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Catalytic Decomposition of CFC-112 and CFC-113 in the Presence of Ethanol

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Iron (III) chloride supported on activated charcoal was extremely effective for decomposition of CFC-112 and CFC-113 into CO and CO_2 in the presence of ethanol at the the low temperature.

The decomposition of chlorofluorocarbons (CFCs) under various reaction conditions has been discussed in recent review.[1)] These reactions were conducted under fairly severe conditions.

In this letter, we report that CFCs such as CFC-112 (CCl_2F-CCl_2F) and CFC-113 (CCl_2F-$CClF_2$) were readily decomposed into CO and CO_2 in the presence of ethanol with iron (III) chloride catalyst supported on activated charcoal. Twenty grams of activated charcoal (Wako Pure Chemical Ind.) were soaked in the 100 ml aqueous solution of iron(III) chloride (4.06 g, 0.025 mol) and the solution was evaporated to dryness in oven under the atmospheric pressure. The activated charcoal was cylindrical in form, 7 mm in length and 4 mm in diameter, with a surface area of 1340 m^2g^{-1}. The reaction was carried out with a flow type system.[2)] The reactor was made of stainless steel with 40.0 cm in length and 2.0 cm in diameter. The catalyst was placed in the reactor. The reactor was heated in a vertical electric furnace. CFCs were mixed with ethanol in molar ratio of 1 : 4. The mixed solution was fed into evaporator by using a microfeeder at a rate of 10 ml/h and was preheated to

150 ^{o}C. The mixed gas evaporated through it was passed to the reactor. The quantitative analysis of the reaction products were performed with gas chromatography (Porapak Q, active carbon). Samples were collected from the gaseous and condensed effluents which were passed to the reactor three to four hours after the reaction started.

Shown in Table 1 are the product compositions for the catalytic decomposition of CFC-112 in the presence of ethanol with iron(III) chloride catalyst supported on activated charcoal at various temperatures.

Table 1. Catalytic decomposition of CFC-112 at various temperatures

Temp	Products / Fed CFC-112 × 100 (mol/mol)				
^{o}C	CO	CO_2	$C_2F_2Cl_2$	$CHFClCFCl_2$	$CFCl_2CFCl_2$[a]
150	1.0	7.0	-	3.4	92.6
175	2.0	12.8	20.1	10.2	62.3
200	7.0	26.2	32.3	4.3	46.8
230	6.0	36.0	39.4	2.8	36.8
265	34.0	107.2	27.9	-	1.5

a) Unreacted CFC-112.

CFC-112 was decomposed over the catalyst into CO and CO_2, accompanied with dechlorination and substitution. A fraction of ethanol was converted into acetaldehyde and ethyl acetate, while a large portion of ethanol was changed into ethyl chloride, diethyl ether and ethylene. Needless to say, CFCs stayed unchanged in the absence of the catalyst. Figure 1 shows the catalytic activity for the decomposition of CFC-112 in the presence of ethanol with the passage of time. It can be seen from Fig. 1 that the conversion of CFC-112 gradually decreased at the initial period in the reaction but was almost constant after that.

On the other hand, the ethanol only was passed over the catalyst in order to confirm the catalytic effects of iron (III) chloride at 250 ^{o}C. Ethyl chloride was formed from ethanol by the reaction with iron (III) chloride followed by trace formation of CO and CO_2. However, in this case, the formation of ethyl chloride was rapidly decreased with the

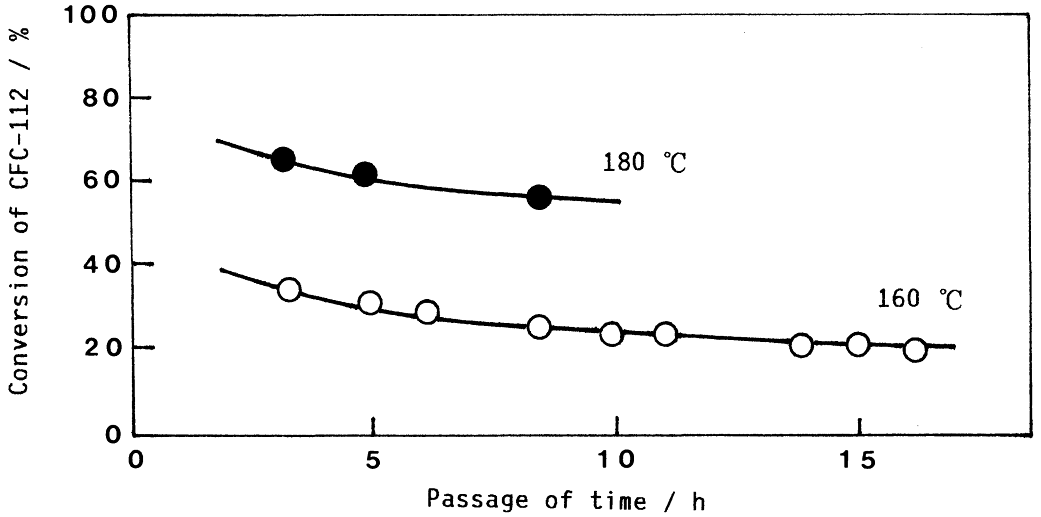

Fig. 1. The effect of the reaction time on the conversion of CFC-112.

passage of time. From these results, it could be anticipated that the durability of catalytic activity are continued for a long time with some improvements of the catalyst. Similarly, Table 2 shows the product composition of CFC-113 in the presence of ethanol. As can be seen from the table, CFC-113 was almost completely decomposed into CO and CO_2 at about 300 ^oC.

Figure 2 shows the relationship between the ratio of the amount of

Table 2. Catalytic decomposition of CFC-113 at various temperatures

Temp	Products / Fed CFC-113 × 100 (mol/mol)					
^oC	CO	CO_2	C_2F_3Cl	$C_2F_2Cl_2$	$CHFClCF_2Cl$	$CF_2ClCFCl_2$[a)]
140	3.6	14.6	-	-	6.4	84.5
190	11.0	38.2	-	-	6.1	69.3
200	9.8	44.8	0.4	-	3.0	69.3
240	10.2	40.8	1.4	1.1	18.8	53.2
250	19.0	74.8	1.4	0.4	13.0	38.3
280	33.6	105.8	1.4	-	18.4	10.5
290	35.0	121.8	0.6	-	15.3	5.7

a)Unreacted CFC-113.

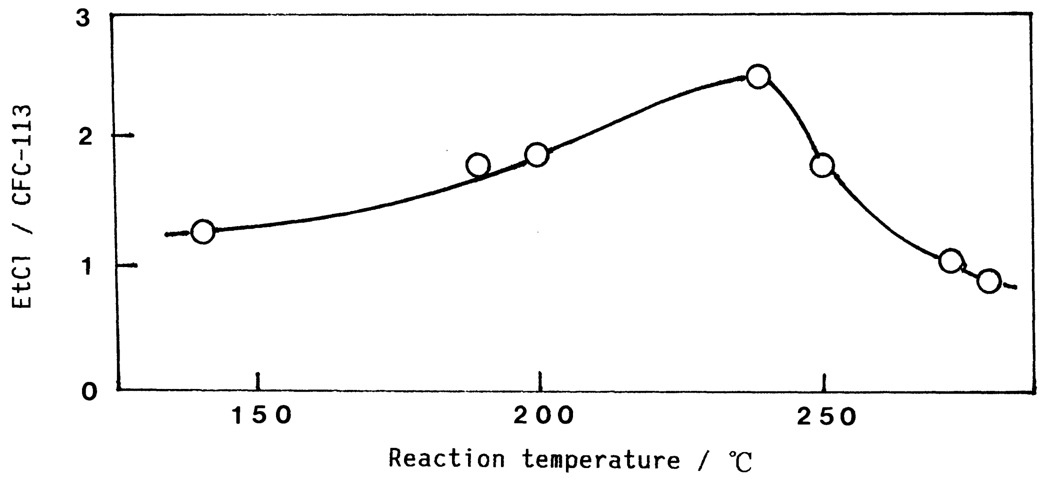

Fig. 2. The effect of the reaction temperature on the formation of ethyl chloride.

ethyl chloride formed to that of CFC-113 decomposed and the reaction temperature. If chlorines of CFC-113 were converted to the form of EtCl, the theoretical value of EtCl/CFC-113 would be 3.0. The ratio of EtCl/CFC-113 has a peak point at about 240 °C. It can be seen from fig. 2 that the chlorines freed from the decomposition of CFC-113 were almost recovered as those of EtCl at about 240 °C. The remainder of the chlorines were quantitatively recovered as hydrogen chloride.

These reaction equations can be written as follows.

$$CClF_2CCl_2F = CF_2CFCl + Cl_2 \quad (1)$$

$$CClF_2CCl_2F + CH_3CH_2OH = CClF_2CHClF + CH_3CHO + HCl \quad (2)$$

$$CClF_2CCl_2F + CH_3CH_2OH \longrightarrow CO + CO_2 + CH_3CH_2Cl + HF \quad (3)$$

Reactions 1 and 2 proceeded smoothly at low temperature, whereas reaction 3 was favorable at higher temperature. Hydrogen fluoride reacted immediately with reactor wall into various metal fluorides.

References

1) K. Mizuno, Kagaku, 45, 86 (1990).

2) K. Shinoda and K. Yasuda, Bull. Chem. Soc. Jpn., 58, 3082 (1985).

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