

Binary Adsorption Kinetics and Equilibrium Measurement on CMS Using the Isotope Exchange Technique

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Introduction

The Isotope Exchange Technique (IET) can be used to simultaneously measure multicomponent gas adsorption equilibria and self-diffusivities of the components in a single, isothermal experiment without disturbing the adsorbed phase. The key advantages of this technique are (i) experiments simultaneously provide multicomponent adsorption kinetics and equilibrium, (ii) the equilibrium state is not perturbed, (iii) the experiment is completely isothermal, (iv) the method is a direct measurement of uptake with time, (v) there is complete control over the pressure, temperature, initial, and final loadings of all components, and (vi) the experiments are immediately replicated by injection of a second isotope plug

In this work, we present the use of the isotope exchange process to measure isothermal binary adsorption kinetics and equilibrium for nitrogen/oxygen on Takeda CMS.

Experimental

Figure 1 is a simplified schematic of the experimental apparatus. The general experimental procedure is outlined here; details are provided elsewhere.¹ A gas mixture is allowed to flow across an adsorbent sample until equilibrium is achieved. The gas phase composition is continuously monitored with a mass spectrometer. A plug of isotope-enriched gas is added to the closed-loop system, without disturbing the system pressure, temperature, or composition. The concentration of the isotopic species instantaneously increases, then decays to a final equilibrium composition. The adsorption equilibrium can be calculated from the initial and final gas-phase equilibrium concentrations of the isotopic species,

$$n_i^m = \bar{y}_i V \rho \left(\frac{y_i^{*m} - y_i^{*\infty}}{y_i^{*\infty} - y_i^{*0}} \right)$$

The transient change in concentration after injection can be used to calculate the fractional uptake rate,

$$f(t) = \frac{y_i^{*m} - y_i^{*o}}{y_i^{*m} - y_i^{*o}}$$

where y_i^{*o} is the concentration of the isotope of component i and the superscript denotes the time during the experiment; where o is before injection, m is immediately upon injection, and ∞ is at the final equilibrium, and t is any time after injection and before the final equilibrium.

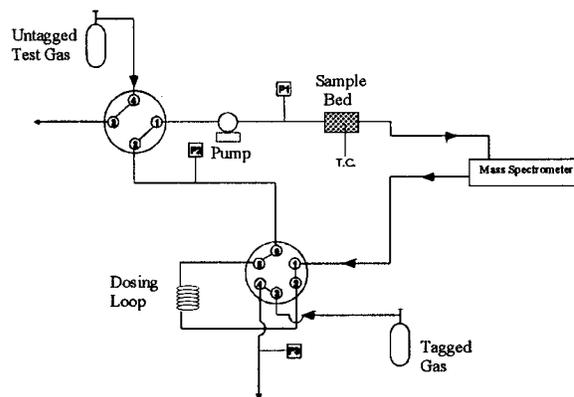


Figure 1. Simplified Schematic of Isotope Exchange Technique Experimental Setup.

Results and Discussion

The adsorption of pure nitrogen and nitrogen from air on Takeda carbon molecular sieve (CMS) were measured at various pressures at 10, 30, 50°C. The uptake rates are compared to the Fickian model,

$$\frac{\partial C}{\partial t} = \frac{D}{r^2} \left(\frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) \right)$$

where C is the concentration profile throughout the adsorbent pellet, and the linear driving force model (LDF),

$$\frac{\partial n_i^m}{\partial t} = k_m [n_i^m(e) - n_i^m(t)]$$

where $n_i^m(e)$ is the equilibrium moles that would be adsorbed if the gas and solid phase concentrations were in equilibrium. Figure 2 shows the typical shape of the uptake of nitrogen and oxygen as a function of the square root of time. Also included on these graphs are lines that correspond to the best-fit LDF model and the Fickian model at various D/a^2 values. Clearly, neither oxygen nor the nitrogen can be modeled by the Fickian model. All data collected were consistent with the LDF model.

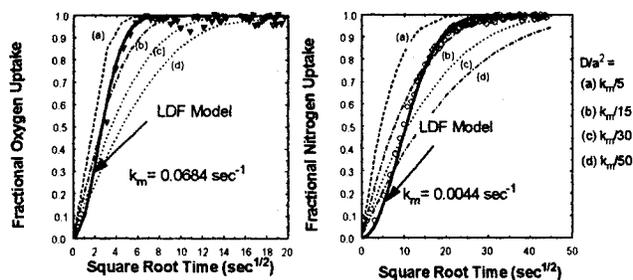


Figure 2. Comparison of (a) Oxygen and (b) Nitrogen Uptake Curves with LDF and Fickian Diffusion Models for Air Adsorption on Takeda CMS.

Figure 3 shows that the extracted k_m values for nitrogen increase with partial pressure. However, the presence of oxygen does not significantly alter the nitrogen kinetics.

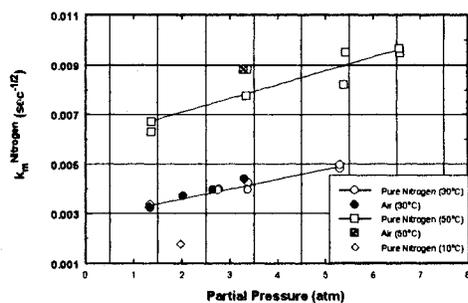


Figure 3. Nitrogen Mass Transfer Coefficient dependence on Nitrogen Partial Pressure.

The data for kinetics of pure nitrogen at 0.68 mmoles/g of CMS at the three temperatures were used to determine an activation energy for k_m of 7.3 kcal/mole, compared to an isosteric heat of adsorption of 3.7 kcal/mole.

A series resistance model showed a calculated resistance two orders of magnitude greater than the k_m values measured. Therefore, kinetics

were controlled by transport through the pellet and not diffusion through a concentration boundary layer on the pellet surface.

An adsorption-desorption experiment was performed, and it was found that the adsorption and desorption kinetics were identical for this system.

Conclusions

The Isotope Exchange Technique can be used to simultaneously measure multicomponent gas adsorption equilibria and kinetics in a single, isothermal experiment. Isotherms and nitrogen self-diffusivities for pure nitrogen and air were measured. It was found that the CMS did not exhibit thermodynamic selectivity for air separation but exhibited a kinetic selectivity for oxygen over nitrogen. It was also found that the mass transfer resistance for self-diffusion of nitrogen and oxygen on CMS were described well by a linear driving force model, which is consistent with the theory that the mass transport resistance was controlled by the pore mouth restriction. Calculations showed that the observed kinetics were not due to diffusion through a concentration boundary layer. Also for the system, the desorption rate was identical to the uptake rate.

¹ Rynders, R. M., Rao, M. B., and Sircar, S., *AICHE J. submitt999ed for publication.*