

## A New HCN Production from $\text{CCl}_2\text{F}_2$ (CFC12) and Ammonia over $\text{NiTiO}_3$ , Ni metal, and Pt/C Catalysts

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$\text{NiTiO}_3$ , Ni metal, and Pt/C are effective catalysts for the formation of HCN from CFC12 and  $\text{NH}_3$  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.*<sup>1</sup> reported that CFC11 reacts with water vapour in an Ar plasma to give  $\text{CO}_2$ , HCl, HF,  $\text{Cl}_2$ , and  $\text{F}_2$ .

We have reported<sup>2</sup> that 1,1,2-trichloro-1,2,2-trifluoroethane (CFC113) reacts with hydrogen to give  $\text{C}_2\text{H}_2\text{F}_2$  and  $\text{CH}_4$  over the Pd(1 wt%)/ $\text{TiO}_2$  catalyst at 420–820 K,  $\text{C}_2\text{H}_2\text{F}_2$  and  $\text{C}_2\text{H}_3\text{F}_3$  over the Pt(1 wt%)/ $\text{TiO}_2$  catalyst at 520–570 K, and  $\text{C}_2\text{F}_3\text{Cl}$  over Ni(10 wt%)/ $\text{TiO}_2$  and Co(10 wt%)/ $\text{TiO}_2$  at 470–620 K, respectively.

Ueda *et al.*<sup>3</sup> also reported that dechlorination to  $\text{C}_2\text{F}_3\text{Cl}$  takes place over NiO,  $\text{Fe}_2\text{O}_3$ , and  $\text{Cr}_2\text{O}_3$  at 723 K. Okazaki and Kurosaki<sup>4</sup> studied the decomposition of CFC113 and reported that CFC113 reacts with water vapour >673 K, and

decomposition into CO,  $\text{CO}_2$ , HCl, and HF only takes place over zeolite catalysts. However, little is known about the reaction of  $\text{CCl}_2\text{F}_2$  (CFC12) which has been utilized as a refrigerant. We have discovered a new catalytic reaction of CFC12 with  $\text{NH}_3$ . HCN is now industrially manufactured by the partial oxidation of  $\text{CH}_4$  and  $\text{NH}_3$  in the presence of oxygen. The new CFC12 decomposition reaction could replace the partial oxidation.

The  $\text{NiTiO}_3$  catalyst was prepared as follows. An aqueous solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  containing dispersed  $\text{TiO}_2$  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  $\text{NiTiO}_3$  and  $\text{TiO}_2$ .

Activated charcoal (Wako) on which  $\text{H}_2\text{PtCl}_6$  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<sub>3</sub> over various catalysts.<sup>a</sup>

Catalyst	Temp./K	Conversion (%)	Selectivity (%)					
			CO	CO <sub>2</sub>	HCN	CF <sub>2</sub> ClH	CF <sub>2</sub> H <sub>2</sub>	CFH <sub>3</sub>
NiTiO <sub>3</sub> (50 wt%)	773	72.7	6.8	10.4	81.8	0.6	0.1	0.3
	823	98.0	18.8	12.9	66.2	1.4	0.2	0.4
	673	32.6			75.4	1.7		
Ni	723	87.7			b	98.3	0.6	
	768	100			b	23.0	b	
	723	50.1						
Pt/C (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

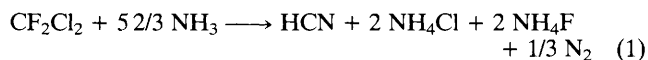
<sup>a</sup> Reactant gas, CF<sub>2</sub>Cl<sub>2</sub> 5, NH<sub>3</sub> 30, N<sub>2</sub> 65 mol%. Selectivity is based on the CFC12 consumed. <sup>b</sup> Trace amount.

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

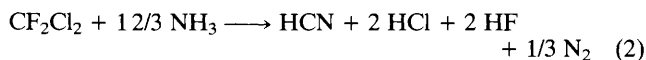
The results of the steady-state flow reaction are shown in Table 1. With the NiTiO<sub>3</sub> catalyst, a small amount of CFC12 was converted at 723 K and 72.7% of CFC12 reacted at 773 K to give HCN at 81.8% selectivity. Almost 100% conversion was attained at 823 K, but the selectivity of HCN reduced to 66.2% and the by-products were CO and CO<sub>2</sub>. Since no oxygen is present in the reactant gas, CO and CO<sub>2</sub>, for example, are thought to be formed from the reaction of CFC12 with the NiTiO<sub>3</sub> 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<sub>3</sub> 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<sub>2</sub> over Ni powder catalyst is observed, which supports the above hypothesis. The reaction of CFC12 with NH<sub>3</sub> 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<sub>3</sub>, so the reaction can be written as equation (1).



But HCN was formed selectively when the ratio of NH<sub>3</sub>:CFC12 was *ca.* 2, therefore, the basic reaction is thought to be equation (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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## References

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