

# Catalytic Dehydrochlorination of 1,2-Dichloroethane into Vinyl Chloride over PAN-ACF

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## Introduction

Vinyl chloride monomer (VCM) has been produced commercially through the pyrolysis of 1,2-dichloroethane (1,2-DCE) around 500°C. This process has been established, being proved to give vinyl chloride at a very high selectivity about 99% and a reasonable conversion of about 50%. However the coking on the reactor wall is a major hindrance for long term operation, requiring decoking every two months.

The catalytic dehydrochlorination at lower temperatures has been studied to solve the problem. Although the basic zeolite<sup>1),2)</sup> and active carbon<sup>3),4)</sup> were reported to lower the reaction temperature, coking still took place on the catalysts to limit its life. Vinyl chloride may be polymerized and carbonized in the pores of the catalysts. Polyacrylonitrile-based active carbon fibers (PAN-ACF) are believed to have shallow pores and distinct basicity caused by nitrogen atoms contained in a PAN-ACF. The basic elimination at lower temperature and short residence of the product in the shallow pore may prevent coke formation on the catalyst<sup>5)</sup>.

In the present study several kinds of ACFs were examined for the dehydrochlorination of 1,2-DCE. The catalytic activity of ACFs under some reaction conditions were studied.

## Experimental

The dehydrochlorination was carried out by using a flow reactor with fixed catalyst bed. The reactor tube 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 by a liquid pump and then vaporized before 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 the 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 were used as catalysts, Mesophase pitch-CF was obtained from Tonen. The properties of ACFs are summarized in **Table 1**.

## Results

**Figure 1** shows the activities of ACFs. The PAN-ACF has exhibited most excellent catalytic activity among the ACFs for the dehydrochlorination of 1,2-DCE. The conversion and selectivity over PAN-ACF at 360°C after two hours were 50% and 99.9% respectively. The major by-products were ethylene, acetylene and 1,1-dichloroethane, all of which were produced in yields lower than 0.1%, although their yields were much the same as those obtain by the conventional thermal reaction at 500°C. The yields of methyl chloride, ethyl chloride and butadiene were less than 0.01%.

**Figure 2** illustrates conversions by time on stream, which the PAN-ACF and a mixture of PAN-ACF and Pitch-CF were packed respectively. Although the reaction temperature was controlled at 360°C in both cases, the temperatures at the center of the catalyst bed were 310°C and 340°C, respectively, because of the high thermal conductivity of mixed Pitch-CF. This temperature distribution causes a variation in the conversion, the latter bed giving a much higher conversion although it decreased by the time on stream probably because of deactivation by deposited carbon.

**Figure 3** illustrates the variation of conversion in the long run at 360°C and 300°C. The conversion at 360°C was around 55% for the initial 30h and then decreased rather rapidly to 15% by 80h after the reaction started. The reaction was much more stable at 310°C, the conversion being about 10-15% for 100h.

## Conclusion

PAN-ACF was found to be an excellent catalyst for the dehydrochlorination of 1,2-DCE into VCM. Its poor thermal conductivity induced a large temperature gradient between the skin and center of the sample's bed because of the endothermic reaction of dehydrochlorination to form VCM. Blending Pitch-CF with PAN-ACF reduced that gradient. The reaction temperature of 300°C provided a stable conversion for at least 100h.

## References

1. Y. Hosose, J. Kawamura, and K. Sekizawa, Jpn. Kokai Tokkyo Koho, 381232 (1991).
2. H. Hirakawa, S. Fujii, Y. Hosose, and K. Sekikawa, Jpn. Kokai Tokkyo Koho, 3141232 (1991).
3. K. Okamoto, N. Tanaka, K. Adachi, and H. Shingu, *Bull. Chem. Soc. Jpn.*, **39**, 1522

- (1966).
- J. J. Prinsloo, P. C. Van Berge, and J. Zlotnick, *J. Catal.*, **32**, 466 (1987).
  - I. Mochida, Y. Yasumoto, Y. Watanabe, H. Fujitsu, Y. Kojima, and M. Morita, *Chem. Lett.*, **6**, 197(1994).

Table 1. Properties of active carbon fiber

| ACFs / CF  | elemental analysis / wt % |     |     |      |     | S. A. m <sup>2</sup> /g |
|------------|---------------------------|-----|-----|------|-----|-------------------------|
|            | C                         | H   | N   | O    | Ash |                         |
| PAN-ACF    | 78.1                      | 1.4 | 4.5 | 16.0 | 0.3 | 850                     |
| Pitch-ACF  | 93.9                      | 0.9 | 0.3 | 4.6  | 0.5 | 1550                    |
| Phenol-ACF | 92.3                      | 0.9 | 0.3 | 6.3  | 0.3 | 1000                    |

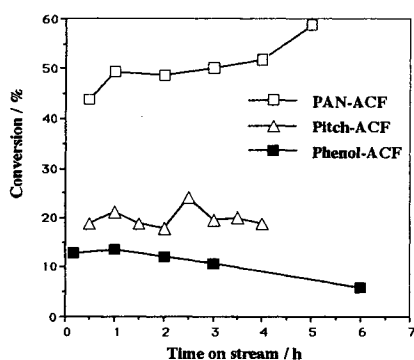


Figure 1. Activity of each ACF  
 Reaction temperature 360 °C  
 Amount of catalyst 300mg  
 Flow rate of 1,2-DCE 0.17 ml/min.

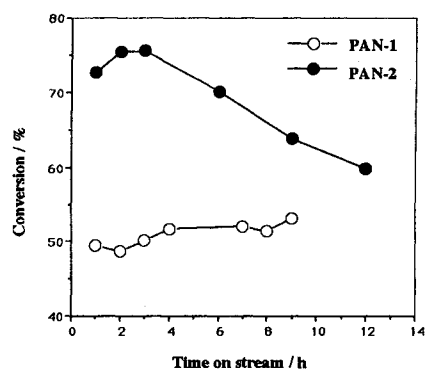


Figure 2. Effect of mixing a carbon fiber  
 Temperature at the center of the catalyst bed PAN-1 : 310°C, PAN-2 : 340°C  
 PAN-1 as PAN-ACF 300mg  
 PAN-2 as PAN-ACF 300mg + CF 300mg  
 Reaction temperature 360°C  
 Flow rate of 1,2-DCE 0.17ml/min.

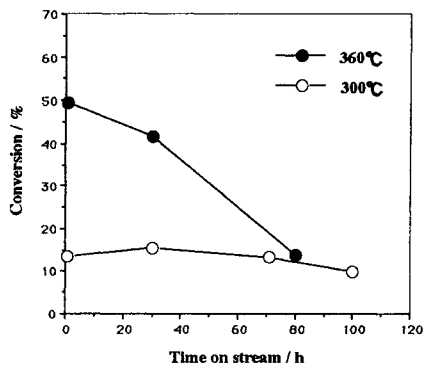


Figure 3. Long reactions at 360°C and 300°C  
 Amount of catalyst 300mg  
 Flow rate of 1,2-DCE 0.17 ml/min.