

PREPARATION OF CARBON MOLECULAR SIEVES FOR OXYGEN SEPARATION FROM AIR

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Introduction

Carbon molecular sieves (CMS) have been traditionally used in pressure swing adsorption (PSA) processes to separate and recover high purity N₂ (99%) from air. The separation process relies on O₂ preferentially adsorbing in the micropores of the CMS. Low purity O₂ (35-50%) is the byproduct of the desorption cycle. To produce higher purity O₂ (80-95%) for such applications as oxygen enriched combustion or gasification [1], zeolite sorbents would be needed. However, zeolites are expensive and tend to adsorb water, which decreases separation efficiency. An alternative to zeolites would be a new class of CMS that could be used to recover high purity O₂ from air. An existing patent [2] claims an 83% O₂ stream can be obtained from a two stage process using coal-based CMS made by carbon deposition (Figure 1a, CMS1 is O₂ selective).

Almost all microporous carbons adsorb more O₂ than N₂; however, recent results [3] and [4] suggest that the surface chemistry of carbon can be modified so that more N₂ than O₂ is adsorbed based on differences in equilibrium adsorption capacities. This type of sorbent could be used to produce higher purity O₂ from the products of the desorption cycle of an air separation PSA process (Figure 1b, CMS2 is N₂ selective). The objective of this study [5] is to develop CMS from bituminous coal and to develop a process that can be used to recover high purity O₂ (up to 90%) from air. In this paper, we focus on production of CMS that will increase the percent O₂ in the products of desorption, i.e., CMS1 with high O₂ capacity and O₂/N₂ selectivity.

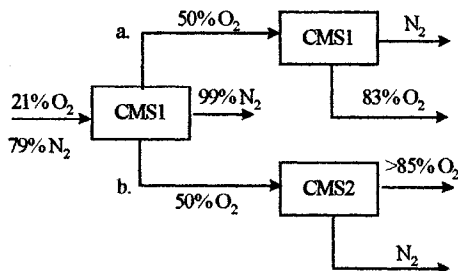


Figure 1. Proposed processes for producing high purity oxygen.

Experimental

Carbon molecular sieves were prepared from pelletized Illinois bituminous coal (IBC-102). Cylindrical coal pellets (0.5 cm diameter, 1 cm length) were prepared by

mixing IBC-102 coal (-100 mesh) with 5% by mass corn starch and feeding this mixture through a California pellet mill. Pelletized coal chars were prepared in a fixed bed reactor (FXB). The three major processing steps were pyrolysis, activation, and carbon deposition. About 2 g of coal pellets were placed in a ceramic boat inside a 2 in. ID tube furnace and heated under flowing N₂ to 700-1000°C and held for 0.5h. To increase adsorption capacity of these chars, physical (CO₂, 875°C, 1h) and chemical activation (coal/KOH = 1 by mass, N₂, 800°C, 1h) methods were employed. To further modify pore structure and narrow pore size distribution to the desired 3-4 Å range, carbon deposition (3-12% benzene, 650-850°C, 0.3-2.0h) was employed. The O₂ and N₂ adsorption capacities (25°C, 500 torr) of prepared chars were evaluated at 30 s intervals using a volumetric adsorption apparatus (Autosorb-1, Quantachrome Corp). Volumes adsorbed were calculated using the ideal gas law. Prior to all adsorption experiments, char samples were outgassed (120°C, 10⁻³ torr) for 8 h. Single point N₂ BET surface areas were measured using a Monosorb flow apparatus.

Results and Discussion

The effect of heat treatment temperature (HTT) during pyrolysis on the molecular sieve properties of pelletized chars are presented in Table 1. The pelletized chars exhibit no sieving effects, and the greatest O₂ capacity was attained for the char treated at 800°C. Since O₂ capacity is important, the sample was further activated with CO₂. Activating the char with CO₂ further increased its O₂ capacity (after 2 min. adsorption) from 7.0 to 10.0 cm³/g but decreased selectivity from 1.04 to 0.95. The KOH activated char had the highest O₂ capacity, but the lowest O₂/N₂ selectivity. Selectivity is defined as the ratio of O₂ capacity to N₂ capacity. These two activated chars have O₂ capacities significantly higher than those recently reported in the literature [6] for activated carbons (8 cm³/g). Table 1 also shows the molecular sieve properties of chars prepared from 12 x 40 mesh IBC-102 coal at 600-1000°C [7]. The O₂ capacities of these four chars also go through a maximum at HTT = 800°C; however, these chars exhibit significant sieving effects, e.g., at HTT = 900°C, the O₂/N₂ selectivity is 3.46. Commercial CMS for nitrogen recovery from air typically have N₂ BET surface areas < 10 m²/g.

To increase selectivity of the activated pelletized chars, carbon deposition (CD) with benzene was performed in one or two steps. CD with 12% benzene (balance N₂) at 800°C imparts some selectivity to the CO₂ activated pellet as shown in Table 2. But, CD with 3% benzene at 650°C does little to affect the O₂/N₂ selectivity of this char.

Table 1. Effect of HTT and Activation.

Sample	O ₂ (cm ³ /g)	N ₂ (cm ³ /g)	O ₂ /N ₂	N ₂ BET (m ² /g)
Pellets, 700°C	6.37	6.15	1.04	86
Pellets, 800°C	7.01	6.98	1.00	--
Pellets, 900°C	3.83	3.66	1.05	--
Pellets, 1000°C	3.39	3.19	1.06	--
Pellets, 800°C, CO ₂ , 875°C, 1h	10.02	10.55	0.95	350
KOH activated	13.91	15.31	0.91	1220
12 x 40, 600°C	6.00	3.71	1.62	12
12 x 40, 800°C	7.02	5.22	1.34	5
12 x 40, 900°C	4.46	1.29	3.46	--
12 x 40, 1000°C	0.17	0.00	--	2

Better results were achieved at higher temperatures (800°C) presumably because benzene will crack at the pore entrance before it has a chance to diffuse into the pore, thereby increasing selectivity while preserving the internal adsorption capacity of the pore. At lower temperatures (650°C), the benzene does not crack as readily and it will be able to diffuse into the pores and crack. An even layer of carbon deposits within the pore would tend to decrease capacity, but not change selectivity. Table 2 shows that CD on the KOH activated char had little effect on selectivity, but decreased both O₂ and N₂ adsorption capacities. The results seem to indicate that either benzene has cracked within the pores and not at the pore entrance or the pores were too large to begin with.

Table 2. Single Step Carbon Deposition.

Sample	O ₂ (cm ³ /g)	N ₂ (cm ³ /g)	O ₂ /N ₂	N ₂ BET (m ² /g)
Pellets, CD, 12%, 800°C, 20 min	8.05	2.72	2.96	--
CD, 3%, 650°C, 1h	9.26	9.27	1.00	--
CD, 3%, 650°C, 2h	8.79	9.19	0.96	--
KOH, CD, 9%, 800°C, 20 min	1.54	3.27	2.12	25
KOH, CD, 9%, 850°C, 20 min	1.10	1.08	0.97	3

A two step CD process could significantly increase selectivity while maintaining capacity [8]. The molecular sieve properties of chars after a two step CD process are presented in Table 3. The first step involves depositing most of the carbon at the pore entrance using a concentrated stream of benzene for a short period of time. The second step involves using a less concentrated stream of benzene to fine-tune the pore opening to achieve a desired selectivity. Table 3 shows that our

best results thus far were attained using this two step process. An effective CMS should have high selectivity (> 10) as well as high capacity (> 6 cm³/g) when using CD. The higher the selectivity, the purer the product; the higher the capacity, the higher the product recovery.

Table 3. Two Step Carbon Deposition.

Sample	O ₂ (cm ³ /g)	N ₂ (cm ³ /g)	O ₂ /N ₂	N ₂ BET (m ² /g)
Pellets, CD, 12%, 800°C, 20 min, 650°C, 3%, 1h	7.65	2.65	2.89	62
Pellets, CD, 12%, 800°C, 20 min, 3%, 750°C, 1h	6.03	1.94	3.11	46
Pellets, CD, 12%, 800°C, 20 min, 3%, 800°C, 1h	6.88	2.05	3.36	49
Pellets, CD, 12%, 800°C, 10 min, 3%, 850°C, 1h	1.67	0.65	2.58	18

Conclusions

The two-step CD process using pellets seems to be the most promising thus far (O₂/N₂=3.36). Further research on CO₂ activated pellets will be continued. Activation with KOH does not appear suitable for making O₂ selective CMS probably due to the initial pore size of KOH activated char. Altering the surface chemistry of KOH activated char (O₂/N₂ = 0.91) will be pursued to make the material more N₂ selective.

Acknowledgments

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