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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

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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

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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.

Table 2
Properties of the HS-MgF_2 samples

Sample[a]	BET area (m^2 g^{-1})	Pore size (Å)	Pore vol. (cm^3 g^{-1})
HS-MgF_2	342	27	0.23
15 mol.% FeF_3 in HS-MgF_2	346	22	0.18
15 mol.% AlF_3 in HS-MgF_2	190	47	0.22

[a] In all cases the gel precursors were fluorinated using HF/N_2 (volumetric flow ratio = 4:20).

Since in all cases the materials are amorphous to X-rays, the term doped is not used here as regular distributions of the metal(III) species throughout the host cannot be proved, although they are likely to occur. In view of the stoichiometry, which was determined from the composition of the alkoxide mixtures used to prepare the sol–gels, HS-MgF_2 should be regarded as the host component. In the crystalline rutile phase of MgF_2, doping with a trivalent cation, results in an increase in Lewis acidity; this is an application of the Tanabe model, originally developed for doped oxides, to mixed metal fluorides [5,17].

2.2. *Examination of the vapour phase above reaction mixtures by FTIR*

Contact between an HS-AlF_3 sample, which had been prepared via the CCl_2F_2/N_2 route (sample CFC1 in Table 1) and Bu^{t}Cl vapour at room temperature results in the immediate observation of HCl in the vapour phase above the solid. After 1 h, there were no features in the spectrum that could be assigned obviously to Bu^{t}Cl, although a complex series of bands, possibly arising from a mixture of olefins and other hydrocarbon fragments [18], was present. The characteristic absorbance due to HCl increased further over the next 7 h. After 24 h, volatile material was removed from the cell and a fresh aliquot of Bu^{t}Cl added. On recording a second series of spectra, similar observations were made, except that the peaks assignable to hydrocarbon species differed from before. Their nearest match was with *trans*-but-2-ene, which is the expected product from dehydrochlorination of Bu^{t}Cl [15]. Repetition of this procedure with a different sample (CFC3 in Table 1) led to identical results. Samples prepared using aHF/N_2 at the second stage were not studied using FTIR but in view of the radiochemical results, to be described below, it can be assumed reasonably that similar behaviour would have been observed.

The application of this method and procedure to β-AlF_3 under identical conditions results in a far milder reaction, which leads to the slow formation of HCl in the vapour over a period of several hours [9]. Nanoscopic AlF_3, HS-AlF_3, therefore is far more reactive than the β-modification with respect to room temperature dehydrochlorination. This could be the result simply of the far greater BET area of the former but it is considered that the particle structure of HS-AlF_3 is as important, if not more. We return to this point below.

In contrast to the above behaviour, no HCl was detected by FTIR above HS-MgF_2 or the M'F_3/HS-MgF_2 samples, in all cases prepared using aHF/N_2 as the gel fluorinating agent, when they were exposed to Bu^{t}Cl over 24 h periods. These experiments therefore differentiate clearly between HS-AlF_3 and the HS-MgF_2-based materials.

2.3. *Interactions involving chlorine-36 labelled anhydrous HCl*

2.3.1. *With HS-AlF_3 materials*

The [^{36}Cl] surface count behaviour observed when a series of anhydrous H^{36}Cl aliquots is successively exposed to HS-AlF_3, samples CFC1 and 3 prepared by the CCl_2F_2/N_2 route, at room temperature is illustrated in Fig. 1.

In both examples, Fig. 1(a) and (b), the interactions observed at the surface are substantial. In Fig. 1(a), when HS-AlF_3 (CFC1 in Table 1) is exposed successively to aliquots of H^{36}Cl, using pressures of 45 Torr for 1–3 and 60 Torr for 4–8; there is a build-up of [^{36}Cl] on the surface, at least until addition 7. The species is strongly bound as evidenced by the slow decrease in surface count observed (counts 9–12) over several days after removal of the last H^{36}Cl aliquot, during which time the sample was stored in the evacuated counting cell and pumped intermittently. This behaviour indicates that the species is not simply physically adsorbed but that it is chemically

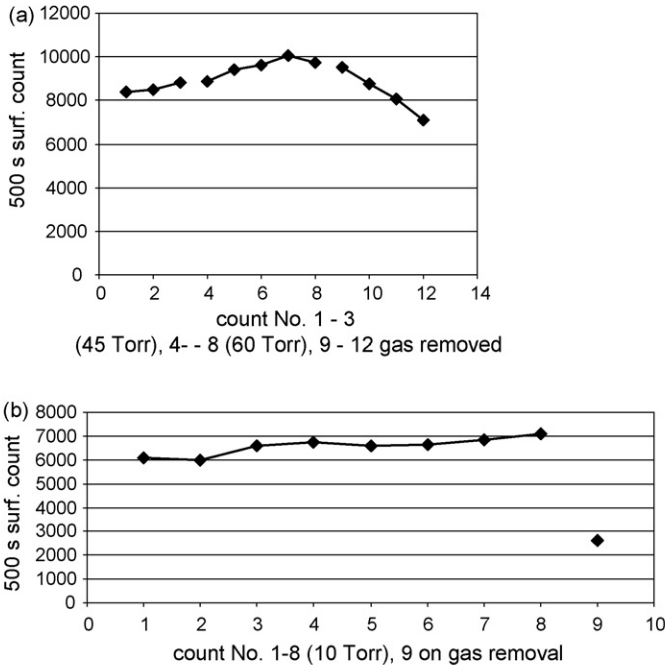

Fig. 1. Surface count values from HS-AlF_3, samples, CFC1(BET, 186 m^2 g^{-1}) and CFC3 (BET, 180 m^2 g^{-1}), from precursors fluorinated by CCl_2F_2/N_2, after exposures to [^{36}Cl]-labelled HCl, showing some pressure dependence in trace (a) and retention after removal of the last aliquot of H^{36}Cl in both cases.

adsorbed. The differences observed in the surface count behaviour between Fig. 1(a) and (b) are probably attributable largely to the smaller pressure of $H^{36}Cl$ used in the latter case. Using a smaller aliquot pressure, 10 Torr, the build-up of retained material on the surface during the addition sequence (using sample CFC3 of Table 1) is not so marked, Fig. 1(b) but the rather large relative error, ±5.8%, on the mean surface $[^{36}Cl]$ count, indicates that a build-up probably does occur. In this example, the surface count determined immediately after the removal of volatile material from the counting cell, was ca. 40% of the mean. In this case therefore, the surface counts observed during the series of additions are the result of both physical and chemical adsorption processes.

The results of analogous experiments using HS-AlF_3 samples fluorinated in the second stage of synthesis with HF/N_2 (samples HF1 and HF3 in Table 1) are shown in Fig. 2.

Similar to the situation shown in Fig. 1(a), the behaviour of the $[^{36}Cl]$ surface counts in Fig. 2(a), sample HF1 prepared using aHF/N_2, indicates a dependence on the aliquot vapour pressure, mean count for additions 1–4 (45 Torr) = 4234 $(500\ s)^{-1}$ (±3.8%), for additions 5–9 (55 Torr) = 5243 $(500\ s)^{-1}$ (±3.1%). Unlike the situation where HS-AlF_3 has been prepared via CCl_2F_2/N_2 fluorination however, the $[^{36}Cl]$ surface count decreased almost to background when volatile material was removed. The experiment shown in Fig. 2(b), using sample HF3 of Table 1, employed $H^{36}Cl$ of far greater $[^{36}Cl]$ specific activity, in order to detect any strongly adsorbed species that might be present. The mean $[^{36}Cl]$ surface count over aliquots 1 9 was 26,312 $(500\ s)^{-1}$ (±3.1%); that measured immediately after removal of volatile material, point 10 in Fig. 2(a), was ca. 40% but those determined after a further 24 h corresponded to ca. 53% (±1.1%) of the mean value determined during the additions. The increased surface count observed is considered to reflect diffusion of $[^{36}Cl]$ species from within the bulk, where due to $[^{36}Cl]$ self absorption they will not be detected by the Geiger-Müller counters, to the exterior surface of the sample where they can be detected. This process is slow but is a feature of the results throughout this study. It has enabled useful inferences to be made about the nature of the bulk materials.

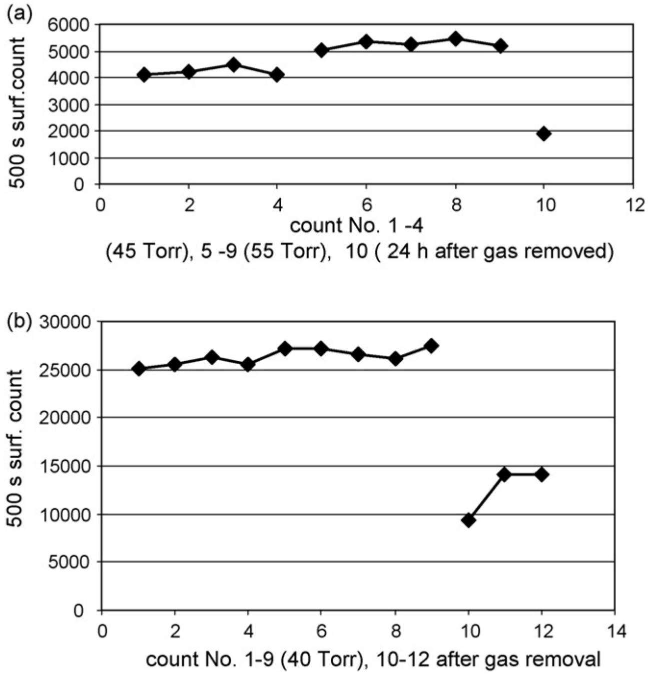

Fig. 2. Surface count values from HS-AlF_3, samples, HF1 (BET, 205 $m^2\ g^{-1}$) and HF3 (BET, 420 $m^2\ g^{-1}$) from precursors fluorinated by HF/N_2 flow, after exposures to $[^{36}Cl]$-labelled HCl, showing some pressure dependence but effectively zero retention after removal of the last aliquot of $H^{36}Cl$ in trace (a) and some retention in trace (b).

2.3.2. With HS-MgF_2 materials

$[^{36}Cl]$ Surface count data for the three materials HS-MgF_2, 15 mol.% FeF_3 in HS-MgF_2 and 15 mol.% AlF_3 in HS-MgF_2, all of which were synthesised with aHF/N_2 at the second stage, are compared in Fig. 3.

Although a mean value of the surface count in Fig. 3(a) over eight determinations can be determined, its relative error (±4.5%) compared with the errors on individual determinations (ca. 1.5%) suggests that successive exposures of $H^{36}Cl$ to HS-MgF_2 result in progressive, small increases in the surface count. A large fraction (ca. 50–54%) of the $[^{36}Cl]$ activity deposited on the surface is retained after HCl removal. Determination 9 in Fig. 3(a) was made immediately after removal of $H^{36}Cl$ above the solid, while determination 10 was made 24 h later. It is concluded that both physically and chemically adsorbed $H^{36}Cl$ are formed during the sequence of additions.

The behaviour of $H^{36}Cl$ towards HS-15 mol.% FeF_3/MgF_2, shown in Fig. 3(b), is rather similar. There is no real evidence for a 'mean' surface count over the eight determinations made; successive exposures result in progressive, small increases in the surface count. Retention of the $[^{36}Cl]$ activity deposited on the surface is essentially complete; this indicates that chemical adsorption of $H^{36}Cl$ dominates. The situation with HS-15 mol.% AlF_3/MgF_2, Fig. 3(c), is also very similar. In this case the surface count increases 24 h after removal of $H^{36}Cl$

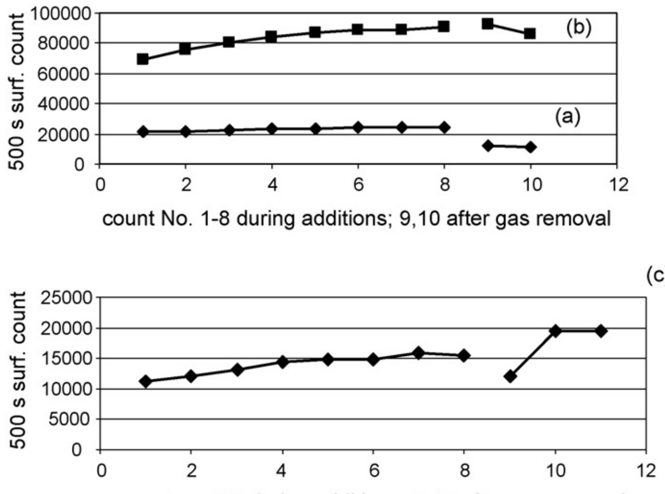

Fig. 3. Comparisons among $[^{36}Cl]$ surface count data from (a) HS-MgF_2 vs. $H^{36}Cl$ (25 Torr aliquots) (b) 15 mol.% HS-FeF_3 in HS-MgF_2 vs. $H^{36}Cl$ (20 Torr aliquots) and (c) 15 mol.% HS-AlF_3 in HS-MgF_2 vs. $H^{36}Cl$ (10 Torr aliquots).

vapour, determinations 10 and 11 in Fig. 3(c), to a value which is greater than that observed (count 8) at the end of the sequence of $H^{36}Cl$ exposures. Evidently the exterior surface of the sample is not saturated by the end of count 8, so migration of $H^{36}Cl$ from the relatively large-diameter pores (Table 2) in the bulk material to the surface where they are detected is possible. A similar phenomenon was encountered in the [^{36}Cl]-labelled Bu^{t}Cl experiment described below.

2.4. Interactions involving chlorine-36 labelled Bu^{t}Cl

The behaviour of anhydrous $H^{36}Cl$ towards the solid fluorides described above provides a good basis from which to interpret the behaviour of [^{36}Cl]-labelled Bu^{t}Cl towards the solids. There are similarities in behaviour in all cases; however, due to the sensitivity of the [^{36}Cl] method [15], subtle differences are also apparent.

2.4.1. With HS-AlF_3

When aliquots of [^{36}Cl]-labelled Bu^{t}Cl are successively exposed to HS-AlF_3, CFC1 in Table 1, in agreement with the observations made by FTIR, $H^{36}Cl$ is formed but from the [^{36}Cl] experiment, it is clear that not all the $H^{36}Cl$ is evolved to the vapour phase. A proportion of the surface counts observed as a result of each addition could be due to physically adsorbed $H^{36}Cl$, however, the substantial count observed after the last aliquot of $H^{36}Cl$ was removed indicates a strongly bound (chemically adsorbed) species. Furthermore, the increase observed in going from this count to that determined one day after and which was slightly greater than the value determined at the end of the addition sequence, suggests strongly that adsorption of [^{36}Cl]-Bu^{t}Cl and subsequent $H^{36}Cl$ adsorption occur also at sites located other than at the exterior surface. This point is considered further below.

Similar behaviour was observed when sample CFC2 in Table 1 was exposed to a series of seven aliquots (all 35 Torr) of [^{36}Cl]-Bu^{t}Cl. In this experiment, there was a build-up of [^{36}Cl] activity on the surface as successive aliquots of [^{36}Cl]-Bu^{t}Cl were added. Most of the $H^{36}Cl$ generated was adsorbed strongly.

In contrast to these observations exposure of [^{36}Cl]-Bu^{t}Cl to HS-AlF_3, which had been fluorinated using aHF/N_2 (sample HF1 in Table 1), resulted in the formation of $H^{36}Cl$ that was physically adsorbed. These three experiments illustrate well the unexpectedly different behaviour with respect to $H^{36}Cl$ retention, depending on the second stage fluorinating agent used in the samples' synthesis.

No dehydrochlorination activity could be detected when HS-AlF_3, that had been prepared *via* the aHF/N_2 route but which had also been subjected to an additional N_2 flow at 520 K (sample HF2 in Table 1), was exposed to [^{36}Cl]-Bu^{t}Cl. Although the counting statistics were satisfactory, there was no evidence even for physically adsorbed $H^{36}Cl$. This could have been a reflection of the far smaller BET area (72 vs. 205 $m^2 g^{-1}$) of the sample, although, in other studies using this Geiger-Müller monitoring method, positive results have been obtained for materials that have even smaller BET areas (e.g. [9]).

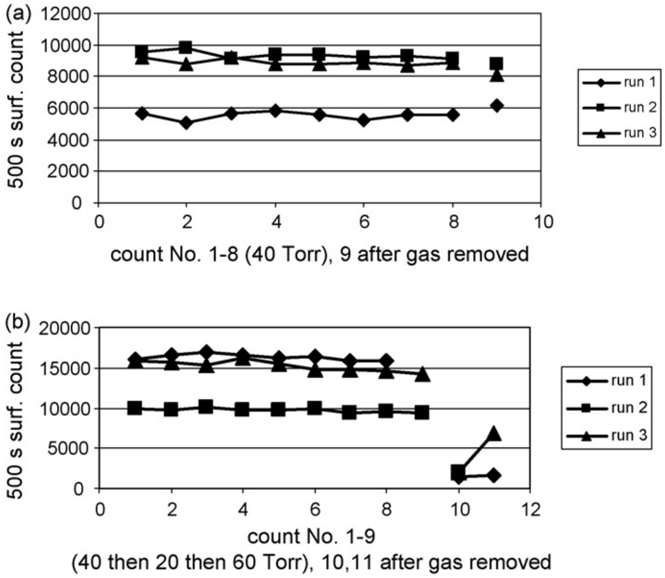

Fig. 4. Comparison of the behaviour of [^{36}Cl]-Bu^{t}Cl towards HS-AlF_3; (a) sample, CFC3 (BET, 180 $m^2 g^{-1}$) from a precursor fluorinated by CCl_2F_2/N_2, (b) sample HF3 (BET, 420 $m^2 g^{-1}$) from a precursor fluorinated by HF/N_2. Data points are from sequential exposures carried out in each case as three sets (runs 1–3) of aliquot additions.

Samples CFC3 and HF3 (Table 1) were used in a more extensive test of the possibility that the adsorption behaviour of $H^{36}Cl$, which is formed via dehydrochlorination over HS-AlF_3, can depend on the fluorination reagent used, CCl_2F_2/N_2 or aHF/N_2. Each material was used separately in a series of three consecutive experiments where three sets of eight or nine [^{36}Cl]-Bu^{t}Cl aliquots were added successively to the sample. The [^{36}Cl] specific activity was identical in all cases to facilitate comparisons among different runs. The results are compared in Fig. 4 and Table 3; the latter summarises mean surface counts and the counts obtained after removal of [^{36}Cl]-Bu^{t}Cl vapour and weakly adsorbed species.

Surface counts were greater for sample HF3, reflecting its greater specific surface area, Table 1. More significant however is the different behaviour observed between the two samples with respect to the retention of [^{36}Cl] activity. When CCl_2F_2/N_2 was used in the second stage fluorination, CFC3 in Table 1, retention determined at the end of each run was at least 90% of the mean surface count determined. Data from runs 2 and 3 are effectively identical, Table 3, indicating that the sample becomes saturated with respect to the formation of chemically adsorbed $H^{36}Cl$. However, there was no evidence that the presence of strongly bound $H^{36}Cl$ inhibited subsequent dehydrochlorination of [^{36}Cl]-Bu^{t}Cl and this suggests that dehydrochlorination and subsequent adsorption of $H^{36}Cl$ occur at different sites. In contrast, there was little evidence for strongly adsorbed $H^{36}Cl$ using HS-AlF_3 that had been synthesised via the aHF/N_2 fluorination route, HF3 in Table 1, at least until the end of run 3, Fig. 4(b) and Table 3. The behaviour observed indicates that $H^{36}Cl$ is retained within the bulk material and is evident at the exterior surface only some time after volatile species have been removed.

Table 3
[^{36}Cl] Surface counts from multiple exposures of [^{36}Cl]-Bu^{t}Cl to HS-AlF$_3$ samples prepared either using CCl$_2$F$_2$/N$_2$ or HF/N$_2$

Compound[a]	Run no.	Mean surface count, (500 s)$^{-1}$ (no. of points)	Rel. error (%)	Retained surface count, (500 s)$^{-1}$	Rel. error (%)
CFC3	1	5531 (8)	4.7	6166	2.3
	2	9357 (8)	2.4	8796	1.7
	3	8904 (8)	2.2	8122	1.9
HF3	1	16303 (8)	2.4	1446 then 1645[b]	7.1, 6.0[b]
	2	9705 (9)	2.7	2011	5.2
	3	15197 (9)	4.2	1957 then 6780[b]	5.4, 2.1[b]

[a] Codes correspond to those in Table 1; reagents used were, for CFC3, CCl$_2$F$_2$/N$_2$ and for HF3, HF/N$_2$.
[b] Determined immediately on removal of volatile material then 24 h later.

2.4.2. With HS-MgF$_2$ materials

The behaviour of [^{36}Cl]-Bu^{t}Cl towards HS-MgF$_2$ and the materials containing 15 mol.% FeF$_3$ or AlF$_3$ in HS-MgF$_2$ as host, is compared in Fig. 5.

In all three cases the [^{36}Cl] specific activity of [^{36}Cl]-Bu^{t}Cl used was identical; a further factor facilitating comparisons, at least between HS-MgF$_2$ and 15 mol.% FeF$_3$ in HS-MgF$_2$, is the near identity of their BET areas and pore volume parameters, Table 2.

The relative error (±5.8%) on the mean surface count obtained when HS-MgF$_2$ was exposed to a series of [^{36}Cl]-Bu^{t}Cl aliquots at room temperature, Fig 5(a), is a little larger than errors on individual values (ca. ±3%) and it is possible that there is a very small increase with each addition. Retention of [^{36}Cl] surface activity is significant (63% of the mean) and an apparent increase to a value slightly greater than that observed during the exposures to [^{36}Cl]-Bu^{t}Cl is observed after 24 h. This observation suggests that the interaction is not confined to the surface but involves bulk material, as with the similar observations described above.

Comparison between the behaviour of [^{36}Cl]-labelled HCl and Bu^{t}Cl suggests strongly that HCl is formed on exposure of HS-MgF$_2$ to Bu^{t}Cl. As no HCl was observed in the vapour above the solid by FTIR, in contrast to the situation with HS-AlF$_3$, Section 2.2, it appears that any HCl formed is trapped on the surface or in the bulk. The extent of the dehydrochlorination reaction at HS-MgF$_2$ is far less than that at HS-AlF$_3$; its observation using [^{36}Cl] labelling is a reflection of the great sensitivity of the technique. Dehydrochlorination can be detected by the deposition of [^{36}Cl] species on the surface and is observed at a level below that at which HCl is observable, using FTIR, in the vapour phase above the surface.

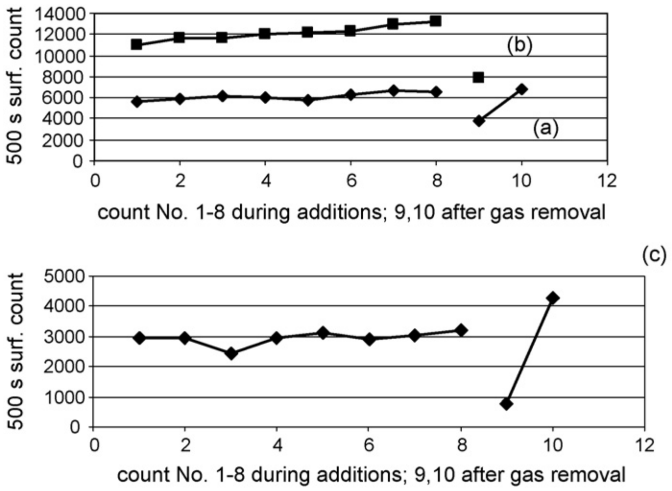

Fig. 5. Comparisons among [^{36}Cl] surface count data from (a) HS-MgF$_2$ vs. [^{36}Cl]-labelled Bu^{t}Cl (30 Torr aliquots), (b) 15 mol.% HS-FeF$_3$ in HS-MgF$_2$ vs. [^{36}Cl]-labelled Bu^{t}Cl (30 Torr aliquots) and (c) 15 mol.% HS-AlF$_3$ in HS-MgF$_2$ vs. [^{36}Cl]-labelled Bu^{t}Cl (30 Torr aliquots).

The material, 15 mol.% FeF$_3$ in HS-MgF$_2$ behaves in a manner very similar to HS-MgF$_2$ when exposed to [^{36}Cl]-Bu^{t}Cl, Fig. 5(b), but it is probably more reactive. The relative error on the mean surface count (±5.6%) is larger than errors on individual values (ca. ±2%) and it is possible that there is a very small increase with each addition rather than there being a true mean. Retention of [^{36}Cl] surface activity is significant (64% of the nominal mean value). The observations are almost identical to those described above for HS-MgF$_2$; however, surface counts are significantly higher, suggesting that the interaction is not confined to MgF$_2$-derived sites.

The degree of interaction between 15 mol.% AlF$_3$ in HS-MgF$_2$ and [^{36}Cl]-Bu^{t}Cl appears to be the smallest of the three samples studied in this series. This is consistent with its BET area being little more than 50% of those of the other two solids (Table 2). As a consequence, the surface counts are not determined particularly precisely (the relative error on the mean value from eight determinations is ±7.5% and relative errors on single values ca. 6%). Retention of [^{36}Cl] surface activity, though significant after 24 h and at this point greater than the mean value during the series of exposures, is very small initially, Fig. 5(c). These findings, as with those described above for the H^{36}Cl interaction with this solid, Fig. 3(c), suggest very strongly that bulk interactions are more important than those on the surface and this is consistent with the larger pore diameter of the material. In all other respects however, the behaviour of the material is rather similar to those described above for HS-MgF$_2$ and the FeF$_3$/HS-MgF$_2$ materials; the differences, in degree rather than in type, probably originate as a result of the smaller BET area.

2.5. The Lewis acidity of HS-AlF$_3$ and HS-MgF$_2$

Making comparisons among solid Lewis acids can be more problematic than among molecular acids, even though the solids may be closely related. Comparisons among molecular Lewis acid fluorides are made often on the basis of the F^- ion affinities of the isolated molecules, for example the pF scale [19]. From these computations and related work [20], it has been established quantitatively that antimony pentafluoride and its oligomers are benchmarks for molecular strong Lewis acid fluorides. For solid acids, not only are the intrinsic strengths of the different types of Lewis acid present on the surface an important consideration but their surface site densities and the morphology of the surface, which may conflict with the steric requirements of adsorbed species, will often be crucial in determining the apparent effectiveness of a solid Lewis acid. Using a multi-technique approach, including FTIR measurements of adsorbed pyridine, temperature programmed desorption (TPD) of NH_3 and catalytic behaviour in probe reactions, notably its catalytic activity in C_1 halofluorocarbon dismutation reactions and isomerisation of $CBrF_2CBrFCF_3$, it has been established that HS-AlF_3 is one of the most effective solid Lewis acids presently known [10–13]. It is comparable in its behaviour to that of solid aluminium chlorofluoride, $AlCl_xF_{3-x}$, $x = 0.05–0.25$ [21,22]. This conclusion is supported by the [^{36}Cl]-tracer studies described here, as the behaviour of $AlCl_xF_{3-x}$ towards [^{36}Cl]-Bu^{t}Cl [15] is very similar to that described above for HS-AlF_3.

Crystalline MgF_2 is not usually considered to be a strong acid; the pure compound is, at best, a weak Lewis acid [23]. It has been used mainly therefore as a catalyst support rather than as an acid catalyst [24,25]. Although MgF_2 of small particle size has been prepared using aqueous or aqueous-organic sol–gel [26] or microwave [27] techniques, the properties of the solids will be rather different than those reported in the present work, where non-aqueous sol–gel conditions have been used for syntheses of the precursors [14]. Crystalline MgF_2 is a useful host for a range of metal trifluorides, M'F_3, providing the size of the M' cation is not too different from that of Mg^{2+} [17]. Providing this condition is met and the concentration of the dopant cation is not too great, the surface Lewis acidity of the doped solid exceeds that of undoped MgF_2 [28]. Paradoxically, this effect (originally derived to account for acidity in doped oxides and described as the Tanabe model [17]) has been observed from solids prepared both via conventional aqueous co-precipitation and via the non-aqueous sol–gel method [28]. These findings have led to the synthesis of Lewis acid heterogeneous catalysts containing Fe^{III} or Cr^{III} [29].

Notwithstanding these previous studies, the behaviour of HS-MgF_2 towards room temperature dehydrochlorination of Bu^{t}Cl was not predicted. It does confirm however, that sol–gel prepared MgF_2, as well as the amorphous solids in which FeF_3 or AlF_3 is present, can exhibit Lewis acidity. They are less effective than HS-AlF_3, since in all cases activity was detected only by using the very sensitive [^{36}Cl] method.

Additional evidence for the behaviour of HS-MgF_2, 15 mol.% FeF_3/HS-MgF_2 and 15 mol.% AlF_3/HS-MgF_2 as Lewis acids comes from the results of NH_3 TPD experiments and from their catalytic behaviour in the dismutation of chlorodifluoromethane, Eq. (1), a representative of a class of C_1 halocarbon dismutation reactions that has been used extensively to probe surface Lewis acidity in fluorides and fluorinated oxides [30].

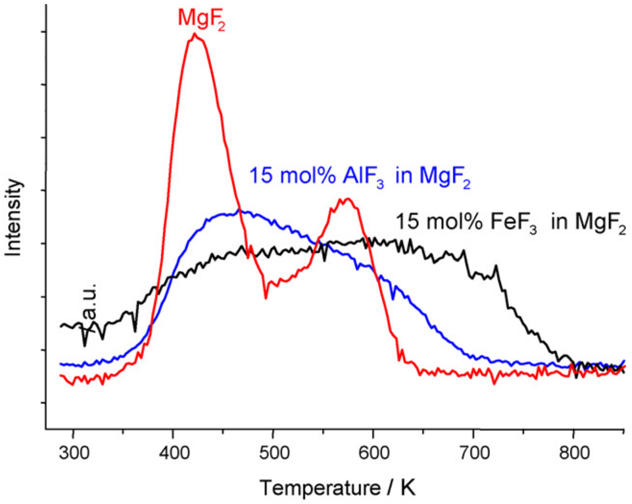

Fig. 6. Comparison among NH_3 TPD data from HS-MgF_2 based samples.

$$5CHClF_2 \rightarrow 3CHF_3 + CHCl_2F + CHCl_3 \quad (1)$$

TPD traces for NH_3 desorption from the three solids are shown in Fig. 6. Deconvolution of the signals, Table 4, indicates the presence of three maxima and therefore three different types of acid site, in each case. The behaviour is related to TPD observations made previously for HS-AlF_3 [13]. Although the temperature maxima in 15 mol.% AlF_3/HS-MgF_2 are rather similar to those in HS-MgF_2 alone and are only slightly shifted to higher temperatures, 15 mol.% FeF_3/HS-MgF_2 has sites that are significantly stronger, as indicated by the NH_3 desorption temperatures.

Conversion data for $CHClF_2$, determined under flow conditions at 623 K in the presence of the three solids, show an identical trend, Table 5. In Fig. 7 the temperature at which the onset of reaction can be detected and the variations of conversion with temperature, in both cases at HS-MgF_2, are shown. The only products detected are those given in Eq. (1) and they were observed in the expected molar ratios.

Thus TPD and dismutation probe reaction results are both in agreement with the [^{36}Cl]-Bu^{t}Cl dehydrochlorination study. All three HS-MgF_2-based solids behave as Lewis acids; 15 mol.% FeF_3/HS-MgF_2 has stronger Lewis sites, possibly Fe^{III}-based, than are found in HS-MgF_2 alone. Although the [^{36}Cl] study does not allow an unambiguous distinction to be made between

Table 4
Peak maxima from NH_3 TPD deconvolution

Compound[a]	$T_{max}(1)$ (K)	$T_{max}(2)$ (K)	$T_{max}(3)$ (K)	$T_{max}(4)$ (K)
HS-MgF_2	422	474	573	–
15 mol.% FeF_3 in HS-MgF_2	–	497	614	703
15 mol.% AlF_3 in HS-MgF_2	438	513	573	–

[a] The analogous data for HS-AlF_3 from [13] are T_{max} = 500, 599, 669, 773 K.

Table 5
Conversion of $CHClF_2$ in its dismutation at 623 K

Catalyst	Equilibrium conversion of $CHClF_2$ (%)
HS-MgF_2	41
15 mol.% FeF_3 in HS-MgF_2	100
15 mol.% AlF_3 in HS-MgF_2	63

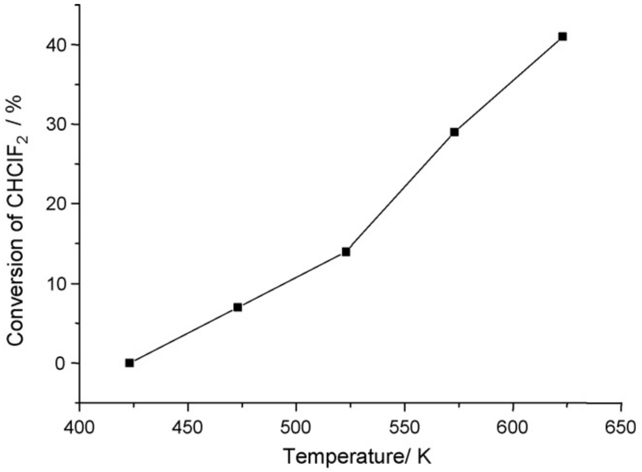

Fig. 7. Conversion of $CHClF_2$ vs. temperature over HS-MgF_2.

15 mol.% AlF_3/HS-MgF_2 and HS-MgF_2, the TPD and dismutation results suggest that the former may have slightly stronger Lewis acid sites.

2.6. *Adsorption of anhydrous HCl*

A second surprising feature of the [^{36}Cl] radiotracer study is the observation of strongly adsorbed $H^{36}Cl$ in the vast majority of the situations examined. The proposal to account for this, although speculative, does rationalize the observations made. It can be summarised as follows. Strong adsorption of $H^{36}Cl$ occurs irrespective of its origin, [^{36}Cl]-Bu^{t}Cl or $H^{36}Cl$, and the solid involved. In many cases adsorption involves regions of the solid other than the exterior surface, defined as the surface at the gas–solid interface. It appears that the migration of strongly adsorbed HCl from sites at the interior surface to the exterior is a slow process. The extent to which $H^{36}Cl$ is adsorbed strongly at HS-AlF_3 appears to depend on the fluorinating agent, CCl_2F_2/N_2 or anhydrous HF/N_2, used to perform the second stage of the synthesis.

Although interactions between HCl and metal fluorides have not been widely studied, those involving oxides are well known. Dissociative adsorption, which is the normal situation for HCl at aluminas, involves formation of an Al–Cl bond with H^+ bound to an adjacent oxygen or replacement of surface Al–OH by Al–Cl and the loss of H_2O [31]. Dissociative adsorption of HCl at fluorides is not likely unless hydrolysis has occurred on the surface to some extent. The effects of surface hydroxyl group formation on crystalline MgF_2 are well documented [25,32] but there was no evidence for surface hydrolysis here.

Associative adsorption of HCl at coordinatively unsaturated Al^{III} sites, postulated to occur at the strong Lewis acid η-alumina [33], is a realistic possibility for HS-AlF_3 and, by implication, for the other solids examined here. The solids are composed of aggregates of very small particles (nanoparticle solids [12]), which will have properties that are very different from those of the bulk, crystalline analogues. This has been emphasised recently in a molecular dynamics simulation of cubic α-AlF_3 nanoparticles in which significant structural rearrangements occur, particularly at the edges and corners of the particles [34]. Coordinatively unsaturated, Lewis acid Al^{III} sites are located largely in these regions, their environments being reminiscent of the structural motifs found in metastable β-AlF_3 [16] and other modifications derived from structurally more open precursors [35]; it has been known for many years that modifications of AlF_3 that have structures more open than that of crystalline α-AlF_3 are good Lewis acid heterogeneous catalysts [30,35,36].

We have shown previously that anhydrous HCl is strongly adsorbed at hydrated surface sites of β-AlF_3 [9]. If hydrated or hydroxylated sites were to be present at HS-AlF_3 they would contribute to the HCl adsorption observed. It seems more likely however that the main contribution arises from a direct interaction between HCl, acting as a Lewis base, and coordinatively unsaturated Al^{III} sites located at corners or edges of particles. Many of the latter will be located remote from the gas–solid exterior surface and will not be detectable by [^{36}Cl] Geiger-Müller counters until $H^{36}Cl$ migrates to the exterior surface. Since there is no evidence for immediate poisoning of Bu^{t}Cl dehydrochlorination by prior-adsorbed HCl, the latter is likely to be adsorbed at different sites than those used for dehydrochlorination.

Finally, the difference in behaviour of the two types of HS-AlF_3 examined here can be rationalized by considering the subsequent behaviour of the fluorinating reagent used, CCl_2F_2/N_2 vs. anhydrous HF/N_2. The former will be, at best, weakly adsorbed on the surface while the latter will be adsorbed strongly. It is proposed that the extent to which HCl is adsorbed strongly at an HS-AlF_3 surface is reduced by the presence of prior-adsorbed HF. Removal of the latter is favoured by treatment at high temperature but this also apparently leads to sintering and a reduction in BET area.

3. Experimental

3.1. *Synthesis of the amorphous solids*

All experiments were conducted under non-aqueous conditions using Schlenk technique. Solvents were dried by standard methods and stored over molecular sieve. HS-Aluminium fluoride was prepared according to the literature [13] as follows. Dried *iso*propanol was added to aluminium isopropoxide (Aldrich 98%+) and stirred. A stoichiometric quantity of HF dissolved in *iso*propanol was added with stirring; a translucent gel was formed immediately. This was aged at room temperature for 24 h and evaporated under vacuum at 343 K to obtain the dry Al-F-gel (precursor).

Fluorination of the dry Al-F-gel was performed in a continuous flow fixed-bed tube reactor, consisting of a nickel tube, i.d. = 5 mm, located in a furnace. The desired amount of the sample was placed in the center of the reactor on a silver wool plug. Mixtures of CCl_2F_2/N_2 or aHF/N_2 were flowed for the times and temperatures shown in Table 1 using mass flow controllers and a thermocouple for temperature measurement.

HS-Magnesium fluoride was prepared according to [14b]. Magnesium methoxide was prepared from magnesium metal and methanol. It was reacted in alcoholic solution with a stoichiometric quantity of anhydrous HF dissolved in alcohol, to yield a sol or gel. The latter was dried at 343 K under vacuum to a dry gel, which was further fluorinated with HF/N_2 at somewhat higher temperatures (volumetric flow rates, 4 $cm^3 min^{-1}$ of aHF and 20 $cm^3 min^{-1}$ of N_2) yielding the high surface area HS-MgF_2. Mixed metal solids were prepared in a similar way as for HS-MgF_2. The second metal was introduced by adding 15 mol.% of its alkoxide, aluminium isopropoxide or iron(III) methoxide (Alfa Aesar, 98%) to the magnesium methoxide solution.

The specific surface area, pore size distribution, and pore volume of the samples were determined using dinitrogen as adsorbate at 77 K and a Micromeritics ASAP 2020 volumetric adsorption analyzer. The sample was loaded and outgassed in vacuum at 273 K 10 h before the measurements to remove physically adsorbed water. The specific surface areas were determined according to the BET method and pore size distributions and pore volumes were calculated via the Barret-Joyner-Halenda (BJH) method.

3.2. Chlorine-36 experiments

Anhydrous hydrogen chloride labelled with [^{36}Cl] was prepared by a modified literature procedure [37] from a standard solution prepared from a commercial sample of aqueous $Na^{36}Cl$ and conc. HCl (10 cm^3). This was diluted further with conc. aqueous HCl (normally to 10 cm^{-3} using 1–5 cm^{-3} of the standard) and allowed to react with 98% H_2SO_4 dropwise at room temperature. Purification involved low temperature trap to trap distillation over P_4O_{10}, finally distillation *in vacuo* and storage in a stainless steel or Monel pressure vessel over P_4O_{10}. *Tert*-butyl chloride labelled with [^{36}Cl] was prepared according to the literature [38] as modified for the labelled compound [9]. Typically 2-methylpropan-2-ol (1.66 g, 23.0 mmol) and an aliquot (up to 10 cm^3) of the standard aqueous $H^{36}Cl$ solution were mixed and shaken intermittently over 2 h. The organic layer was washed with aqueous $NaHCO_3$ then water, dried over $CaSO_4$ then activated 3A sieves *in vacuo*. Material with higher specific count rate was prepared similarly by using a more highly radioactive standard $H^{36}Cl$ solution.

The principles behind the Geiger-Müller direct monitoring method as applied to the study of room temperature dehydrochlorination of [^{36}Cl]-labelled Bu^tCl have been described recently [15] as has the procedure for monitoring $H^{36}Cl$ adsorption at β-AlF_3 through multiple exposures of $H^{36}Cl$ to the solid [9]. Samples of HS-solids to be studied were added to the Pyrex counting cell *in vacuo* via an evacuable Pyrex dropping ampoule fitted with a high vacuum PTFE/Pyrex stopcock (J. Young), the ampoule having been charged previously with the solid sample in a glove box. A sample (normally 250–500 mg) was spread as thinly as possible in a Pyrex boat positioned directly below one of the G.-M. counters; the arrangement being made to approximate to the requirement for an infinitely thin layer of solid. The solid and the cell were thoroughly outgassed, then a measured pressure of [^{36}Cl]-labelled anhydrous HCl or Bu^tCl was expanded into the cell from a calibrated, gas-handling manifold. The cell was isolated from the remainder of the vacuum system, 15 min were allowed for equilibration and the counts from each G.-M. counter recorded simultaneously on two scaler-timers for a period of 500 s. The vapour was removed from the cell and the sequence, gas admission, equilibration then counting, repeated. Usually eight or nine aliquots were used for each experiment. After removal of the last aliquot, the counts were recorded from both counters. The cell was left evacuated over a period of at least 18 h, usually with intermittent pumping before additional counts were recorded. Background counts were obtained regularly, before and after each experiment, and counters were replaced when contamination appeared to have occurred. Before using a new batch of labelled HCl or Bu^tCl, the intercalibration factor of the two counters was re-determined.

The interaction between each solid and Bu^tCl vapour was studied also using FTIR spectroscopy and a Pyrex cell, path length 10 cm, KBr end windows and a depression below the beam path to contain the solid. The latter was added *in vacuo* using an evacuable ampoule similar to that used in the G.-M. experiments described above. A spectrum of a measured pressure of Bu^tCl vapour was recorded before the solid was added, immediately afterwards and at intervals over a 24–36 h period.

3.3. Temperature programmed desorption of NH_3

Experiments were carried out in a fixed bed flow reactor over a temperature range 353–773 K. Before the TPD experiment, the sample (200 mg) was outgassed for 1 h in a flow of argon (10 $cm^3 min^{-1}$) to desorb material from the surface, then was exposed at 393 K to a stream of NH_3. The excess of NH_3 was eliminated by argon flow at 393 K for 1 h. After allowing the sample to cool to 353 K, the TPD program (10 K min^{-1}, up to 773 K, held for 30 min) was started. Desorbed NH_3 was monitored continuously via FTIR spectroscopy (FT-IR System 2000, PerkinElmer), absorbed in acid and the total quantity determined by back titration with sodium hydroxide.

3.4. Catalytic dismutation of $CHClF_2$

The dismutation of $CHClF_2$ over the HS-MgF_2 solids was tested in a flow system. A sample of the solid (ca. 1 g) was placed in a nickel tube flow reactor through which a mixture of $CHClF_2$ diluted with N_2, ratio 1:4, was passed. A residence time of 2 s was set by adjusting the gas flow with a mass flow meter. The composition of the exhaust gas phase was determined by in-line GC with FID using a 10% SE 30 Chromosorb column. The reaction temperature was varied from 473 to 623 K. The activity of each catalyst was tested from 623 K downwards, cooling by 50 K steps and holding each temperature for 5 min to make a measurement. Data were reproduced several times.

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