Available online at www.sciencedirect.com
ScienceDirect
Journal of Fluorine Chemistry 127 (2006) 1446–1453
JOURNAL OF FLUORINE CHEMISTRY
www.elsevier.com/locate/fluor

γ-Alumina-supported boron trifluoride: Catalysis, radiotracer studies and computations

Thomas M. Klapötke [a], Fiona McMonagle [b], Ronald R. Spence [b], John M. Winfield [b,*]

[a] *Department of Chemistry and Biochemistry, Ludwig-Maximilian University of Munich, Butenandtstr. 5-13(D), D-81377 Munich, Germany*
[b] *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 γ-alumina and amorphous chromia, in both cases at room temperature, has been studied using [^{18}F]-labelled BF_3. Although the resulting γ-alumina surface has some catalytic activity for the room temperature fluorination by anhydrous HF of CH_3CCl_3 under static conditions, its activity is far lower than that of γ-alumina, which has been fluorinated with SF_4, nominally at room temperature. A possible explanation for the observed behaviour is given.

Keywords: Boron trifluoride; Sulfur tetrafluoride; Alumina; Catalysis; [^{18}F] 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_3 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_2, from the reaction with surface Al–OH [4], Si–OBF_2, 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_3 is adsorbed on perfect NiO (0 0 1) is –OBF_3 but adsorption at a Ni-site is favoured on an O-deficient surface [8].

Supporting a complex such as BF_3,OEt_2 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_3,$2H_2O$ in EtOH is used to prepare a silica-supported BF_3 catalyst, a higher coverage of stronger Brönsted surface sites is obtained than is the case when BF_3,OEt_2 is used as the precursor [10].

Our interest in BF_3 supported on γ-alumina arose from studying the behaviour of γ-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_4-fluorinated γ-alumina can be fine tuned by modification of the conditions used for the fluorination [14]. Boron trifluoride might therefore be an alternative to SF_4 in these applications.

Here the behaviour of γ-alumina treated with BF_3 is compared with those of γ-alumina and amorphous chromia,

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

0022-1139/$ – see front matter © 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 1,1,1-trichloroethane, 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.

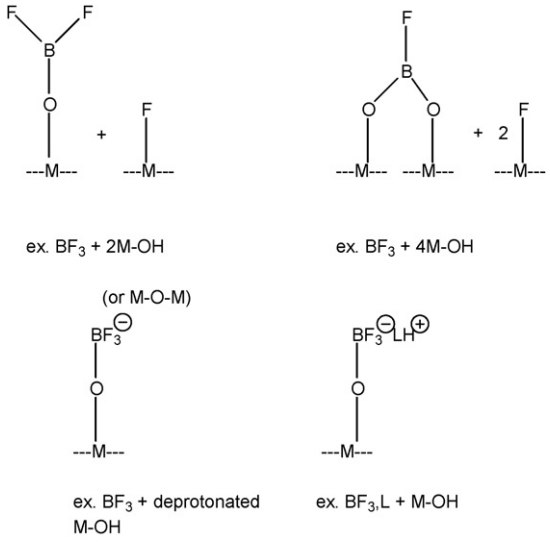
2. Results and discussion

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

The use of [^{18}F]-labelled BF_3, whose specific count rate has been experimentally determined, is a convenient way of establishing the stoichiometry of the interaction of BF_3 with solid oxides. The results of sequential $BF_2{}^{18}F$ additions to γ-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 $BF_2{}^{18}F$ in each case, were 2.05 and 1.45 mg atom F (g solid)$^{-1}$, respectively, equivalent to 3.9 and 2.75 wt.% F. The corresponding figure obtained previously for the uptake of fluorine by γ-alumina after exposure to $SF_3{}^{18}F$ under comparable conditions is 15 mg atom F (g solid)$^{-1}$ (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≡2F). This will lead to surface Al^{III} atoms in a disordered O/F environment that can function as very strong Lewis sites [14]. From a recent surface science study of γ-alumina fluorination by $CHClF_2$, 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_3 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 γ-alumina is easily envisaged, particularly when L in Scheme 1 is H_2O (cf. Ref. [10]), the promotion of Lewis acidity at a coordinatively unsaturated surface Al^{III} will be dependent on the inductive effect of a neighbouring $-OBF_2$ group. This is likely to be smaller than in the SF_4-fluorinated case where more than one F is bound directly to a surface Al^{III} [14]. Interestingly, although DRIFTS of adsorbed pyridine on BF_3-treated γ-alumina indicated that both Lewis and Brönsted sites were present, there were no marked differences from the spectra of pyridine adsorbed on SF_4-treated γ-alumina.

2.2. Reactions of BF_3- and SF_4-treated γ-alumina and SF_4-treated chromia with 1,1,1-trichloroethane

The reaction used to compare the catalytic properties of γ-alumina and amorphous chromia after exposure to BF_3 or SF_4 involved exposure of the fluoride-treated solids to 1,1,1-trichloroethane vapour at room temperature. The chemistry of chlorocarbons in the presence of acidic solids is complex and

Table 1
Uptake of [^{18}F] by γ-alumina (0.505 g) and amorphous chromia (0.535 g) on exposure to $BF_2{}^{18}F$ aliquots (ca. 1 mmol)[a] at room temperature for 1 h

Aliquot no.	$BF_2{}^{18}F$ count rate (count min^{-1})[b]	Solid count rate (count min^{-1})		$BF_2{}^{18}F$ recovered (%)
		Initial[b]	After $BF_2{}^{18}F$ removal[c]	
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

[a] $BF_2{}^{18}F$ specific count rates, 10,923 count min^{-1} (mg atom F)$^{-1}$.
[b] Relative error <2%.
[c] Relative error <1%.