Chemical Vapor Deposition of Some Heterocyclic Compounds over Active Carbon Fiber to Control Its Porosity

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Chemical vapor deposition (CVD) of heterocyclic compounds was examined over commercial pitch-based active carbon fiber (ACF). The ACF treated with pyridine, pyrrole, and thiophene showed excellent performance in the gas separation of CO_2/CH_4. Thermal stability of the aromatic compounds around 700 °C appears an important factor to restrict its decomposition on the pore wall where the compound is adsorbed and carbonized.

In previous studies,[1-4] pore size of active carbon fiber (ACF) was modified as designed by the selective chemical vapor deposition (CVD) of benzene where the deposition temperature was selected carefully. In this system, we suggested the following scheme of carbonization which restricts the pore wall. Benzene which was one of the best organic compound for achieving a molecular sieving capability, is adsorbed on the pore wall by catalytic action of ACF surface where it is condensed into non-volatile substances within a short time. The adsorbed species are carbonized into isotropic carbon because of little rearrangement of adsorbed species into graphitic layer stacking. The adsorption leading to such a carbonization is restricted to the pore wall and not on the outer surface of ACF. Under the flow conditions, adsorption on the outer surface is low and the residence time is not be long enough for the carbonization. Thus, carbonization on the pore wall continued to thicken the carbon coating on the wall as long as benzene could diffuse in to the pore. When the pore width was reduced by the carbon coating to be less than the molecular thickness of benzene (0.37 nm),[5] the carbonization stopped automatically. The pore width of 0.37 nm is in-between the molecular sizes of CH_4 (0.38 nm) and CO_2 (0.33 nm), and can distinguish them with true molecular sieving ability.[6]

In this letter, CVD of some heterocyclic compounds onto a ACF was tried to control their porosity and surface functionality, since they are thermally stable enough to give molecular sieving ability to the ACF like benzene. In addition, heterocyclic functions are expected to be introduced on the ACF surface. The treated ACFs were evaluated in the gas separation of CO_2/CH_4.

Some of physical and chemical properties of a commercial pitch based ACF used in the present study are listed in Table 1. After outgassing at 150 °C for 4 h, BET surface area was measured by N_2 adsorption at -196 ℃, using a Simazu ASAP 2000 apparatus. Pyrolysis of heterocyclic compounds (pyridine, pyrrole, furan, and thiophene) were performed by flowing a helium stream containing controlled amounts of the organic compounds (2 vol%) at 150 ml min^{-1} over the ACF (200 mg) suspended in a quartz basket in a micro balance (CAHN 1000). A thermocouple, in a glass tube, was inserted directly below the quartz basket. The sample was heated in the He flow to the fixed temperature at a programmed rate of 10 ℃ min^{-1} and maintained at the temperature for 1 h. Then, a prescribed amount of organic compound was supplied by a micro feeder into the He gas flow to be sent to the heated ACF for a fixed period. The weight uptake of the sample was recorded continuously by the balance. The organic species produced from organic compounds were analyzed at the outlet of the reactor, using GC-MS (Simazu, GC-17A-QP-5000) with a detector mainly used to detect heavy products (>50 a.m.u.). Products deposited on the reactor wall were recovered and analyzed by GC. Adsorptions of CO_2 and CH_4 on the ACFs were carried out separately using a volumetric adsorption apparatus. Each ACF was evacuated to 1.3×10^{-3} kPa at 150 ℃ for 1 h prior to the adsorption study. The gas volumes adsorbed by ACF within a given time interval at 30 ℃ were determined from the change of pressure in the closed system. The initial pressure of each gas to be adsorbed was fixed at 101.3 kPa. The amount adsorbed (S.T.P.) vs. time was plotted to determine the rate of the adsorption. CO_2 adsorption capacity is defined in the present paper as the amount of CO_2 adsorbed in 2 min. CO_2 selectivity is defined as the ratio of CO_2 adsorbed in 2 min to CH_4 adsorbed in 2 min. These parameters are more reflective of kinetic properties than equilibrium properties, as are appropriate parameters for PSA application.

The weight increases of ACF during the pyrolysis of organic compounds at 725 °C are illustrated in Figure 1, where the concentration of organic compounds were 2 vol% in He flow. Pyridine increased the weight of ACF slowly upto 110 mg g^{-1} within 40 min when the weight gain ceased. Pyrrole, furan, and thiophene showed similar profiles of weight increase and

Table 1. Some properties of active carbon fiber

Sample	Mean pore diameter (nm)	Elemental analyses (%)			
		C	H	N	O
as-received ACF[a]	1.36	88.7	0.9	0.7	9.7
Treated ACF by pyridine[b]	—	90. 8	1.0	2.6	5.6
Treated ACF by pyrrole[b]	—	91.9	1.0	2.4	4.7

a Activated carbon fiber from coal tar pitch, fiber diameter 10-15 μ m.
b Carbon deposition amount : 110 mg g^{-1}

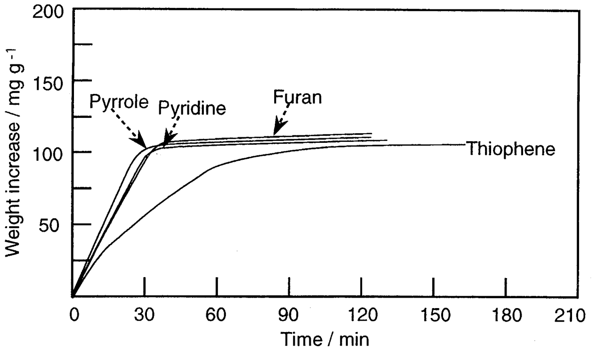
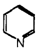
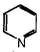
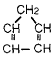
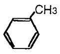


Figure 1. Weight increase of ACF by contacting with organic compounds at 725 ℃.

Table 2. Products of the pyrolysis reaction

organic compound	reaction temperature (℃)	products at the outlet of the reactor
	725	 > dimer trace (mol ratio)
	725	 71% $CH_2=CH-CH=CH_2$ 17%  8%  3%  1% (T.I.C. ratio ; > 50 a.m.u.)
	780	 > dimer trace (mol ratio)

saturation level. However, the time to achieve the saturation with pyridine was slightly longer than that with pyrrole, but much shorter than that with thiophene.

Table 2 shows GC-MS (heavy products (; >50 a.m.u.) were detected) analysis of products at the outlet of the reactor. Only pyridine was detected in the gas phase after the pyrolysis of pyridine at 725 °C while a small amount of dimer was found on the reactor wall. Thiophene stayed also unchanged at this temperature, although very little amount of its dimer was also detected like pyridine. In contrast, furan was reactive to show 29% conversion, producing mainly butadiene (17% yield), cyclopentadiene, and benzene (>50 a.m.u.).

Figure 2 illustrates adsorption profiles of CO_2 and CH_4 on as-received and treated ACFs. As-received ACF adsorbed both CO_2 and CH_4 very rapidly within 1 min, and adsorptions of both CO_2 and CH_4 were apparently saturated by 2 min. After 2 min, the as-received ACF adsorbed 37 ml g^{-1} (S.T.P.) of CO_2 and 16 ml g^{-1} (S.T.P.) of CH_4, giving a CO_2 selectivity (CO_2/CH_4) of 2.3. The ACF, which gained weight by CVD of pyridine to 110 mg g^{-1} of the saturation level, showed an excellent CO_2/CH_4 adsorption selectivity of about 50, while CO_2 adsorption capacity decreased only slightly to 86% of that on the original ACF. The adsorption of CH_4 was markedly reduced by CVD to less than 1 ml g^{-1} (S.T.P.), thus dramatically improving the selectivity. Pyrrole and thiophene provided excellent selectivity for CO_2/CH_4 adsorption as pyridine, when 110 mg g^{-1} of weight increase was obtained at 700 and 780 °C, respectively. CVD of pyrrole and thiophene at 725 °C allowed similar sieving ability when the same weight increase was obtained, although the time to obtain the weight increase varied by the temperatures. The ACF treated by furan was found to have poor CO_2/CH_4 kinetic adsorption selectivity by reducing both adsorption. The CO_2 adsorption was very slow and no saturation was observed by 5 min.

ACFs defined as points where the weight gains of the ACF were 110 mg g^{-1} (saturation level), obtained a considerably increased nitrogen content after CVD treatment from pyridine and pyrrole (see Table 1).

In the present study, pyridine, pyrrole, furan, and thiophene were used as the carbon precursor of CVD, because they possess similar molecular shape and thickness like benzene although hetero atom is included in their ring. An activated pitch based ACF could be successfully controlled in its pore at the nano-scale by carbon deposition from pyridine, thiophene and pyrrole at a specific range of temperature (around 700 °C) to obtain molecular sieving activity sufficient to separate CO_2 from CH_4 . In addition, treated ACF by pyridine and pyrrole possessed nitrogen atom. Surface functionality was also modified by heterocyclic compounds.

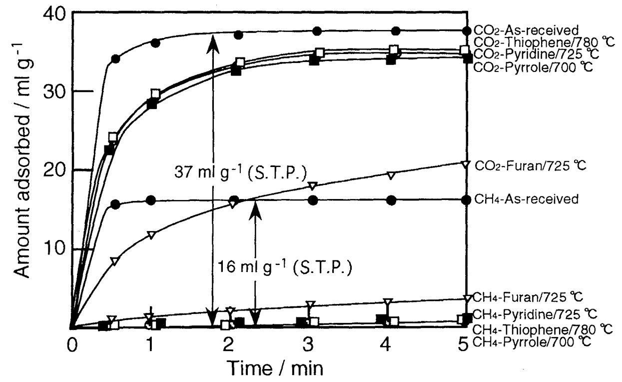


Figure 2. Adsorption profiles of CO_2 and CH_4 over as-received and treated ACFs.

Initial pressure : 101.3 kPa Final pressure : 66.7 ~ 80.0 kPa

Although furan showed the similar profile of weight increase of ACF by carbon deposition, the molecular sieving selectivity was not improved at all. The kinetic adsorption capacity for both CO_2 and CH_4 was also significantly diminished. Only furan was decomposed among the compounds examined at this temperature range. A variety of sizes and shapes of decomposed products does not allow the control of pore size, although the carbonization appears to be limited on the ACF surface. Thermal stability of the aromatic compound is a key factor to get molecular sieving activity by CVD, because such stability restricts their penetration into the pore of the designed diameter for successive adsorption and activation.

References and Notes

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