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HCN Formation from CCl_2F_2 (CFC12) over Iron Group Metal Catalysts

Dichlorodifluoromethane (CCl_2F_2, CFC12), which has been widely used as a refrigerant, has high ozone depressive potential and therefore should not be released into the atmosphere. Studies on the decomposition of CFCs into CO_2, HCl, and HF have been reported (*1*, *2*). However, a better way to handle chlorofluorocarbons is to convert used CFCs into raw materials for use by the chemical industry. We have previously studied the reaction of CFC 12 with NH_3 and found that a new reaction, HCN formation, takes place over $NiTiO_3$ and Pt catalysts supported on activated charcoal (*3*). We report the catalysis by iron group metals for CFC 12–NH_3 reaction.

Ni powder (Wako Pure Chem., 99.6%, 80–120 mesh), Fe powder (Wako Pure Chem., 95%, 100 mesh), and Co powder (Wako Pure Chem., 99%, 60–80 mesh) were used as catalysts without further purification. The catalytic reaction was carried out in an ordinary flow type reaction system using a 10-mm-i.d. stainless-steel reactor with a fixed catalyst bed. Two cubic centimeters of catalyst were used for experiments and the feed gas rate was 60 cm^3/min. CFC 12, HCN, and NH_3 were analyzed by GC with Porapak Q and chromosorb columns. Analysis was carried out after 30 min, at which point the reaction had reached steady state.

The results of metal catalysts are presented in Table 1. Reaction between CFC 12 and NH_3 took place at >570 K and 100% conversion was achieved over the Fe catalyst. The major product was HCN; however, its selectivity did not exceed 20%. With increased conversion, most of the reacted CFC was not recovered. The deposition of amorphous carbon was observed on the Fe catalyst after the reaction at temperatures up to 773 K.

The Co catalyst was less active and the conversion reached only 49% even at 823 K. However, it showed a relatively high selectivity to HCN in the range of 64–80%. The conversion curve of the Ni catalyst was similar to that of the Fe catalyst but the selectivity to HCN was significantly higher than the other catalysts. The selectivity to HCN was 98.8% at 723 K and a reasonably high selectivity, ca. 75%, was maintained at elevated temperatures such as 773–823 K.

The reaction was carried out using metal powder catalysts and the results are shown in Table 1. No reactions took place up to 723 K. Although the consumption of a small amount of CFC 12 was observed at 773 K, no homogeneous reactions accompanied the catalytic reactions by metals at this temperature. The conversion of CFC 12 reached 27.2% at 823 K. However, only 30.2% of the reacted CFC 12 was recovered as $CClF_2H$. About 71–74.5% of reacted CFC 12 was recovered as CH_4, $CClF_2H$, and HCN. This suggests a contribution of homogeneous reactions or a heterogeneous reaction on the wall of the reactor.

The surface areas of the metal catalysts measured by the BET method are also listed in Table 1. The Co catalyst has the surface area ca. 4.5 times greater than that of the Ni catalyst and that of the Fe catalyst is much smaller than the others. Taking into account the surface area of the catalysts, the order of the activity of CFC 12 conversion is Fe > Ni > Co.

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TABLE 1

CFC 12–NH_3 Reaction over the Metal Powder Catalysts

Catalyst	Temp (K)	Conv. (%)		Selectivity (%)[a]			SA[b] (m^2)	Feed gas composition (mol%)
		CFC	NH_3	CH_4	$CClF_2H$	HCN		
Fe	623	13.2	7.5			6.7		CFC 13.3
	673	16.7	9.6	7.1		19.4	0.10	NH_3 29.5
	723	65.9	36.7	4.0	1.2	16.4		N_2 57.2
	773	99.8	89.0	1.0		1.0		
Co	723	3.6	7.5	12.6				CFC 13.8
	773	16.5	13.5	7.4	12.4	80.2	8.6	NH_3 34.5
	823	39.8	43.1	1.7	5.3	64.0		N_2 51.7
Ni	623	0.6	10.0			+		CFC 13.7
	673	37.6	39.0		+	37.6		NH_3 36.7
	723	47.9	65.2	+	1.2	98.8	1.9	N_2 49.6
	773	100	100	+	0.3	74.4		
	823	100	100	+	+	74.5		
None	723	0	0					CFC 12.4
	773	6.5	28.7		tr			NH_3 35.6

Note. Catalyst: 2 cm^3; Fe, 5.32 g (100 mesh); Co, 7.19 g (60–80 mesh); Ni, 4.22 g (80–120 mesh). Feed gas: 60 cm^3/min.

[a] Reacted CFC basis.

[b] Surface area.

Since Ni metal powder has a high potential to convert CFC 12 into HCN, the effects of initial concentration of CFC 12 on the HCN formation was examined and the results are shown in Table 2. Under the reaction condition (a) of Table 2, the initial CFC concentration was 5 mol%, HCN formed at >623 K, and the selectivity was extremely high, 98.3%, at 723 K. However, at temperatures higher than 768 K, although the conversion of CFC reached almost 100%, the selectivity to HCN decreased drastically and coke formation became dominant.

When the concentration of CFC was raised to 14 mol%, condition (b) in Table 2, the selectivity to HCN gave a maximum at 723 K similar to (a). With increasing reaction temperature, the conversion reached 100% at around 773 K and the selectivity to HCN decreased slightly, but a relatively high value such as ca. 75% was maintained even at >773 K. When CFC concentration was raised to 26.2%, condition (c) in Table 2, the conversion increased sharply at temperatures between 723 and 773 K and approached 100% at 823 K. Almost all the CFC 12 was converted to HCN at 773 K and extremely high selectivity, 84.6%, was maintained even at 823 K. These results lead to the conclusion that the higher CFC concentration in the feed gas, the more selective the HCN formation.

A similar tendency was observed in the case of condition (d), in spite of the much smaller NH_3/CFC ratio. It can be said from these results that 14–26 mol% of initial CFC 12 concentration is preferable for selective HCN formation over the Ni powder catalyst.

The stoichiometry of the reaction was examined using the reaction data at 723 K in Table 2 (a), where excess NH_3 was present and the HCN selectivity was extremely high. CFC 12, 107 μmol, and NH_3, 571 μmol, were consumed to form HCN per minute. The ratio of NH_3/CFC is about 5.34 and this value is near 16/3. Thus the reaction stoichiometry can be represented by

TABLE 2

Reaction of CFC12 with NH_3 over Ni Metal Catalyst

Feed gas composition (mol%)		React. temp. (K)	Conv. (%)		Selectivity (%)				
			CFC12	NH_3	CH_4	CH_3F	CHF_2Cl	CH_2F_2	HCN
(a) CFC	5.0	629	24.0	22.8			1.0		27.3
NH_3	30.9	673	32.7	31.2		0	1.0	0	52.1
N_2	64.1	723	87.7	73.8		0	0.6	0	98.3
		768	100	94.4		0	+		23.0
		823	100	98.6		0.1		0.1	0.8
(b) CFC	14.0	673	37.6	39.0			+		43.6
NH_3	38.0	723	47.9	65.2		+	1.0		99.0
N_2	48.0	773	100	100		+	0.4		74.7
		823	100	100		+	+		74.5
(c) CFC	26.2	773	65.9	81.1			1.0		99.0
NH_3	40.7	823	96.7	100		+	1.1		84.8
N_2	33.1								
(d) CFC	15.0	623	22.0	36.9	0.2		3.0		96.6
NH_3	15.0	673	35.9	63.6	0.7		1.5		97.8
N_2	70.0	723	61.5	100	0.5		1.3		98.2
		773	83.4	100	3.9		0.8		95.2
		823	85.4	100	14.7	0.1	0.9		8.0

Note. Catalyst: Ni (80–120 mesh), 4.54 g (2 cm^3), + trace amount.

$$CCl_2F_2 + \tfrac{17}{3}NH_3 = HCN + 2NH_4Cl + 2NH_4F + \tfrac{1}{3}N_2. \quad (1)$$

According to this equation, 2 mol each of NH_4Cl and NH_4F should be formed, but actually white powder deposited on the wall of the reactor just downstream from the catalyst bed during the reaction under the conditions of (a) in Table 2. This white powder was determined to be NH_4Cl by means of elemental analysis. The HCN formation from CFC 12, however, required less NH_3, in the cases of (b) and (c). For example, the ratio of the reacted NH_3/CFC was about 3.8 in the reaction at 723 K in Table 2 (b), although the NH_3/CFC ratio was significantly lower than $\frac{17}{3}$, selective formation of HCN was observed. Thus the basic reaction may be represented by

$$CCl_2F_2 + \tfrac{5}{3}NH_3 = HCN + 2HCl + 2HF + \tfrac{1}{3}N_2. \quad (2)$$

The results when initial NH_3/CFC was unity are shown in Table 2 (d). At temperatures below 673 K, where the conversion of NH_3 does not reach 100%, the conversion of CFC 12 is near the theoretical value, which is three-fifths of the conversion of NH_3 according to Eq. (2). G°_{298} for Eqs. (1) and (2) are calculated to be -107.3 and -34.0 kcal/mol, respectively. The occurrence of these reactions is supported thermodynamically. Even in the situation where all of the NH_3 feed was consumed, HCN formed selectively as shown for the results at 773 K. Neglecting the formation of CH_4 and $CClF_2H$, the mole ratio of consumed NH_3 to formed HCN is near 1.21, which is significantly smaller than $\frac{5}{3}$. These results suggest the presence of another reaction path of HCN formation. This reaction path is worth studying, specifically because the reaction that consumes less NH_3 is favorable for an industrial process. HCN is now manufactured practically by the oxidation of CH_4 and NH_3 using the Pt catalyst at higher temperatures such as >1273 K. The catalytic reaction discussed here is thought to be useful in the treatment of used refrigerant for the protection of the global environment.

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