

Available online at www.sciencedirect.com





Journal of Fluorine Chemistry 127 (2006) 1446-1453

www.elsevier.com/locate/fluor

### $\gamma$ -Alumina-supported boron trifluoride: Catalysis, radiotracer studies and computations

Thomas M. Klapötke<sup>a</sup>, Fiona McMonagle<sup>b</sup>, Ronald R. Spence<sup>b</sup>, John M. Winfield<sup>b,\*</sup>

<sup>a</sup> Department of Chemistry and Biochemistry, Ludwig-Maximilian University of Munich, Butenandtstr. 5-13(D), D-81377 Munich, Germany <sup>b</sup>Department of Chemistry, University of Glasgow, Glasgow, G12 8QQ Scotland, UK

Received 4 April 2006; received in revised form 9 May 2006; accepted 10 May 2006

Available online 19 May 2006

Dedicated to Prof. Dr. Boris Žemva on the occasion of his receiving the 2006 ACS Award for Creative Work in Fluorine Chemistry.

#### Abstract

The irreversible adsorption of boron trifluoride on calcined  $\gamma$ -alumina and amorphous chromia, in both cases at room temperature, has been studied using [<sup>18</sup>F]-labelled BF<sub>3</sub>. Although the resulting  $\gamma$ -alumina surface has some catalytic activity for the room temperature fluorination by anhydrous HF of CH<sub>3</sub>CCl<sub>3</sub> under static conditions, its activity is far lower than that of  $\gamma$ -alumina, which has been fluorinated with SF<sub>4</sub>, nominally at room temperature. A possible explanation for the observed behaviour is given.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Boron trifluoride; Sulfur tetrafluoride; Alumina; Catalysis; [18F] Exchange; MP2 and MP4 calculations

#### 1. Introduction

Boron trifluoride is a moderately strong Lewis acid [1] that has been used widely as an acid catalyst in both small- and large-scale reactions [2]. When added to a reaction mixture as a complex,  $BF_3$ , L, where  $L = Et_2O$  or  $H_2O$  for example, particularly in a protic medium, it functions also as a Brönsted acid [3]. Exposure of high surface area oxides to BF<sub>3</sub> at room temperature results in irreversible adsorption [4– 7]. IR spectroscopic examinations of the resulting surfaces have suggested that surface species such as Al-OBF<sub>2</sub>, from the reaction with surface Al-OH [4], Si-OBF2, from the reaction with surface Si-O-Si groups [5], or the ion pair, Al- $OBF_3^-H^+$  [7] can be formed. Alumina treated with  $BF_3$ behaves as a hydrocarbon alkylation catalyst [6] and it has been claimed that this material is a solid super acid [7]. On the basis of a very recent DFT computational study, it has been concluded that the favoured species when BF<sub>3</sub> is adsorbed on perfect NiO (001) is -OBF<sub>3</sub> but adsorption at a Ni-site is favoured on an O-deficient surface [8].

Supporting a complex such as BF<sub>3</sub>,OEt<sub>2</sub> on alumina results in a milder catalyst than is the case when the complex is used in solution and this has been exploited for a variety of syntheses [9]. Subtle effects are possible, for example if the complex BF<sub>3</sub>,2H<sub>2</sub>O in EtOH is used to prepare a silica-supported BF<sub>3</sub> catalyst, a higher coverage of stronger Brönsted surface sites is obtained than is the case when BF<sub>3</sub>,OEt<sub>2</sub> is used as the precursor [10].

Our interest in BF<sub>3</sub> supported on  $\gamma$ -alumina arose from studying the behaviour of  $\gamma$ -alumina which had been fluorinated with sulfur tetrafluoride as a Lewis/Brönsted acid catalyst for room temperature halogen exchange involving chlorohydrocarbons [11], isomerization of 1,1,2-trichlorotrifluoroethane [12] and dismutation of 1,1,1-trichlorotrifluoroethane [13]. The acidity of SF<sub>4</sub>-fluorinated  $\gamma$ -alumina can be fine tuned by modification of the conditions used for the fluorination [14]. Boron trifluoride might therefore be an alternative to SF<sub>4</sub> in these applications.

Here the behaviour of  $\gamma$ -alumina treated with BF<sub>3</sub> is compared with those of  $\gamma$ -alumina and amorphous chromia,

<sup>\*</sup> Corresponding author. Tel.: +44 141 330 5134; fax: +44 141 330 4888. E-mail address: johnwin@chem.gla.ac.uk (J.M. Winfield).

<sup>0022-1139/\$ -</sup> see front matter (C) 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.jfluchem.2006.05.010

which in each case have been fluorinated with  $SF_4$ . The basis of the comparison is their behaviour with respect to fluorine-18 isotopic exchange reactions and their behaviour towards 1,1,1trichloroethane, the reagent used previously to prepare supported organic layer catalysts [11]. An additional insight into the behaviour of  $BF_3$  compared with  $SF_4$  is provided by a computational study at the MP2 and MP4 levels of theory. Although such computations involving molecular  $Al^{III}$ -containing species do not represent the real situation for the solids studied here, they are helpful in comparing the fluorination abilities of the two molecular fluorides used.

#### 2. Results and discussion

# 2.1. Uptake of $[^{18}F]$ -labelled boron trifluoride by $\gamma$ -alumina and amorphous chromia at room temperature

The use of [<sup>18</sup>F]-labelled BF<sub>3</sub>, whose specific count rate has been experimentally determined, is a convenient way of establishing the stoichiometry of the interaction of BF<sub>3</sub> with solid oxides. The results of sequential BF<sub>2</sub><sup>18</sup>F additions to  $\gamma$ alumina and to amorphous chromia, prepared by the 'volcano' thermal decomposition of ammonium dichromate, are shown in Table 1. The uptakes of fluorine so determined, after four additions of BF<sub>2</sub><sup>18</sup>F in each case, were 2.05 and 1.45 mg atom F (g solid)<sup>-1</sup>, respectively, equivalent to 3.9 and 2.75 wt.% F. The corresponding figure obtained previously for the uptake of fluorine by  $\gamma$ -alumina after exposure to SF<sub>3</sub><sup>18</sup>F under comparable conditions is 15 mg atom F (g solid)<sup>-1</sup> (28.5 wt.%) [15].

A key difference between the two fluorides is that  $SF_4$  when it functions as a fluorinating agent, has the ability to replace surface oxygen atoms by fluorine ( $O\equiv 2F$ ). This will lead to surface  $AI^{III}$ atoms in a disordered O/F environment that can function as very strong Lewis sites [14]. From a recent surface science study of  $\gamma$ alumina fluorination by CHCIF<sub>2</sub>, it has been concluded that subsurface insertion of F is required also in order to promote the Lewis acidity required for Cl/F halogen exchange [16].

Some of the species that, on the basis of previous studies [4,5,7,10], could be formed on the surface of alumina after exposure to BF<sub>3</sub> are shown in Scheme 1.



Scheme 1. Possible surface species (M = Al or Si) [4,5,7,10].

Although the promotion of Brönsted acidity on  $\gamma$ -alumina is easily envisaged, particularly when L in Scheme 1 is H<sub>2</sub>O (cf. Ref. [10]), the promotion of Lewis acidity at a coordinatively unsaturated surface Al<sup>III</sup> will be dependent on the inductive effect of a neighbouring –OBF<sub>2</sub> group. This is likely to be smaller than in the SF<sub>4</sub>-fluorinated case where more than one F is bound directly to a surface Al<sup>III</sup> [14]. Interestingly, although DRIFTS of adsorbed pyridine on BF<sub>3</sub>-treated  $\gamma$ -alumina indicated that both Lewis and Brönsted sites were present, there were no marked differences from the spectra of pyridine adsorbed on SF<sub>4</sub>-treated  $\gamma$ -alumina.

## 2.2. Reactions of $BF_3$ - and $SF_4$ -treated $\gamma$ -alumina and $SF_4$ -treated chromia with 1,1,1-trichloroethane

The reaction used to compare the catalytic properties of  $\gamma$ alumina and amorphous chromia after exposure to BF<sub>3</sub> or SF<sub>4</sub> involved exposure of the fluoride-treated solids to 1,1,1trichloroethane vapour at room temperature. The chemistry of chlorocarbons in the presence of acidic solids is complex and

Table 1

Uptake of [1	<sup>18</sup> F] t	уγ	-alumina	(0.505 g	g) and amor	phous of	chromia	(0.535	g) on ex	posure	to $BF_2^1$	<sup>8</sup> F alie	quots	(ca.	1 mmol)	<sup>a</sup> at room	temp	erature	for	1 h
--------------	--------------------	----	----------	----------	-------------	----------	---------	--------	----------	--------	-------------	---------------------	-------	------	---------	----------------------	------	---------	-----	-----

Aliquot no.	BF2 <sup>18</sup> F count rate (count min <sup>-1</sup> ) <sup>b</sup>	Solid count rat	$BF_2^{18}F$ recovered (%)	
		Initial <sup>b</sup>	After BF2 <sup>18</sup> F removal <sup>c</sup>	
γ-Alumina				
1	5614	3836	9992	40.1
2	5848	10210	10872	66.5
3	5202	10431	10872	82.8
4	6931	11080	11305	92.4
Chromia				
1	5829	6920	6448	71.6
2	4948	7628	6232	106.5
3	5310	6083	6762	96.0
4	5465	7731	7017	97.3

<sup>a</sup>  $BF_2^{18}F$  specific count rates, 10,923 count min<sup>-1</sup> (mg atom F)<sup>-1</sup>.

<sup>b</sup> Relative error <2%.

<sup>c</sup> Relative error <1%.



(iii) surfaced catalysed, + HF

Scheme 2. Behaviour of CH<sub>3</sub>CCl<sub>3</sub> on SF<sub>4</sub>-fluorinated γ-alumina [19,20].

much of it is imperfectly understood [17]. However, it is well established that CH<sub>3</sub>CCl<sub>3</sub> in the presence of solid aluminium(III) chloride undergoes rapid dehydrochlorination at room temperature with concurrent formation on the inorganic surface of a purple organic layer which contains partially dehydrochlorinated oligomers, derived from the primary dehydrochlorinated product, 1,1-dichloroethene [17,18]. Similar behaviour has been observed also on the Brönsted and Lewis acid,  $\gamma$ -alumina that had been chlorinated using carbon tetrachloride [19]. On SF<sub>4</sub>fluorinated  $\gamma$ -alumina, these reactions are accompanied by the fluorination of CH<sub>3</sub>CCl<sub>3</sub> to give the HCFC, CH<sub>3</sub>CCl<sub>2</sub>F, an observation that was crucial in the use of the material as a catalyst for room temperature halogen exchange [11,20]. The reactions involved are summarised in Scheme 2.

In the present comparative study, reactions were carried out in both Monel and Pyrex vessels. The former resulted in greater conversions to  $CH_3CCl_2F$  over the  $SF_4$ -fluorinated solids, probably because the *in situ* fluorinations resulted in more active surfaces. Reactions in Pyrex enabled colour changes, an indicator of laydown of organic material (reaction ii in Scheme 2), to be observed. Exposure of  $SF_4$ -fluorinated  $\gamma$ -alumina to  $CH_3CCl_3$ resulted in the formation of a purple layer, though less intense than that produced from a reaction in Monel; the colour developed on  $BF_3$ -treated  $\gamma$ -alumina was blue but the green colour of  $SF_4$ fluorinated chromia was unchanged by the exposure to  $CH_3CCl_3$ . In situ FTIR monitoring of the vapours above the solids showed the disappearance of  $CH_3CCl_3$  and the appearance of  $CH_2=CCl_2$ and  $CH_3CCl_2F$  had attained apparent equilibrium after 2 h exposure. GC and mass balance data for these reactions on the three materials studied are given in Tables 2 and 3.

The behaviour of  $\gamma$ -alumina treated with BF<sub>3</sub> differed from that of the SF<sub>4</sub>-fluorinated materials in that little or no CH<sub>3</sub>CCl<sub>2</sub>F was produced and laydown of organic material occurred to a smaller extent. The production of the primary dehydrochlorination product, CH<sub>2</sub>=CCl<sub>2</sub>, was, however, substantial and there was some evidence that the surface was not 'saturated' by the deposition of the organic layer after the first addition of CH<sub>3</sub>CCl<sub>3</sub> (Table 3). It appears that the 'pool' of labile fluorine, potentially available for the fluorination of CH<sub>3</sub>CCl<sub>3</sub> or the hydrofluorination of CH<sub>2</sub>=CCl<sub>2</sub>, on BF<sub>3</sub>treated  $\gamma$ -alumina is considerably smaller than on the SF<sub>4</sub>fluorinated oxides. Examining the catalytic behaviour of the materials in the fluorination of CH<sub>3</sub>CCl<sub>3</sub> by anhydrous HF at room temperature substantiated this, Table 4. The behaviour of  $\gamma$ -alumina, fluorinated using SF<sub>4</sub> then conditioned with CH<sub>3</sub>CCl<sub>3</sub>, was as expected by comparison with previous work [11]. The chromia analogue showed similar behaviour, although the utilisation of the available fluorine was lower. However,  $\gamma$ -alumina, treated with BF<sub>3</sub> then CH<sub>3</sub>CCl<sub>3</sub> exhibited little or no catalytic ability with respect to fluorination.

Table 2

Volatile product analyses from the reactions of  $CH_3CCl_3$  (3 mmol) with fluorinated<sup>a</sup> oxide samples (0.5 g)

Reaction no.	Oxide	Fluoride	Vessel	GC analysis of product mixture (mol%)				
				CH <sub>3</sub> CCl <sub>3</sub>	CH2=CCl2	CH <sub>3</sub> CCl <sub>2</sub> F		
1	γ-Alumina	$SF_4$	Monel	71.0	5.3	22.9		
2	γ-Alumina	$SF_4$	Pyrex	68.8	17.5	13.5		
				89.4	8.3	2.2		
3	Chromia	$SF_4$	Monel	43.1	18.4	36.5		
4	Chromia	$SF_4$	Pyrex	60.7	21.6	17.3		
				80.6	13.8	5.1		
5	γ-Alumina	$BF_3$	Monel	53.9	42.0	4.1		
6	γ-Alumina	$BF_3$	Pyrex	63.7	32.7	2.3		
				88.5	13.5	0		

Reaction conditions were room temperature for 3 h.

<sup>a</sup> In situ fluorination in Monel; samples for Pyrex reactions were prefluorinated and transferred in a glove box.

Table 3			
Mass balance data for reactions	between	fluorinated oxid	es and CH <sub>2</sub> CCl <sub>2</sub> <sup>a</sup>

Oxide	Fluoride	Mass of CH <sub>3</sub> CCl <sub>3</sub> (g)	Mass of solid (g)		Change in mass (%)	
			Before reaction	After reaction		
γ-Alumina	$SF_4$	0.3822	0.5355	0.7756	44.8	
		0.3409	0.7756	0.7885	1.7	
Chromia	$SF_4$	0.3463	0.4490	0.7285	62.2	
		0.4094	0.7285	0.7379	1.3	
γ-Alumina	BF <sub>3</sub>	0.3700	0.4555	0.5343	17.3	
	-	0.3369	0.5343	0.7025	31.5	

<sup>a</sup> Two additions in each case. In Pyrex.

#### Table 4

Products from room temperature reactions under static conditions of anhydrous HF (1.0 mmol) with CH<sub>3</sub>CCl<sub>3</sub> (3.0 mmol) over supported organic layer catalysts<sup>a</sup>

Products identified by GC analysis (mol%)									
CH <sub>3</sub> CCl <sub>3</sub>	CH2=CCl2	CH <sub>3</sub> CCl <sub>2</sub> F	CH <sub>3</sub> CClF <sub>2</sub>	CH <sub>3</sub> CF <sub>3</sub>					
a/SF <sub>4</sub> /CH <sub>3</sub> CCl <sub>3</sub>									
88.8	0.1	7.5	-	2.0					
92.0	0.4	6.2	0.4	_					
78.8	0.2	19.6	_	0.5					
84.2	_	4.4	11.4	_					
95.0	-	4.8	_	0.1					
SF <sub>4</sub> /CH <sub>3</sub> CCl <sub>3</sub>									
93.4	0.5	5.3	0.3	0.2					
81.9	2.7	14.3	0.6	_					
97.5	0.4	2.1	-	_					
95.0	1.5	3.5	_	_					
97.3	0.8	1.7	0.1	_					
a/BF <sub>3</sub> /CH <sub>3</sub> CCl <sub>3</sub>									
98.6	0.9	0.4	_	0.4					
	$\begin{tabular}{ c c c c c } \hline Products identified \\\hline \hline CH_3CCl_3 \\ \hline 88.8 \\ 92.0 \\ 78.8 \\ 84.2 \\ 95.0 \\\hline SF_4/CH_3CCl_3 \\ 93.4 \\ 81.9 \\ 97.5 \\ 95.0 \\ 97.5 \\ 95.0 \\ 97.3 \\\hline a/BF_3/CH_3CCl_3 \\ 98.6 \\\hline \end{tabular}$	$\begin{tabular}{ c c c c } \hline Products identified by GC analysis (mol%) \hline \hline CH_3CCl_3 & CH_2=CCl_2 \\ \hline & CH_3CCl_3 & 0.1 \\ \hline & 92.0 & 0.4 \\ \hline & 92.0 & 0.4 \\ \hline & 78.8 & 0.2 \\ \hline & 84.2 & - \\ \hline & 95.0 & - \\ \hline & SF_4/CH_3CCl_3 & 0.5 \\ \hline & 81.9 & 2.7 \\ \hline & 97.5 & 0.4 \\ \hline & 95.0 & 1.5 \\ \hline & 97.3 & 0.8 \\ \hline & a/BF_3/CH_3CCl_3 & \\ \hline & 98.6 & 0.9 \\ \hline \end{tabular}$	$\begin{tabular}{ c c c c c } \hline Products identified by GC analysis (mol%) \hline \hline CH_3CCl_3 & CH_2=CCl_2 & CH_3CCl_2F \\ \hline a/SF_4/CH_3CCl_3 & & & & & & & & & & & & & & & & & & &$	$\begin{tabular}{ c c c c c } \hline Products identified by GC analysis (mol%) \hline \hline CH_3CCl_3 & CH_2=CCl_2 & CH_3CCl_2F & CH_3CCIF_2 \\ \hline & & & & & & & & & & & & & & & & & &$					

<sup>a</sup> Catalysts prepared *in situ*. Reaction time 2 h in each case.

On the basis of our previous model for supported organic layer catalysts [20], it is concluded that both fluorinated precursors have the ability to oligomerise  $CH_2$ = $CCl_2$  (reaction ii in Scheme 2) hence forming an organic layer supported on the partially fluorinated surface that is able to trap  $CH_3CCl_3$  at the surface. Both fluorinated oxides therefore are capable of behaving as Lewis acids; in the case of the  $SF_4$ -fluorinated oxide the active site has been proposed to involve  $Al^{III}$  in a disordered oxide/fluoride environment [14], while the active site in the BF<sub>3</sub>-alumina is likely to be identical or related to one of the species shown in Scheme 1. More important however, is the finding that the degree of fluorination is substantially less in the latter material (Table 1).

As a result, the pool of labile fluoride that can be replenished by HF in a catalytic situation will be correspondingly less.

#### 2.3. $[^{18}F]$ Exchange and uptake involving $BF_3$

We have shown previously [20] that fluorine-18 exchange between [<sup>18</sup>F]-labelled HF, SF<sub>4</sub> or BF<sub>3</sub> and SF<sub>4</sub>-fluorinated  $\gamma$ alumina occurs at room temperature. [<sup>18</sup>F] Exchange between these fluorides and SF<sub>4</sub>-fluorinated  $\gamma$ -alumina, subsequently conditioned with CH<sub>3</sub>CCl<sub>3</sub> as described above, was also observed, indicating that deposition of the organic layer did not inhibit the interactions [20]. [<sup>18</sup>F] Exchange behaviour between

Table 5

Room temperature [18F]-exchange after 1 h between BF2<sup>18</sup>F and fluorinated or fluorinated-plus-conditioned oxides<sup>a</sup>

[ <sup>18</sup> F]-BF <sub>3</sub> (mmol)	Oxide	Fluorinating agent	Conditioning agent	Exchange factor, f <sup>b</sup>
1.03-3.00 (five expts.)	γ-Alumina	SF <sub>4</sub>	None	0.88–0.26 <sup>c</sup>
1.03-3.00 (five expts.)	γ-Alumina	$SF_4$	CH <sub>3</sub> CCl <sub>3</sub>	$0.77 - 0.25^{\circ}$
0.35-3.00 (five expts.)	Chromia	$SF_4$	None	0.54-0.38
0.35-3.00 (five expts.)	Chromia	$SF_4$	CH <sub>3</sub> CCl <sub>3</sub>	0.54-0.26
1.0–1.50 (two expts.)	γ-Alumina	BF <sub>3</sub>	None	>0.90
1.0-1.50 (two expts.)	Chromia	BF <sub>3</sub>	None	$\geq 1$

<sup>a</sup> Samples 0.5 g in each case.

 $^{b}$  Defined as  $S_{0}-S_{t}\!/S_{0}-S_{\infty}\!,$  errors  $\leq\pm0.06.$ 

<sup>c</sup> Ref [20].

 $BF_2^{18}F$  and the solids described here is compared in Table 5 using exchange factors, f, derived from determination of the specific count rates of  $BF_2^{18}F$  before and after exposure. Although some variation was observed from replicate experiments, as has been noted previously [20], the exchange factors, f, derived from chromia which has been fluorinated using  $SF_4$ , appear to be rather similar to those from  $SF_4$ -fluorinated materials, if it is assumed that the fluorine content is 15 mg atom F (g chromia)<sup>-1</sup>. Because of the smaller F content of the oxides that have been fluorinated using  $BF_3$ , the f values are less precise than in the  $SF_4$  cases but it appeared that [<sup>18</sup>F] exchange was essentially complete (Table 5).

Further information relating to the interactions of BF<sub>3</sub> with these materials was obtained by monitoring the interaction with time in a closed double-limb counting vessel. The [<sup>18</sup>F] growth curve obtained on exposure of BF<sub>2</sub><sup>18</sup>F (0.35 mmol) to SF<sub>4</sub>fluorinated  $\gamma$ -alumina (0.528 g) at room temperature for 80 min is shown in Fig. 1. The rapid increase in [<sup>18</sup>F] activity detected from the solid over the first 20 min after admission of BF<sub>2</sub><sup>18</sup>F can be attributed most obviously to an exchange process, with an apparent *f* value of 0.8. However, the remainder of the curve, particularly the decrease in activity observed after 70 min, indicates that another process also occurs.

It is suggested that  $BF_2^{18}F$  is also adsorbed weakly on the solid, despite its acidic nature and that the reduction in [<sup>18</sup>F] activity is the result of its partial desorption. Consistent with this is the observation that a further small decrease in the count rate from the solid was observed on the removal of volatile material by condensation. Addition of unlabeled  $BF_3$  to the vessel resulted in a further decrease in the [<sup>18</sup>F] activity from the solid and the observation of a vapour [<sup>18</sup>F] count, indicating that exchange is observed when  $\gamma$ -alumina that had been treated with  $SF_4$  then  $CH_3CCl_3$  was exposed to  $BF_2^{18}F$  and also using the analogous chromia materials.

#### 2.4. Computations

In order to explore the differences in the fluorination behaviour of  $SF_4$  and  $BF_3$  towards  $\gamma$ -alumina from a different standpoint, the reactivities of both fluorides towards  $H_2AIOH$ 



Fig. 1.  $[^{18}F]$  Growth curve on  $SF_4$  fluorinated  $\gamma\text{-alumina}$  after addition of  $BF_2{}^{18}F.$ 

(as a model for surface –OH groups) and  $H_2AI$ –O–Al $H_2$  (as a model for bridging AI–O–AI groups) were calculated ab initio using Møller–Plesset perturbation theory. The species OSF<sub>2</sub> (formed by Eqs. (1) and (2)) and trimeric BOF, a six-membered B–O heterocycle, Fig. 2 (formed by Eqs. (3) and (4)) were assumed to be reasonable reaction products from the fluorides formed from these molecular fluorination reactions (as opposed to the experimentally observed, gas–solid reactions).

$$SF_4(g) + H_2AIOH(g) \rightarrow OSF_2(g) + HF(g) + H_2AIF(g)$$
(1)

$$SF_{4}\left(g\right) \,+\, H_{2}Al \text{-}O \text{-}AlH_{2}\left(g\right) \rightarrow OSF_{2}\left(g\right) \,+\, 2H_{2}AlF\left(g\right) \tag{2}$$

$$\begin{array}{l} BF_{3}\left(g\right) \,+\, H_{2}AlOH\left(g\right) \\ \rightarrow \,(1/3)(BOF)_{3}\left(g\right) \,+\, HF\left(g\right) \,+\, H_{2}AlF\left(g\right) \end{array} \tag{3}$$

$$\begin{aligned} BF_{3}\left(g\right) &+ H_{2}Al - O - AlH_{2}\left(g\right) \\ &\rightarrow (1/3)(BOF)_{3}\left(g\right) + 2H_{2}AlF\left(g\right) \end{aligned} \tag{4}$$

The computational results are summarised in Table 6 and Table 7 summarizes the reaction energies and enthalpy values for reactions (1)–(4). The electronic energies ( $\Delta E^{\text{el}}$ ) were computed ab initio (Table 7), which, after zero point energy (zpe, see Table 6) correction and correction for the translational ( $\Delta U(1)^{\text{tr}} = (3/2)$  RT,  $\Delta U(2)^{\text{tr}} = (3/2)$  RT,  $\Delta U(3)^{\text{tr}} = (1/2)$  RT,  $\Delta U(4)^{\text{tr}} = (1/2)$  RT) and rotational term ( $\Delta U(1)^{\text{rot}} = \text{RT}$ ,  $\Delta U(2)^{\text{rot}} = (3/2)$  RT,  $\Delta U(3)^{\text{rot}} = 0$  RT,  $\Delta U(4)^{\text{rot}} = (1/2)$  RT) and for the work term ( $p\Delta V(1) = \text{RT}$ ,  $p\Delta V(2) = \text{RT}$ ,  $p\Delta V(3) = (1/3)$  RT,  $p\Delta V(4) = (1/3)$  RT), were converted into the reaction enthalpy ( $\Delta H$ ) at 298 K (Table 7) [21].

The reaction enthalpy values (Table 7) indicate clearly that for the reaction of SF<sub>4</sub> with H<sub>2</sub>AlOH (as a model for surface – OH groups) and H<sub>2</sub>Al–O–AlH<sub>2</sub> (as a model for bridging Al–O– Al groups) the fluorination is thermodynamically highly favourable in both cases. In contrast to the fluorination with SF<sub>4</sub>, the reaction of BF<sub>3</sub> with H<sub>2</sub>AlOH (as a model for surface –



Fig. 2. MP2(FU)/6-31G(2d,p) computed structure for (BOF)<sub>3</sub>.

#### Table 6

Computed total energies (E) and zero point energies (zpe)

	Molecule	pg	-E (a.u.)	NIMAG	zpe (kcal $mol^{-1}$ )
MP2/cc-pVDZ MP2(FU)/6-31G(2d,p) MP4(FU,SDQ)/6-31G(2d,p)//MP2(FU)/6-31G(2d,p)	HF	$C_{\infty \mathrm{v}}$	100.221047 100.236447 100.241135	0 0	6.0 6.0 a
MP2/cc-pVDZ MP2(FU)/6-31G(2d,p) MP4(FU,SDQ)/6-31G(2d,p)//MP2(FU)/6-31G(2d,p)	SF <sub>4</sub>	$C_{2v}$	796.068720 796.192710 796.201612	0 0	7.3 7.3 a
MP2/cc-pVDZ MP2(FU)/6-31G(2d,p) MP4(FU,SDQ)/6-31G(2d,p)//MP2(FU)/6-31G(2d,p)	H <sub>2</sub> AlOH	Cs	318.825853 318.862416 318.879895	0 0	16.9 17.3 a
MP2/cc-pVDZ MP2(FU)/6-31G(2d,p) MP4(FU,SDQ)/6-31G(2d,p)//MP2(FU)/6-31G(2d,p)	OSF <sub>2</sub>	Cs	671.904781 672.009930 672.014862	0 0	5.8 5.9 a
MP2/cc-pVDZ MP2(FU)/6-31G(2d,p) MP4(FU,SDQ)/6-31G(2d,p)//MP2(FU)/6-31G(2d,p)	H <sub>2</sub> AlF	$C_{2v}$	342.836072 342.868103 342.883264	0 0	9.8 10.0 a
MP2/cc-pVDZ MP2(FU)/6-31G(2d,p) MP4(FU,SDQ)/6-31G(2d,p)//MP2(FU)/6-31G(2d,p)	H <sub>2</sub> AlOAlH <sub>2</sub>	$D_{ m 2d}$	561.431557 561.476079 561.502945	0 0	19.7 20.2 a
MP2/cc-pVDZ MP2(FU)/6-31G(2d,p) MP4(FU,SDQ)/6-31G(2d,p)//MP2(FU)/6-31G(2d,p)	BF <sub>3</sub>	$D_{3\mathrm{h}}$	323.839020 323.912181 323.919524	0 0	7.8 8.0 a
MP2/cc-pVDZ MP2(FU)/6-31G(2d,p) MP4(FU,SDQ)/6-31G(2d,p)//MP2(FU)/6-31G(2d,p)	(BOF) <sub>3</sub>	$D_{3\mathrm{h}}$	598.828152 599.004757 599.020339	0 0	23.4 23.9 a

pg = point group; NIMAG = number of imaginary frequencies.

<sup>a</sup> For the MP4 single point calculation the zpe values were taken from the MP2(FU) calculation.

OH groups) is thermodynamically neutral ( $\Delta H \approx 0$ ) whereas the reaction of BF<sub>3</sub> with H<sub>2</sub>Al–O–AlH<sub>2</sub> (as a model for bridging Al–O–Al groups) is thermodynamically slightly favourable with  $\Delta H \approx -9$  kcal mol<sup>-1</sup>.

Although our comparison of molecular computations with a study of the behaviour of different fluorinated surfaces is not entirely logical, we feel it is informative and therefore justified. The situation is not unlike the current situation for solid Lewis acid binary fluorides. Values of  $F^-$  ion affinities computed for isolated molecular fluorides [1] have not only featured in

#### Table 7

Calculated reaction energies and enthalpies for reactions (1)-(4)

Reaction	Level of theory	$\frac{\Delta E^{\text{electronic}}}{(\text{kcal mol}^{-1})}$	$\Delta H^{\circ}$ (kcal mol <sup>-1</sup> )
1	MP2/cc-pVDZ MP2(FU)/6-31G(2d,p) MP4//MP2	-42.2 -37.2 -36.2	-42.7 -37.8 -36.8
2	MP2/cc-pVDZ MP2(FU)/6-31G(2d,p) MP4//MP2	-48.1 -48.5 -48.2	-47.4 -47.7 -47.4
3	MP2/cc-pVDZ MP2(FU)/6-31G(2d,p) MP4//MP2	-1.0 -1.0 +1.0	-1.6 -1.9 +0.2
4	MP2/cc-pVDZ MP2(FU)/6-31G(2d,p) MP4//MP2	-6.9 -10.2 -10.9	-6.2 -9.6 -10.3

discussions of acidity in molecular fluorides [22] but have also acted as a spur for the development of new forms of highly acidic solid fluorides having extended structures [23].

#### 3. Conclusions

Consistent with previous studies, promotion of surface acidity, both Lewis and Brönsted, on  $\gamma$ -alumina results from its treatment with BF<sub>3</sub> at room temperature. The surface fluorinecontaining species formed are labile with respect to exchange but the pool of labile fluorine is significantly smaller than when SF<sub>4</sub> is used as the fluorinating agent. As a result, BF<sub>3</sub>-supported  $\gamma$ -alumina is an effective catalyst for the dehydrochlorination of CH<sub>3</sub>CCl<sub>3</sub> but, unlike SF<sub>4</sub>-fluorinated  $\gamma$ -alumina, it is an ineffective catalyst for halogen exchange involving CH<sub>3</sub>CCl<sub>3</sub>. Although the basis for the theoretical findings is very different from the experimental reaction conditions, the findings themselves are in good accord with the experimental observation that BF<sub>3</sub> and SF<sub>4</sub> are very different in their fluorination behaviour towards  $\gamma$ -alumina.

#### 4. Experimental

#### 4.1. General reagents, methods and instrumentation

Vacuum, Pyrex and Monel metal systems, and glove box techniques were used throughout. Sulfur tetrafluoride and boron

trifluoride were commercial products and were purified before use by trap to trap distillation *in vacuo* over dried NaF. The chlorohydrocrbons, CH<sub>3</sub>CCl<sub>3</sub> and CH<sub>2</sub>=CCl<sub>2</sub>, both 99% pure, Aldrich, were degassed, vacuum distilled to remove the stabilisers, 1,4-dioxane and hydroquinone monomethyl ether, respectively; the purified reagents were stored *in vacuo* under subdued light over activated 3A molecular sieves. Samples were degassed again before use to remove any volatile decomposition products that might have been formed during storage.

 $\gamma$ -Alumina (Degussa C) was a fine powder that was caked  $(500 \text{ g with deionised water, } 350 \text{ cm}^3)$  heated, then sieved to give a particle size range of 400-1680 µm. Chromia was prepared as a fine green powder by the ammonium dichromate volcano reaction [24]. A sample of each oxide (typically 10 g) was heated under dynamic vacuum in a Monel metal pressure vessel for 6 h at 23 K. Treatment with SF<sub>4</sub> was according to a published procedure [11] and consisted of sequential exposure of an oxide sample (0.5 g), contained in a Monel metal vessel, to three aliquots (3 mmol) of SF<sub>4</sub> for 3 h, nominally at room temperature. After each addition the volatile product, a mixture of OSF<sub>2</sub> and SO<sub>2</sub>, was examined by FTIR spectroscopy; some reactions were followed also by observing pressure changes (Heise Bourdon gauge) during the additions. Conditioning of the SF<sub>4</sub>-fluorinated oxides (0.5 g) with CH<sub>3</sub>CCl<sub>3</sub> or CH<sub>2</sub>=CCl<sub>2</sub> (3 mmol in each case) and the investigation of catalytic halogen exchange reactions between CH<sub>3</sub>CCl<sub>3</sub> and anhydrous HF (3:1 mole ratio at room temperature using a Monel metal vessel) in the presence of fluorinated then conditioned oxides (0.5 g) both used published procedures [11]. In addition, some experiments were carried out in Pyrex in order to be able to carry out mass balance measurements and to be able to observe colour changes. B.E.T areas, determined using Micromeritics 2400 equipment, were as follows: heat treated  $\gamma$ -alumina, 110; after fluorination with SF<sub>4</sub>, 90; after fluorination then conditioning with  $CH_3CCl_3$ , 94 m<sup>2</sup> g<sup>-1</sup>. Corresponding values for chromia were 52, 44 and 47  $m^2 g^{-1}$ , respectively.

A parallel investigation of  $BF_3$ -fluorinated oxides was performed in a manner similar to that described above, the difference being the stoichiometry of  $BF_3$  used at the fluorination step. In view of the results of the [<sup>18</sup>F]-BF<sub>3</sub> fluorination study, sequential addition of four aliquots of  $BF_3$ (1 mmol) was adopted.

Vapour phase samples for FTIR spectroscopy were contained in a Pyrex cell fitted with AgCl windows. The cell had a depression below the light path to enable the spectra of volatile components directly above fluorinated oxides to be obtained. Investigations of hydrochlorocarbon loss from the vapour phase during conditioning of fluorinated oxides were made; kinetics were complex and did not follow any simple reaction order. Diffuse reflectance infrared Fourier transform spectra (DRIFTS) were made using a Nicolet Auxiliary Experiment Module attached to a Nicolet 5DXC FTIR spectrometer. Handling and scan times were kept as short as possible to minimise hydrolysis. Volatile product mixtures from conditioning or catalytic reactions were analysed by off line GC (Varian 3400 instrument, FID, 50 m capillary column, He carrier gas).

#### 4.2. Fluorine-18 tracer experiments

The procedures and methods for preparation of the isotope <sup>18</sup>F], labelling of inorganic fluorides and counting equipment and procedures have been described elsewhere [25-27]. Experiments that involved the interactions of [<sup>18</sup>F]-labelled  $BF_3$  with  $\gamma$ -alumina or with fluorinated  $\gamma$ -alumina samples were carried out in calibrated Pyrex double limbed counting vessels, each limb being fitted with a PTFE/Pyrex vacuum stop cock; the latter enabled the individual limbs to be isolated one from the other. The dimensions of each limb were identical and were such that the lower portion of a limb was a snug fit with the scintillation well counter. At the beginning of an experiment a sample (normally 0.5 g) of the solid to be investigated was loaded into one limb in the glove box. The vessel was connected to a vacuum line, evacuated and a measured quantity of  $[^{18}F]$ -BF<sub>3</sub>, whose specific count rate had been determined previously, condensed into the other limb. The gas was allowed to warm to room temperature and to contact the solid. Each limb was counted alternately as the interaction proceeded to an apparent equilibrium. Counts due to the solid were obtained by subtraction of the vapour-only count (obtained from one limb) from the vapour-plus-solid count (obtained from the other). The efficiency of vapour phase counting was far smaller than that from the solid, justifying the simple subtraction method used. At the end of each experiment, any gas that remained was removed by vacuum distillation and the final solid count determined. In some cases an inactive aliquot of BF3 was added to determine the transfer of radioactivity from solid to vapour phase.

#### 4.3. Computational methods

All calculations were performed with the program package Gaussian 98 [28]. All structures, energies, zero point energies (zpe) and vibrational data were calculated at the electron correlated MP2 level of theory [29] using either a polarized standard double-zeta 6-31G(2d,p) basis set or Dunning's correlation consistent cc-pVDZ double-zeta basis set [30]. In order to account for contribution of the core orbitals to the binding energy, which is structure-dependent [31], the more expensive MP2(FULL)/6-31G(2d,p) method, where all electrons are included in a correlation calculation for the computation of the structures and energies, was applied. The zero point energies for the MP4 single point calculation (MP4(FULL,SDQ/6-31G(2d,p)//MP2(FULL)/6-31G(2d,p)) were taken from the MP2(FULL)/6-31G(2d,p) calculations.

The usually very poor agreement between experiment and uncorrelated Hartree–Fock calculation for fluorine containing non-metal molecules clearly shows the great importance of electron correlation for accurate predictions for fluorine containing non-metal compounds [32]. Note that the  $F_2$ molecule is unbound if electron correlation is not taken into account [33,34]. Whereas the CCSD(T) method has generally been shown to be reliable for covalently bound non-metal compounds [32,35] often the less expensive MP2 method in combination with a double-zeta basis set gives very good structural results and vibrational frequencies[21,35].

#### Acknowledgement

We thank the EPSRC for a studentship (to F. McM).

#### References

- K.O. Christe, D.A. Dixon, D. McLemore, W.W. Wilson, J.A. Sheehy, J.A. Boatz, J. Fluorine Chem. 101 (2000) 151–153.
- [2] G.A. Olah (Ed.), Friedel-Crafts and Related Reactions, vol. 1, Interscience, New York, London, 1963;
  M. Houe-Grant (Ed.), Fluorine Chemistry: a Comprehensive Treatment. Encyclopedia Reprint Series, John Wiley and Sons, New York, 1995, p. 60.
- [3] D. Fărcașiu, J.Q. Li, J. Phys. Chem. 98 (1994) 6893-6896.
- [4] K.H. Rhee, M.R. Basilà, J. Catal. 10 (1968) 243-251.
- [5] B.A. Morrow, A. Devi, J. Chem. Soc.: Faraday Trans. I 68 (1972) 403– 422.
- [6] Yu.I. Kozorezov, I.P. Erofeeva, Zh. Fiz. Chim. 49 (1975) 666–668, Chem. Abstr. 83 (1975) 42931y;

Yu.I. Kozorezov, N.M. Pikalo, I.P. Erofeeva, Zh. Fiz. Khim. 51 (1977) 1166–1169, Chem. Abstr. 87 (1977) 73773k;

Yu.I. Korezov, V.I. Lisin, Neftekhimiya 17 (1977) 396–400, Chem. Abstr. 87 (1977) 101864m;

Yu.I. Kozorezov, A.N. Kuleshova, Kinet. Katal. 18 (1977) 813–814, Chem. Abstr. 87 (1977) 117268f.

- [7] M. Marczewski, H. Marczewska, K. Witoslawski, Bull. Soc. Chim. Fr. 128 (1991) 366–371.
- [8] W. Wang, Y. Zhang, K. Ding, J. Li, J. Fluorine Chem. 126 (2005) 1463– 1466.
- [9] S.H. Baek, M. Srebnik, R. Mechoulam, Tetrahedron Lett. 26 (1985) 1083– 1086;

S.H. Baek, Y.C. Kim, Y.O. Kim, Bull. Korean Chem. Soc. 15 (1994) 507–508, Chem. Abstr. 121 (1994) 157232s;

S.-H. Baek, C.N. Yook, D.S. Han, Bull. Korean Chem. Soc. 16 (1995) 293–296, Chem. Abstr. 122 (1995) 239992z.

 K. Wilson, J.H. Clark, Chem. Commun. (1998) 2135–2136; see also: J.H. Clark, J.E. Johnstone, M.S. White, Chem. Commun. (1996) 2523–2524;
 P.M. Price, J.H. Clark, D.J. Macquarrie, J. Chem. Soc.: Dalton Trans.

(2000) 101–110; C.R. Quinn, J.H. Clark, S.J. Tavener, K. Wilson, Green Chem. 5 (2003)

602–605.

- [11] J. Thomson, G. Webb, J.M. Winfield, D. Bonniface, C. Shortman, N. Winterton, Appl. Catal. A 97 (1993) 67–76.
- [12] H. Bozorgzadeh, E. Kemnitz, M. Nickkho-Amiry, T. Skapin, J.M. Winfield, J. Fluorine Chem. 107 (2001) 45–52.
- [13] H. Bozorgzadeh, E. Kemnitz, M. Nickkho-Amiry, T. Skapin, J.M. Winfield, J. Fluorine Chem. 110 (2001) 181–189;
  H. Bozorgzadeh, E. Kemnitz, M. Nickkho-Amiry, T. Skapin, G.D. Tate, J.M. Winfield, J. Fluorine Chem. 112 (2001) 225–232.
- [14] 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.
- [15] A. Bendada, G. Webb, J.M. Winfield, Eur. J. Solid State Inorg. Chem. 33 (1996) 907–916.
- [16] O. Boese, W.E.S. Unger, E. Kemnitz, S.L.M. Schroeder, Phys. Chem.: Chem. Phys. 4 (2002) 2824–2832.
- [17] A.E. Kulikova, E.N. Zil'berman, Russ. Chem. Rev. 40 (1971) 256– 271.
- [18] J.H. Gough, M.D. Sutherland, Aust. J. Chem. 24 (1971) 1737–1738;
   D.G. McBeth, J.M. Winfield, B.W. Cook, N. Winterton, J. Chem. Soc.: Dalton Trans. (1990) 671–676.
- [19] J. Thomson, G. Webb, J.M. Winfield, J. Mol. Catal. 68 (1991) 347-354.

- [20] A. Bendada, D.W. Bonniface, F. McMonagle, R. Marshall, C. Shortman, R.R. Spence, J. Thomson, G. Webb, J.M. Winfield, N. Winterton, Chem. Commun. (1996) 1947–1948.
- [21] T.M. Klapötke, A. Schulz, Quantenmechanische Methoden in der Hauptgruppenchemie, Spektrum, Heidelberg, 1996, pp. 92–100;
  T.M. Klapötke, A. Schulz, R.D. Harcourt, Quantum Chemical Methods in Main-Group Chemistry, Wiley, Chichester, New York, 1998, pp. 89–98.
  [22] H.D. Lucher, H.P. Bachetter, L. Pacamara, Chem. (2) (2003)
- [22] H.D.B. Jenkins, H.K. Roobottom, J. Passmore: Inorg. Chem. 42 (2003) 2886–2893;
   H.D.B. Jenkins, I. Krossing, J. Passmore, I. Raabe, J. Fluorine Chem. 125 (2004) 1585–1592.
- [23] E. Kemnitz, U. Groβ, S. Rüdiger, C.S. Shekar, Angew. Chem. Int. Ed. 42 (2003) 4251–4254;
   S.K. Ruediger, U. Groβ, M. Feist, H.H. Prescott, S. Chandra Shekar, S.I.
- Troyanov, E. Kemnitz, J. Mater. Chem. 15 (2005) 588–597. [24] D. Klissurski, K. Hadjiivanov, A. Davydov, J. Catal. 111 (1988) 421–424.
- [25] K.W. Dixon, J.M. Winfield, J. Chem. Soc.: Dalton Trans. (1989) 937–942.
- [26] T. Baird, A. Bendada, G. Webb, J.M. Winfield, J. Mater. Chem. 1 (1991)
- 1071–1077. [27] A.W. Baker, D. Bonniface, T.M. Klapötke, I. Nicol, J.D. Scott, R.R.
- Spence, M.J. Watson, G. Webb, J.M. Winfield, J. Fluorine Chem. 102 (2000) 279–284.
  [28] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C.
- Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala,
  Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B.
  Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko,
  P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith,
  M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C.
  Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 98,
  Revision A.3, Gaussian Inc., Pittsburgh, PA, 1998.
- [29] C. Møller, M.S. Plesset, Phys. Rev. 46 (1934) 618-622;

R.J. Bartlett, D.M. Silver, J. Chem. Phys. 62 (1975) 3258–3268;
J.A. Pople, J.S. Binkley, R. Seeger, Int. J. Quant. Chem.: Quant. Chem. Symp. 10 (1976) 1–19;

J.A. Pople, R. Seeger, R. Krishnan, Int. J. Quant. Chem: Quant. Chem. Symp. 11 (1977) 149–163;

S. Sæbø, J. Almlöf, Chem. Phys. Lett. 154 (1989) 83-89;

M. Head-Gordon, J.A. Pople, M.J. Frisch, Chem. Phys. Lett. 153 (1988) 503–506;

M.J. Frisch, M. Head-Gordon, J.A. Pople, Chem. Phys. Lett. 166 (1990) 275–280, and 281–289;

M. Head-Gordon, T. Head-Gordon, Chem. Phys. Lett. 220 (1994) 122–128.

[30] A.D. McLean, G.S. Chandler, J. Chem. Phys. 72 (1980) 5639–5648;
R. Krishnan, J.S. Binkley, R. Seeger, J.A. Pople, J. Chem. Phys. 72 (1980) 650–654;
D.E. Woon, T.H. Dunning Jr., J. Chem. Phys. 98 (1993) 1358–1371;
R.A. Kendall, T.H. Dunning Jr., R.J. Harrison, J. Chem. Phys. 96 (1992) 6796–6806;
T.H. Dunning Jr., J. Chem. Phys. 90 (1989) 1007–1023;
K.A. Betterrer, D.E. Wase, T.H. Durning In., Phys. 100 (1994)

K.A. Peterson, D.E. Woon, T.H. Dunning Jr., J. Chem. Phys. 100 (1994) 7410–7415.

- [31] F. Wang, R.D. Harcourt, J. Phys. Chem. A 104 (2000) 1304–1310.
- [32] J.B. Foresman, A. Frisch, Exploring Chemistry with Electronic Structure Methods, 2nd ed., Gaussian Inc., Pittsburgh, 1993.
- [33] W. Kutzelnigg, Angew. Chem. Int. Ed. Engl. 12 (1973) 546-562.
- [34] T.M. Klapötke, in: E. Riedel (Ed.), Moderne Anorganische Chemie, Walter de Gruyter, Berlin, New York, 1999, pp. 34–40.
- [35] D.A. Dixon, D. Feller, Computational Thermochemistry of Fluorinated Compounds 14th ACS Winter Fluorine Conference, St. Petersburg, FL, abstract no. 29, January 17–22, 1999.