A study on the hydrodechlorination reaction of dichlorodifluoromethane over Pd/AlF₃ catalyst

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Abstract

The hydrodechlorination reaction of dichlorodifluoromethane (CF_2Cl_2) has been studied under an atmospheric pressure at 130–210°C over Pd/AlF₃ catalyst. The effects of various reaction conditions on the catalyst performance in terms of the reaction rate and product distributions were extensively investigated and the adsorption behaviours of H_2, CF_2Cl_2, CHF_2Cl, CH_2F_2 and CH_3F on the catalyst surface are compared. In addition, the plausible reaction scheme has been proposed based on the experimental observations. Under the assumption that the formation of two main products, CH_2F_2 and CH_4, proceeds through the hydrogenation of intermediate species, CF_2^*, the reaction rate constants have been calculated by fitting the experimental data with the reaction rate expression.

Keywords: Dichlorodifluoromethane; Hydrodechlorination reaction; Adsorption behaviour; Reaction scheme

1. Introduction

Chlorofluorocarbons (CFCs) have been widely used as refrigerants, blowing agents, propellants or cleaning agents due to their outstanding properties such as stability, nontoxicity, nonflammablity, good thermodynamic properties and so on. However, production and use of CFCs are currently being phased out under international agreements, Montreal Protocol, because of global environmental concerns. Chlorine atoms dissociated from CFCs are believed to be responsible for diminishing the ozone content of the stratosphere.

Thus, the safe destruction of recovered CFCs is urgently needed. It would be particularly desirable if recovered CFCs can be converted to harmless and preferably to useful chemicals. Various technologies for treating CFCs before being released to air have been proposed in recent years. These technologies are mainly based on catalytic or non-catalytic decomposition processes. Catalytic decomposition technology includes oxidation [1,2], hydrolysis [3,4] and hydrogenation [5,6]. CF_2Cl_2 (CFC-12) may be catalytically transformed to CH_2F_2 (HFC-32) via hydrodechlorination. HFC-32 is thought to be one of the most promising candidates for

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replacing CHF_2Cl (HCFC-22) which has been mainly used as low-temperature refrigerants.

The reaction of CF_2Cl_2 with hydrogen has been studied by Du Pont Inc. at 500–700°C over Pt, Ag, Co and Cu catalysts [7]. The maximum selectivity to $CHFCl_2$ and C_2F_4 was found to be 39%. Aida et al. [3] compared the performance of Au/Al_2O_3 and Au/Co_3O_4 catalyst for the decomposition of CF_2Cl_2. Au/Al_2O_3 was found to have a higher activity than Au/Co_3O_4. They concluded that Au/Co_3O_4 had only a high oxidation activity, while Au/Al_2O_3 had both oxidation and hydrolysis activity. Coq et al. [5] studied the hydrogenation of CF_2Cl_2 in the gas phase at atmospheric pressure over Pd black and Pd supported on alumina, graphite, or AlF_3, and found the highest selectivity to CH_2F_2 over Pd/AlF_3 catalyst.

In this work, extensive experimental investigations on the hydrodechlorination reaction of CF_2Cl_2 have been carried out under an atmospheric pressure at 130–210°C over Pd/AlF_3 catalyst. The plausible reaction scheme has been proposed based on the experimental results and adsorption characteristics. The reaction rate constants were calculated by fitting the experimental data with the reaction rate expression.

2. Experimental

2.1. Preparation and characterizations of Pd / AlF₃ catalyst

A catalyst containing 3.45 wt.% of Pd on AlF_3 was prepared by the conventional impregnation of AlF_3 with aqueous $PdCl_2$ solution. The necessary amount of $PdCl_2$ was dissolved in 20 cm³ of 0.1 N HCl solution, and then it was added to 5 g of AlF_3. The solution was evaporated at about 60°C in a rotary evaporator for several hours. After drying at 120°C overnight, the impregnated catalyst was calcinated at 450°C in the electric furnace for 2–3 h. Prior to the reaction, the calcinated catalyst was reduced in situ in a hydrogen stream.

The specific surface area of the catalyst were measured using an area meter Model II (Strohlein Instrument, Germany), which was a
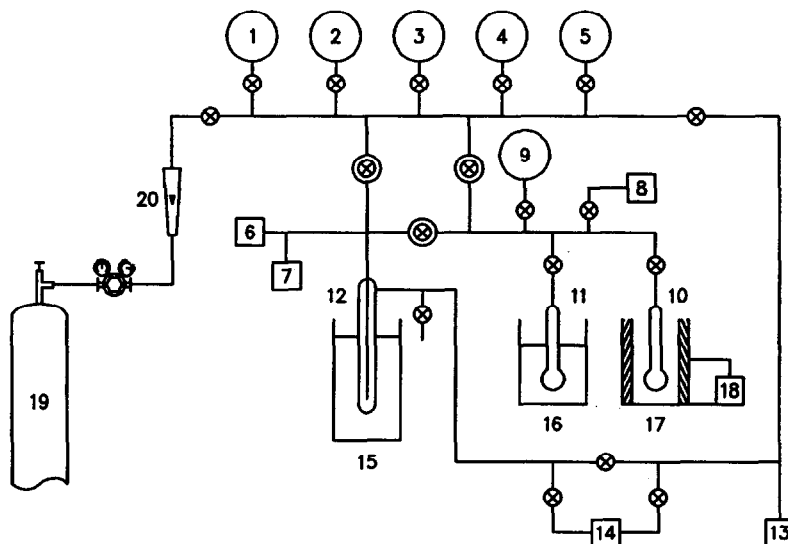

Fig. 1. Volumetric apparatus for adsorption experiment. 1: H_2 reservoir; 2: CFC reservoir; 3: N_2 reservoir; 4: O_2 reservoir; 5: He reservoir; 6: ion vacuum gauge; 7: convection vacuum gauge; 8: Baratron vacuum gauge; 9: standard volume (22.01 ml); 10: 1/4 in. chemisorption cell; 11: 3/8 in. chemisorption cell; 12: liquid N_2 (to remove vaporized silicon oil); 13: rotary vacuum pump; 14: diffusion pump; 15: liquid N_2 duar; 16: liquid N_2 duar; 17: electric heater; 18: temperature controller; 19: gas bomb; 20: flow meter.

single point BET apparatus. The surface area of calcinated catalyst was found to be 36.5 m^2/g.

2.2. Adsorption

The adsorption experiments of H_2, CF_2Cl_2, CHF_2Cl, CH_2F_2, and CH_3F were conducted in a conventional volumetric apparatus as shown in Fig. 1. A rotary vacuum pump and a diffusion pump were used to connect with the volumetric apparatus, and the liquid nitrogen trap was installed between the apparatus and the pumps for the removal of vaporized silicon oil. The pressure change during the adsorption step was measured by a pressure gauge (MKS Instruments, USA).

After 0.3 g of catalyst was charged to the volumetric apparatus, the volume of the apparatus was measured using He gas. The reduction of catalyst was performed under the hydrogen flow of 20 cm^3/min at 300°C for 1 h. After the reduction, adsorbed hydrogen was discharged through a vacuum line for 1 h. Then the apparatus was cooled to 150°C to perform hydrogen chemisorption experiment.

The hydrogen of high purity grade at a certain pressure was introduced into the adsorption apparatus and the equilibrium pressure was measured after 30 min. Adsorbed hydrogen was discharged through a vacuum line for 1 h. And then, the hydrogen at a different pressure was introduced again and the same procedure was repeated. The adsorption equilibrium isotherm of hydrogen was determined from the adsorption amounts obtained for various pressures. In the same way, the adsorption isotherms were obtained for CF_2Cl_2, CHF_2Cl, CH_2F_2, and CH_3F.

2.3. Reaction

The reaction of CF_2Cl_2 with hydrogen was carried out at atmospheric pressure in a continuous flow system with a fixed-bed reactor made of nickel tube (0.3 m × 1/2 in.). The schematic diagram of the apparatus is shown in Fig. 2. 0.25 g of Pd/AlF$_3$ catalyst was placed in the reactor. The catalyst was reduced in situ under flowing hydrogen (N_2:30 cm^3/min, H_2:15 cm^3/min) at 450°C for 4 h. Before being sub-
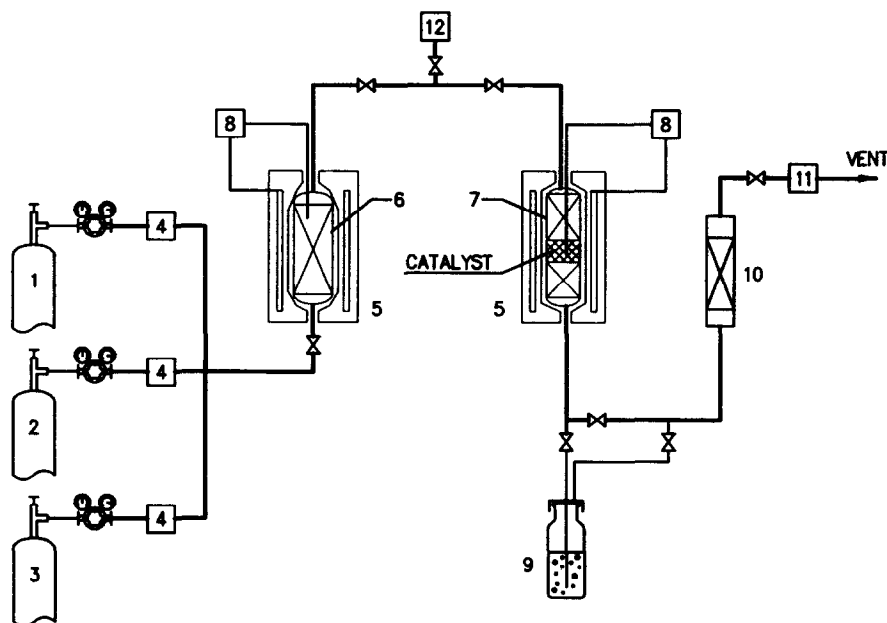

Fig. 2. Schematic diagram of reaction system. 1: CFC-12 cylinder; 2: H_2 cylinder; 3: N_2 cylinder; 4: mass flow controller; 5: electric furnace; 6: preheater; 7: reactor; 8: temperature controller; 9: NaOH solution (HCl and HF trap); 10: CaCl$_2$ (drying agent); 11: sampling port; 12: pressure gauge.

jected to the main reaction, the catalyst was again pretreated under the flow condition of 8.0 cm^3/min of CF_2Cl_2, 8.0 cm^3/min of H_2 and 4.8 cm^3/min of N_2 at 210°C until the catalyst activity was stabilized. The Pd catalyst has been reported to undergo changes in activity and selectivity during the initial period of time in the hydrogenation reaction [5].

The flow rate of each reactant was controlled by mass flow controller (Matheson Model 8270). The effluent from the reactor was bubbled through a scrubber with 0.1 N NaOH solution to remove any HCl and HF formed, and then the remaining moisture was removed through a $CaCl_2$ dryer. Even though CHF_2Cl has been known to be hydrolyzed in NaOH solution, the product gas composition was hardly affected by the hydrolysis in our experiments. The temperature of catalyst bed in the reactor was measured by a thermocouple and controlled with a precision of ±1°C by a temperature controller. The reaction products were analyzed using the gas chromatograph equipped with a Porapak Q column (2 m × 1/8 in.) and the mass spectrometer equipped with a HP-1 capillary column (50 m × 0.2 mm).

3. Results and discussion

The CF_2Cl_2 hydrodechlorination reaction over Pd/AlF$_3$ catalyst was investigated varying the reaction conditions such as feed composition, reaction temperature and so on.

$$CF_2Cl_2 + H_2 \rightarrow products$$
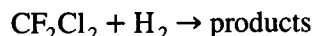
Considering that the dissociation energy of C–Cl bond is known to be smaller than that of C–F bond [8], there is a possibility that the reaction proceeds through a consecutive scheme:

$$CF_2Cl_2 \rightarrow CHF_2Cl \rightarrow CH_2F_2 \rightarrow CH_3F \rightarrow CH_4$$

As a result of reaction, however, CH_2F_2 and CH_4 were produced as major products, which usually occupied more than 90% of the total products. CHF_2Cl and CH_3F, on the other hand, were detected only as trace amounts.
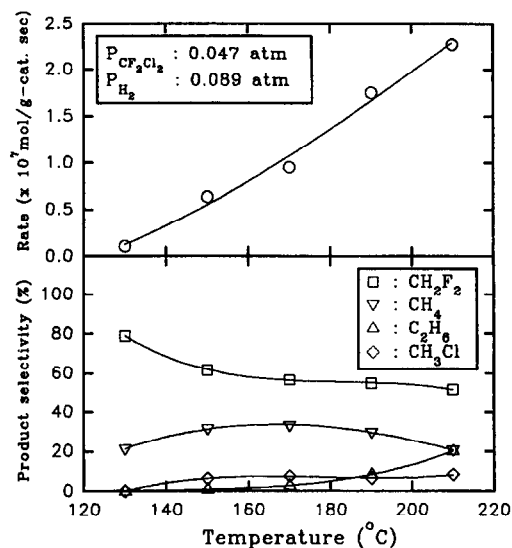

Fig. 3. Effect of temperature on reaction rate and product selectivity in the hydrogenation of CF_2Cl_2 over Pd//AlF$_3$ catalyst.

Fig. 3 shows the effects of the reaction temperature on the reaction rate and product distributions. It is readily seen that the reaction rate increased rapidly as the reaction temperature was raised from 130°C to 210°C. With increasing the reaction temperature, CH_2F_2 was found to decrease slowly while CH_4 showed a maximum at 170°C. C_2H_6 increased gradually and reached to about 20% at 210°C. CH_3Cl also held a small portion among all the products in a higher temperature. From these results in the product distributions with CF_2Cl_2 conversion (or reaction rate) change, it can be assumed that $CH2_*^*$ or CH_3^* would be formed through the hydrogenation of CF_2Cl_2 on Pd surface and react with each other or Cl* to produce C_2H_6 or CH_3Cl. In other words, it can be said that the main reaction in CF_2Cl_2 hydrodechlorination did not proceed through a consecutive scheme. Coq et al. [5] drew a similar conclusion and suggested the removal reactions of two halogen atoms during one sojourn at the catalyst surface:

$$CF_2Cl_2 \rightarrow CH_2F_2; CHF_2Cl$$
$$\rightarrow CH_3F; CH_2F_2 \rightarrow CH_4$$
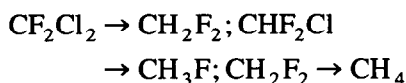
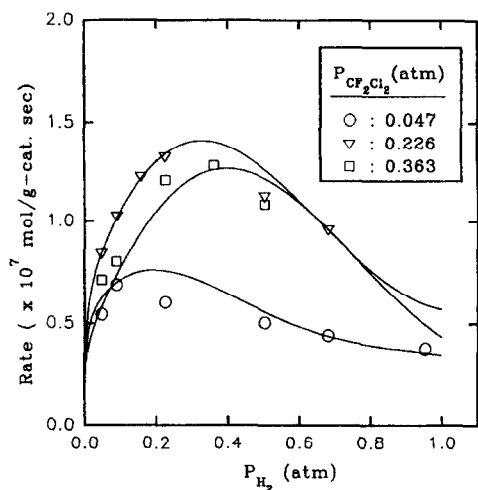In a way, the formation of byproduct, CH_3Cl, may be attributed to AlF$_3$ used as support.

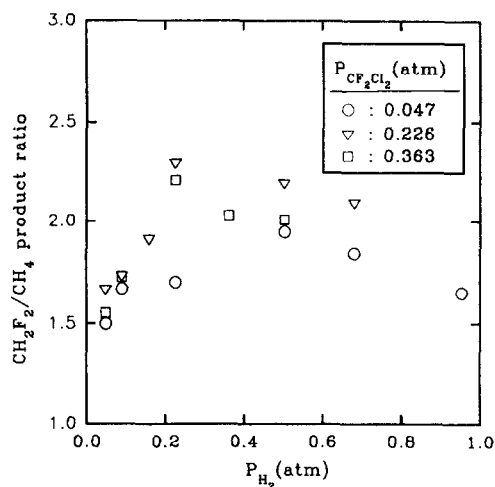Fig. 4. Effect of hydrogen pressure on reaction rate at various CF_2Cl_2 pressure at 150°C over Pd//AlF$_3$ catalyst.

Fig. 5. Effect of hydrogen pressure on CH_2F_2/CH_4 product ratio of various CF_2Cl_2 pressures at 150°C over Pd//AlF$_3$ catalyst.

CH_3Cl can be obtained by F/Cl exchange from the intermediate product, CH_3F, on AlF$_3$ which has been reported to be a good catalyst in the preparation of CF_3CFCl_2 from $CFCl_2CF_2Cl$ [9]. However, this effect can be neglected because of much lower reactivity on AlF$_3$ than Pd surface. The activity of AlF$_3$ alone was found experimentally to be negligible for the hydrodechlorination reaction in the experimental range of 130–210°C.

The effects of the feed composition on the overall reaction rate are shown in Fig. 4. The reaction rate had a maximum value at a specific hydrogen pressure for given CF_2Cl_2 pressures. This result indicates that there is competitive adsorption between CF_2Cl_2 and hydrogen on catalyst surface.

Fig. 5 illustrates the effect of hydrogen pressure on the CH_2F_2/CH_4 ratio at various CF_2Cl_2 pressures. The CH_2F_2/CH_4 ratio showed a maximum value at a certain hydrogen pressure depending upon the CF_2Cl_2 pressure change, while it showed little change with change in CF_2Cl_2 pressures. Therefore, the reaction appeared to be more strongly influenced by hydrogen pressure rather than CF_2Cl_2 pressure.

The adsorption experiments were also carried out in order to compare the adsorption ability of CF_2Cl_2 and hydrogen on the catalyst surface.

The adsorption equilibrium curves for reaction products as well as reactants were obtained as shown in Fig. 6. The order of adsorption ability was found to be $H_2 > CF_2Cl_2 > CHF_2Cl > CH_2F_2 > CH_3F$. These results show that carbon–chlorine compounds were adsorbed more easily than carbon–fluorine compounds on the catalyst surface.

Fig. 7 compares the adsorption isotherms of CF_2Cl_2 depending upon the adsorption models. The adsorption isotherms obtained from two
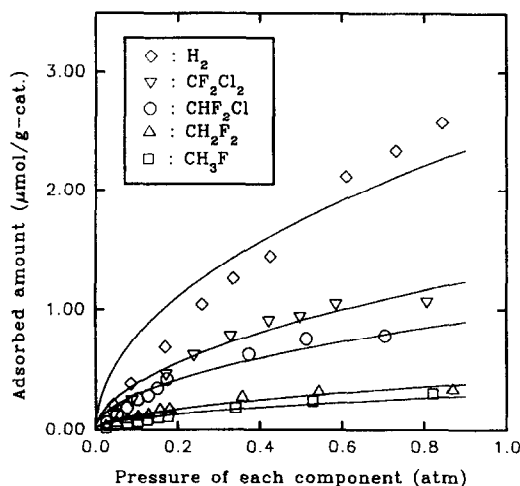

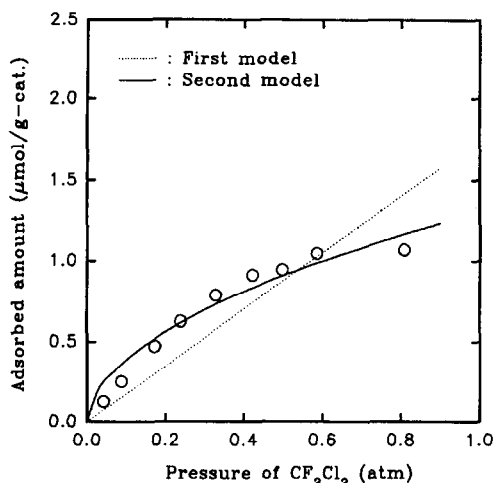Fig. 6. Adsorption equilibria for various components at 150°C over Pd//AlF$_3$ catalyst.

Fig. 7. Comparison of isotherm models for CF_2Cl_2 adsorption at 150°C over $Pd//AlF_3$ catalyst.

adsorption models were compared with the experimental results. It was assumed in the first model that CF_2Cl_2 was physically adsorbed to form $CF_2Cl_2^*$. Coq et al. [5] used a classical Langmuir–Hinshelwood model with competitive adsorption of CF_2Cl_2 and H_2 as a kinetic model, which involved this adsorption model. On the other hand, in the second model it was assumed that CF_2Cl_2 was dissociatively adsorbed to form CF_2Cl^* and the adsorbed CF_2Cl^* was further dissociatively adsorbed to form CF_{2*}^*. As indicated in Fig. 7, the second model was found to be much better than the first model in predicting the adsorption behaviour of CF_2Cl_2.

Based on the above experimental observations, a plausible reaction scheme modified from Coq's one [5] has been proposed as shown in
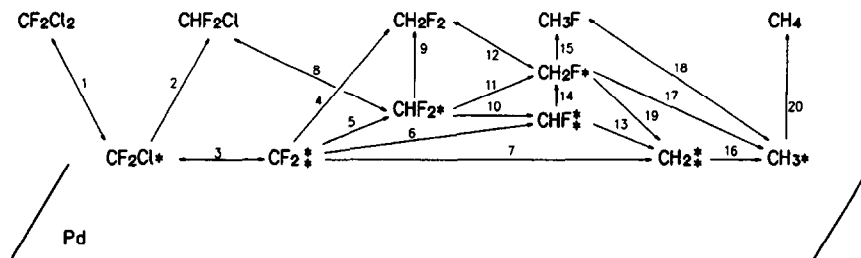
Fig. 8. Since the major products of the reaction were found to be CH_2F_2 and CH_4, their formation was postulated to proceed through the hydrogenation of intermediate species such as CF_{2*}^*, CHF_2^*, CHF_*^*, CH_{2*}^* and so on. Since no appreciable amounts of CHF_2Cl and CH_3F were formed during the reaction, this postulation is more likely acceptable rather than the consecutive scheme of

$$CF_2Cl_2 \rightarrow CHF_2Cl \rightarrow CH_2F_2 \rightarrow CH_3F \rightarrow CH_4$$

In particular, CF_{2*}^* is regarded as a most important species among various intermediates in the proposed reaction scheme for the formation of CH_2F_2 and CH_4 by the hydrodechlorination of CF_2Cl_2.

The reaction rate was calculated and compared with the experimental data under the assumption that other intermediate species, except for CF_{2*}^* in Fig. 8, were consumed as soon as they were formed and the formation of two main products, CH_2F_2 and CH_4, was dependent only upon the hydrogenation rate of CF_{2*}^*. For simplicity, other reaction routes for the formation of CH_2F_2 and CH_4 were neglected in predicting the reaction rate of CF_2Cl_2 hydrodechlorination. Thus, the assumptions adopted for this study can be summarized as follows.

1. CF_2Cl_2 and H_2 are dissociatively adsorbed on catalyst surface.

$$H_2 + 2^* \rightleftharpoons 2H^* \tag{1}$$

$$CF_2Cl_2 + 2^* \rightleftharpoons CF_2Cl^* + Cl^* \tag{2}$$
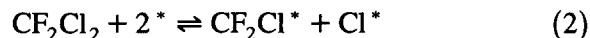
2. CF_2Cl^* is further dissociated to form CF_{2*}^*. The formation of CHF_2Cl from CF_2Cl^*
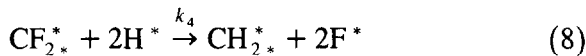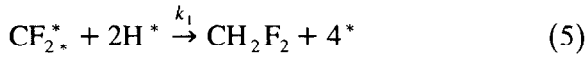

Fig. 8. Reaction scheme.

is assumed very slow or negligible from the experimental results.

$$CF_2Cl^* + 2^* \rightleftharpoons CF_{2*}^* + Cl^* \tag{3}$$
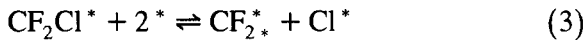
3. Cl^* reacts with H^* to produce HCl.

$$Cl^* + H^* \rightleftharpoons HCl + 2^* \tag{4}$$

4. Formation of two main products, CH_2F_2 and CH_4 is controlled by the step of the hydrogenation of CF_{2*}^*.

$$CF_{2*}^* + 2H^* \xrightarrow{k_1} CH_2F_2 + 4^* \tag{5}$$

$$CF_{2*}^* + H^* \xrightarrow{k_2} CHF_2^* + 2^* \tag{6}$$

$$CF_{2*}^* + H^* \xrightarrow{k_3} CHF_*^* + F^* \tag{7}$$

$$CF_{2*}^* + 2H^* \xrightarrow{k_4} CH_{2*}^* + 2F^* \tag{8}$$
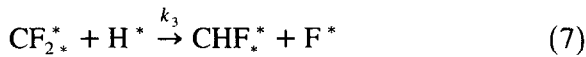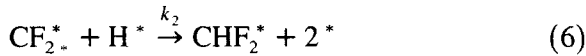
The adsorption equilibrium of each component and the active site balance can be expressed as follows.

$$K_{H_2} = \frac{\theta_H^2}{P_{H_2}\theta_v^2} \tag{9}$$

$$K_{CF_2Cl_2} = \frac{\theta_{CF_2Cl}\theta_{Cl}}{P_{CF_2Cl_2}\theta_v^2} \tag{10}$$

$$K_{CF_2Cl} = \frac{\theta_{CF_2}\theta_{Cl}}{\theta_{CF_2Cl}\theta_v^2} \tag{11}$$

$$K_{HCl} = \frac{\theta_H\theta_{Cl}}{P_{HCl}\theta_v^2} \tag{12}$$

$$\theta_H + \theta_{CF_2Cl} + 2\theta_{CF_2} + \theta_{Cl} + \theta_v = 1 \tag{13}$$

where θ_i is the surface coverage of component i and subscript v denotes the vacant site.

Under the above assumptions, the overall reaction rate for the formation of CH_2F_2 and CH_4 was defined as

$$\begin{aligned}
R &= k_1\theta_{CF_2}\theta_H^2 + k_2\theta_{CF_2}\theta_H + k_3\theta_{CF_2}\theta_H \\
&\quad + k_4\theta_{CF_2}\theta_H^2 \\
&= k_{2H}\theta_{CF_2}\theta_H^2 + k_H\theta_{CF_2}\theta_H \\
&= \frac{A}{2}\theta_v^3\left\{k_{2H}K_{H_2}P_{H_2}\theta_v + k_H\left(K_{H_2}P_{H_2}\right)^{1/2}\right\}
\end{aligned} \tag{14}$$

where $k_{2H} = k_1 + k_4$ and $k_H = k_2 + k_3$

$$\theta_v = \frac{-B + \left(B^2 + 4A\right)^{1/2}}{2A}$$

$$A = \frac{2K_{H_2}K_{CF_2Cl_2}P_{H_2}P_{CF_2Cl_2}}{\left(K_{HCl}P_{HCl}\right)^2}$$

$$B = \left(K_{H_2}P_{H_2}\right)^{1/2} + \frac{K_{HCl}P_{HCl}}{\left(K_{H_2}P_{H_2}\right)^{1/2}}$$

$$+ \frac{K_{CF_2Cl_2}P_{CF_2Cl_2}\left(K_{H_2}P_{H_2}\right)^{1/2}}{K_{HCl}P_{HCl}} + 1$$

K_{H_2}, $K_{CF_2Cl_2}$ and K_{CF_2Cl} were determined from the experimental data using the adsorption equilibrium relations (9), (10) and (11). K_{HCl} and the reaction constants, k_{2H} and k_H, at 150°C were calculated by fitting the rate expression (14) with the experimental data using a modified Levenberg–Marquardt algorithm. The values of these parameters calculated are shown in Table 1.

Fig. 9 and 10 illustrate the change in the surface coverage of each component depending upon the H_2 and CF_2Cl_2 pressures at 150°C. The surface coverages of each component were calculated from Eqs. 9–13 with equilibrium constants obtained above, assuming the competitive adsorption on the basis of Langmuir isotherm model [10]. By comparing Figs. 9 and

Table 1
Value of parameters

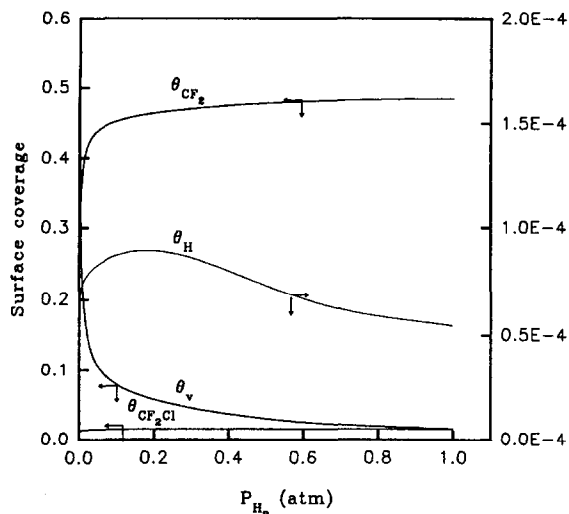| Parameters	Values
K_{H_2}	1.229×10^{-5} (atm^{-1})
$K_{CF_2Cl_2}$	1.806×10^{-6} (atm^{-1})
K_{CF_2Cl}	1.815×10^{-4} (–)
K_{HCl}	3.263×10^{-7} (atm^{-1})
k_{2H}	14.741 (s g-cat./mol)
k_H	5.169×10^{-4} (s g-cat./mol)

Fig. 9. Surface coverage of each component with hydrogen pressure at $P_{CF_2Cl_2} = 0.047$ atm and 150°C over Pd//AlF$_3$ catalyst.

10, it can be seen that the surface coverage of H* is strongly influenced by CF_2Cl_2 pressure. This means that the adsorption of CF_2Cl_2 and H$_2$ on catalyst surface proceeds competitively. In addition, the surface coverage of H* and Cl* was found to be very low compared to that of other components. This indicates that the formation of HCl took place much faster than other reactions.
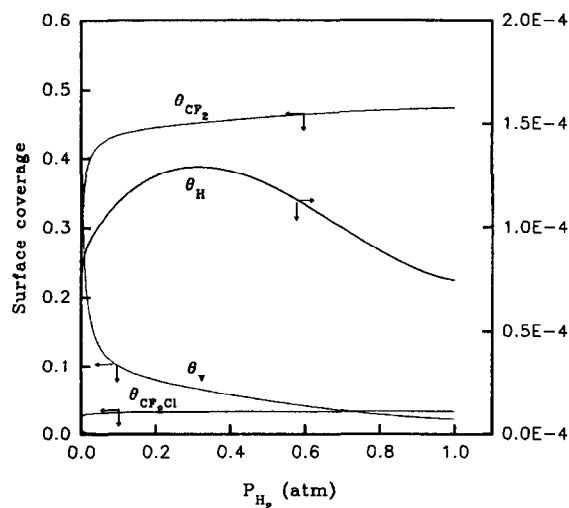

Fig. 10. Surface coverage of each component with hydrogen pressure at $P_{CF_2Cl_2} = 0.226$ atm and 150°C over Pd//AlF$_3$ catalyst.

Using the parameters obtained and rate expression (14), the overall reaction rate was calculated for H$_2$ and CF_2Cl_2 pressure change. The calculated results, the solid lines in Fig. 4, were found to be in good accordance with the experimental data. These results strongly support the proposed reaction scheme for the hydrodechlorination of CF_2Cl_2. The formation of major products, CH_2F_2 and CH_4, can be explained and estimated by the hydrogenation of intermediate species, CF_{2*}^*, rather than the consecutive scheme of

$$CF_2Cl_2 \rightarrow CHF_2Cl \rightarrow CH_2F_2 \rightarrow CH_3 \rightarrow CH_4$$
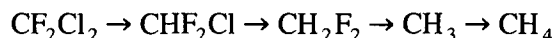
As shown in Fig. 8, CF_{2*}^* reacts with H* and 2H* to form CH_2F_2, CHF_2^*, CHF_*^* and CH_{2*}^* by paths 4–7. Since the reactions of H* and 2H* with CF_{2*}^* have the rates of the same order of magnitude, and CHF_2^* produces CH_2F_2 by path 9 as well as CHF_*^* by path 10, it was difficult to estimate the CH_2F_2/CH_4 product ratio.

4. Conclusion

The major products of CF_2Cl_2 hydrodechlorination reaction was found to be CH_2F_2 and CH_4. The competitive behaviours between CF_2Cl_2 and H$_2$ during the reaction was confirmed from the experimental results and adsorption characteristics. In predicting the adsorption behaviour of CF_2Cl_2 on Pd surface, the model for dissociative adsorption with the formation of CF_2Cl^* and CF_{2*}^* was found to be superior to the model for physical adsorption. The formation of the products could be explained by the direct hydrogenation of intermediate species, CF_{2*}^*, rather than by the consecutive scheme of

$$CF_2Cl_2 \rightarrow CHF_2Cl \rightarrow CH_2F_2 \rightarrow CH_3 \rightarrow CH_4$$
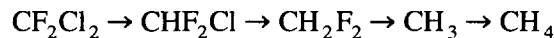
A reaction scheme for the CF_2Cl_2 hydrodechlorination was proposed and the overall reaction rate expression derived from the scheme was confirmed experimentally to describe the reaction well.

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