

Available online at www.sciencedirect.com



Journal of Fluorine Chemistry 121 (2003) 83-92



www.elsevier.com/locate/jfluchem

Dynamic behaviour of chlorofluoroethanes at fluorinated chromia aerogels and fluorinated zinc(II) or magnesium(II) doped chromia aerogels

Hamid Bozorgzadeh^a, Erhard Kemnitz^a, Mahmood Nickkho-Amiry^b, Tomaž Skapin^{c,*}, John M. Winfield^b

^aInstitute of Inorganic Chemistry, Humboldt University, Brook-Taylor Str. 2, D-12489 Berlin, Germany ^bDepartment of Chemistry, University of Glasgow, Glasgow G12 8QQ, UK ^cDepartment of Inorganic Chemistry and Technology, "Jožef Stefan" Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

Received 7 October 2002; received in revised form 27 November 2002; accepted 6 December 2002

Abstract

The preparation and characterisation of two series of fluorinated chromia aerogel materials, lightly doped with zinc(II) or magnesium(II), are described. They behave as heterogeneous catalysts for transformations of 1,1,2-trichlorotrifluoroethane under HF-free conditions and at moderate temperatures. Product distributions depend critically on the contact time. When the latter is very long (static conditions) the surface becomes chlorinated, notwithstanding its fluorinated nature. Rather surprisingly, in view of previous work, the catalytic behaviour of the materials is almost identical to that of the undoped fluorinated chromia aerogel. The nature of reactions occurring under HF-free conditions and low levels of doping achievable are discussed as possible factors in determining catalytic behaviour. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Fluorinated chromia aerogel; Zinc(II); Magnesium(II); CFC; Catalysis

1. Introduction

Recently we investigated the possibility of converting CCl_2FCClF_2 (CFC-113), which was in the past largely used as a solvent, to the alternative refrigerant, CH_2FCF_3 (HFC-134a), in a process where anhydrous hydrogen fluoride is not used. The optimal reaction scheme for the planned conversion consists of three steps:

 $CCl_2FCClF_2 \rightarrow CCl_3CF_3 \rightarrow CCl_2FCF_3 \rightarrow CH_2FCF_3$

Work carried out to date has demonstrated that conversion of CCl_2FCClF_2 under HF-free conditions is possible on aluminium- or chromium-based catalysts, but the catalytic behaviour of the two groups of catalysts differs significantly [1,2]. High conversion with high selectivity for the two target asymmetric intermediates, CCl_3CF_3 and CCl_2FCF_3 , was observed only when fluorinated γ -alumina or β -AlF₃ were used as catalysts [2,3]. On similar chromium-based catalysts, the conversion was considerably lower, with the preferential formation of the symmetric product, CClF₂CClF₂. It was concluded that on aluminium-based catalysts isomerisation was the dominant reaction, followed by the dismutation of the asymmetric product, CCl₃CF₃, to give CCl₂FCF₃ and CCl₃CClF₂ [2]. A [³⁶Cl] radiotracer study demonstrated that in these two reactions surface Al-Cl groups are not formed, indicating that the processes involved are intramolecular [4]. In contrast, the formation of labile chlorine- and fluorinecontaining species on the surface of chromium-based catalysts that were in contact with CFCs had been established earlier by using [³⁶Cl]- or [¹⁹F]-labelled compounds [5]. From previous studies it is also known that labile halogen species are involved in intermolecular halogenation reactions [5–7] that, depending on specific conditions, can be described as concerted dismutation processes or as non-concerted halogen exchange. Comparative studies clearly show that on chromium-based catalysts these halogenation reactions prevail over isomerisation even under HF-free conditions [1,2]. As a result, chromium-based catalysts exhibit lower selectivity for the asymmetric products. Chromium-based materials can be therefore considered inferior catalysts for the conversion of CCl₂FCClF₂ to CCl₂FCF₃ under HF-free

^{*} Corresponding author. Tel.: +386-1-477-3557; fax: +386-1-423-2125. *E-mail address:* tomaz.skapin@ijs.si (T. Skapin).

conditions, especially when compared to similar aluminiumbased catalysts [2].

Doping chromium-based materials with divalent cations, such as magnesium(II) or zinc(II), has often been used to improve the behaviour of catalysts in reactions involving CFCs, HCFCs and HFCs [8,9]. For example, it was demonstrated that the introduction of small quantities of zinc(II) on chromia promotes significantly its catalytic ability in the fluorination of CH_2CICF_3 with HF to give CH_2FCF_3 [9]. This reaction is limited by the small equilibrium constant and therefore requires highly active catalysts that are less prone to coking. For the same reaction, introduction of MgF₂ was claimed to promote activity, selectivity and durability of CrF₃-based catalysts [10]. However, doping $AlF_{3-x}(OH)_x$ with magnesium(II) resulted in a progressive reduction of Lewis acidity when the magnesium(II) content was increased. A distinctive reduction in catalytic activity for CCl₂F₂ dismutation was observed when the nominal Mg content was greater that that required by the atom ratio Mg:Al = 1.9 [11]. In contrast, a synergic effect was observed when $CrF_{3-x}(OH)_x$ was doped in a similar way. In this latter case, an increase in Lewis acidity paralleled the increased magnesium(II) content, the highest normalised catalytic activity in the same test reaction was observed with the atomic ratio Mg:Cr = 1:3 [12]. These findings demonstrate that significant modification of surface and catalytic properties can be achieved by doping. However, the real promotional effect depends on many parameters, including, the selected dopant-host pair, the dopant loading and dispersion, and the nature of the reaction under investigation. Seldom can it be anticipated. In some specific cases, the acidic properties of fluorinated doped materials that may be relevant for catalysis can be qualitatively predicted by using the Tanabe model [13], originally developed for mixed oxides and extended recently to fluoride systems [14].

In this paper we report the results of an investigation to determine the effect of Zn^{II} or Mg^{II} doping at low levels, on the catalytic properties of fluorinated chromia aerogels with respect to the behaviour of CCl_2FCClF_2 .

2. Results and discussion

2.1. Pure and doped chromia aerogels

Modification of the general procedure to obtain pure chromia aerogels by the chromium(VI) oxide/alcohol route [15,16] allows the preparation of aerogels doped with aliovalent cations. In this way two series of zinc(II) or magnesium(II) doped aerogels were prepared, denominated as Cr/ Zn or Cr/Mg, respectively. Some properties of the pure and doped chromia aerogels used in this work are summarised in Table 1. The main limitations to the procedure were imposed by the solubility of the dopant compounds in the alcohol. Two methods of dopant addition were therefore tested for Cr/Zn aerogels (more details can be found in Section 4). For the preparation of highly doped aerogels, the dopant compound must be dissolved in bulk ethanol before an aqueous solution of CrO₃ is added (method B, Table 1). Using this method, the highest value achievable for the atomic ratio M^{II} :Cr is ca. 26 × 10⁻³ and even so, loss of Zn^{II} during the latter stages of the preparation is significant (cf. later). Higher doping levels could possibly be obtained by using additional dopant deposition, for example by impregnation as used in the earlier work [9], but this would be likely to result in the destruction of the internal structures of the

Table 1

Some properties of zinc(II) or magnesium(II) doped chromia aerogels before and after fluorination

Sample (method) ^a	M ^{II} /Cr ratio ^b	(×10 ³)			BET ^c (m ²	F-content ^d (%)		
	Calculated	Found ^c			S			VH
		S	VH	F				
Cr	0	_	_	_	482	329	271	12.7
Zinc								
Cr/Zn-1 (A)	1.29	0.74	1.36	0.82	490	330	272	11.3
Cr/Zn-2 (A)	2.61	1.01	1.77	2.00	489	335	293	12.0
Cr/Zn-3 (B)	2.60	1.56	2.05	1.46	486	385	327	12.7
Cr/Zn-4 (A)	6.49	4.46	4.62	4.87	492	390	369	14.6
Cr/Zn-5 (B)	6.49	3.92	3.67	4.44	504	389	296	13.1
Cr/Zn-6 (B)	25.99	18.94	18.49	21.54	535	392	350	12.9
Magnesium								
Cr/Mg-1 (B)	2.53	_	-	_	495	338	318	12.7
Cr/Mg-2 (B)	6.49	_	-	_	500	361	317	12.9
Cr/Mg-3 (B)	25.93	-	-	-	518	328	336	12.9

^a Method of M^{II} -acetate (M = Zn or Mg) addition (see Section 4).

^b M^{II}/Cr atom ratio; determined only for the zinc(II) doped series.

^c Stages of preparation: starting aerogel after autoclave treatment (S), vacuum heated (VH) and fluorinated (F).

^d Total F-content in fluorinated samples.

aerogels. Pure chromia aerogel, denominated as Cr, was used as a reference material.

Comparisons among the data in Table 1 show that neither the identity of the dopant, its quantity, nor the method of dopant introduction have any decisive effects on the properties determined at the dopant levels employed. Chromia precursors prepared in the autoclave (preparation stage S) are completely amorphous to X-rays and have extraordinarily high surface areas in the range of $500 \text{ m}^2 \text{ g}^{-1}$. An important feature of the autoclave-prepared doped chromias is a large amount of organic residue, identified by photoacoustic FTIR spectroscopy (PAS) as acetate species with characteristic bands at 1350, 1444 and 1547 cm^{-1} . Evacuation at 723 K (preparation stage VH) eliminates a considerable part of the organic residue with only partial reduction of the surface area. Further reduction of the surface area is observed after fluorination with CHF₃ at 623 K (preparation stage F). The extent of the fluorination is very similar for all aerogels. Fluorinated aerogels remain amorphous and retain relatively high surface areas. This indicates that the bulk structure of the oxide aerogel precursors is largely conserved throughout the preparation sequences. In this respect the current materials resemble closely the behaviour of pure chromia aerogels reported earlier [2,16] and differ significantly from similarly treated alumina-based aerogels [17]. Bulk transformation to crystalline aluminium fluoride occurs in the latter case, yielding materials with considerably reduced surface areas.

Comparison within each series of doped aerogels, shows that surface areas of highly doped materials are the highest, as evidenced by the two highly doped samples, Cr/Zn-6 and Cr/Mg-3. When conventional impregnation techniques are used for the preparation of doped catalysts, the opposite trend is usually observed due to the pore clogging and/or filling processes induced by the dopant species. Such processes, resulting in the loss of internal surface area, seem to be less important when doped catalysts in the form of aerogels are prepared. In the technique used here, both constituents are homogeneously mixed in the liquid phase from which the solid aerogel structure is formed during the autoclave treatment under supercritical conditions. Even if pore clogging and/or filling processes did occur, they are of less importance in view of the very open structure of the solid aerogel network. The use of acetates as the dopant source has an additional beneficial effect. It was previously found that ethanol-derived chromia aerogels, in which the organic residue consisted mainly of thermally stable acetate species, had relatively high mechanical stability and could be prepared in large pieces or monoliths [18]. It is likely that the additional acetate, present in the dopant precursors, contributed further to consolidate the solid structure of doped aerogels.

Chemical analyses of the complete zinc doped series were performed to follow the behaviour of zinc in each preparation step (Table 1). The Zn/Cr atom ratios determined are considerably lower than those calculated for the majority of the samples, indicating that part of the zinc is lost during preparation. A more definitive comparison involving the various preparation stages is not justified due to the significant scattering in the data. However, the results clearly show that the majority of zinc is lost during supercritical drying and that the fluorination step had practically no effect on the final zinc content. The preparation route used here enabled the preparation of fluorinated Cr/Zn aerogels in which a considerable portion of the original zinc is retained. The scattering of results observed indicates that dopant distribution throughout the batch of the aerogel may not be uniform. A more precise determination of zinc distribution was not possible due to the poor mechanical characteristics of the present samples.

Photoacoustic FTIR spectroscopy of adsorbed pyridine (PAS-py) is a valuable tool to determine the nature of surface acidic sites in different fluorinated materials based on alumina or chromia [19]. PAS-py spectra of representative pure and doped chromia aerogels are shown in Fig. 1. For all aerogels, remarkably similar spectra were recorded that indicate the presence of Lewis acid sites. Introduction of



Fig. 1. Photoacoustic spectra of adsorbed pyridine (PAS-py) for CHF_3 treated pure Cr (A), doped Cr/Zn-6 (B), and Cr/Mg-3 (C) chromia aerogels. Pyridine adsorption at 423 K; prior to pyridine adsorption the samples were pre-treated in a flow of nitrogen at 423 K (upper bold trace) or 873 K (bottom trace). L: bands of pyridine bonded to Lewis acid sites, B: possible position of bands for pyridine bonded to Brønsted acid sites (if present).

dopant species at the levels used here has therefore not modified the Lewis acidity of the chromia surface. Very similar surface characteristics are retained also after thermal treatment up to 873 K, as shown by the corresponding lower traces in Fig. 1. Disappearance of some minor bands in the 1500–1600 cm^{-1} region can be attributed to the elimination of the last traces of organic residue retained after the evacuation and fluorination steps. A slight shift of approximately 1 cm^{-1} to lower wavenumber could possibly be interpreted as a slight reduction in the strength of Lewis acid sites, probably as a consequence of a partial loss of fluorine in the thermolysis reactions that take place at higher temperatures (see later). The remarkable thermal stability under non-oxidising conditions, previously reported for fluorinated pure chromia aerogels [16], is confirmed also in the present study for the doped materials.

PAS spectra (not presented) show broad features in the 950, 1630 and 3400 cm^{-1} regions, indicating that some hydration/hydroxylation of fluorinated chromia aerogels always occurs, even if the samples are in contact with ambient air for very short periods of time during manipulation. Dissociative water adsorption leading to the formation of surface hydroxyl groups, and non-dissociative water adsorption, evidenced by the presence of molecular water, are both well documented for crystalline and amorphous chromia [20,21]. Similar behaviour towards water is apparently exhibited also by fluorinated chromia aerogels. It is reasonable to assume that water adsorption on these materials is additionally promoted by their very high surface area and due to the increased Lewis acidity induced by fluorination. In temperature programmed desorption (TPD) investigations, performed as an extension of previous ammonia TPD studies [16], practically continuous desorption of water from such aerogels, preconditioned at 373 K, was detected by FTIR over the whole range, 373-873 K, investigated. A distinctive maximum in water desorption at approximately 433 K was always observed. This peak indicated the desorption of physisorbed or weakly bonded water. Desorption at higher temperatures could be associated with the condensation of surface hydroxyl groups. Desorption of water from fluorinated chromia aerogels resembles therefore that previously observed for amorphous chromia [21]. Desorption of HF commenced at 493-533 K, depending on the pre-treatment procedure used. As expected, the onset of HF desorption from evacuated samples was always shifted to higher temperatures. Corresponding initial losses of fluorine on heating up to 873 K ranged from 28 to 35%. In addition, loss of fluorine was almost complete when fluorinated aerogels were heated under ambient air atmosphere at 723 K. It was concluded that HF, detected in TPD experiments, originated from desorption of physisorbed HF and from hydrolysis of metal fluoride species affecting the fluoride phase, the latter process becoming increasingly important at higher temperatures. It appears that when contact with water cannot be completely excluded, formation of surface hydroxyls, Cr-OH, and a partial replacement of Cr-F bonds by Cr-O in

extensively pre-fluorinated chromia, are likely to occur to some extent, even at the intermediate temperature (623 K) that is relevant for the catalytic work reported here. Under these conditions, however, such hydrolytic modifications of fluorinated surfaces seem to have a negligible effect on the Lewis acidity of surface chromium sites because the intermediate hydroxylation (Cr–F \rightarrow Cr–OH) is compensated for by the dehydroxylation (2Cr–OH \rightarrow Cr–O–Cr + H₂O) a process that creates new Lewis acid surface sites. Since these processes involve just a small fraction of the surface, they do not result in any measurable change in the overall acidity. As ZnF₂ is highly hygroscopic, these transformations will be facile also at zinc(II) sites.

A change in Lewis acidity can therefore be detected using PAS-py measurements, only from samples treated under more drastic conditions (873 K). However, hydration/hydroxylation of the fluorinated chromia aerogels does not result in the formation of Brønsted acidic sites that can be detected by pyridine adsorption at 423 K (Fig. 1). Using the same method, very low or negligible Brønsted acidity was previously found also for fluorinated conventional chromia [19], iron(III) or magnesium(II) doped chromium hydroxyfluorides [12] and mixed MgF₂/CrF₃ catalysts [22]. Similarly, a very small surface coverage of ammonia bound to Brønsted acid sites was determined by using FTIR spectroscopy in an earlier study of reduced amorphous chromia [23]. On basis of the Tanabe model [13,14], incorporation of a metal(II) species in the Cr₂O₃ or CrF₃ lattice should result in the creation of Brønsted sites. However, since this model does not allow any conclusion to be drawn regarding the strength of the acid sites, it seems that they are very weak and can not be detected by PAS-py. Such sites can be rather regarded as weakly basic in nature, thus explaining their behaviour in contact with H³⁶Cl (mentioned later).

By using a radio-labelled probe molecule, H³⁶Cl, it was possible to determine the role of water on surface properties of differently fluorinated aluminium-based materials [24]. A similar approach has been used in the present study to examine the behaviour of fluorinated chromia aerogels towards H³⁶Cl at room temperature. In Table 2 the results for fluorinated pure and zinc(II) doped chromia aerogels are compared with those obtained with some aluminium-based materials. The most interesting feature is the extremely high proportion of H³⁶Cl that was retained on the surface of fluorinated chromia aerogel and its zinc(II) doped derivative. The fractions of [³⁶Cl] retained are far greater than was the case for β -AlF₃ or fluorinated γ -alumina (Table 2 and [24]) and are comparable with, or greater than, that retained by calcined y-alumina under identical conditions. It has been shown previously [25] that the latter material is chlorinated by HCl under these conditions, with surface hydroxyl groups being replaced by Al–Cl bonds. It appears that the situation is similar for the chromia aerogels and, despite the fact that their surfaces have been extensively pre-fluorinated, they contain sufficient Cr-OH groups that are basic enough to interact with HCl, for example to replace Cr-OH by Cr-Cl bonds. Table 2

Surface [³⁶Cl] count rates determined from γ -alumina, CHF₃-fluorinated chromia aerogel and CHF₃-fluorinated, zinc(II) doped chromia aerogel in the presence of H³⁶Cl at room temperature and after its removal

Surface [³⁶ Cl] count rate ^a (count n	Activity of [³⁶ Cl]				
In the presence of H ³⁶ Cl	After removal of H ³⁶ Cl ^c	retained [®] (%)			
Fluorinated Cr aerogel					
5892	4994	79			
5868 ^d	3623	62			
Fluorinated Cr/Zn-2 aerogel					
4954	4821	97			
5413	4398	81			
γ-Alumina					
4510	2956	66			
4440	3153	71			
4519	2943	65			
β -AlF ₃ or fluorinated γ -alumina ^e	7–11				

^a Saturation values.

^b Estimated relative error $\pm 10\%$.

^c Removed under static vacuum.

^d In contact for 1 h before removal of H³⁶Cl.

^e Range of values reported for fluorinated aluminium-based materials taken from [24].

Based on PAS-py results discussed earlier, it is reasonable to conclude that non-acidic hydroxyl groups, capable of interacting with H³⁶Cl at room temperature, may originate from processes that follow the surface rehydration of fluorinated chromia aerogels.

2.2. Catalytic behaviour

2.2.1. Steady flow conditions

The influences of the dopants at different concentrations on the catalytic activity and selectivity in HF-free conversion of CCl₂FCClF₂ were studied under dynamic flow conditions. Results are collected in Table 3; distributions of the two major products for both series of doped catalysts are compared in Fig. 2. Comparisons among the results show that there were no major differences between the catalytic behaviour of pure and doped chromia aerogels. Similarly, there is apparently no effect arising from the extent of dopant loading. Conversion of CCl₂FCClF₂ is in the range 50–59%; the two major products are CCIF₂CCIF₂ and CCl₃CCIF₂ and the extent of isomerisation to CCl₃CF₃ is very low. Halogen balances for the identified volatile products always show a partial loss of chlorine. In general, the behaviour of the present catalysts resembles very much that exhibited by chromia aerogels treated in a similar way and used in our previous study [2]. Formation of the two main products, CClF₂CClF₂ and CCl₃CClF₂, is consistent with the previously proposed intermolecular models [2,5,6], in which labile halogen species, denoted as "F" or "Cl", on the surface of chromia-based catalysts are involved (Eqs. (1) and (2)). Depending on whether these reactions proceed in a concerted or non-concerted manner, they can be described either as dismutation or as halogen exchange. Based on the present data, a clear distinction between both options is not possible:

$$CCl_2FCClF_2 + "F" \to CClF_2CClF_2 + "Cl"$$
(1)

$$\operatorname{CCl}_2\operatorname{FCClF}_2 + \operatorname{''Cl''} \to \operatorname{CCl}_3\operatorname{CClF}_2 + \operatorname{''F''}$$
(2)

Formation of other minor products can be explained by similar fluorination or chlorination sequences. Although competitive catalytic reactions, such as isomerisation, probably also occur, they are of lesser importance under the conditions used in flow experiments. The final result of all these transformations is the formation of chlorine- and fluorine-rich by-products. The formation of the highly fluorinated product, CClF_2CF_3 , which may be formed by fluorination of either CCl_2FCF_3 or $\text{CClF}_2\text{CClF}_2$ (Eqs. (3) and (4)), is

Table 3 Reaction of CCl₂FCClF₂ (CFC-113) under steady flow conditions at 623 K and contact time 1 s

Catalyst	CFC ^a products (mol%)											
	1110	110	111	112	112a	113	113a	$114 + 114a^{b}$	115			
Cr	1.00	0.22	1.32	2.00	17.11	47.11	0.69	29.67	0.21	3.03:2.91		
Cr/Zn-1	1.32	0.19	1.51	1.89	19.47	43.35	1.80	30.24	0.24	3.02:2.96		
Cr/Zn-2	3.11	0.15	1.38	1.93	16.68	41.26	2.14	33.06	0.30	3.03:2.91		
Cr/Zn-3	0.90	0.11	1.13	1.73	18.70	50.01	0.68	26.60	0.14	3.01:2.97		
Cr/Zn-5	2.09	0.17	1.59	2.02	19.08	41.84	2.15	30.79	0.26	3.00:2.97		
Cr/Zn-6	0.84	0.12	1.16	1.74	18.75	49.36	1.14	26.74	0.14	3.01:2.95		
Cr/Mg-1	2.09	0.14	1.47	2.14	18.37	43.31	1.82	30.44	0.22	3.01:2.95		
Cr/Mg-2	2.05	0.09	1.11	1.81	17.31	46.46	1.32	29.62	0.23	3.02:2.94		
Cr/Mg-3	2.16	0.12	1.51	2.06	18.42	44.07	1.72	29.73	0.21	3.00:2.96		

^a Key for compounds: 1110, CCl₂=CCl₂; 110, CCl₃CCl₃; 111, CCl₃CCl₂F; 112, CCl₂FCCl₂F; 112a, CCl₃CClF₂; 113, CCl₂FCClF₂; 113a, CCl₃CF₃; 114, CCl₂CClF₂; 114a, CCl₂FCCF₃; 115, CClF₂CF₃.

^b The two isomers were not separated by GC, the sums of both are given. GC/MS and ¹⁹F NMR indicate that 114 prevails, typical molar ratios were 114/ $114a \ge 6.25$.



Fig. 2. Distribution of the main products, CCl_2FCF_3 (CFC-114a), $CClF_2CClF_2$ (CFC-114) and CCl_3CClF_2 (CFC-112a), and unconverted CCl_2FCClF_2 (CFC-113) obtained under steady flow conditions at 623 K and contact time of 1 s for the fluorinated zinc(II) (Cr/Zn) and magnesium(II) (Cr/Mg) doped chromia aerogel series in comparison with the fluorinated undoped chromia aerogel (Cr).

evidently limited under HF-free steady flow conditions used here:

$$CCl_2FCF_3 + "F" \to CClF_2CF_3 + "Cl"$$
(3)

$$CClF_2CClF_2 + "F" \to CClF_2CF_3 + "Cl"$$
(4)

It appears that under these conditions the reactions leading to chlorine-rich products complete more easily, presumably due to kinetic effects. The observed trends reflect well the large differences in the reactivity of different members of the $C_2Cl_{6-n}F_n$ series. It is well known that the reactivity of these molecules increases rapidly with increasing number of chlorine atoms. As a consequence, completely chlorinated products are readily formed even with the relatively short contact times used in flow experiments. The unsaturated compound, $CCl_2=CCl_2$, is formed in the final step by the dechlorination of CCl_3CCl_3 , according to Eq. (5). Formation of $CCl_2=CCl_2$ with the liberation of chlorine that was not detectable by GC, accounts for the deficit in chlorine balances observed in all catalytic tests (Table 3):

$$CCl_3CCl_3 \rightarrow CCl_2 = CCl_2 + Cl_2 \tag{5}$$

2.2.2. Behaviour of surface halogen species

A series of catalytic tests under static conditions was performed for representative pure and zinc(II) doped chromia aerogel catalysts in order to obtain supplementary information on the course of the HF-free conversions mentioned before. In contrast to the flow experiments, the results obtained under static conditions, involving much longer contact times, represent a closer approach to the equilibrium situation where the contributions of different competitive reactions may become significant or predominant. The behaviour of CCl₂FCClF₂ and CCl₃CF₃ under static conditions is summarised in Table 4. In all cases a distinctive deficiency in the chlorine balance is observed. This is most likely to be the result of the formation of completely chlorinated products, CCl₃CCl₃ and CCl₂=CCl₂, which were not detected by the ¹⁹F NMR analytical method used. In addition, chemical analyses of used catalysts, discussed later, indicated that deposition of chlorine, both organic and inorganic, was substantial. The data given in Table 4 are representative therefore for the volatile fraction in which highly fluorinated products prevail and do not accurately

Table 4

Reaction of CCl₂FCClF₂ (CFC-113) or CCl₃CF₃ (CFC-113a) with CHF₃-fluorinated chromia aerogel or zinc(II) doped chromia aerogel at 623 K under static conditions

Catalyst ^a	Test no. ^a	CFC ^c reactant	Duration (h)	CFC ^e p	CFC^{c} products in the volatile fraction $(mol\%)^{b}$							
				111	112	112a	113	113a	114	114a	115	
Cr	Ι	113	24	0.41	4.33	4.67	7.73	14.39	45.10	18.40	4.97	3.64:2.36
Cr/Zn-2	II	113	24	4.85	8.10	8.60	8.27	32.21	13.10	14.67	10.20	3.22:2.68
	III	113	72	7.12	3.23	7.34	1.07	21.37	6.04	21.70	32.13	3.67:2.33
	V	113	72	2.70	0.60	14.1	1.60	23.60	5.40	17.00	35.00	3.72:2.28
	IV	113a	72	6.40	6.65	4.12	1.58	46.60	1.30	16.40	16.95	3.28:2.72

^a Numbers correspond to tests given in Table 5.

^b Determined by ¹⁹F NMR spectroscopy from the combination of volatile and less volatile fractions, only fluorinated products were detected. ^c For CFC key, see footnote in Table 3. reflect their true equilibrium concentrations. As with the flow experiments, the behaviour of the zinc(II) doped chromia towards CCl_2FCClF_2 is very similar to that of the analogous undoped material. With very long contact times, used in static experiments, high conversions of CCl_2FCClF_2 are observed with the formation of significant quantities of the highly fluorinated product, $CClF_2CF_3$. This compound is very likely to be formed by the fluorination steps given in Eqs. (3) and (4). There is a direct correlation between the contact time and the amount of $CClF_2CF_3$ formed. Under the HF-free conditions used here these fluorination steps seem to be very slow and have high activation energies. Accordingly, very low conversion to $CClF_2CF_3$ is observed with the much shorter contact times used in flow experiments.

Catalytic tests in which the asymmetric isomer, CCl₃CF₃, was used as the starting substance, indicates that even under the extreme conditions used in static experiments, the reactivity of this compound is much lower than that observed for the more symmetric isomer, CCl₂FCClF₂. This finding correlates well with the comparative investigations performed under flow conditions on conventional chromia catalysts, pre-treated with CCl₂F₂ and used in a previous study [2]. Under flow conditions, conversion of CCl₂FCClF₂ was several times higher than that observed for CCl₃CF₃. The main highly fluorinated product was CClF₂CClF₂ when starting with CCl₂FCClF₂, while the asymmetric CCl₂FCF₃ prevailed in the case of CCl₃CF₃. The difference reflects the kinetic and thermodynamic stability of the CF₃– group.

Different halogen-containing species, present on the surface of fluorinated chromia, are recognised to be the key factors determining the catalytic behaviour of these materials [5,7,9]. Catalytic work performed within this study gives additional evidence in this respect. To obtain a deeper insight in the behaviour of an individual halogen, chemical analyses of some pure or zinc(II) doped chromia aerogels before and after catalytic tests under static conditions were performed. Results are summarised in Table 5. Comparison of initial and final fluorine contents demonstrated that the level of fluorine remained practically constant, within the experimental error, for all chromia aerogels investigated. Deviations from this general behaviour, most evident in the case of catalytic test III (Table 5) could be ascribed primarily to the possible differences between aliquots of the same catalyst used for each test. As already mentioned, scattering of results from the determination of the metals ratio suggests that the homogeneity of catalysts might be low, even if they originated from the same batch of aerogel. Nevertheless, it can be concluded that fluorine, initially present in the prefluorinated chromia, has not contributed significantly to the fluorine balance among the organic products. Bulk fluorine is evidently not involved in catalytic halogenation reactions that are believed to be the main processes taking place under the HF-free conditions investigated here. This conclusion is supported by a previous investigation [7] where, using $[^{18}F]$ as a radiotracer, three types of fluorine-containing species were identified in fluorinated chromia catalysts. Only the labile fluorine species, representing a minor fraction of the total fluorine present, was catalytically active.

Incorporation of chlorine in used catalysts was remarkably high, irrespective of the type of catalyst or chlorofluoroethane used as the starting substance. Longer contact times had apparently no effect on the levels of chlorine incorporated, indicating that its deposition is relatively fast. In previous investigations [2] deposition of organic residue was always observed after prolonged catalytic tests under HF-free static conditions. Identification of CCl₃CCl₃ and $CCl_2 = CCl_2$ suggested that the organic residue consisted mainly of fully chlorinated and less volatile compounds. In order to differentiate among possible forms of chlorine present in used catalysts, solvent extractions on the solids were performed. Two different solvents, chloroform and diethyl ether, were tested and both gave comparable results (Table 5). Slightly better extraction results were usually obtained with chloroform. This may be correlated with its better solvent properties for chlorinated hydrocarbons. It should be also pointed out that the use of the highly

Table 5 Chemical analyses of fluorinated chromia aerogels used in HF-free catalytic reactions under static conditions at 623 K

Catalyst	Test no.	CFC reactant	Duration (h)	Initial $F^{-}(\%)^{a}$	After ca	talytic test F ⁻	(%) ^a	$\mathrm{Cl}^{-}(\%)^{b}$)	
						Extracted	Extracted		Extracted	1
						CHCl ₃	Ether		CHCl ₃	Ether
Cr	Ι	113	20	12.2	11.8	11.9	12.2	13.0	7.0 ^a	8.7
Cr/Zn-2	II	113	24	11.5	9.8	8.9		10.8	6.2 ^a	
	III	113	72	11.5	18.4	18.9		17.1	10.7 ^a	
	IV	113a	72	11.5	8.2	7.9		14.7	9.5 ^a	
	V	113	72	11.5	11.0	10.7	9.8	12.6	7.2	7.5
	VI	113	72	12.0	13.7	13.3		8.0	6.1	
Cr/Zn-3	VII	113	72	12.7	16.1	16.9		12.0	7.6	

^a Sample decomposition in alkaline melt.

^b Sample pyrohydrolysis.

chlorinated solvent, chloroform, has, evidently, not interfered with chlorine determinations. In the analytical data obtained from catalysts after extraction, a considerable reduction in chlorine content was observed while there were no distinctive changes in fluorine values. The latter findings confirmed that the fluorine content of the organic residue was negligible. The presence of extractable chlorine in used catalysts that had been treated in vacuo for 2 h at 423 K provided further evidence that the deposit consisted of high boiling fully chlorinated products. Chlorine found in extracted catalysts was still significant and indicated the part of the total chlorine that is strongly retained by chromia, very probably bound directly to Cr. Current investigations gave clear evidence that substantial incorporation of chlorine is possible, even in cases when chromia has been extensively pre-fluorinated. These findings complement therefore very well the work with H³⁶Cl, described earlier.

Based on the results discussed so far, the following rationalisation for the behaviour of halogens on fluorinated chromia aerogel surfaces can be made. First it must be pointed out that the behaviour of doped and undoped chromia aerogels observed in the present study resembles very much that of pure chromia aerogels reported here and earlier [2]. Introduction of dopants at the levels used in the present study has therefore a negligible effect on the catalytic processes under discussion. Fluorination of all chromia aerogels yielded materials with remarkably similar characteristics. Only partial fluorination is indicated in all cases. It is assumed that fluorination of oxide aerogel precursors proceeds predominantly on their surfaces, by the gradual replacement of surface Cr-OH groups and Cr-O-Cr clusters with Cr-F bonds. The interior of the chromia particles consists mainly of unconverted oxide. As demonstrated, the highly fluorinated chromia surfaces formed in this way, are very susceptible to water adsorption and, consequently, easily loose some fluorine. Depending on the specific conditions, new Cr-O-Cr clusters or Cr-OH groups in a distorted fluoride environment are formed. These species represent the active sites that may interact with reactive halogen species. High retention of H³⁶Cl after adsorption at room temperature is clear evidence for such strong interaction. In catalytic reactions under HF-free conditions, the reactive halogen species originate from CCl₂FCClF₂ and its products in reactions similar to those given in Eqs. (1) and (2). Due to the small differences in bond energies, the formation of both Cr-F and Cr-Cl bonds is thermodynamically possible [2]. This was clearly demonstrated by photoelectron and Auger electron spectroscopy in the case of conventional chromia where both halogens were detected on the surface after treatment with different HCFCs or CFCs [26]. The situation encountered on fluorinated chromia differs therefore distinctively from that observed for fluorinated alumina materials where the formation of Al-F over Al–Cl bonds is strongly favoured [2,4]. According to previous studies [5,7], some of the halogen species formed on chromia may be labile and, as such, can be involved in fluorination and chlorination cycles exemplified by Eqs. (1) and (2). Present catalytic tests performed under static conditions show that labile fluorine species gradually form highly fluorinated compounds. Although these processes are slow, the compounds formed are stable and highly volatile. Incorporation of fluorine in these compounds can be therefore regarded as a sink for the active fluorine species. On the other hand, tests performed under static and flow conditions clearly demonstrate that the labile chlorine species easily form less stable and less volatile compounds that are deposited on chromia and may, finally, decompose to yield Cl₂. The partially fluorinated chromia aerogels used in static experiments are therefore subjected to strong chlorination conditions. As a result, additional halogenation takes place, converting some of the oxide, unconverted in the pre-fluorination step, to chloride. Formation of significant quantities of CCl₂=CCl₂ in flow experiments suggests that additional chlorination of prefluorinated chromia aerogels is likely to occur also under these conditions. This aspect may become relevant in situations when the time on-stream is long.

2.2.3. Role of the dopant

Catalytic behaviour of zinc(II) or magnesium(II) doped chromia aerogels in contact with CCl₂FCClF₂, under flow or static conditions, was unexpectedly similar to the corresponding undoped materials. This situation parallels well the similarity in other properties determined for these materials. It appears that the introduction of an aliovalent cation at levels used here has no effect on catalytic reactions studied. Dopants do not promote the lability of surface halides involved in intermolecular halogenations that are believed to be the dominant reaction mechanisms when CCl₂FCClF₂ is contacted with chromia catalysts under HF-free conditions. Isomerisation, the most plausible competitive reaction, especially when long contact times are used, is also not influenced by doping. Lack of any observable effect induced by doping can be explained both by the nature of catalytic reactions investigated here and by the method used for doping. Earlier it was proposed [9] that the promotional role of zinc(II) in the catalytic fluorination of CH₂ClCF₃ by HF that leads to CH₂FCF₃, is due to the formation of ZnF₂ 'islands' on the surface and their consequent effect on the adsorbed state of HF. The current findings are not inconsistent with this assumption, since the reactions studied here do not involve HF as a reagent. The nature of the adsorbed state of CCl₂FCClF₂ and its subsequent reactions with surface labile halide species (cf. earlier) are the important factors here. Adsorption of CCl₂FCClF₂ is likely, following earlier work [5], to occur at coordinatively unsaturated Cr^{III} sites that have a disordered O/F environment.

The degree of inhomogeneity in the distribution of dopant observed for some samples and the intrinsic surface levels of the dopant are also relevant. In the study referred to [9], the best results were obtained with a low level of Zn^{II} but this was incorporated by aqueous impregnation of conventionally prepared chromias. Using this method, Zn^{II} may react with surface/subsurface layers only, thus the dopant concentration on the surface could be higher than in the present work, where both bulk and surface are doped. For chromia-based catalysts doped with Mg^{II} obtained by co-precipitation [12], the best catalytic activities have been obtained using samples having significantly higher levels of the dopant (ca. 25%) than was possible here, as discussed earlier (Section 2.1). From the present work it appears that if high levels of doping are required, these are not compatible with the use of aerogel materials.

3. Conclusions

Doping of chromia aerogels with low levels of either Zn^{II} or Mg^{II} with subsequent fluorination leads to stable materials that have catalytic activity for transformations of CCl_2FCClF_2 . However, the promotional effect of M^{II} , observed in a previous study [9], was not observed. This is accounted for by a combination of two factors. The level of doping achievable from solution impregnation of aerogel materials is limited. The catalyst–substrate interactions, required for catalytic fluorination using anhydrous HF (the reaction studied in [9]) and those appropriate for dynamic behaviour of CCl_2FCClF_2 under HF-free conditions, studied here, are apparently different.

4. Experimental

4.1. Preparation of catalytic materials

The preparation procedure for chromia aerogels consisted of three separate steps, preparation of oxidic precursors (stage S), conditioning (stage VH) and fluorination (stage F). Precursor aerogels were prepared from an aqueous solution of chromium(VI) oxide (Merck, minimum 99%) and a large excess of ethanol (Carlo Erba, minimum 99.8%). The liquid mixtures thus obtained were dried in the autoclave at supercritical conditions (573 K). Two series of chromia aerogels doped with magnesium(II) or zinc(II) cations were prepared. For both series hydrated metal acetates (Merck, minimum 99.5%) were the dopant sources. Due to the limited solubility of metal(II) acetates in ethanol, two methods of dopant addition were tested for the zinc(II) doped series. Method A: CrO₃(aq.) (81 g, 43.2 wt.% CrO₃) was mixed with the majority of ethanol (280 cm^3) , then a corresponding quantity of zinc(II) acetate, dissolved in 100 cm³ of ethanol, was added. Method B: corresponding quantity of zinc(II) acetate was dissolved in 380 cm³ of ethanol, then $CrO_3(aq.)$ (same quantity as in A) was added to the solution. For higher dopant loadings only method B could be used. For the magnesium(II) doped series only method B was used.

Before fluorination, precursor chromia aerogels were conditioned at 723 K under dynamic vacuum to reduce the quantity of organic contaminants. This procedure preserved substantially the morphology of the precursor. Fluorination of conditioned oxidic aerogels (4–5 g) was performed under flow conditions at 623 K with trifluoromethane, CHF₃ (Matheson, minimum 98%; 20 g h⁻¹) for 4 h. Other details for the preparation of chromia aerogels starting from CrO₃ and alcohols are given elsewhere [15,16,18].

4.2. Catalyst characterisation

All solids were examined by X-ray powder diffraction. Specific surface areas were determined by the BET method using nitrogen as the adsorbate. Temperature programmed desorption and infrared photoacoustic spectroscopy of chemisorbed pyridine (PAS-py) were performed according to the procedures reported earlier [19]. The framework vibrations of the solids were used as an internal reference to obtain the normalised PAS-py spectra. When transferring the sample to the photoacoustic cell, a short contact with ambient air could not be prevented, due to the technical characteristics of the cell used.

Chromium and zinc contents for the zinc(II) doped series were determined by redox titration or inductively coupled plasma atomic emission spectroscopy (ICP-AES), respectively, after decomposition in carbonate (alkaline) melts. Total fluorine and chlorine contents were determined with the respective ion-selective electrodes following the total decomposition in carbonate (alkaline) melts or by pyrohydrolysis. Separate tests with model materials shoved that both decomposition methods gave comparable results. Absolute differences in fluorine or chlorine values obtained by both methods were usually lower than 1%. Samples of chromia aerogels used in some experiments under static conditions were extracted with chloroform or ether. Before extraction, used catalysts were evacuated at 423 K for 2 h. For each extraction two aliquots of fresh solvent were used. In each extraction the solid sample was shaken with the solvent for 30 min then solvent was removed by filtration. Extracted solids were dried at 322 K and cooled in a desiccator.

The behaviour of representative chromia aerogels and γ -alumina towards [³⁶Cl]-labelled anhydrous hydrogen chloride at room temperature was examined using a Geiger-Müller direct monitoring method, originally developed for [¹⁴C] adsorption measurements [27]. Two, intercalibrated Geiger-Müller counters were positioned within the evacuable Pyrex counting vessel to enable [³⁶Cl] activity from the vapour phase and from the vapour plus surface to be monitored concurrently. The fraction retained on the surface was obtained from the difference of the two values. It should be noted that due to the strong self-absorption of the β^- emitter [³⁶Cl], only the activity from the surface can be monitored in this way. Incorporation of H³⁶Cl into the bulk solid is therefore not detectable by this technique. Further details can be found in previous reports [4,24].

4.3. Catalytic reactions

Catalytic reactions of CCl_2FCClF_2 were studied under steady flow and static conditions, usually at 623 K. Experimental methods for both sets of experiments and analytical methods for the quantification of reaction products were the same as those used in the previous studies [2,4]. The contact time for experiments performed under steady flow conditions was 1 s, for static experiments the contact times ranged from 24 to 72 h.

Acknowledgements

We thank the European Union for support of this work under contract ENV4-CT97-0601. Additional funding for T. Skapin was provided by the Ministry of Education, Science and Sport of the Republic of Slovenia.

References

- M. Blanchard, L. Wendlinger, P. Canesson, Appl. Catal. 59 (1990) 123–128.
- [2] H. Bozorgzadeh, E. Kemnitz, M. Nickkho-Amiry, T. Skapin, J.M. Winfield, J. Fluorine Chem. 110 (2001) 181–189.
- [3] H. Bozorgzadeh, E. Kemnitz, M. Nickkho-Amiry, T. Skapin, J.M. Winfield, J. Fluorine Chem. 107 (2001) 45–52.
- [4] H. Bozorgzadeh, E. Kemnitz, M. Nickkho-Amiry, T. Skapin, G.D. Tate, J.M. Winfield, J. Fluorine Chem. 112 (2001) 225–232.
- [5] L. Rowley, J. Thomson, G. Webb, J.M. Winfield, A. McCulloch, Appl. Catal. A: Gen. 79 (1991) 89–103.
- [6] A. Farrokhnia, B. Sakakini, K.C. Waugh, J. Catal. 174 (1998) 219–230.

- [7] J. Kijowski, G. Webb, J.M. Winfield, Appl. Catal. 27 (1986) 181– 193.
- [8] L.E. Manzer, M.J. Nappa, Appl. Catal. A: Gen. 221 (2001) 267-274.
- [9] D.W. Bonniface, J.R. Fryer, P. Landon, J.D. Scott, W.D.S. Scott, M.J. Watson, G. Webb, J.M. Winfield, Green Chem. 1 (1999) 9–11.
- [10] H. Kim, H.S. Kim, B.G. Lee, H. Lee, S. Kim, J. Chem. Soc., Chem. Commun. (1995) 2383–2384.
- [11] E. Kemnitz, A. Hess, G. Rother, S. Troyanov, J. Catal. 159 (1996) 332–339.
- [12] B. Adamczyk, A. Hess, E. Kemnitz, J. Mater. Chem. 6 (1996) 1731– 1735.
- [13] K. Tanabe, T. Sumijoshi, K. Shibata, T. Kiyoura, J. Kitagawa, Bull. Chem. Soc. Jpn. 47 (1974) 1064–1066.
- [14] E. Kemnitz, Y. Zhu, B. Adamczyk, J. Fluorine Chem. 114 (2002) 163–170.
- [15] J.N. Armor, E.J. Carlson, W.C. Conner, React. Solids 3 (1987) 155– 159.
- [16] T. Skapin, E. Kemnitz, J. Non-Cryst. Solids 225 (1998) 163-167.
- [17] T. Skapin, E. Kemnitz, Catal. Lett. 40 (1996) 241-247.
- [18] T. Skapin, J. Non-Cryst. Solids 285 (2001) 128-134.
- [19] A. Hess, E. Kemnitz, J. Catal. 149 (1994) 449-457.
- [20] A. Zecchina, S. Coluccia, E. Guglielminotti, G. Ghiotti, J. Phys. Chem. 75 (1971) 2774–2783.
- [21] M. Schraml-Marth, A. Wokaun, H.E. Curry-Hyde, A. Baiker, J. Catal. 133 (1992) 415–430.
- [22] H. Lee, H.D. Jeong, Y.S. Chung, H.G. Lee, M.J. Chung, S. Kim, H.S. Kim, J. Catal. 169 (1997) 307–316.
- [23] M. Schraml-Marth, A. Wokaun, H.E. Curry-Hyde, A. Baiker, J. Catal. 133 (1992) 431–444.
- [24] C.H. Barclay, H. Bozorgzadeh, E. Kemnitz, M. Nickkho-Amiry, D.E.M. Ross, T. Skapin, J. Thomson, G. Webb, J.M. Winfield, J. Chem. Soc., Dalton Trans. (2002) 40–47.
- [25] J. Thomson, G. Webb, J.M. Winfield, J. Mol. Catal. 67 (1991) 117– 126.
- [26] E. Kemnitz, A. Kohne, I. Grohmann, A. Lippitz, W.E.S. Unger, J. Catal. 159 (1996) 270–279.
- [27] A.S. Al-Ammar, G. Webb, J. Chem. Soc., Faraday Trans. I 74 (1978) 195–205.