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Conversion of 1,1,2-Trichloro-1,2,2-trifluoroethane (CFC113) over TiO_2-Supported Metal and Metal Oxide Catalysts

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CCl_2FCClF_2 was converted to $C_2H_2F_2$ and CH_4 over Pd/TiO_2 at 420-820 K in the presence of hydrogen. $C_2H_2F_2$ and $C_2H_3F_3$ were mainly formed over Pt/TiO_2 at 520-570 K and dechlorination to CF_3Cl took place over Ni/TiO_2 and Co/TiO_2 at 470-620 K. The CeO_2/TiO_2 catalyst and the catalyst containing La themselves reacted with CFC113 to give CeF_3/TiO_2 and LaF_3/TiO_2 after the reaction at 820 K, respectively. $MnTiO_3$ catalyzed the reaction to C_2F_3Cl at relatively high temperatures of 770-820 K.

Chloro-radicals derived from chlorofluorocarbons (CFCs) by the photoreaction in the stratosphere catalyze the decomposition of ozone molecules into dioxygen molecules. It would be a better way that CFCs used are collected, separated into the components, and then those are again utilized. At least, spent CFCs should be decomposed to safety materials before release into the atmospheric environment. There are many technical reports on the production of CFCs. On the other hand, there are few studies on the catalytic conversion of CFCs. Okazaki et al.1) reported that Fe_2O_3 supported on active charcoal catalyzed the decomposition of CCl_4 by water vapor at 843 K and was also effective for the decomposition of several CFCs such as CCl_3F, CCl_2F_2, $CClF_3$, $CHClF_2$, and $C_2F_3Cl_3$ at 570-860 K. Tomioka et al.2) studied the reaction of 1,1,2-trichloro-1,2,2-trifluoroethane (CFC113) with hydrogen over various metal oxides and found that the dechlorination of CFC113 to chlorotrifluoroethylene took place over NiO, Fe_2O_3, and Cr_2O_3 at 723 K. Tajima et al.3) also studied the decomposition of CFC113 and reported that CFC113 began to react with water vapor at 673 K, and only the decomposition into CO, CO_2, HCl, and HF took place over zeolites but the disproportionation also proceeded concurrently over γ-Al_2O_3 to give $C_2Cl_2F_4$, $C_2Cl_4F_2$, and C_2ClF_5. However, chemistry concerning to the catalytic conversion of CFCs has been less known. This paper deals with the conversion of CFC113 over various metal and metal oxide catalysts supported on TiO_2 in the presence of hydrogen.

Catalysts were prepared through the following procedure. Hydrous titanium oxide was added into an aqueous solution of metal nitrate and the water was evaporated to dryness on a hot plate. The powder obtained was subjected to the calcination in the air at 773 K for 5 h, followed by the reduction in a hydrogen stream at 773 K (573 K for Pd and Pt). Catalytic reaction was carried out using an ordinary glass tubular flow type reactor with fixed catalyst bed inside. The gas effluent from the reactor was washed with an aqueous solution of NaOH (5 mol/L) to remove HCl and/or HF formed then it was analyzed by GC using a Porapak Q column for the separation of CFCs.The reactor was kept at desired temperature for 1 h prior to analysis. The selectivity of a product A is defined as $100r_A/r_F$ (%), where r_A is the rate of CFC113 converted to A and r_F is that of total CFC113 consumption.

The results of the reaction are shown in Fig. 1 and Table 1. As can be seen from the figure, CFC113 reacted with hydrogen over the Pd, Pt, and Ni catalysts even at 420 K. The Pd catalyst showed so much higher catalytic activity that most of the reactant disappeared at 520 K. The conversion of CFC113 approached to 100% at 570 K over the Pt and Ni catalysts, at 620 K over the Co catalyst, and at 670 K over the catalyst containing La or Cu. However the conversion of CFC113 did not exceed 85-90 % over the catalysts containing Cr or Ce. The catalyst containing Mn was effective only at the temperatures higher than 820 K. Chlorine atoms of CFC113 molecules were removed selectively by hydrogen over the catalysts containing noble metals. As shown in Table 1, over the Pd catalyst,

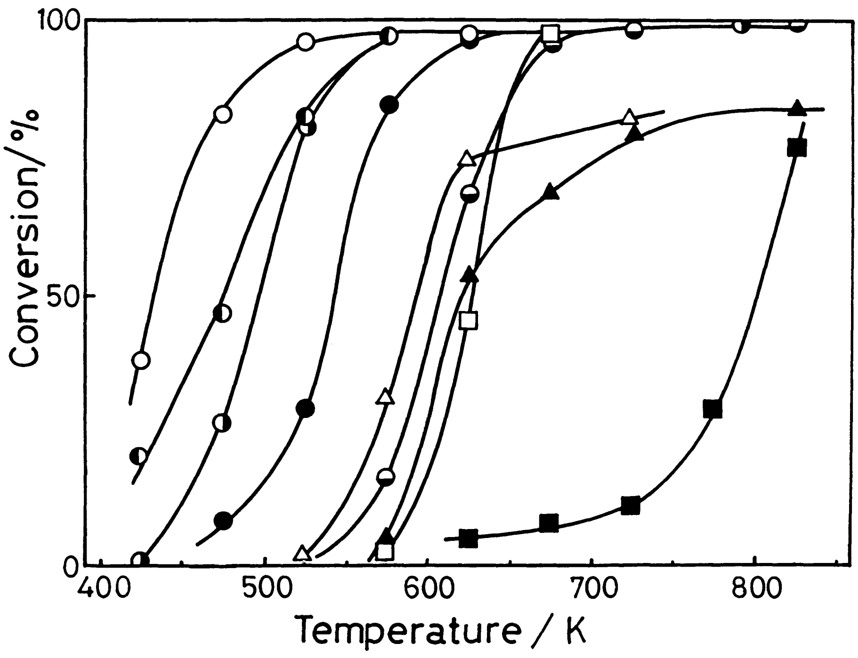

Fig. 1. Catalytic reaction of CFC113 over the TiO_2-supported metal and metal oxide catalysts.

○ Pd, ◐ Pt, ◑ Ni, ● Co, △ Cr, ◒ Cu, ▲ Ce, □ La, ■ Mn

$C_2H_2F_2$ was formed at lower temperatures, which was successively converted to methane. The chief products were $C_2H_2F_2$ and $C_2H_3F_3$ over the Pt catalyst. The rate of C_2F_3Cl formation increased with reaction temperature then reached a maximum at about 573 K then decreased with the temperature and the formation of methane became dominant at >620 K over the Ni catalyst.

The crystalline phases of the catalysts before and after the reaction were analyzed by XRD. The XRD patterns of the catalysts before reaction revealed that each metal was supported on TiO_2 in the cases of Cu and Pt. On the other hand, only Cr_2O_3 or CeO_2 was supported on TiO_2. The catalysts containing Mn and Ni gave the diffraction peaks ascribed to the binary oxides such as $MnTiO_3$ and $NiTiO_3$ suggesting that the catalysts are composed of the surface binary oxide layer and the TiO_2 core. The catalysts containing Co, Pd, and La only gave the diffraction peaks attributed to TiO_2.

After the reaction, Cu and Pt species on TiO_2 remained unaltered, and the supported species were changed to the metals in the cases of Pd and Co. The $NiTiO_3$ catalyst was changed into Ni metal and TiO_2. It is obvious that these metals are effective for the dechlorination of CFC113 and replacement reaction of chlorine with hydrogen. The XRD patterns of the catalysts

Table 1. Reaction of CFC113 over the TiO_2-supported catalysts

Cata-	Temp	Conv.	Selectivity / %								
lyst	K	%	CH_4	C_2H_6	$C_2H_2F_2$	C_2HF_3	$C_2H_3F_3$	C_2F_3Cl	CO	CO_2	unknown[a)]
Pd	473	83.0	14.8		50.0						17.8
	523	96.3	25.3		51.0		0.6	0.3			4.2
	623	97.0	65.7		32.2			0.7			
	723	97.7	78.6		4.5				19.9		
	823	98.8	67.8						20.5		
Pt	523	82.9	1.4		33.0		46.2	7.0	2.2	20.2	5.2
	573	97.7	7.3		48.4				11.3	34.8	
Ni	523	81.3			1.9	13.9	12.2	34.8		1.3	10.9
	573	97.1	3.6		1.7	4.9	9.6	65.0	3.6	1.5	10.1
	673	98.4	69.3		1.9	1.8		8.9	11.1		2.3
Co	623	96.6	1.6			5.1		62.6	3.6		24.2
	723	97.3	20.0		0.7	12.5		29.5	30.3	3.0	1.3
Cr	573	30.5							97.0		2.1
	723	81.9		0.6	0.6			4.5	32.1	0.5	58.2
Cu	573	16.0			7.9			49.5	7.5	20.1	15.1
	773	99.0	1.2	0.9	1.4	0.6		33.8	35.1	2.7	19.0
Ce	673	68.3							99.9		
	823	83.6			5.6				56.7		
La	773	99.5			1.3				62.7	0.8	24.5
Mn	773	28.8						73.2			21.6
	823	76.8						74.7			7.5

Catalyst:1.00 g, W/F=1.20 $g\cdot s\cdot cm^{-3}$, Feed gas composition:CFC113 0.8 mol%, H_2 19.0 mol%, balance He. a) Substances detected by GC but not identified.

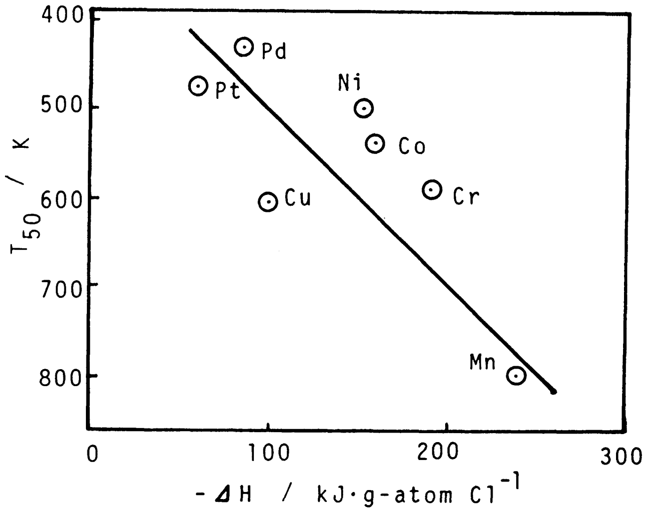

Fig.2. Relation between catalytic activity of the metals and heat of formation of metal chlorides.

containing La and Ce composed of the diffraction peaks of LaF_3 and CeF_3 except for those due to TiO_2, respectively. The chemical reaction between metal oxides and CFC113 might take place in these catalysts because significant amount of CO was formed in spite of the absence of oxygen in the reaction gas mixture. The Cr_2O_3 catalyst remained unchanged after the reaction at 823 K for 2 h, however, the possibility of the occurrence of the chemical reaction between the catalyst and CFC113 can not rule out in this stage because the chief product was CO. The $MnTiO_3$ catalyst, on which dechlorination to C_2F_3Cl proceeded selectively, also remained unchanged after the reaction. Those results suggest that both metals and metal oxides can catalyze the same type of reaction.

Figure 2 shows the relation between the catalytic activity of the supported metal catalysts and the heat of formation of metal chlorides. The temperatures where the conversion reached 50% were plotted on the vertical axis and the heat of formation of metal chlorides horizontally as a parameter of the bond strength between metal atom and chlorine atom adsorbed thereupon. It seems reasonable to assume that the right hand side of the volcano shape appeared in the figure. So that the bond strength between chloride ion and surface metal ion is thought to be one of the key factors in this reaction. Studies on the detailed reaction mechanism are now in progress.

References

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