MODIFICATION OF PORES OVER MOLECULAR SIEVING CARBON AND ACTIVATED CARBON FIBERS

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INTRODUCTION

Pressure swing adsorption (PSA) technique using molecular sieves has been established in the gas separation. Some natural gas resource are known to carry very high contents of CO_2 [1] . Hence it is crucial for the combustion and transportation of such a resource to remove CO_2 from CH_4.

Recently, pitch and PAN based activated carbon fibers have been commercialized. Its homogeneous micropore developed in the fiber surface exhibits rapid adsorption and desorption. Such carbons can be unique adsorbent when molecular sieving ability is endowed.

In the present study, several specific carbon adsorbents such as commercial molecular sieving carbon, pitch and PAN based active carbon fibers were treated at their surface by chemical vapour deposition (CVD) of benzene at 1000K to endow the molecular sieving ability for the selective adsorption of CO_2 in CH_4.

EXPERIMENTAL

Three commercial carbon adsorbents (molecular sieving carbon, pitch and PAN based activated carbon fibers) used in the present study are listed in Table 1 along with some of their physical and chemical properties.

Benzene pyrolysis was performed by flowing it to the carbon material stored in a quartz basket using a microbalance.

The gas volume adsorbed by the sample within a given time interval at 303K was determined from the change of pressure in a closed system. The initial pressure of both gases to be adsorbed was fixed at 760 torr. The amount adsorbed vs time was plotted to get the kinetic selectivity in adsorption. The kinetic selectivity and adsorption capacity were defined in the present paper as the ratio of adsorbed CO_2 and CH_4 by 2min and the amount adsorbed CO_2 by 2min, respectively.

The micropore volume distribution was determined from the adsorption isotherms of three probe gases (CO_2, C_2H_6, n-C_4H_{10}) at 298K according to DR equation. The kinetic dimensions of such gas molecules are reported to be 0.33, 0.40, and 0.43nm, respectively [2] .

RESULTS

Figure 1 illustrates the adsorption profiles of as-received ACFs and modified ones by CVD at room temperature. As-received pitch ACF adsorbed both CO_2 and CH_4 very rapidly within 1 min, where adsorptions of both CO_2 and CH_4 were basically saturated. The kinetic selectivity of CO_2/CH_4 was 2.4 at 2min, their adsorption capacity being 37.3ml/g CO_2 and 15.8ml/g CH_4, respectively. As-received PAN ACF exhibited similar profiles, giving rather poor CO_2/CH_4 kinetic selectivity of 2.8. Pitch ACF modified exhibited much improved selectivity of 45 by 2min. The capacity was reduced slightly to 31ml/g by 2min, 18% of CO_2 adsorption capacity being lost by CVD. The adsorption of CH_4 was markedly reduced by CVD to be less than 1ml/g, improving the selectivity. PAN ACF modified exhibited further higher selectivity ca. 100 by 2min. It is noted that the decrease of CO_2 adsorption capacity is less than 10%, and CH_4 adsorption doesn't take place within at least 5 min.

Figure 2 illustrates the kinetic selectivity of CO_2/CH_4 adsorption over modified MSC and ACFs vs. weight increases by CVD, using 2vol% benzene in He at 1000K.

MSC reduced its CO_2 adsorption very gradually according to the weight increase upto 30mg/g by CVD, while its CH_4 adsorption was reduced very drastically at 20mg/g from 17ml/g to 4ml/g, increasing drastically the selectivity. Further reduction of CH_4 adsorption was observed by more weight increase, reaching basically to zero by 31mg/g where the selectivity as high as 100.

Pitch ACF reduced both adsorption by CVD modification, although that of CH_4 was more rapid with weight increase. The selectivity increased sharply at the weight increase of 110mg/g to 50. More CVD was effective to the increase of selectivity, but reduction of CO_2 adsorption was inevitable.

PAN ACF reduced CH_4 adsorption as soon as CVD started, the selectivity significantly increased to ca. 100 at weight increase of 15mg/g, which was the smallest amount of desorption.

The micropore volumes of MSC, ACF, and modified ones measured with three probe molecules are plotted against their minimum dimensions in Figure 3, where CO_2, C_2H_6, and n-C_4H_{10} were used as probe molecules. As-received MSC exhibited pore volume of 0.20ml/g regardless of the probe molecules, indicating its pore size larger than 0.43nm. Modified MSC exhibited sharp decrease in the volume of pores with the larger size, indicating the significant narrowing of the pore size by chemical vapour deposition

without significant reduction of pore volume.

As-received Pitch ACF exhibited micropore volume of 0.26ml/g, regardless of the probe molecules, indicating again that the pore size is larger than 0.43nm. Modified ACF exhibited sharp decrease in the volume of pores with the increasing size, although the volume of pores less than 0.34nm was also reduced by 35% to 0.17ml/g.

DISCUSSION

Kinetically selective adsorption of CO_2 and CH_4 relies basically on differences in their shape and polarity. The latter property may be important for the selective adsorption of CO_2 on some oxides of basicity or polarity [3] . In contrast, the carbon adsorbent may distinguish them by their molecular shape and size because the adsorbent is rather non-polar and carries slit-type pores of narrow mouth due to its graphitic layer structure, of which size is variable according to its carbonization and activation. The kinetic diameters of CO_2 and CH_4 have been reported 0.33 and 0.38 nm, respectively [2] . CO_2 and CH_4 are planar and spherical molecules, respectively. Hence, slit width of the carbon adsorbent is the major key to distinguish the substrates when it is designed to range between 0.33 and 0.38.

The CVD of benzene on to the MSC and two types of activated carbon fiber was proved in the present study to be effective for the emphasize their molecular sieving ability, depending probably on their pore structure. The pyrolytic carbon deposited on the neighboring wall of the pore can control the slit-width. The CVD under the present conditions improved markedly the kinetic selectivity for CO_2/CH_4 with least reduction of CO_2 adsorption capacity. In a PSA procedure, the rate of adsorption to reach the saturation is another key for the efficiency. Pores of ACFs which are directly open from their surface assure the rapid adsorption and desorption.

REFERENCES

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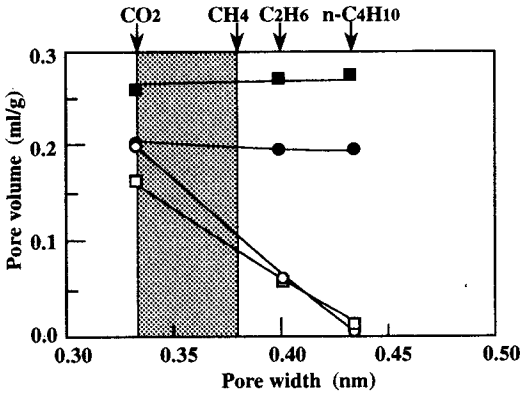

Figure 3 Micropore volume distribution before and after CVD over MSC and Pitch-ACF.

● as-received MSC ■ as-received Pitch-ACF
○ modified MSC □ modified Pitch-ACF

Table 1 Some properties of as-received carbons.

Dose	Elemental analyses (%) C	H	N	O	Ash	BET surface area (m^2/g)	CO_2 adsorption capacity* (mg/g)
MSC[1]	90.6	0.7	0.4	7.4	0.9	410	72
ACF-1[2]	88.7	0.9	0.7	9.7	-	700	83
ACF-2[3]	77.5	1.8	9.7	11.0	0.1	450	73

1) molecular sieving carbon
2) activated carbon fiber from pitch
3) activated carbon fiber from polyacrylonitrile
* 303K, 1atm using gravimetric system

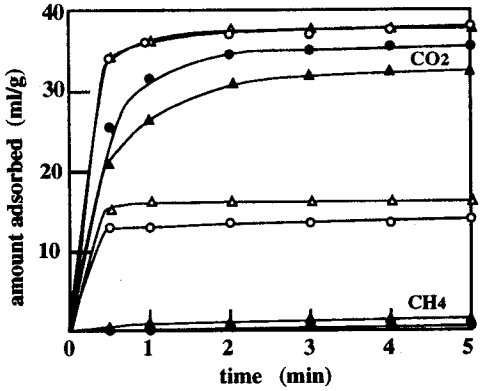

Figure 1 Adsorption profiles of CO_2 and CH_4 over modified ACFs for CO_2/CH_4 kinetic separation at 303K.

Initial pressure : 760 torr Final pressure : 500 ~ 600 torr

▵ as-received Pitch-ACF ▲ modified Pitch-ACF
○ as-received PAN-ACF ● modified PAN-ACF

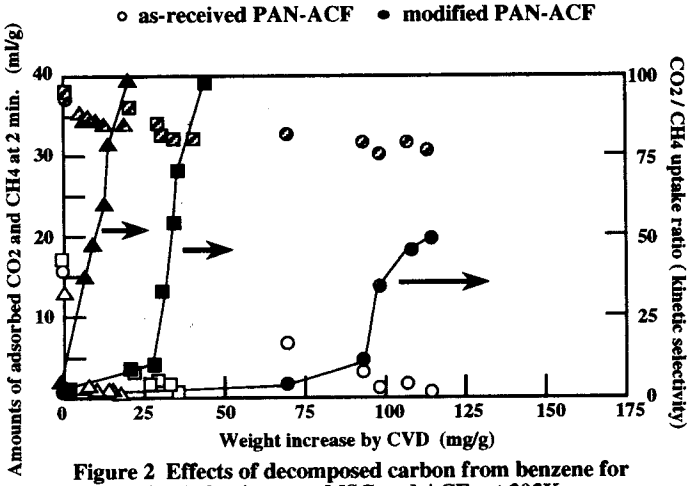

Figure 2 Effects of decomposed carbon from benzene for adsorption behavior over MSC and ACFs at 303K.

Adsorption pressure; 500 ~ 600 torr

on the condition of 2vol% C_6H_6 concentration

Over Pitch-ACF
- ◍ amount adsorbed CO_2 at 2min
- ○ amount adsorbed CH_4 at 2min
- ● CO_2/CH_4 uptake ratio at 2min

Over PAN-ACF
- ◬ amount adsorbed CO_2 at 2min
- △ amount adsorbed CH_4 at 2min
- ▲ CO_2/CH_4 uptake ratio at 2min

Over MSC
- ▨ amount adsorbed CO_2 at 2min
- □ amount adsorbed CH_4 at 2min
- ■ CO_2/CH_4 uptake ratio at 2min