that main-term diffusivities determined for the mixture agree well with pure component diffusivities.

Cussler (1976) indicated that the diffusion coefficients are generally not symmetric and the cross-term diffusion coefficients are often ten percent or less of the main-term values; but as the cross-term value depends on the choice of solvent, it may be small for one choice and be much larger with another solvent. Both positive and negative values for D_{ij} have been reported from these studies (Marutovsky and Bülow, 1987; Carlson and Dranoff, 1987). Marutovsky and Bülow (1987) obtained a negative cross diffusion coefficient for a binary n-hexane-ammonia mixture in NaCaA zeolite. They explained the occurrence of the negative value by the replacement (non-equilibrium rearrangement) of ammonia by n-hexane. Some experimental results showed that the diffusivities of the fast diffusing molecules were affected by the co-existence of the slow diffusing molecules (Masuda et al., 2000; Bowen et al., 2004).

The experiments and studies for mass transfer of N_2-O_2 mixtures are limited. Yasuda and Matsumoto (1989) applied the batch frequency response method to systems of binary N_2-O_2 gas mixtures on 4A zeolite at 273 K and a low pressure about 10 torr. They showed that the main-term O_2 diffusivity (D_{11}) decreases with increasing concentration of N_2 and approaches that of pure N_2, whereas the N_2 diffusivity (D_{22}) is almost unaltered with increasing concentration of O_2. For cross-term diffusivities, their D_{21} is always larger than D_{12}. Also from their theory, the cross-term diffusivities should always have the same sign. Chen et al. (1994) used the DAB technique to measure diffusivities of O_2, N_2, and their mixtures (composition similar to air) in Bergbau-Forschung CMS. They suggested that their predictive model provided good agreement with the experimental uptake curves. All of the diffusivities are positive by their model. Their pure component diffusivities are almost 10 times less than those we determined, which may result from different origin of CMS and different pretreatment. They showed that the diffusivity results changed almost 20 times with

Table 2. Parameters for transport diffusivities 1: O_2, 2: N_2.

D_{11}/r_p^2 (s^{-1})	D_{12}/r_p^2 (s^{-1})	D_{21}/r_p^2 (s^{-1})	D_{22}/r_p^2 (s^{-1})
1.28×10^{-3}	-2.57×10^{-4}	4.62×10^{-5}	1.07×10^{-4}

different regeneration temperatures. We also noticed the same phenomena in our pure component experiments. Their mixture concentration is very similar to one in our study, which can be predicted well with their predictive model with positive cross-term diffusivities. But for our equimolar mixture, it showed somewhat discrepancy. Krishna (2000) used Maxwell-Stefan theory to obtain good agreement with Chen's experimental data. We also tried Maxwell-Stefan theory, and it worked well for air composition, but not well for other concentrations.

Conclusions

A new flow-through FR method has been developed to measure moderately fast diffusion processes for both pure and binary systems. Mass-transfer rate measurements for N_2 and O_2 and their mixtures in Takeda CMS have been performed using this technique. This method has the advantages of maintaining isothermal conditions and linear behavior. It can also provide simple and fast determination of transport mechanism.

Multicomponent diffusivities can be extracted from the experimental data by the combined resistance model. Main-term diffusivities agree with pure component diffusivities. For the binary system with two more parameters (D_{ij}), the transport behavior can be described well over the entire concentration range. A negative cross-term diffusivity for co-diffusion, has been reported for the system investigated.

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