

ADSORPTION OF GASES AND VAPOURS ON CARBON MOLECULAR SIEVES

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Introduction

The use of carbon molecular sieves in the separation and purification of gas mixtures has considerable commercial interest. Carbon molecular sieves can be prepared by carbon deposition on a microporous carbon substrate derived from a wide range of precursor materials. The carbon deposition is a pore blocking technique which controls the kinetic selectivity for gases. The pressure swing adsorption (PSA) technique is based on the difference between the kinetics of adsorption of oxygen and nitrogen with the former being much faster than the latter although the equilibrium capacities for both gases are very similar¹.

In the present investigation the kinetics of adsorption of oxygen, nitrogen, argon, neon and water vapour on a carbon molecular sieve have been studied.

Experimental

Materials used The carbon molecular sieve used in this study was prepared by carbon deposition on a microporous substrate to introduce kinetic selectivity and was suitable for separating oxygen and nitrogen.

Adsorption Kinetics The kinetic measurements were carried out using an Intelligent Gravimetric Analyser (IGA) supplied by Hiden Analytical. The instrument consists of a fully computerised microbalance which automatically records the weight of the carbon sample as a function of time with the gas pressure and sample temperature under computer control. After outgassing the sample at 10^{-8} bar and 383 K; the pressure and temperature were set to the desired value under computer control and the weight uptake measured as a function of time under isothermal conditions until equilibrium was attained. The approach to equilibrium was monitored in real time and a computer algorithm used to establish when 99% gas uptake was achieved. After equilibrium was achieved, the pressure was increased to the next desired value and weight versus time recorded. The weight versus time data were used to calculate the kinetic data for each pressure step thereby providing adsorption kinetic data for different amounts

of pre-adsorbed gas/vapour. Adsorption experiments were also carried out in helium flowing at 1 bar pressure with various partial pressures of gases.

Results

The carbon dioxide adsorption isotherm at 273 K for the carbon molecular sieve was Type 1 and the micropore volume derived from the Dubinin-Radushkevich equation was $0.152 \text{ cm}^3 \text{ g}^{-1}$. A comparison of typical uptake curves for oxygen and nitrogen are shown in Figure 1. It is apparent that the adsorption kinetics differ markedly while the equilibrium adsorption capacities are very similar. The gas adsorption follows a linear mass transfer driving force model for a range of pressure increments from 10 to 100 kPa over the pressure range 0-900 kPa. Typical graphs of $\ln(1-M_t/M_e)$ against time are shown in Figure 2. M_t and M_e are the amounts adsorbed at time t and equilibrium respectively. The rate constants for oxygen adsorption are over 20X greater than those for nitrogen. The rate constants increase with increasing initial pressure for a given pressure increment. The gas uptakes for both gases were very similar and approximately linear at low pressure when Henry's law was obeyed. The adsorption temperatures used in this study were well above the critical temperatures of the gases and therefore it is not possible to express the pressures in terms of relative pressure since the saturated vapour pressure does not exist under the aforementioned conditions. In these circumstances a virial equation approach must be used for comparing adsorption characteristics for example using graphs of $\ln(n/p)$ against n where n and p are the amount adsorbed and pressure respectively. This graph allows calculation of the virial coefficients. The carbon molecular sieves also adsorb argon, neon and water vapour. The gas uptakes for both these gases and water vapour also follow similar kinetic rate laws to oxygen and nitrogen. However the rate constants for water vapour adsorption show a different trend with initial pressure. Initially the rate constant decreases with increasing pressure and reaches a minimum in the region where bridging between water molecule clusters occurs before

increasing at high p/p_0 (See figure 3). Clearly these different trends in the variation of rate constant with amount of pre-adsorbed gas/vapour can be attributed to the different mechanisms of adsorption. The pore volume calculated from the amount of water vapour adsorbed at high p/p_0 was lower than the micropore volume. Similar results have been obtained for active carbons and this has been attributed to the lower density of adsorbed water in microporous materials.

Conclusions

The rate constants for oxygen and nitrogen adsorption on the CMS differ by a factor of x20 indicating a kinetic rather than a thermodynamic effect. The rates of adsorption of nitrogen and oxygen increase slightly with increasing amounts of initial preadsorbed gas for a given pressure step for both pure gases and gas/helium mixtures. Molecular sieving effects are also observed for argon and neon. The adsorption of water vapour on the CMS is similar to that on active carbons where there is no kinetic selectivity for gases.

References

1. Chagger, H.K., Ndaji, F.E., Sykes, M.L. and Thomas, K.M., *Carbon*, 1995, **33**, 1411.

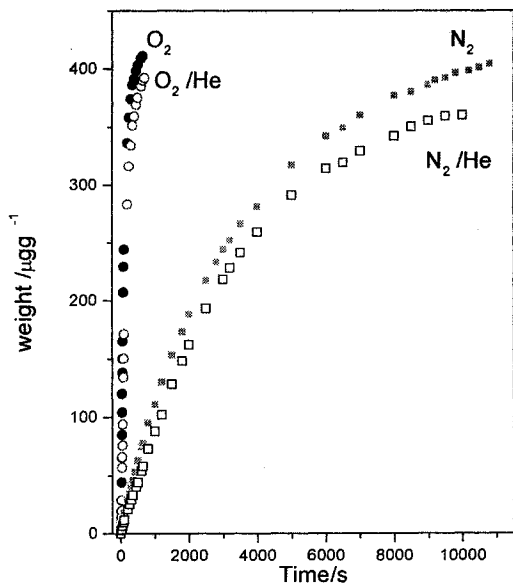


Figure 1: The variation of adsorption of oxygen and nitrogen with time on the CMS at 293K a) Pure gases: pressure change 55-66 kPa b) gas/helium mixtures, partial pressure changes: nitrogen 40.3-50.2kPa, Oxygen 41.2-48.9kPa.

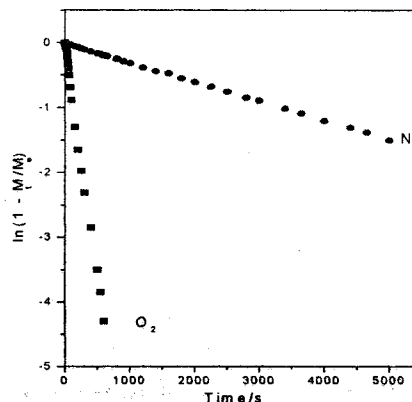


Figure 2: The variation of $\ln(1 - M/M_0)$ against time for the adsorption of nitrogen and oxygen on the CMS at 293K: Pressure increment 55-66kPa.

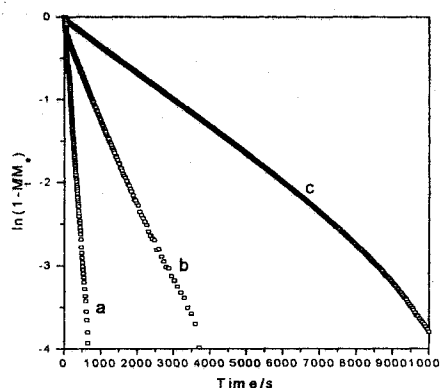


Figure 3: The variation of water vapour uptake with time on the CMS at 293K: Pressure Range a) 0 -101Pa, b) 1617-1719Pa, c) 913-1015Pa

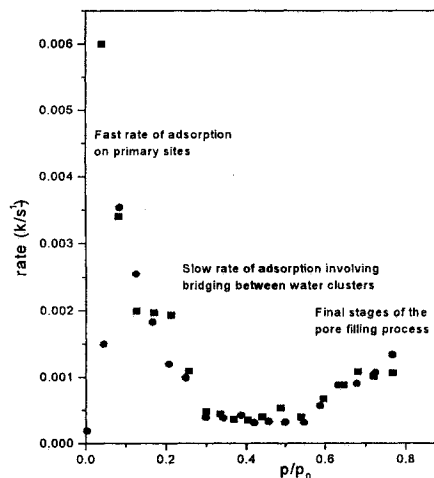


Figure 4: The variation of rate constant for water vapour adsorption/desorption on the CMS as a function of vapour pressure at 293K