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DISPROPORTIONATION OF CF_3Cl CATALYZED BY $Al_2O_3 \cdot Cr_2O_3$

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A mixed oxide of Al_2O_3 and Cr_2O_3 ($Al_2O_3 \cdot Cr_2O_3$) showed catalytic activity higher than that of Al_2O_3 or Cr_2O_3 in the disproportionation of CF_3Cl. Maximum conversion ($>$30 %) was obtained when the reaction was carried out over the mixed oxide (atomic ratio of Cr/Al : 1/9) at 450°C.

Disproportonation of chlorofluorohydrocarbons is an important route for the preparation of various types of chlorofluorocarbon products.$^{1)}$ In general, the disproportionation reactivity of chlorofluorohydrocarbon decreases with an increase in the number of fluorine atoms bound to one carbon atom.$^{2)}$ Therefore, disproportionation of CF_3Cl designated by the following equation

$$2\ CF_3Cl \longrightarrow CF_2Cl_2 + CF_4 \qquad (1)$$

is difficult to achieve. And studies relating to the disproportionation of CF_3Cl are not found in the literature except for by-product formation of a small amount of CF_4 reported in some patents.$^{3)}$ Recently, since CF_4 has been widely employed as an effective etching agent in the LSI industry, a new and more advantageous process for its preparation is desirable.

It is already known that disproportionations of $CFCl_3$$^{4)}$ and $CF_2Cl_2$$^{2)}$ are greatly promoted by Al_2O_3 catalyst. Although disproportionation of CF_3Cl is also catalyzed by Al_2O_3, the conversion of CF_3Cl is rather low (less than about 8 %). Furthermore, the catalytic activity decreases significantly during the reaction.$^{2)}$ This decrease is possibly due to the formation of stable aluminum fluorides on the surface.

Such metal oxides as Al_2O_3, Cr_2O_3, TiO_2, ZrO_2 and MgO, are not converted to volatile metal chlorides in contact with chlorofluorohydrocarbons at high temperatures. Therefore, the catalytic activities of these metal oxides in the disproportionation of CF_3Cl were examined for comparison with that of mixed oxides of Al_2O_3 and Cr_2O_3. Except for TiO_2, all of the simple and mixed oxides were prepared from solutions or mixed solutions of respective metal nitrates by neutralization with aqueous ammonia. The precipitated hydroxides were heat-trated at 600°C in air. The TiO_2 was prepared from titanium isopropoxide because titanium nitrate cannot be commercially obtained.

The disproportionation reaction was carried out in a flow system at atmospheric pressure using a glass reactor packed with 0.2 g of the metal oxides. Gaseous CF_3Cl (the purity was above 99.5 %), kindly supplied by Mitsui Fluorochemical Co., was diluted to 50 % with He and fed to the reactor at the constant rate of 2.22 l per hour. In order to examine any change in catalytic activity with time, the reactions were continued for 180 min. The products were analyzed by gas chromatography using a 5 m column Porapack N. The formation of high boiling species such as $CFCl_3$ and CCl_4 was found, besides CF_2Cl_2 and CF_4. The former two probably formed by the disproportionation of CF_2Cl_2 and $CFCl_3$. However, since the amounts of $CFCl_3$ and CCl_4 were relatively small (the sum of the two was less than 2 - 3 %), the conversion of CF_3Cl to CF_4 was approximately expressed as follows,

$$\text{Conversion (\%)} = \left(1 - \frac{(CF_3Cl)}{2 \times (CF_4) + (CF_3Cl)} \right) \times 100$$

where (CF_3Cl) and (CF_4) denote the amount of each component in the effluent gas, and $2 \times (CF_4)$ is assumed to be the amount of CF_3Cl consumed by equation (1). Figure 1 shows the conversions over Al_2O_3, Cr_2O_3 and the mixed oxides at 400°C and the conversion over Cr_2O_3 at 500°C. The TiO_2, ZrO_2 and MgO did not show any catalytic activity even at a temperature as high as 500°C. The formation of CF_4, which was not found up to 500°C in the absence of metal oxide, was observed over Al_2O_3 catalyst at lower temperatures. Over Cr_2O_3 catalyst, the conversion of CF_3Cl to CF_4 reached about 5 % at 500°C, while CF_4 was not formed at 400°C. In contrast to the catalytic activities of simple oxides such as Al_2O_3 and Cr_2O_3, those of the mixed oxides were generally higher. However, the catalytic activity of the mixed oxides varied significantly with time, depending on the atomic ratio of Cr to Al. An addition of a small amount of Cr component to Al_2O_3 enhanced the catalytic activity at 400°C remarkably. Induction periods were observed in the

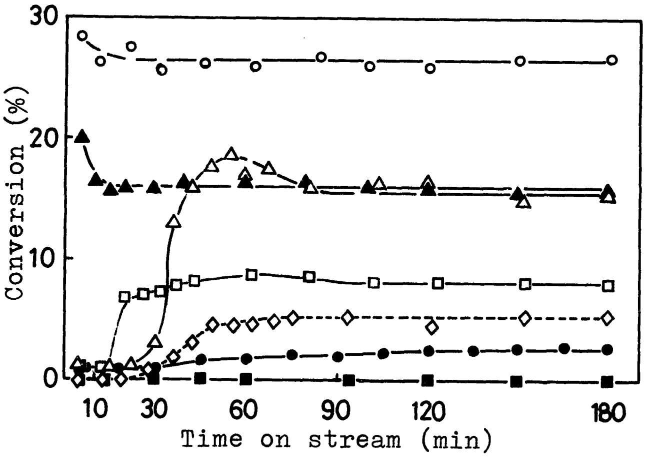

Fig.1 Disproportionation of $CClF_3$ at 400°C

Cr/Al
—●—: 0/10
—○—: 1/9
—▲—: 1/3
—△—: 1/1

Cr/Al
—□—: 3/1
—■—: 10/0
--◇--: 10/0 (reaction at 500°C)

reactions over the catalysts containing a large amount of Cr component just as in the case of Cr_2O_3 at 500°C.

As the reaction temperature was raised to 450°C, the catalytic activity of the mixed oxides became more pronounced, and the induction period in the reaction catalyzed by Cr_2O_3-rich mixed oxide almost disappeared. Figure 2 shows the effect of the atomic ratio of Cr to Al on the catalytic activity of the mixed oxide at 450°C. The addition of a small amount of Cr component greatly enhanced the catalytic activity similar to the reaction at 400°C (Fig.1), and about a 33 % conversion was attained over the mixed oxide with the ratio of Cr/Al = 1/9.

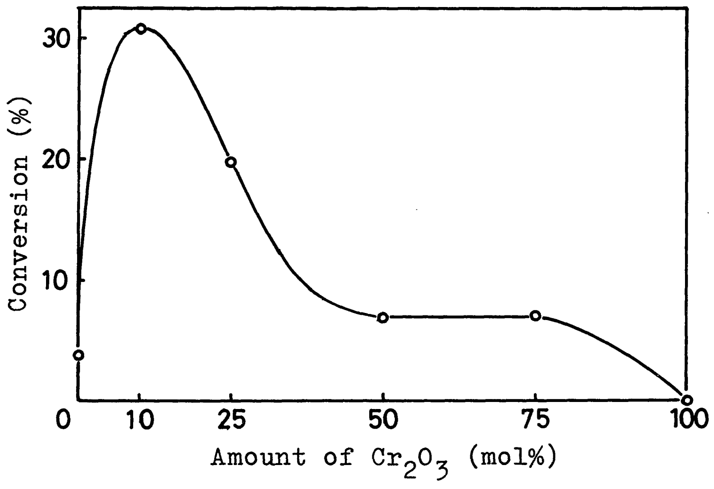

Fig.2 Effect of Cr_2O_3 content in $Al_2O_3 \cdot Cr_2O_3$ on catalytic activity at 450°C

Unlike the catalytic activity of Al_2O_3 which decreased with reaction time, that of $Al_2O_3 \cdot Cr_2O_3$ remained almost unchanged during times up to 180 min. When the reaction temperature was further raised to 500°C, the catalytic activity of Al_2O_3-rich mixed oxide remarkably decreased with the lapse of reaction time. The Al_2O_3 contained 8.02 wt % of fluorine after use as a catalyst at 450°C for 3 h. In contrast, $Al_2O_3 \cdot Cr_2O_3$ with the ratio of Cr/Al = 1/9 contained only 2.98 wt % of fluorine after reaction under the same conditions. The fact suggests that the replacement of a small amount of aluminum ion in Al_2O_3 with chromium ion might prevent the introduction of too many fluorine atoms, or the formation of stable aluminum fluorides, resulting in an increase in the activity and prolonging of the catalytic life. Since the radius of chromium(III) ion is relatively close to that of aluminum ion, such a replacement is considered to take place easily. However, as Cr_2O_3 (or partially fluorinated chromia) itself is not as active as Al_2O_3 or fluorinated alumina, the catalytic activity of the mixed oxide decreases with a further increase in the atomic ratio of Cr to Al as shown in Figures 1 and 2.

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