

Dismutation of CFC-12 to CFC-13 over Chromia–Alumina Catalyst†

A. Venugopal, K. S. Rama Rao, P. S. Sai Prasad and P. Kanta Rao*

Catalysis Section, Physical and Inorganic Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500 007, India

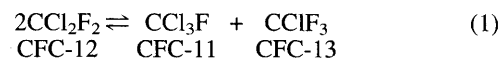
Selective transformation of CCl_2F_2 (CFC-12) to fluorine-rich CClF_3 (CFC-13) in the absence of HF over a chromia–alumina catalyst has been achieved.

Chlorofluorocarbons (CFCs) have become a major cause for concern in recent times due to their ozone depleting behaviour in the stratospheric region. In order to abate this environmental problem, much attention is focussed on the development of CFC alternatives *i.e.* HCFCs or HFCs, which are commonly prepared in the presence of HF by halogen exchange reactions over a catalyst. Another approach, dismutation of CFCs, leads to fluorine-rich and chlorine-rich compounds in the absence of HF. A process for the selective preparation of the former is a challenging task. Conversion of CCl_2F_2 into CClF_3 has hitherto been reported at very high temperatures, using a plasma torch in the presence of O_2 .¹ In this communication a novel approach to dismutation of CCl_2F_2 to mostly CClF_3 over a Cr_2O_3 – Al_2O_3 catalyst is reported.

Using fresh chromia–alumina catalyst‡ for the dismutation of CCl_2F_2 , no product formation was observed for the first 45 min, except the evolution of carbon oxides. Formation of chromium and aluminium oxy/hydroxy halides, the probable active sites for the reaction, might be the reason for this behaviour. Similar observations over a Cr_2O_3 based catalyst were also reported by Bechadargue *et al.*³ during the dismutation of a mixture of CCl_2F – CClF_2 (CFC-113) and CCl_3 – CF_3 (CFC-113a) and Coulson *et al.*⁴ during dismutation of CHClF_2 (HCFC-22).

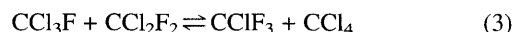
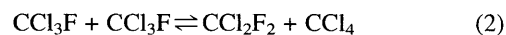
Characterization of fresh and used catalysts revealed that new phases were formed during the reaction. For example, the BET surface area of the fresh catalyst ($185 \text{ m}^2 \text{ g}^{-1}$) has been drastically reduced after the reaction, to $45 \text{ m}^2 \text{ g}^{-1}$. EPR spectra of the catalysts reveal (Fig. 1) the presence of γ -phase Cr^{5+}

species⁵ in the fresh catalyst ($g = 1.97$, $\Delta H_{pp} = 42 \text{ G}$) and the formation of β -phase electronically coupled Cr^{3+} species^{5,6} with a g value of 1.98 and ΔH_{pp} of 508 G, and amorphous carbon ($g = 2.001$, $\Delta H_{pp} = 21 \text{ G}$) in the used catalysts.⁷ A comparison of the carbon content of the catalyst after 45 min of activation ($3.01\% \text{ m/m}$) and after 40 h of steady state operation ($3.23\% \text{ m/m}$) revealed a negligible amount of coke formation during the reaction. The presence of a γ - Al_2O_3 phase in the fresh catalyst and γ - Al_2O_3 and $\text{AlF}_{1.65}(\text{OH})_{1.35} \cdot x\text{H}_2\text{O}$ ($x = 0.375$) phases in the used catalyst has been detected by X-ray diffraction (XRD). No crystalline phases due to any chromium oxides or oxy-halides were observed in either fresh or used catalysts. Generally, dismutation of CCl_2F_2 is expected to produce CCl_3F and CClF_3 in equal proportions. During the initial unsteady state where the catalyst interacts with the reactant CFC to produce the active species, formation of CCl_3F and CClF_3 [eqn. (1)] in equimolar proportions might not be expected.



However, in our study, a 1 : 1 ratio of CCl_3F and CClF_3 is not observed even after attaining a steady state (Table 1). This may be attributed to the participation of one of the products in further dismutation reactions. The dismutation reactivity of a CFC decreases with the decrease in the number of chlorine atoms or with the increase in the number of fluorine atoms attached to the carbon. It was also reported that for CClF_3 to participate in a dismutation reaction high temperatures of $>673 \text{ K}$ are required.⁸

Thus, the reactivity of the reactants and products of dismutation of CCl_2F_2 are in the order: $\text{CF}_4 < \text{CClF}_3 < \text{CCl}_2\text{F}_2 < \text{CCl}_3\text{F}$. Formation of CF_4 was not observed in the product mixture. A conversion of 80% for CCl_2F_2 was observed with the selectivities of 60, 30 and 5% towards CClF_3 , CCl_4 and CCl_3F , respectively, at a contact time of 0.4 s. The formation of CCl_4 may be explained as due to the participation of CCl_3F either along with the reactant or by itself in a secondary reaction [eqns. (2) and (3)].



Based on the values of the heat of formation of each component in eqns. (2) and (3) calculated by the semi-empirical method using AM1 Hamiltonian,⁹ the heats of reaction have been found to be -13.3 and $-22.9 \text{ kcal mol}^{-1}$ respectively ($1 \text{ cal} = 4.184 \text{ J}$). Hence the more probable secondary reaction of CCl_3F would be by the path shown in eqn. (3).

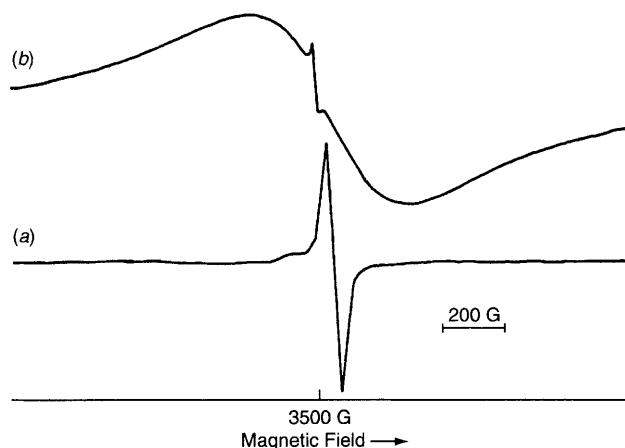


Fig. 1 EPR spectra of (a) fresh and (b) used catalysts

Table 1 Conversion and selectivity data in the dismutation of CFC-12 to CFC-13

Pretreatment	Flow rates/ l h^{-1}		Contact time/s	Conversion (%)	Selectivity (%)		
	Hydrogen	CFC-12			CFC-13	CFC-11	CCl_4
Hydrogen ^a	1.46	1.66	0.27	86	70	10	20
Hydrogen	2.30	1.66	0.22	86	60	8	30
Hydrogen	7.32	4.14	0.07	65	62	17	20
— ^a	—	1.66	0.40	80	60	5	30

^a Time on stream for 40 h.

When the catalyst is pretreated with hydrogen at a flow rate of 4.4 l h^{-1} for 3 h at 573 K prior to the reaction at the same temperature, the subsequent conversion is dependent mainly on the feed rate of CCl_2F_2 . A maximum conversion of 86% is achieved with 70, 20 and 10% selectivities for CClF_3 , CCl_4 and CCl_3F , at feed rates for H_2 and CCl_2F_2 of 1.46 and 1.66 l h^{-1} , respectively. After attaining the steady state, the reaction was carried out continuously for a period of 40 h, during which no deactivation was observed. The conversion of CCl_2F_2 decreased when the flow rates of H_2 and CCl_2F_2 were increased to 7.32 and 4.14 l h^{-1} , respectively. At these flow rates, the selectivities towards CClF_3 , CCl_3F and CCl_4 were 62, 17 and 20% respectively. Obviously, at lower contact times, CCl_3F might be desorbed from the catalyst surface without a sufficient amount participating in the secondary reaction.

The overall reaction may thus proceed according to eqns. (1) and (3) and to a lesser extent by eqn. (2), accounting for the higher selectivity towards fluorine-rich CClF_3 , through the catalytic dismutation of CCl_2F_2 in the absence of HF.

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Footnotes

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‡ 10% m/m Cr_2O_3 impregnated on $\gamma\text{-Al}_2\text{O}_3$ (Harshaw, Al-111-61E, sieved to 18/25 BSS mesh, BET surface area $234 \text{ m}^2 \text{ g}^{-1}$), synthesised using CrO_3 as a precursor and then dried and calcined in air at 673 K for 5 h, was used

for the dismutation of CCl_2F_2 . The reaction was performed in a fixed bed micro-reactor (catalyst 0.5 ml, reaction temperature 573 K) interfaced with an on-line gas chromatograph equipped with a thermal conductivity detector. The product analysis was carried out using a 30% squalane ChW (HP) column (length 10', diameter $\frac{1}{8}$ " and GC-MS (VG Micromass 7070 H, UK, 30 eV, 100 μA , EI mode). The ion masses of the CFCs from the mass spectra are in line with those reported recently by Simmonds *et al.*² The catalyst was characterized by BET surface area using a conventional all-glass high vacuum unit (10^{-6} Torr) and X-ray diffraction patterns were recorded on a Phillips PW 1051 diffractometer using Ni-filtered $\text{Cu-K}\alpha$ radiation. EPR spectra were recorded at room temperature on a Bruker ER 200 D-SRC X-band spectrometer with 100 KHz modulation. The carbon content of the catalyst was determined on a Perkin-Elmer 240-B microanalyser.

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