Carbon, Vol. 30, No. 6, pp. 837–844, 1992
Printed in Great Britain.

0008-6223/92 $5.00 + .00

F35 — 936

CARBON MOLECULAR SIEVES WITH STABLE HYDROPHOBIC SURFACES

S. K. VERMA* and P. L. WALKER, JR.
Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802, U.S.A.

(*Received* 26 *February* 1991; *accepted in revised form* 28 *February* 1992)

Abstract—The effect of interactions of O_2 and H_2O with CMS surfaces on their performance was studied under ambient conditions by using O_2 and Ar as molecular probes. Such interactions deteriorate the adsorption-desorption behavior of CMS and exhibit an adverse impact on their performance. Treatments of CMS with Cl_2 and H_2 were investigated for stabilizing their surfaces. Treatment with H_2 at 5.5 MPa and 150°C was found to eliminate strong interactions with O_2 and H_2O by passivating the active sites, thus resulting in a stable CMS surface.

Key Words—Carbon molecular sieve, adsorption, diffusion, uptake rate, O_2, Ar, interactions.

1. INTRODUCTION

Use of carbon molecular sieves (CMS) in gas separations, specially O_2 and N_2, has been constantly growing. The micropore structure of such carbons is unique, since the slit-like apertures or the so-called "constrictions" of their micropores are of a size similar to the molecular dimensions of the adsorbing species. In the separation of gases, molecules smaller than the size of the micropore constrictions rapidly diffuse through them into the associated micropore volume. On the other hand, a larger molecule is denied access to the volume behind the constrictions[1]. A small change in the effective size of the constriction can affect the rate of diffusion of an adsorbing gas molecule to a considerable extent, so that its non-activated diffusion through the pore constriction now becomes activated.

Carbon surfaces exhibit a strong affinity for O_2 even at room temperature. Interactions of O_2 with carbon result in the formation of certain specific types of carbon-oxygen surface complexes. Oxygen is, therefore, held to the carbon surface, in part, more strongly than just by physical adsorption. Oxygen interactions and chemisorption at or near a pore constriction can eventually reduce its effective size, thereby offering diffusional restrictions for some freely adsorbing gas molecules. Prevention of such surface reactivity towards O_2 can, therefore, yield more stable CMS.

In addition, the hydrophobicity of CMS is of prime importance. Carbons exhibit a hydrophobic character to some extent. However, it has been reported that water can preferentially hydrogen bond to specific sites, such as surface oxides present on the carbon surface[2,3]. Sorption of water on carbon becomes significant at relative vapor pressures (rvp) > ~0.4. The weak dispersion interactions of water molecules with the carbon surface are believed to be enhanced in narrow micropores[2]. However, since the overlap of the potential field from pore walls of a slit-like pore can enhance the interaction energy significantly[1], this interaction energy at the pore constriction is expected to be considerably higher than inside the pore. The existence of constrictions of molecular dimensions that offer maximum interactions of the adsorbent walls with an adsorbate is of prime importance in CMS-type carbons. Thus, due to a high interaction energy, sorption of water vapor at the pore constrictions can occur at a relatively much lower vapor pressure. Water held strongly at or near the pore constrictions of a CMS can affect the diffusion rate of gases during the adsorption and desorption steps and thus significantly change its performance in a Pressure Swing Adsorption system.

Suzuki and Doi[4] have reported that adsorption of small amounts of water on a CMS from a humid gas stream dramatically diminishes diffusivities of gases such as O_2 and N_2, and adversely impacts equilibrium adsorption. Therefore, the hydrophobic behavior of CMS surfaces needs to be preserved in order to enhance their stability in performance. Pierce, *et al.*[5] have reported that treatment of a Saran char, which exhibited high water sorption at low rvp, with H_2 at 600°C diminishes its hydrophilic behavior considerably. After the H_2 treatment, significant water sorption commenced only at rvp > ~0.45. Stoeckli and Kraehenbuehl[6] have also shown that a MSC reduction in H_2 at 650°C modified its surface so that water adsorption was displaced to a higher rvp.

The present study investigates the effects of O_2 and H_2O, that are abundantly available in the atmosphere and interact strongly with a carbonaceous surface, on the stability of CMS surfaces. Efforts were also focused at improving the hydrophobicity of CMS surfaces in order to prevent their strong specific interactions with O_2 or H_2O.

*Present address: Calgon Carbon Corp., Pittsburgh, PA 15230.

2. EXPERIMENTAL

Freshly prepared samples of CMS were used in this study. These samples were generated *via* carbon deposition on CMS-B, a microporous carbon with an average pore dimension of 0.5 nm[7], from cracking or propylene at 700°C for 3 minutes[8]. The temperature and time of cracking of propylene were optimized to produce the highest achievable uptake rate of O_2 and the lowest uptake rate of Ar. The uptake of O_2 and Ar was investigated to evaluate the sieving properties of these carbons as reported earlier[7]. The reproducibility of an adsorption run was found to be within ± 0.05 cc/g.

In order to investigate the stability of CMS, both freshly made samples and those pretreated in Cl_2 and H_2 were tested for repeat performance for uptake of O_2 and Ar. Treatment with Cl_2 was carried out by flowing a Cl_2 stream (0.1 MPa) through a sample of CMS at 450°C for 15 hours. After exposure, the carbon was degassed at 450°C for 1 hour to eliminate the physisorbed Cl_2. Treatment in H_2 was conducted in two different ways. First, a sample of CMS was treated by flowing a H_2 stream (0.1 MPa) through the carbon bed maintained at 250°C for 40 hours. Second, another sample of a freshly prepared CMS, maintained at 150°C, was exposed to a 5.5 MPA pressure of H_2 for 72 hours. After each treatment, the performance of CMS samples was tested volumetrically for uptake rates of Ar and/or O_2 under ambient conditions in a manner discussed elsewhere[7]. Following such tests, the samples were kept under dry (<1 ppm H_2O) and/or moist air (rvp of ~1.0) in a desiccator for specified time periods. After storage, each sample was reevaluated for O_2 and Ar uptake.

3. RESULTS AND DISCUSSION

3.1 *Effect of adsorption cycles*

Stability of CMS surfaces toward O_2 was investigated by following adsorption-desorption (vacuum)-adsorption cycles for Ar and O_2 gases under ambient conditions on a freshly prepared sample of CMS, designated as CMS-I. The order of diffusion runs, regeneration conditions, selectivity ratios, and volume uptakes at 8 and 30 minutes are summarized in Table 1. It was found in a number of diffusion runs on a similar sample of CMS that uptake of O_2 does not change significantly after 30 minutes. It was, therefore, concluded that the amount of O_2 physically adsorbed in this period closely represents the equilibrium O_2 loading on the CMS. On the other hand, the rate of loading of Ar is quite slow, with equilibrium not being reached in 30 minutes. However, 30-minute loading values for Ar are considered for the sake of comparison. Selected gas diffusion runs on the untreated CMS-I are plotted in Fig. 1 A. In these runs, the surface of the CMS was exposed to O_2 for the first time in Run 2. Runs 1 and 2 indicate that this CMS exhib-

Table 1. Adsorption-desorption cycles of O_2 and Ar on a CMS and effects of storage in dry or moist air

Diffusion run	Gas used	Degassing conditions: Temp (°C)	Degassing conditions: Time (h)	Uptake (cc/g, STP) at (min): 8	Uptake (cc/g, STP) at (min): 30	O_2/Ar ratio at (min): 1	O_2/Ar ratio at (min): 5
1	Ar	700	1	0.20	1.28		
2	O_2	110	1	5.05	5.83	∞	54
3	Ar	25	1	0.13	1.06		
4	O_2	25	1	4.22	4.79	∞	224
5	Ar	25	1	0.22	1.07		
6	O_2	25	1	3.85	4.43	∞	167
7	Ar	25	1	0.10	0.95		
8	O_2	25	1	4.01	4.53	∞	209
9	Ar	25	1	0.10	0.95		
10	O_2	25	1	3.89	4.36	∞	∞
11	Ar	110	1	0.11	1.01		
12	O_2	25	1	3.91	4.47	∞	∞
13	O_2	110	1	4.07	4.67	—	—
14	O_2	110	1	4.02	4.68		
15	Ar	110	1	0.11	0.85	∞	∞
Part a. After storage in dry air at 25°C for 35 days							
16a	O_2	25	1	2.47	4.02	—	—
17a	O_2	110	1	4.47	5.61	—	—
18a	O_2	110	1	4.31	5.61	—	—
Part b. After storage in moist air at 25°C for 35 days							
16b	Ar	25	1	nil	0.26		
17b	O_2	25	1	2.48	4.50	∞	∞
18b	O_2	110	1	3.44	5.15	—	—
19b	O_2	110	1	3.66	5.16	—	—

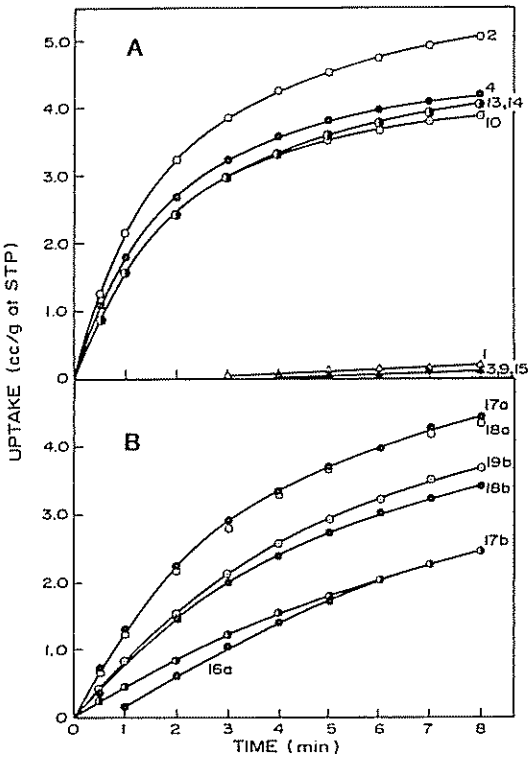

Fig. 1. Diffusion of O_2 and Ar in (A) untreated CMS-I and (B) untreated CMS-I stored in (a) dry air and (b) wet air. See Table 1 for description of runs.

its a high selectivity for O_2 adsorption. Following this, eight diffusion runs (No. 3–10) were made, exposing the CMS alternately to Ar and O_2. After each diffusion run, the CMS was regenerated by degassing only at ambient temperature for 1 hour. As seen in Fig. 1 A, for Runs 3 and 4 both O_2 and Ar uptake rates are diminished. In absolute terms, the effect is more pronounced in the case of O_2. However, the selectivity ratio, after a 5-minute period, is increased due to a greater fractional lowering of Ar uptake. In subsequent runs, Ar does not show a further detectable change in its rate of diffusion. By contrast, the uptake rate of O_2 continues to diminish through Run 10, though at a reduced rate. Even for the 30-minute adsorption period, some decrease in loading capacity is noted. As seen in Table 1, compared to the O_2 loading in Run 2, the O_2 loading at 30 minutes in Run 10 is reduced by about 25%.

If it is assumed that the difference in O_2 uptake between Runs 2 and 10 represents the greater amount of oxygen chemisorbed in Run 2, an estimate can be made of the surface area it would occupy. Assuming that this amount of oxygen (1.47 cc/g) is adsorbed dissociatively on the carbon surface, it is calculated that this amount of oxygen covers ~7 m^2/g of the total area. This coverage was determined assuming 0.083 nm^2 as the area covered by one oxygen atom [9]. Assuming that the total area of the CMS is ~680 m^2/g[8], it means that this chemisorbed oxygen occupies roughly 1% of the surface. It is possible that the reduction in O_2 uptake between Runs 2 and 10 is due to a combination of reduction in physically adsorbed and chemisorbed oxygen. Reduction in physically adsorbed O_2 would occur if chemisorbed oxygen blocked some pore apertures. Thus the above calculation for the difference in amount of chemisorbed oxygen between Runs 2 and 10 represents an upper limit.

At the fourth O_2 adsorption cycle (Run 8), it appears that O_2 uptake becomes nearly reversible, and that the most reactive sites are now occupied by chemisorbed oxygen. It is expected that this strongly held oxygen is also responsible for some lowering in Ar uptake rate. No interactions of Ar with the CMS surface are expected other than its physical adsorption. However, the O_2 held at sites located at pore constrictions reduces their effective size and thus restricts entry of Ar molecules, ultimately causing lowering of Ar uptake.

In order to investigate effects of ambient O_2 and moisture on the performance of CMS, the carbon after Run 15 was divided into two portions. One portion was kept under dry air in a desiccator for 35 days. After this period, the sample was tested for O_2 uptake under ambient conditions. Insufficient sensitivity was available to measure any Ar uptake in 8 minutes. Results are included in Table 1 and diffusion plots are shown in Fig. 1 B. Storage in dry air for 35 days, followed by degassing at 25°C, results in a sharp decrease in the rate of O_2 uptake into the CMS. Compare runs 14 and 16a in Table 1. The effect is particularly marked for short adsorption times. Weight uptake of 0.5% was recorded after the storage period (as is in Table 2). This may be caused by some strong interactions of oxygen with carbon. However, this does not appear to be the case since, upon degassing at 110°C, most of the weight gained during storage is lost. Comparing Run 17a with Run 2, it is interesting to find that most of the adsorption of O_2 at 8- and 30-minute periods is recovered to the level of fresh CMS though the initial diffusion rate is lower in Run 17a. Therefore, for regeneration of CMS after extended storage or usage under dry atmospheric conditions, heat treatment at about 110°C appears to be quite helpful in improving its performance.

It is curious, though, that heating to 110°C following storage yielded a sieve showing a superior uptake of O_2 than that found in Run 14, since it was found earlier that heating to 110°C produced little improvement in O_2 uptake (Runs 13 and 14). It is as if some of the oxygen originally chemisorbing on the CMS during diffusion runs was made susceptible for removal by outgassing at 110°C following the 35 days of storage in dry air. Alternatively, it may be possible that some of the oxygen chemisorbed in Run 2, which was effective in reducing O_2 diffusion rates in subsequent cycles (Runs 4, 6, 8, 10, 12, 13, and 14), diffused away from sites on which it was originally

Table 2. Weight gain of CMS samples during storage for 35 days

Carbon	Pretreatment	Dry air		Moist air	
		Wt. gain %	Wt. loss on regeneration* %	Wt. gain %	Wt. loss on regeneration* %
CMS-I	none	0.5	0.4	14.7	11.5
CMS-II	Cl_2, 450°C	—	—	13.9	13.2
CMS-III	H_2, 250°C	0.5	—	14.4	13.4
CMS-IV	H_2, 150°C 5.5 MPa	0.0	0.0	12.6	12.2†

*Regeneration by degassing at 110°C, 1 hour.
†Regeneration by degassing at 25°C, 1 hour.

chemisorbed during 35 days of storage. For example, oxygen atoms may have diffused to basal plane sites and chemisorbed. Possibly, on basal plane sites, chemisorbed oxygen atoms are less effective at blocking O_2 diffusion into the CMS.

The second portion of CMS-I after run 15 was stored for 35 days under a relative humidity of near 100% at ambient temperature. This sample shows a weight gain of 14.7% during the storage period (as Table 2). Results of the uptake of O_2 and Ar on this sample measured after this period are presented in Table 1 and Fig. 1 B. In Run 17b, the O_2 uptake at 30 minutes (equilibrium) is similar to that observed in Run 14 made on CMS-I prior to its storage under moist air. However, the rate of diffusion in Run 17b in the first few minutes of adsorption is significantly reduced in comparison to Run 14 (as in Fig. 1 B). Such a decrease in the initial diffusion rate of O_2 will exhibit a deleterious effect upon the performance of CMS in a PSA unit using a short time cycle.

In agreement with results following storage in dry air, degassing at 110°C significantly enhances O_2 uptake following storage in moist air (Runs 18b and 19b). However, regeneration is not as successful as that found in the former case. Regeneration results in a weight loss of only 11.5%, thus leaving a significant amount of H_2O in the sieve. Comparison of Run 18b with Run 14 is interesting. Oxygen uptake in Run 14 exceeds that in Run 18b in the first 8 minutes; however, uptake at equilibrium (30 minutes) is greater for Run 18b. That is, the initial diffusion of O_2 into the sieve is reduced as a result of exposure to moist air and subsequent degassing at 110°C. Presumably H_2O remaining in the sieve is blocking some pore entrances to O_2 uptake. But, despite the presence of some H_2O in the pore system, O_2 uptake at equilibrium is not reduced—in fact, it is increased. It is as if O_2 physically adsorbs more strongly onto H_2O molecules than onto oxygen complexes or the carbon-free surface.

In any case, repetitive adsorption-desorption runs with O_2 and long-term storage in either dry or moist air reduces the initial diffusion rate and, in some cases, equiblibrium uptake of O_2 on the CMS. Obviously, it is important to attempt to stabilize the CMS so that these effects are minimized.

3.2 *Effect of Cl_2 treatment*

As shown previously, water adsorbs preferentially on oxygen complexes which are chemically bonded to carbon surfaces[2,3]. It is thought that they are hydrogen bonded to such groups. It is not surprising that heating untreated CMS-I, previously exposed to moist air, to 110°C did not remove all H_2O from the sample. To remove the interaction of H_2O with the oxygen complexes, the carbon sites active for oxygen chemisorption need be passivated (covered) with some chemically bound species, which, in turn, does not preferentially interact with H_2O. One such possible species is atomic chlorine, which chemisorbs on carbon-active sites, forming a covalent bond[10]. Puri[11] and Puri and Bansal[12] have also shown that chlorine can be chemically bound to the carbon surface. This chemically bound chlorine is desorbed only at a significantly higher temperature (1200°C). Tobias and Soffer[13] have reported that Cl_2 reacts with carbon at the double bonds and exchanges with chemibound hydrogen.

In this study, chlorine was chemisorbed on a freshly prepared sample of CMS-I by treating it with 0.1 MPa Cl_2 at 450°C for 15 hours prior to its exposure to O_2 or air. The physisorbed Cl_2 was removed by degassing CMS at 450°C for 1 hour. Results of O_2 and Ar adsorption on the chlorine-treated CMS-I sample are presented in Table 3. Compared to Runs 1 and 2 of Table 1, the chlorine-treated carbon (CMS-II) shows reduction in uptake of both O_2 and Ar. The 8-minute uptake of O_2 in Run 3 (Table 3) is substantially lower than that seen on the untreated CMS-I sample (Run 2, Table 1). It is suggested by Tobias and Soffer[13] that treatment with Cl_2 at about 500°C enables activated adsorption of chlorine into pores smaller than 0.38 nm and probably leads to closure of some narrow pore openings. The chlorine chemisorbed at certain pore constrictions eventually makes some pores inaccessible to O_2, thus lowering its uptake rate. Further cycling in Runs 4, 5, and 6 led to a continuing decrease in O_2 diffusion rates into the

Table 3. Effect of treatment of CMS-I with Cl_2 at 0.1 MPa, 450°C on its storage stability

Diffusion run	Gas used	Degassing conditions: Temp (°C)	Degassing conditions: Time (h)	Uptake (cc/g, STP) at (min): 8	Uptake (cc/g, STP) at (min): 30	O_2/Ar ratio at (min): 1	O_2/Ar ratio at (min): 5
1	Ar	110	1	0.26	0.98	—	—
Treated with 0.2 MPa Cl_2 at 450C, 10 hours							
2	Ar	110	10	nil	0.26		
3	O_2	110	1	1.91	4.01	∞	∞
4	Ar	25	1	nil	0.05		
5	O_2	25	1	1.34	2.77	∞	∞
6	O_2	25	1	0.94	2.48	—	—
After storage in moist air for 35 days							
7	O_2	25	1	0.31	0.87	—	—
8	O_2	110	1	0.68	1.84	—	—
9	O_2	110	15	1.00	2.43	—	—

CMS and reduction in equilibrium capacity for O_2. Obviously, this treatment in Cl_2 at 450°C did not block all the carbon-active sites for subsequent chemisorption of oxygen during diffusion runs in O_2.

Following Run 6, the sample was exposed to moist air for 35 days, resulting in a weight gain of 13.9%. This exposure results in another sharp decrease in O_2 uptake at 8 and 30 minutes on the CMS degassed at 25°C. Subsequent degassing at 110°C for 1 hour removed most of the water picked up during the 35-day exposure and resulted in some enhancement in O_2 uptake rate and amount. Further degassing at 110°C for 15 hours restored the sample activity to that seen in Run 6.

From studies of Walker and Janov[3], passivation of carbon active sites is expected to reduce H_2O adsorption at rvps below 0.5. However, at rvps between 0.5 and 1.0, water adsorption increases sharply, so that at 1.0 water uptake is essentially the same whether the surface has been passivated or not. Thus weight gains on samples CMS-I and CMS-II, exposed to a H_2O rvp of ~1.0, are essentially the same. The difference lies in the ability to regenerate the samples at 110°C following water uptake. Chlorine chemisorbed on some of the most active carbon sites on which oxygen chemisorbed in the case of the untreated CMS-I sample. Thus, it would be expected that removal of H_2O from CMS-II at 110°C would be more successful than from CMS-I. Such is seen to be the case, with regeneration producing a 95% weight recovery for sample CMS-II but only a 78% weight recovery for sample CMS-I.

3.3 *Effect of H_2 treatment*

Hydrogen appears to be an attractive species for blocking the active sites on the CMS surface. Being a small atom, chemisorption of hydrogen at pore constrictions may not alter their size to an extent that may seriously affect the rate of diffusion of the gas desired to be adsorbed on CMS. As mentioned above, previous reports[5,6] indicate that chemisorption of hydrogen reduced the sorption of H_2O at lower rvps and displaced the isotherm to a higher rvp. Puri reported[11] that chemisorbed hydrogen is evolved as H_2 when carbon is degassed above 500°C. Chen and Yang, from molecular orbital calculations, examine the feasibility and relative strengths of chemisorption of hydrogen on the two prismatic faces of graphite. Chemisorption of atomic hydrogen is stable, with C—H bond strengths of ~89 and 71 kcal/mol on the $(10\bar{1}0)$ and $(11\bar{2}0)$ faces, respectively[14].

In this study, chemisorption of hydrogen was carried out at moderate temperatures and at two different pressures. The first treatment in H_2 was conducted at 0.1 MPa. A virgin sample of CMS was prepared by carbon deposition from pyrolysis of propylene on CMS-B at 700°C for 3.1 minutes. Therefore, a slightly higher carbon deposition resulted as compared to that in the case of the CMS-I and CMS-II samples. Consequently, the initial O_2 diffusion rate on this CMS-III sample is relatively smaller than that observed on the CMS-I and -II samples. The CMS-III sample was treated with H_2 prior to any exposure to O_2 or air by flowing the gas through the carbon bed maintained at 250°C for a 40-hour period. At this temperature, gasification of the carbon in H_2 to produce CH_4 was found to be insignificant. After treatment, the sample was degassed and several Ar and O_2 adsorption runs were made. The sequence of various adsorption-desorption cycles made on this carbon, the adsorption data, and selectivity ratios are presented in Table 4. Selected plots of Ar and O_2 uptake are shown in Fig. 2 A. Some loss in Ar uptake is observed between Runs 1 and 2. This appears to be caused by the decrease in size of some pore constrictions due to chemisorption of hydrogen. Uptake of both gases at 8 or 30 minutes is reduced further during Runs 4 and 5. This occurs due to some strong interactions of the CMS surface with O_2 during the adsorption run. Some oxygen is strongly held to the carbon surface during Run 3 and is not easily desorbed upon degassing at ambient temperature. Be-

Table 4. Effect of treatment of CMS with H_2 at 0.1 MPa, 250°C on its storage stability

Diffusion run	Gas used	Degassing conditions: Temp (°C)	Degassing conditions: Time (h)	Uptake (cc/g, STP) at (min): 8	Uptake (cc/g, STP) at (min): 30	O_2/Ar ratio at (min): 1	O_2/Ar ratio at (min): 5
1	Ar	110	1	0.26	1.02	—	—
Treated with 0.1 MPa H_2 at 250°C, 40 hours							
2	Ar	110	1	0.17	0.83		
3	O_2	110	1	4.34	5.97	∞	37.5
4	Ar	25	1	0.12	0.67		
5	O_2	25	1	3.72	4.92	∞	∞
6	Ar	25	1	0.12	0.62		
7	O_2	25	1	3.47	4.62	∞	237
8	Ar	25	1	0.13	0.64		
9	O_2	25	1	3.58	4.74	∞	222
Part a, After storage in dry air at 25°C for 35 days							
10a	O_2	25	1	2.17	4.00	—	—
11a	O_2	110	1	3.07	5.48	—	—
12a	O_2	110	20	3.15	5.43	—	—
Part b, After storage in moist air at 25°C for 35 days							
10b	Ar	25	1	nil	nil		
11b	O_2	25	1	1.18	3.04	∞	∞
12b	O_2	110	1	2.84	5.09	—	—
13b	O_2	110	20	2.84	5.09	—	—

yond Run 5, it appears that adsorption of O_2 and Ar becomes nearly reversible after regeneration by degassing at 25°C. Obviously, some of the active sites on the carbon surface have reacted with H_2. As discussed previously, there are discrete types of sites available for chemisorption of hydrogen that exhibit different potential energy configurations due to the geometrical arrangement of carbon atoms on the carbon surface[14–16]. Thus, some active sites are still left unreacted following treatment with H_2 at 250°C. These active sites then react with O_2 during diffusion runs in O_2. When all the remaining sites, which are inactive to hydrogen chemisorption at 250°C and 0.1 MPa, are covered with oxygen, adsorption on the CMS becomes reversible for both O_2 and Ar, though the diffusion rate is considerably reduced.

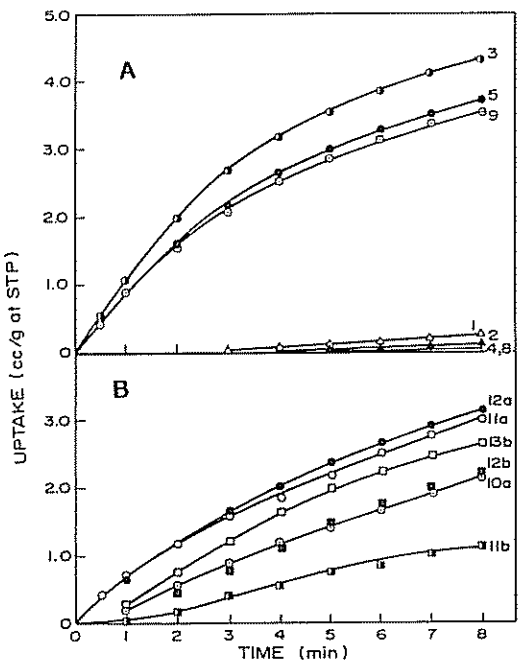

Fig. 2. Diffusion of O_2 and Ar in (A) CMS-III before and after treatment with H_2 and (B) CMS-III stored in (a) dry air and (b) wet air. See Table 4 for description of runs.

Storage studies on the above H_2-treated sample were conducted in the usual way. Results of O_2 and Ar uptake are included in Table 4 and diffusion plots are presented in Fig. 2 B. Storage in dry air, followed by degassing at 25°C for 1 hour, is seen to reduce O_2 uptake at 8 and 30 minutes. Further degassing at 110°C for 1 hour increases the rate of O_2 diffusion into the CMS, but the rate is still below that found prior to storage (compare Run 11a with Run 9). Interestingly, equilibrium uptake of O_2 at 30 minutes in Run 11a is greater than that found in Run 9. Further outgassing at 110°C for 20 hours (Run 12a) produced little additional improvement in the sieve behavior. Obviously H_2 treatment at 0.1 MPa and 250°C was not successful in improving sieve behavior over that of the untreated CMS-I sample, as seen by comparing Run 17a (Table 1) with Run 11a (Table 4). Treatment in H_2 reduced the initial diffusion rate of O_2 into the sieve, without noticeably improving its stability during storage in dry air. In fact, weight gain during storage in dry air was the same for the untreated and H_2-treated samples.

Results for storage of the H_2-treated sample in moist air are also given in Table 4. As expected for

Table 5. Effect of treatment of CMS with H_2 at 5.5 MPa, 150°C on its storage stability

Diffusion run	Gas used	Degassing conditions: Temp (°C)	Degassing conditions: Time (h)	Uptake (cc/g, STP) at (min): 8	Uptake (cc/g, STP) at (min): 30	O_2/Ar ratio at (min): 1	O_2/Ar ratio at (min): 5
1	Ar	110	1	0.41	1.26	—	—
Treated with 5.5 MPa H_2 at 150°C, 72 hours							
2	Ar	110	1	nil	nil		
3	O_2	110	1	2.97	3.85	∞	∞
4	Ar	25	1	nil	0.10		
5	O_2	25	1	3.01	3.91	∞	∞
6	Ar	25	1	nil	0.40		
7	O_2	25	1	3.19	4.03	∞	∞
8	Ar	25	1	nil	0.37		
9	O_2	25	1	3.06	3.89	∞	∞
10	O_2	25	1	3.12	4.01		
11	Ar	25	1	nil	0.48	∞	∞
Batch kept in moist air at 25°C for 35 days							
12	O_2	25	1	2.02	3.43	—	—
13	O_2	110	1	3.18	4.96	—	—
14	O_2	110	1	3.31	5.06	—	—

exposure to moist air at a relative humidity close to 1.0, weight pick-up is essentially the same as that found for the untreated sample. However, regeneration at 110°C resulted in removal of more H_2O from the sample than was removed during regeneration of the untreated sample, as seen in Table 2 (93% *vs* 78%). Again, treatment in H_2 was not successful in removing the effect of storage in wet air on subsequent sieve behavior in O_2. Regeneration at 110°C for 1 hour (Run 12b in Table 4) yielded an inferior sample to that produced by regeneration of the untreated sample under the same conditions (Run 18b in Table 1). These results show that chemisorption of hydrogen affects the nature of interactions of water with the CMS surface. However, to achieve a completely non-reactive surface, all the active sites on the CMS have to be passivated by chemisorption of hydrogen, so that none are left for strong interactions to occur between O_2 and/or H_2O and the CMS surface.

An effort in this direction was made by treating CMS with H_2 at a high pressure. A sample of CMS, designated as CMS-IV, was prepared by pyrolysis of propylene on CMS-B at 700°C for 4.3 minutes. Following an Ar diffusion run, the sample was exposed to 5.5 MPa H_2 at 150°C for 72 hours. Results from the subsequent diffusion runs are summarized in Table 5 and Fig. 3. Uptake of Ar in 8 or 30 minutes is not measurable after this hydrogen treatment. The key result is that the uptake of O_2 over the first 8 minutes and equilibrium adsorption in 30 minutes is essentially unchanged in a series of adsorption-desorption cycles (Runs 3 through 10). This is interpreted to mean that this high pressure exposure to H_2 had essentially passivated the carbon surface against the subsequent chemisorption of oxygen during diffusion runs.

Following Run 11 in Ar, CMS-IV was given the usual storage in moist air. As seen in Table 2, this storage resulted in a weight gain of 12.6%. However, regeneration at 25°C removed essentially all of the H_2O picked up during storage, that is, 97%. This again is indicative that the water taken up during storage was hydrogen-bonded to very few surface oxygen groups. Regeneration at 110°C resulted in complete recovery of the ability of the original carbon to take up O_2 in the first 8 minutes. In fact, if anything, uptake rate of O_2 was slightly enhanced (compare Run 13 with Runs 3 and 10). Interestingly, equilibrium uptake was significantly enhanced following regeneration of the sample stored in moist air.

It is certain that we have not optimized conditions for the passivation of CMS surfaces by exposure to H_2 in this study[17]. It is clear, though, that such passivation exhibits great potential for reducing (essentially removing) oxygen chemisorption on carbon

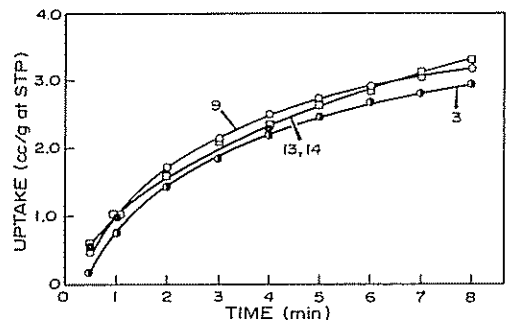

Fig. 3. Diffusion of O_2 in CMS-IV after treatment with H_2 at 5.5 MPa, 150°C, 72 hours. See Table 5 for description of runs.

surfaces. Such passivation can stabilize the carbon surface and lead to reproducible performance of the material. This is important for all kinds of applications ranging from the use of carbons in adsorption processes to their use in composites.

4. CONCLUSIONS

Oxygen and H_2O seriously affect the performance of CMS due to their strong interactions with the active centers on the CMS surface. Chemisorption of hydrogen at 5.5 MPa H_2 pressure and 150°C was found to passivate essentially all such active sites. Such a treatment stabilizes the CMS surface to allow consistently stable performance for extended usage and/or storage.

REFERENCES

1. D. A. Everett and J. C. Powl, *Trans. Faraday Soc.* **72**, 619 (1976).
2. M. M. Dubinin, *Carbon* **18**, 355 (1980).
3. P. L. Walker, Jr. and J. Janov, *J. Coll. Interface Sci.* **28**, 449 (1968).
4. M. Suzuki and H. Doi, *Carbon* **20**, 441 (1982).
5. C. Pierce, J. W. Wiley, and R. N. Smith, *J. Phys. Chem* **53**, 669 (1949).
6. H. F. Stoeckli and F. Kraehenbuehl, *Carbon* **19**, 353 (1981).
7. S. K. Verma and P. L. Walker, Jr., *Carbon* **28**, 175 (1990).
8. S. K. Verma and P. L. Walker, Jr., *Carbon* **30**, 829 (1992).
9. N. R. Laine, F. J. Vastola, and P. L. Walker, Jr., *J. Phys. Chem.* **67**, 2030 (1963).
10. Y. Ishikawa, L. G. Austin, D. E. Brown, and P. L. Walker, Jr. In *Chemistry and Physics of Carbon* (Edited by P. L. Walker, Jr. and P. A. Thrower), Vol. 12, p. 39. Marcel Dekker, New York (1975).
11. B. R. Puri. In *Chemistry and Physics of Carbon* (Edited by P. L. Walker, Jr.), Vol. 6, p. 191. Marcel Dekker, New York (1970).
12. B. R. Puri and R. C. Bansal, *Carbon* **6**, 189 (1967).
13. H. Tobias and A. Soffer, *Carbon* **23**, 281 (1985).
14. J. P. Chen and R. T. Yang, *Surface Science* **216**, 481 (1989).
15. R. C. Bansal, F. J. Vastola, and P. L. Walker, Jr., *J. Coll. Interface Sci.* **32**, 187 (1970).
16. R. C. Bansal, F. J. Vastola, and P. L. Walker, Jr., *Carbon* **9**, 185 (1971).
17. R. C. Bansal, F. J. Vastola, and P. L. Walker, Jr., *Carbon* **12**, 355 (1974).