

ADSORPTION CHARACTERISTICS OF CARBON MOLECULAR SIEVES: DECONVOLUTING COMPETING ADSORPTION PROCESSES

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Introduction

Air separation can be achieved by the Pressure Swing Adsorption (PSA) process. This is a commercially important process allowing the separation of a mixture of gases into its components. The adsorbent used in PSA is a carbon molecular sieve (CMS), which utilizes kinetic differences in the adsorption of nitrogen and oxygen.[1,2] Adsorption dynamics have been investigated previously for pure oxygen and nitrogen on CMS materials and show kinetic selectivity despite the similar molecular dimensions of the adsorptives.[3] However, in gas mixtures, the components may compete with each other for adsorption sites in the porous structure. It is important to understand this competitive adsorption process to improve the efficiency of CMS materials to allow tailoring and optimization of the selective porous structure.

Experimental

Materials Used CMS-44, was obtained from Air Products and Chemicals Inc., Pennsylvania, USA. Oxygen (99.99%), nitrogen (oxygen free), helium (99.99%) and air were supplied by BOC Limited, UK. Special gas mixtures of 20% oxygen /balance helium and 80% nitrogen/balance helium were supplied by Air Products Plc. U.K.

Instrumentation The Intelligent Gravimetric Analyzer (IGA) is an ultrahigh vacuum system that allows isotherms and corresponding kinetics of adsorption/desorption to be determined, for set pressure steps.[4] The balance and pressure control system were isothermal to $\pm 0.05\text{K}$ to eliminate changes due to variation in the external environment. The carbon sample ($100 \pm 1\text{mg}$) was out-gassed until constant weight, at a pressure of $<10^{-6}\text{ Pa}$ at 503K .

Static Gas Isotherms The pressure was gradually increased, over $\sim 30\text{s}$ to prevent disruption of the microbalance, until the desired value was achieved. Pressure control was achieved via the use of two transducers with ranges $0\text{-}0.2$ and $0\text{-}10\text{ kPa}$, each with an accuracy of 0.02% of the specified range. The pressure was maintained at the set point by active computer control of the inlet/outlet valves throughout the duration of the experiment. The mass uptake was measured as a function of time and the approach to equilibrium monitored in real time with a computer algorithm. After equilibrium was established, the pressure was increased to the next set value, and the subsequent uptake measured until equilibrium was re-established. The increase in weight due to adsorption was used to calculate the kinetic parameters, for each step, using an appropriate kinetic model. Errors in the calculated rates were typically better than $\sim 2\%$.

The sample temperature was monitored throughout the experiment and the variation was minimal (<0.1 K). The isotherms were repeatable to an accuracy of better than 1%.

Results and Discussion

Adsorption isotherms for pure oxygen and nitrogen gases on CMS-44 at 293K are shown in Figure 1. It is evident that the uptakes for the two components are equal at equivalent pressures, on an amount adsorbed basis.

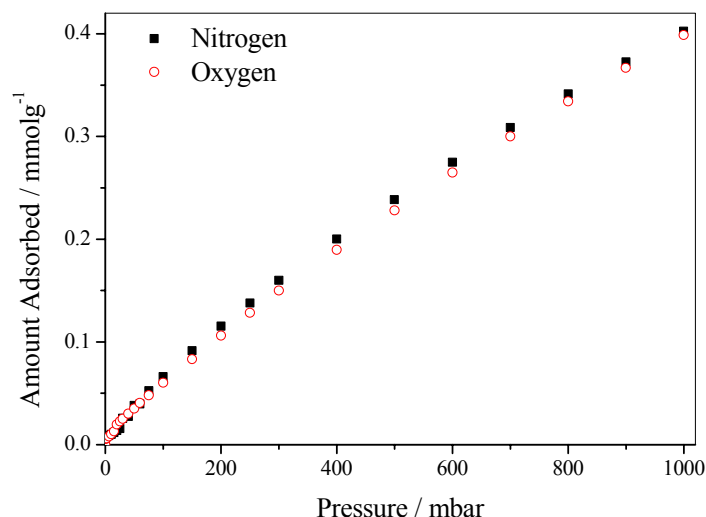


Figure 1. Adsorption isotherms for pure oxygen and nitrogen gases on CMS-44 at 293K

A Linear Driving Force Mass Transfer Model (LDF) has been used previously to evaluate the adsorption/desorption dynamics of pure gases and vapors on activated carbons, carbon molecular sieves, porous silicas and porous molecular frameworks.[5-10] The LDF model can be described by the equation:

$$\frac{M_t}{M_e} = 1 - e^{(-kt)} \quad (1)$$

where M_t is the mass at time t , M_e is the equilibrium mass and k is the rate constant for adsorption. The rates obtained for adsorption of pure oxygen and nitrogen on CMS-44 are shown in Figure 2. It is evident that the adsorption is significantly faster for oxygen. Both nitrogen and oxygen adsorption exhibit an increase in rate constant with increasing pressure. The kinetic selectivity of CMS-44 was found to be $k_{O_2}/k_{N_2} = 32.0$, which compares well with other values [3].

Figure 3 shows the adsorption isotherms obtained for the adsorption of air on CMS-44 at 293K. Combined adsorption uptakes for pure oxygen and nitrogen in the appropriate proportions were used to produce the second isotherm shown in Figure 3 and the two plots show excellent agreement.

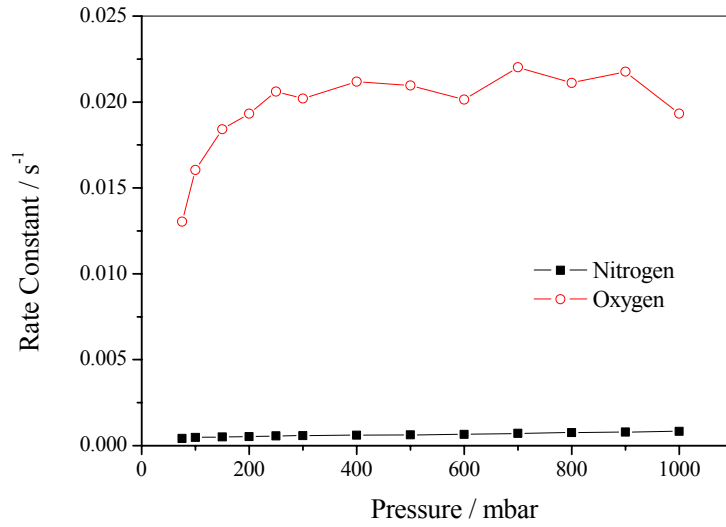


Figure 2. Adsorption kinetics for oxygen/nitrogen on CMS-44 at 293K.

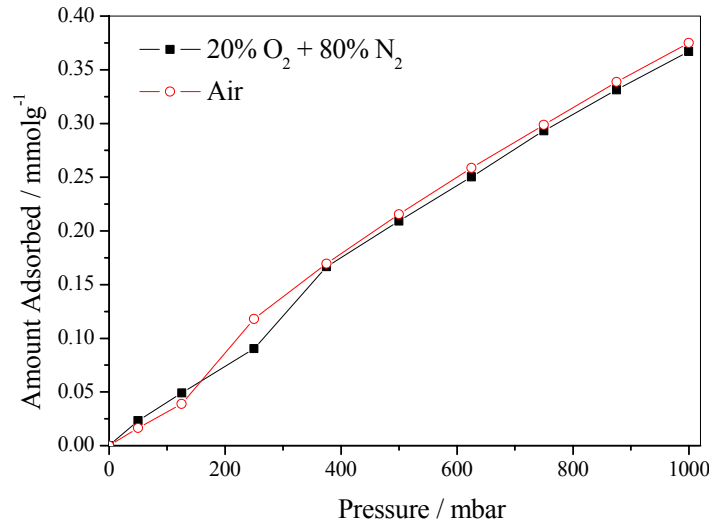


Figure 3. Comparison of Pure gas and air adsorption at 293K.

The rate constants for adsorption of air (oxygen/nitrogen mixture) and argon/oxygen were determined using a double exponential model, which is based on the existence of two barriers to diffusion and is expressed as:

$$\frac{Mt}{Me} = A_1(1 - e^{-k_1 t}) + A_2(1 - e^{-k_2 t}) \quad (2)$$

k_1 and k_2 are kinetic rate constants for two processes, $A_1 + A_2 = 1$, hence $A_2 = 1 - A_1$. The proportions of the two gases are known to be 20% oxygen and 80% nitrogen (argon) making $A_1 = 0.2$ and $A_2 = 0.8$. Hence the variables are constrained to two parameters, the rate constants k_1 and k_2 . The model may be used as the 'pure' gases have kinetics that fit the LDF model, hence the combined adsorption kinetics can be

modeled by a combination of the two LDF rate curves. A representative fit is shown in Figure 4. The deconvoluted rate constants for adsorption of oxygen and nitrogen in air on CMS-44 show that the kinetics are only significantly different for oxygen, where typically a reduction of ~75% in the rate constant was observed whereas the rate constants for nitrogen adsorption the reduction was only ~ 2%.

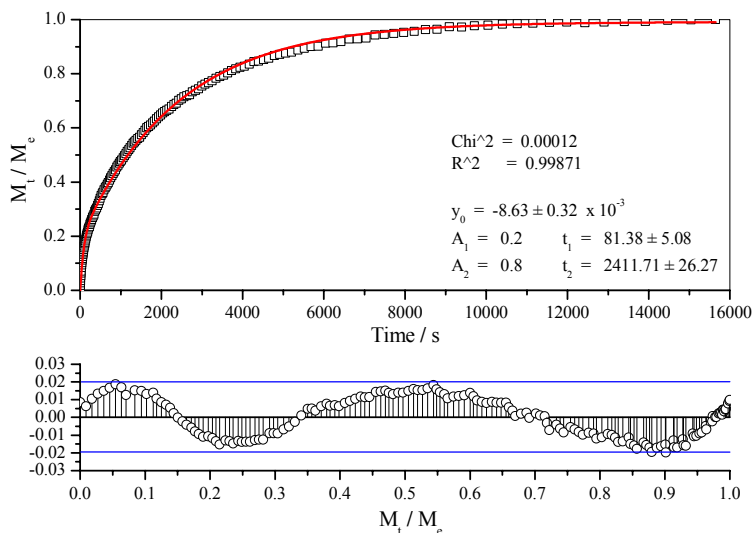


Figure 4: Representative fit for adsorption of 875mbar 20% oxygen in argon at 293K.

The observed reduction in rate constants is similar to the results obtained by O'koye *et al.* where the rate of adsorption of oxygen was 30 – 37% slower in helium than for the pure gas and a reduction of < 5% occurred for nitrogen in helium. Since helium was not adsorbed significantly under the conditions used, diffusion effects are important.[3]

Conclusions

The adsorption of oxygen and nitrogen in a mixture is more complex than single component adsorption with both competitive adsorption and diffusion effects. This suggests that the determination of adsorption characteristics of air are much more important in the assessment of CMS performance than those of the pure gases. The results show that the effect of competitive adsorption of species has a considerable effect and must be taken into consideration in the development of systems.

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