First Principles Characterisation of Aluminium Trifluoride Catalysts

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Abstract.
The recently discovered high surface area AlF₃ catalyst is characterised with respect to surface composition and structure using calculations based on density functional theory. Under typical reaction conditions the surfaces are found to expose five fold coordinated Al reaction centres and to preferentially adsorb water. The acidic centres are probed using NH₃ adsorption which binds strongly indicating strong Lewis acidity. The predicted temperature probed desorption spectrum has features from competing surfaces and features due to strong intermolecular interactions, which are used to interpret the observed spectrum.

1. Introduction
Many processes of scientific and technological importance are strongly influenced by the structure and chemical reactivity of solid surfaces. The detailed characterisation of surfaces through diffraction, spectroscopy and microscopy has been dominated by studies under ultra-high vacuum conditions as this facilitates both the operation of the experimental probe and the preparation of well characterised surfaces. First principles simulation has played a significant and growing role in the characterisation of surfaces. Calculations of surface structure and formation energy for a free surface in contact with vacuum are now sufficiently reliable and efficient that they are now an essential component of most projects in surface science. In recent years both experiment and simulation have been extended to the characterisation of surfaces under reaction conditions. In this article the recent advances in the underlying theory will be reviewed and then applied to the characterisation of an important new class of nano-structured catalysts for which experimental data that illuminates the atomistic structure of the reaction centres is currently unavailable.

The catalytic fluorination of hydrocarbons is of great industrial importance. This process facilitates the large-scale production of hydrochlorofluorocarbons for a wide range of applications including aerosol propellants, refrigerants and solvents. The catalysts used are typically Lewis acids. High surface area aluminium fluoride (HS-AlF₃) has recently been produced and shown to have a Lewis acidity comparable to that of the widely used Swarts catalysts based on antimony pentafluoride [1, 2]. HS-AlF₃ may be an attractive alternative in a number of reactions including halogen exchange hydrofluorocarbon production [3, 4, 5, 6].

The surface science of fluorinated aluminas is relatively poorly developed and so little is known about the composition and structure of the surfaces exposed in HS-AlF₃. Studies that have been...
performed include solid state NMR [7, 8, 9], powder X-ray diffraction [7, 8, 10, 11, 12, 13, 10], infrared spectroscopy [11, 12, 14], X-ray photoelectron spectroscopy [7, 14, 15] and temperature programmed desorption [16]. In the absence of detailed characterisation, models of the reactive surfaces have been developed from observations of chemical activity [17] and are based on the (100) plane of $\beta$-AlF$_3$.

In the current paper we review our first principles calculations of the thermodynamic stability of AlF$_3$ surfaces as a function of F$_2$ chemical potential [18, 19]. The structure and composition of the surfaces and the morphology of crystallites are reviewed. The acidic sites presented by these surfaces are characterised by simulating the adsorption (and desorption) of NH$_3$ [20], chosen to probe the acidity of the surfaces sites. Hydroxylation and molecular adsorption of HF and H$_2$O on the $\alpha$-AlF$_3$ (01T2) is considered and the structure and energetics of this surface as a function of HF and H$_2$O chemical potentials is presented for the first time.

2. Methodology

Calculations were performed using the CRYSTAL code [21]. Electronic exchange and correlation were treated using the hybrid-exchange (B3LYP) approximation to density functional theory. This functional has been shown to provide reliable geometric and electronic structures and energetics in a wide range of materials [22]. Triple valence local Gaussian basis sets for Al and F, developed in previous studies, have been used throughout [19]. A 6-31G* basis set was used for oxygen [23] and a 8-21G* basis set was used for hydrogen [23] to describe H$_2$O molecules and OH$^-$ groups. A 7-311G basis set [23] with an additional polarisation function of $d$ symmetry, with an exponent of 0.8 was used for N and a 5-11G* basis set [23] was used for H to describe the NH$_3$ molecule.

Structures were fully optimised, within symmetry constraints, using a combination of damped molecular dynamics and Broyden-Fletcher-Goldfarb-Shanno (BFGS) [24] algorithms. Optimisation was considered to be complete when the residual forces were below $1.0 \times 10^{-4}$ Hartrees Bohr$^{-1}$. The binding energies of molecules were corrected, where possible, for basis set superposition error (BSSE) using the counterpoise scheme [25].

2.1. The Free Energy of Surface Formulation

The relative stability of surfaces of different composition in contact with reactive gases is determined by the free energy of surface formation which can be calculated from first principles. The formalism in the context of metal oxides is now well established [26, 27, 28, 29] and is applied here to the specific reaction conditions of AlF$_3$ [30]. As an example we consider an AlF$_3$ surface with adsorbed hydroxyl groups, H$_2$O and HF exposed to an atmosphere containing gaseous H$_2$O, H$_2$ and HF. The methodology is trivially extended to other systems. Modelling the AlF$_3$ surface as a periodic slab of material, the surface free energy is given by [31]

$$
\gamma(T, P_{F_2}, P_{O_2}, P_{H_2}, P_{tot}) = \frac{1}{2A} \left[ G_{slab}(T, P_{tot}) - N_{Al}\mu_{Al}(T, P_{tot}) \right. \\
\left. -N_{F} \frac{1}{2} \mu_{F_2}(T, P_{F_2}) - N_{O} \frac{1}{2} \mu_{O_2}(T, P_{O_2}) - N_{H} \frac{1}{2} \mu_{H_2}(T, P_{H_2}) \right] 
$$

(1)

where $A$ is the area of the unit cell. $G_{slab}$ is the Gibbs free energy per unit cell of the slab and $N_{Al}$, $N_{F}$, $N_{O}$ and $N_{H}$ are respectively the total number of Al, F, O and H ions within the system. $P_{F_2}$, $P_{O_2}$ and $P_{H_2}$ are the partial pressures of the F$_2$, O$_2$ and H$_2$ gaseous species and $P_{tot}$ is the total pressure. $\mu_{Al}$, $\mu_{F_2}$, $\mu_{O_2}$ and $\mu_{H_2}$ are the chemical potentials of Al, F$_2$, O$_2$ and H$_2$ respectively. The condition that the bulk aluminium fluoride is in equilibrium is;

$$
G_{bulk}(T, P_{tot}) = m\mu_{Al}(T, P_{tot}) + n \frac{1}{2} \mu_{F_2}(T, P_{F_2}) 
$$

(2)
where $G_{\text{bulk}}$ is the Gibbs free energy per formula unit of the bulk crystal $\text{Al}_m\text{F}_n$. Similarly, $\text{HF}$ and $\text{H}_2\text{O}$ are in equilibrium with their constituent atoms, hence

$$\frac{1}{2}\mu_2(T,P_{H_2}) + \frac{1}{2}\mu_2(T,P_{F_2}) = \mu_{HF}(T,P_{HF}) \quad (3)$$

$$\mu_{H_2}(T,P_{H_2}) + \frac{1}{2}\mu_{O_2}(T,P_{O_2}) = \mu_{H_2O}(T,P_{H_2O}) \quad (4)$$

Equations 2, 3 and 4 can now be used to eliminate $\mu_{Al}$, $\mu_{F_2}$ and $\mu_{O_2}$ from equation 1 to obtain

$$\gamma(T,P_{HF},P_{H_2O},P_{H_2}) = \frac{1}{2A} \left\{ G_{\text{slab}}(T,P_{tot}) - \frac{N_{Al}}{m} G_{\text{bulk}}(T,P_{tot}) \right. - \left( N_{F} - \frac{n}{m} N_{Al} \right) \mu_{HF}(T,P_{HF}) - N_{O} \mu_{H_2O}(T,P_{H_2O})$$

$$- \frac{1}{2} \left( \frac{n}{m} N_{Al} - N_{F} - 2N_{O} + N_{H} \right) \mu_{H_2}(T,P_{H_2}) \right\} \quad (5)$$

Treating the gaseous species as ideal gases, their chemical potentials dependence on P and T is:

$$\mu_X(T,P_X) = \mu_X(T,P_X^0) + kT \ln \left( \frac{P_X}{P_X^0} \right) \quad (6)$$

This chemical potential can be referred to the athermal limit and the DFT calculations by rewriting equation 6 as,

$$\mu'_X(T,P_X) = [\mu_X(T,P_X) - \mu_X(0,P_X^0)] + E_{\text{DFT}}(T=0) \quad (7)$$

The term in square brackets in equation 7 can be obtained from thermodynamical reference tables [32], as described previously [30]. In the current study the Gibbs free energies of the slab and bulk crystal are computed at the athermal limit and their temperature dependence is ignored as it is negligible compared to that of the gaseous species. The small PV term due to the change in volume of the bulk phases is also neglected.

2.2. Simulating Temperature Programmed Desorption

Temperature programmed desorption (TPD) is simulated using a lattice Monte Carlo model. The rate of desorption, $r_{\text{des}}$, calculated using the Redhead equation [33]. Determination of an accurate rate of desorption is dominated by the accuracy of the calculation of the binding energy. The attempt frequency is estimated from a calculation of the vibrational frequency of the bond between the surface and adsorbed molecule.

3. Results

3.1. Bulk Phases

The various crystalline forms of AlF$_3$ consist of arrangements of corner sharing AlF$_6$ octahedra. The most stable phase is $\alpha$-AlF$_3$, which has a close packed corundum-like structure, as shown in figure 1a. The metastable $\beta$-phase has a more open structure of the hexagonal tungsten bronze (HTB) type and is shown in figure 1b. The equilibrium lattice constants for the $\alpha$ and $\beta$ unit cells and the non-symmetry fixed positions of the atoms were computed and are within 2% of those observed.
3.2. Clean (ex situ) Surfaces

3.2.1. α-AlF₃
In the absence of detailed characterisation it is natural to assume that the α-AlF₃ basal plane (0001) will be the stable surface, in a (1x2) reconstruction which preserves the stoichiometry. Analysis of the bonding also suggests that the (1x1) (01T2) surface will be stable. The computed formation energies for various terminations of the two surfaces as a function of fluorine chemical potential are presented in figure 2. Stoichiometric terminations are predicted to be the most stable at all realistic fluorine chemical potentials. At very high fluorine chemical potential, molecular adsorption of F₂ on the stoichiometric (01T2) surface is predicted. The preference for stoichiometric terminations and non-dissociative adsorption of F₂ is consistent with the highly ionic nature of AlF₃.

The computed energy of the stoichiometric (01T2) surface is 0.94 Jm⁻², somewhat lower than that of the (0001) surface, which is 1.18 Jm⁻². The crystal morphology is therefore predicted to be dominated by the (01T2) surface, as observed [34]. The predicted structure of the (1x1) (01T2) surface is shown in figure 3a. This surface exposes a network of alternating 6-fold coordinated Al ions (Al(6)) and 5-fold coordinated Al ions (Al(5)). The Al(5) ions being likely Lewis acid centres. The metastable (1x2) (0001) surface is shown in figure 3b, this surface exposes Al(5) and Al(4) ions. In principle one might expect the Al(4) ions to be more reactive than the Al(5) ions. There is, however, an important difference in the coordination geometry of these sites. The Al(4) is almost perfectly tetrahedrally coordinated whereas the Al(5) ion is in an highly distorted and truncated octahedral geometry. Given the stability of tetrahedrally coordinated ions in metal oxide systems, the tetrahedral Al ions are expected to be less reactive than Al(5) ions. This observation is contrary to previous suggestions that the very strong Lewis acid sites on AlF₃ materials may be due to Al(4) ions [35].

3.2.2. β-AlF₃
The open β structure is capable of supporting a variety of low index surfaces with multiple possible stoichiometric terminations. Formation energies were computed for fully relaxed geometries of the stoichiometric (100), (010) and (001) surfaces. Typical low energy surface structures are shown in figure 4. The energies of the most stable (100), (010) and (001) surfaces are 0.85, 0.74 and 0.79 Jm⁻² respectively and are consistent with a simple model of surface stability based on Al and F coordination numbers [19].

There are a number of characteristic local geometries which occur on these surfaces and on those of the α-phase. For example the β(100) and α(01T2) surfaces both have surface layers containing Al(5) and Al(6) ions in which the Al(5) ions are bound to five bidentate (“bridging”)
Figure 2. Surface energies of various terminations of the (a) (01\text{\text{-\text{T2}}}) and (b) (0001) surfaces as a function of the fluorine chemical potential ($\mu'_F$) and the fluorine partial pressure at 300K.

Figure 3. The structure of the $\alpha$-AlF$_3$ (a) (01-12) and (b) (0001) stoichiometric surfaces.

Figure 4. The lowest energy $\beta$-AlF$_3$ (100), (010) and (001) surfaces.

ions and the Al$_{(6)}$ have an additional monodentate ("dangling") F ion. A Wulff plot [36] of the equilibrium crystallite morphology of the $\beta$ phase is displayed in figure 5. The surface area of the resultant crystallite is composed of: 3% {001}, 59% {010} and 38% of the {001} surface [19].
3.3. The Effect of Reactive Gases: (in situ) Surfaces

As the surface sites of α-AlF₃ (0112) have been found to be representative of the surfaces of the α and β phases their stability in the presence of H₂O and HF is used here as a model for all AlF₃ surfaces. In principle, a reliable prediction of the surface structure and geometry under reaction conditions (i.e. the surface phase diagram) requires an exploration of all possible surface compositions and geometries. Initial structures and surface compositions were guided by the need to maintain charge neutrality. The surface formation energy for structures in which 1, 2 or 3 surface F ions are replaced by OH ions was computed. Molecular adsorption of H₂O and HF was also considered for all surfaces. The resultant surface phase diagram is represented as a function of the HF and H₂O chemical potentials (converted also to partial pressures and temperatures) in figure 6. Under typical reaction conditions (i.e at temperatures around 600K), the clean surface with water adsorbed (3F + H₂O) above the Al(5) ions is predicted to be the thermodynamically stable phase. If the partial pressure of HF is very low then the surface is also likely to be partially hydroxylated via OH replacement of surface F ions (e.g. 1F2OH + H₂O). At high HF and low H₂O partial pressures HF adsorbs on the clean surface. HF can also adsorb on hydroxylated surfaces but then transfers a proton to a surface OH group forming an H₂O and a surface F ion. This is the observed refluorination process of the hydroxylated surface by HF.

3.4. Characterising the Acidic Sites

The theoretical definition of Lewis acidity is fraught with difficulties. The general definition of an electron pair acceptor gives rise to a number of possible quantifications of acidity, none of which is entirely satisfactory. Here the acidic sites are characterised by computing the binding energy of the Lewis base NH₃. This well defined process is commonly used both experimentally
The TPD curves obtained from: (a) Lattice Monte Carlo simulations parameterised from the NH$_3$ DFT binding energies from two low energy $\beta$-AlF$_3$ (100) (labelled T1 and T6). (b) Kemnitz et al [41] and the results obtained from our lattice Monte Carlo simulations, shifted by 70°C to higher temperatures.

Figure 7. The TPD curves obtained from: (a) Lattice Monte Carlo simulations parameterised from the NH$_3$ DFT binding energies from two low energy $\beta$-AlF$_3$ (100) (labelled T1 and T6). (b) Kemnitz et al [41] and the results obtained from our lattice Monte Carlo simulations, shifted by 70°C to higher temperatures.

and theoretically for this purpose [37, 38, 39].

The binding energies of NH$_3$ to the Al$_{(5)}$ centres on two low energy $\beta$-AlF$_3$ (100) terminations have been calculated as a function of NH$_3$ coverage [20]. The terminations, labelled for historical reasons [40] as T1 and T6, represent Al$_{(5)}$ ions bound to 5 bidentate ions (T1), and Al$_{(5)}$ ions bound to 4 bidentate and a monodentate F ion (T6). This data is used to build a model of the surface adsorption energy that can be used in lattice Monte Carlo simulations to predict TPD spectra, shown in figure 7a. The predicted spectra contains three peaks, which can be assigned to the superposition of two spectra from each termination, each of which contains two peaks. The peak that occurs at the lower temperature from each termination is due to desorption from regions of high local coverage in which NH$_3$ is destabilised by, direct and surface mediated, inter-molecular repulsions. The peak that occurs at the higher temperature is due to low coverage desorption in which most or all neighbouring sites are unoccupied.

The predicted spectrum is compared to that measured on several polycrystalline $\beta$-AlF$_3$ samples [41] in figure 7b. The experimental spectra are all generally consistent with the predicted spectrum. Each consists of three distinct peaks/shoulders, at around 200°C, 300°C and 420°C. The spacing of the peaks is in excellent agreement with the prediction while the absolute temperature is slightly higher (70°C) than that predicted. This strongly indicates that the sites on the model surface are representative of the local geometries that occur on $\beta$-AlF$_3$ samples under reaction conditions. It is notable that this data also assigns the number and the position of the peaks in the TPD spectrum to a combination of surface site and inter-molecular interactions and mitigates strongly against the simplistic interpretation of peaks in TPD spectra as indicative of particular surface sites or species.

4. Conclusions
The composition and structure $\alpha$- and $\beta$-AlF$_3$ low index surfaces have been established using hybrid exchange density functional theory. Under typical reaction conditions the surfaces are found to expose five fold coordinated Al reaction centres and to preferentially adsorb water. NH$_3$ adsorbs strongly to the reaction centres as expected for a strong Lewis acid. The predicted TPD spectrum has features from competing surfaces and features due to strong inter-molecular interactions and is in good agreement with the observed spectrum.
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