Aluminum Chloride as a Solid Is Not a Strong Lewis Acid

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Aluminum Chloride as a Solid Is Not a Strong Lewis Acid

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Received: January 9, 2006; In Final Form: March 9, 2006

Aluminum chloride is used extensively as Lewis acid catalyst in a variety of industrial processes, including Friedel−Crafts and Cl/F exchange reactions. There is a common misconception that pure $AlCl_3$ is itself a Lewis acid. In the current study, we use experimental and computational methods to investigate the surface structure and catalytic properties of solid $AlCl_3$. The catalytic activity of $AlCl_3$ for two halide isomerization reactions is studied and compared with different AlF_3 phases. It is shown that pure solid $AlCl_3$ does not catalyze these reactions. The (001) surface of crystalline $AlCl_3$ is the natural cleavage plane and its structure is predicted via first principles calculations. The chlorine ions in the outermost layer of the material mask the Al^{3+} ions from the external gas phase. Hence, the experimentally found catalytic properties of pure solid $AlCl_3$ are supported by the predicted surface structure of $AlCl_3$.

Introduction

$AlCl_3$ is commonly used as a catalyst in many industrial processes. Together these processes account for more than 40% of the $AlCl_3$ produced annually.[1] These processes are all examples of Friedel−Crafts catalytic reactions catalyzed by strong Lewis acids.[2] This has led to a common assumption that pure $AlCl_3$ is a strong Lewis acid.

Principally, $AlCl_3$ and AlF_3 phases should behave quite similarly concerning their Lewis acidity[3] and their Lewis acid-dependent catalytic performance. However, generally AlF_3 is regarded as a weak Lewis acid and a poor catalyst because of the experiments performed with the crystalline α- and β-AlF_3 phases. Actually, large differences between the different phases of AlF_3 are observed,[4] which can be explained by the substantial differences in the accessibility of the aluminum sites at the surface. The surface of well crystallized α-AlF_3 shows no Lewis acidity or catalytic activity,[4] and theoretical calculations have shown that the Al atoms are effectively covered by fluorine atoms.[5] Conversely, the structure of beta-AlF_3, which shows moderate Lewis acidity and catalytic activity,[4] has been shown to contain under-coordinated 5-fold aluminum ions at the surface,[6] thus, explaining the observed moderate surface acidity and catalytic activity of this phase.

Just like α-AlF_3, solid $AlCl_3$ is a highly ordered crystalline material.[7] Therefore, catalytic inertness should also be expected for the solid, highly crystalline phase. This is in contrast to traditional opinion based on its widespread use as catalyst.

To gain insight into the Lewis acid properties of solid $AlCl_3$ its catalytic activity for reactions, which are known to proceed exclusively when catalyzed by Lewis acids, has been investi-

gated experimentally and compared with different AlF_3 phases, which differ markedly in their respective degree of order. That means, a high degree of disorder is the prerequisite of under-coordinated surface Al-sites, and consequently, differently accessible surface Lewis-acid sites resulting in different catalytic properties of the chemically equally composed phases. The composition and structure of the natural cleavage plane, the (001) surface of $AlCl_3$, has also been predicted using first principles calculations

The details of the experimental work are first discussed followed by the main results of the experiments. The theoretical methodology is then described and it is followed by its main finding. The findings of the two studies are then compared and the agreement between the results is discussed.

Experimental Methodology

The catalytic test reactions selected are specifically Lewis acid catalyzed and truly heterogeneous, as opposed to reactions where $AlCl_3$ becomes dissolved in the reaction mixture, e.g., in Friedel−Crafts reactions. The reactions used (viz. reaction 1 and 2) are isomerizations of fully halogenated compounds.

$$CCl_2FCClF_2 \rightarrow CCl_3CF_3 \qquad \text{(Reaction 1)}$$

$$CBrF_2CBrFCF_3 \rightarrow CF_3CBr_2CF_3 \quad \text{(Reaction 2)}$$

Reaction 1 is of economic interest, CCl_3CF_3 is a sought after resource for the increasingly important CF_3 chemistry.[8,9] The reaction can be performed under defined heterogeneous solid/gaseous and solid/liquid conditions, since CCl_2FCClF_2 is a very poor solvent for inorganic compounds. The equation for reaction 1 given above does not fully represent the possible reaction path, because consecutive dismutation reactions of CCl_3CF_3 may take place depending on the catalyst and the temperature needed for this reaction. The isomerization reaction of CCl_2FCClF_2 was shown to occur via an intramolecular reaction path, whereas

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TABLE 1: Isomerization of CCl$_2$FCClF$_2$ (Reaction 1) and CBrF$_2$CBrFCF$_3$ (Reaction 2) over AlCl$_3$ and Different Al-fluoride Catalysts

| | reaction 1 | | | | | | | | | | | | reaction 2 |
| | liquid phase 53°C | | | liquid phase 53°C | | | gas phase | | | gas phase | | | |
catalyst	time [min]	X^a [%]	Y^b [%]	time [min]	X^a [%]	Y^b [%]	temp [°C]	X^a [%]	Y^b [%]	temp [°C]	X^a [%]	Y^b [%]	X^a [%]
AlCl$_3$	**60**	**9**	**5**	**180**	**92**	**71**	**50**	**1.5**	**1.4**	**100**	**1.6**	**0.4**	**0**
HS−AlF$_3$	45	7	7	300	24	22	50	82	59	100	94	83	≈100
ACF	2	10^c	9^c	20	99^c	94^c	50	100	96	100	100	96	≈100
α-AlF$_3$				300	0					300	0		0
β-AlF$_3$				300	0					300	0		0

^{a} Conversion. ^{b} Yield of CF$_3$CCl$_3$. ^{c} At 25°C.

the dismutation reactions of the C$_2$Cl$_{6-x}$F$_x$ analogues occur rather via an intermolecular reaction path.[10] However, for both types of reactions, surface Lewis acid sites of crucial strength are necessary. The weaker the surface sites the higher the reaction temperature needed and, consequently, the less selective the reaction is.

Reaction 2 was selected because it proceeds only under the catalytic influence of the strongest Lewis acids such as SbF$_5$.[11]

AlCl$_3$ and, for comparison, 4 aluminum fluorides, α-AlF$_3$, β-AlF$_3$, HS−AlF$_3$ (high surface AlF$_3$[12]), and ACF (aluminum chlorofluoride[13]), were tested as catalysts in reaction 1 both under solid/liquid and solid/vapor phase conditions, and in reaction 2 under solid/liquid conditions. Temperature programmed desorption of adsorbed NH$_3$ (TPD) was attempted.

Experimental. AlCl$_3$ (Sigma-Aldrich) was freshly sublimed in a Cl$_2$-stream and stored in a drybox. The BET surface area was not detected because a totally inert sample transfer to the BET apparatus could not be realized and contact to moisture of air would change the surface. HS−AlF$_3$ was prepared as described elsewhere.[12] It had a specific surface area (SA-BET/N$_2$) of 210 m^2/g. ACF was prepared as described in detail elsewhere.[13] The product correlated with the formula AlCl$_{0.13}$F$_{2.87}$ (SA-BET/N$_2$ 101 m^2/g). β-AlF$_3$ was prepared according to ref 14. Phase purity was confirmed by XRD (SA-BET/N$_2$ 26 m^2/g). α-AlF$_3$ (ACROS) was used as supplied (SA-BET/ N2 13m^2/g).

Catalytic Reactions. *CCl$_2$FCClF$_2$ Isomerization, Vapor Phase.* The reaction was carried out passing a mixture of CCl$_2$FCClF vapor and N$_2$ through a bed of 2.8 mL catalyst kept in a metal tube reactor (40 cm × 0.5 cm), with a contact time of 3.7 s. The products were trapped in cold CDCl$_3$ and analyzed by ^{19}F NMR.

Liquid Phase. About 5 mL of CCl$_2$FCClF$_2$ was stirred with ∼500 mg of the respective catalyst (corresponding to a molar ratio of about 7:1) at 53 °C (AlCl$_3$, β-AlF$_3$, HS−AlF$_3$) or at 25 °C (ACF) for 4−5 h in a glass bulb equipped with a reflux condenser. The reaction mixture was subjected to ^{19}F NMR analysis at regular intervals.

CBrF$_2$CFBrCF$_3$ Isomerization. About 0.1 g of the catalyst was added to 1 mL CBrF$_2$CBrFCF$_3$, and the mixture was shaken for 2 h at room temperature; after the catalyst has settled down, the supernatant liquid was analyzed by ^{19}F NMR.

Temperature Programmed Desorption of Ammonia (NH$_3$-TPD). The sample (about 0.2 g) was first heated under nitrogen up to 300 °C, then at 120 °C exposed to NH$_3$. After flushing the excess NH$_3$ at 120 °C with N$_2$ for 1 h and cooling to 80 °C the TPD program was started (10°/min up to 500 °C, keeping for 30 min). Desorbed NH$_3$ was monitored continuously via IR spectroscopy (FT−IR System 2000, Perkin-Elmer).

Experimental Results

The hypothesis of this work is that, in analogy to perfectly crystalline α-AlF$_3$, a perfectly crystalline AlCl$_3$-surface should not exhibit any under-coordinated surface Al-site, that means it should not provide Lewis acidic surface sites and, consequently, should not be catalytically active as long as no change of the surface constitution/morphology takes place.

Therefore, to prevent any chemical impact on the AlCl$_3$ surface, catalytic reactions were selected, which (i) are exclusively catalyzed by Lewis acid sites, and (ii) the partners of which can neither AlCl$_3$ nor AlF$_3$ dissolve. Additionally, reaction 1 was carried out under gas-phase conditions making dissolution of the catalyst impossible.

AlCl$_3$ has previously been used for reaction 1.[15] However, neither in liquid CCl$_2$FCClF$_2$ at room temperature over 3 h nor with CCl$_2$FCClF$_2$ vapor up to 100 °C did AlCl$_3$ give any indication of catalytic activity. In a separate run, the amount of AlCl$_3$ was enlarged to such an extend that under assumption of a BET/N$_2$-surface area of about 10 m^2/g the same absolute surface area was provided. Even under these conditions, no conversion was observed. But upon repeating the reaction with refluxing CCl$_2$FCClF$_2$, the isomerization started slowly (Table 1), reaching 3% conversion after 30 min, 9% after 1 h, 92% after 3 h, and completeness was obtained in 4 h. In reaction 2, AlCl$_3$ did not show any catalytic activity.

Both α-AlF$_3$ and β-AlF$_3$, the latter reported[16,17] to be an active halogen exchange catalyst, did not show any catalytic activity either for reaction 1 up to 300 °C in the gas-phase reaction (with β-AlF$_3$, the reaction is reported to start above 327 °C,[14] crystallized α-AlF$_3$ did not show catalytic activity under either condition, even not using a large excess of catalyst) or for reaction 2 (Table 1).

Freshly prepared HS−AlF$_3$ as well as ACF were active catalysts under both liquid and vapor phase conditions for both reactions 1 and 2 (Table 1). In the vapor phase of reaction 1 the catalytic activity of HS−AlF$_3$ and ACF was almost comparable at 100−200 °C, but at 50 °C HS−AlF$_3$ needed more extended contact time than ACF to reach 100% conversion. However, the selectivity of HS−AlF$_3$ was lower than that of ACF, and with decreasing contact time, the activity was more drastically decreased than with ACF. In the liquid phase of reaction 1, HS−AlF$_3$ was not as active as ACF, after 5 h of reaction time the conversion had reached only 24%; however, in reaction 2 both aluminum fluorides were equally highly active.

Temperature programmed desorption of adsorbed NH$_3$ (TPD) provides information about strength and quantitative distribution of acid sites on solids. Attempted TPD was not successful with AlCl$_3$ because of its too-ready sublimation (starting already at ca. 120 °C), whereas, in case of the aluminum fluorides, it was
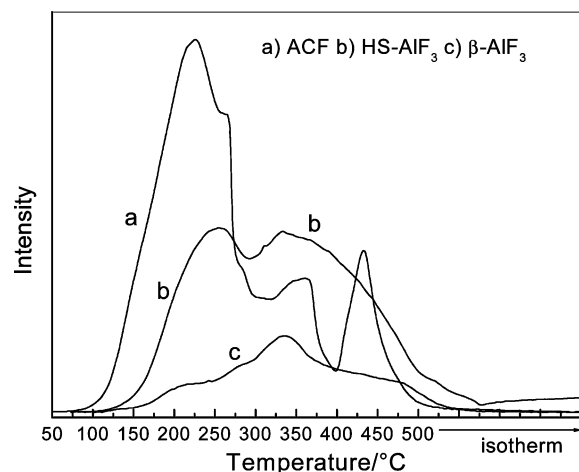
Figure 1. NH_3−TPD of ACF, HS−AlF_3, and β-AlF_3. (Note that ACF decomposes above 400 °C giving rise to additional NH_3 liberation, whereas HS−AlF_3 is thermally stable up to 560 °C.)

successful. The TPD curves for the fluorides are shown in Figure 1 indicating superior Lewis acidity of ACF and HS−AlF_3.

Theoretical Methodology

The relative stability of a surface with variable stoichiometry is determined by minimization of the surface free energy. The effect of an external atmosphere of chlorine on the surface structure of $AlCl_3$ is included in the first priciples calculation via the inclusion of a chlorine chemical potential.[18−20] The same methodology has been used by us in studies of AlF_3[5,6]

Calculations were performed using a linear combination of atomic orbitals scheme as implemented in the CRYSTAL code.[21] The B3LYP hybrid exchange functional, which has been shown to provide reliable structures and energetics in a wide range of materials,[22] was employed to approximate electronic exchange and correlation. Local Gaussian basis sets for the Al^{3+} and Cl^- ions where obtained from standard sources.[23]

The relative charges on the atoms were calculated using a mulliken partition of the total charge density. This is a somewhat arbitrary choice, since there is no unique method of performing the partition of the charge density. However, the choice of a given scheme is still extremely useful in comparing the results of calculations performed using similar basis sets.[24] Therefore, it provides a useful tool for comparing charge distributions of bulk and surface calculations, and for examining the effects of differing treatments of electronic exchange and correlation.

The bulk unit cell of $AlCl_3$ is defined by 10 parameters. These consist of four lattice parameters and six fractional coordinates to define the atom positions. The lattice parameters are the a, b, and c lattice vectors of the unit cell and the angle between the b lattice vector and the ac plane. There are five fractional atom coordinates required for the chlorine ions and one parameter required for the aluminum ions.

We began our investigation by performing a full structure optimization of the bulk geometry of $AlCl_3$. Optimization was performed by energy minimization using an unconstrained Broyden−Fletcher−Goldfarb−Shanno (BFGS) algorithm as implemented in the DOMIN software.[25] The atomic positions were allowed to relax in all directions consistent with the symmetry. To optimize the bulk cell unit of $AlCl_3$ the stresses arising from changes in lattice parameters were calculated by numerical differentiation with a finite difference step of 0.002 Å. The optimization of atomic positions was performed using analytic derivatives of the energy.

TABLE 2: Optimized Bulk $AlCl_3$ Structure[a]

parameter	this study	experimental
a	6.053 Å	5.914 Å
b	10.500 Å	10.234 Å
c	6.160 Å	6.148
B	107.04°	108.25°

atom	x(fractional)	y (fractional)	z(fractional)
Al	*0.0*	0.1660 (0.1662)	*0.0*
Cl_1	0.2069(0.2147)	*0.0*	0.2220 (0.2263)
Cl_1	0.2481 (0.2482)	0.1810 (0.1787)	0.2249 (0.2248)

[a] Values shown in *italics* are constrained by summetry and were not optimized.

The results of the lattice optimization and the atom positions for the bulk $AlCl_3$ are shown in Table 2. The calculated equilibrium lattice constants for the unit cell and the nonsymmetry fixed positions of the atoms are in close agreement with those observed from experimental study.[26] The maximum deviation of any parameter is 3.6%, and the mean deviation is 1.3%.

$AlCl_3$ has a layered structure. From our knowledge of such structures it is highly likely that the (100) surface will be the natural cleavage plane and, consequently, will dominate the surface morphology of any real sample.

The (001) surface of the $AlCl_3$ was obtained by cleaving the bulk crystal to produce a two-dimensional slab of material. The boundary condition perpendicular to the slab is that the wave function should decay to zero at infinity. The optimized surface structures were obtained by energy minimization with respect to the atomic positions using analytical first derivatives and the same BFGS algorithm that was used to calculate the optimized bulk structures. The geometry of each of the structures was assumed to have converged when the residual forces along all allowed symmetry directions were below 5×10^{-4} Hartrees/Bohr.

The initial termination considered consisted of a slab terminated by a complete layer of chlorine atoms. Due to the stability of the individual layers it would seem probable that this will be the most stable surface structure available. The optimization was repeated for increasing slab thickness. The geometry and surface energy were found to have converged to better than 0.01 Å and 0.001 Hartrees for a nine layer slab, e.g., three layers of the ClAlCl repeat unit. This was then used for all subsequent calculations.

Three further surface structures of $AlCl_3$ were considered. These are obtained by successive removal of chlorines. These surfaces are terminated by a layer containing two Cl ions, one Cl ion, and an Al ion, and are denoted as 2Cl, 1Cl, and Al, respectively. The geometry of each of these slabs was also fully relaxed and their relative energies were evaluated as a function of external chlorine chemical potential.[18−20]
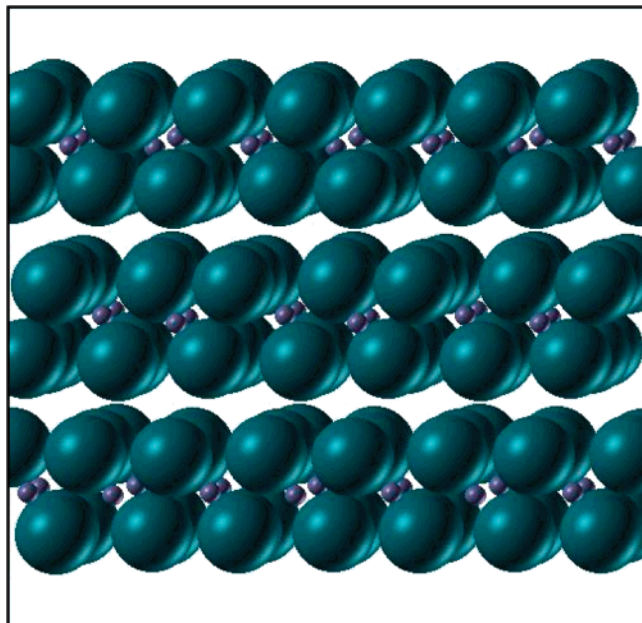
Theoretical Results

The free energies as a function of external partial pressure of chlorine are plotted in Figure 2 for each of the four terminations. It can be seen that the termination involving a complete layer of Cl ions is the most stable at all chlorine chemical potentials. The surface energy of this termination is 0.030 Jm^{-2}. This is likely to be an underestimate of the surface energy as the individual layers of $AlCl_3$ interact only via van der Waals type interactions which are underestimated by density functional calculation. This is a very low value for a surface energy and indicates that real samples will be dominated by the (001) surface.
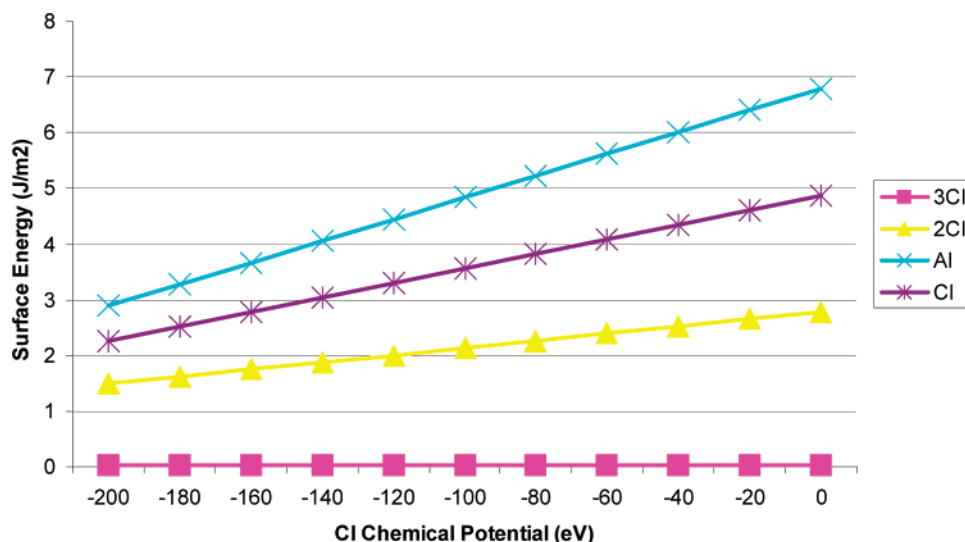
Figure 2. Dependence of surface energy from Cl chemical potential for differently terminated $AlCl_3$ surfaces (terminated by Al atoms; or by Al covered by 1, 2, or 3 chlorine atoms, respectively).
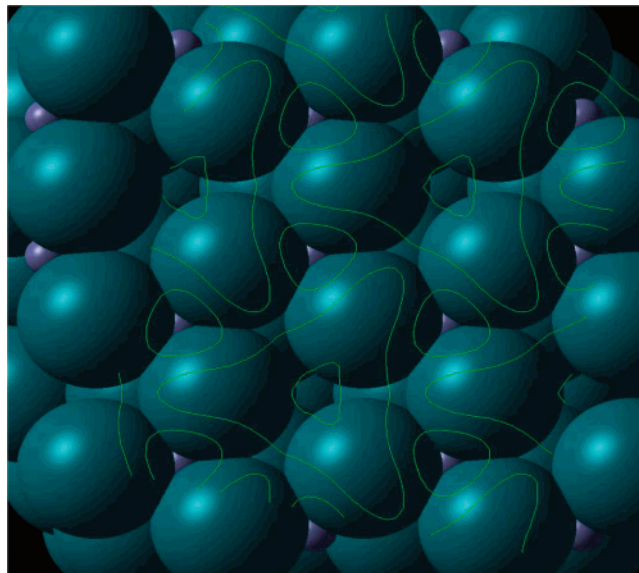

Figure 3. Optimized chlorine terminated $AlCl_3$ slab.

Figure 4. "Exemplary" Lewis acid $AlCl_3$ is not a strong Lewis acid in the solid state! Thus, it resembles α- and β-AlF_3 as proven by catalytic experiments. Responsible are halogen atoms forming the outer surface and covering the aluminum sites as shown by surface energy calculations.

The surface has undergone only a very small reconstruction from the bulk cleaved surface. The largest single atom displacement is 0.0334 Å. The optimized structure is shown in Figure 3. It can be seen that the surface layer is structurally very similar to that of the bulk.

The mulliken analysis shows that there is very little difference in the ion charges between the bulk terminated and the relaxed surfaces. The charge on the bulk Al is 11.092 compared to 11.109 on the Al ions in the surface layer. The charge on the bulk Cl ions is 17.640 and 17.628, the charge on the Cl ions in the surface layer is 17.601 and 17.603.

Within Lewis octet theory, a Lewis acid is defined as an electron pair acceptor species. A common measure of Lewis acidity is to measure the adsorption energies of electron donating species such as ammonia onto the surface of the $AlCl_3$. High absorption energies indicate strong Lewis acidity.

Lewis acids all have a vacant orbital and/or an available LUMO and all species with full or partial positive charge behave as Lewis acids. Therefore, an alternate approach that should allow the characterization of possible acid sites on the surface is to consider the electrostatic potential on a plane 1 Å above the surface. A large positive potential would indicate an electron acceptor species and, hence, Lewis acidity.

It is found that there is a relatively weak negative potential above the chlorines and weak positive potential immediately above the Al^{3+} ions, this is shown in Figure 4.

Comparison

The predictions discussed concerning the Lewis acidity of crystalline $AlCl_3$, based on our theoretical calculations, are fully confirmed by the results of the catalytic test reactions 1 and 2. The results from the catalytic reactions also support previous work on the theoretical calculations for the alpha-AlF_3 and beta-AlF_3 surfaces.[5,6]

In solid $AlCl_3$, the surface Al sites are completely covered by chlorine atoms in its energetically favored state, it behaved like α-AlF_3: it did not exhibit catalytic activity to be attributed to Lewis acidity. The slowly starting isomerization with

refluxing CCl_2FCClF_2 cannot be seen as counter-evidence; on the contrary, it was the result of a heterogeneous fluorination reaction between CCl_2FCClF_2 and $AlCl_3$ resulting in partial formation of ACF, the real catalytically active agent. The elemental analysis proved that $AlCl_3$ is partially fluorinated (18.6% F; 57.4% Cl; $AlCl_3$ requires 79.75% Cl). It is known that $AlCl_3$ is converted into ACF by CCl_3F in a highly exothermic halogen exchange reaction, whereas CCl_2FCClF_2 is much less reactive and needs extended heating.[27] Studying reaction 1 with [^{36}Cl] labeled $AlCl_3$, Winfield et al.[28] reported that adsorption of CCl_2FCClF_2 at $AlCl_3$ sites results exclusively in chlorination of the CCl_2FCClF_2, while isomerization occurs exclusively at $AlCl_2F$ sites. Hence, it is concluded that isomerization occurs only at a surface of aluminum (III) in a disordered environment, rather than at the regularly ordered crystalline $AlCl_3$ surface. Therefore, for the reaction with CCl_2FCClF_2, $AlCl_3$ can be seen as precursor rather than a catalyst. Upon contact with CCl_2FCClF_2, vapor, up to 125 °C, fluorination of $AlCl_3$ to form ACF did not occur, this is in line with the behavior of CCl_3F which reacts with $AlCl_3$ as a liquid but not as a gas,[29] consequently almost no isomerization of CCl_2FCClF_2 was detectable, even when a large excess of $AlCl_3$ was used.

Crystalline α-AlF_3, where the surface Al sites are almost totally blocked by fluorine atoms, and β-AlF_3, the Lewis surface sites of which are too weak, were also not catalytically active. In contrast, HS−AlF_3[12] and ACF[13] are highly disordered so that Al sites are accessible resulting in the predicted very high Lewis acidity[3] and, consequently, very high catalytic activity. ACF, being the more distorted material, exhibited a somewhat higher activity than did HS−AlF_3 in reaction 1 only. The high selectivity toward CCl_3CF_3, observed for reaction 1, in both cases is mainly due to the low temperature needed because of the high Lewis acidic strength of surface sites in ACF and HS−AlF_3.

The observation that reaction 2 proceeded quantitatively only under the catalytic influence of HS−AlF_3 and ACF provides evidence that Al−F and Al−F−Cl compounds can principally exhibit Lewis acidity about as high as SbF_5 in agreement with calculated strength.[3] However, solid $AlCl_3$ was similar to α-AlF_3 and β-AlF_3, it was not active in reaction 2; these solids are far from being strong Lewis acids, as long as they exist in highly crystalline phases, due to the type of surface termination by halogens.

In solvents $AlCl_3$ behaves quite differently: the aluminum is tetrahedrally coordinated forming quasi-tetrahedral complexes of the type $AlCl_3$·L or, depending on the electron donor ability of the solvent, even ionic equilibria including $AlCl_4^-$ species are formed. The degree of electron polarizability and charge transfer, respectively, can be seen by the shift of the IR absorption bands of solvent molecules adsorbed at solid $AlCl_3$. Not surprisingly, $CHCl_3$, a compound whose properties are closely related to CCl_3F, shows no solvent interactions.[30]

Although AlF_3 should be about as Lewis acidic as $AlCl_3$ (according to ab initio calculated fluoride affinity data[3]), the latter cannot be replaced by AlF_3 in nearly all reactions catalyzed by $AlCl_3$ because AlF_3 is not soluble in the reaction mixtures used. A comparison of the differences of standard enthalpies of formation for gaseous and condensed state for $AlCl_3$ (ΔH_f = 121 kJ/mol) and AlF_3 (ΔH_f = 301 kJ/mol) and the large differences in Al−X binding energies shows the reason for the AlF_3 insolubility. Only in a very highly disordered state as in ACF and in HS−AlF_3 Al sites will become accessible to potential reactants resembling somewhat the dissolved state of $AlCl_3$, so that the predicted high Lewis acidity becomes reality and the materials are highly catalytically active.

Conclusion

According to Christe et al.[3] and our own calculations[31] all aluminum halides should be strong Lewis acids. However, as long as $AlCl_3$, like AlF_3, exist in a solid crystalline state, they cannot be regarded as being Lewis acidic. The explanation for the fact that solid $AlCl_3$ and crystalline AlF_3 phases do not behave as strong Lewis acids, as expected from the earlier theoretical calculations, is that their surfaces are chlorine or fluorine terminated, respectively, giving any reactant no opportunity to coordinate Al^{3+} sites. This is in agreement with our surface energy calculations for solid $AlCl_3$. If the aluminum halide structure becomes disordered, as in HS−AlF_3 or ACF and most extremely upon dissolution of $AlCl_3$, these compounds exhibit strong Lewis acidity. However, in solution, $AlCl_3$ is no longer a solid, and hence, it is no longer a heterogeneous catalyst. Consequently, it is not a question whether the surface area of the AlX_3-phase is large, but rather if coordinatively unsaturated Al-sites are accessible for a reactant or not. Well crystallized AlF_3 and $AlCl_3$ surfaces, respectively, do not exhibit under-coordinated surface Al-sites, but HS−AlF_3 and ACF do. Hence, it is not surprising that increasing the amount of well crystallized AlX_3 (X = F, Cl), to provide the same absolute surface area, does not result in catalytic activity.

On the other hand, if suitable synthesis procedures are applied, resulting in strongly distorted solid phases, as for ACF or HS−AlF_3, strong solid Lewis acids may be obtained because of coordinatively unsaturated Al-surface sites giving access for suitable reactants.

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