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Selective Hydrodechlorination of CFC-113 to 1-Chloro-1,2,2-trifluoroethylene over Supported Ni Catalysts

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Various metal oxides have been examined as catalysts for the hydrodechlorination of CFC-113 to form 1-chloro-1,2,2-trifluoroethylene (CFC-1113). NiO was most effective and over silica gel- or Y zeolite-supported Ni catalyst, 100% conversion of CFC-113 and 96% selectivity to CFC-1113 were attained.

The decomposition of ozone layer in the stratosphere, which may be caused by chlorine atoms dissociated from chlorofluorocarbons (CFCs), is becoming serious problem today. Various technologies for treating CFCs before being released to air have already been proposed.[1),2)] These technologies are mainly based on catalytic or non-catalytic decomposition processes. Apart from such processes, we have attempted the selective hydrodechlorination of CFC-113 to CFC-1113 over solid catalysts (eq. 1), since HFC-134a as possible substitute of CFC-12 could be synthesized from CFC-1113 via hydrodechlorination and hydrofluorination.

$$CCl_2FCClF_2 + H_2 \longrightarrow CClF{=}CF_2 + 2HCl \qquad (1)$$

Table 1 summarizes the results of screening test by the use of various metal oxide catalysts, all of which are commercially available and are treated in an Ar stream (56 $ml \cdot min^{-1}$) at 450 °C for 2 h before the reaction. The reactions were carried out under an atmospheric pressure by using a continuous flow reaction system with a fixed-bed reactor (Pyrex). The reaction conditions are depicted in footnote in the tables. Transition metal oxide catalysts, such as Fe_2O_3, NiO, Co_2O_3, and CoO, were found distinctively active for the CFC-113 conversion to CFC-1113. In particular, NiO catalyst is highly active, yielding CFC-1113 selectively (89%) at high conversion (56%) of CFC-113. The catalytic activity of NiO was quite stable for a prolonged reaction time though it was revealed by XRD measurement that NiO was completely reduced to metallic Ni during the reaction. Such reduction was also observed on Co_2O_3, CoO, and CuO. Fe_2O_3 showed high selectivity but its surface seems to be damaged by chlorine during the reaction because unidentified XRD peaks were observed for the used catalyst. Cr_2O_3 catalyst showed poor activity, while the obtained selectivity was extremely high (99.2%) and no

Table 1. Hydrodechlorination of CFC-113 over metal oxide catalysts[a)]

Catalyst	Conversion of CFC-113/%	Selectivity to CFC-1113/%
MgO	3.1	19.2
Al_2O_3	70.7	0
SiO_2	0.3	0
TiO_2	94.3	-
Cr_2O_3	8.0	99.2
Fe_2O_3	28.0	98.9
CoO	13.5	91.0
Co_2O_3	31.7	78.1
NiO	56.1	88.7
CuO	10.3	73.4
ZnO	4.2	73.5

a) Total flow rate; 95 ml·min^{-1}, carrier gas; Ar, partial pressure of CFC-113; 10 kPa, H_2/CFC-113=3, reaction temperature; 450 °C, catalyst amount; 1.0 g (32-60 mesh).

Table 2. Hydrodechlorination of CFC-113 over supported Ni catalysts[a)]

Catalyst	Amount of loading /wt%	Conversion of CFC-113 /%	Selectivity to CFC-1113[d)] /%
Ni/SiO_2	20	100	84.5
Ni/SiO_2	5	100	95.8
Ni/MgO	20	30.7	88.8
Ni/C	20	39.5	67.1
Ni/Y-Zeolite	-[b)]	96.0	94.8
NiO[c)]	-	72.2	89.4

a) Reaction conditions, see Table 1.

b) Amount of Ni loading was not determined.

c) Prepared by hydrolysis of aqueous solution of nickel nitrate with KOH, followed by calcination at 450 °C.

d) By-products consisted mainly of CFC-123a, CFC-133, and trifluoroethylene.

deactivation was observed without the phase change as ascertained by XRD analysis. The highest conversion was attained with TiO_2 catalyst. However, CFC-1113 was not formed and the decomposition of CFC-113 mainly took place. The formation of a titanium compound around the outlet of the reactor suggests that TiO_2 is extremely unstable under the reaction atmosphere. Al_2O_3 also showed high activity but CFC-1113 was not formed. Main products were $CClF_3$, CH_2FCClF_2, $C_2F_4Cl_2$, $CCl_2{=}CFCl$, $C_2Cl_4F_2$, $CCl_2{=}CCl_2$. MgO and ZnO were less active and SiO_2 was inactive.

We further conducted the reaction by the use of supported form of Ni which resulted in the most effective catalyst element (Table 1). SiO_2, MgO, active carbon, and Y-zeolite were chosen as supports. The catalysts were prepared by an evaporation to dryness method using aqueous Ni nitrate solution except Ni/Y-zeolite catalyst which was prepared by an ion-exchange method. All catalysts were pre-reduced in a H_2 stream (56 ml·min^{-1}) at 450 °C for 2h.

The results are shown in Table 2. Over Ni/SiO_2 and Ni/Y-zeolite catalysts, most of CFC-113 in the feed was converted into CFC-1113 in the selectivity over 94%. It is obvious that the supported catalyst is superior to the unsupported one. In addition, no appreciable changes in catalytic activity were observed within 7 h reaction for both the catalysts. When the amount of Ni loading on SiO_2 decreased from 20 to 5 wt%, the selectivity was appreciably improved without the change of the high conversion. The result suggests that a highly dispersed Ni is suitable for the selective formation of CFC-1113. Ni/MgO and Ni/C catalysts showed lower activity and lower selectivity in comparison with the SiO_2-supported catalysts.

References

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