Catalytic Dehydrochlorination of 1, 2-Dichloroethane over Pyridine Deposited Pitch-Based Active Carbon Fiber

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Pitch-based active carbon fiber (pitch-ACF) modified by pyridine chemical vapor deposition (CVD) showed excellent catalytic activity for dehydrochlorination of 1, 2-dichloroethane (1, 2-DCE) into vinyl chloride (VC). Compared with polyacrylonitrile-based ACF (PAN-ACF), the present ACF of 2% weight increase by CVD showed long life over 300 h at 360 °C (conversion: ca. 20%; VC selectivity: 99.7%; contact time: 5.8 x 10^{-3}).

The pyrolysis of 1, 2-dichloroethane (1, 2-DCE) at 500 °C has been commercialized to produce vinyl chloride (VC) at a reasonable conversion of 50% and high selectivity above 98%.[1, 2] However, deposition of pyrolytic carbon on the reactor wall decreases its thermal conductivity to disturb the temperature control, and carbon precipitation in the transfer line and heat-exchanger brings about plugging problems.[3] Hence frequent decoking treatment is necessary. The problems involved in the pyrolysis can be solved by using a catalyst. When the catalytic reaction proceeds selectively at lower temperature, the coke deposition can be avoided to allow the continuous long operation.[4, 5]

Active carbon fibers (ACFs) have been recognized to carry shallow slits near the surface of the fiber, hence ACFs absorb and desorb substrates very rapidly in spite of very large surface.[6] In addition, nitrogen as well as oxygen functional groups can be introduced on the wall surface of the slits. Pyridinic nitrogen is expected to catalyze the base catalyzed elimination reaction. The present authors reported catalytic activity of polyacrylonitrile-based ACF (PAN-ACF) with 4.5 wt% nitrogen for the dehydrochlorination of 1, 2-DCE into VC.[7] A contact time of 5.8 x 10^{-3} g·min/ml allowed a conversion of 50% (Figure 2) and high selectivity of 99.9% at 360 °C. The nitrogen content has been found to be correlated to the initial activity. However, the catalyst's life is a problem, catalytic activity being lost by 45 h by probably the carbon deposition in the pores, because the surface area decreased from 850 to 244 m^2/g and the catalyst's weight increased by about 24 wt% after the deactivation. The coke is assumed to be derived from polyvinyl chloride (PVC) which is produced in the pore through the radical polymerization probably catalyzed by the ACF's surface.

In the present study, chemical vapor deposition (CVD) of pyridine on the surface of the pore wall is applied to introduce the basicity on the pitch-based ACF (pitch-ACF) with a very large surface area. CVD carbon was also expected to reduce the radical initiation on the surface.

The pitch-ACF and PAN-ACF supplied from Osaka Gas Co., Ltd. and Toho Rayon Co., respectively, were used in the present study. Their properties are summarized in Table 1. CVD of pyridine was performed in a Cahn micro-balance on to the pitch-ACF in the quartz basket from pyridine (2 vol%) carried by a helium flow (150 ml/min). CVD temperature was controlled by a thermo-couple placed just below the quartz basket. Weight gain of sample was continuously recorded by the micro-balance.

The surface of ACF was characterized by ESCA (ESCA-1000; Shimadzu Corporation) with Mg Kα radiation. The operating pressure was below 4 x 10^{-5} Pa and the acceleration voltage was 10 kV. The obtained spectra were corrected by the standard peak of C 1s at 284.6 eV.

Dehydrochlorination was carried out with a flow type reactor. ACF of 300 mg was packed in the reactor and 1, 2-DCE was fed by a micro-feeder (0.17 ml/min). Reaction temperature was controlled by a thermo-couple on the reactor wall.

Figure 1 shows weight gain of the ACF by CVD of pyridine. At a temperature range below 650 °C, the weight gain was very slow. At 725 °C, the weight increased rapidly to reach the saturated weight of 46% within 2 h. No further increase of weight may indicate that CVD is restricted on the pore wall and that CVD is stopped when pyridine cannot get into the pore.[8] Four pyridine-modified ACFs with different quantity of deposition were prepared at 725 °C, their weight gains being 2, 8, 16, and 25 wt%, respectively, as shown in Table 1. The nitrogen content of the ACF increased and its surface area decreased as expected according to the deposition amount.

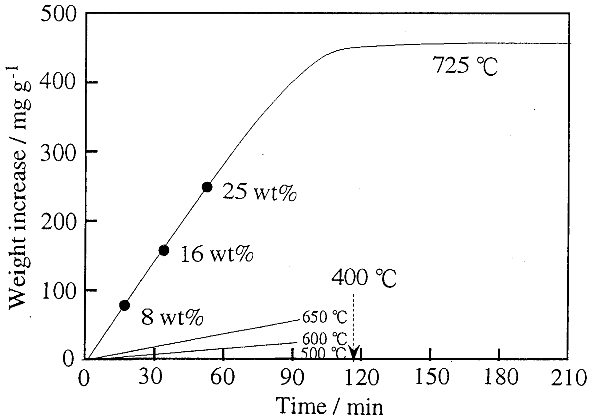

Figure 1. Process of deposition of pyridine.

Table 1. Some properties of ACFs

ACFs	Elemental analysis (wt%)				S. A. (m^2/g)
	C	H	N	O(diff.)	
PAN-ACF	78.1	1.4	4.5	16.7	850
Pitch-ACF	93.9	0.7	0.3	4.6	2149
Pyr 2-ACF	95.4	0.8	0.7	3.1	1962
Pyr 8-ACF	95.3	0.7	1.5	2.4	1883
Pyr 16-ACF	94.5	0.6	2.3	2.4	1593
Pyr 25-ACF	93.4	0.6	3.0	2.9	1265
Bzn 16-ACF	96.9	0.9	0.2	1.2	1500

The profiles of the catalytic elimination over the ACFs at 360 °C are shown in Figure 2. The pitch-ACF, as-received, showed a very low catalytic activity and a short life time. The ACFs modified by pyridine exhibited much better performances. ACF of 2% weight gain showed the longest life time more than 350 h, although it showed lower initial activity than that of the pitch-ACF. ACF of 8% weight gain gave a higher initial conversion of 40% and longer life time of about 300 h. ACF of 16% weight gain gave a much higher initial conversion of 60%, however its deactivation was more rapid. Although ACF of 25% weight gain showed the almost same initial activity to that of the ACF of 16% weight gain, the deactivation was much faster.

Benzene CVD ACF of 16% weight gain exhibited a smaller surface area but minimum of nitrogen content. The conversion on the particular ACF was rather low to be 16%, however the life time was prolonged to reach 200 h.

After the reaction, the weight gains of the pitch-, Pyr 2, Pyr 8, Pyr 16, Pyr 25, and Bzn 16-ACF were 18, 71, 61, 42, 24, and 29 wt%, respectively. Longer reaction increased the gain.

There were found two peaks of N 1s in ESCA spectra of pyridine deposited ACFs as shown in Figure 3. One peak around 398 eV has been assigned to pyridinic nitrogen and the other around 401 eV to quaternary nitrogen.[9] The pitch-ACF showed no peaks as expected. Pyridine deposition produced two peaks. The intensity of pyridinic nitrogen was a little stronger than that of quaternary nitrogen on the ACF of 8% weight gain. More deposition intensified the quaternary nitrogen which exceeded the pyridinic nitrogen on the ACF of 24% weight gain. ACF of 2% weight gain obtained a little increase of nitrogen, no definite ESCA peak being observed. Pyridinic and quaternary nitrogens disappeared after the reaction, while pyrrolic nitrogen (400 eV) appeared. HCl may stay on the basic site of ACF.

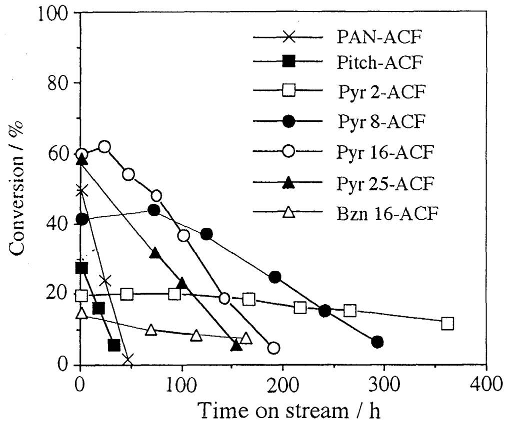

Figure 2. The effect of modification by pyridine and benzene. Reaction temperature was 360 ℃. Amount of catalyst was 300 mg. W/F was 5.8 x 10^{-3}g · min/ml.

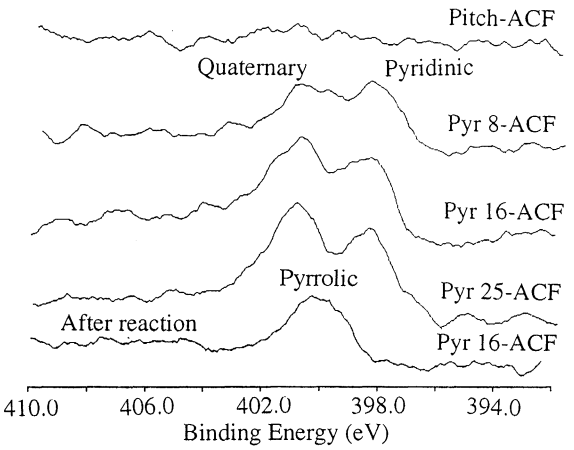

Figure 3. N 1s ESCA spectra of ACFs.

The present letter describes the promising activity of the pitch-ACF coated with deposited pyridine for the selective elimination of 1, 2-DCE into VC for a long life at least several hundreds of hours. Quaternary nitrogen would be stabilized by surrounding π-electrons, while pyridinic nitrogen can be the basic site for the catalytic activity. The site is neutralized with HCl formed by the elimination reaction. Hence, the desorption of HCl from the basic site may be the rate determining step.

The Pyr 2-ACF showed lower initial activity than that of the pitch-ACF. Significant contribution of radical elimination is suggested on the pitch-ACF. Such activity is lost rapidly by the carbon formation from VC.

More amount of pyridine deposition increased the nitrogen content on the ACF surface; however quaternary nitrogen is more emphasized. Hence the increase of the initial activity is rather limited.

The catalyst life as well as the activity is a key factor for a practical application. The carbon derived from PVC is assumed to cause the deactivation. Radical polymerization of VC seems to be effectively reduced by the CVD coating of the surface, however the narrower pore may hold VC to accelerate its polymerization and the deactivation. Thus, the optimum deposition of pyridine on the ACF of rather large pore is designed to obtain a reasonable activity and a longer life.

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