Available online at www.sciencedirect.com

ScienceDirect

Journal of Fluorine Chemistry 129 (2008) 366–375

JOURNAL OF FLUORINE CHEMISTRY

www.elsevier.com/locate/fluor

# A comparative study of surface acidity in the amorphous, high surface area solids, aluminium fluoride, magnesium fluoride and magnesium fluoride containing iron(III) or aluminium(III) fluorides

Mahmood Nickkho-Amiry [a,1], Gehan Eltanany [b], Stefan Wuttke [b], Stephan Rüdiger [b], Erhard Kemnitz [b], John M. Winfield [a,*]

[a] *Department of Chemistry, University of Glasgow, Joseph Black Building, Glasgow G12 8QQ, UK*
[b] *Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Straße 2, 12489 Berlin, Germany*

Received 24 October 2007; received in revised form 21 January 2008; accepted 22 January 2008
Available online 13 February 2008

## Abstract

The behaviour of the sol–gel prepared, amorphous solids, high surface area (HS) aluminium fluoride and magnesium fluoride in promoting room temperature dehydrochlorination of *tert*-butyl chloride ($Bu^tCl$), in their catalytic activity for the dismutation of chlorodifluoromethane and in the temperature programmed desorption of ammonia is similar, indicating that, unexpectedly, both solids exhibit significant surface Lewis acidity. Using a similar approach, it has been demonstrated that surface Lewis acidity in HS-$MgF_2$ is enhanced by the incorporation of amorphous iron(III) fluoride and probably also by amorphous aluminium(III) fluoride. A second, unexpected feature is the substantial retention of anhydrous hydrogen chloride by all the solids, which is observed by the use of chlorine-36 labelling, when they are exposed at room temperature either to $Bu^tCl$ or to HCl directly. The detailed behaviour of $H^{36}Cl$ towards HS-$AlF_3$ depends on the fluorinating agent, dichlorodifluoromethane or anhydrous hydrogen fluoride, which is used in the second stage of HS-$AlF_3$ synthesis. This observation and the pattern of the results obtained overall lead to the proposal that strongly adsorbed HCl behaves as an unconventional Lewis base towards these solids.

*Keywords:* Aluminium fluoride; Magnesium fluoride; Lewis acid; Dehydrochlorination; Chlorine-36

## 1. Introduction

The dehydrochlorination of 1,1,1-trichloroethane has been used as an operational test of surface acidity on various types of solid, both by ourselves and by others. The original study involved resublimed aluminium(III) chloride [1]. Subsequently, the room temperature dehydrochlorination of $CH_3CCl_3$ in the presence of γ-alumina, either chlorinated using carbon tetrachloride [2] or fluorinated using sulfur tetrafluoride [3], has been used as an indication of surface Lewis acidity in these materials. Dehydrochlorination of $CH_3CCl_3$ has been observed also above 400 K on γ-alumina [4] and various mixed metal fluorides, $MF_2/M'F_3$ [5]. In the γ-alumina case, the direct involvement of surface Lewis acid sites was demonstrated by selective poisoning with Lewis base molecules [4]. Dehydrochlorination is inhibited over halide catalysts even by trace quantities of the Lewis base, $H_2O$ [1–3].

Although the hydrochloroethane, $CH_3CCl_3$, is peculiarly susceptible to dehydrochlorination, this type of behaviour can be observed in other chloroalkanes, notably 2-chloropropane, 1,2-dichloropropane and *tert*-butyl chloride ($Bu^tCl$). Catalytic dehydrochlorination of the chloropropanes has been investigated over various oxide catalysts [6,7]. Lewis acidic oxides effectively promote dehydrochlorination, with $WO_3$ and silica-alumina catalysts having the greatest dehydrochlorination activities and the lowest threshold temperature of reaction (<400 K) [6,7]. However, the most acidic catalyst of those used, zeolite ZSM-5, had one of the lowest activities for dehydrochlorination. This was ascribed to the high activity of ZSM-5 in competing reactions, for example oligomerisation, cracking and aromatisation [6]. The probe molecule, *tert*-butyl

---

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

[1] Present address: Islamic Azad University of Jouybar, Jouybar, Iran.

0022-1139/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2008.01.017

Table 1
Synthesis conditions and properties of the HS-$AlF_3$ samples

| Sample code | Reagent used in gel fluorination | Fluorination conditions | BET area ($m^2\ g^{-1}$) |
|---|---|---|---|
| CFC1 (orange) | $CCl_2F_2/N_2$ (5:20)[a] | 573 K, 10 h | 186 |
| CFC2 (off-white) | $CCl_2F_2/N_2$(5:20) | 433 K, 2 h then 473, 2 h then 573 K | 170 |
| HF1 (off-white) | $HF/N_2$ (3:40) | 413 K, 4 h then $N_2$ alone, 10 h | 205 |
| HF2 (off-white) | $HF/N_2$ (3:40) | As for sample HF1 then $N_2$ at 520 K, 3 h | 72 |
| CFC3 (off-white) | $CCl_2F_2/N_2$ (7:20) | 423 K, 3 h then 473 K, 2 h, then 573 K | 180 |
| HF3 (off-white) | $HF/N_2$ (1:20) | 393 K, 4 h | 420 |

[a] Volumetric flow ratio in parentheses.

chloride is particularly interesting, since, in the presence of acidic solids, it may behave as an alkylation agent or may undergo dehydrochlorination, depending on the conditions used [8,9].

The solids studied in this paper are all amorphous materials, which have been synthesised under sol–gel conditions. An aluminium(III) fluoride gel is fluorinated further under flow conditions at moderate temperatures, using a chlorofluorocarbon, hydrochlorofluorocarbon or anhydrous hydrogen fluoride, in all cases diluted with dinitrogen, to give anhydrous materials whose stoichiometry is $AlF_3$. This material, which normally has a very high surface area (hence its designation as HS-$AlF_3$), has been studied previously in great detail by a variety of techniques [10–13]; it is capable of behaving as a very strong solid Lewis acid [10–12]. Using a similar synthetic approach but starting from magnesium methoxide rather than aluminium *iso*propoxide, results in the preparation of the analogous magnesium fluoride, HS-$MgF_2$ [14]. Mixed fluorides containing iron(III) or aluminium(III) can be prepared via the sol–gel route starting from mixtures of the corresponding metal alkoxides.

The methodology developed to study the surface acidity of these compounds involves the use of $Bu^tCl$ as the probe molecule with a combination of chlorine-36 radiotracer monitoring and FTIR spectroscopy. Details have been given elsewhere [15] but the central principle involves using the [$^{36}Cl$]-labelled compounds, $Bu^tCl$ or anhydrous HCl, to observe the formation of strongly or weakly adsorbed (chemically or physically adsorbed) labelled surface species. The distinction between these is made on the basis of whether the [$^{36}Cl$]-labelled surface species is removed easily or with difficulty under static or dynamic vacuum at room temperature. FTIR spectroscopy is used to monitor formation of HCl and hydrocarbon products and disappearance of $Bu^tCl$ in the vapour directly above the surface and hence to judge the extent of dehydrochlorination. By analogy with previous reports of its significant Lewis acidity [10–13], HS-$AlF_3$ promotes the room temperature dehydrochlorination of $Bu^tCl$. However, the adsorption behaviour of HS-$AlF_3$ towards anhydrous HCl depends on the reagent used in the second fluorination step in its synthesis and this is unexpected. Unexpected also is the behaviour of HS-$MgF_2$ as a good Lewis acid, not only with respect to $Bu^tCl$ dehydrochlorination at room temperature but also in the more conventional tests for a solid Lewis acid, temperature programmed desorption (TPD) of $NH_3$ and the catalytic dismutation of the HCFC, chlorodifluoromethane.

## 2. Results and discussion

### 2.1. Some properties of the metal fluoride samples used

Details of the six, amorphous HS-$AlF_3$ samples studied are contained in Table 1. They are identified by the codes, CFC 1, 2 or 3 and HF 1, 2 or 3, to distinguish the fluorination reagent $CCl_2F_2/N_2$ or $aHF/N_2$ used at the second synthetic stage. They differ in their Brunauer, Emmett, Teller (BET) areas but apart from one sample (HF2), the values determined are all of the order of 170 $m^2\ g^{-1}$ or greater. The colour of HS-$AlF_3$ can vary from off-white to orange, although variation in colour does not appear to indicate a large difference in surface properties.

The most important factor that affects their subsequent dehydrochlorination behaviour is the reagent used to perform the fluorination in the second stage of their synthesis. There is always a possibility when using dichlorodifluoromethane, or the HFC, chlorodifluoromethane, which is an alternative, of retaining organic matter on the surface after fluorination; in the present study however, residual carbon was always no more than 0.3%. Using $HF/N_2$ instead of $CCl_2F_2/N_2$ has, at least, two consequences. Firstly, the reaction enthalpy should be markedly higher with HF, therefore the reaction is carried out at lower temperature. Secondly, and this is more important, the HF behaves as Lewis base, reacting with the strong Lewis acid sites, which become thereby blocked. A similar situation has been demonstrated previously [9] for HF on β-$AlF_3$, a modification that has the hexagonal tungsten bronze structure [16]. Retention of small quantities of HF after the second stage fluorination using this reagent is therefore a probability. To desorb the HF the samples have been additionally heated for the indicated times in an $N_2$ flow, the temperatures employed were in case of sample HF2 about 100 K higher than in case of sample HF1. This can be seen as an explanation for the observed differences in surface area.

BET areas and pore data for the three samples based on HS-$MgF_2$ that were used are given in Table 2. These samples were all prepared using $aHF/N_2$ as the fluorination reagent for the second stage. At the beginning of the study significant Lewis acidity for the HS-$MgF_2$ surface was not expected, hence the use of the ‘cleaner’ $aHF/N_2$ reagent.