Investigating the Lewis acidity of aluminium fluoride surfaces

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Abstract. The current study employs state of the art hybrid-exchange density functional theory (DFT) to investigate the Lewis acidic sites on the β-AlF₃ (100) surface. It is shown that the strong Lewis base, NH₃, binds to the surface with a binding energy of up to 1.9 eV. This demonstrates that the material is strongly Lewis acidic. We also consider the binding of the weak Lewis base CO to the surface. We calculate the shift in its stretch frequency compared to the gas phase molecule. Shifts are compared to experimental data and are shown to be typical of strong Lewis acidity.

1. Introduction

Recently there has been much interest in the use of aluminium fluorides (AlF₃’s) as strong Lewis acid catalysts. High surface area AlF₃ can now be prepared that has a Lewis acidity comparable to that of the widely used Swarts catalysts based on antimony pentafluoride [1]. This material is of interest as strong Lewis acid catalysts are used in the large-scale production of chlorofluorocarbons and hydrofluorocarbons [2, 3] which are used in a wide range of applications including aerosol propellants, refrigerants and solvents.

Many experimental studies have been performed to investigate the structure and chemical properties of AlF₃’s, including solid state NMR, powder x-ray diffraction, infrared spectroscopy, x-ray photoelectron spectroscopy and temperature programmed desorption [4, 5]. However, the majority of the traditional surface science techniques used to determine surface structure require large, pure, crystalline samples. Unfortunately, producing suitable AlF₃ crystals is very difficult. Consequently, very little is known about the detailed atomic-scale surface structure of these fluorides.

AlF₃ exists in several different crystalline forms. It is thought that the chemically active surfaces of the high surface area AlF₃ are related to that of the hexagonal tungsten bronze β-phase. To enable a better understanding of the catalytic properties of the high surface area material we have studied the atomic scale structure and properties of the β-AlF₃ (100) surface. We previously identified two different low energy terminations that we predict to exist (or co-exist) on surfaces of β-AlF₃ [6]. These terminations expose under coordinated Al ions that we predict to be Lewis acidic. Similar sites are likely to occur on the high surface area material.

In this study we quantify the Lewis acidic nature of these sites by calculating the binding energy of the strong Lewis base NH₃ to the Lewis acid sites. We also calculate the adsorption...
of the weak Lewis base CO to these surfaces and calculate the stretch frequency of the adsorbed molecule and compare this to experimental data.

2. Methodology
Calculations were performed using the CRYSタル code[7]. The B3LYP hybrid exchange functional, which has been shown to provide reliable structures and energetics in a wide range of material [8], was employed throughout. Local Gaussian basis sets were obtained from standard sources, as specified elsewhere [9, 10].

Structures for the clean β-AlF3 were taken from our previous study [6]. The probe molecules (NH3 and CO) were adsorbed above under coordinated Al sites. Structures were fully optimised using a combination of damped molecular dynamics and BFGS optimisers. The atomic positions were allowed to relax in all directions consistent with the symmetry of the system. The structure was considered to be converged when the residual forces along all allowed symmetry directions were below 2.5x10^{-4} Hartrees per Bohr and atomic displacements were less than 10^{-3} Bohr between optimisation steps.

The binding energies for the probe molecules (NH3 and CO) were calculated as the energy of the clean surface and the energy of the molecule in a vacuum subtracted from the energy of the system comprising of the AlF3 surface with the given molecule adsorbed on it. A negative binding energy, therefore, denotes the formation of a bond between the surface and the molecule. Binding energies were corrected for basis set superposition error using the counterpoise scheme [11].

The vibrational frequencies of the CO molecules were computed by construction of the force constant matrix via finite differencing of the analytic gradients followed by diagonalisation [12].

3. Results and Discussion
The two low energy β-AlF3 (100) terminations are referred to as the T1 and T6 surfaces [6]. These surfaces are shown in figure 1 with NH3 and CO molecules adsorbed above their under coordinated Al ions. The T1 surface contains two rows that contain under coordinated Al ions. The sites above these Al ions on the upper most row are labelled A sites, and those on the lower row, B sites. On the T6 surface all the under coordinated Al ions are identical, however molecules can either adsorb from above (A type binding) or from below (B type binding). The concentration of under coordinated Al sites on the T6 surface is twice that of the T1 surface.
Table 1. Binding energies (BE) of NH$_3$ on the T1 and T6 surfaces.

| Coverage (Monolayers) | Type of Site | T1 BE (eV) | T6 BE (eV) |
|-------------------|-------------|-----------|-----------|
| 0.5               | A           | -1.91     | -1.38     |
| 0.5               | B           | -1.81     | -1.40     |
| 1                 | A           | -1.61     | -1.40     |
| 1                 | B           | -1.53     | -1.41     |

3.1. NH$_3$ Adsorption

We considered coverage levels from one quarter monolayer to a full monolayer of NH$_3$ on the β-AlF$_3$ surfaces within a (1x2) unit cell. Figures 1a and 1b show the geometries of full monolayer adsorption on these two surfaces. The binding energies of NH$_3$ at two possible half monolayer coverages and at a full monolayer coverage on the T1 and T6 surfaces are displayed in table 1. It can be seen that the binding energies are significantly greater on the T1 surface compared to the T6 surface. The binding energies decrease with increasing levels of NH$_3$ coverage on the T1 surface. The data shown in table 1 is taken from a sample of the possible adsorption geometries. Depending on the level of coverage the binding energy was found to vary between 1.50 eV and 1.96 eV on the T1 surface. Although, from the data shown in table 1, it appears that the binding energies on the T6 surface are not strongly dependant of the level of coverage, this is not true. The binding energy is strongly dependant on the availability of next nearest neighbours on this surface. Binding energies were found to vary between 1.15 eV and 1.80 eV depending on the coverage of neighbouring sites. The detailed results of these calculations will be published elsewhere. In comparison, the binding energy of NH$_3$ to strong Lewis acid sites on the zeolite Mordenite is 1.68 eV [13]. It can be concluded from these results that the surfaces are strongly Lewis acidic and that the sites on the T1 surface are in general stronger than those on the T6 surface.

3.2. CO Adsorption

We considered full monolayer and half monolayer adsorption of CO to the β-AlF$_3$ surfaces within a (1x1) unit cell. Figures 1c and 1d show the geometries of the full monolayer adsorption to the two surfaces. The binding energies and the shifts in the CO stretch frequencies (compared to a CO molecule in vacuum) are displayed in table 2. It can be seen from table 2 that there is poor correlation between binding energy strength and CO stretch frequency. CO is a weak Lewis base, hence the strength of its binding energy is not a reliable method of quantifying Lewis acidity [14].

The numbers given in brackets in table 2 refer to the absolute values obtained from our quasi harmonic B3LYP calculations. However it is widely known that such calculations over-estimate vibrational frequencies (largely due to the neglect of anharmonicity). For example, we calculated the gas phase CO frequency to be 2199 cm$^{-1}$ compared to the experimentally value of 2143 cm$^{-1}$. A study involving 125 different molecules [15] proposes that a scaling factor of 0.9679 should be used to allow comparison between quasi harmonic B3LYP values and experimental values for gas phase molecules. A similar study for molecules adsorbed on organometallic surfaces proposes a scaling factor of 0.9550 [16]. We have applied these two scaling factors to our data in table 2. For comparison, computational studies (using the GGA functional and no scaling factors) have shown CO shifts of around 100 cm$^{-1}$ for strong Lewis acid centres on the zeolite Mordenite [14].
Table 2. Binding energies and stretch frequencies for CO adsorbed to the T1 and T6 surfaces.

| Coverage (Monolayers) | Type of Site | Binding energies (eV) T1 | Binding energies (eV) T6 | CO stretch shift (cm⁻¹) T1 | CO stretch shift (cm⁻¹) T6 |
|-----------------------|--------------|-------------------------|-------------------------|---------------------------|---------------------------|
| 0.5                   | A            | -0.39                   | -0.34                   | 75 (109)                  | 53 (85)                   |
| 0.5                   | B            | -0.55                   | -0.14                   | 69 (102)                  | 59 (92)                   |
| 1                     | A            | -0.51                   | -0.36                   | 72 (105)                  | 51 (83)                   |
| 1                     | B            | -0.67                   | -0.15                   | 65 (98)                   | 53 (85)                   |

The IR spectra of \(\beta\)-AlF\(_2\)(OH)\(_0\)\(_.4\) has recently been measured by our collaborators, led by Marco Daturi, at the university of Caen [17]. This study showed four distinct CO shifts; one low intensity shift at 92 cm\(^{-1}\) (thought to be due to defect sites) and three others at 72 cm\(^{-1}\), 56 cm\(^{-1}\) and 40 cm\(^{-1}\). It is tempting to assign the shifts of 72 cm\(^{-1}\) and 56 cm\(^{-1}\) to under coordinated Al ions in environments seen on our T1 and T6 surfaces respectively. We are currently investigating the effect of OH groups on the CO stretch frequencies to allow an improved interpretation of this data.

4. Conclusions
We have shown that under coordinated Al sites on the \(\beta\)-AlF\(_3\) (001) surface display high Lewis acidity. The strength of the Lewis acidic sites have been quantified using two different methods. The binding energies of NH\(_3\) adsorption and the shifts in the CO stretch frequency of adsorbed molecules show that these sites are strong Lewis acids.

We have compared our results to experimental data and it appears that our model of Lewis acid sites occur on real samples. It is likely that such sites will also exist on the highly catalytic high surface area AlF\(_3\) material.

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