Effect of temperature on oxygen-argon separation on carbon molecular sieves

Carbon molecular sieves (CMS) are used as adsorbents in the separation of O_2, N_2 and Ar from air by pressure swing adsorption (PSA). Due to its aperture-cavity type pore structure, a CMS for this application exhibits greater selectivity for O_2 uptake. The economics of this process or other competitive technologies, such as cryogenic and membrane separations, is largely impacted by the product recovery and purity profiles. There is great demand for ultra high purity Ar in many chemical, metallurgical and electronic processes. High purity gases are also desired in numerous laboratory processes. Trace impurities such as O_2 and CO_2 are left behind during recovery of other gases. Such trace impurities can be efficiently removed by flowing the product gas of a traditional separation process through a column of CMS that selectivity adsorbs the impurities.

In previous publications [1-3] we have described methods for preparation of CMS for separation of O_2 from N_2 or Ar. The performance of CMS was evaluated by following diffusion of these gases under ambient conditions. In this study we have investigated the adsorption of these gases at lower temperatures.

The carbons used in this study were CMS-A and modified CMS-B. CMS-A is a pelletized commercial molecular sieve adsorbent for separation of O_2 and N_2 in air; it is classified as a 0.3-0.4 nm CMS [1]. CMS-B is a granular carbon of pore size of about 0.5 nm [1]. The modified sample of CMS-B was prepared by depositing carbon from propylene cracking [3]. This treatment produced a CMS-B sample that exhibited properties similar to a 0.3-0.4 nm CMS. Physical properties of the carbons used are discussed elsewhere [1-3]. The rate of gas diffusion on these carbons and their adsorption capacities were measured volumetrically in a manner reported earlier [1]. Carbons were degassed at 383 K for 1 h prior to gas adsorption.

Physical data for O_2, N_2 and Ar, reported elsewhere [2], indicate that boiling and critical temperatures of these gases lie in a very close range. Therefore, their equilibrium capacity on a carbon should be essentially similar under specific adsorption conditions. In a CMS, separation of O_2 from Ar or N_2 occurs because the critical pore dimension (CPD) of CMS is below the minimum dimension of Ar or N_2, thus restricting the entry of these molecules. It can be said that the diffusion of these gases becomes activated. Rao et al [4] have reported that there are two types of energy barriers for the adsorbing molecule, one at the entrance of the pore of critical dimension and the second for diffusion within the pore. However, the relative rate of diffusion of adsorbing species is dependent on the magnitude of the energy barrier at the pore entrance which is the largest of the two types of energy barrier. Using the Lennard-Jones [6-12] potential, Walker and co-workers [5] estimated that the diffusion of gases becomes activated when the pseudographitic basal planes are closer to each other than the sum of the kinetic diameter of the diffusing species and 0.16 nm.

Therefore, small changes in slit thickness will clearly produce very large changes in activation energy for diffusion. The rate of diffusion of these gases is thus temperature dependent. Below ambient temperatures (closer to the critical temperatures) the molecules are much less energetic to overcome the resistance offered by the pores that have entrances in close range of the size of the adsorbing molecule. On the other hand, molecules of size smaller than the CPD are rapidly adsorbed since their diffusion is non-activated.

Uptake rates of O_2 and Ar at 298, 273 and 189 K on a sample of CMS-A are shown in Fig. 1. As reported earlier [2], rates of diffusion of these gases vary in accordance to the minimum dimension of the molecule, being higher for the smaller O_2 molecule and lower for the larger Ar molecule. At 298 K, uptake of O_2 levels off at ~4.5 cc/g, requiring only 8 min. Taking the area occupied by a physically adsorbed molecule of O_2 at 298 K as 0.27 nm^2, it is estimated that 1 cc O_2 (STP) covers ~ 7.3 m^2 of surface. Or at saturation uptake of O_2 at 298 K, it is estimated that ~ 33 m^2/g of surface is occupied. Taking the total surface area of CMS-A as 575 m^2/g [1], fractional coverage is only ~ 0.057. Uptake of Ar at 298 K in 8 min is ~ 1.2 cc/g, or the ratio of O_2 to Ar uptake (selectivity) is 3.8.

Upon decreasing the adsorption temperature to 273 K, the rate of uptake of O_2 remains unchanged but the rate of Ar uptake is diminished. As a result, the selectivity of the carbon in 8 min is enhanced to ~ 5.6. When adsorption was carried out at 189 K, it is seen that the rate of Ar uptake is further reduced. Even though the rate of uptake of O_2 is initially reduced, longer time
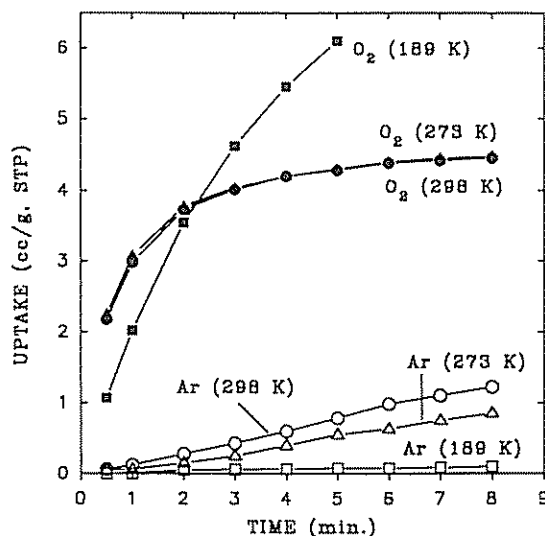

Figure 1   Uptake of O_2 and Ar on CMS-A.

uptake is enhanced. Selectivity of the carbon at 189 K is sharply increased to ~ 7.8.

The results show the desirability of reducing adsorption temperature to enhance the separation of O_2 from Ar. Since the activation energy for O_2 diffusion into a CMS is lower than that for Ar [6], a reduction in temperature will reduce the Ar diffusion parameter more drastically than the of O_2. This is desirable for greater separation. Also a reduction in temperature will enhance O_2 and Ar uptake at equilibrium. Enhancement at equilibrium will be about equal since their isosteric heats of adsorption on a CMS are very similar (~ 17-18 kJ/mole) [7-8]. However, because the diffusion parameter for Ar is much less than that of O_2 on the CMS, in a reasonable cycle time for pressure swing adsorption, Ar uptake will be much more removed from its equilibrium value than that for O_2. As a result, it is seen in Fig. 1 that O_2 uptake at 8 min at 189 K (~ 7.8 cc/g) is greater than O_2 uptake in 8 min at 298 K, whereas Ar uptake at 189 K is sharply reduced over that at 298 K. Or, for an 8 min cycle, thermodynamics dominates for O_2 uptake and kinetics dominates for Ar uptake.

Figure 2 shows plots of O_2 and Ar uptake at 298 and 189 K on a CMS sample prepared from CMS-B by deposition of carbon [3]. Again the advantage of operating below ambient temperature on the separation of O_2 from Ar is seen. At 298 K, the Ar uptake on this
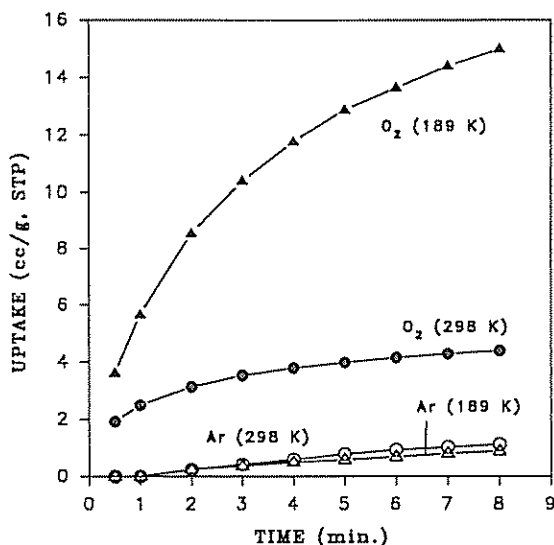
CMS is lower than that on CMS-A. Just like CMS-A, the uptake rate of Ar on this carbon is diminished upon reducing the adsorption temperature to 189 K. Over the first minute, this carbon shows no discernible uptake of Ar. By contrast, the O_2 uptake rate and amount adsorbed are increased 2-3 fold by operating at 189 K, thus causing a significant improvement in selectivity to ~ 19.

Calgon Carbon Corporation   S.K.VERMA
Pittsburgh, PA 15230

Ehime University   Y. NAKAYAMA
Binkyo-cho, Matsuyama
Ehime 790, JAPAN

Department of Materials Science   P.L.WALKER, Jr.
  and Engineering
The Pennsylvania State University
University Park, PA 16802

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Figure 2   Uptake of O_2 and Ar on CMS-B.