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Decomposition of Chlorofluorocarbons by the Reaction with Water Vapor Catalyzed by Iron Oxide Supported on Activated Carbon

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Chlorofluorocarbons such as $CClF_3$ and CCl_2FCClF_2 were readily decomposed by the reaction with water vapor at temperatures higher than 450 °C in the presence of iron oxide supported on activated carbon.

Decomposition of chlorofluorocarbons(CFCs) is a subject of increasing importance as concern for protecting the ozone layer surrounding the earthe. The decomposition is, in general, very difficult due to the extremely high stabilty of CFC molecules. Recently, special technique such as plasma-treatment and reduction with Na naphthalenide have been reported to be effective for the decomposition.[1)] However, for the practical disposal of a small amount of CFCs, a simpler and more convenient method is desired.

For the decomposition of CFCs, the reactions with water vapor look promising, since such reactions are thermodynamically possible as suggested by the ΔG^o value for the following example reaction.[2)]

$$CClF_3 + 2\ H_2O \longrightarrow CO_2 + HCl + 3\ HF \qquad \Delta G^o = -40.6\ \text{kcal/mol}$$

Hence, we tried to find an effective catalyst working under appropriate reaction conditions. In this study, $CClF_3$ was adopted as a primary CFC sample, since it is the most inactive owing th the exceedingly strong C-Cl and C-F bonds. CCl_2F_2 and CCl_2FCClF_2 were adopted as samples since they are widely used as a refrigerant and a solvent in semiconductor industry, respectively. For comparison, CF_4 was used as an another sample. All CFCs and CF_4 were reacted with water vapor diluted with He(molar ratio,CFC:H_2O:He=0.06:0.44:0.50) in a gas-phase flow system under atmospheric pressure in the temperature range 350 - 590 °C.

Reaction products, such as CO_2, CO, HCl, and HF, and unreacted CFC $^{3)}$ were analyzed by gas chromatography using a 3 m column of Porapak Q. A certain product, probably CX_3COX (X is Cl or F), which was obtained in the CCl_2FCClF_2 reaction in addition to the other products described above, was also analyzed by gas chromatography. Various metal oxides were used as catalysts in the form of granules (20-32 mesh). Except for some commercial products, most of the oxides were prepared by neutralization of a metal nitrate solution with 28% NH_3 water, followed by separation as metal hydroxides and heat-treatment in air at 600 °C for 3 h.

For selected metal oxides, catalytic activities were measured after being supporting on activated carbon (Kurarey Co., GC-1) by evaporation to dryness method. The supported oxides were dried at 120 °C overnight, and heat-treated in He at 600 °C for 30 min immediately before use as catalysts.

As shown in Table 1, some metal oxides were catalytically active for the CFC reaction with water vapor. In particular, iron oxide supported on activated carbon exhibited a high catalytic activity. This is contrasted to the fact that iron oxide alone was quite inactive as a catalyst. Furtheremore, activated carbon itself had little catalytic activity. Thus, the catalytic activity of iron oxide supported on activated carbon was attributable to highly dispersed iron oxide or some active compound formed by interaction between iron oxide and activated carbon. The catalytic activity of the supported iron oxide increased with an increase in iron oxide amount up to 3 wt% as Fe_2O_3 (Fig. 1). Then the activity gradually decreased while increasing the amount to more than 10 wt%. The decrease was ascribable to segregated iron oxide particles on the activated carbon.

The reaction of $CClF_3$ with water vapor over the supported iron oxide proceeded at temperatures higher than 450 °C, and the reactivity increased almost linearly with reaction temperature up to 570 °C as shown in Fig. 2. The reactivity was well maintained after a little decrease in the first 30 min of the run.

CCl_2F_2 and CCl_2FCClF_2 on the supported iron oxide catalyst reacted with water vapor at much lower temperatures as compared to the case of $CClF_3$ (Fig. 2). The higher reactivities of these CFCs were attributed to their weaker C-Cl and C-F bonds than those in $CClF_3$.$^{4)}$ In contrast to CCl_2F_2 and CCl_2FCClF_2, CF_4 hardly reacted with water vapor even at 590 °C. The inactivity was not explained merely by the strong C-F bond (bond energy= 123±2 kcal/mol$^{4)}$) of the molecule. The existence of C-Cl bond seems essential to the decomposition of CFC by the reaction with water vapor.

Table 1. Catalytic decomposition of $CClF_3$ with water vapor over various metal oxides[a)]

Catalyst	Conversion of $CClF_3$ to CO_2 and CO/mol%		
	Running time		
	15 min	60 min	120 min
Al_2O_3	45.4	43.5	42.7
SiO_2-Al_2O_3 (Al 80 atm%)	51.8	46.1	44.0
SiO_2-Al_2O_3 (Al 15 atm%)	28.4	17.4	15.4
H^+-M	13.6	5.9	4.1
Na^+-M	1.1	0	-
H^+-Y	8.1	4.7	-
Na^+-Y	1.8	1.1	-
Nb_2O_5	1.4	1.1	-
CaO	1.3	0	-
MgO	0	0	-
ZnO	0	-	-
Fe_2O_3	0	-	-
Cr_2O_3	0	-	-
ZrO_2	0	0	-
TiO_2	0	0	-
SiO_2	0	0	-
WO_3	0	-	-
3wt%Fe_2O_3/Carbon	96.4	87.2	82.2
3wt%Cr_2O_3/Carbon	24.0	23.3	21.5
3wt%Al_2O_3/Carbon	3.7	4.0	-
3wt%NiO/Carbon	24.4	25.5	25.1
3wt%CoO/Carbon	14.4	14.4	-
3wt%CuO/Carbon	43.1	36.6	29.5
Carbon (Activated carbon)	2.2	2.0	-

a) Reaction temperature: 570 °C; W/F: 37.3 or 24.3 $g.h.mol^{-1}$(for activated carbon and activated carbon-supported metal oxide).

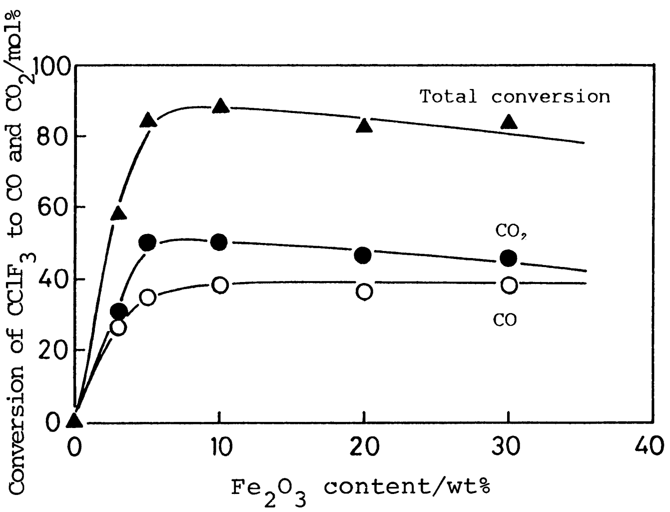

Fig. 1. Relationship between catalytic activity and Fe_2O_3 content in Fe_2O_3/Carbon.

Reaction temperature: 530 °C. Contact time: W/F=24.3 g.h.mol^{-1}

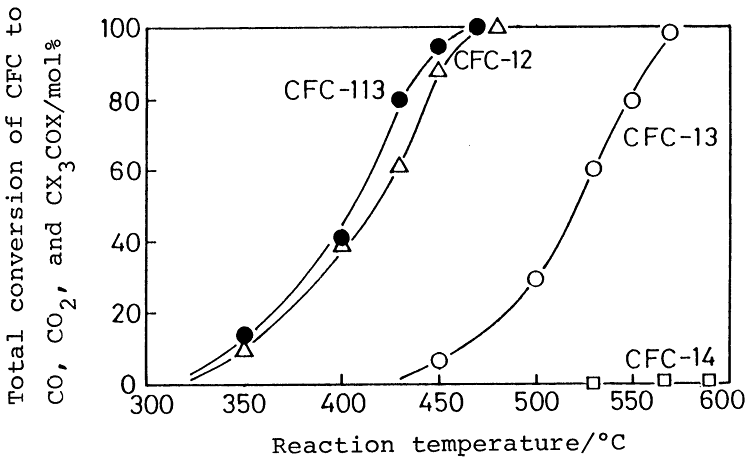

Fig.2. Catalytic decomposition of CFCs with water vapor over Fe_2O_3/carbon.

References

1) "Destruction Technologies of CFCs (Interim Report)," Ministry of International Trade and Industry of Japanese Government, April,1989.
2) The ΔG value was calculated using the data reported by K.A.Kobe and D.H.Kobe (Petroleum Refiner, 38, (12) 117(1959) (for $CClF_3$) and those listed in "CRC Handbook of Chemistry and Physics," 59th ed, ed by R.C.Weast, CRC Press, Florida(1979).
3) Halocompounds other than HF and HCl were not found in the products for halomethane reactions. Thus, more than 97% of the halogen components was recovered as HF, HCl, and unreacted CFC for the $CClF_3$ reaction shown in Fig. 1.
4) G.Glocker, J.Phys.Chem., 63, 828(1959); H.H.Semenov, "Some Problems of Chemical Kinetics and Reactivity," Translated by J.E.S.Bradley, Pergamon Press, New York(1958).

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