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Catalytic reactions of chlorofluoroethanes at fluorinated alumina and chromia aerogels and xerogels

A comparison of reaction pathways in alumina- and chromia-based catalysts

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Dedicated to the memory of Dr. Drago Lutar (1947–2000)

Abstract

The differences in the dynamic behaviour of 1,1,2-trichlorotrifluoroethane over fluorinated alumina or chromia catalysts at moderate temperatures are significant. Alumina-based catalysts favour the isomerization of CCl_2FCClF_2 followed by the dismutation of CCl_3CF_3 so formed. Fluorinated chromias are less selective since halogen exchange and isomerization reactions both occur. An explanation in terms of the differences in Al–X, X = Cl or F, bond energies compared with their Cr–X counterparts is suggested. The identity of the catalyst precursor has little effect in the chromium case and no effect in the case of aluminium. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Aerogel; Xerogel; Alumina; Chromia; Chlorofluoroethane

1. Introduction

Combination of sol–gel chemistry with different drying techniques enables the preparation of materials consisting of micro- to nanometer-sized particles, arranged either in aerogel or xerogel structures. Besides other specific properties, such solids possess interestingly high surface areas and distinctively different porosity. In addition, materials with high surface areas very often provide better catalytic activity than is found using those of low surface area. The combined synthetic approach is therefore frequently used to prepare catalysts based, particularly, on metal oxides [1,2].

For heterogeneous catalytic fluorination and related reactions, aluminium(III) and chromium(III) oxides are used as catalysts. As has been shown by numerous authors [3–6], the oxidic catalysts become, at least in the surface region, fluorinated during use. Due to this fluorination, drastic changes in the chemical composition, for example, formation of fluorides or/and oxofluorides, and in the topological properties occur. Although metal oxides obtained by conventional precipitation processes have been investigated extensively, little is known about the ability of aerogel- or xerogel-derived materials to function as catalysts in fluorination and related reactions.

In recent investigations, we have studied the surface changes of aerogel and xerogel alumina and chromia following gas phase fluorination [7,8]. Due to the synthesis procedure, both groups of starting oxides exhibit high surface areas and are either of low crystallinity or are completely amorphous to X-rays. Fluorination yields materials with distinctive differences. Even at moderate temperatures, a high degree of fluorination is obtained when alumina-based precursors are used. Bulk conversion to crystalline fluoride phases is observed; the main consequences are large reductions in porosity and surface area. In contrast, fluorination of chromia-derived materials is limited mainly to the surface; the bulk characteristics of the precursors are only partly modified and there is much lower overall incorporation of fluorine. Fluorinated alumina aerogels or xerogels

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generally exhibit surface areas that are an order of magnitude smaller than similarly treated chromia materials and have up to six times higher fluorine contents.

We have recently shown that conversion of 1,1,2-trichlorotrifluoroethane (CFC-113) to 1,1-dichlorotetrafluoroethane (CFC-114a) can be achieved at moderate temperatures under flow conditions using the catalysts, β-aluminium(III) fluoride or γ-alumina, pre-fluorinated with dichlorodifluoromethane or sulfur tetrafluoride. Since aluminium-based catalysts favour the formation of asymmetric isomers, 1,1,1-trichlorotrifluoroethane (CFC-113a) is also a major product [9]. This work is part of a larger study designed to develop routes for the conversion of CCl_2FCClF_2 to environmentally acceptable compounds. The investigation of fluorinated aerogel and xerogel materials was an obvious extension and we have studied the catalytic behaviour of materials derived from alumina and chromia with respect to their behaviour towards CCl_2FCClF_2. There are significant differences in the distributions of products obtained using alumina- or chromia-derived catalysts and the reasons for the differences have been explored by investigating the effect on product distribution of varying the contact time between catalyst and the organic reactant.

2. Results and discussion

2.1. Properties of the catalysts

Table 1 summarises the characteristic data of the catalysts used for this investigation. The general behaviour of both groups of catalysts resembled the behaviour of alumina- [7,10] or chromia-based [8] aerogels or xerogels previously reported.

Conditioning at 723 K in air transformed raw alumina-based aerogels or xerogels to high surface area, γ-alumina materials. A partial shrinkage of the aerogel structure occurred. This resulted in a slight reduction of porosity and in a beneficial increase of the mechanical strength of the pellets. A very high degree of fluorination was observed even at the relatively low temperatures used in the present work (623 K). Oxide was converted largely to crystalline fluoride. In highly fluorinated samples the only phase detected by XRD was α-AlF_3; the presence of an amorphous phase was also evident. In line with the previous investigations [7,10], bulk crystallisation of the fluoride phase reduced considerably the surface area and porosity of the starting oxide. The higher surface areas of fluorinated

Table 1
Some properties of the catalysts

Sample[a]		Preparation		BET surface area ($m^2\,g^{-1}$)	F content (%)	Form	XRD analysis[b]
		Reagent	Temperature (K)				
Alumina							
Aerogel	Al/A/S	Ethanol	573	319	–	Soft pellets	AlOOH (boehmite)
	Al/A/AH	Air	723	320	–	Soft pellets	γ-Alumina (LC)
	Al/A/F	CHF_3	623	94	58.6	Soft pellets	α-AlF_3 + AM
	Al/A/H	HF/N_2	623	68	60.7	Soft pellets	α-AlF_3 + AM
Xerogel	Al/X/S	Air	393	306	–	Hard pellets	nd
	Al/X/AH	Air	723	284	–	Hard pellets	γ-Alumina (LC)
	Al/X/F	CHF_3	623	24	58.2	Hard pellets	α-AlF_3 + AM
	Al/X/H	HF/N_2	623	50	46.5	Hard pellets	γ-Alumina (LC)
Alumina/F		CCl_2F_2	623	51	19.3	Hard pellets	γ-Alumina + AM
β-AlF_3		$AlF_3 \cdot 3H_2O$	693	30	nd[c]	Hard pellets	β-AlF_3
Chromia							
Aerogel	Cr/A/S	Methanol	573	594	–	Soft pieces	AM
	Cr/A/VH	Vacuum	723	355	–	Soft pieces	AM
	Cr/A/F	CHF_3	623	255	13.1	Soft pieces	AM
	Cr/A/H	HF/N_2	623	214	21.3	Soft pieces	AM
Xerogel	Cr/X/S	Methanol	473	518	–	Pieces	AM
	Cr/X/VH	Vacuum	723	256	–	Hard pieces	AM
	Cr/X/F	CHF_3	623	80 (50–104)	8.8	Heterogeneous powder	AM + α-chromia (LC)
	Cr/X/H	HF/N_2	623	148	15.9	Hard pieces	AM
Chromia/F		CCl_2F_2	623	38	2.5	Hard pellets	AM
β-CrF_3		$(NH_4)_3CrF_6$	723	36	nd[c]	Hard pellets	β-CrF_3

[a] Al/A: alumina aerogel; Al/X: alumina xerogel; Cr/A: chromia aerogel; Cr/X: chromia xerogel; S: starting material; AH: air treated; F: CHF_3; H: HF/N_2; VH: vacuum treated.

[b] Phases detected by XRD, LC: low crystallinity; AM: amorphous.

[c] nd: not determined.

alumina aerogels can be ascribed primarily to the differences in the initial porosity of alumina aerogels or xerogels [7].

Raw chromia materials prepared by the CrO_3–methanol route were green, completely amorphous to X-rays and had extraordinarily high surface areas. Organic residue present after the autoclave treatment consisted of surface formiate species that were removed by evacuation at 723 K, as indicated by FTIR. In line with previous findings [8], thermal decomposition of the organic phase resulted in partial reduction of chromia, yielding brown-black, pyrophoric materials. Subsequently, the colour was unaffected by both successive treatment steps, re-oxidation on exposure to air and fluorination, suggesting that the change in colour occurring during evacuation was due primarily to the presence of traces of the organic decomposition products. In the previous work on ethanol-derived materials [8], only a partial elimination of thermally more stable acetate species was observed under similar evacuation conditions. In the case of the methanol-derived materials used in the present study, the almost complete removal of the organic residue resulted in the formation of highly reactive chromia materials with lower mechanical stability. Both characteristics are believed to be responsible for considerable reductions in surface area that were observed at all steps that led to the fluorinated product (Table 1). This reduction is most evident in the case of a more compact xerogel. The organic precursor (alcohol) therefore influenced directly the morphology of fluorinated CrO_3-derived chromia aerogels and xerogels but it had a negligible effect only on the extent of fluorination. Compared with similarly treated alumina materials, fluorinated chromia aerogels or xerogels had much lower fluorine contents. Fluorinated chromia materials were amorphous with relatively high surface areas. It was evident that, in the case of chromia, the fluorination was limited to the surface with the bulk of the oxidic precursor being affected to a much lower extent.

2.2. *Catalysis under steady flow conditions*

Representative results of the catalytic investigations in which CCl_2FCClF_2 was allowed to react under flow conditions are summarised in Table 2 and Fig. 1. All data are mean values obtained from at least three different runs. Under the reaction conditions employed, the degree of conversion was not affected within experimental error by the contact time (gas flow) above 0.5 s, nor by the gas phase composition of

Table 2
Product distribution (mol%) for the reactant CCl_2FCClF_2 (CFC-113) at various catalysts for different temperatures

Catalyst	CFC[a]	115	114/114a[b]	113	113a	112	112a	111	110	1110	Halogen balance[c]		
	T (K)										ΣCFC	n_F	n_{Cl}
Al/A/CHF_3[d]	633	0.4	26.0	3.9	54.8	0.9	7.3	2.8	1.4	2.5	100	2.99	3.01
	693	2.0	31.9	4.7	43.3	0.9	6.0	2.0	0.7	8.4	99.9	2.98	3.02
Al/A/HF	593	0.6	23.4	3.1	59.0	0.7	6.9	2.6	1.6	2.1	100	3.01	2.99
	633	1.0	24.7	3.4	55.8	0.8	6.9	2.6	1.4	3.4	100	2.99	3.01
	693	2.9	29.7	4.2	45.2	0.8	6.1	2.1	0.8	8.2	100	2.97	3.03
Al/X/CHF_3[d]	573	0.0	3.0	88.8	5.7	0.2	2.0	0.1	0.1	0.0	99.9	3.00	3.00
	633	3.7	24.5	3.2	52.8	0.7	6.6	2.4	1.4	4.7	100	3.04	2.96
	693	7.8	27.3	3.8	41.5	0.7	5.6	1.9	0.9	10.5	100	3.09	2.91
Al/X/HF	573	1.8	24.8	4.6	53.4	0.7	8.1	2.3	1.2	3.1	100	3.04	2.96
	633	7.4	24.2	3.4	46.6	0.7	6.2	2.3	1.2	7.9	99.9	3.07	2.93
	693	12.0	25.2	3.7	35.7	0.7	5.1	1.8	0.8	15.0	100	3.08	2.92
Cr/A/HF	573	0.0	14.5	72.2	0.0	1.0	11.9	0.3	0.0	0.2	100	3.00	3.00
	633	0.2	29.4	46.7	0.7	2.0	17.0	1.3	0.1	2.6	100	3.00	3.00
	693	1.2	42.3	24.0	5.8	1.9	13.4	2.0	0.4	8.9	99.9	2.98	3.02
Cr/A/CHF_3	573	0.0	15.6	69.2	0.0	1.2	13.4	0.4	0.0	0.2	100	3.01	2.99
	633	0.1	25.6	52.7	0.0	2.0	16.0	1.1	0.1	2.4	100	3.03	2.97
	693	0.7	37.9	31.5	4.3	2.0	13.5	1.6	0.2	8.3	100	3.07	2.93
Cr/X/CHF_3	573	0.2	26.4	47.5	1.6	1.8	20.4	1.3	0.2	0.6	100	2.99	3.01
	633	0.8	36.3	27.6	7.1	2.2	19.0	2.7	0.5	3.8	100	2.98	3.02
	693	3.3	39.7	13.3	16.4	1.7	12.4	2.9	0.8	9.5	100	2.95	3.05
Cr/X/HF	573	0.2	24.9	52.8	0.0	1.5	19.2	1.0	0.1	0.3	100	3.01	2.99
	633	0.9	35.7	30.3	4.5	2.1	19.8	2.5	0.4	3.8	100	3.01	2.99
	693	3.8	41.8	15.4	11.6	1.7	12.4	2.6	0.6	10.1	100	3.08	2.92

[a] 113 — CCl_2FCClF_2; 113a — CCl_3CF_3; 114 — $CClF_2CClF_2$; 114a — CCl_2FCF_3; 115 — $CClF_2CF_3$; 112 — CCl_2FCCl_2F; 112a — CCl_3CClF_2; 111 — CCl_3CCl_2F; 110 — CCl_3CCl_3; 1110 — C_2Cl_4 key for compounds.

[b] These isomers could not be separated by GC, therefore the sums of both compounds are given here.

[c] Ratio F:Cl = n_F:n_{Cl}.

[d] A: aerogel; X: xerogel.

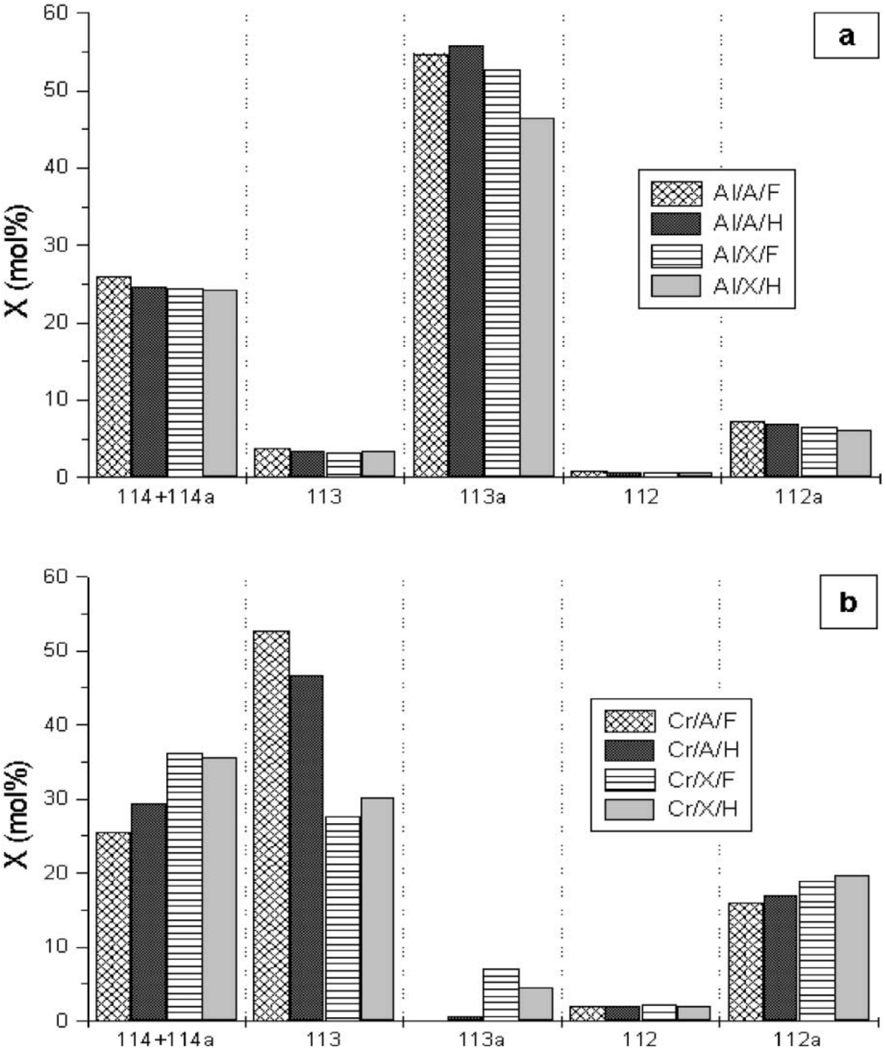

Fig. 1. Main products from the reaction of CCl_2FCClF_2 ($T = 633$ K, $t_r = 1$ s) on (a) fluorinated alumina-based catalysts; (b) fluorinated chromia-based catalysts.

the CFC up to 40% (carrier gas N_2). Although the precursor alumina aerogel (Al/A) and xerogel (Al/X) oxides are quite different in their properties (cf. Table 1), the fluorinated materials behaved very similarly towards CCl_2FCClF_2 (Table 2 and Fig. 1a) and in both cases the behaviour was similar to that of fluorinated γ-alumina [9]. Thus, the surface properties of the different precursors were irrelevant as a result of progressive fluorination and they were independent of the identity of the fluorinating agent used.

In accordance with the earlier findings [11], it might be concluded that the similar catalytic behaviour shown by all these fluorinated aluminium oxide phases to that of β-AlF_3 indicated that the active sites formed on the surface were very similar to those of β-AlF_3 (cf. Table 2). However, XRD examination yielded no evidence for the suggestion. The only crystalline phase identified by X-ray analysis after extensive fluorination was α-AlF_3 and even this phase was not observed in every case. Since it has been found previously that this phase shows no [11] or very little [12] catalytic activity, the activity observed here must be due either to X-ray-amorphous β-AlF_3 or to very strongly disordered α-AlF_3 which provides suitable, catalytically active, surface Al-sites which are not present in the crystalline phase. We cannot distinguish between these possibilities.

Rather different behaviour was observed when chromium-based catalysts were used (Table 2 and Fig. 1b). For all Cr-based catalysts, considerable amounts of CCl_2FCClF_2 remained unconverted under conditions comparable to those used with the aluminium catalysts. Smaller quantities of the isomerization product, CCl_3CF_3 (CFC-113a) were formed. Formation of $C_2Cl_2F_4$ isomers (CFC-114/114a) was significant and for some catalysts, the proportion of this fraction was greater than was observed using the alumina-based catalysts. The significance of the isomer ratio is discussed below. The generally lower degrees of conversion of CCl_2FCClF_2 experienced using chromia-derived aerogel catalysts indicated a lower activity compared with the chromia xerogels. In view of the surface area and the pore

Table 3
Reaction of CCl_2FCClF_2 with fluorinated alumina and chromia aerogels and xerogel catalysts under static conditions

Catalyst	Fluorinating agent	Reaction conditions		CFC-113 (mmol)	Conversion[a] (%)							Organic retention[b] (%)
		T (K)	Time (h)		112/112a	113	113a	114	114a	115	116	
Al/A/H	HF	548	23	2.67	8.4	2.8	57.8	1.6	13.4	7.3	t[c]	8.7
Al/X/H	HF	573	24	3.73	10.5	1.9	55.3	1.3	10.2	6.7	t	14.2
Al/A/F	CHF_3	593	24	2.93	1.8	3.4	64.1	1.5	9.8	2.5	t	16.9
Al/X/F	CHF_3	593	40	5.55	5.2	4.2	57.7	2.1	14.6	4.4	t	11.6
Cr/A/H	HF	573	24	4.91	8.1	19.6	9.2	54.4	7.3	0.5	–	0.75
Cr/X/H	HF	573	22	3.00	2.8	10.0	16.8	43.9	18.1	2.8	–	5.5
Cr/A/F	CHF_3	623	22	8.10	9.8	1.9	18.0	36.5	20.2	10.8	–	2.75
Cr/X/F	CHF_3	623	24	4.75	9.9	10.5	27.9	30.0	15.3	6.0	–	0.35

[a] Determined by ^{19}F NMR spectroscopy; defined as mmol products/mmol reactant 113. Key for compounds: 116 — CF_3CF_3; 115 — $CClF_2CF_3$; 114 — $CClF_2CClF_2$; 114a — CCl_2FCF_3; 113 — CCl_2FCClF_2; 113a — CCl_3CF_3; 112 — CCl_2FCCl_2F; 112a — CCl_3CClF_2.

[b] Defined as (mmol identified products − mmol reactant 113)/mmol reactant 113.

[c] t: trace.

size of the precursor aerogel oxide (Table 1), the opposite would have been expected. In contrast to the aluminium catalysts therefore, it appeared that the chromium oxide materials contained surface sites whose exact nature depended on the topology of the starting oxides.

2.3. Catalysis under static conditions

Product distributions from reactions carried out under static conditions and therefore with very long contact times, are summarised in Table 3. The pattern of results was generally similar to that obtained under flow conditions (Table 2) at a corresponding temperature. Many of the minor differences that were observed can be rationalised on the basis that reactions under static conditions were likely to reflect more nearly the equilibrium situation. The most important finding from these experiments was that the chromia catalysts favoured the formation of the symmetric isomer, $CClF_2CClF_2$, over the asymmetric isomer, CCl_2FCF_3. Thus, the behaviour of chromia was clearly differentiated from that of alumina. The behaviour of all four alumina catalysts was identical, in agreement with the finding from the flow experiments. There may have been very minor differences in the product distributions observed from the four chromia catalysts, particularly when HF was used as the fluorinating agent, but these were not investigated in sufficient detail for the differences to be considered definitive.

2.4. Comparisons between fluorinated γ-alumina and fluorinated chromia catalysts using short contact times

In order to explore the difference in the behaviour of fluorinated alumina and chromia in more detail, the ratios of $C_2Cl_3F_3$ and $C_2Cl_2F_4$ isomers were determined, by GC or ^{19}F NMR spectroscopy as appropriate, after flow of CCl_2FCClF_2 over γ-alumina fluorinated using CCl_2F_2 or amorphous chromia fluorinated using CCl_2F_2. The contact time for CCl_2FCClF_2 on the catalyst was varied and by this means, information concerning the primary product or products formed from CCl_2FCClF_2 could be obtained. Representative data from GC and from ^{19}F NMR analyses are contained in Tables 4 and 5. The differences in product distributions obtained using fluorinated alumina or chromia catalysts were very similar to those described above (Table 2). Moreover, the importance of the asymmetric isomer, CCl_3CF_3, in the products from reactions over fluorinated alumina was very apparent. Different reaction pathways were indicated for alumina and chromia catalysts and those suggested are described below.

Table 4
Product distributions determined by GC analysis for the reactant CCl_2FCClF_2 (CFC-113) by varying the contact time (t_c) at 633 K

Catalyst	t_c (s)	115	114 + 114a[a]	113	113a	112	112a	111	110	1110
Alumina/CCl_2F_2	0.25	0.6	27.7	5.6	50.2	1.0	8.6	2.6	1.1	2.6
	1.08	1.9	28.4	3.9	50.0	0.8	6.4	2.3	1.1	5.2
	7.5	0.2	24.2	3.5	46.7	0.8	6.5	2.6	1.5	7.9
Chromia/CCl_2F_2	0.25	0.1	21.0	63.0	–	1.5	13.6	0.5	–	0.8
	7.5	1.8	41.4	13.3	18.3	1.7	15.1	3.4	1.0	4.1

[a] The GC values indicate the molar percentages of the products CFC-114 and -114a since they could not been separated by GC. For the CFC code, see footnotes in Tables 2 and 3.

Table 5
^{19}F NMR ratio $CClF_2CClF_2$:CCl_2FCF_3 (CFC-114 and -114a) after contact of CCl_2FCClF_2 (CFC-113) with fluorinated γ-alumina and fluorinated chromia under flow conditions at 633 K

Catalyst	Contact time (s)	^{19}F NMR ratio CFC-114:CFC-114a
γ-Alumina/CCl_2F_2	0.25	1:13
	1.08	1:5.2
	7.50	1:5
Chromia/CCl_2F_2	0.25	1:0.14
	7.50	1:0.46

2.5. Fluorinated aerogels and xerogels based on alumina or chromia-prefluorination and catalytic activity

The data in Table 1, in which previously reported data [13,14] for the β-MF_3, M = Al, Cr, phases and for fluorinated M_2O_3 phases are included for comparison, indicate a significant difference between alumina- and chromia-based aerogels/xerogels in the degree of fluorination obtained under the same experimental conditions. This parallels the situation for the conventionally prepared oxides and is in accordance with the thermodynamic situation [6]. Thus, the formation of AlF_3 is strongly favoured whereas that of $AlCl_3$ is not favourable. The thermodynamic situation for CrX_3 is quite different; as a consequence, formation of both CrF_3 and $CrCl_3$ is to be expected when using a reagent such as CCl_2F_2. Moreover, the thermodynamic driving force for the formation of CrF_3 is significantly lower than that for AlF_3. In agreement with the thermodynamic expectations, a very high yield of conversion into AlF_3 is indicated from the F-contents and from the XRD-analyses (Table 1). Although there is no evidence for the complete fluorination of any of the aluminium-based aerogels and xerogels under the conditions used here, it is not unreasonable to conclude that in these materials, the surface after extensive use will consist largely of AlF_3.

Our results will be discussed on the basis that in both systems we are dealing with highly, although not necessarily completely, fluorinated surfaces. Much of the previous reported work in this area has used the terms "chromia/alumina" and "fluorinated chromia/alumina" interchangeably. This creates confusion because even untreated chromia becomes partially fluorinated rapidly, at least on the surface, in a CFC-related catalytic situation. Therefore, it seems reasonable to assume the formation of surface Cr or Al atoms that are in disordered O/F co-ordination environments. Under comparable prefluorination and reaction conditions however, the extent of the fluorination of chromia will be significantly less than that of alumina.

In the case of aluminium-derived catalysts, independent of the exact catalyst employed, almost the same conversion of the reactant CCl_2FCClF_2 was observed and the product distribution was identical within the experimental uncertainty (Tables 2 and 3). The data observed from sample Al/X/CHF_3 at 573 K under flow conditions (Table 2) appear at first sight to be anomalous but they reflect the fact that the catalysts become active just in this temperature region. Too much significance should not be attached to these data therefore. Taken overall, the product distribution data obtained using Al-based catalysts lead to the conclusion that topological differences in the precursors, which are the result of the different synthesis methods, have become irrelevant due to the high degree of fluorination.

A different situation is encountered when using the chromia-based catalysts. Most importantly, the conversion of the reactant CCl_2FCClF_2 is significantly lower and the product distribution is quite different compared with alumina-based catalysts. Usually, aerogels provide larger surface areas and greater pore volumes than the respective xerogels and, thus, are often catalytically more active. However, in the present case, fluorinated chromia aerogels are catalytically less active than the corresponding xerogels although their surface areas are approximately double those of the fluorinated xerogels. The fluoride content is significantly higher in aerogels compared with xerogels. By comparison with conventionally prepared oxidic materials, smaller surface areas might have been expected [7]. Since it is known that aerogels contain significantly more interior surface due to a more highly developed pore structure, our conclusion is that under the prefluorination conditions used here, the interior surface is fluorinated only to a small extent. In contrast, the exterior surface is fluorinated extensively and to a higher degree than the xerogels.

The considerations outlined above lead to the following proposals for the prefluorination of chromia aerogels and xerogels. Fluorination of the oxide using HF or CHF_3 starts at the outer surface thus blocking the access of the fluorinating agent to the inner pores. Although access of the fluorinating agent to inner pore sites is, at best, restricted, N_2, which is used for BET-surface determination, can enter them. The BET-surface areas of fluorinated aerogels are still comparably high, although they reveal a higher degree of fluorination. Due to the denser topology of chromia xerogels, the extent of their fluorination is smaller, thus leaving the surface with higher ratios of oxygen to fluorine. Consequently, the fluorinated chromia xerogels exhibit a memory of their original topology. It is possible that the Cr^{III}-sites at the oxofluoro surface exist in a more distorted, coordinatively less saturated environment. For example, it has been shown recently, that surface Cr^{III} located in a strongly distorted $CrO_{6-x}F_x$-octahedral environment is capable of behaving as a good Lewis-acid [15]. For whatever reason, the more heavily fluorinated Cr^{III} surface sites of aerogels exhibit less catalytic activity than their oxofluoride xerogel counterparts.

2.6. Pathways for chlorofluoroethane reactions on aluminium- and chromium-based catalysts

Variation of the contact time of the reactant CCl_2FCClF_2 with fluorinated alumina and fluorinated chromia catalysts has enabled the formation of key products in the mixtures to be studied in more detail. As shown above, differences in the product distributions between the alumina- and chromia-based systems are obvious using a contact time of ca. 1 s. Differences in reactivity between aerogels and xerogels were found only in the chromia system and, even so, the product distributions were comparable. They are similar to those found using conventionally prepared fluorinated chromia (Table 2). Therefore, fluorinated aluminium and chromium oxides were employed for these investigations, allowing a more straightforward comparison between this work and previous studies to be made.

2.6.1. The aluminium system

The dominant product from the reaction of CCl_2FCClF_2 over fluorinated alumina using a very short contact time is the asymmetric isomer, CCl_3CF_3. From this observation it is concluded that the initial reaction is the isomerization of CCl_2FCClF_2 (Eq. (1)).

$$CCl_2FCClF_2 \rightarrow CCl_3CF_3 \quad (1)$$

The other important products are CCl_2FCF_3 and, to a lesser extent, CCl_3CClF_2. The formation of these directly from CCl_3CF_3, without the intervention of other species, is supported by the behaviour of CCl_3CF_3 itself as a reactant under identical conditions. We have concluded that these observations are best accounted for by the dismutation of CCl_3CF_3 as the second step (Eq. (2)).

$$2CCl_3CF_3 \rightarrow CCl_2FCF_3 + CCl_3CClF_2 \quad (2)$$

Thermodynamically, this reaction is favoured, however, from the kinetic point of view it demands a very high activation energy since a CF_3– group is a very stable entity. We might conclude that this reaction requires very strong acid sites that are unique to fluorinated alumina and that have no equivalent on fluorinated chromia as suggested by Kolditz et al. [3] and Blanchard and coworkers [4]. This is an attractive hypothesis but there is no clear experimental evidence at present.

Activation of C–F bonds is a topic, which is receiving increasing attention and it has been reviewed relatively recently [16]. Activation of C–F bonds in C_6F_6 and related polyfluoroaromatics has been demonstrated using a variety of electron rich organometallic complexes (e.g. [17–20]) and the literature dealing with activation of sp^3 C–F bond activation is now considerable (e.g. [21–29]). In many cases activation is the result of the coordination of a perfluoroalkyl ligand to an electron rich transition metal complex [21,22,26,27] but metal-based systems that incorporate a redox active component have also been described [23,24,29]. One report describes the activation of a CF_3– group via an hypervalent $(F–C–F)^+$ interaction which is postulated to be the result of the interaction of the CF_3– group with a carbocation [25]. Activation of the CF_3– group is also the result of the dissociative adsorption of CF_3I on a copper(1 1 1) surface [30]. In this case, desorption leads to the formation of CF_2 and CuF. Although none of these examples is an exact analogy for the dismutation of CCl_3CF_3 (Eq. (2)), the examples do lend credibility to a postulated adsorbed state of the type, $Al^{\delta+} \ldots F \ldots C$.

2.6.2. The chromium system

In contrast, the situation on chromia is more straightforward, at least to the extent that there are precedents in the literature. For chromia, the energetic difference between an Cr–F and an Cr–Cl bond is small and it has been shown that labile halogen, which may originate either from HX or from a chlorofluoroethane, is present on the chromia catalyst surface [31]. It has also been demonstrated that a highly fluorinated chromia surface from which HF has been desorbed, is capable of fluorinating CCl_4 to both CCl_3F and to CCl_2F_2 concurrently [32]. Using these precedents, it is suggested that the first reaction of CCl_2FCClF_2 at a fluorinated chromia surface is an intermolecular fluorination (Eq. (3)) closely followed by an intermolecular chlorination (Eq. (4)).

$$CCl_2FCClF_2 + \text{``F''} \rightarrow CClF_2CClF_2 + \text{``Cl''} \quad (3)$$

$$CCl_2FCClF_2 + \text{``Cl''} \rightarrow CCl_3CClF_2 + \text{``F''} \quad (4)$$

In each case, ‘‘F’’ and ‘‘Cl’’ denote surface halogen species.

In the present instance, it is not possible to state if the reactions are concerted, i.e. a dismutation, or non-concerted, i.e. an halogen exchange. Under the conditions used here (cf. Table 4), it appears that isomerization of CCl_2FCClF_2 to CCl_3CF_3 does not compete very well, although it does occur to some extent. The other reactions, which result in additional products using longer contact times, can be rationalised on a similar basis.

3. Conclusions

Bond energy relationships are a key factor in rationalising the difference in the dynamic behaviour of CCl_2FCClF_2 over fluorinated alumina catalysts at moderate temperatures compared with their chromia counterparts. There is a large inequality in Al–X, X = F or Cl, bond energies in the former case compared with the near equality of Cr–X bond energies in the latter case. Intermolecular halogen exchange between C–Cl bonds and surface Al–F is thermodynamically unfavourable and isomerization of CCl_2FCClF_2 dominates to give the thermodynamically preferred isomer. At fluorinated chromia surfaces in contrast, halogen exchange and isomerization processes are competitors and these catalysts are less selective as a result. The question of how far the exact surface sites on fluorinated chromias are determined by the nature of the oxide precursor and the fluorination treatment, remains unresolved, although from the product distributions obtained, there is no reason to believe that these factors are of prime importance. For fluorinated aluminas however, these factors are unimportant and the nature of the oxidic precursor appears to be irrelevant.

4. Experimental

4.1. Catalyst preparation

Aerogels and xerogels were prepared from inorganic metal precursors according to procedures previously described for alumina- [10] or chromia-based [8,33] materials. Only the basic preparation steps are described here. Alumina materials were obtained from gelatinous precipitates prepared by the addition of an excess of aqueous ammonia to the solution of aluminium chloride until the pH was 10. After filtration and washing, precipitates were extruded to form uniform wet pellets. A portion of the pellets was dried at 393 K to constant mass to form hard and considerably shrunken alumina xerogels (Al/X/S samples). The second part of the gelatinous pellets was dried partially to increase its mechanical strength and immersed in ethanol to achieve the water–alcohol exchange. Alcohol-exchanged pellets were dried in an autoclave pre-pressurised with dinitrogen (50 bar). The autoclave was heated over 2 h to 573 K; the maximum pressure was kept below 160 bar. After a 1 h stabilisation period, the autoclave was depressurised over 1 h at a constant temperature, 573 K. The hot autoclave was evacuated and refilled several times with N_2 to reduce the amount of organic residue. Soft alumina aerogel pellets (Al/A/S samples) were obtained.

Chromia-based materials were prepared from an aqueous solution of chromium(VI) oxide that was added slowly to intensively stirred and cooled methanol. A large excess of methanol was used, the methanol to CrO_3 molar ratio was normally 30:1. The liquid mixture was transferred into the autoclave that was pre-pressurised with N_2 (50 bar) and heated over 3 h to 473 K to prepare the chromia xerogel (Cr/X/S samples), or to 573 K to prepare the chromia aerogel (Cr/A/S samples). All further steps of the autoclave treatment were identical to those described for alumina aerogel.

Before fluorination, all materials were conditioned at 723 K to eliminate or reduce the amount of inorganic and/or organic contaminants. Alumina materials were heated in air (/AH samples). For chromia materials, a vacuum treatment (/VH samples) was used to preserve the morphology [8]. Fluorination of adequately conditioned oxidic materials from both groups was performed for 4 h at 623 K under flow conditions with either pure trifluoromethane, (/F samples), or anhydrous HF (20 vol.%) diluted with N_2 (/H samples). The total quantity of fluorinating agent used was always in large excess over that required for complete fluorination. From the results of earlier work, the presence of chromium in higher oxidation states than 3+ can be excluded, since it has been shown that under these reaction conditions any $Cr^{>3+}$ becomes immediately reduced to Cr^{3+} [34].

CFC-fluorinated γ-alumina was obtained by fluorinating commercially available γ-alumina (Degussa, p.a.) with a specific surface area of 180 $m^2\,g^{-1}$, a size range between 160 and 325 μm and a bulk density of 0.58 g cm^{-3} with CCl_2F_2 (CFC-12). 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 623 K for 2 h at a flow rate of 3.5 l h^{-1}. After activation with CCl_2F_2, the catalysts exhibited a surface area of 51 $m^2\,g^{-1}$ and contained 19.3% fluoride and less than 0.5% chloride. Before use, all catalyst samples were left in contact with a N_2/CCl_2FCClF_2 gas stream. The fluorinated product phases were amorphous to X-rays, therefore X-ray phase analysis revealed pure γ-alumina.

CFC-fluorinated chromia was obtained by fluorinating Cr_2O_3 obtained by thermal decomposition of ammonium dichromate (volcano reaction) with CCl_2F_2 (CFC-12). After pressing the Cr_2O_3-powder into pellets and cutting, the fraction from 0.3 to 0.6 mm was taken. These pellets were loaded into the flow reactor, dried at 573 K for 2 h at a flow rate of 3.5 l h^{-1} and finally activated with CCl_2F_2 at 623 K. The catalyst exhibited a surface area of 38 $m^2\,g^{-1}$ and contained 2.5% fluoride. As described for fluorinated alumina, all catalyst samples were left in contact with an N_2/CCl_2FCClF_2 gas stream before use. The fluorinated product phases were amorphous to X-rays, therefore X-ray phase analysis revealed only pure chromia.

4.2. Catalyst characterisation

All solids were characterised by X-ray powder diffraction (XRD 7 Seiffert-FPM, Freiburg; Cu Kα radiation), by determination of their specific surface areas using the BET method and N_2 as adsorbate (ASAP 2000, Micromeritics) and by analysis for fluoride. Details have been given previously [9].

4.3. Catalysis under steady flow conditions and experiments using short contact times

Kinetic investigations were carried out in a stainless steel flow system with online GC-analysis as described previously [9]. On-line quantitative analyses were performed using a capillary gas chromatograph (HP 5890, Hewlett Packard, column Pona, 50 m, 0.5 μm polydimethylsiloxane). In some cases, GCMS (Shimadzu QP 5000) was used for product analyses; this was particularly useful for identification of isomeric mixtures. The uncertainty in the kinetic measurements was within the range ±3% in all cases. For short contact time experiments, the quantity of catalyst used and the gas velocity were both varied, thus, enabling contact times as short as 0.1 s to be achieved. The conversion and selectivity were detected using GC but since this method did not separate the isomers, $CClF_2CClF_2$ and CCl_2FCF_3, but rather gave their sum, NMR-spectroscopy was used to determine their ratio. For NMR analyses, the total product gas stream was absorbed in a flask filled with trichloromethane for 5 min. From this solution, NMR-determination was performed and the relative intensities of $CClF_2CClF_2$

and CCl_2FCF_3 were determined and the quantitative ratio determined using the GC-determined sum of the isomers. Mixtures of CCl_2FCClF_2 and CCl_3CF_3 were often analysed in a similar fashion, although base-line separation of the isomers was normally possible by GC.

4.4. Catalysis under static conditions

The behaviour of CCl_2FCClF_2 in the presence of fluorinated alumina or chromia aerogel and xerogel materials under static conditions was investigated using standard vacuum and glove box ($H_2O < 2$ ppm) techniques. Reactions were carried out in prefluorinated stainless steel (75 cm^3) or Monel metal (90 m^3) pressure vessels equipped with stainless steel or Monel valves (Whitey) and appropriate fittings. A vessel was loaded with a sample of a catalyst (0.5 g) in the glove box, heated at 523 K for 2 h in vacuo, allowed to cool and a weighed quantity (2–4 mmol) of CCl_2FCClF_2 added by vacuum distillation. The reactivity of each mixture was tested over 24 h periods at 295, 523, 573 and 623 K, in order to establish optimum reaction conditions. In these preliminary studies off-line analyses were by FTIR spectroscopy (Nicolet Impact 410) and GC (Varian 3400, Chrompack capillary column, 30 m, FI detection). The latter technique enabled quantitative analyses to be made of components in the $C_2Cl_{6-n}F_n$ series but did not, in general, separate individual isomers. A fresh sample of each mixture was heated for a period in the range 22–40 h at a temperature in the range 548–623 K, individual temperatures being chosen to achieve substantial or complete conversion of CCl_2FCClF_2. Material that was volatile at room temperature was collected by vacuum distillation, weighed and the components present, including isomers, identified by GC and ^{19}F NMR spectroscopy (Bruker WP200 SY). Quantitative analyses using the latter technique were made with the aid of spectra of authentic samples and by literature comparisons [35–37]. Less volatile material was removed by distillation at 323 K under dynamic vacuum, weighed and the components present identified by GCMS (Jeol JMS-700) and ^{19}F NMR spectroscopy.

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