Korean J. of Chem. Eng., 13(1), 75-81 (1996)

SYNTHESIS OF HFC-134a BY ISOMERIZATION AND HYDROGENATION

Dong Jin Suh, Tae-Jin Park†, Byung-Gwon Lee* and Kun-You Park*

Division of Chemical Engineering, *Division of Environmental & CFC Technology,
Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, Korea

(Received 5 July 1995 • accepted 6 September 1995)

Abstract—For the preparation of HFC-134a, the isomerization of CFC-114 and the hydrogenation of CFC-114a were investigated. Both reactions were catalyzed by $AlCl_3$ and supported Pd catalysts, respectively. For the comparison purpose, the isomerization of CFC-113 was carried out also. With virgin $AlCl_3$ catalyst, both isomerization reactions proceeded after a certain induction period probably because the catalyst needed the activation by the halogen exchange. The catalyst deactivated gradually with the time on stream. However, the deactivation rate could be reduced by removing impurities from the reactants. Isomerization rate of CFC-114 was much slower than that of CFC-113. Palladium supported on carbon catalyzed the hydrogenation reaction quite selectively while the selectivity declined when the support was replaced with different supports. The catalytic activity and selectivity to desired products increased in the following order. Pd/kieselguhr<Pd/silica-alumina≅Pd/silica gel<Pd/TiO_2<Pd/Al_2O_3<Pd/C

Key words: HFC-134a, Isomerization, Hydrogenation, $AlCl_3$, Pd Catalysts

INTRODUCTION

Chlorofluorocarbons (CFCs) have been widely used throughout the world as refrigerants, blowing agents, cleaning solvents, and aerosol propellants. Ironically, the high stability and inertness of CFCs, which make them so valuable, have led to their downfall. Once released at ground level into the atmosphere, they rise slowly into the stratosphere, where they are degraded by high-energy radiation from the sun and release chlorine-containing free radicals that trigger a catalytic ozone depletion cycle. Following detailed, though not definitive studies, agreement was reached on a major global environmental treaty, the Montreal Protocol, to phase out CFC production by the turn of the century. A race by all CFC producers then began to find suitable and environmentally acceptable substitutes. The strategy is to reduce its atmospheric lifetime by introducing hydrogen into the molecule so that it is removed from the atmosphere by reaction with hydroxyl radicals in the stratosphere.

Of particular interest to the refrigerant industry is 1,1,1,2-tetrafluoroethane (HFC-134a), which can be obtained by vapor phase catalytic fluorination of trichloroethylene using anhydrous hydrogen fluoride [Firth and Foll, 1973]. Also it is known that HFC-134a can be derived from the intermediate 1,2,2,2-tetrafluorodichloroethane (CFC-114a) by catalytic hydrogenation [Gervasutti et al., 1981; Kim et al., 1993]. This intermediate is, in turn, the isomer of the more readily obtainable 1,1,2,2-tetrafluoro-1,2-dichloroethane (CFC-114). The isomerization of such chlorofluoroethanes by treatment with aluminum trihalide is well documented in the art [Zawalski, 1990].

The purpose of this investigation is to develop an improved process for producing HFC-134a by the isomerization of CFC-114, followed by hydrogenation. An attempt has been made to suggest optimum reaction conditions for obtaining high yield to the desired products. In the present work, prior to relatively difficult CFC-114 isomerization, the CFC-113 isomerization experiment was also carried out in the presence of an activated aluminum chloride catalyst in order to investigate the general characteristics of chlorofluorocarbons isomerization.

EXPERIMENTAL

1. Isomerization of CFC-113

CFC-113 isomerization experiments have been carried out in a 500 ml three neck flask, equipped with a reflux condenser, a thermowell, and a sampling tube that permits periodical withdrawal of condensed samples. The flask was charged with 300 ml (468 g) of CFC-113, anhydrous aluminum trichloride, and if necessary, chromium and manganese powder. With vigorous agitation by using a hot plate stirrer, the flask was brought to reflux for 8 hours. The reaction mixture was then cooled to room temperature for 1 hour, and agitation was stopped for 10 hours to allow settling of the catalyst particles. Crude isomerized product was then carefully siphoned off leaving the active catalyst heel in the bottom of the flask. The subsequent reaction cycles were repeated by adding approximately equivalent amount of fresh CFC-113. The condensed reaction mixture which was diluted with methanol was injected into a gas chromatograph equipped with a thermal conductivity detector (TCD) for the analysis. CFCs were separated in a 10 ft.×1/8 in.-O.D. SP alloy column packed with 60/80 Carbopack B/5% Fluorocol (Supelco Cat. No. 1-2425). Helium at 28 ml/min was used as carrier gas. The temperature of the column was kept at 80℃ for 25 min, programmed from 80℃ to 130℃ at 5℃/min, and finally held at 130℃ for 5 min.

2. Isomerization of CFC-114

As shown in Fig. 1, the reaction system consisted of a 12 ounce Fisher bottle for the low temperature experiments below 80℃ and a 300 ml autoclave for high temperature runs. The reactors were charged with anhydrous aluminum trichloride, chromium and manganese powders. After the reactor being sealed and eva-

---

† To whom correspondence should be addressed.

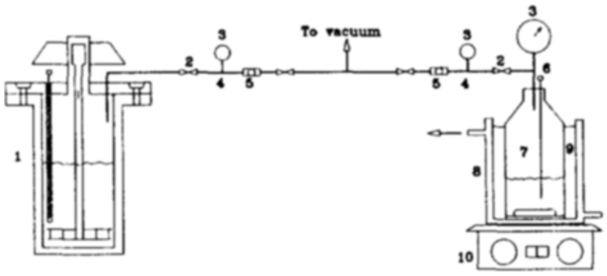

Fig. 1. Schematic diagram of CFC-114 isomerization apparatus.

1. Autoclave
2. Sampling valve
3. Pressure gauge
4. Sampling tube
5. Sampling port (septum)
6. Thermowell
7. Fischer bottle
8. Constant temperature circulator
9. Silicone oil
10. Magnetic stirrer

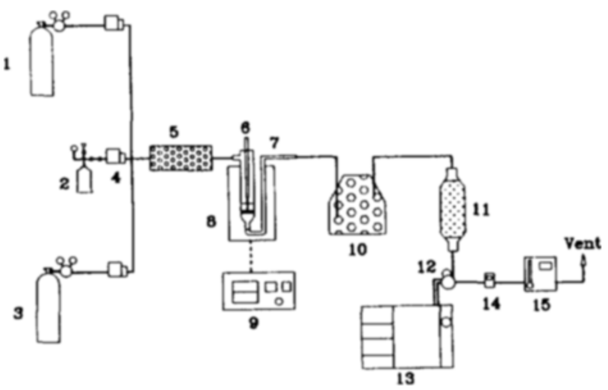

Fig. 2. Schematic diagram of CFC-114a hydrogenation apparatus.

1. Hydrogen
2. CFC-114/114a
3. Nitrogen
4. Mass flow controller
5. Gas mixer
6. Thermowell
7. Reactor
8. Furnace
9. Temperature programmer
10. Alkali scrubber
11. Dryer
12. 6-port switching valve
13. Gas chromatograph
14. Mass flow meter
15. Bubble flow meter

cuated slowly, 100 ml (145 g) of CFC-114 (originally containing 7.4% of CFC-114a) was quickly charged. Agitation was begun and the reactor was heated up to the reaction temperature. The reaction mixture could be taken through the evacuated sampling tube. The crude product was withdrawn from the reactor to blank Fisher bottle cooled by dry ice, and then the catalytic heel was separated from the product mixture. Subsequent experiments were performed with thus-obtained active catalyst heel and freshly supplied CFC-114 reactant. The crude product was purified by distillation and recrystallization. The vapor composition was periodically analyzed by a gas chromatograph as described above. The temperature of the column was kept at 40℃ for 20 min, programmed to 90℃ at 5℃/min, and finally held at 90℃ for 10 min.

3. Hydrogenation of CFC-114a

0.8% Palladium on charcoal extrudate (type 47, 0.8R86) obtained from Johnson Matthey was ground, sieved, and a fraction of 120-200 mesh was used as a reference catalyst. A typical reactant was an isomeric mixture of CFC-114 and CFC-114a at 61.3 : 38.7 mole ratio. Hydrogenation experiments were carried out at atmospheric pressure by using a conventional continuous flow reaction apparatus as shown in Fig. 2. The reactor consisted of a U-shaped Pyrex glass tube equipped with a glass axial thermocouple well and catalyst samples were held in place by quartz wool. The product stream was scrubbed with 10% NaOH aqueous solution to remove hydrogen halides, and dried with $CaCl_2$. Prior to hydrogenation test, the catalyst bed was heated up to 120℃ in 30 min and held at this temperature for an hour under a H_2 flow of 15 cc/min. After heating to the desired reaction temperature (normally 200℃), a mixture of CFC-114a (2 cc/min) and H_2 (6 cc/min) was fed to the reactor through mass flow controllers. Analysis of the reaction product was done by an on-line gas chromatograph with a thermal conductivity detector (TCD) equipped with a 20 ft. Carbopack B/Fluorocol column whose temperature was kept at 40℃ for 10 min, programmed to 70℃ at 5℃/min, and kept at this final temperature for 5 min.

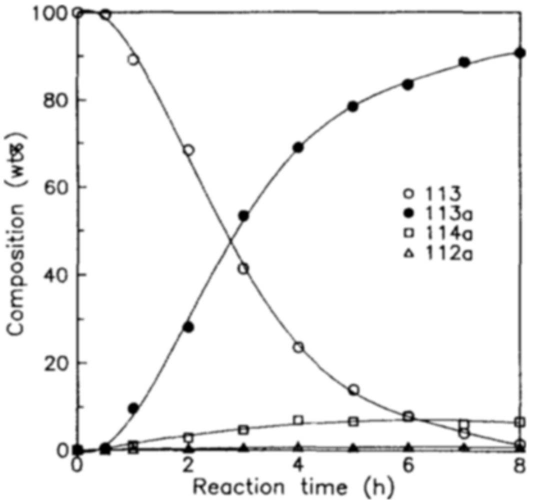

Fig. 3. Reaction profile of the first batch of CFC-113 isomerization. (CFC-113/$AlCl_3$=30; $AlCl_3$/Cr, Mn=600; molecular sieve 5A treated CFC-113).

RESULTS AND DISCUSSION

1. Isomerization

1-1. Catalyst Activation

In the first batch of CFC-113 isomerization, the reaction appeared to proceed after an induction period of about 30 minutes as shown in Fig. 3. This phenomenon was observed only in the first batch with fresh catalysts. During this induction period, the aluminum trihalide catalyst which can be expressed by the formula $AlCl_{3-x}F_x$ may be generated by the halogen exchange reaction between $AlCl_3$ and CFC-113. This is evidenced by the fact that the halogen exchanged product, CFC-112a, was produced significantly only in the first batch, as shown in Table 1. That is, taking into account the relative proportions of the two by-products, the major route to the CFC-112a formed in the first batch was not the disproportionation reaction but the catalyst activation. As shown in Fig. 4, similar behavior was observed for CFC-114 isomerization experiments. During the catalyst activation step, CFC-113a was formed by the transfer of Cl from the catalyst surface to the reactants and vice versa for F. However, such activation normally required more than 1 hour due to relatively slow rate

Table 1. Results of CFC-113 isomerization experiments*

Batch no.	Reaction time (h)	Product composition (wt %)			
		113	113a	114a	112a
1	7.5	0.33	89.20	0.39	10.08
2	4.0	-	96.62	1.18	2.20
3	1.0	-	96.33	1.93	1.75
4	1.25	-	96.49	1.85	1.66
5	2.67	-	96.63	1.68	1.69
6	2.5	-	96.40	1.91	1.69
7	2.0	-	96.30	1.76	1.94
8	2.0	-	96.15	1.89	1.96
9	2.0	-	96.95	1.57	1.49
10	5.0	-	96.25	1.57	2.18
11	4.0	-	95.79	1.67	2.54
12	7.0	-	96.00	1.23	2.77
13	8.0	0.24	95.48	1.10	3.19
14	8.0	3.35	92.30	1.18	3.17

*Molecular sieve treated CFC-113; CFC-113/AlCl$_3$=3.0.

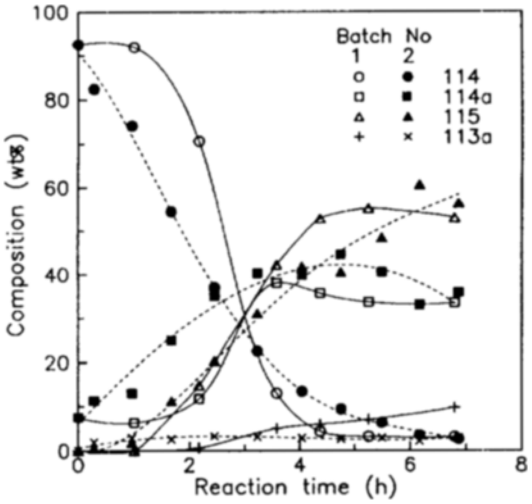

Fig. 4. Reaction profile of CFC-114 isomerization at 120°C.
(CFC-114/AlCl$_3$=10; AlCl$_3$/Cr, Mn=200; molecular sieve 5A treated CFC-114).

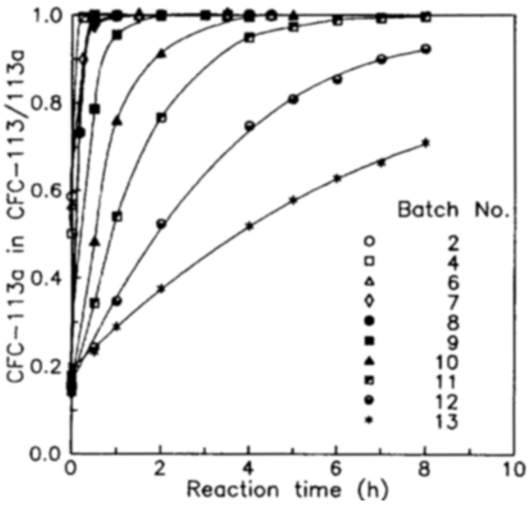

Fig. 5. Reaction profile of CFC-113 isomerization as a function of the batch number.
(CFC-113/AlCl$_3$=30; AlCl$_3$/Cr, Mn=600; molecular sieve 5A treated CFC-113)

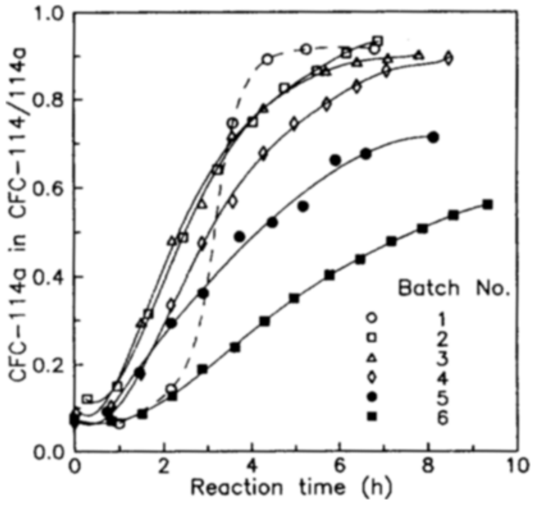

Fig. 6. Reaction profile of CFC-114 isomerization at 120°C as a function of the batch number.
(CFC-114/AlCl$_3$=10; AlCl$_3$/Cr, Mn=200; molecular sieve 5A treated CFC-114)

of halogen exchange.

1-2. Catalyst Lifetime Extension

Anhydrous aluminum trichloride fumes in air and has the strong odor of HCl from reaction with atmospheric moisture. It reacts vigorously with water to give HCl and catalytically inert alumina. Thus, the presence of even minute amount of moisture in the reactants may result in the loss of the active catalyst. To remove moisture and other possible contaminants, chlorofluorocarbon reactants were pretreated with molecular sieve 5A dried at 400℃ for 10 hours, and catalyst lifetime could be extended significantly.

It was reported that a metal promoter has a beneficial effect on the lifetime of the AlCl$_3$ catalyst [Zawalski, 1990]. The metal component could be selected from stainless steel, chromium, manganese, molybdenum, tungsten and combinations thereof. In our experiments, however, the presence of chromium and manganese powder was found to have very little influence on the normal lifetime of CFC isomerization catalysts. On the other hand, their presence reduced the initial deactivation rate. For instance, the time required to complete the isomerization using these metal promoters was found to be the same for a total of 8 batches whereas the isomerization acitivity of the activated catalyst without a metal promoter began to decline only after the 4th batch operation.

1-3. Characteristics of CFC Isomerization

Compared with CFC-113 isomerization (Fig. 5), the isomerization rate from CFC-114 to CFC-114a was quite slow, and the rate of catalyst deactivation was more pronounced (Fig. 6). In addition, the final product contained a minor portion of the nonisomerized CFC-114. It is economically impractical to separate CFC-114 from CFC-114a by distillation since the difference between the boiling points of the two isomers is only 0.6℃. Accordingly, it is presently

Table 2. Results of CFC-114 isomerization experiments*

Batch no.	Reaction time (h)	Product composition (wt %)					114a (%) in 114/114a
		114	114a	115	113a	12	
1	6.8	3.12	33.47	52.85	9.75	0.81	91.46
2	6.87	2.58	35.85	56.19	4.90	0.49	93.28
3	7.10	4.62	38.93	51.06	5.19	0.20	89.39
4	7.07	4.79	30.78	61.80	1.19	1.43	86.53
5	8.13	15.22	38.70	42.78	0.92	2.37	71.77
6	15.65	19.14	47.51	31.20	1.44	0.71	71.28

*Molecular sieve treated CFC-114; 120℃; CFC-114/$AlCl_3$=10; $AlCl_3$/Cr, Mn=200.

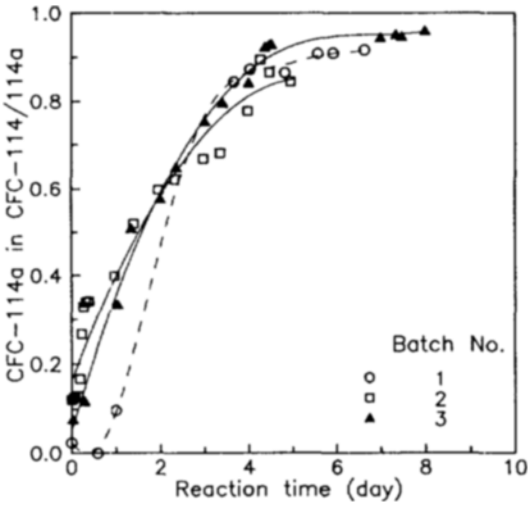

Fig. 7. Reaction profile of CFC-114 isomerization at low temperature.
(80℃ for the first batch, 70℃ for the 2nd and 3rd batches; CFC-114/$AlCl_3$=10; $AlCl_3$/Cr, Mn=200; molecular sieve 5A treated CFC-114)

difficult to obtain a high purity product of CFC-114a substantially free of CFC-114 by this method.

From the study of the behavior of CFC-113 in the isomerization and disproportionation, it was found that the isomerization rate from CFC-113 to CFC-113a was much higher than the disproportionation rate to CFC-112a and CFC-114a. On the other hand, as shown in Table 2, the disproportionation of CFC-114 to CFC-113a and CFC-115 was quit significant under the reaction conditions employed. The CFC-114a product could not be obtained without undesirably high levels of CFC-113a and CFC-115. The selectivity to CFC-114a was improved to some extent by decreasing the reaction temperature, but the reaction rate decreased drastically. For example, Fig. 7, in comparison with Fig. 6, indicates that the reaction rate decreased roughly by 20 times when the temperature was reduced from 120℃ to 70℃.

As mentioned before, the catalyst activation via halogen exchange in CFC-113 occurred more readily than that in CFC-114. However, an attempt to activate the catalyst by employing CFC-113 in place of CFC-114 led to no detectable change in the characteristics of the subsequent isomerization of CFC-114.

2. Hydrogenation

According to the experimental results of the aforementioned isomerization process, it is inevitable that obtained CFC-114a contains considerable amount of unreacted CFC-114. However, fortunately, HFC-134a can be prepared by selective hydrogenation of

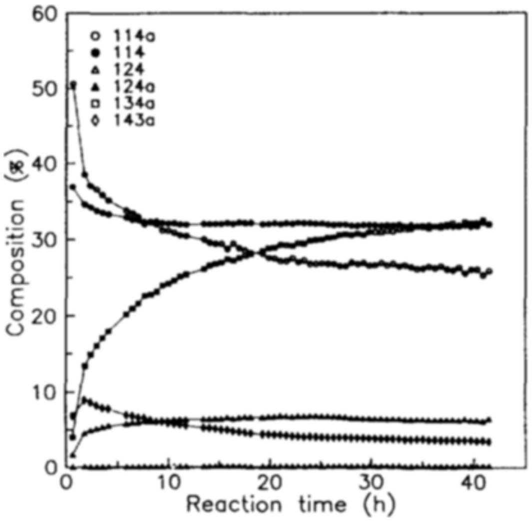

Fig. 8. Product composition of CFC-114/114a hydrogenation.
(0.8% Pd/C, 0.5g; 200℃; H_2/CFC=3; H_2 flow rate, 6 cc/min)

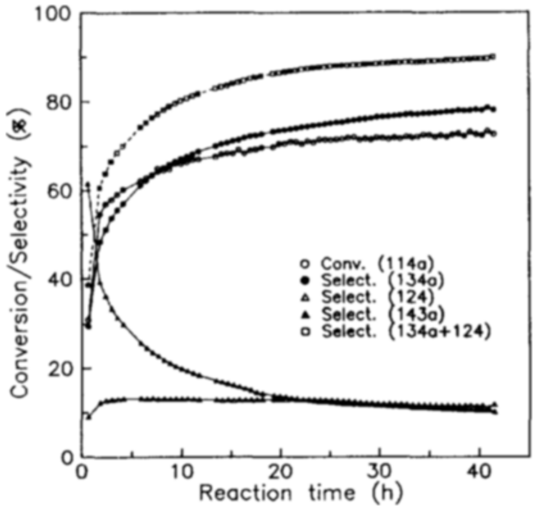

Fig. 9. Conversion and product selectivity of CFC-114/114a hydrogenation at 200°C.
(0.8% Pd/C, 0.5 g; H_2/CFC=3; H_2 flow rate, 6 cc/min)

CFC-114a over a hydrogenation catalyst such as palladium supported on carbon even though CFC-114 coexists with the starting CFC-114a since the reactivity of CFC-114 is quite low. The reaction product in the presence of supported palladium catalysts at a temperature lower than 250℃ included HCFC-124, HCFC-124a, HFC-134a, HFC-143a, and less than 0.5% of other by-products. Only by using highly active catalysts, HFC-143 began to be observed at temperatures higher than 250℃, but its content was normally less than 0.1%. Thus the overall hydrogenation pathway in the operating range can be described as the following sequence:

$CF_3CCl_2F \rightarrow CF_3CHClF \rightarrow CF_3CH_2F \rightarrow CF_3CH_3$
(CFC-114a) (HCFC-124) (HFC-134a) (HFC-143a)

$CClF_2CClF_2 \rightarrow CHF_2CClF_2 \cdots CHF_2CHF_2$
(CFC-114) (HCFC-124a) (HFC-134)

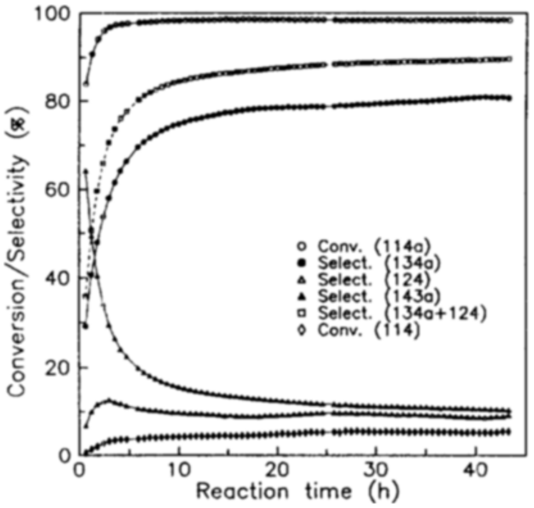

Fig. 10. Conversion and product selectivity of CFC-114/114a hydrogenation at 250°C.
(0.8% Pd/C, 0.5 g; H_2/CFC=3; H_2 flow rate, 6 cc/min)

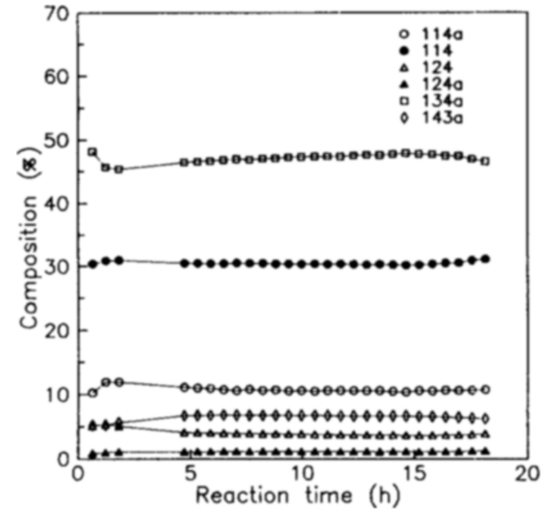

Fig. 11. Product composition of CFC-114/114a hydrogenation over 5% Pd/C at 200°C.
(5.0% Pd/C, 0.08 g; H_2/CFC=3; H_2 flow rate, 6 cc/min)

2-1. Catalyst Aging

Typical results with 0.8% Pd/C catalyst at 200°C are presented in Fig. 8 and Fig. 9. There was considerable aging in the first 20 hours of reaction. While CFC-114a conversion and HFC-134a selectivity increased with time on stream, the unwanted HFC-143a decreased almost continuously. The HCFC-124 yield showed some initial growth, but generally it was not influenced by aging. Less than 0.2% of HCFC-124a was obtained by only monohydrogenation from CFC-114 at very low conversion levels.

Since the metal catalyst in a reduced form is pyrophoric, it is generally supplied in a stabilized form to make it possible to utilize and handle in the air. Therefore the overall increase of catalyst activity with aging may be explained by reduction of the catalyst to catalytically active metallic state by contacting with excess hydrogen during the reaction. This explanation can be confirmed by comparing the data in Fig. 9 and Fig. 10. Although general trends of the aging phenomenon were not changed at 250°C, the transient period was getting shorter due to enhanced reduction rate.

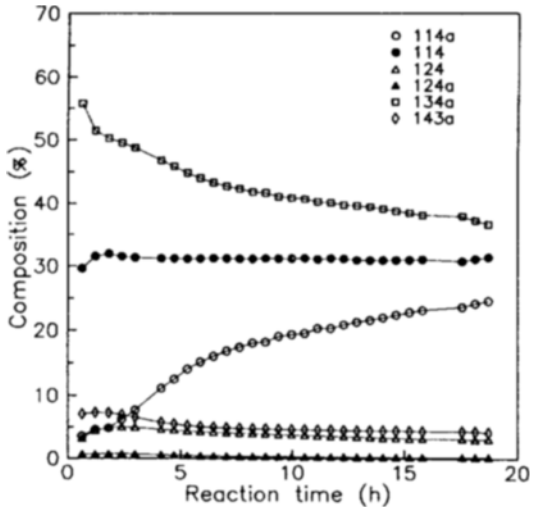

Fig. 12. Product composition of CFC-114/114a hydrogenation over 5% Pd/Al_2O_3 at 200°C.
(5.0% Pd/Al_2O_3, 0.08 g; H_2/CFC=3; H_2 flow rate, 6 cc/min)

Obviously it is easier to reduce the catalyst when the metal loading is high. By using the same metallic amount of 5% Pd/C supplied from Engelhard, the effect of metal loading on aging was studied. Fig. 11 shows, for the high metal loading catalyst, there was no remarkable characteristic change in the product distribution with time on stream. This observation indicates that the catalyst was fully reduced during pretreatment even under mild conditions, and no further reduction occurred thereafter.

Clear differences in aging phenomena were found between carbon supported catalysts and alumina based one as can be seen in Fig. 12. With 5% Pd/Al_2O_3 obtained from Engelhard, both the overall conversion and HFC-134a selectivity decreased continuously with time. This apparent deactivation for Pd/Al_2O_3 cannot be attributed to sintering because the sintering was found to be much more extensive on carbon supports than on alumina [Suh et al., 1994]. The following characteristics of alumina may be involved in the catalyst deactivation. In contrast to catalytically inert carbon supports, the alumina support is capable of facilitating the formation of the organic compounds which contaminate the catalytic surface by inducing undesirable secondary reactions. In addition, alumina may be attacked by acidic gases such as HF and HCl produced, which in turn causes a significant loss of their surface area. From this point of view, carbon would be a suitable support for CFC hydrogenation catalysts.

2-2. Support Effects

Catalytic activity for CFC-114a hydrogenation over supported Pd appeared to be markedly affected by the support used. The results of the reaction for 5% Pd catalysts on various supports and the corresponding Pd dispersions and specific surface areas are listed in Table 3. On the general basis of the conversion-selectivity correlations, the catalytic activity and selectivity to desired products increased in the following order.

Pd/kieselguhr<Pd/silica-alumina≃Pd/silica gel<Pd/TiO_2<Pd/Al_2O_3<Pd/C

Table 3. CFC-114a hydrogenation characteristics and properties of 5% Pd catalysts on various supports*

Support	Disp.[a] (%)	Surf. area (m^2/g)	150℃ Conv.[b]	150℃ Sel.[c]	200℃ Conv.[b]	200℃ Sel.[c]	250℃ Conv.[b]	250℃ Sel.[c]
Carbon	28.0	1000	53.0	94.5	93.5	90.7	99.4	86.1
Al_2O_3	42.1	210	26.2	89.5	64.0	88.6	87.9	88.1
Silica gel	16.1	300	4.1	80.1	26.3	64.6	55.6	58.7
Silica-alumina	19.0	410	4.1	79.9	27.6	63.3	48.5	65.0
TiO_2	26.8	50	11.0	77.4	44.6	68.4	65.0	74.7
Kieselguhr	17.1	16	4.0	63.4	19.5	52.5	45.7	43.8

*H_2/CFC=3; H_2 flow rate, 6 cc/min; catalyst charge, 0.1 g; time on stream, 10h

[a] Dispersion measured by oxygen-hydrogen titration cycles [5]

[b] Conversion of CFC-114a (%)

[c] Selectivity of HCFC-124+HFC-134a (%)

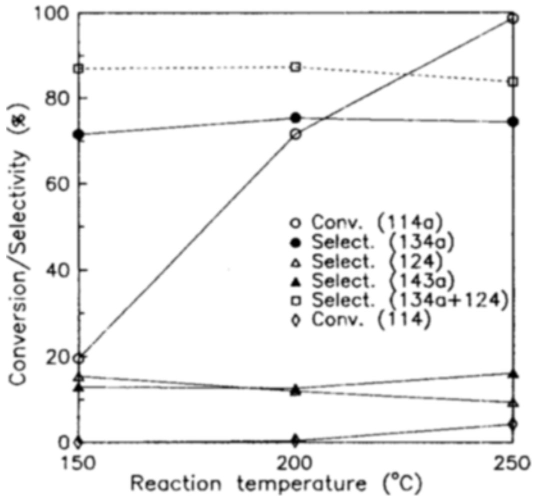

Fig. 13. Effect of reaction temperature on conversion and selectivity of CFC-114/114a hydrogenation.
(0.8% Pd/C, 0.5 g; H_2/CFC=3; H_2 flow rate, 6 cc/min; after 10 h)

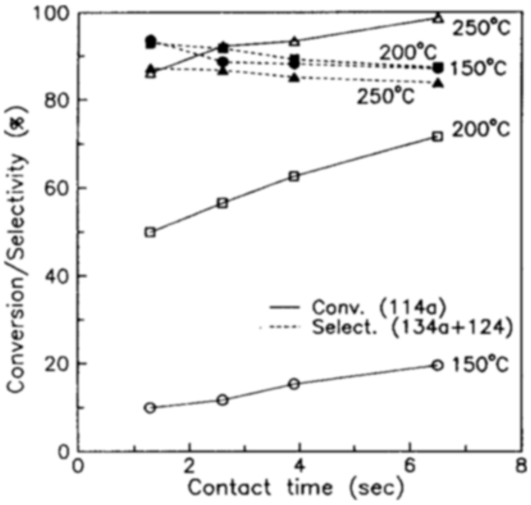

Fig. 14. Effect of contact time on conversion and selectivity of CFC-114/114a hydrogenation.
(0.8% Pd/C; H_2/CFC=3; H_2 flow rate, 6 cc/min; after 10 h)

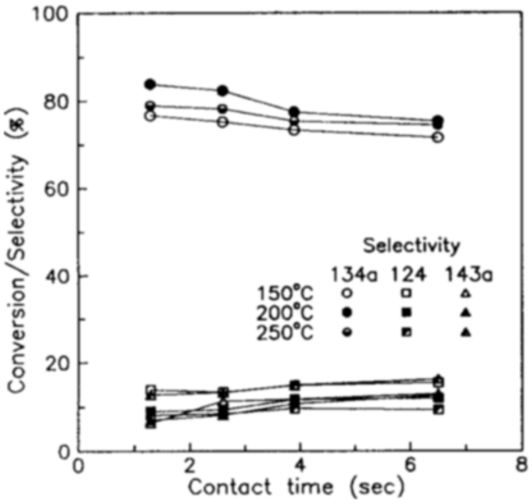

Fig. 15. Effect of contact time on selectivity of CFC-114/114a hydrogenation.
(0.8% Pd/C; H_2/CFC=3; H_2 flow rate, 6 cc/min; after 10 h)

This order may be explained by active metal surface area expressed as Pd dispersion, and the chemical resistance to acidic products such as HF and HCl. Except for the carbon supported catalyst, our results are similar to the ones reported by Kim et al. [1993]. The disagreement on the carbon supported catalysts may be due to the different carbon supports and pretreatment conditions. Under our moderate reaction and treatment conditions, the sintering effect may be insignificant. As pointed out for alumina supported Pd catalyst earlier, similar results have been obtained for the catalyst deactivation by using other conventional supports other than carbon. Relatively faster deactivation was observed during the first 3 hours. In addition, over such catalysts, the formation of side-products was more pronounced at the temperatures above 200℃. Particularly, Pd supported on kieselguhr with the lowest catalytic activity showed the lowest selectivity to desired products. Such unique characteristics are attributed to the fact that kieselguhr contains some mineral substances which can promote undesirable chemical reactions.

2-3. Effects of Reaction Parameters

The influences of temperature, contact time, and H_2/CFC ratio were presented in Fig. 13-16. While the maximum selectivity to HFC-134a was observed at about 200℃, the selectivity to HCFC-124 decreased with increasing the reaction temperature. In the operating range examined, the maximum selectivity to these two desired products was obtained at 200℃. However, compared with

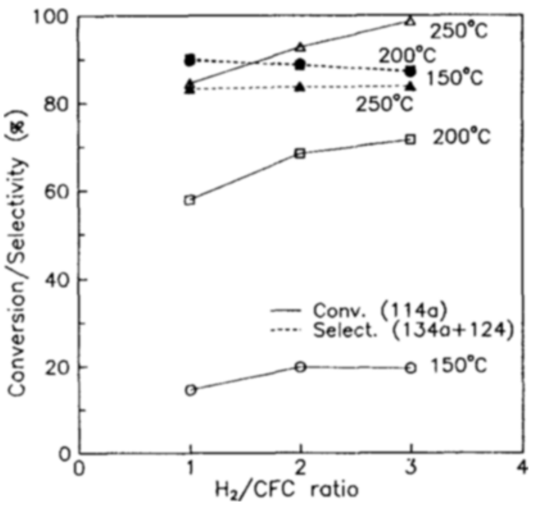

Fig. 16. Effect of H_2/CFC ratio on conversion and selectivity of CFC-114/114a hydrogenation.

(0.8% Pd/C, 0.5 g; total flow rate, 8 cc/min; after 10 h)

CFC-114a, conversion and the selectivity to each product were not appreciably affected by the reaction parameters. For temperatures above 200℃, the hydrogenation of CFC-114 to HCFC-124a began to occur to some extent. As shown in Fig. 16, the conversion of CFC-114a increased with increasing H_2/CFC molar ratio up to 2, the stoichiometric value for obtaining HFC-134a, and no further increase was observed. According to this result, it is suggested to use 2 moles of hydrogen per mol of CFC-114/114a for economic viewpoint.

It was found that the catalytic activity of Pd/C depended to some extent on the pretreatment process used. Since Pd/C catalysts are prone to sinter under elevated temperatures in the hydrogen atmosphere [Chang et al., 1985; Pope et al., 1971], the pretreatment temperature should not exceed 400℃. When supported on activated carbons with mineral impurities which can be catalyst poisons or promote undesirable reactions, the temperature should be much lower.

CONCLUSIONS

For the isomerization reactions of CFC-113 and CFC-114, $AlCl_3$ catalyst was quite active and selective, but the virgin catalyst required a certain period of activation. The experimental results indicate that the activation is through the exchange of chlorine with fluorine. To prevent the deactivation of the isomerization catalyst, the removal of impurities contained in the reactants was quite effective but the addition of metal components was not. Isomerization rate of CFC-114 was much slower than that of CFC-113 and the complete conversion appeared to be unobtainable.

Palladium catalysts supported on various supports were tested for the hydrogenation of CFC-114a. The catalytic activity and selectivity to desired products increased in the following order.

Pd/kieselguhr$<$Pd/silica-alumina$\cong$Pd/silica gel$<$Pd/$TiO_2$$<$Pd/$Al_2O_3$$<$Pd/C

Pd/C was quite selective catalyst for the production of HFC-134a while the other catalysts exhibited lower selectivity. The supports other than carbon appeared to catalyze side-reactions probably because of the support itself or impurities contained in the support.

NOMENCLATURE

CFC : chlorofluorocarbon
CFC-12 : dichlorodifluoromethane (CCl_2F_2)
CFC-112a : tetrachloro-1,1-difluoroethane (CCl_3CClF_2)
CFC-113 : 1,1,2-trichlorotrifluoroethane (CCl_2FCClF_2)
CFC-113a : 1,1,1-Trichlorotrifluoroethane (CCl_3CF_3)
CFC-114 : 1,2-dichlorotetrafluoroethane ($CClF_2CClF_2$)
CFC-114a : 1,1-dichlorotetrafluoroethane (CF_3CCl_2F)
CFC-115 : chloropentafluoroethane (CF_3CClF_2)
HCFC-124 : 2-chloro-1,1,1,2-tetrafluoroethane (CF_3CHClF)
HCFC-124a : 1-chloro-1,1,2,2-tetrafluoroethane (CHF_2CCl_2F)
HFC-134 : 1,1,2,2-tetrafluoroethane (CHF_2CHF_2)
HFC-134a : 1,1,1,2-tetrafluoroethane (CF_3CH_2F)
HFC-143 : 1,1,2-trifluoroethane (CHF_2CH_2F)
HFC-143a : 1,1,1-trifluoroethane (CF_3CH_3)

REFERENCES

Chang T.-C., Chen, J.-J. and Yeh, C.-T., "Temperature-Programmed Reduction and Temperature-Resolved Sorption Studies of Strong Metal-Support Interaction in Supported Palladium Catalysts", *J. Catal.*, **96**, 51 (1985).

Firth, R. A. and Foll, G. E., "Process for Producing Fluorinated Hydrocarbons", US Patent 3,755,477 (1973).

Gervasutti, C., Marangoni, L. and Marra, W. J., "Hydrogenolysis of Dichlorotetrafluoroethane Isomeric Mixtures for the Formation of 1,1,1,2-Tetrafluoroethane", *J. Fluorine Chem.*, **19**, 1 (1981).

Kim, D.-W., Ihm, S.-K., Park, K.-Y., Lee, B.-G., "Hydrogenation of CFC over Palladium Catalysts", *Hwahak Konghak*, **31**(6), 831 (1993).

Pope, D., Smith, W. L., Eastlake, M. J. and Moss, R. L., "The Structure and Activity of Supported Metal Catalysts VI. Measurement of Dispersion in Palladium-Charcoal Catalysts", *J. Catal.*, **22**, 72 (1971).

Suh, D. J., Park, T.-J. and Ihm, S.-K., "Hydrogen/Oxygen Titration Method for Measurement of Pd Dispersion on Supported Catalysts", *J. Catal.*, **149**, 486 (1994).

Zawalski, R. C., "Process for Preparing Chlorofluorocarbons via an in situ Generated Activated Aluminum Trichloride Catalyst and Products Resulting Therefrom", US Patent 4,925,993 (1990).