PREPARATION OF CARBON MOLECULAR SIEVES BY PROPYLENE PYROLYSIS OVER NICKEL-IMPREGNATED ACTIVATED CARBONS

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Abstract—Exploratory runs have shown it to be possible to produce a sieve for the separation of O_2 from Ar by depositing carbon from propylene in or over an activated carbon (AC) previously impregnated with Ni. It is thought that preferential cracking of propylene at the Ni sites within the pores of the AC particles and/or at the particle exterior surface introduces apertures of size 0.54–0.57 nm—the size required for this separation.

1. INTRODUCTION

An activated carbon (AC) possesses high surface area and extensive adsorption capacity. If its pore structure can be modified to generate constrictions for molecular sieving, such a carbon can produce an excellent carbon molecular sieve (CMS). Walker et al.[1] have proposed the 'gate' principle, suggesting that the constrictions or the gates of size in the range of molecular dimensions can be created in the pore structure of an AC by coating them with a thermosetting polymer. Deposition of carbon, using chemical vapor deposition, has also been used to modify the structure of microporous carbons[2–4]. Deposition of a thin layer of carbon on the outer surface of the host is anticipated to create such gates, leaving behind the interior micropore volume essentially unchanged. However, for separation of gases, of molecular sizes in close range, earlier efforts on modifying the pore structure of activated carbons into an aperture-cavity type pore structure by carbon deposition[2,3] have proved only partially successful. Generally, because of a wide pore-size distribution in an AC, such a treatment causes a continuous shrinkage of pores of all sizes, thereby simply moving the distribution downward to a smaller average pore-size. It leaves behind a relatively small pore volume in pores between 0.54 and 0.57 nm in width, that is, pores that allow separation of O_2 from Ar or N_2[5].

It was suggested earlier[2] that carbon deposition from the cracking of propylene at temperatures below about 973K can prove helpful in modifying the pore structure of activated carbons, since cracking at relatively low temperatures prevents sintering of AC. Hoffman[6], LaCava et al.[7], and more recently, McAllister and Wolf[8] have shown that pyrolysis of propylene on carbon surfaces is significantly enhanced in the presence of Ni. Therefore, in the presence of Ni, carbon deposition from pyrolysis of propylene can be achieved at a relatively lower temperature and specifically at the Ni sites on the carbon matrix. If Ni is impregnated near the outer surface of the AC, it can lead to deposition of carbon closer to the outer surface of the host for a favorable generation of an aperture-cavity system in the pore structure where little or none previously existed, while leaving behind sufficiently high adsorption capacity in the micropores. These apertures will be preferably formed due to more rapid deposition of carbon over nickel particles than over the non-impregnated carbon surface.

2. EXPERIMENTAL

2.1 Carbons used

Two commercial microporous carbons were used in this study. CMS-A is a carbon molecular sieve adsorbent derived from coal and used for the separation of O_2 from N_2 or Ar[9]. Physical properties of this carbon are given in Table 1. The relatively large surface area, measured by CO_2 adsorption at 298 K, and low surface area, measured by N_2 adsorption at 77 K, is characteristic of carbons having pores or apertures predominantly in the narrow size range 0.54 to 0.57 nm[5].

AC-B is an activated carbon derived from coconut hulls. It has a broader distribution of pore size in the micropores than does CMS-A, with the peak in the distribution located at a larger pore size (>0.57 nm) than that for the CMS sample. Surface areas, as measured by both CO_2 and N_2, are very large for this AC, with the N_2 area being larger than the CO_2 area due to some capillary condensation of N_2 in the larger micropores. AC-B carbon has an open porosity of 58%, as calculated from its total open

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Table 1. Physical properties of carbons

| Carbon | Particle size (mm) | Particle density (g/cc) | Surface area (m²/g) | |
			CO₂ (298 K)	N₂ (77 K)
CMS-A	4 × 1.5	1.356	575	<1
AC-B	4.7 × 2.0	0.845	1367	1706

pore volume of 0.688 cc/g, determined from its particle and methanol densities[2]. Of the total pore volume, ~44% is located in macropores and transitional pores of size between 2×10^4 nm and 6 nm, as measured by mercury porosimetry.

2.2 Addition of Ni to the activated carbon

In this study AC-B was loaded with Ni up to 5% by weight. Nickel was impregnated on the carbon from a concentrated solution of $Ni(NO_3)_2 \cdot 6 H_2O$ by the incipient-wetness technique. A volume of solution essentially equivalent to the pore volume of the carbon was injected into the carbon bed to reach the point of incipient wetness. By this method most of the solution is expected to be adsorbed into the pores. The loading level for Ni can be varied by injecting solutions of varied Ni concentration. After impregnation, the carbon was dried at 383 K for 2 h. The sample was then held at 773 K in N_2 for 4 h in order to decompose the $Ni(NO_3)_2$. It was subsequently treated with H_2 at 773 K for 4 h for reduction of the oxide to Ni. No significant gasification of carbon was observed at the treatment temperature. The sample was cooled in H_2 and then stored under vacuum.

2.3 Carbon deposition by cracking of propylene

The carbons were first degassed at either 823 K or 973 K, and then held isothermally at these temperatures before exposure to propylene. Treatment in propylene was carried out by flowing a stream at 100% propylene through the carbon bed at 0.1 MPa total pressure and flow rate of 100 cc/min for a specified period. Following this treatment, the carbon was degassed at the same temperature or, in some cases, a higher temperature. Molecular sieve properties of various carbons were measured after treatment by adsorption of O_2 and Ar, volumetrically, under ambient conditions, as discussed elsewhere[9].

The rate of pyrolysis of propylene on the carbons was measured by using a Cahn Electrobalance. The carbon sample, held in a quartz boat, was suspended in a quartz reactor tube. The system could be connected either to the desired gas stream or to vacuum for degassing the carbon to 10^{-4} MPa. Change in weight of the carbon was recorded as a function of time on a continuous chart recorder.

3. RESULTS AND DISCUSSION

3.1 Carbon deposition

Carbon deposition on AC-B at 823 K, before and after addition of 5% Ni, was studied over a 5 h period. Results are shown in Fig. 1 by plots designated AC-B and AC-B/Ni—Run 1. As expected, the rate of carbon deposition from propylene over the Ni-containing sample is significantly greater than that over the original AC-B. The interesting finding is that carbon deposition on the AC-B sample has essentially stopped at 28% weight gain after 5 h, whereas deposition is still continuing on the Ni-impregnated sample following a weight gain of ~56% in 5 h. Since the open porosity in AC-B is ~58%, if the true densities of the base carbon and the deposited carbon were equal, a potential weight gain of 58% within the pore system would be possible.

Following the initial 5 h runs, each carbon was held at 1123 K under vacuum for 1 h to clean the surface prior to re-exposure to propylene at 823 K. In the case of the as-received AC-B, negligible deposition of carbon was recorded during the second exposure. However, the Ni-impregnated carbon showed an additional loading of ~13% in 5 h. Apparently, upon degassing at 1123 K prior to the second exposure, some of the Ni sites were regenerated and, consequently, catalyzed further pyrolysis of propylene. LaCava et al.[7] have reported that heat treatment at elevated temperature diffuses some deposited carbon away from Ni, to leave behind active Ni sites.

Clearly, a superior CMS would be one that could be described as an aperture-cavity solid. The apertures would be of a size that would admit O_2 without requiring activated diffusion, but not admit Ar without activated diffusion being required. For apertures
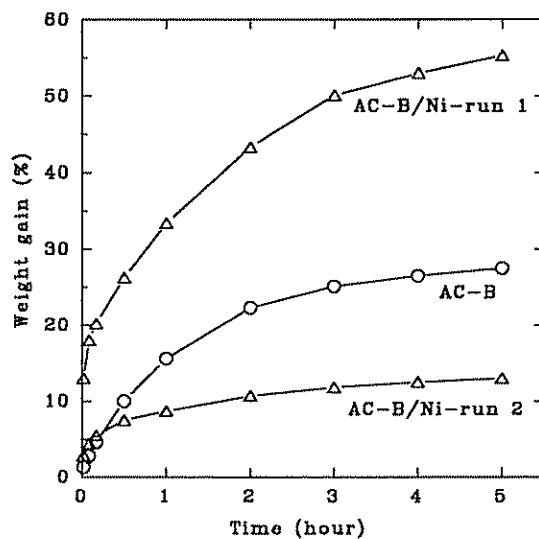

Fig. 1. Weight gain produced by deposition of carbon from the cracking of propylene at 823 K over AC-B before and after 5% Ni addition.

being composed of the basal plane of trigonally bonded carbon atoms, the aperture size (thickness) should be between 0.54 and 0.57 nm[5] to fulfill this requirement. Also most desirably, the ratio of the surface area in the cavities to that in the apertures of a correct size and location should be at a maximum. Even though all microporous carbons are thought to be, more or less, aperture-cavity solids, it is clear that commercial activated carbon AC-B does not have apertures of the appropriate size and/or location to separate O_2 from Ar effectively. It was selected as a precursor for the production of a suitable CMS, however, since it had a very large surface area in micropores; and, hopefully, little carbon deposition would have converted it to an excellent sieve for separating O_2 from Ar. Such was not the case, as previously reported[2].

Nickel has been added to AC-B in this study in an attempt to produce apertures of the desirable size and location following carbon deposition from propylene. It was thought that Ni particles, to the extent that they had access to the pore system of AC-B, would catalyze carbon deposition from propylene producing apertures along the pores. We expected then that the amount of carbon that could be introduced into the pore system of AC-B before deposition stopped would be markedly reduced compared to that of carbon deposition in the original AC-B. However, as seen in Fig. 1, such was not the case. Carbon deposition over the Ni-impregnated sample not only exceeded the rate of deposition over the as-received AC-B sample, but also greatly exceeded the amount that could be deposited. Deposition even exceeded that which apparently could be accommodated within the pore system of the AC-B. Apparently, much of the carbon deposition occurred at the exterior surface of the AC-B 4.7×2.0 mm particles. If non-uniform impregnation of AC-B with Ni in fact did occur, with the majority of the Ni residing at or close to an exterior surface, this could be a desirable situation. It could result in a minimum loss of surface area for adsorption within most of the interior of the particles. That is, the gate principle would be operative if apertures of appropriate size were formed at or slightly within the exterior surface of the particles[1,2].

3.2 Uptake of O_2 and Ar on carbons

Uptake of O_2 and Ar on commercial CMS-A is shown in Fig. 2. 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 (STP) O_2 occupies 7.3 m^2 of surface. Or at saturation coverage, O_2 covers ~30 m^2/g CMS-A surface. This represents a fractional coverage of only 0.052, based on the CO_2 surface area of 575 m^2/g. It is thought that adsorption is in the Henry's Law region, where uptake is directly proportional to adsorbate pressure[10].

As discussed previously, we have not yet been successful in producing a comparable or better sieve than CMS-A using carbon impregnation from pro-
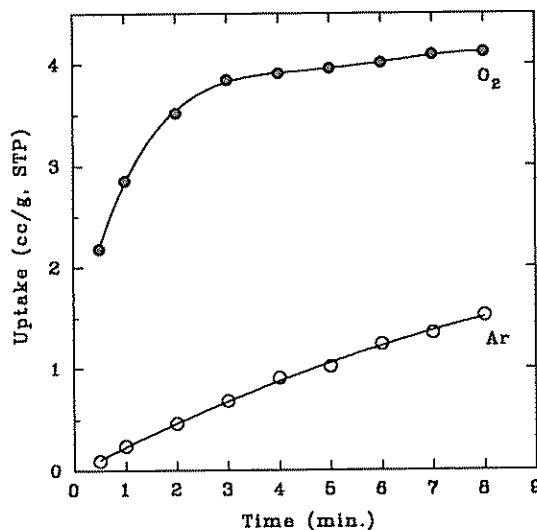

Fig. 2. Uptake of O_2 and Ar on commercial sieve CMS-A.

pylene of the activated carbon AC-B[2]. One useful criterion to evaluate the quality of sieving achieved by a carbon is to compare the ratio of O_2 to Ar volume taken up in a fixed period of time, say, in 3 min[9]. This ratio for the CMS-A sample is 6.4. Some of our attempts to produce a superior sieve by carbon infiltration of AC-B/Ni will now be described.

Several conditions were selected for deposition of carbon in AC-B before and after impregnation with Ni. In one case, a carbon loading of 28% was achieved upon pyrolysis of propylene on either AC-B/5% Ni at 823 K for 30 min or AC-B at 973 K for 13 min. Figure 3 presents results for uptake of O_2 and Ar at ambient temperature and 0.1 MPa pressure. Run 3 represents uptake on the non-im-
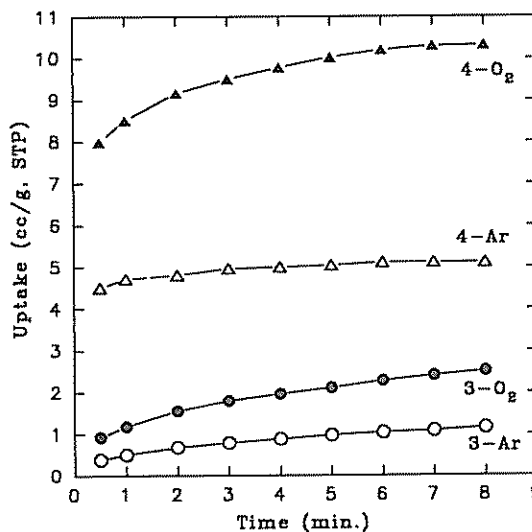

Fig. 3. Uptake of O_2 and Ar on AC-B (run 3) and AC-B/ 5% Ni (run 4) following deposition of 28% carbon.
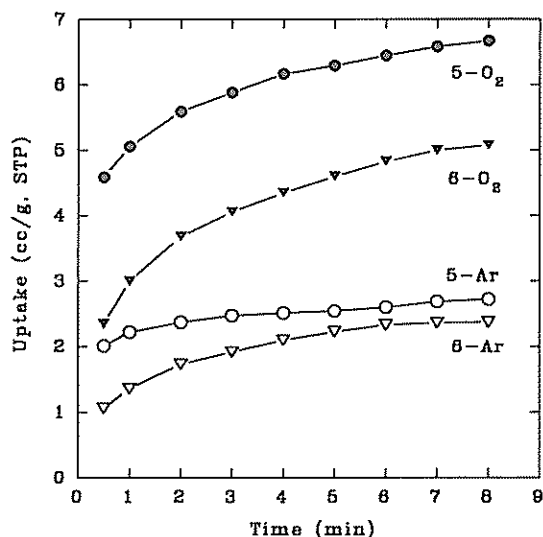
Fig. 4. Uptake of O_2 and Ar on AC-B/5% Ni following deposition of 43% (run 5) and 53% (run 6) carbon.

pregnated AC-B sample; run 4 represents uptake on the impregnated AC-B/5% Ni sample. These results are conistent with conclusions derived from Fig. 1. That is, at equivalent loadings of deposited carbon, the pore volume in sample AC-B is much more closed to propylene than it is in sample AC-B/5%wt. Thus, it would be expected that gas uptake rate would be less in impregnated sample AC-B.

Results shown in run 3 are consistent with previous results, which show the failure of producing a good CMS from AC-B[2]. That is, uptake rate and capacity for Ar are reduced to an unacceptably low level only when it is accompanied by too much reduction of O_2 uptake. Unsatisfactory sieving results, with the ratio of O_2 volume uptake to Ar volume uptake at 3 min equaling only 1.9.
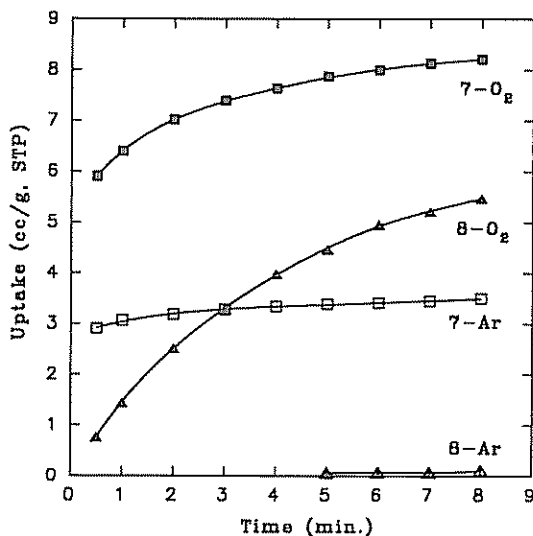

Fig. 5. Uptake of O_2 and Ar on AC-B/3.2% Ni following deposition of 31% (run 7) and 36% (run 8) carbon.

More carbon was deposited on other samples of AC-B/5% Ni by extending deposition times to 2 and 4 h at 823 K. In 2 h and 4 h, it is estimated that weight gains of 43% and 53%, respectively, were achieved. Figure 4 shows the effects of these treatments on O_2 and Ar uptake. Uptakes of both gases are sharply reduced, compared to uptakes found in run 4 (Fig. 3). Uptake volume ratios are improved, however, to 2.4 (run 5) and 2.2 (run 6).

Another sample of AC-B was impregnated with 3.2% Ni. This carbon was first exposed to propylene at 823 K for 80 min, followed by degassing at 1123 K. It is estimated that a weight gain of 31% resulted from the deposited carbon. Uptake of O_2 and Ar on this sample is shown in Fig. 5 (run 7). Uptakes of O_2 and Ar in 3 min are less than those found for run 4, Fig. 3, despite essentially the same amount of carbon deposited. Run 7 shows a superior ratio of O_2 to Ar uptake in 3 min, however: 2.5 compared to 1.9.

A portion of the carbon-laden sample from run 7 was further exposed to propylene at 823 K for 30 min, followed by degassing at 1123 K for 1 h. It is estimated that an additional weight increase of 5% resulted. Uptake of O_2 and Ar on this sample is shown in Fig. 5 (run 8). A striking result is achieved. No uptake of Ar is detected, within the sensitivity of the volumetric measuring equipment, for at least 4 min. Less than 0.12 cc/g is taken up in 8 min. This low level of Ar uptake is accompanied by a significant O_2 uptake. Oxygen uptake of 3.3 cc/g in 3 min is almost as great as uptake on the commercial sieve CMS-A. At 8 min, O_2 uptake on the infiltrated AC-B/3.2% Ni sample exceeds that found on the CMS-A sample. The shape of the O_2 uptake curves are different. For very short times, uptake is more rapid on the CMS-A sample; but total capacity is reached in about 3 min. Uptake on the infiltrated AC-B/3.2% Ni sample continues even past 8 min. For very short cycle times (~0.5 min), CMS-A may exhibit superior sieving behavior; for longer cycle times, the impregnated AC-B/Ni sample would be superior.

4. CONCLUSIONS

Exploratory runs have shown that it is possible to produce a molecular sieve for the separation of O_2 from Ar by depositing carbon from propylene over and in an activated carbon previously impregnated with Ni. By using the incipient wetness technique, it was thought that Ni could be distributed evenly through the porous network of the carbon prior to carbon deposition—at least in the macropores (>20 nm) and transitional pores (2–20 nm). However, measurements of carbon deposition from propylene on both the original AC and a sample impregnated with Ni suggest that extensive amounts of the Ni reside at the surface of the AC particles. Thus, it is not clear at this time whether satisfactory sieving was achieved primarily by the introduction

of new apertures of size 0.54–0.57 nm within the pore system or by depositing on pore mouths at exterior surfaces of the particles. It is clear, in any case, that the addition of a catalyst for the cracking of a hydrocarbon presents an additional useful variable for the production of carbon sieves from AC.

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