

Reactivity of fluorinated γ -alumina and β -aluminium(III) fluoride surfaces towards hydrogen halides and *tert*-butyl chloride

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The Lewis acids β -aluminium(III) fluoride and γ -alumina, fluorinated at room temperature with sulfur tetrafluoride, both interact with hydrogen fluoride and chloride, as demonstrated by radiotracer measurements using [¹⁸F] and [³⁶Cl]. The different behaviour of HCl towards the two surfaces is rationalised by considering plausible surface sites and, in the case of β -AlF₃, the role of residual water. Both materials promote dehydrochlorination of *tert*-butyl chloride. β -Aluminium(III) fluoride also has some catalytic activity in Friedel–Crafts alkylation whereas oligomerisation of Bu⁺Cl dominates on fluorinated γ -alumina. The different behaviour appears to be due to the presence of both Lewis and Brønsted surface acidity on γ -alumina that has been fluorinated under static conditions. A description for this surface is proposed.

Introduction

It has been recognised for many years that the acidity of a γ -alumina surface can be promoted by partial fluorination of its surface¹ and that this results in the formation of Al–F bonds.² Fluorinated aluminas have been used widely as acidic catalysts or catalyst supports, for example in hydrocarbon chemistry.³ The bulk conversion of alumina to aluminium(III) fluoride, although highly favourable thermodynamically,⁴ is kinetically slow and it is therefore important that the materials that result from pre-fluorination processes are characterized in some detail.

The situation is made more complicated by the existence of several metastable AlF₃ phases in addition to the thermodynamically stable α -AlF₃. The α -phase has a close-packed structure⁵ whereas β -AlF₃ has a more open structure of the hexagonal tungsten bronze (HTB) type.⁶ The other phases that have been characterized structurally are related to β -AlF₃.⁷ Although α -AlF₃ has little or no catalytic activity, the β -phase is an active heterogeneous catalyst for the dismutation of chlorofluoromethanes and hydrochlorofluoromethanes.^{8,9} The β -, η -, θ - and κ -phases are active catalysts for the fluorination of CHCl₃ or CCl₃CF₃ by anhydrous hydrogen fluoride.¹⁰

The catalytic behaviour of γ -alumina, pre-fluorinated using CCl₂F₂ or CHClF₂, in C₁ dismutation reactions is rather similar to that of β -AlF₃. It has been suggested therefore, that in their activated form, the former materials have a surface structure that resembles that of β -AlF₃.⁸ Although this is undoubtedly a simplification, the available evidence indicates that fluorinated alumina and the metastable AlF₃ phases are closely related in their surface properties. This developing situation has been reviewed recently, emphasising the results of X-ray photoelectron studies, which are particularly informative.¹¹ γ -Alumina, fluorinated using CCl₂F₂ or sulfur tetrafluoride under flow conditions, and β -AlF₃ are also good heterogeneous

catalysts for the isomerization of 1,1,2-trichlorotrifluoroethane to the thermodynamically preferred isomer, 1,1,1-trichlorotrifluoroethane, under flow conditions at moderate temperatures,¹² suggesting that in all cases, strong Lewis acid surface sites are present.¹³

We now report the results of a detailed comparison of the chemical reactivity of fluorinated γ -alumina and β -AlF₃ surfaces towards hydrogen fluoride, hydrogen chloride and *tert*-butyl chloride, which are generally regarded as very weak Lewis bases. *tert*-Butyl chloride was chosen as one of the probe molecules, since the catalytic behaviour of SF₄-fluorinated γ -alumina and β -AlF₃ in the alkylation of activated aromatics differs.¹⁴

The isolated AlF₃ molecule is recognised as a very strong Lewis acid¹⁵ and species of the type AlF₃(FH)_{*n*}, *n* = 1¹⁶ or 2¹⁷ have been identified as vapour phase products from thermal decomposition of α -AlF₃ or Al(OH)F₂(H₂O). From several computational studies, at various levels,^{18–20} of these and related species, it can be concluded that AlF₃(HF) is a credible molecular species, the most recent study giving a computed value for the dissociation energy of *ca.* 67 kJ mol^{–1}.²⁰ It was therefore of interest to examine the possible interaction between HF vapour and solid β -AlF₃, in which HF could be co-ordinated at surface Lewis acid sites or could be included in the hexagonal channels that are present in the structure.⁶ This aspect of the study was extended to determine whether there might be analogous interactions between β -AlF₃ or fluorinated γ -alumina and anhydrous HCl.

We have shown previously that acid–base interactions that involve a fluorinated surface can be studied using radiolabelled probe molecules²¹ and that the progress of the fluorination of an oxide surface can be monitored by labelling the fluorinating agent with the short-lived isotope, fluorine-18 (*t*_{1/2} = 110 min).^{22,23} The high sensitivity of the radiotracer approach is a great advantage in situations where acid–base interactions are likely to be weak or difficult to observe by spectroscopic methods. A similar approach was adopted in the present work using [¹⁸F]- and [³⁶Cl]-labelled hydrogen halides and [³⁶Cl]-

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labelled *tert*-butyl chloride. FTIR spectroscopic measurements on SF₄-fluorinated γ -alumina using pyridine as a probe molecule and mass spectrometric measurements of HCl and H₂O desorption from β -AlF₃ have been used to supplement the results from radiotracer experiments. Interpretations are offered for the behaviour of β -AlF₃ in terms of its structure⁶ and the structural model previously proposed for the surfaces of β -MF₃, M = Cr and Al, fluorides.^{11,24} The data are used also to propose a description for a fluorinated γ -alumina surface that is the result of the fluorination by SF₄.

Experimental

Standard vacuum and glove box (H₂O < 1 ppm) were used throughout. Except where described below, instrumentation and experimental methods have been described previously.^{12,25}

Preparation of materials

β -Aluminium(III) fluoride was prepared by the temperature programmed dehydration⁶ of AlF₃·3H₂O (5.0 g, Aldrich, purity 97%) under He (30 cm³ min⁻¹), heating from room temperature to 493 K at 5 K min⁻¹, held at 493 K for 1 h, heating to 723 K at 10 K min⁻¹, held at 723 K for 2 h, finally allowed to cool to room temperature under He flow. The β -AlF₃ so formed was transferred in a sealed vessel to a N₂ glove box (H₂O *ca.* 1 ppm) where subsequent manipulations were performed. Its identity was confirmed by XRD. Samples prepared in Berlin or Glasgow showed identical behaviour. Its BET area = 26 m² g⁻¹.¹²

Fluorinated γ -alumina was prepared under both flow and static conditions. γ -Alumina (Degussa, BET area = 110 m² g⁻¹) was calcined under N₂ flow at 523 K, then fluorinated under SF₄/N₂ flow for 2 h at 523 K (F, 47.1%; BET area = 67 m² g⁻¹).¹² Fluorinations under static conditions were performed in a Monel metal pressure vessel (Hoke, 90 cm³) attached to a Monel vacuum line.^{23,25} Typically, γ -alumina (1.5 g), previously caked, sieved to produce 500–1000 μ m particles and calcined *in vacuo* for 8 h at 523 K, was allowed to react with SF₄ (9.0 mmol, 99%, Fluorochem) for 2 h, nominally at room temperature. Volatile products, a mixture of OSF₂ and SO₂, whose components were identified by FTIR spectroscopy, were removed by distillation and the process repeated twice. The product, an off-white solid, was transferred to and handled subsequently in, a glove box. It could be stored for short periods in FEP; storage in Pyrex led to etching, indicating that HF was lost slowly from the solid. For this reason, smaller quantities (0.5 g) were prepared for use *in situ*, with the appropriate adjustment of the quantity of SF₄. Fluorinations were carried out also using SF₄/OSF₂ mixtures. Single point determinations of BET area (Coulter SA 3100 instrument) gave values in the range 80–90 m² g⁻¹. The imprecision was possibly a result of the corrosive nature of the material. Fluorine content was not determined directly but a value of *ca.* 22% was inferred from a previous [¹⁸F] study of the fluorination carried out under very similar conditions.²³

Anhydrous [³⁶Cl]-labelled hydrogen chloride was prepared from conc. aqueous HCl (10 cm³), to which was added H³⁶Cl (1–2 cm³, specific activity *ca.* 925 kBq cm⁻³) and 98% H₂SO₄. Trace H₂O was removed by trap to trap distillation over P₂O₅, the product being stored in an evacuated stainless steel vessel over P₂O₅.²⁶

2-Methylpropan-2-ol (1.66 g, 23.0 mmol) was shaken with conc. aqueous HCl (5.66 cm³) containing aqueous H³⁶Cl (1.0 cm³, 925 kBq) over a 2 h period. The lower aqueous layer was discarded and the organic layer washed with aqueous NaHCO₃ then H₂O.²⁷ The *tert*-butyl [³⁶Cl]chloride so formed, was dried over CaSO₄ then over 3A sieves *in vacuo*; the yield was *ca.* 70%. The [³⁶Cl] specific count rate of the vapour was 195 count min⁻¹ kPa⁻¹. No impurities in an inactive sample were detected using ¹H, ¹³C NMR or FTIR spectroscopy.

Reactions under Friedel–Crafts conditions

These were performed in a Pyrex three-necked flask, equipped with a septum cap for the introduction of reagents, an He gas inlet and a gas outlet, fitted with a condenser. β -Aluminium(III) fluoride or fluorinated γ -alumina (0.5 g in each case) was loaded in the glove box and the apparatus flushed with He. A mixture of dried toluene (224.0 mmol) and dried Bu'Cl was introduced *via* the septum and the mixture stirred magnetically at a constant rate to minimise diffusion effects. Samples of the liquid phase (0.5 cm³) were withdrawn at regular intervals and analysed by GC (AMS Model 93, 15 m capillary column, FID), response factors being determined by calibration with authentic samples of the products. Confirmatory measurements were made using GCMS (Hewlett Packard 5971 mass selective quadrupole detector at 70 eV interfaced to a Hewlett Packard 5890 series II GC, HP1 15 m column) and by ¹³C{¹H} NMR spectroscopy.

Radiotracer experiments

The preparation of the isotope [¹⁸F], *t*_{1/2} 110 min, β^+ (γ) emitter, the preparation of H¹⁸F and the counting procedures used have been described elsewhere.²⁸ Interactions between H¹⁸F and β -AlF₃ or fluorinated γ -alumina (0.5 g for both solids) were studied using an evacuable Ni tube reactor equipped with a tube furnace, valves (Whitey), an FEP counting tube and a Monel vessel to contain H¹⁸F or CCl₂FCClF₂. The apparatus was calibrated and well seasoned with HF before use. The reactor was loaded with solid in the glove box, supporting the solid on a plug of fine Monel gauze, and transferred to a Monel vacuum line. A measured quantity of H¹⁸F (normally 1–2 mmol), whose [¹⁸F] specific count rate (values in the range 45000–8000 count min⁻¹ [mg atom F]⁻¹) had been determined, was introduced and the reactor heated at 573 K for 0.5–0.75 h. Uncombined H¹⁸F was removed by distillation, quantified and counted. The solid was tipped into the FEP tube and counted. After [¹⁸F] had decayed completely, the solid was weighed. Labelled β -AlF₃ or F- γ -alumina (0.5 g), prepared as above, were exposed to CCl₂FCClF₂ (0.4–0.8 g) for 0.75–1.0 h at 523–548 K using a similar procedure.

The behaviour of β -AlF₃ or fluorinated γ -alumina towards [³⁶Cl]-labelled HCl or Bu'Cl was examined using the Geiger–Müller direct monitoring method, developed in Glasgow for [¹⁴C] adsorption measurements²⁹ and used subsequently for a variety of inorganic applications, including those with [³⁶Cl] and [³⁵S].²¹ An evacuable Pyrex counting vessel with a gas handling facility was used for measurements at ambient temperature. Two Geiger–Müller counters were positioned to enable [³⁶Cl] activity from the vapour phase and from the vapour plus surface (due to self-absorption of the β^- emitter [³⁶Cl]), activity from the bulk was not detected) to be monitored concurrently. The counting tubes were intercalibrated using H³⁶Cl, counts being recorded simultaneously on two scalers, enabling [³⁶Cl] counts from the surface of a solid placed below one of the counters to be determined by subtraction. Powdered β -AlF₃ or fluorinated γ -alumina (0.5 g) samples were spread as thinly as possible in order to approach the required criterion of an infinitely thin solid layer. Cell and solid were thoroughly degassed before a measured pressure of labelled H³⁶Cl or [³⁶Cl]-Bu'Cl vapour was added *via* a calibrated gas-handling manifold. Counting times were chosen to enable substantial counts (normally 10⁴ to minimise counting errors) to be accumulated. Pressures of volatile components were in the range 1300–6700 Pa. At the conclusion of an adsorption isotherm determination or of an addition sequence, volatile material was removed by distillation and the count from [³⁶Cl] material retained on the solid determined.

The interaction between β -AlF₃ or fluorinated γ -alumina and Bu'Cl vapour was also studied by FTIR using a 10 cm Pyrex cell containing a depression to hold solid below the beam. It was

fitted with KBr windows and an evacuable ampoule from which solid (0.5 g) could be added to the cell after a measured pressure of vapour had been added from a calibrated Pyrex vacuum manifold. The cell was supported in the spectrometer to ensure that positioning was reproducible. Spectra were recorded at regular intervals over periods up to 20 h.

Fluorination of γ -alumina with [^{18}F]- or [^{35}S]-labelled sulfur tetrafluoride

Samples of calcined γ -alumina (0.08, 0.10, 0.15 and 0.24 g), contained in Pyrex double limb counting vessels designed for the well of a NaI(Tl) well scintillation counter, were exposed to aliquots of SF_3^{18}F (2 mmol), prepared as previously described.²¹ The counts developed from the solids were monitored with time. Subtraction of the very small counts determined from the vapour phase, together with the determination of the [^{18}F] specific count rate of SF_3^{18}F (as SF_4py), enabled the uptakes of [^{18}F] to be determined. The fluorination of calcined γ -alumina at room temperature using $^{35}\text{SF}_4$, which was prepared as previously described,²¹ was carried out in a manner similar to that described above for the [^{36}Cl] experiments.

Desorption from β - AlF_3 studied by mass spectrometry

Desorption of H_2O and HCl was studied using a quartz reactor with an on line coupled mass spectrometer. Before desorption was determined, the samples were heated for 1 h at 313 K in the reactor under Ar ($p = 150$ Pa); the system was then heated at a rate of 10 K min^{-1} from 313 to 673 K. The variation of the gas phase composition during constant heating was analysed using a quadrupole mass spectrometer (QMG421I Pfeiffer Vacuum GmbH). Three experiments in which β - AlF_3 was treated in different ways, were performed.

(a) When untreated β - AlF_3 was examined, the water release was so great that no measurement was possible due to saturation of the detector. It was necessary to calcine β - AlF_3 *in situ* at 523 K, then allow the sample to cool to room temperature before following the procedure described above. (b) A fresh sample of β - AlF_3 was transferred into a Schlenk tube and exposed to HCl vapour flow for 30 min at room temperature. The treated sample was transferred under inert conditions into the reactor, held at 313 K for 1 h under Ar (150 Pa) in order to remove any weakly bound HCl and heated at a constant rate as described above while desorption of HCl and H_2O was monitored. (c) A β - AlF_3 sample was calcined under Ar at 573 K for 2 h. After cooling to room temperature, the sample was exposed to HCl for 30 min as described above. The sample was transferred to the reactor and desorption monitored.

X-Ray photoelectron spectroscopy

The XPS measurements were performed using an ESCALAB 220 iXL spectrometer (Fisons Instruments) consisting of two vacuum chambers: the analyser and the fast entry air lock/preparation chamber. The powdered sample was fixed on carbon conductive tape (Pelco International) at the top of the sample holder and transferred into the UHV chamber. The X-ray source was monochromatic focussed $\text{Al(K}\alpha)$ radiation (1486.6 eV) with an input power of 150 W. The charge on the sample was equalised with the instrument's charge compensation facility. The final peak position was determined using the C1s peak (shifted to 285.0 eV) corresponding to absorbed carbon species. The XPS-measurements were performed at a constant pass energy of 25 eV. The ESCALAB was calibrated routinely with the XPS lines of Au, Ag, and Cu.³⁰

Results and discussion

The aluminium(III) compounds

β -Aluminium(III) fluoride is a well characterized solid and was prepared by temperature programmed thermal decomposition

of $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$, *via* an amorphous intermediate, $\text{AlF}_3 \cdot x\text{H}_2\text{O}$.⁶ γ -Alumina was fluorinated under three sets of conditions, its properties being very dependent on those used.

Fluorination under flow conditions at 523 K for 2 h using a SF_4/N_2 gas stream¹² produced a solid with F content of 47.1%. These conditions are similar to those used to fluorinate alumina with other fluorinating agents.³¹ Fluorination under static conditions, nominally at room temperature, was carried out using three successive additions of SF_4 .²⁵ The procedure was based on a [^{18}F] radiotracer study of the fluorination, from which an estimated value for the fluorine content was *ca.* 22%.²³ Experiments in which γ -alumina was fluorinated in a double limb Pyrex counting vessel using a single aliquot of [^{18}F] labelled SF_4 , resulted in a rapid increase in [^{18}F] from the solid during the first 20 min and a constant value thereafter. The [^{18}F] activity retained corresponded to an average (determined from four samples) fluorine content of 5.2%. Similar experiments using [^{35}S]-labelled SF_4 and a Geiger–Müller direct monitoring counting cell²⁹ led to an immediate uptake of [^{35}S] by the surface. The count rate decreased steadily over the next 0.5 h, then increased slowly over the next 0.5 h. When material that was volatile at room temperature, a mixture of OSF_2 and SO_2 , was removed, the count rate decreased to background. Two further additions of $^{35}\text{SF}_4$ to the same sample resulted in an identical pattern for the behaviour of the [^{35}S] count rate, although the maximum value observed *in situ* increased from addition to addition.

Comparing this behaviour with the [^{18}F] experiments described above and with our previous [^{18}F] study,²³ which demonstrated that the extent of the fluorination increased with each SF_3^{18}F treatment, suggests the following rationalisation. An initial fluorination of the surface leads to the replacement of some surface Al-OH and Al-O-Al groups by Al-F , together with the formation of OSF_2 , SO_2 and HF . The increasing [^{35}S] count rates that were observed *in situ* over the course of the three additions of $^{35}\text{SF}_4$, suggest that SO_2 and possibly also OSF_2 , can be adsorbed weakly at the new Al^{III} -centred Lewis sites that have been created by the fluorination. Adsorption at basic surface fluoride sites is an alternative possibility. There was no evidence from the [^{35}S] measurements however that sulfur-containing species were permanently retained on the surface. In contrast, the [^{18}F] results indicated that loss of HF from the surface at room temperature was very small.

Brønsted and Lewis acidity of SF_4 -fluorinated γ -alumina

FTIR studies of adsorbed pyridine (py) or other basic probe molecules is a convenient method of obtaining information on the nature of surface acid sites.³² This method has been successfully applied, using photoacoustic detection, to the study of β - AlF_3 and fluorinated alumina surfaces and has yielded useful information concerning the relative importance of Lewis and Brønsted sites.⁹ γ -Alumina, fluorinated with SF_4 under flow or static conditions, was examined in this way. The spectrum of py adsorbed on the material previously fluorinated at 523 K under flow conditions, was similar to those obtained previously on CFC-fluorinated alumina.⁹ The relative intensities of py bands at 1452 and 1492 cm^{-1} indicated qualitatively that, although both types of site were present, Lewis sites predominated. Exposure of the sample to moist air followed by py treatment, resulted in the almost complete loss of IR bands associated with Lewis acidity but this could be restored by heating the sample at 423 K under N_2 flow. The relative intensities of the 1452 and 1492 cm^{-1} bands of py adsorbed on γ -alumina that had been fluorinated at room temperature under static conditions, were reversed compared with those in the spectrum described above and indicated qualitatively that Brønsted sites predominated. This situation was particularly obvious for a sample that had been exposed to moist air.

The most obvious origin of the Brønsted acidity at the surface of γ -alumina that has been fluorinated with SF_4 under

static conditions, is the HF that is produced from the primary fluorination of the surface by SF₄. Dissociative adsorption of HF at the surface should lead to the formation of new Brønsted sites and this suggestion is consistent with the [¹⁸F] observations made above. Formation of such sites is less likely under flow conditions at higher temperature, since HF desorption will be more favoured. A second possibility is that a sulfito species was formed, due to the incomplete removal of SO₂ during the surface fluorination. Some evidence for this suggestion is the observation of a peak, binding energy = *ca.* 167 eV and attributable to S^{IV}, in the S(2p) X-ray photoelectron spectrum of γ-alumina that had been fluorinated under static conditions. No S(2p) peak was observed in the spectrum of material fluorinated under flow conditions. Although this second explanation appears to be inconsistent with the [³⁵S] results reported above, very small quantities of ³⁵SO₂ retained immediately below the surface may not have been detected by Geiger–Müller counting due to self-absorption of the [³⁵S] β[−] radiation. Formation of sulfito groups on or near the surface cannot be completely excluded therefore. Irrespective of its exact origin, it appears that Brønsted surface acidity is enhanced by fluorination at lower temperatures under static conditions.

Surface modification of oxidic solids, such as mesoporous silicas, by small changes in the pretreatment regime is now a well established technique.³³ An example relevant to the present work is the enhancement of surface Brønsted acidity on mesoporous silica by treatment with BF₃(H₂O)₂. Enhancement is less pronounced in silica which has been treated with BF₃(OEt)₂.³⁴ Exposure of both materials to py results in the observation of IR bands associated with Lewis and Brønsted acidity, the latter being more obvious when the pretreatment was with BF₃(H₂O)₂.³⁴

The behaviour of H¹⁸F or H³⁶Cl towards β-AlF₃ and fluorinated γ-alumina

Exposure of β-AlF₃ (5.9 mmol) to H¹⁸F (1.0 mmol, specific count rate = 49482 count min^{−1} [mg atom F]^{−1}) at 473 K for 1 h produced a [¹⁸F]-labelled solid. The specific count rate of the H¹⁸F recovered (0.75 mmol) was 7974 count min^{−1} [mg atom F]^{−1}. This result indicated that both [¹⁸F] exchange and retention of HF by β-AlF₃ had occurred. Repetition with β-AlF₃ (6.2 mmol) and H¹⁸F (0.75 mmol) at 548 K for 1 h gave similar results, the proportion of HF retained being 21%. Since it is believed that HF is adsorbed on fluorinated γ-alumina (*cf.* above), [¹⁸F] exchange with H¹⁸F vapour should be extensive. This has been demonstrated previously at room temperature.³⁵ The interaction between SF₄-fluorinated γ-alumina and H¹⁸F at 473 K was substantial and the great extent to which H¹⁸F was retained by the solid made it impossible to quantify precisely the degree of the exchange. However, in view of the substantial [¹⁸F] exchange observed at room temperature,³⁵ the situation at higher temperatures will be similar.

Exposure of the solids that had been labelled with [¹⁸F] by this means, to CCl₂FCClF₂ at 548 or 523 K for 1 h did not lead to any measurable incorporation of [¹⁸F] in the organic compound. A fraction, 22%, of the H¹⁸F was lost from β-AlF₃ during heating but evidently fluorination of CCl₂FCClF₂ did not occur. Experimental limitations due to the short *t*_{1/2} of [¹⁸F] prevented longer exposure times from being used.

The room temperature adsorption isotherm for H³⁶Cl on γ-alumina, determined using the Geiger–Müller direct monitoring technique,²⁹ indicated that physical adsorption and retention of a significant fraction of [³⁶Cl] on removal of H³⁶Cl, both occurred. This is not surprising, since we have previously shown, by [³⁶Cl] labelling, that γ-alumina can be chlorinated under these conditions. The chlorine so deposited is strongly bound, although it is labile with respect to room temperature exchange with HCl vapour.³⁶ Unexpectedly however, both γ-alumina, fluorinated by SF₄ under static conditions, and

β-AlF₃ interacted at room temperature with H³⁶Cl, albeit to a small extent. The fractions of [³⁶Cl] surface activity retained by samples of both solids after removal of H³⁶Cl under static vacuum are given in Table 1.

The effects on the [³⁶Cl] surface count rates from the solids of their exposure to successive aliquots (*ca.* 6.6 kPa) of H³⁶Cl, each aliquot being removed by condensation *in vacuo* before the next was added, are shown in Figs. 1 and 2. For the first four

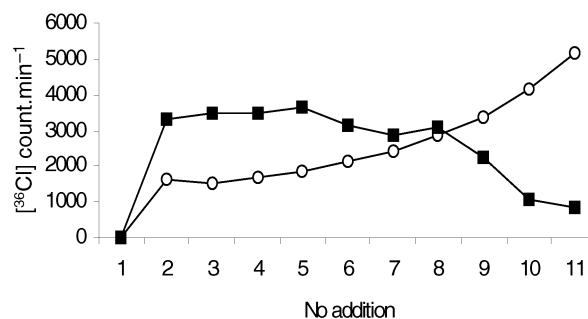


Fig. 1 Variation of the [³⁶Cl] count rate (count min^{−1}) from the surface of β-AlF₃ (■) and the vapour phase (○) with the sequential addition of H³⁶Cl aliquots. No. 1 is the value of the surface count rate prior to the first addition of H³⁶Cl.

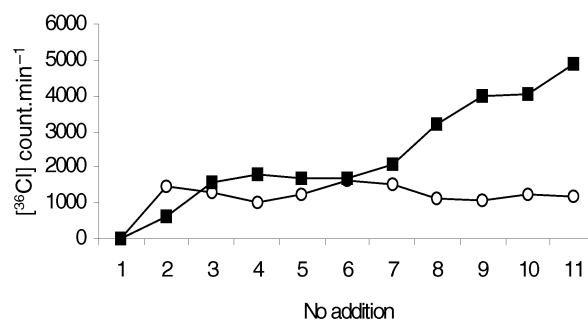


Fig. 2 Variation of the [³⁶Cl] count rate (count min^{−1}) from the surface of fluorinated γ-alumina (■) and the vapour phase (○) with the sequential addition of H³⁶Cl aliquots. No. 1 is the value of the surface count rate prior to the first addition of H³⁶Cl.

additions to β-AlF₃ a plateau in the [³⁶Cl] surface count rate was observed. Subsequent additions resulted in a decrease and a concomitant increase in the vapour phase count, Fig. 1. Due to the self-absorption of β[−] radiation emitted from [³⁶Cl], any incorporation of H³⁶Cl into the bulk solid would not have been detectable. Pumping the solid over several hours after the last addition removed most, but not all, of the [³⁶Cl] activity from the surface. Using an identical procedure for fluorinated

Table 1 [³⁶Cl] Surface count rates determined from β-AlF₃ and SF₄-fluorinated γ-alumina samples in the presence of H³⁶Cl at room temperature and after its removal

Surface [³⁶ Cl] count rate ^a /count min ^{−1}		
In the presence of H ³⁶ Cl	After removal of H ³⁶ Cl ^c	[³⁶ Cl] Activity retained ^b (%)
β-AlF ₃		
856	96	11
1548	159	10
536	40	7
434	39	9
F-γ-alumina		
4582	365	8
1595	123	8
2038	195	9.5

^a Saturation values. ^b Estimated error ±5%. ^c Under static vacuum.

γ -alumina resulted in small but definite increases in the surface count rate over the sequence of additions, Fig. 2. Most, but not all, of the [^{36}Cl] activity was removed on pumping at the end of the first cycle of additions. In both cases, repetition of the sequence using the same samples produced rather similar behaviour to those observed during the first series of additions.

The behaviour observed for $\beta\text{-AlF}_3$ over the series of H^{36}Cl additions indicates that a change in the surface occurred during the sequence. The decreasing surface and increasing vapour [^{36}Cl] count rates observed towards the end of each series of additions, indicate that the extent of the interaction with the surface decreased. It is tempting to postulate that this is due to the incorporation of HCl in the hexagonal channels of the HTB structure. However, the 'diameter' of a 'free' channel in $\beta\text{-AlF}_3$ (243 pm)⁶ is probably too small for HCl to be accommodated readily, making reasonable assumptions about its size (H—Cl = 127 pm, van der Waals radii of Cl and H = 180 and 120 pm respectively).³⁷ Since the great sensitivity of radiotracer methods can result in ambiguity in interpretation when hygroscopic materials are involved, for example, due to the presence of adventitious H_2O from transfer of H^{36}Cl through Pyrex, the effect of H_2O on the adsorption/desorption of HCl at $\beta\text{-AlF}_3$ was studied using mass spectrometry.

The quantity of H_2O evolved from uncalcined $\beta\text{-AlF}_3$ on heating was too great to be measured but if the solid was calcined *in situ* at 523 K prior to a desorption study, evolution of H_2O could be observed above 543 K. Evolution of H_2O from uncalcined $\beta\text{-AlF}_3$ that had been exposed to HCl flow at room temperature was observed above 373 K, Fig. 3, but no HCl was detected, Fig. 4. Treatment of $\beta\text{-AlF}_3$, freshly calcined at 573 K,

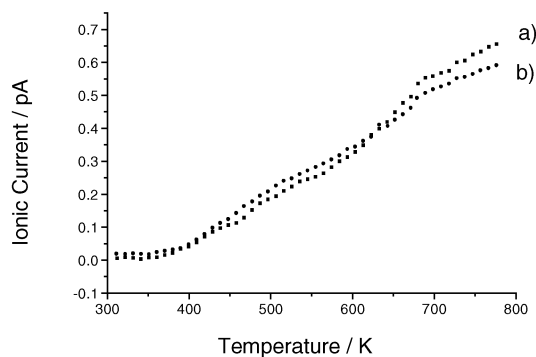


Fig. 3 Desorption of H_2O from $\beta\text{-AlF}_3$; (a) freshly calcined at 573 K and subsequently treated with HCl at room temperature; (b) not calcined but treated with HCl at room temperature.

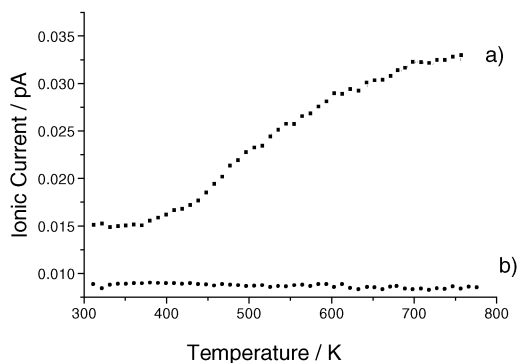


Fig. 4 Desorption of HCl from $\beta\text{-AlF}_3$; (a) freshly calcined at 573 K then treated with HCl at room temperature, (b) not calcined but treated with HCl at room temperature.

with HCl at room temperature led to desorption of both H_2O (Fig. 3) and HCl (Fig. 4) above *ca.* 373 K.

Combining the radiotracer and mass spectrometric observations indicates that some H_2O is retained by $\beta\text{-AlF}_3$ even when

it has been calcined. Partial removal of H_2O from uncalcined $\beta\text{-AlF}_3$ can be achieved by HCl treatment at room temperature. Adsorption of HCl on $\beta\text{-AlF}_3$ is not observed unless the level of H_2O is already low but, when this condition is fulfilled, adsorption is observed and some HCl is retained by calcined $\beta\text{-AlF}_3$. A co-operative effect between HCl and adsorbed H_2O is indicated. Their behaviour on $\beta\text{-AlF}_3$ can be rationalised by considering the role of the F-terminated hexagonal channels in the solid structure⁶ and a plausible model for a predominant surface plane constructed by cleavage along the channel direction. This plane contains exposed, co-ordinately unsaturated Al^{III} sites in a fluoride environment that are expected to be strongly Lewis acidic.^{11,24} Both structural features are represented diagrammatically in the Scheme (I). The intermediate in the preparation of $\beta\text{-AlF}_3$ is amorphous $\text{AlF}_3 \cdot x\text{H}_2\text{O}$, $x < 0.5$, from which pure $\beta\text{-AlF}_3$ can be obtained by heating at 723 K *in vacuo*.⁶ In the present work this step was conducted under He flow, followed by calcination *in vacuo* at 523 K for several hours. It is proposed that residual H_2O is trapped within the channels, that it is lost slowly and that this process leads to some hydration and hydroxylation of the surface (II in Scheme 1). Although surface hydrolysis can occur during prolonged exposure to moist air, for example, previous XPS work²⁴ indicates that the surface atom ratio $\text{O}^{2-} : \text{Al}^{3+}$ in $\beta\text{-AlF}_3$ can be as high as 0.25, in view of the handling procedures used here, extensive hydrolysis of the surface was unlikely.

Adsorption of HCl on $\beta\text{-AlF}_3$ is visualised as HCl becoming hydrogen bonded to co-ordinated H_2O (III, Scheme 1). A computational study of the isolated complexes, $\text{AlF}_3(\text{H}_2\text{O})_n$, $n = 2$ or 3, in which one H_2O molecule is directly co-ordinated to Al^{III} , the remainder being involved in O—H—O and O—H—F bonding,³⁸ is a possible precedent for this suggestion. Most, but not all, of the HCl is lost under vacuum at room temperature (Table 1) and desorption of HCl and H_2O are both observed by mass spectrometry above 373 K (Figs. 3 and 4). In principle, coordinatively unsaturated Al^{III} sites are generated by this sequence (III, Scheme 1). The decreasing [^{36}Cl] surface count rates observed over the latter part the sequence of H^{36}Cl additions (Fig. 1) is consistent with the decreasing hydration of the surface, if the proposal for the adsorbed state is accepted.

A very small fraction of HCl was retained on the surface after pumping for several hours (*ca.* 2–3% of the saturation [^{36}Cl] surface count rate from GM monitoring). This suggests that chlorination of the surface OH groups can occur (IV, Scheme 1) in addition to weak adsorption, when $\beta\text{-AlF}_3$ is exposed to HCl.

The increasing incorporation of [^{36}Cl] on the fluorinated γ -alumina surface with repeated exposure of the surface to aliquots of H^{36}Cl , Fig. 2, might be the result of the chlorination of unfluorinated surface hydroxyl groups. Although this may occur to a small extent, *cf.* the situation for $\beta\text{-AlF}_3$ (Scheme 1), by analogy with the situation for unfluorinated γ -alumina,³⁶ it would be expected that a substantial proportion of [^{36}Cl] activity would be retained on the surface. This is contrary to the experimental findings that *ca.* 10% was retained when H^{36}Cl was removed under static vacuum (Table 1) and that only 2–3% was retained after pumping over several hours. A more speculative rationalisation is that the adsorbed H^{36}Cl is weakly hydrogen bonded to surface fluoride. This would account for the build up of [^{36}Cl] activity observed throughout the sequence of experiments. The hydrogen bonded dimer, HF—HCl , is known to exist in the vapour phase³⁹ but is only weakly bound.^{39,40} Its existence on a surface is therefore problematic. Estimated values of $X^--\text{HY}$, X and Y = F and Cl, dissociation energies, derived from gas phase ion-molecule reactions studied by mass spectrometry,^{41,42} are greater than the corresponding values for the neutral dimers.⁴⁰ Dissociation energies estimated for F^--HY are 161 (Y = F) and 250 kJ mol^{-1} (Y = Cl).⁴² Therefore the formation of surface species of the type $(\text{Al})\text{—F}^--\text{HCl}$ is more plausible.

The uptakes of HF by β -AlF₃ and fluorinated γ -alumina are significantly greater than their HCl counterparts. However, the proposals made above are relevant to these systems also with two additional considerations. Incorporation of HF in the channels of β -AlF₃ is a possibility and the presence of oligomers on the surface cannot be discounted.

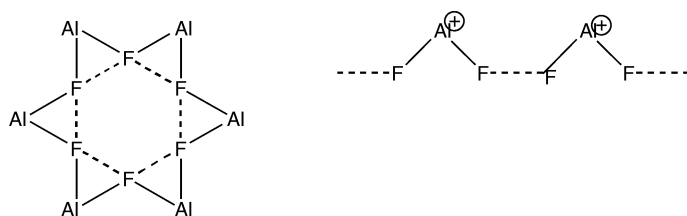
The behaviour of *tert*-butyl chloride on β -AlF₃ and fluorinated γ -alumina

The Lewis acid properties of β -AlF₃ and fluorinated γ -alumina make them candidates for Friedel–Crafts catalysts, being possible replacements for aluminium(III) chloride in this respect. Although preliminary results indicated that both β -AlF₃ and SF₄-fluorinated γ -alumina demonstrated some activity in the room temperature alkylation of toluene by *tert*-butyl chloride,¹⁴ a detailed examination of fluorinated γ -alumina revealed a more complex situation. Unlike the situation for CCl₂FCClF₂ isomerisation,¹² there were significant differences between the behaviour of Bu'Cl towards β -AlF₃ and that

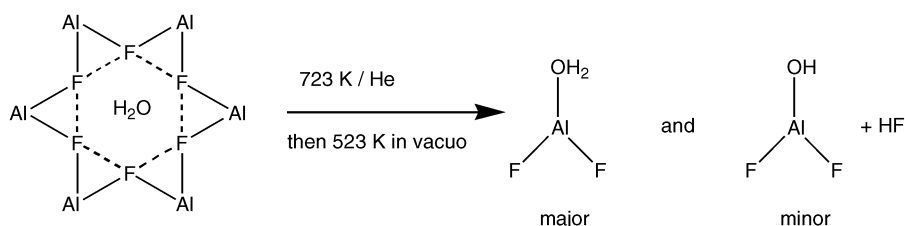
towards γ -alumina, fluorinated using pure SF₄ under static conditions.

A stirred mixture of Bu'Cl and toluene (1 : 10 mol ratio) reacted at room temperature in the presence of solid β -AlF₃ to give a mixture of mono-alkylated products (conversion 46%, *para* : *meta* = 84 : 16) within 10 min, although further conversion was not observed thereafter. The behaviour of γ -alumina, fluorinated using a mixture of SF₄ and OSF₂ under static conditions, was similar, the conversion being 36% after 50 min (*para* : *meta* = 97 : 3). Alkylation of benzene under identical conditions produced small initial conversions to mono- and di-alkylated products; conversions were 5 and 8% respectively for β -AlF₃ and fluorinated γ -alumina and the mono : di product ratios were 79 : 21 and 89 : 11. In all cases unchanged Bu'Cl was present.

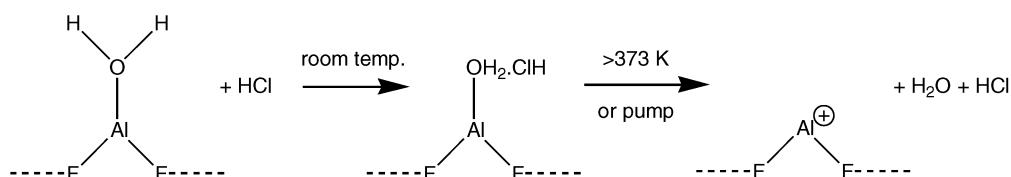
γ -Alumina fluorinated by pure SF₄ had no Friedel–Crafts activity at room temperature, although consumption of Bu'Cl was significant (55–60% over 1 h). The decrease in solution concentration was particularly marked, 37%, after 5 min. The same phenomenon was observed in the absence of hydro-



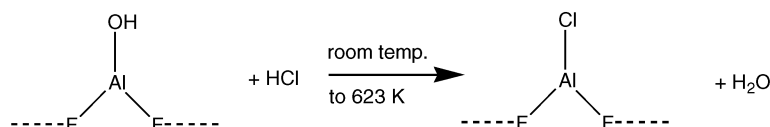
(I) Hexagonal channel and Lewis acid sites in β -AlF₃



(II) Formation of hydrated (major) and hydroxylated (minor) sites



(III) Adsorption/desorption of HCl



(IV) Chlorination of hydroxylated sites

Scheme 1

carbon. Under these conditions, consumption of Bu'Cl was accompanied by the appearance of an orange layer on the solid whose colour was discharged on the admission of moist air. Analysis of the liquid reaction mixture by GCMS indicated that two non-chlorine containing species were present, tentatively identified as $(\text{CH}_3)_2\text{C}=\text{CH}_2$, the obvious dehydrochlorination product from Bu'Cl, and a C_{16} hydrocarbon, whose mass corresponded to a tetramer derived from the olefin but whose structure was undetermined.

Consumption of Bu'Cl by SF_4 -fluorinated γ -alumina was rapid also under solid-gas conditions at room temperature, as indicated by FTIR and ^{36}Cl tracer studies. The solid became coated with a yellow material. There was no evidence from FTIR for the evolution of HCl into the vapour phase, although with the pressure of Bu'Cl used, it should have been readily detectable. Similarly, when SF_4 -fluorinated γ -alumina was exposed to ^{36}Cl -Bu'Cl, there was an initial, substantial decrease in the ^{36}Cl count rate detected from the gas phase, followed by a small, continuous decrease thereafter. However, no count rate from the surface was observed. The surface changed colour during exposure from colourless \rightarrow yellow \rightarrow purple.

Exposure of $\beta\text{-AlF}_3$ to Bu'Cl under identical conditions resulted in its incomplete consumption and the evolution of some HCl. However, ^{36}Cl monitoring of the surface provided no evidence for a substantive interaction involving ^{36}Cl -labelled species. The behaviour of γ -alumina, fluorinated using a SF_4/OSF_2 mixture, was similar to that of $\beta\text{-AlF}_3$, although the surface of the solid became purple with time.

γ -Alumina fluorinated using SF_4 is known to promote dehydrochlorination in chloroalkanes^{25,35} and therefore dehydrochlorination of Bu'Cl in the presence of these solids is not surprising. The distinctive behaviour of SF_4 -fluorinated γ -alumina towards Bu'Cl can be rationalised by assuming that $(\text{CH}_3)_2\text{C}=\text{CH}_2$, formed by the initial dehydrochlorination reaction, undergoes rapid oligomerisation. The absence of detectable ^{36}Cl from the surface suggests that the organic layer so formed covers HCl adsorbed on the surface, preventing its observation by ^{36}Cl monitoring and its escape to the vapour phase. In this system therefore, the dehydrochlorination-oligomerisation route suppresses Friedel-Crafts activity, in contrast to the situation with $\beta\text{-AlF}_3$ or γ -alumina fluorinated using an SF_4/OSF_2 mixture. It is concluded that the different behaviour is the result of the combination of very strong Lewis surface sites and significant Brønsted acidity on SF_4 -fluorinated γ -alumina.

Conclusion: the nature of the SF_4 -fluorinated γ -alumina surface

The similarity in catalytic behaviour found for $\beta\text{-AlF}_3$ and SF_4 -fluorinated γ -alumina surfaces towards $\text{CCl}_2\text{FCClF}_2$ and other chlorofluoroethanes, is the result of their Lewis acidity. In catalytic situations where the presence of Lewis sites on the surface is the only factor of importance, very similar behaviour for the two materials is to be expected, as has been observed.¹²

The behaviour of H^{18}F and H^{36}Cl towards $\beta\text{-AlF}_3$ and fluorinated γ -alumina is formally similar and in both cases unexpected. It has, however, a different origin. For $\beta\text{-AlF}_3$ the phenomenon can be rationalised in terms of the structure of the bulk⁶ and the proposed model for the surface of $\beta\text{-AlF}_3$,^{11,24} however the situation for fluorinated γ -alumina is not so straightforward.

The characteristic feature of fluorinated γ -alumina is that Brønsted and Lewis acidity can both be important. The nature of the surface formed is highly dependent on the exact conditions used for its preparation. Fluorination using SF_4 under static conditions and at lower temperature, results in a material with a lower fluorine content but one in which Brønsted and Lewis acidity are both manifest. This is rationalised as a result

of incomplete removal of HF when fluorination is conducted under static conditions and this is responsible for the ability of the material to interact further with HF and to interact with HCl. It seems likely also that Brønsted acidity is a factor in accounting for the different behaviour of SF_4 -fluorinated γ -alumina compared with $\beta\text{-AlF}_3$ towards Bu'Cl.

γ -Alumina has a defect (tetrahedral Al^{III}) spinel structure whose stoichiometry only approximates to Al_2O_3 and whose surface is stabilised by the presence of hydroxyl groups.⁴³ It is well established that surface hydroxyls on γ -alumina exist in several different environments and have, as a consequence, different acidities.⁴⁴ They have an indirect influence on coordinatively unsaturated Al^{III} Lewis acid sites, since three types of Lewis site can be correlated with different types of $-\text{OH}$ that are their nearest neighbours.⁴⁵ Fluorination of the surface with SF_4 , nominally at room temperature, will result in partial replacement of $\text{Al}-\text{OH}$ groups by $\text{Al}-\text{F}$ and the formation of OSF_2 , SO_2 and HF. Under static conditions HF can be adsorbed dissociatively to form $\text{F}-\text{Al}(\text{OH})-\text{Al}$ groups which can potentially function as Brønsted sites and sites at which HCl adsorption or further HF adsorption can occur. Under flow conditions above room temperature, most if not all, of the HF formed is expected to be lost from the surface, therefore the formation of new Brønsted sites will be relatively less important. In this situation, Lewis acidity predominates. The surface properties are similar to those that result from fluorination with a chlorofluorocarbon or a hydrochlorofluorocarbon.³¹ Enhanced Lewis acidity is the result of the replacement of surface oxygen atoms by fluorine ($\text{O} \equiv 2\text{F}$) resulting in surface Al^{III} atoms which have a disordered O/F environment. New, strong Lewis sites are created with the inevitable disruption of the surface structure. It could be argued that the surface that results from room temperature fluorination would be more disordered and so have stronger Lewis sites. However, we have no direct information on this point.

Ab initio calculations, at the SV-321G level, on small clusters that are relevant to γ -alumina and its chlorinated analogues suggest that both Brønsted and Lewis acid character are associated with Al^{III} atoms occupying tetrahedral rather than octahedral sites.⁴⁶ Replacement of OH groups by Cl, up to two Cl atoms per $\text{Al}-\text{O}-\text{Al}$ cluster, results in significant increases in both types of acidity. In some respects, γ -alumina which has been fluorinated by SF_4 under static conditions resembles material that has been chlorinated using CCl_4 ,³⁶ although, unlike the material fluorinated under static conditions, chlorinated γ -alumina is an efficient Friedel-Crafts catalyst at room temperature.¹⁴ The two materials also differ in the extent to which halogenation occurs and in the extent of the interactions that involve hydrogen halide. Notwithstanding these differences in properties however, Brønsted and Lewis acidity in SF_4 -fluorinated γ -alumina is more likely to be associated with tetrahedral Al^{III} sites.

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