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Hydrodehalogenation Reaction on Carbon-Supported Palladium Catalyst†

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In this study, dichlorodifluoromethane was hydrodehalogenated on Pd/carbon catalyst. Activated carbon and activated carbon fiber were used as a catalyst support. The main products were difluoromethane, methane, chlorofluoromethane, hydrogen chloride and hydrogen fluoride. The activity of catalysts was tested in microreactor. The reaction variables were temperature, reactant composition and reactant flow rate. The reaction temperature affected on reaction severely. But the effects of reactant composition and reactant flow rate on reaction were mild. Nitrogen and carbon dioxide was adsorbed on catalysts to characterize catalysts. Specific surface area (nitrogen, BET eqn.), narrow micropore volume (carbon dioxide, Dubinin-Radushkevich eqn.), total micropore volume (nitrogen, alpha-s plot), total pore volume area (nitrogen, Gurvitsch eqn.) was calculated.

Key Words: Dehalogenation, Activated carbon, Fiber, Palladium, Catalysis.

INTRODUCTION

The chlorofluorocarbons are responsible for the ozone depletion. Several agreements and protocols were reached to reduce or give up chlorofluorocarbon production. It has been studying to decompose or convert chlorofluorocarbons to less harmful materials. Incineration, pyrolysis, catalytic conversion may be used to do so. Active carbon-supported palladium catalysts are widely used in heterogeneous hydrogenation of liquid-phase reactants. Because of its merits on such as high surface area, sufficient strength, heat and chemical stability and chemical inertness, activated carbons are favoured as supports for activated metals. Recently, activated carbon fiber was developed and supposed to be the substitute of conventional activated carbons. As most of the pores of activated carbon fibers are micropore and their pore size distributions are narrow, they may show the molecular sieving effect and may show shape-selectivity in catalysis. In this study, CF_2Cl_2 was dehalogenated with hydrogen on carbon supported palladium catalysis. The main products were CF_2H_2, CH_4, CF_2HCl, HCl and HF. Activated carbon and activated carbon fiber were used as carbon supports[1]. Palladium was deposited on carbon to be a dehalogenation catalyst. Its catalytic activity was tested on gas phase heterogeneous dehalogenation reaction.

EXPERIMENTAL

Sample preparation: Activated carbon(bituminous based) and activated carbon fiber (coal tar pitch based) referred in the following activated carbon and activated carbon fiber were used as carbonaceous catalyst supports. Activated carbons were sieved to particle size ranging from 0.8 to 1.7 mm. Felt-type activated carbon fiber was crushed by Fine Impact Mill and sieved to 20 mesh size. Then, the fraction which is smaller than 20 mesh size was used as a adsorbent.

Catalyst preparation: Palladium was deposited on activated carbon fiber by precipitation and reduced by formaldehyde. $PdCl_2$ was the precursor of palladium catalyst. Pitch-based activated carbon fiber was offered by Osaka Gas Co. Prepared catalysts were filtered, washed with hot distilled water and stored in the glass bottle in wet state. Catalysts were evacuated at 373K for 15 h to avoid sintering of palladium particle.

Porosity analysis: The adsorption of nitrogen at 77 K was performed in a gravimetric apparatus equipped with Cahn balance in order to investigate the pore structure. Specific surface areas (BET equation), total pore volumes (Gurvitsch rule[2]) and total micropore volumes (α_s-plot)[3] were calculated from the nitrogen adsorption isotherms. Narrow micropore volumes (Dubinin-Radushkevich equation[4]) and mean pore radii (Dubinin equation[5]) were obtained from the adsorption isotherm of carbon dioxide at 273 K. The wide micropore volumes were calculated by substracting narrow micropore volumes from total micropore volumes.

Hydrodehalogenation reaction: CF_2Cl_2 and hydrogen were fed into the reactor. CF_2Cl_2 was dehalogenated at atmospheric pressure in a micro-reactor. The products were sampled

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on line and analyzed by gas chromatography (TCD, 5 % Fluorcol 143 HMW on 60/80 Carnopack B). The standard reaction condition was as follows; temperature 473 K, catalyst quantity 0.5 g, reactant composition (CF_2Cl_2 26 vol. % hydrogen 74 vol. %), reactant flow rate 19 cc/min.

RESULTS AND DISCUSSION

Porosity of catalysts: Table-1 shows the porosity of manufactured catalysts. The specific surface area and total pore volume of activated carbon fiber supported catalyst is almost two times larger than those of activated carbon supports catalyst. The pore size distribution of activated carbon supported catalyst is almost similar in micropore and mesopore compared to microporous activated carbon fiber supported catalyst.

TABLE-1
POPOSITIES OF CATALYST

Sample	5 wt. % Pd on AC	5 wt. % Pd on ACF
Specific surface area (m^2/g)	840	1623
Narrow micropore volume (cc/g)	0.271	0.319
Wide micropore volume (cc/g)	0.030	0.583
Total pore volume (cc/g)	0.533	0.923

Hydrodehalogenation reaction on activated carbon supported palladium catalyst: Fig. 1 illustrates the temperature effect on product composition and conversion. The stoichiometry of hydrodehalogenation reaction may be explained as follows;

$$CF_2Cl_2 + H_2 \rightarrow CF_2HCl + HCl$$
$$CF_2Cl_2 + 2H_2 \rightarrow CF_2H_2 + 2HCl$$
$$CF_2Cl_2 + 4H_2 \rightarrow CH_4 + 2HCl + 2HF$$
$$CF_2HCl + H_2 \rightarrow CF_2H_2 + HCl$$
$$3CF_2Cl_2 + 7H_2 \rightarrow CF_2HCl + CF_2H_2 + CH_2 + 5HCl + 2HF$$

The conversion reached more than 90 % resulting in CF_2H_2 and CH_4 mainly. Trace amounts of CF_2HCl were detected. The conversion increased with reaction temperature linearly. It seemed that a formal series reaction was preceded as follows:

$$CF_2Cl_2 \rightarrow CF_2H_2 \rightarrow CH_4$$

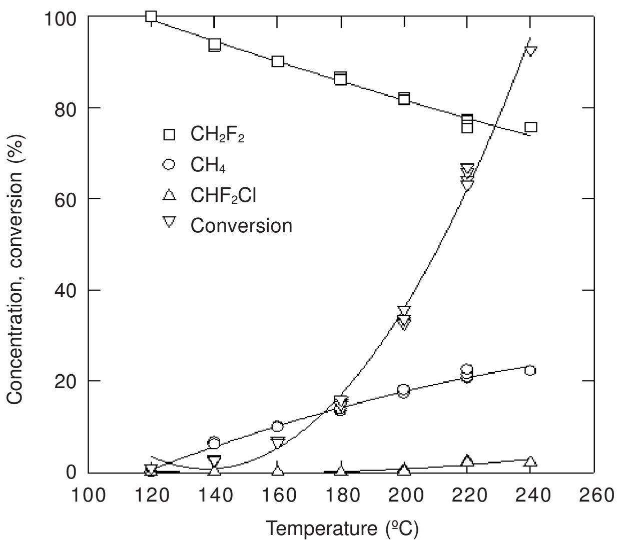

Fig. 1. Effect of temperature on the hydrodehalogenation of CF_2Cl_2 (catalyst; Pd on activated carbon)

The ratio of CF_2H_2 to CH_4 is shown in Fig. 2. The selectivity to CF_2H_2 decreased as temperature increased. It means that the selectivity to CH_4 increased as temperature increased. Gervasutti reported CF_3CH_3/CF_3CH_2F selectivity ratio decreases as CF_3CFCl_2 dechlorinated on Pd/C catalyst[6]. Weiss reported when CCl_4 is hydrodechlorinated on Pt catalyst, the produced ratio of $CHCl_3/CH_4$ is in the range of 4-6 regardless of the conversion of CCl_4[6]. In the case of CF_2Cl_2, the selectivity of CF_2H_2 and CH_4 may be determined primarily by the desorption rate of : CF_2 radical and the formation rate of CH_4 on catalyst surface.

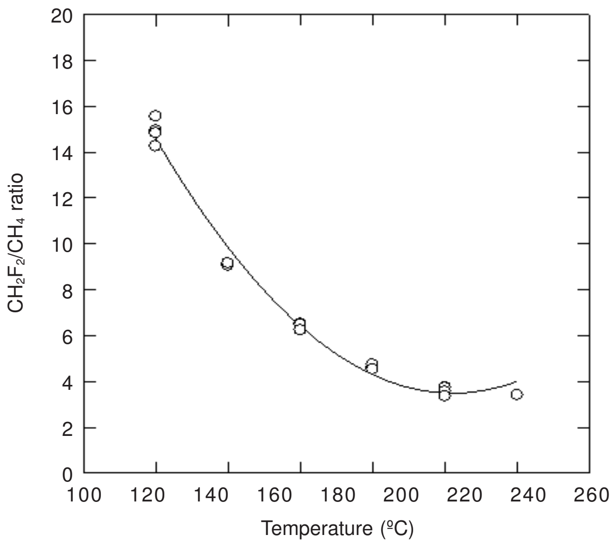

Fig. 2. Effect of temperature on the ratio of CH_2CF_2 to CH_4 (catalyst; Pd on activated carbon)

Fig. 3 illustrates the effect of reactant composition on the hydrodehalogenation of CF_2Cl_2 on Pd/AC catalyst. As the concentration of CF_2Cl_2 in reactant increases, the concentration of produced CF_2H_2 increases and that of CH_4 decreases. The selectivity to CF_2H_2 was increased with CF_2Cl_2 concentration because of low conversion resulting from hydrogen shortage. The feed composition had a little influence on product selectivity in the range of this study (CF_2Cl_2 concentration was 20-75 vol. %).

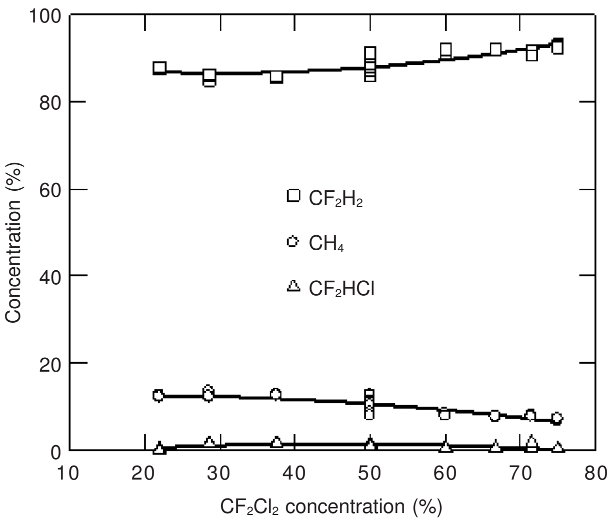

Fig. 3. Effect of reactant composition on the hydrodehalogenation of CF_2Cl_2 (catalyst; Pd on activated carbon)

Fig. 4 shows the effect of reactant flow rate on the hydrodehalogenation of CF_2Cl_2. The concentration of reactant CF_2Cl_2 was 26 vol. % and space time was 3,600-7,200 h^{-1}. The flow rate of reactant had a little influence on product selectivity in the range of this study. The selectivity to CF_2H_2 was increased with reactant flow rate. It was resulted from low conversion because of short contact time.

The effect of reactant flow rate on the ratio of CF_2H_2 to CH_4 was shown in Fig. 5. The ratio increased a little according to the increase of reactant flow rate.

Hydrodechlorination reaction on activated carbon fiber supported palladium catalyst: The reaction results on activated carbon fiber support catalyst are shown in Fig. 6. CF_2Cl_2 reacted with hydrogen resulting in up to 94 vol. % of CF_2H_2 and CH_4 mixture and lower than 6 vol. % of CF_2HCl. As the reaction temperature increased, the selectivity to CF_2H_2 decreased and the selectivity to CH_4 increased. The conversion shows concave parabola having minimum value around 140 ºC. Product composition and conversion were affected by reaction temperature. Although the trend was similar to that of activated carbon support catalyst, the conversion and selectivity were different (Fig. 2). The conversion was higher than that of activated carbon support catalyst at low temperature, but it was inversed at high temperature. The selectivity to CF_2H_2 was slightly higher than that of activated carbon support catalyst. It was concluded that the dehalogenation of CF_2Cl_2 with hydrogen was affected severely by reaction temperature and mildly by reactant flow rate and reactant composition. The selectivity to CF_2H_2 is inversely proportional to conversion.

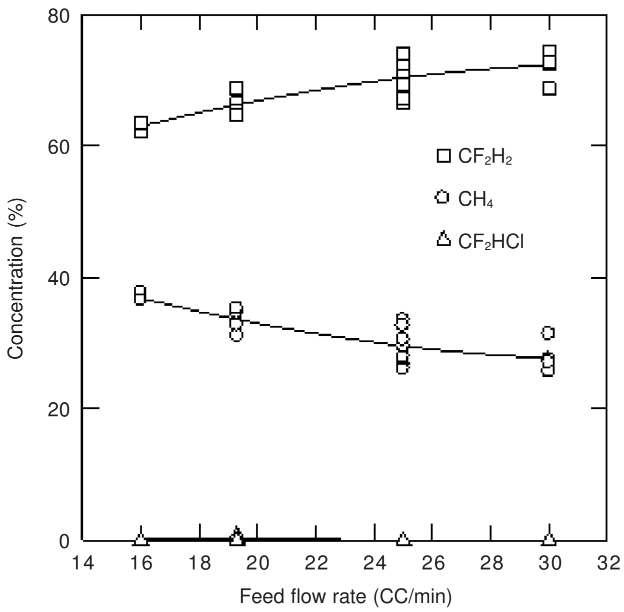

Fig. 4. Effect of reactant flow rate on the hydrodehalogenation of CF_2Cl_2 (catalyst; Pd on activated carbon)

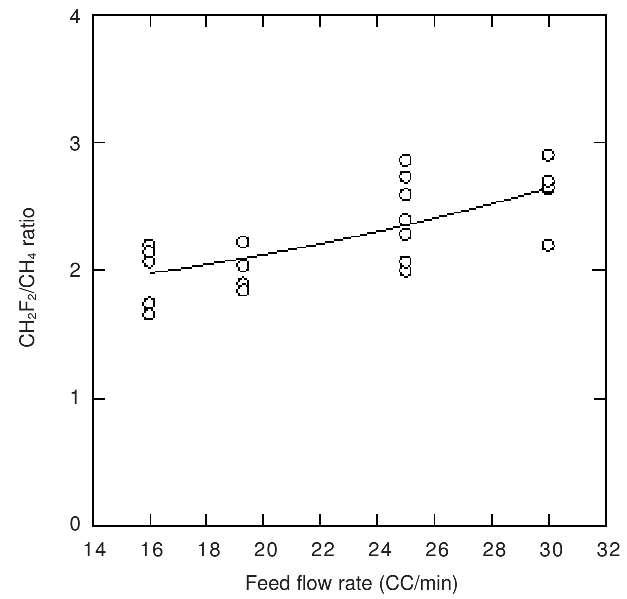

Fig. 5. Effect of reactant flow rate on the ratio of CH_2CF_2 to CH_4 (catalyst; Pd on activated carbon)

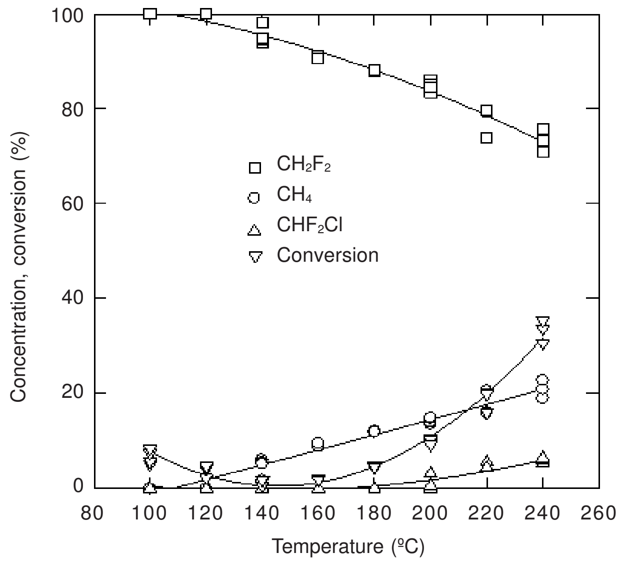

Fig. 6. Effect of temperature on the hydrodehalogenation of CF_2Cl_2 (catalyst; Pd on activated carbon fiber)

The effect of temperature on the ratio of CF_2H_2 to CH_4 was shown in Fig. 7. The ratio decreased according to the increase of reaction temperature.

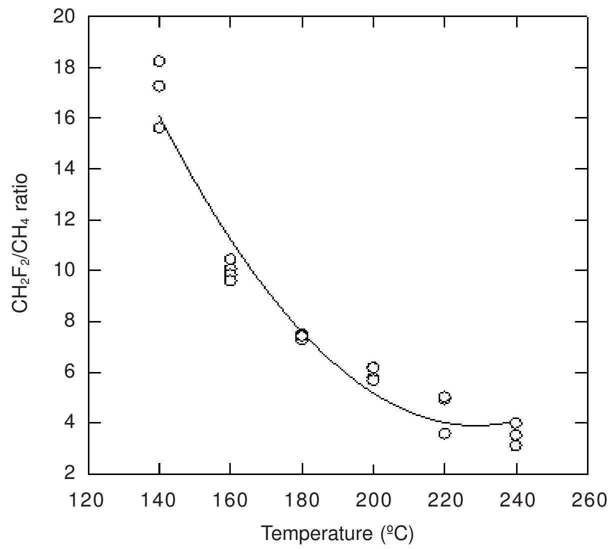

Fig. 7. Effect of temperature on the ratio of CH_2CF_2 to CH_4 (catalyst; Pd on activated carbon fiber)

Conclusion

Dichlorodifluoromethane was hydrodehalogenated on palladium/carbon catalyst. Main products were difluoromethane, methane, chlorofluoromethane, hydrogen chloride and hydrogen fluoride. The temperature affected on hydrodehalogenation reaction considerably. But the effects of reactant composition and reactant flow rate on reaction was a little. The selectivity to CF_2H_2 is inversely proportional to conversion.

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