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Review

Investigation of fluorinated surfaces by means of radio-labelled probe molecules

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Dedicated to Prof. Neil Bartlett for his forthcoming 75th birthday.

Abstract

Acid–base reactions and interactions are at the heart of inorganic fluorine chemistry and are now recognised as forming a very important part of the chemistry, catalytic or non-catalytic, that occurs on inorganic fluorinated surfaces. This review traces the use that has been made of radioactive isotopes, particularly the short-lived β^+ emitter, fluorine-18, and the very long-lived chlorine-36, which is a β^- emitter, to investigate a variety of surface-related phenomena. Attention is concentrated on solid Lewis acids, including aluminium(III) fluoride derivatives, fluorinated γ-alumina and fluorinated chromia.

Keywords: Fluorine-18; Chlorine-36; Lewis acid; Fluoride ion; Fluorinated chromia; Fluorinated alumina; Aluminium trifluoride; Aluminium chlorofluoride

Contents

1. Introduction

One of the characteristics of contemporary surface chemistry and heterogeneous catalysis is the widespread use that is made of the range of instrumentally based techniques available for investigation of surface properties and catalytic phenomena. In contrast, techniques that use radioactive isotopes as tracers, which are at the heart of this review, are 'classical' and will seem to many to be old-fashioned and laborious. It is the authors' contention that this proposition is incorrect; the relative simplicity of their use has been a distinct advantage in catalytic systems, where corrosive species like binary fluorides, anhydrous HF being a prime example, are involved and in situations where surfaces

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may be hydrolytically unstable; the latter property can lead to marked changes in the nature of a surface, even after minimal exposure of a surface to moist laboratory atmosphere. These are recurring themes in a review that traces the use that has been made of radio-isotopes, particularly fluorine-18 and chlorine-36, in the *in situ* study of surface phenomena involving Lewis acid–base interactions or reactions that are relevant to heterogeneous catalysis or materials chemistry.

The 'local' context of the work to be reviewed should be noted. The Chemistry Department at the University of Glasgow has a long history in radioactivity, dating from the appointment of Frederic Soddy to the (first) Lectureship in Physical Chemistry at the University in 1904. In the next 10 years Soddy and his co-workers clarified the relationships among the natural radioelements and the Periodic Table (including coining the word 'isotope'), work for which, together with subsequent studies, he was awarded the 1921 Nobel Prize. Radiochemical studies of solids and surfaces in the Department date from 1957 onwards, directed initially by S. (Sam) J. Thomson and later by G. (Geoff) Webb [1]. Much of this later work was focussed on heterogeneous catalysis involving hydrocarbons at supported metal surfaces [2]. In turn this activity became very relevant, not least for JMWs education, to the radiotracer examinations of catalysis in fluorine chemistry, an activity that took its first tentative steps in the late 1960s with investigations into catalysis by caesium fluoride [3,4].

The two radioactive isotopes that are at the heart of this account present an interesting contrast. Fluorine-18 is the longest-lived of several radioactive isotopes of the element. Its half-life is 110 min [5]; it is a positron (β^+) emitter, which is detected by the subsequent γ annihilation ($e^+ + e^-$) radiation of 0.51 MeV. The isotope is used extensively in positron emission tomography (PET), a non-invasive diagnostic technique used, for example, for tumour imaging and in investigations of Parkinson's disease. Chemists play a key role in the synthesis of [^{18}F]-labelled radiopharmaceuticals [6]. In contrast, chlorine-36 has a very long half-life, 3.0×10^5 years [5], and, apart from the radiological hazard associated with its use, can be treated as though it were a stable isotope. It is a reasonably energetic, $E_{\max} = 0.714$ MeV [5], β^- emitter; like all such emitters the radiation is subject to extreme attenuation by matter, the phenomenon of self-absorption. The phenomenon can be exploited in the investigations of gas–solid heterogeneous systems, since the detection of β^- radiation from [^{36}Cl] will be limited to the surface of a solid, whereas the γ radiation from [^{18}F] can be detected from both the surface and from a bulk solid.

2. Illustrations of experimental methodology

In order to appreciate the strengths and the limitations of the application of radiotracers to fluorides which are described below, three aspects of the experimental methodology used, together with some results obtained, are now described.

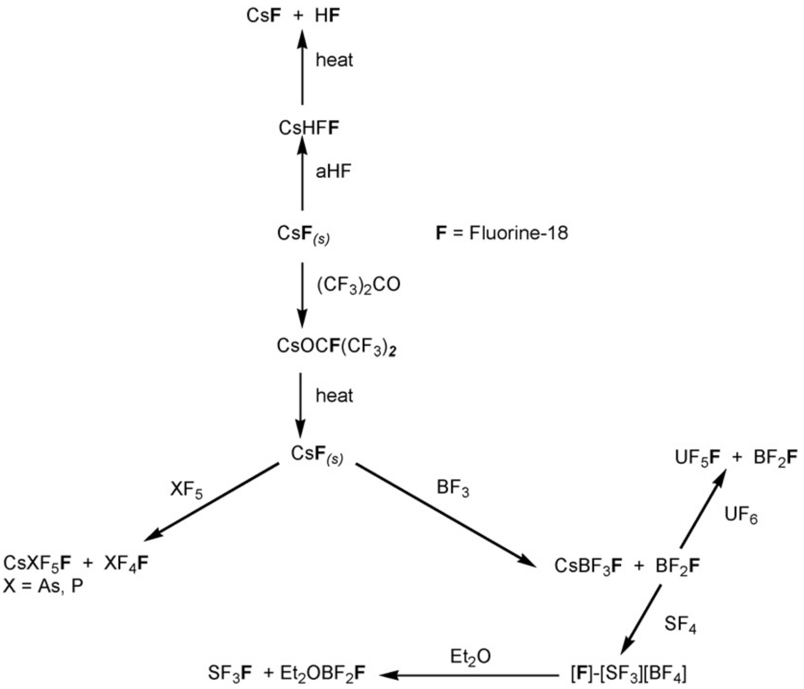
2.1. Synthesis of some radio labelled probe compounds

The isotope [^{36}Cl] is available commercially as an aqueous solution of $^{36}Cl^-$. From this starting point, both anhydrous $H^{36}Cl$ and $^{36}ClCl$ (statistically the probability of labelling both atoms can be discounted) are prepared readily using classic synthesis methods [7,8]. Replacement of C–H by C–^{36}Cl in several hydrochlorofluorocarbons can be achieved *via* UV photolysis with $^{36}ClCl$, for example [^{36}Cl]-CCl_2FCF_3 from $CHClFCF_3$ [8] and [^{36}Cl]-CCl_2FCClF_2 from CH_2FCHF_2 [9]. Replacement of C–OH by C–^{36}Cl is a route to labelled alkyl chlorides, for example $(CH_3)_3C^{36}Cl$ from aq. conc. $H^{36}Cl$ and $(CH_3)_3COH$ [10].

Several methods for the preparation of [^{18}F] are available; the choice will depend crucially on the time required for travel between the locations of the nuclear installation and the laboratory where the tracer chemistry is to be performed. For many years we prepared fluorine-18 using a research nuclear reactor located a short drive from the Department. Neutron irradiation of [^{6}Li] yields tritium, which in turn bombards [^{16}O] to give [^{18}F]. The two-step process is not particularly efficient; it is feasible only if the two target isotopes are in intimate contact and this is achieved by using a compound that contains both isotopes, for example Li_2CO_3, as the target. An additional consideration is the requirement to separate unused [^{3}H] from the product $Li^{18}F$. This is accomplished by an acid distillation, liberating $H^{18}F$, which is neutralised to form $Cs^{18}F$ (the yield of material being typically 1.5–2.5 MBq). Providing the latter is well dried, it is a versatile starting point for synthesis of a wide variety of labelled fluorides (see below); however, the whole sequence is time-consuming and produces relatively low specific activity material. Although specific activity (or specific count rate) is an unfamiliar term to most, it can be regarded as akin to a concentration term; a typical unit is MBq (mg atom F)$^{-1}$. The specific activity achievable is inadequate for radiopharmaceutical syntheses but is sufficiently high for most tracer purposes [3]. More recently it has been possible to take advantage of the increasing interest in [^{18}F] for PET use and prepare material of higher specific activity from the nuclear reaction, $^{20}\mathrm{Ne}(d,\alpha)^{18}\mathrm{F}$, carried out in a medical cyclotron. Although this route nominally produces no-carrier-added (NCA) [^{18}F], i.e. containing no [^{19}F], in practice this is not achieved as a little F_2 is added to the irradiation chamber to remove material adsorbed on the chamber walls. An aqueous solution of $^{18}F^-$ is transported to Glasgow and converted as previously described to solid $Cs^{18}F$ (typically 50–450 MBq) [11]. Although the closest medical cyclotron to Glasgow is the John Mallard Scottish PET Centre, Aberdeen, the time loss as a result of the 3 h road journey to Glasgow is offset by the higher specific activities $Cs^{18}F$ routinely produced.

Some syntheses of volatile target molecules, labelled with [^{18}F] by reaction with the primary [^{18}F]-labelled compound, solid $Cs^{18}F$, are shown in Scheme 1.

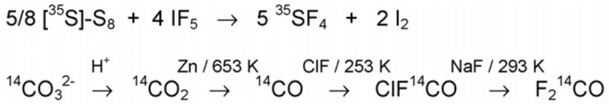
The importance of Lewis acid–base reactions is obvious; in most cases [^{18}F] isotopic exchange with no chemical change is involved [3,11–16]. These exchange reactions have the advantage of occurring relatively quickly at moderate temperatures (typically temperatures in the range 323–373 K



Scheme 1. Some reactions leading to [^{18}F]-labelled binary fluorides starting from solid Cs^{18}F [3,11–16].

are used) but, because normally all F atoms are exchangeable, the radio-label is distributed statistically throughout and, as a result, specific activities may be relatively low. An important observation made early on was that the kinetic performance of Cs^{18}F in the [^{18}F] exchange reactions could be improved significantly if the compound had been activated by prior formation and subsequent thermal decomposition of the alkoxides, Cs$^+$[OC^{18}F(CF$_3$)$_2$]$^-$ or Cs$^+$[OCF$_2$^{18}F]$^{-1}$ [14]. These are available readily by reaction between CsF and (CF$_3$)$_2$CO or F$_2$CO [17]. The treatment introduces an extra stage into the labelling process but is justified by the increased level of [^{18}F] incorporation achievable. The reason is likely to be due to the increase in BET area of CsF, from 0.31–0.19 to 3.01–2.09 m^2 g^{-1}, which is the result of the (CF$_3$)$_2$CO pre-treatment [14], as determined *via* radio krypton [^{85}Kr] ($\boldsymbol{\beta}^-$, $t_{1/2}$ 10.6 years [5]) physical adsorption [18]. The observed ten-fold increase is too great to be the result solely of particle size reduction. It is ascribed tentatively to the development of a meso- or macro-porous structure to some extent on thermal decomposition of the alkoxide anion [14].

In situations where a radiotracer other than [^{18}F] is required to explore some facet of the chemistry of a covalent fluoride, radio-isotope incorporation makes use of conventional synthesis. Two examples, the synthesis of sulfur-35 ($\boldsymbol{\beta}^-$, $t_{1/2} = 87$ days [5]) labelled SF$_4$ [19] and carbon-14 ($\boldsymbol{\beta}^-$, $t_{1/2} = 5720$ years [5]) carbonyl fluoride [20], in each case from commercially available labelled materials, are given in Scheme 2.



$$5/8\,[^{35}S]\text{-}S_8 + 4\,IF_5 \rightarrow 5\,^{35}SF_4 + 2\,I_2$$

$$^{14}CO_3^{2-} \xrightarrow{H^+} {}^{14}CO_2 \xrightarrow{Zn\,/\,653\,K} {}^{14}CO \xrightarrow{ClF\,/\,253\,K} ClF^{14}CO \xrightarrow{NaF\,/\,293\,K} F_2{}^{14}CO$$

Scheme 2. Syntheses of two labelled fluorides.

2.2. *H^{18}F interaction with diamond*

One of the main reasons for using [^{18}F] is the great sensitivity of the isotopic tracer technique, for example 50 MBq (50×10^6 disintegrations s^{-1}) corresponds to 7.9×10^{-13} mol. In situations where a reasonably high specific activity, measured in MBq (mg atom F)$^{-1}$, can be obtained for a probe compound, precise measurements of stoichiometry become possible. This situation is easily achieved for anhydrous HF (aHF, Scheme 1) and its interactions with a variety of materials, particularly surface interactions, have been examined. Although [^{18}F] labelling on its own is seldom definitive, combined with other methods that give chemical/structural information, it is extremely useful. The behaviour of aHF towards diamond powders is a case in point [11].

Valuable information relating to the effects of the surface fluorination of diamond powders and films, whose surfaces are terminated by bonds to hydrogen or oxygen, has been obtained by a variety of methods, including diffuse reflectance FTIR and mass spectrometry [21], microscopy [11] and XPS [11], making use in the latter case of comparative XPS data from other fluorinated carbon-based materials [22]. Armed with this information and using stoichiometry data, Table 1, for the uptakes of aH^{18}F by diamond powders whose surfaces have been treated in various ways, it is possible to describe the nature of HF interactions with the diamond surfaces, both fluorinated and unfluorinated. The uptakes are determined from the product of the specific count rate, experimentally determined for the batch of aH^{18}F used and measured in count min^{-1} (mg atom F)$^{-1}$, and the count rate, count min^{-1}, of the diamond sample after treatment with H^{18}F.

The behaviour is not explicable simply in terms of physical adsorption of HF. Uptake is greatest at an O-terminated surface,

Table 1
Uptakes of $H^{18}F$ at ambient temperature by diamond powders[a]

Sample pre-treatment	Uptake of $[^{18}F]$ (mg atom F) g^{-1}
H-terminated surface	0.58–0.90 (five experiments)[b]
O-terminated surface	0.84–1.12 (three experiments)[c]
H_2 flow then F_2, ambient	0.118[d]
H_2 flow then F_2, 673 K	0.090[d]
H_2 then O_2 flows, F_2, ambient	0.361–0.531 (two experiments)[d]
H_2 then O_2 flows, F_2, 623 K	0.139–0.183 (two experiments)[d]

[a] Typical conditions, pre-treated diamond powder (1 μm; 1.0 g), $H^{18}F$ (3.5 mmol), Monel vessel, 0.75 h.
[b] Relative error 1.4%.
[c] Relative error 0.5%.
[d] ±0.001.

followed by an H-terminated, with a F-terminated surface producing the smallest uptakes. A specific H-bonding interaction between HF and surface functional groups such as C=O, COC and OH is proposed to account for the observed interaction. Adsorbed $H^{18}F$ is labile with respect to exchange with, or displacement by, HF, however no $[^{18}F]$ exchange is observable between $H^{18}F$ and surface C–F containing groups [11]. Fluorination of O-terminated diamond reduces but does not eliminate, all O-functionality on the surface [21]; even after high temperature fluorination, XPS indicates the presence of some surface O and this is consistent with the smaller, though still measurable, uptake of $H^{18}F$ observed in Table 1.

A similar pattern of behaviour is observed for H-terminated diamond versus $H^{18}F$, although the uptakes are smaller than those in the O-terminated case. A specific interaction of the type F–H–H–C, which is weaker than a conventional F–H–O–C hydrogen bond, is postulated [11].

2.3. $H^{36}Cl$ interaction with aluminium(III) chlorofluoride (ACF)

Direct monitoring of events taking place at a surface by means of a β^- emitting isotope such as $[^{14}C]$ or $[^{36}Cl]$ is possible using a Geiger-Müller direct monitoring method. Although developed originally to study adsorption phenomena involving $[^{14}C]$-labelled hydrocarbons at supported metal heterogeneous catalysts [2], we have applied it extensively to the study of fluorinated surfaces. The apparatus consists of two end window Geiger-Müller counting tubes mounted within an evacuable Pyrex vessel equipped with a moveable Pyrex boat and gas handling system, Fig. 1.

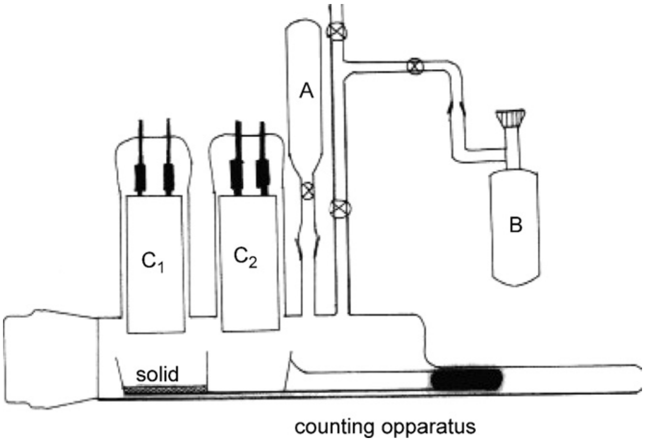


Fig. 1. Geiger-Müller direct monitoring equipment. C_1 and C_2 are two inter-calibrated end window Geiger-Müller counting tubes; A is an evacuable ampoule, originally containing the solid fluoride; B is an evacuable ampoule from which the labelled volatile probe compound is dispensed.

The information available from the technique is illustrated first by a very simple experiment involving exposure of a $[^{36}Cl]$-labelled probe molecule, $H^{36}Cl$, to a surface, which is contained in the boat directly below counter C_1. The possible chemical events that could occur thereafter are illustrated schematically in Fig. 2.

The way in which physical and/or chemical adsorption can be recognised in a real chemical system is illustrated by the output from a GM experiment, Fig. 3.

This records the effect of repeated exposures of $H^{36}Cl$ aliquots to the solid strong Lewis acid, aluminium chlorofluoride, $AlCl_xF_{3-x}$, where $x = 0.05–0.3$ [23–25].

Adsorption of $H^{36}Cl$ at the ACF surface is indicated by observation of a surface count. Its magnitude increases very slightly with each addition of $H^{36}Cl$, although the increases are only marginally greater than the standard deviations on the individual points. More importantly, a substantial fraction of the surface $[^{36}Cl]$ activity is retained on the removal of material

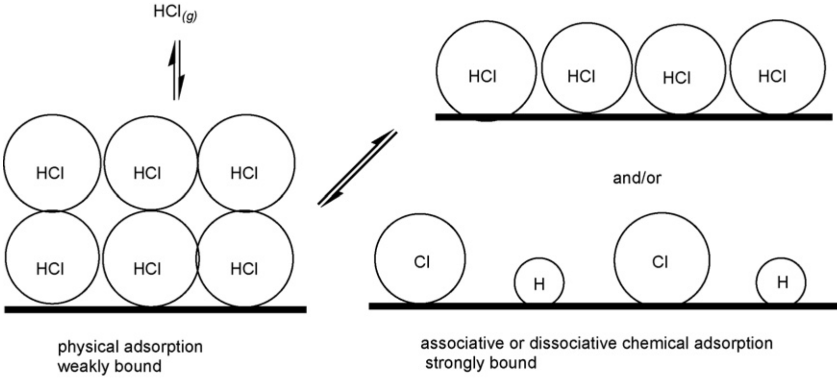


Fig. 2. Three possibilities for the HCl probe, physical adsorption, associative chemical adsorption or dissociative chemical adsorption.

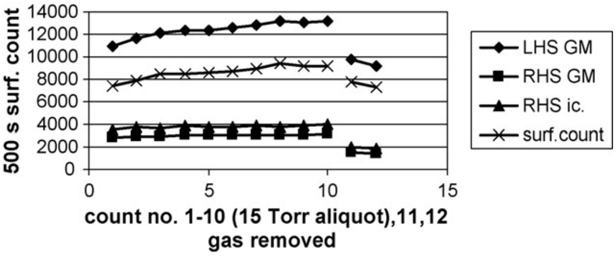


Fig. 3. Sequential exposure of 10 aliquots of $H^{36}Cl$ (15 Torr) to ACF. LHS GM (C_1) counts surface + the volume of gas directly above; RHS GM (C_2) counts an equivalent volume of gas; RHS ic is the intercalibrated count from C_2; surf. count is C_1–ic. C_2. See also Fig. 1.

volatile at room temperature, count no. 11. As is evident from Fig. 3, a substantial count from the surface is observable also on the following day (count 12). This indicates that chemical adsorption of HCl on ACF is an important component of the interaction, although the counts determined in the presence of $H^{36}Cl$ (nos. 1–10) will reflect both physical and chemical adsorption. The experiment cannot distinguish between associative and dissociative adsorption modes (Fig. 2); the latter is found more commonly on aluminas but the former has been observed also [26]. We return to this point when considering the behaviour of *t*-butyl chloride at Lewis acid surfaces in the next section.

3. Lewis acid surfaces: fluorinated chromia, fluorinated γ-alumina, β-aluminium(III) fluoride and aluminium(III) chlorofluoride (ACF)

Amorphous chromia and the defect spinel, γ-alumina, are both widely used acidic heterogeneous catalysts and catalyst supports. They are linked together in fluorine chemistry as catalysts for the halogen exchange reaction, Eq. (1):

$$\mathrm{C{-}Cl + HF \rightarrow C{-}F + HCl} \qquad (1)$$

used originally for the large scale production of CFCs and more recently HCFCs and HFCs, the latter being one of the classes of refrigerants and foam blowing agents developed following the Montreal Protocol.

In reality it is the fluorinated materials that should be considered, since the oxides' surfaces do not survive the action of HF vapour at moderate temperatures. Although linked by usage, fluorinated chromia and fluorinated alumina behave differently and, as shown in Section 4 of this review, behave as catalysts for different types of reactions. One important factor is the thermodynamics of fluorination of Cr^{III} *vis a vis* Al^{III}. This has been considered by calculating free energy changes for the fluorination of Cr_2O_3 and Al_2O_3 by gaseous reagents such as HF, $CHCl_2F$ and $CHClF_2$ and for the chlorination of these solids by HCl or the hydrochlorofluoromethanes specified above. From the magnitudes of the data it can be concluded that, for reactions of alumina, Al–F bond formation is favoured strongly over formation of Al–Cl bonds. In the chromia reactions the energetics are more balanced and Cr–F and Cr–Cl bond formation are both likely [27], see also Ref. [28].

3.1. Fluorination of amorphous chromia

The application of [^{18}F] and [^{36}Cl] to the behaviour of chromia and fluorinated chromia catalysts at various stages of the catalyst lifetime, illustrates the chromia situation very well. Treatment with $H^{18}F$ under flow conditions at 623 K leads to the slow replacement of Cr–O bonds by Cr–F and the differentiation of three types of surface fluoride, weakly bound (presumed to be adsorbed HF), catalytically active and inert. The latter type is presumed to be Cr^{III}–F because of its similar behaviour to that of CrF_3 [29]. Fluoride uptake by a 'working' fluorinated chromia catalyst, as determined by quantitative determination of [^{18}F], is in the range 1.0–1.4 mg atom g^{-1}. Uptakes of chlorine by laboratory-fluorinated chromia after treatment at 623 K under flow conditions with $H^{36}Cl$ are in the range 64–88 μg atom g^{-1}. Similar behaviour is observed after flow of $C_2Cl_2F_4$ isomers over fluorinated chromia catalysts [7]. Subsequent flow of HF at 623 K or reactions that involve $C_2Cl_2F_4$ isomers or CCl_2FCClF_2 lead to the removal of a large fraction of the [^{36}Cl] activity and from observations of this type, the halogen exchange model for fluorinated chromia catalysis was developed. A summary of its main features has been given elsewhere [28].

The metal(II)-doped chromia catalysts, developed more recently, appear to follow similar principles, as determined by their behaviour towards $H^{18}F$ [30]. Unlike chromia where complete conversion of Cr–O to Cr–F bonds is never achieved under laboratory conditions, the metal (II) dopants, Zn^{II} or Ni^{II}, which are added to the unfluorinated catalyst precursor as $ZnCl_2$ or $[Ni(H_2O)_6][NO_3]_2$, are readily converted to their fluorides. It appears possible that a function of the MF_2 dopant is to provide an additional pathway for the catalytically active surface fluoride species to be replenished by HF [30]. Despite much intensive research, much of which has been reviewed elsewhere [28], the exact nature of the catalytically active site(s) for fluorination and chlorination has not been elucidated. However, the evidence favours disordered chromium oxofluoride(chloride) sites; this has been reinforced recently from a static TOF-SIMS study [31].

3.2. Fluorination of γ-alumina

The use of a number of different fluorinating reagents for γ-alumina has been reported [28]. Anhydrous HF is used universally for large-scale operations, whereas, for laboratory studies, CFCs and more recently HCFCs have been employed. Following a chance observation that the exposure of γ-alumina to SF_4 led to a very exothermic interaction, we have made extensive use of this reagent. The use of SF_4 results in a fluorinated alumina whose surface has both Brønsted and Lewis acid character. In contrast, CFC or HCFC activation of γ-alumina leads exclusively to Lewis acidity [28]. Progress of the fluorination by SF_4 can be followed conveniently by [^{18}F] labelling [32]. Successive addition of four aliquots of $SF_3{}^{18}F$ to calcined γ-alumina, nominally at ambient temperature results in a total F uptake of *ca.* 15 mg atom F (g alumina)$^{-1}$, corresponding to a fluorine content of *ca.* 22%. A single exposure of $SF_3{}^{18}F$ leads to an F content of *ca.* 5.2% [10]. From these and related studies involving [^{35}S]-labelled SF_4, OSF_2 and SO_2, the following rationalisation of the fluorination process becomes possible [10]. Initially, some surface Al–OH and Al–O–Al groups are replaced by Al–F with the formation of OSF_2, SO_2 and HF. Under the static conditions used, HF becomes dissociatively adsorbed, with the formation of F–Al–(OH)–Al surface species. Partial replacement of O by 2F results in enhancement of surface Lewis acidity. A key factor in the utility of SF_4 appears to be its ability to transfer 2F to the surface simultaneously, a property that it shares with, for example, $CHClF_2$ [28] but not with BF_3; using the latter reagent the fluorination level is lower [33].

Fluorination of γ-alumina under flow conditions, normally at elevated temperatures, gives rise to higher levels of F incorporation, for example flowing SF_4 diluted with N_2 over γ-alumina at 523 K for 2 h results in an F content of 47.1% [34], a value rather similar to those obtained with CFC or HCFC reagents [35]. However, the major difference between materials fluorinated under flow conditions and those fluorinated under static conditions is the absence of Brønsted surface acidity in the former case. This is rationalised by the more facile loss of HF from the surface under the flow conditions normally used [10].

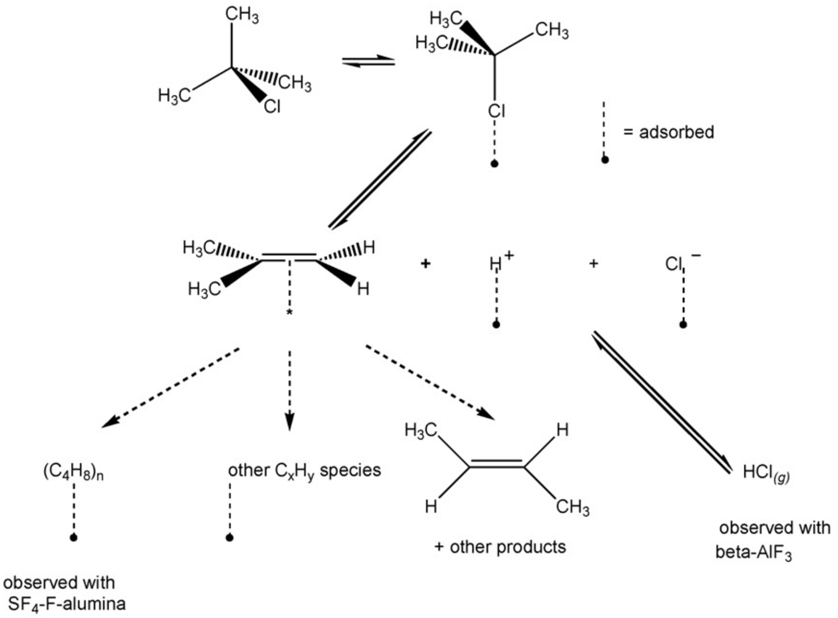
As for fluorinated chromia, the nature of the new, strong Lewis acid surface sites created by fluorination is not known with any certainty. It is generally supposed however, that the strong Lewis acid sites are Al^{III} surface atoms in a disordered O/F environment. This is in accord with a detailed Surface Science study of γ-alumina which has been fluorinated using $CHClF_2$. It was concluded additionally that sub-surface insertion of F is required to promote Lewis acidity [36].

3.3. Dehydrochlorination of hydrochlorocarbons: the use of $H^{36}Cl$ as a surface probe

One of the most striking reactions of the hydrochlorocarbon, 1,1,1-trichloroethane, is its behaviour at room temperature in the presence of an aluminium metal surface, the so-called 'bleeding reaction'. The reaction occurs also in the presence of solid aluminium trichloride that has been resublimed *in vacuo*; it consists of a rapid dehydrochlorination of CH_3CCl_3 to give $CH_2{=}CCl_2$ followed by oligomerisation of the latter and further loss of HCl from the oligomeric mixture that coats the solid $AlCl_3$ surface [37]. Similar, though less violent, chemistry occurs when γ-alumina, which has been chlorinated by CCl_4 in order to promote its surface Lewis and Brønsted acidity, is exposed to CH_3CCl_3 [38]. Not surprisingly, γ-alumina that has been fluorinated by SF_4 is also a suitably acidic surface on which to perform the chemistry. The combination of a pool of labile F, demonstrated by its room temperature [^{18}F] exchange behaviour towards $H^{18}F$, $SF_3{}^{18}F$ and $BF^{18}F$ [39], and an oligomeric layer, with which hydrochlorocarbons are miscible, makes the fluorinated alumina–chlorocarbon oligomer composite an active catalyst for room temperature F-for-Cl halogen exchange reactions on C_2 and C_3 hydrochlorocarbons, CH_3CCl_3 and others, that are susceptible to dehydrochlorination [40].

Although *tert*-butyl chloride is less reactive than CH_3CCl_3 with respect to dehydrochlorination, it is proving to be a useful probe molecule in the investigation of acidic surfaces. Its use is connected directly to the dehydrochlorination that is observed on an acidic surface. Some of the possibilities that could result from the adsorption of a *t*-BuCl molecule *via* its Cl atom at a Lewis acid surface site are shown in Scheme 3.

The utility of the probe stems from the HCl formed on dehydrochlorination of *t*-BuCl at room temperature. If HCl is



Scheme 3. Possible events and reactions following the adsorption of *t*-BuCl.

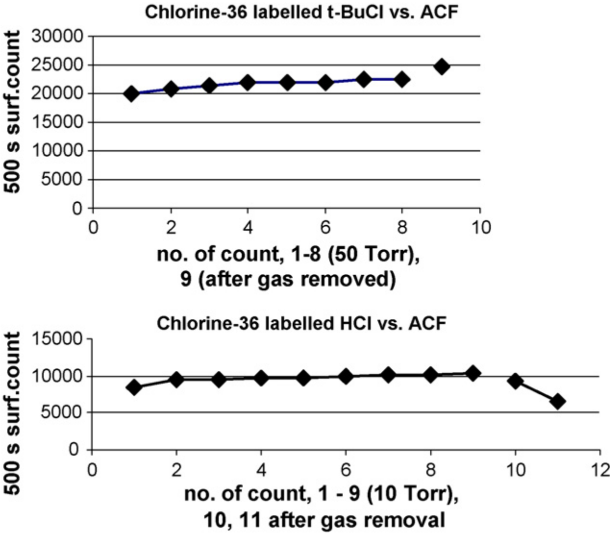


Fig. 4. [^{36}Cl] Surface count rate relationships from the successive additions of ^{t}Bu^{36}Cl or H^{36}Cl to $AlCl_xF_{3-x}$.

evolved to the vapour phase, it can be detected easily from its characteristic IR spectrum by monitoring the vapour directly above the solid by FTIR using an evacuable cell. If HCl remains strongly adsorbed at the surface, this will be manifest as surface radioactivity (Figs. 1 and 3), by [^{36}Cl] labelling. Weakly bound H^{36}Cl (*cf.* Fig. 2) will give rise to a surface count that is easily lost on pumping. The chemical events depicted in Scheme 3 imply that there will often be a close relationship or identical behaviour between *t*-Bu^{36}Cl and H^{36}Cl as they interact with a Lewis acidic surface. This is illustrated well by the [^{36}Cl] surface count behaviour when the probes interact with $AlCl_xF_{3-x}$, $x = 0.05$–0.3, Fig. 4.

In each case there is a small but measurable increase in the [^{36}Cl] surface count with each successive addition. The very similar behaviour is rationalised on the basis that *t*-Bu^{36}Cl is dehydrochlorinated rapidly on the surface at room temperature; in both cases therefore it is the surface count from adsorbed H^{36}Cl that is measured. The behaviour as volatile material is removed by pumping, counts 9–11 in the two cases (Fig. 4), though not completely identical, does indicate that a substantial fraction of H^{36}Cl is adsorbed strongly. The behaviour in the *t*-Bu^{36}Cl case suggests that, in addition to chemisorbed H^{36}Cl on the surface, some is located in the bulk material and migrates to the surface on pumping. There are two possible ways of accounting for the strongly adsorbed HCl. Firstly, it is possible that HCl, which is of course a strong Brønsted acid, is trapped by hydroxyl or oxo groups, which have been formed by trace hydrolysis of the surface. Secondly, it is possible to envisage adsorption of HCl, which is also a very weak Lewis base, at the very strong surface Lewis sites on ACF. The former explanation is preferred, since it is clear from the relationship between the [^{36}Cl] count and the number of aliquots of *t*-Bu^{36}Cl added, that the activity of the Lewis acid sites is not affected.

Rather different behaviour is observed when SF$_4$-fluorinated γ-alumina, prepared under static conditions as outlined above, is exposed to *t*-BuCl [10]. No surface [^{36}Cl] count was detected, neither was HCl detected in the vapour phase. Evidently, HCl is completely retained by the solid and the surface is covered with a coloured organic layer derived from the dehydrochlorination product, $(CH_3)_2C{=}CH_2$, Scheme 3. Although it is undoubtedly a strong Lewis acid, the material shows no activity towards Friedel Crafts alkylation, presumably because the ‘self condensation’ process is preferred. The behaviour observed is reminiscent of that observed with CH_3CCl_3 described above. This behaviour is in contrast with that of β-aluminium(III) fluoride [41] and γ-alumina, which has been fluorinated with SF$_4$ that contains OSF$_2$ as an impurity; both have moderate-to-low Friedel Crafts alkylation catalyst activity [42]. Moderate yields of monoalkylated products are formed from toluene and *t*-butyl chloride at room temperature and small yields of monoalkylated products are formed from corresponding reactions that involve benzene [42].

Although HCl is detected in the vapour phase after exposure of *t*-BuCl to β-AlF$_3$ at room temperature, Scheme 3, there is no evidence for a substantial interaction between *t*-BuCl and the surface [10]. Apparently, dehydrochlorination of *t*-BuCl does occur but subsequent events are a consequence of the method of preparation and the resulting hexagonal tungsten bronze structure of β-AlF$_3$ [41]. This AlF$_3$ modification is prepared by temperature programmed dehydration of the trihydrate. Inevitably, not all H$_2$O is lost, some remaining in the hexagonal channels, from which H$_2$O is desorbed slowly during use. The great sensitivity of the H^{36}Cl probe has enabled the H^{36}Cl–H$_2$O–β-AlF$_3$ interactions to be observed during a cycle of successive H^{36}Cl aliquot addition then removal, confirmatory evidence being provided by monitoring the HCl adsorption–desorption process by mass spectrometry [10]. It is believed that HCl can be hydrogen bonded to hydrated surface Al^{III} sites, which, in the presence of the Brønsted acid, HCl, behave as H-bond acceptors, i.e. Brønsted base, sites. In addition, HCl is capable of reacting with hydroxylated, Al–OH, sites forming Al–Cl groups. Liquid scintillation counting of [^{36}Cl] distributions before and after exposure of β-AlF$_3$ and related materials to H^{36}Cl at 623 K overnight, has enabled Cl atom surface densities, and by inference OH surface densities, to be estimated [43]. The values obtained are not unreasonable by comparison with other methods of estimation.

4. Reaction pathways and mechanisms

Results from radiotracer experiments have played a very useful role in the determination of reaction pathways and, in favourable circumstances, mechanisms. Separate labelling experiments with [^{36}Cl] and [^{35}S] enabled the mechanism of SF$_4$ chlorofluorination by ClF, a reaction that occurs readily at room temperature in the presence of activated CsF [44], to be elucidated. The reaction involves the surface reaction between weakly adsorbed SF$_4$ and ClF; the monitoring cell shown in Fig. 1 enabled the disappearance of [^{36}Cl] and [^{35}S] activities on the surface to be monitored with time. Competing, poisoning reactions involve the formation of the anions $[SF_5]^-$ and $[ClF_2]^-$, evidence that these species are formed on the surfaces coming from [^{35}S] and [^{36}Cl] surface count rate behaviour and from vibrational spectroscopy [20,45]. The ionic fluorides, CsF

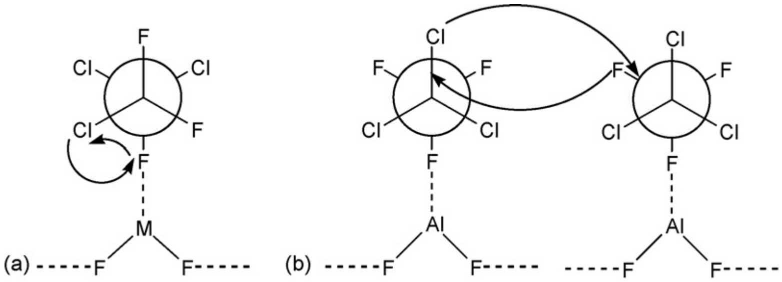


Fig. 5. Schematic representations of possible adsorbed states for (a) CCl_2FCClF_2 prior to isomerisation to $CCCl_3CF_3$, M = Cr, Al, and (b) CCl_3CF_3 prior to its dismutation.

or KF, supported on fluorinated γ-alumina, are also both active catalysts; supported CsF at the optimum loading being comparable in activity with the unsupported compound, whereas supported KF is less active. These reactions have been reviewed in some detail elsewhere [46].

A second mechanistic area in which radiotracer experiments involving [^{18}F] and [^{36}Cl] have been crucial is the catalytic fluorination, normally using aHF, of C–Cl to C–F compounds (Eq. (1)), notably CFCs and their HFC and HCFC replacements. Fluorinated chromia and fluorinated alumina catalysts, although they lead nominally to very similar product mixtures, are very different surfaces from a mechanistic point of view. The underlying thermodynamics were outlined in Section 3. The mechanistic consequence is that a halogen exchange sequence of reactions is operative on fluorinated chromia (for detailed descriptions see Refs. [28,46]), whereas the reactions that occur on fluorinated γ-alumina, or on **β**-AlF_3, which behaves very similarly, are better understood in terms of isomerisation and dismutation reactions; this is true particularly under 'HF free' conditions [47]. The compound CFC-113, CCl_2FCClF_2, has been used most often as a subject for mechanistic study. Its isomerisation to CCl_3CF_3 (Eq. (2)) is:

$$CCl_2FCClF_2 \rightarrow CCl_3CF_3 \qquad (2)$$

thermodynamically very favourable; this reaction has been observed on a variety of surfaces, including fluorinated chromia [48] (see also Ref. [28]), two types of fluorinated γ-alumina and β-AlF_3 [9,47]. In all cases, the isomerisation occurs *via* an intramolecular mechanism. For example [^{18}F] and [^{36}Cl] experiments on fluorinated chromia indicate that, unlike the situation for halogen exchange, there is no transfer of radioactivity to and from the surface during isomerisation [48]. A similar situation is indicated for [^{36}Cl]-CCl_2FCClF_2 on β-AlF_3 [9]. Isomerisation of CCl_2FCClF_2 on fluorinated γ-aluminas and β-AlF_3 is followed by its dismutation, Eq. (3), shown by kinetic life time [46] and [^{36}Cl] measurements [9] to involve:

$$2CCl_3CF_3 \rightarrow CCl_2FCF_3 + CCl_3CClF_2 \qquad (3)$$

halogen transfer between (presumably) adsorbed CCl_3CF_3 species; formation of Al–Cl surface bonds is not involved.

The radiotracer observations, referred to above, indicate that these reactions proceed *via* surface adsorbed states; they give no definitive information regarding the structures of the adsorbed species. Two possibilities are shown in Fig. 5. In both cases adsorption *via* a fluorine ligand is postulated. Although not required for the isomerisation, formation of two species adsorbed via F and at adjacent surface sites, appears to be a requirement for dismutation.

Although now only of historical interest, the isomerisation of CCl_2FCClF_2 (Eq. (2)) was the first step in a large-scale process to introduce a CF_3-group into an organic molecule. The isomerisation was 'catalysed' by solid aluminium(III) chloride. In reality, however, as was pointed out many years ago [49] and confirmed more recently [25,50], isomerisation is accompanied by chlorination and solid $AlCl_3$ is better viewed as the catalyst precursor with the real catalyst being ACF.

5. Conclusions and outlook

As the examples described above demonstrate, information concerning surface phenomena that are related to heterogeneous catalysis can be readily obtained using radiotracer methods under *in situ* conditions for chemically reactive fluorinated surfaces. Although seldom definitive by themselves, in combination with spectroscopic and surface science methods, they are a powerful addition for the investigation of surfaces. Hitherto, fluorine-18 has appeared to be a rather esoteric isotope but with increasing use being made of [^{18}F] in nuclear medicine and the consequent increase in its availability, there should be many more purely chemical applications for this branch of fluorine chemistry in the future.

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