A New HCN Production from CCl_2F_2 (CFC12) and Ammonia over $NiTiO_3$, Ni metal, and Pt/C Catalysts

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$NiTiO_3$, Ni metal, and Pt/C are effective catalysts for the formation of HCN from CFC12 and NH_3 at 673—823 K: 86.2% yield is attained at 723 K over Ni metal.

Chloro-radicals derived from chlorofluorocarbons (CFCs) by irradiation with UV in the stratosphere catalyse the decomposition of ozone into dioxygen. Spent CFCs, therefore, must not be released into the atmosphere.

Wakabayashi *et al.*[1] reported that CFC11 reacts with water vapour in an Ar plasma to give CO_2, HCl, HF, Cl_2, and F_2.

We have reported[2] that 1,1,2-trichloro-1,2,2-trifluoroethane (CFC113) reacts with hydrogen to give $C_2H_2F_2$ and CH_4 over the Pd(1 wt%)/TiO_2 catalyst at 420—820 K, $C_2H_2F_2$ and $C_2H_3F_3$ over the Pt(1 wt%)/TiO_2 catalyst at 520—570 K, and C_2F_3Cl over Ni(10 wt%)/TiO_2 and Co(10 wt%)/TiO_2 at 470—620 K, respectively.

Ueda *et al.*[3] also reported that dechlorination to C_2F_3Cl takes place over NiO, Fe_2O_3, and Cr_2O_3 at 723 K. Okazaki and Kurosaki[4] studied the decomposition of CFC113 and reported that CFC113 reacts with water vapour >673 K, and decomposition into CO, CO_2, HCl, and HF only takes place over zeolite catalysts. However, little is known about the reaction of CCl_2F_2 (CFC12) which has been utilized as a refrigerant. We have discovered a new catalytic reaction of CFC12 with NH_3. HCN is now industrially manufactured by the partial oxidation of CH_4 and NH_3 in the presence of oxygen. The new CFC12 decomposition reaction could replace the partial oxidation.

The $NiTiO_3$ catalyst was prepared as follows. An aqueous solution of $Ni(NO_3)_2{\cdot}6H_2O$ containing dispersed TiO_2 was evaporated to dryness. The powder obtained was calcined at 773 K for 5 h in the air then reduced at 573 K for 3 h in a hydrogen stream. The XRD pattern consisted of the peaks due to $NiTiO_3$ and TiO_2.

Activated charcoal (Wako) on which H_2PtCl_6 was impregnated was dried at 400 K overnight then reduced at 573 K for

Table 1. Product distribution in the reaction of CFC12 with NH_3 over various catalysts.[a]

			Selectivity (%)					
Catalyst	Temp./K	Conversion (%)	CO	CO_2	HCN	CF_2ClH	CF_2H_2	CFH_3
$NiTiO_3$	773	72.7	6.8	10.4	81.8	0.6	0.1	0.3
(50 wt%)	823	98.0	18.8	12.9	66.2	1.4	0.2	0.4
Ni	673	32.6			75.4	1.7		
	723	87.7		[b]	98.3	0.6		
	768	100		[b]	23.0	[b]		
Pt/C	723	50.1						
(1 wt%)	769	78.9		0.5	53.4	7.6	0.5	0.3
	821	100	0.8	0.6	64.6	0.2	0.3	0.2

[a] Reactant gas, CF_2Cl_2 5, NH_3 30, N_2 65 mol%. Selectivity is based on the CFC12 consumed. [b] Trace amount.

4 h in a hydrogen stream. Ni powder (Wako) was reduced at 573 K for 3 h in a hydrogen stream.

The results of the steady-state flow reaction are shown in Table 1. With the $NiTiO_3$ catalyst, a small amount of CFC12 was converted at 723 K and 72.7% of CFC12 reacted at 773 K to give HCN at 81.8% selectivity. Almost 100% conversion was attained at 823 K, but the selectivity of HCN reduced to 66.2% and the by-products were CO and CO_2. Since no oxygen is present in the reactant gas, CO and CO_2, for example, are thought to be formed from the reaction of CFC12 with the $NiTiO_3$ catalyst.

HCN was formed over Ni powder catalyst more selectively, which suggests that metallic nickel catalyses the reaction. Although the catalytic activity of the $NiTiO_3$ cannot be compared with that of Ni powder directly, it is noteworthy that HCN formation takes place even at as low a temperature as 673 K over Ni powder. The yield of HCN reached 86.2% at 723 K, however, carbon recovery fell significantly at 768 K which may be accounted for by carbon deposition on the catalyst. No formation of CO and CO_2 over Ni powder catalyst is observed, which supports the above hypothesis. The reaction of CFC12 with NH_3 was also examined over Co powder catalyst and it was found that the conversion of CFC12 reached 100% at 723 K and the decomposition to carbon was predominant.

Over the Ni powder catalyst, the formation of 97 µmol of HCN required the consumption of 570 µmol of NH_3, so the reaction can be written as equation (1).

$$CF_2Cl_2 + 5\,2/3\ NH_3 \longrightarrow HCN + 2\ NH_4Cl + 2\ NH_4F + 1/3\ N_2 \quad (1)$$

But HCN was formed selectively when the ratio of NH_3: CFC12 was *ca.* 2, therefore, the basic reaction is thought to be equation (2).

$$CF_2Cl_2 + 1\,2/3\ NH_3 \longrightarrow HCN + 2\ HCl + 2\ HF + 1/3\ N_2 \quad (2)$$

The same type of reaction took place over Pt catalyst supported on activated charcoal as shown in Table 1 although the selectivity to HCN was somewhat lower than those of other catalysts.

Spent CFC12 collected after use, can be readily converted to HCN selectively over these catalysts.

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