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Conversion of 1,1,2-trichlorotrifluoroethane to 1,1,1-trichlorotrifluoroethane and 1,1-dichlorotetrafluoroethane over aluminium-based catalysts

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Abstract

Conversion of CCl_2FCClF_2 to CCl_2FCF_3 is achieved in the temperature range, 593–713 K, under flow conditions by using the catalysts, β-AlF_3 or γ-alumina, prefluorinated with CCl_2F_2 or SF_4. Aluminium-based catalysts favour the formation of asymmetric isomers in the chlorofluoroethane series, hence CCl_3CF_3 is also a significant product. More highly chlorinated materials, containing ≥4 Cl atoms, and $CClF_2CF_3$ are minor products. Product composition data provided evidence for the possible pathway $CCl_2FClF_2 \rightarrow CCl_3CF_3 \rightarrow CCl_2FCF_3$. The isomerisation step is believed to be intramolecular and is facile. The apparent fluorination step is best described as a dismutation. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Chlorofluorocarbons (CFCs) which were discovered in 1930 by Thomas Midgley, had a variety of industrial applications. The compounds are highly stable and remarkably unreactive. Hence, once released into the atmosphere, deliberately or inadvertently, they are very long-lived. They are sources of stratospheric chlorine and as such, perturb the O_3/O_2 equilibrium. Therefore, CFCs have been classified as controlled substances in the Montreal Protocol and its amendments. Accordingly, their production and usage have been terminated in the developed countries and will finish by 2010 in developing countries.

This situation resulted in two major research and development activities. The first involves the design and implementation of routes to the large-scale synthesis of CFC-alternatives, notably 1,1,1,2-tetrafluoroethane, CF_3CH_2F (HFC-134a), since it can be used as a 'drop-in' replacement for the widely used refrigerant, CCl_2F_2. Work in this area has been carried out largely by chemical companies in the developed world [1], although our research groups have been heavily involved in researching fundamental aspects of this topic ([2–4] and references therein). The second activity involves devising methods for the destruction of CFCs in situations where recycling is not an option. Equally important is the requirement for stocks of CFCs, presently held in developed and developing countries, to be converted to useful, environmentally-friendly chemical feedstock. Hence, there exists an urgent need either to destroy CFCs or to convert them into useful compounds.

Incineration of CFCs is energy intensive and, if not properly performed, can result in the release of toxic products. Dehalogenation by chemical means is a more elegant alternative; several routes, with or without photochemical intervention, have been described [5–9] but, although they are excellent laboratory methods and could be feasible for CFC removal from gas streams after condensation, scale-up is likely to present economic and technical difficulties. An alternative approach is the catalytic oxygenation over acidic oxide catalysts of C_1 and C_2 CFCs to give CO_2 and hydrogen halides. A variety of catalysts, for example, zeolites, TiO_2, ZrO_2 or V_2O_5, modified in some cases by sulfuric or phosphoric acid, has been reported [10–18]. Relatively high temperatures (ca. 800 K) are required, particularly for C_2 CFCs, and catalyst deactivation due to metal fluoride

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formation is a disadvantage. Because of this constraint, the approach is also more suited to the removal of CFCs from dilute gas streams, rather than for large quantities of CFC containing gases. It should be noted that this approach is not entirely benign from an environmental standpoint.

Another approach is to convert a CFC into a useful chemical reagent or feedstock. One example is HCN production from CCl_2F_2 by heterogeneous catalytic ammonolysis [19–21]. A second is the catalytic hydrodechlorination of CCl_2FCClF_2 (CFC-113) to give halo-olefins, which are then used in further reactions [22–23]. Depending on the catalyst used, $CClF{=}CF_2$ or $CHF{=}CF_2$ may be formed selectively and the CFC-alternative, CF_3CH_2F (HFC-134a), is accessible from the latter by catalytic addition of HF [24].

As illustrated above, more than one type of catalytic reaction can be used and these include halogen exchange with HF, isomerization, dismutation, dehydrohalogenation and hydrodehalogenation. All may be considered as elements of schemes that transform CFCs into useful intermediates for the synthesis of either hydrofluorocarbons (HFCs), the designated substitutes for CFCs or to hydrochlorofluorocarbons (HCFCs), which are transitional compounds. Our objective is to avoid the use of HF as a volatile reagent for the transformation of CCl_2FCClF_2 (CFC-113) to CH_2FCF_3 (HFC-134a) by the sequence of reactions (Eqs. (1)–(3)) that comprises isomerization of CCl_2FCClF_2 to CCl_3CF_3, dismutation of CCl_3CF_3 to give CCl_2FCF_3 and CCl_3CClF_2 and hydrodechlorination of CCl_2FCF_3 to CH_2FCF_3.

$$CCl_2FCClF_2 \rightarrow CCl_3CF_3 \tag{1}$$

$$2CF_3CCl_3 \rightarrow CClF_2CCl_3 + CF_3CCl_2F \tag{2}$$

$$CCl_2FCF_3 + 2H_2 \rightarrow CH_2FCF_3 + 2HCl \tag{3}$$

Each reaction of this multi-step process requires a suitable catalyst. In this paper, we describe the use of three fluorinated aluminium-based catalysts to achieve the conversion of CCl_2FCClF_2 (CFC-113) to CCl_2FCF_3 (CFC-114a).

2. Experimental

2.1. Catalyst preparation and characterization

CFC-fluorinated γ-alumina was obtained by fluorinating, using CCl_2F_2 (CFC-12), γ-alumina (Degussa, p.a.). This had a specific surface area of 255 $m^2\,g^{-1}$, a size range between 160 and 325 μm and a bulk density of 0.58 $g\,cm^{-3}$. The alumina samples were dried by means of a nitrogen stream (flow reactor) at 573 K for 4 h. The solids were then activated with a CCl_2F_2 gas stream at 573 K for 2 h at a flow rate of 3.5 $l\,h^{-1}$. After fluorination, the catalyst had a surface area of 135 $m^2\,g^{-1}$ and contained 21.3% fluoride and less than 0.5% chloride. Before use, all samples were left in contact with an N_2/CCl_2FCClF_2 gas stream. In agreement with an earlier finding [25], X-ray phase analysis revealed pure γ-alumina but there was also evidence for the presence of an amorphous phase.

Sulfur tetrafluoride-fluorinated γ-alumina was also prepared in situ. Thus, alumina was placed in the reactor, calcined at 523 K under dry nitrogen flow (2.5 $l\,h^{-1}$) and finally fluorinated with a SF_4/N_2-gas stream, containing approximately 20% SF_4, at the same temperature for 2 h. The surface area of this SF_4-fluorinated γ-alumina was 67 $m^2\,g^{-1}$ and it contained 47.1% fluoride. XRD analysis indicated the presence of γ-alumina and, possibly, an amorphous phase.

β-Aluminium(III) fluoride was prepared by temperature programmed thermal dehydration of commercial $AlF_3\cdot 3H_2O$ (Aldrich) according to the published synthesis [26]. It was less susceptible to hydrolysis than SF_4-fluorinated γ-alumina. Its surface area was 26.3 $m^2\,g^{-1}$ and its fluorine content 69.7% (AlF_3 req. 67.9%).

All solids prepared were examined by X-ray powder diffraction (XRD 7 Seiffert-FPM, Freiburg; Cu Kα radiation). Specific surface areas were determined by the BET method using N_2 as adsorbate (ASAP 2000, Micromeritics). Fluoride was determined using a published procedure [27]. On the basis of pyridine adsorption FTIR measurements, β-AlF_3 exhibits Lewis surface acidity and γ-aluminas with fluorine contents in the range reported here, exhibit mainly surface Lewis acidity [28]. The surface properties of the solids do not change during considerable periods of use [28,29], although, very small increases in fluorine content are to be expected for the fluorinated γ-aluminas. These will be accompanied by a decrease in Brønsted acidity [17].

2.2. Catalysis under steady flow conditions

Kinetic investigations were carried out in a stainless steel flow system, Fig. 1. Dinitrogen, used as a carrier gas, was adjusted as necessary by a flow control valve. By passage of the controlled N_2 flow through a saturator, containing the CFC held at a fixed temperature, the gas stream was fed with

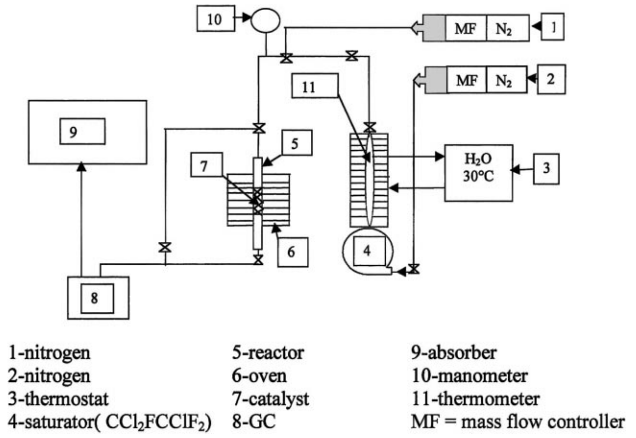

Fig. 1. Apparatus for the temporal investigations under steady flow conditions.

a constant proportion of CFC. This could be varied by change in temperature of the saturator. The CFC/N_2 gas stream was passed via copper gas lines into a nickel catalytic reactor containing a catalyst sample, previously fluorinated, where appropriate, in situ. An adjustable furnace controlled the reactor temperature. Product streams entered a six-port sampling valve via heated copper gas lines to ensure that the less volatile, highly chlorinated components formed, did not condense. On-line quantitative analyses were performed using a capillary gas chromatograph (GC-14A, Shimadzu, column Pona, 25 m). In some cases, GCMS (Shimadzu QP 5000) was used for product analyses; this was particularly useful for identification of isomeric mixtures. The RD uncertainty in the kinetic measurements was within the range ± 3% in all cases.

The near identical boiling points of the $C_2Cl_2F_4$ isomers made their individual quantification by GC problematic, particularly if one isomer was in large excess. Therefore, it was possible that the isomer $CClF_2CClF_2$ would be under-represented in the on-line product analyses. However, independent GC/MS measurements indicated that $CClF_2CClF_2$ was present in the fraction only as a very minor component. Moreover, ^{19}F NMR spectroscopic analysis of product mixtures provided supporting identification that was unambiguous. The spectral parameters obtained, for $CClF_2CClF_2$, δ_F: 71.1; CCl_2FCF_3, δ_F: 77.0(q) and −84.1(d), J_{FF}: 6 Hz (δ values w.r.t. CCl_3F ext.), were in good agreement with the literature [30–33] and with the spectra of authentic samples.

3. Results

3.1. The catalysts

Three closely related catalysts were chosen for this study: β-aluminium(III) fluoride, γ-alumina fluorinated by CCl_2F_2 and γ-alumina fluorinated by SF_4. The preparation and characterization of these materials have been described above. It has been shown previously that β-AlF_3 is a significantly more active catalyst in halogen exchange reactions than the more thermodynamically stable α-phase [28,29]. Fluorination of γ-alumina by any fluorinating agent, including CFCs, results in a significant decrease in surface area, an effect that is due to the crystallisation of the fluoride phase formed during the reaction. The nature of the catalytically active sites formed on the surface, appears to be independent of the CFC used and is related closely to the surface of catalytically active β-AlF_3 [25]. γ-Alumina, fluorinated using SF_4, promotes the dehydrochlorination of unsymmetrical chloroethanes at room temperature and this material has been used as the precursor for supported organic layer catalysts that are active in room temperature halogen exchange [34,35]. Unlike CFC-fluorinated γ-aluminas, whose surface characterisation is well-documented [25], the SF_4-fluorinated material has not been investigated so extensively, althougth the limited characterization data obtained in the present work suggest that it is a similar material.

3.2. Isomerization and dismutation reactions under steady flow conditions

In order to prevent any limitation of the catalytic reactions by diffusion processes in the gas phase, the dependence of the degree of conversion on the residence time was investigated over the range 0.5–5.0 s. In all cases, the conversion rate reached a plateau after ca. 0.8 s residence time. Thereafter, changes in the rate of conversion were negligible. The degree of conversion did not depend significantly on changes in the concentration of CCl_2FCClF_2 in the gas phase over the range 5–35%. Thus, the nominal concentration of feedstock in the gas phase did not influence the results obtained, at least in this concentration range and possible uncertainties in the adjustment of the gas phase feedstock concentration were disregarded. For all investigations described below, the reaction conditions were chosen as a contact time ca. 1 s and 10% v/v for the CFC-reactant concentration.

The characteristic gas phase compositions obtained for the catalysed dismutation/isomerisation reactions of CCl_2FCClF_2 over the three catalysts are summarised in Table 1. Here and in the figures referred to below, the small quantities of the symmetrical isomer, $CClF_2CClF_2$, have been included with the CCl_2FCF_3 fraction, since in all cases, the asymmetric isomer was dominant. In all reactions, a nearly identical Cl/F-balance between the overall products and the CCl_2FCClF_2 feedstock was obtained within experimental error (cf. the last two columns in Table 1). The dependence on temperature of the conversion of CCl_2FCClF_2 to the products, CCl_3CF_3, CCl_2FCF_3 and CCl_3CClF_2 over CCl_2F_2-fluorinated γ-alumina, β-AlF_3 and SF_4-fluorinated γ-alumina are compared in Fig. 2(a)–(c). The product concentrations are given in terms of molar concentrations contained in the gas phase effluent.

Most of the CCl_2FCClF_2 was converted into CCl_3CF_3 and CCl_2FCF_3 as the major products over CCl_2F_2- or SF_4-fluorinated γ-alumina throughout the temperature range investigated. The concentration of CCl_2FCClF_2 was almost unaffected by temperature change, Fig. 2(a) and (c), the formation of the desired product, CCl_2FCF_3, was constant or increased slightly but tetrachloroethene (1110) became relatively more important with increasing temperature, Table 1. The latter almost certainly originated from hexachloroethane, which is not thermally stable and decomposed forming C_2Cl_4 and dichlorine. Thus, an unwanted olefinic product accompanied slight increases in the yield of the desired product, CCl_2FCF_3 and the temperature should be kept as low as possible.

The three catalysts differed in the temperature at which the onset of reaction was observed. No reaction was observed over CCl_2F_2-fluorinated γ-alumina at 520 K, whereas it was detected over SF_4-fluorinated alumina ca.

Table 1
Product distribution (mol%) for the reactant CCl_2FCClF_2 (CFC-113) at various catalysts for different temperatures

Catalyst	T (K)	CFC[a]									Halogen balance[c]		
		113	113a	114a[b]	115	112a	112	111	1110	110	$\sum$CFC	n_F	n_{Cl}
γ-Alumina/CCl_2F_2	593	3.2	58.4	23.8	0.6	7.1	0.7	2.6	2.1	1.5	100.0	3.03	2.97
	633	3.7	57.0	23.8	0.4	8.3	0.8	2.6	1.6	1.4	99.6	3.01	2.99
	713	4.4	34.6	29.7	9.1	4.9	0.8	1.6	14.4	0.6	100.1	3.01	2.99
β-AlF_3	593	82.1	12.9	2.5	0.0	2.2	0.3	0.0	0.0	0.0	100.0	3.00	3.00
	633	24.6	38.1	20.6	0.0	13.0	1.6	1.6	0.2	0.3	100.0	3.01	2.99
	693	6.4	44.6	31.2	0.3	8.1	1.2	2.7	4.4	1.0	99.9	3.01	2.99
γ-Alumina/SF_4	593	2.6	61.7	21.9	1.5	6.2	0.5	2.2	2.0	1.3	99.9	3.04	2.96
	633	3.4	47.8	24.8	6.2	6.0	0.7	2.2	7.8	1.2	100.1	2.99	3.01
	693	3.7	34.2	23.6	14.5	5.2	0.8	1.9	15.3	0.8	100.0	2.94	3.06

[a] 113, CCl_2FCClF_2; 113a, CCl_3CF_3; 114a, CCl_2FCF_3; 115, $CClF_2CF_3$; 112a, CCl_3CClF_2; 112, CCl_2FCCl_2F; 111, CCl_3CCl_2F; 1110, C_2Cl_4; 110, C_2Cl_6.
[b] Includes CFC-114, $CClF_2CClF_2$, shown by NMR spectroscopy to be present as a very minor component.
[c] Ratio F:Cl $= n_F{:}n_{Cl}$.

520 K, Fig. 2(c). In contrast, β-AlF_3 was catalytically inactive below 590 K, Fig. 2(b), and below ca. 640 K, the proportion of unchanged CCl_2FCClF_2 was significant. This is illustrated also in Fig. 3 where the concentrations of all products formed using the three catalysts at 633 K are compared using a logarithmic scale. While SF_4- and CCl_2F_2-fluorinated γ-aluminas exhibited rather similar product distributions, β-AlF_3 showed small but significant differences, at least in the early stage of its catalytic lifetime as studied here. A significantly higher amount of unconverted CCl_2FCClF_2 was present compared with the other catalysts. However, the proportions of CCl_3CF_3 and CCl_2FCF_3 were almost identical whatever catalyst was used. In practice therefore, the selectivity of β-AlF_3 towards the conversion of CCl_2FCClF_2 to the desired product, CCl_2FCF_3, was greater than those of the fluorinated γ-aluminas. The formation of the products, C_2Cl_6 and C_2Cl_4, was also relatively less important, Fig. 3.

In order to obtain more information about the reaction pathway, other members of the series, $C_2Cl_{6-n}F_n$ were used as reactants. The behaviour of CCl_3CF_3 (CFC-113a), CCl_2FCF_3 (CFC-114a) and CCl_3CClF_2 (CFC-112a) over CCl_2F_2-fluorinated γ-alumina at a temperature of 713 K is compared with that of CCl_2FCClF_2 in Fig. 4; more detailed data are given in Table 2. At 713 K there was no difference in the product distribution obtained from feedstock, CCl_2FCClF_2 or CCl_3CF_3, suggesting strongly that the isomerization equilibrium between the two isomers was very rapidly established at this temperature. The product distributions observed using CCl_2FCF_3 or CCl_3CClF_2 as

Table 2
Product distributions (mol%) for various CFC reactants over CCl_2F_2-fluorinated γ-alumina at three temperatures

Reactant[a]	T (K)	CFC[a]									Halogen balance[c]		
		113	113a	114a[b]	115	112a	112	111	1110	110	$\sum$CFC	n_F	n_{Cl}
CFC-113	593	3.2	58.4	23.8	0.6	7.1	0.7	2.6	2.1	1.5	100.0	3.03	2.97
	633	3.7	57.0	23.8	0.4	8.3	0.8	2.6	1.6	1.4	99.6	3.01	2.99
	713	4.4	34.6	29.7	9.1	4.9	0.8	1.6	14.4	0.6	100.1	3.01	2.99
CFC-113a	593	1.6	65.3	21.2	0.2	5.8	0.6	2.3	1.6	1.4	100.0	3.01	2.99
	633	3.8	54.8	26.1	0.6	6.6	0.8	2.3	4.0	1.2	100.2	3.00	3.00
	713	4.3	34.2	31.1	8.2	4.5	0.7	1.2	15.4	0.5	100.1	2.92	3.08
CFC-114a	593	0.2	4.2	93.5	2.1	0.0	0.0	0.0	0.0	0.0	100.0	3.98	2.02
	633	0.6	8.2	84.9	6.4	0.0	0.0	0.0	0.0	0.0	100.1	3.98	2.02
	713	1.3	20.1	52.5	24.3	1.0	0.2	0.1	0.7	0.0	100.2	3.98	2.02
CFC-112a	593	2.2	42.1	7.8	0.3	11.8	1.1	14.6	13.4	6.7	100.0	2.06	3.94
	633	2.5	35.1	9.1	0.6	11.6	1.2	14.8	18.6	6.7	100.2	1.92	4.08
	713	2.4	36.1	8.7	0.5	12.1	1.2	14.3	18.4	6.4	100.1	1.94	4.06

[a] 113, CCl_2FCClF_2; 113a, CCl_3CF_3; 114a, CCl_2FCF_3; 115, $CClF_2CF_3$; 112a, CCl_3CClF_2; 112, CCl_2FCCl_2F; 111, CCl_3CCl_2F; 1110, C_2Cl_4; 110, C_2Cl_6.
[b] Includes CFC-114, $CClF_2CClF_2$, shown by NMR spectroscopy to be present as a very minor component.
[c] Ratio F:Cl $= n_F{:}n_{Cl}$.

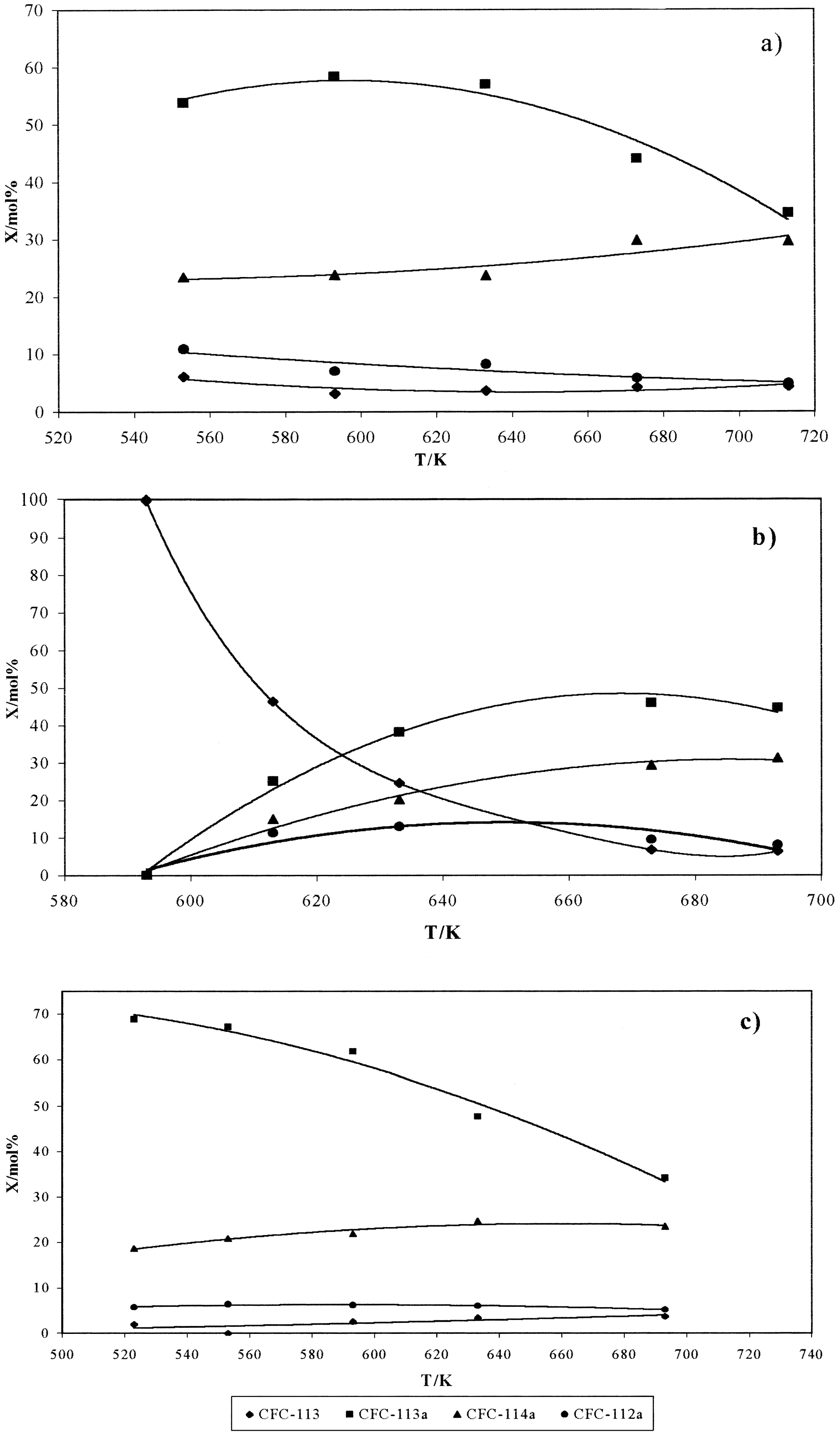

Fig. 2. Variation between temperature (*T*/K) and product composition (*X*/mol%) for CCl_2FCClF_2 over, (a) CCl_2F_2-fluorinated γ-alumina; (b) β-AlF_3; (c) SF_4-fluorinated γ-alumina. Residence time 0.9 s, feed 10 vol.% CCl_2FCClF_2 in N_2. Key for CFCs: (◆) 113, CCl_2FCClF_2; (■) 113a, CCl_3CF_3; (▲) 114a, CCl_2FCF_3; (●) 112a, CCl_3CClF_2.

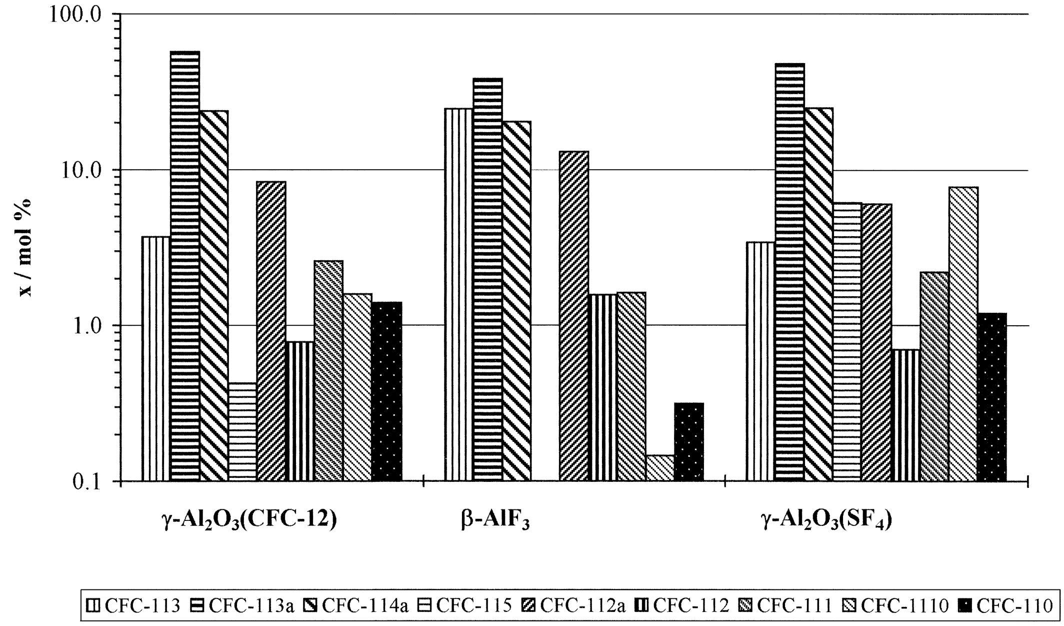

Fig. 3. Product compositions on a logarithmic scale, from the reactions of CCl_2FCClF_2 at 633 K over, (a) CCl_2F_2 (CFC-12)-fluorinated γ-alumina; (b) β-AlF_3; (c) SF_4-fluorinated γ-alumina. Residence time 0.9 s, feed 10 vol.% CCl_2FCClF_2 in N_2. Key for CFCs: 113, CCl_2FCClF_2; 113a, CCl_3CF_3; 114a, CCl_2FCF_3; 115, $CClF_2CF_3$; 112a, CCl_3CClF_2; 112, CCl_2FCCl_2F; 111, CCl_3CCl_2F; 1110, C_2Cl_4; 110, C_2Cl_6.

reactants, Table 2, followed the pattern expected from those obtained using CCl_2FCClF_2 or CCl_3CF_3. Fluorine to chlorine proportions in the reactants determined those found in the products. Thus, using CCl_2FCF_3 as feedstock, the F:Cl ratio in the product mixture overall was 4:2. The corresponding value from CCl_3CClF_2 was 2:4. A greater proportion of $CClF_2CF_3$ was found at 713 K when using CCl_2FCF_3 and greater proportions of the chlorinated compounds, CCl_3CCl_2F, C_2Cl_6 and C_2Cl_4, were observed at all temperatures when CCl_3CClF_2 was used as the reactant. This behaviour suggested that, in these cases also, equilibria were rapidly established.

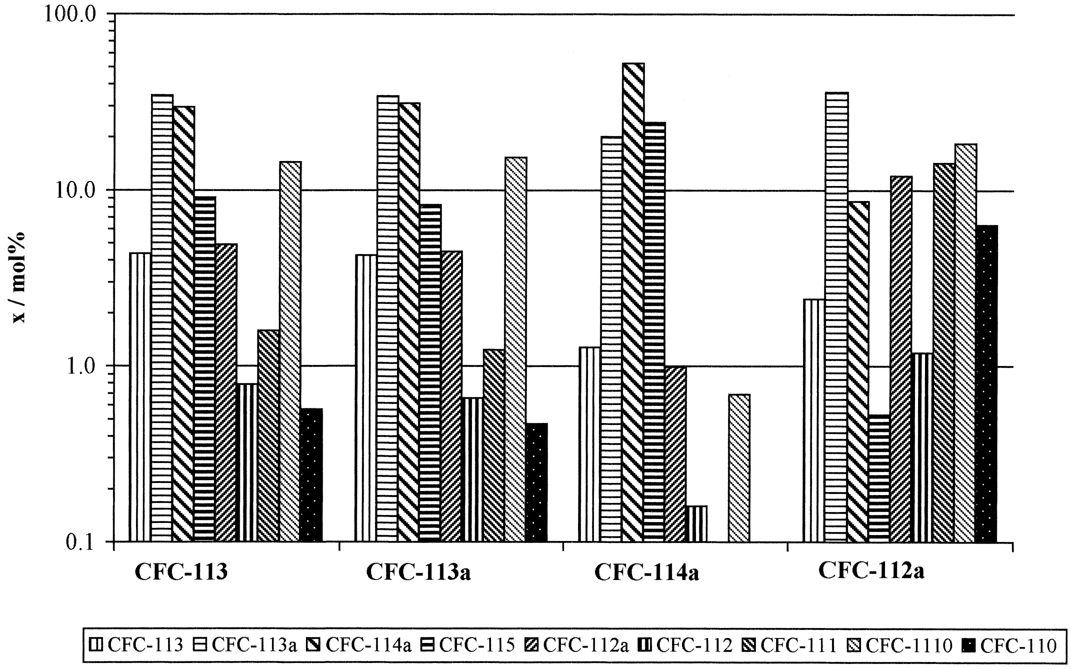

Fig. 4. Product compositions on a logarithmic scale, from the reactions of CCl_2FCClF_2 (CFC-113), CCl_3CF_3 (CFC-113a), CCl_2FCF_3 (CFC-114a) and CCl_3CClF_2 (CFC-112a) over CCl_2F_2-fluorinated γ-alumina at 713 K. Residence time 0.9 s, feed 10 vol.% CFC in N_2. See Fig. 3 caption for CFC key.

4. Discussion

The most noteworthy finding from this study is the relatively large quantities of CCl_2FCF_3 that are formed from CCl_2FCClF_2, in addition to the expected formation of the isomer, CCl_3CF_3 (113a).

Isomerization of CCl_2FCClF_2 in the presence of aluminium(III) chloride under moderate conditions, was first observed many years ago [36]. A re-investigation of the reaction at room temperature, undertaken as a precursor to the present study, has shown that the isomerization, which is intramolecular, occurs not at an aluminium(III) chloride site but at Al(III) in a disordered chlorofluoride environment. The latter site is generated via chlorination reactions between CCl_2FCClF_2, or more highly chlorinated CFCs, and aluminium(III) chloride [37]. At room temperature however, isomerization of $CClF_2CClF_2$ was not observed.

The intramolecular nature of the isomerization of CCl_2FCClF_2 suggests that this species is adsorbed in a dissociative fashion at an isomerization site in contrast to its adsorption at sites where halogen exchange (dismutation) can occur. This implies that the acidity of an isomerization site is greater than that of a Lewis acid site at which halogen exchange occurs but there is, at present, no direct evidence for this proposal. Aluminium chlorofluoride is recognised as a highly Lewis acidic material and on electronegativity grounds, replacement of Cl by F might be expected to increase Lewis acidity. Calculation of F^- ion affinities for *isolated molecular* $AlCl_{3-n}F_n$ species suggests that order is $AlF_3 < AlClF_2 < AlCl_2F < AlCl_3$ [38] or $AlCl_3 < AlClF_2 < AlCl_2F$, AlF_3 [39]. The differences among the data from the two studies are, however, very small and the important conclusion in each case is that significant Lewis acidity is to be expected at a surface Al(III) site in an halogenated environment.

Any rationalisation proposed for the reactions studied here must account for the formation of CCl_3CF_3 and CCl_2FCF_3 as major products and must recognise that fluorination of a C–Cl species by Al–F is thermodynamically unfavourable [3,37]. The isomerization of CCl_2FCClF_2 to the thermodynamically preferred isomer, CCl_3CF_3 (Eq. (1)) is facile and, by analogy with the behaviour on other catalysts [37,40], is proposed to occur via an intramolecular mechanism. It is likely to be site specific. The very similar distributions of products that are observed under flow conditions, irrespective of whether CCl_2FCClF_2 or CCl_3CF_3 are used as feedstock (Table 2), argue strongly that the equilibrium between the two isomers is rapidly established. However, the situation for the isomerization of $CClF_2CClF_2$ (CFC-114), Eq. (4), is less clear.

$$CClF_2CClF_2 \rightarrow CCl_2FCF_3 \qquad (4)$$

Thermodynamically, CCl_2FCF_3 is the more stable isomer and the observation that it is a major product under most conditions (Tables 1 and 2) is not unexpected if thermodynamic control is the major factor. However, the isomerization reaction is not facile kinetically [37,40] and it is therefore unlikely that Eq. (4) is an important pathway to CCl_2FCF_3 in this situation.

The ostensible fluorination steps that convert $C_2Cl_3F_3$ to CCl_2FCF_3 are described most obviously by dismutation reactions. These could involve CCl_3CF_3 (Eq. (2)) or CCl_2FCClF_2 (Eq. (5)).

$$2CCl_2FCClF_2 \rightarrow CClF_2CClF_2 + CCl_3CClF_2 \qquad (5)$$

If the latter reaction were dominant, significant quantities of $CClF_2CClF_2$ would be expected in product mixtures, since, as indicated above, the isomerization to the asymmetric isomer is not facile. The former reaction (Eq. (2)) however, has a severe disadvantage from a kinetic standpoint that catalytic activation of the CF_3 group is required. There is abundant evidence from synthetic work involving these and similar compounds, that the chemical reactivity of both C–Cl and C–F bonds decreases as the fluorine content of the molecule increases [41]. Activation of a CF_3 group, which is required by Eq. (2), is a disadvantage for this pathway, even though the reaction is probably thermodynamically favourable. Similar considerations apply to the formation of the minor product, $CClF_2CF_3$.

Analyses of product distributions in themselves do not permit an unambiguous differentiation to be made between the possible routes to CCl_2FCF_3 from CCl_2FCClF_2. On balance however, the pathway described by Eq. (1) then Eq. (2), is preferred. What has been definitely established, however, is that these aluminium-based catalysts are capable of achieving the conversion of unwanted CCl_2FCClF_2 to CCl_2FCF_3 which can then undergo hydrodechlorination to give the useful compound, CH_2FCF_3.

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