

ADSORPTION OF GASES ON A CARBON MOLECULAR SIEVE USED FOR AIR SEPARATION: LINEAR ADSORPTIVES AS PROBES FOR KINETIC SELECTIVITY

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Introduction

Carbon molecular sieves (CMS) are used widely for the separation of air into its components [1]. In this study the adsorption of linear adsorptives has been investigated to determine the relative importance of factors such as molecular size, shape and electronic structure in determining the adsorption kinetics of gases on CMS. The gases studied include N_2 , CO, C_2H_2 , N_2O and CO_2 . The adsorption kinetics were studied as a function of temperature and pressure, and the activation energies and preexponential factors were determined.

Experimental

The commercial carbon molecular sieve (CMS) used in this study was supplied by the Air Products and Chemicals Inc., U.S. and was prepared by carbon deposition on a microporous substrate. The gases used were supplied by BOC Ltd and had purities $\geq 99.99\%$. Adsorption studies were carried out using an Intelligent Gravimetric Analyser [2] (IGA) supplied by Hiden Analytical Ltd. This apparatus allows isotherms and the corresponding kinetics of adsorption to be determined for the individual pressure steps.

Results and Discussion

N_2O adsorption was studied over the pressure range 0-9 kPa, whereas the other gases were studied over the pressure range 0-100 kPa. The uptakes of all gases were linear at low pressures but deviations occurred as the pressure increased.

Adsorption kinetics: The adsorption kinetics for all the adsorptives except CO_2 and N_2O followed a linear driving force model (LDF) [3,4], where a plot of $\ln(1-M_t/M_e)$ vs. time is linear for 95% of the uptake (see Figure 1).

At low pressures and temperatures the CO_2 followed an LDF model. The adsorption kinetics changed to a barrier resistance/Fickian diffusion model with increasing pressure (Figure 2), and a Fickian diffusion model (Figure 3) was followed for the 90-100 kPa pressure step. The combined barrier resistance/diffusion model [5] is based on the

existence of a barrier resistance at the surface and subsequent diffusion in a spherical microporous system by Fick's law [5]. Figure 2 shows the change in shape of the $\ln(1-M_t/M_e)$ versus time graphs for carbon dioxide adsorption with increasing pressure. This is the first observation of a change in kinetic adsorption mechanism with an increase in pressure. The adsorption kinetics for nitrous oxide can also be described in terms of the combined barrier resistance/diffusion model for the lower temperature region (303-323 K) (Figures 4 & 5). The kinetics for N_2O deviated from this model at higher temperatures.

Comparison of the minimum molecular dimensions [6] shows that there are no simple relationships with adsorption kinetics. For example, comparison of N_2 and CO shows that the latter is the larger molecule while the adsorption kinetics are faster. In addition the relatively fast adsorption kinetics for N_2O and CO_2 compared with Ar and N_2 indicates the length of a molecule is not a major factor in determining the kinetics.

Conclusions

The adsorption kinetics of various probe molecules are a complex function of the size, shape and electronic structure of the adsorptive and the interaction with selective porosity needs to be considered. The kinetic results are consistent with a model [7] which includes two factors in the adsorption dynamics in heterogeneous carbon molecular sieves: (a) diffusion along the pores (b) diffusion through the barrier at the pore entrance. A LDF model is followed when the latter is the rate-determining step. When diffusion along the pores becomes a significant factor, the kinetic model deviates from the linear driving force model and a model based on a combined barrier resistance/diffusion is useful in describing the adsorption kinetics.

References

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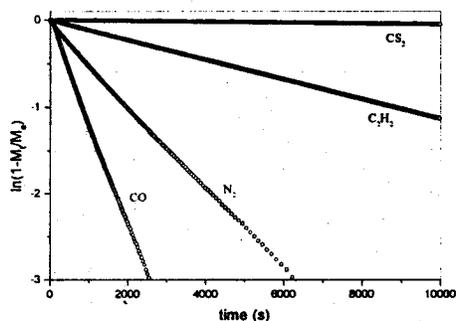


Figure 1: Variation of $\ln(1-M_t/M_e)$ against time for the adsorption of CO (313K, 20-30 kPa), N₂ (313K, 30-40 kPa), C₂H₂ (313K, 20-30 kPa) and CS₂ (343K, 0-0.1 kPa) on CMS A.

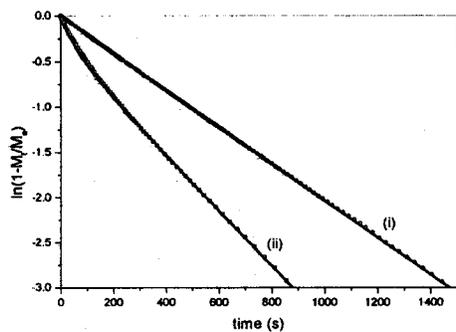


Figure 2: Comparison of the $\ln(1-M_t/M_e)$ versus time graph for CO₂ uptake on CMS A with kinetic models: (I) experimental data (every 20th data point) and calculated from the linear driving force model for pressure increment 0-10 kPa, 313K (-); (ii) experimental data (every 10th data point) and the combined barrier resistance/diffusion model for pressure increment 40-50 kPa, 313K (-).

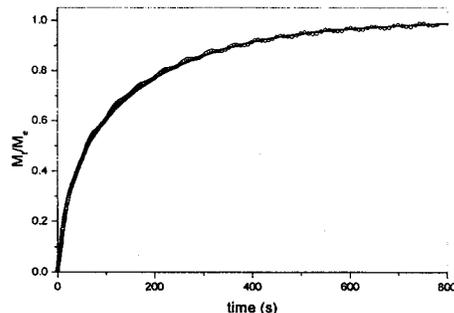


Figure 3: Comparison of the M_t/M_e versus time graph for CO₂ uptake on CMS A for pressure increment 90-100 kPa, 343K with the calculated profile (-) for Fickian diffusion into a spherical particle.

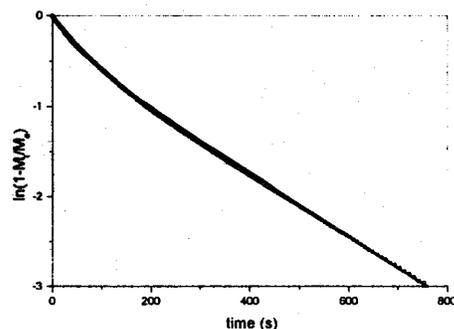


Figure 4: Variation of $\ln(1-M_t/M_e)$ against time for the adsorption of N₂O at 313K for pressure increment 7-8 kPa (every 2nd data point) with the calculated profile (-) for the barrier resistance/diffusion model.

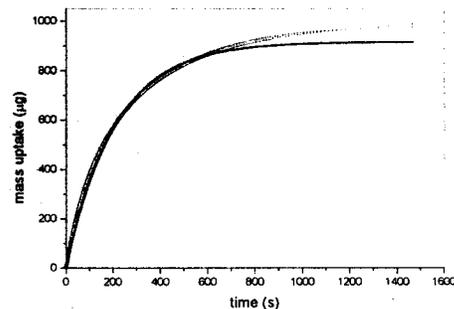


Figure 5: A comparison of the uptake of N₂O on CMS A (313K, 7-8 kPa) with the calculated profile (-) from the LDF model.