

Catalytic Dehydrochlorination of 1,2-Dichloroethane into Vinyl Chloride over  
Polyacrylonitrile-Based Active Carbon Fiber (PAN-ACF)

Isao MOCHIDA, \*Yoshinori YASUMOTO, Yoshiro WATANABE,  
Hiroshi FUJITSU, Yasuhiro KOJIMA, <sup>+</sup> and Makoto MORITA <sup>+</sup>

Institute of Advanced Material Study, Kyushu University, Kasuga, Fukuoka 816

<sup>+</sup>Tosoh Inc., Kaiseicho, Shinnanyo, Yamaguchi 746

A PAN-ACF with large surface area was found to enhance dehydrochlorination of 1,2-dichloroethane into vinylchloride in selectivity above 99% at a conversion level of 21 to 63% in the temperature range of 300-350 °C. The ACF showed stable activity at 325 °C for 100 h. In contrast, other carbon materials were found to show either low activity or short life, although their selectivities were fairly high.

Vinyl chloride (VC),<sup>1)</sup> one of the most important monomer in the polymer industries, has been manufactured from 1,2-dichloroethane (1,2-DCE) through thermal dehydrochlorination around 550 °C. However, the dehydrochlorination at a relatively high temperature suffers the severe coking on the reactor wall, which restricts the continuous operation to only 6 months. The catalytic dehydrochlorination at lower temperatures has been extensively studied to solve the problem. Although the basic zeolites<sup>2,3)</sup> and active carbon<sup>4,5)</sup> were reported to lower the reaction temperature, severe coking takes place on the catalyst to limit its life. Vinyl chloride may be polymerized and carbonized in the pores of the catalysts.

In the present letter, the authors describe the catalytic activity of active carbons and fibers. Their activity, selectivity and life were concerned. Polyacrylonitrile-based active carbon fiber (PAN-ACF) has been proved to carry distinct basicity and shallow pores.<sup>6)</sup> The basic elimination at lower temperature and short residence of the product in the shallow pore may solve the coking problem since the coke is assumed to be produced successively through the radical reactions.<sup>7)</sup>

The dehydrochlorination was carried out, using a flow reactor with the fixed catalyst bed. The flow reactor was made of stainless steel. The reactor tube (diameter 12 mm) was packed with 300 mg of chopped PAN-ACF (20 mm). 1,2-DCE was introduced into the top of the reactor tube with a liquid pump. The flow rate of gaseous 1,2-DCE was 100 ml · min<sup>-1</sup>. The fluent gas was successively sent to a gaschromatograph through a sample valve. The chromatographic column was packed with tricresylphosphite on celite. The reaction temperature was measured with a thermocouple at the center of the catalyst bed. A commercially available PAN-ACF (FE-300, Toho Rayon) was used after the heat treatment at 450 °C in N<sub>2</sub> flow. The length of the packed bed was 30 mm. A coal-based active carbon (C-AC, Diahope 008, Mitsubishi Chem.), a pitch-based ACF (P-ACF, OG-10A, Osaka gas) and a pitch-based carbon fiber (P-CF SG 221, Osaka gas) were also examined. Their analytical data and surface areas are summarized in Table 1. The catalytic reaction was performed in a similar manner as described above.

Table 1. Some Properties of ACFs, CF, and AC

Sample	Analyses / %				Surface area / m <sup>2</sup> · g <sup>-1</sup> (N <sub>2</sub> : BET)
	C	H	N	O	
PAN-ACF	78.1	1.4	4.5	16.0	1141
P-ACF	91.6	0.9	0.6	6.8	710
P-CF	99.8	0.0	0.0	0.0	0.2
C-AC	98	0.7	0.5	0.2	1230

The PAN-ACF exhibited an excellent catalytic activity for the selective dehydrochlorination of 1,2-DCE into VC at a temperature range of 300-375 °C, providing conversions of 20-75% as shown in Fig. 1. The selectivity to VC was always above 99%, reaching 99.8% at its best. The major by-products were ethylene, acetylene, and 1,1-dichloroethane (1,1-DCE), all of which were produced in yields lower than 0.1%, although their yields were much the same to those by the conventional thermal reaction at 510 °C. The yields of methyl chloride, ethyl chloride, and butadiene were less than 0.01%. It should be noted that the selectivity was always very high regardless of the conversion and the reaction temperature. The conversions at 300-375 °C on the same catalyst of continuous use are illustrated in Fig. 1. The conversions were stable for at least several hours below 350 °C, being 21% at 300 °C, 42% at 325 °C, and 63% at 350 °C. However at a higher temperature of 375 °C, the initial conversion of 75% decreased rather rapidly along with the time on stream to 65% after 8 h. The catalyst used at 375 °C for 8h showed the conversion of 43% at 350 °C. The catalyst appeared to be significantly deactivated by coking above 375 °C.

The conversion in this catalytic reaction was further confirmed stable at 325 °C for 100 h as shown in Fig. 2. The conversion started at 55-60% and decreased very gradually to 43-47% in 100 h. No carbonaceous substance was found on the reactor wall as well as the fiber surface.

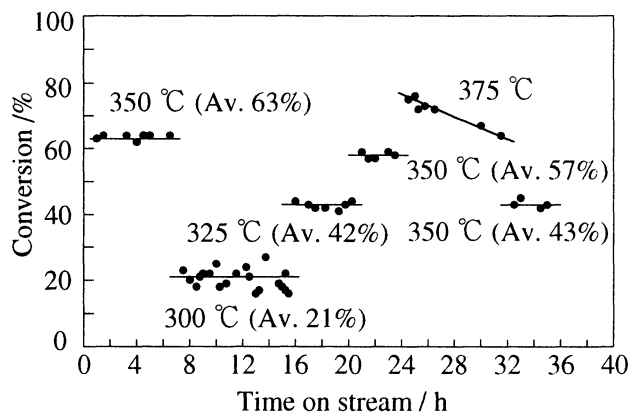


Fig. 1. Conversion of 1,2-DCE over PAN-ACF at some temperatures. W / F = 3 mg · min / ml.

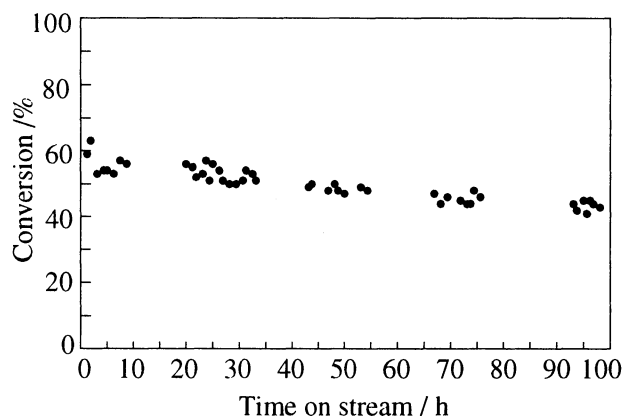


Fig. 2. Conversion change in the continuous operation over PAN-ACF. Reaction temperature and W / F are 325 °C and 6 mg · min / ml, respectively.

The conversions were observed at 350 °C by varying the partial pressure of 1,2-DCE at 0.36, 0.5, and 1 atm. The same conversions were obtained regardless of the partial pressures of 1,2-DCE. The first order in 1,2-DCE is indicated.

The conversions on P-ACF, P-CF, and C-AC are compared at 350 °C in Table 2. P-ACF exhibited at 2h in the time on stream comparable activity and selectivity to those of PAN-ACF; however the activity decreased sharply to 5% at 18 h. C-AC showed lower activity which decreased more rapidly than PAN-ACF, although the selectivity was excellent. P-CF of small surface area showed a very low conversion.

Table 2. Catalytic Activity of ACF, CF and AC for dehydrochlorination of 1,2-DCE <sup>a)</sup>

Sample	2 h <sup>b)</sup>		18 h <sup>b)</sup>	
	Conversion	Selectivity <sup>c)</sup>	Conversion	Selectivity
PAN-ACF	57	99.9	55	99.9
P-ACF	55	99.1	5	99.9
P-CF	0.2	86.2	-	-
C-AC	45	99.5	33	99.7

- a) Reaction temperature and W/F, partial pressure of 1,2-DCE are 350 °C and 3 mg · min / ml, 1 atm.  
 b) 2 and 18 h in the time on stream, respectively. c) Selectivity for VC.

The present letter reports the most stable activity of PAN-ACF among commercially available ACFs and AC for the selective dehydrochlorination of 1,2-DCE into vinylchloride. The selectivity of the catalyst was very high and no carbonaceous substance was found on the reactor wall as well as the fiber surface. Thus, the catalyst appears of value for further examination in the industrial practice. The non-catalytic thermal dehydrochlorination has been assumed to proceed in the gas phase through the radical chain reaction, producing pyrolytic carbons on the reactor wall. The present reaction over PAN-ACF can be principally catalysed by its basic sites because PAN-ACF shows basicity due to a significant content of nitrogen atom which is believed to form the pyridine ring.<sup>8)</sup> PAN-ACF was reported to promote the dehydrochlorination of 1,1,2-trichloroethane into 1,1-dichloroethylene,<sup>9)</sup> which is proved to be produced only on the basic surface, as previously reported.<sup>10)</sup> The basic reaction is expected not to accelerate formation of carbonaceous substance as far as the reaction is operated at relatively low temperature where no radical reaction takes place.

P-ACF and C-AC exhibited significant activity and selectivity in the dehydrochlorination of 1,2-DCE, although they have no distinct basicity. The radical dehydrochlorination may principally take place on these carbon materials. They lost their activities much more rapidly than PAN-ACF. The carbonaceous substances formed on their surface may cause such a deactivation. The substances are formed in the pores of P-ACF and C-AC through the radical reaction of VC. In particular, C-AC carriers pores which developed deep into the center of its grain.<sup>11)</sup> Such deep pores tend to trap the product for a long time because of slow diffusion, accelerating the coke formation through its consecutive reactions. In this sense, the basicity may distinguish PAN-ACF from other ACFs and AC. Shallow pores of PAN-ACF liberate the product rapidly into the gas phase without its consecutive reaction.

## References

- 1) P. Reich, *Hydrocarbon Process.*, **55**, 85 (1976).
- 2) Y. Hosose, J. Kawamura, and K. Sekizawa, Jpn. Kokai Tokkyo Koho, 381232(1991).
- 3) H. Hirakawa, S. Fujii, Y. Hosose, and K. Sekizawa, Jpn. Kokai Tokkyo Koho, 3141232(1991).
- 4) K. Okamoto, N. Tanaka, K. Adachi, and H. Shingu, *Bull. Chem. Soc. Jpn.*, **39**, 1522 (1966).
- 5) J. J. Prinsloo, P.C. Van Berge, and J. Zlotnick, *J. Catal.*, **32**, 466 (1974).
- 6) N. Shindo, K. Tanaka, and Y. Matsumura, *Chem. Eng.*, **32**, 28(1987).
- 7) I. Mochida and H. Fujitsu, "Chemistry and Engineering of Carbon," Asakura, Tokyo(1990), p.210.
- 8) S. Ohtani, K. Okuda, and S. Matsuda, "Carbon Fiber," Kindai Hensyu, Tokyo(1983), p.124.
- 9) I. Mochida, Y. Yasumoto, and H. Fujitsu, 59th Natinal Meeting of the Chemical Society of Japan, March 1990, Abstr., No.1A645.
- 10) I. Mochida, J. Take, Y. Saito, and Y. Yoneda, *J. Org. Chem.*, **32**, 3894 (1967).
- 11) Y. Sanada, M. Suzuki, and K. Fujimoto, "Active Carbon," Kodansha, Tokyo(1992), p.19.

(Received September 22, 1993)