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A Novel Hydrodechlorinative Dimerization of Chlorofluorocarbons over Supported Ni Catalysts

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1,1,1-Trichloro-2,2,2-trifluoroethane or 1,1-dichloro-1,2,2,2-tetrafluoroethane, both of which have CF_3 group, dimerizes over supported Ni catalysts at an elevated temperature (723 K) into corresponding C_4-compounds in good to moderate yields.

We have hitherto investigated the hydrodehalogenation of chlorofluorocarbons(CFCs) in the presence of metal oxide catalysts or supported metal catalysts, and recently reported that Ni metal catalyst has a predominantly strong ability for breaking C-Cl bond rather than C-F bond in the presence of hydrogen and promotes the hydrodechlorination of 1,1,2-trichlorotrifluoroethane to 1-chlorotrifluoroethene selectively.1) Further studies led us to find a novel dimerization of CFCs catalyzed by Ni metal in the presence of hydrogen.

Table 1 summarizes the conversion and product distribution data in the reactions of CFC-113a (1,1,1-trichloro-2,2,2-trifluoroethane) and CFC-114a (1,1-dichloro-1,2,2,2-tetrafluoroethane) over silica-supported Ni (20 wt%) catalysts. Both reactions were carried out under an atmospheric pressure by using a continuous flow reaction system with a fixed-bed reactor made of quartz. The catalyst preparation was described elsewhere.1) Products were identified by mass spectrometry. The details of the reaction conditions are depicted in the footnote of the table.

When a stream of a mixture of CFC-113a and hydrogen (molar ratio; 1:6, argon; diluent) was passed over pre-reduced Ni metal catalyst supported on silica gel at 723 K, the substrate was readily dechlorinated and dimerized at a high conversion. The main products are a mixture of C_4-compounds composed of $CF_3CCl{=}CClCF_3$, $CF_3CH{=}CClCF_3$, $CF_3CH{=}CHCF_3$, and $CF_3C{\equiv}CCF_3$, the first being predominant (cis-trans mixture, total selectivity; 86%). CF_3CHCl_2 and methane are main by-products. The latter was formed clearly at the beginning of the reaction but scarcely when the time on stream was extended (see Fig. 1). The reaction might be better carried out in the presence of a highly excess of hydrogen, since an undesirable deactivation due to coke formation can be prevented.

The catalytic hydrodechlorinative dimerization also takes place when CFC-114a is used as a substrate (Table 1). Two distinctive points emerged from the comparison with the reaction of

Table 1. Hydrodechlorinative Dimerizations of CFC-113a and CFC-114a over 20 wt% Ni/SiO$_2$$^{a)}$

Reactant	Conv. of CFC/%	Product (Selectivity/%)	
113a	100	$CF_3CCl{=}CClCF_3$	(85.2)
		$CF_3CH{=}CClCF_3$	(2.8)
		$CF_3CH{=}CHCF_3$	(1.0)
		$CF_3C{\equiv}CCF_3$	(tr)
		$CF_3\text{-}CHCl_2$	(3.7)
114a	4.5	$CF_3CClF\text{-}CClFCF_3$	(11.5)
		$CF_3\text{-}CHClF$	(56.9)

a) Total flow rate; 65 ml·min^{-1}, partial pressure of CFC; 8 kPa, reaction temperature; 723 K, catalyst amount; 1.0 g (32-60 mesh).

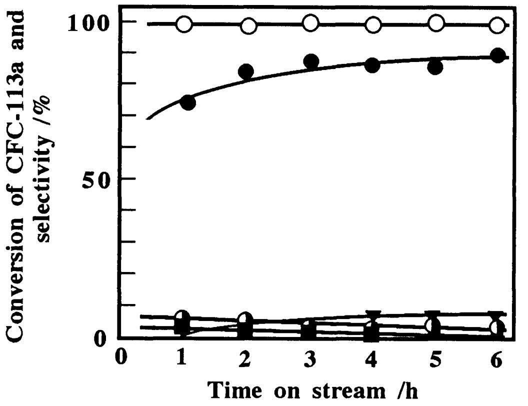

Fig. 1. Hydrodechlorinative dimerization of CFC-113a over Ni/SiO$_2$. The reaction conditions are the same of Table 1. ○ : conversion, ●: $CF_3CCl{=}CClCF_3$, ◐: $CF_3\text{-}CH{=}CClCF_3$, ▼: $CF_3\text{-}CHCl_2$, ■: CH_4.

CFC-113a. First, only a very low conversion of CFC-114a was attained even on the active Ni/SiO$_2$ catalyst because of low reactivity of the substrate; higher stability of C-Cl bond of CFC-114a than that of CFC-113a. The second point concerns product distribution. The main products were a hydrogen-substituted CFC, $CF_3\text{-}CHClF$, and a dimer, $CF_3CClF\text{-}CClFCF_3$. Note that the produced dimer is fully saturated, not olefinic.

In a separate experiment, it was found that the reaction of CFC-113a at a very low conversion (less than 3%) gave two main products, $CF_3\text{-}CHCl_2$ and $CF_3CCl_2\text{-}CCl_2CF_3$, that is, a hydrogen substituted form and a saturated dimer, both of which are exactly the same type of products as observed in the reaction of CFC-114a. Provided that the key step of the catalytic hydrodechlorinative dimerization is a radical C-Cl bond fission, the results allow us to speculate the following reaction scheme. After C-Cl bond breaking on the catalyst surface, $CF_3\text{-}CCl_2$ radical, for example, may be formed and then dimerized to give the saturated C$_4$-compound directly (radical coupling) or through the hydrogen-substituted intermediate. At reaction conditions that provide a high conversion, the C$_4$-dimer formed is further dechlorinated to form various olefinic and acetylenic dimers as detected in the reaction of CFC-113a.

The behavior of CFCs in the atmosphere has been of great concern lately because of environmental problems such as ozone depletion. Heterogeneous catalytic processing of CFCs are, therefore, now attracting wide attention.[2,3] With respect to such environmental problems, we would like to emphasize the potentials of the present novel catalytic process.

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