POSTER

Catalytic Activity of Surface Modified PAN-ACF for the Dehydrochlorination of 1,2-Dichloroethane

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Introduction

The present authors have reported catalytic activity of PAN-based activated carbon fibers (ACF) for the dehydrochlorination of 1,2-dichloroethane (1,2-DCE) into the vinyl chloride monomer (VCM), to replace the conventional pyrolysis, intending a longer run of high productivity. The catalytic reaction is satisfactory in terms of the activity and selectivity, whereas the catalyst's deactivation is a remaining problem when the reaction temperature is high.

In the present study, initial and final catalytic activities of several ACFs on the gas streams were examined. Properties of ACF were correlated to find factors influential on the activity and deactivation in the catalytic dehydrochlorination. Some modification of the ACF surface was also examined to find the stable activity with less deactivation by coking.

Experimental

The dehydrochlorination was carried out by using a flow reactor with fixed catalyst bed. The flow reactor was made of stainless steel and its diameter was 12mm, which was packed with 300mg of ACF. The length of the catalyst bed was 30mm. 1,2-DCE was introduced with a liquid pump and vaporized at the entrance of the reactor tube. The flow rate of 1,2-DCE was 0.17 ml/min. without carrier gas. The effluent gas was successively sent to a gas chromatograph through a sample valve. The reaction temperature was controlled by a thermocouple at the out side of the reactor tube and the temperature at the center of catalyst bed was monitored by another thermocouple. A commercially available PAN-ACF produced by Toho Rayon, Pitch-ACF produced by Osaka gas, Phenol-ACF produced by Kynol, Cellulose-ACF produced by Toyobo were used as catalysts. The properties of ACFs are summarized in **Table 1**.

Heat-treatment was carried out under the flow of hydrogen gas with 100ml/min. at 600°C for 1h.

The oxidation of a PAN-ACF was carried out with concentrated nitric acid (61%). Chopped ACF was dipped in the conc. nitric acid for 1h at ambient temperature, washed by distillated water many times and then dried at 100-200°C under nitrogen gas flow for 1h.

Results

Figure 1 illustrates the activities of as-received ACFs in a long run at 360°C. PAN-ACF-1 of small surface area showed very high activity in the initial minutes, however lost it very rapidly within 2h to be basically inactive. PAN-ACF-2 showed a stable activity for 50h and then lost gradually its activity for the next 40h. Pitch and Phenol-ACF lost their activity within 20h. Unique activity of PAN-ACF-2 is noted.

Cellulose-ACF showed rather interesting activity, which increased from 28% to 40% for the initial 50h, and then decreased very gradually to 10% by 150h.

Figure 2 illustrates the activity of PAN-ACF-2 heat-treated at 600°C in hydrogen gas or oxidized by nitric acid. The initial activity of oxidized ACF was a little lower and the life time was shorter than those of as-received form. On the other hand, heattreated ACF exhibited the absolutely higher initial activity, although the deactivation was very rapid.

Figure 3 illustrates the ESR signal of PAN-ACF-2 and its heattreated ones. The as-received ACF showed a little broad signal at g-value of 2.004. After the heat-treatment, the signal became sharper and smaller.

Reference

1. J. Zawadzki, *Carbon*, **18**, 281 (1980).
2. T. Budinova, N. Petrov, S. Duber, and E. Shebestova, *Carbon*, **32**, 417 (1994).

Table 1. Properties of active carbon fiber

ACF's	elemental analysis / wt % C	H	N	O	Ash	S. A. m^2/g
PAN-ACF-1	77.5	1.8	9.7	11.0	0.3	450
PAN-ACF-2	78.1	1.4	4.5	16.0	0.3	850
Pitch-ACF	89.6	1.1	0.7	8.2	0.3	480
Phenol-ACF	92.3	0.9	0.3	6.3	0.3	1000
Cellulose-ACF	86.5	1.0	1.5	9.9	1.1	1290

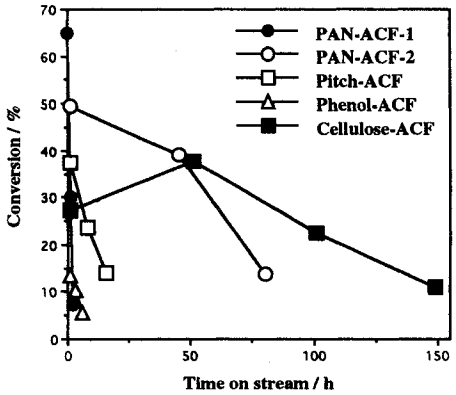

Figure 1. Long reaction of each ACF
Reaction temperature 360 ℃
Amount of catalyst 300mg
Flow rate of 1,2-DCE 0.17 ml/min.

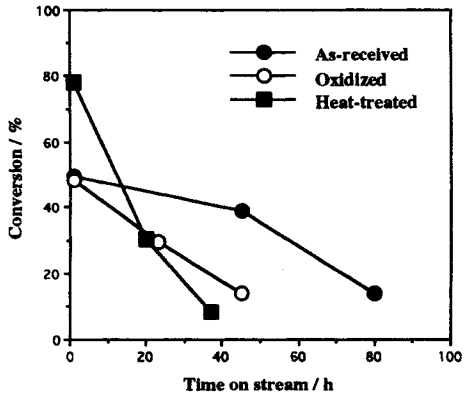

Figure 2. Effect of oxidation by conc. nitric acid and heat-treatment at 600℃
Reaction temperature 360 ℃
Amount of catalyst 300mg
Flow rate of 1,2-DCE 0.17 ml/min.

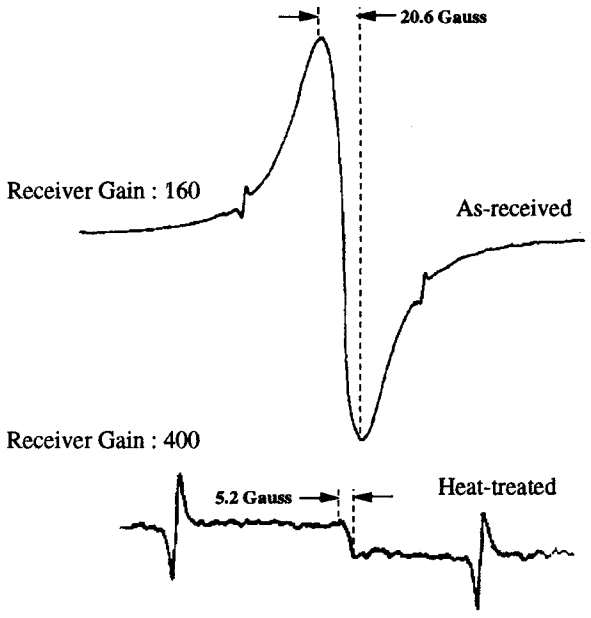

Figure 3. ESR signals of as-received and heat-treated ACF