Structure-Property Relationships in Solid AlF₃ Lewis Acids

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Abstract. Understanding the structural cause of the high Lewis acidity in the novel solid Lewis acid AlF₃ is of crucial importance to tailor this important material property to the specific needs of potential applications. Based on Al and F K-edge XAS studies, we are able to correlate high Lewis acidity with geometric distortions of the [AlF₆] building blocks of AlF₃. These distortions are induced by the presence of i-OPr ligands in the AlF₃-(i-OPr)ₓ precursor material and can only be preserved by the application of a mild fluorinating agent like CCl₂F₂. High Lewis acidity is not caused by electronic modification of the aluminium atom, but by the better exposure of reactants to the acid site in the high surface area materials.

Keywords: Aluminium Fluoride; X-ray absorption spectroscopy; Al K-edge; F K-edge

PACS: 61.10.Ht X-ray absorption spectroscopy: EXAFS, NEXAFS, XANES, etc.; 61.43.-j Disordered solids; 78.30.Hv Other nonmetallic inorganics

INTRODUCTION

High surface areas are desirable for inorganic materials, as their reactivity usually depends on the amount of exposed surface. Oxides with high surface areas can be prepared by sol-gel methods, freeze-drying or using supercritical conditions as xero- or aerogels [1].

Another important factor influencing reactivity is the Lewis acidity. High Lewis acidic materials are needed e.g., for carbon-halide bond cleavages [2]. Although metal oxides like Al₂O₃ do exhibit a moderate acidity, they never reach the strength of solid superacids like SbF₅ [3] or aluminium chloro fluoride (ACF) [4,5].

The acidity of AlF₃ in the gas phase is remarkably high [3], but common preparation methods usually produce a highly crystalline material which exhibits no or only little acidity. This is due to the high lattice energy which leads to the formation of a highly ordered polycrystalline solid.

A recently discovered synthesis route produces AlF₃ with extremely high surface area [6,7]. The synthesis proceeds via a precursor containing fluoride and isopropoxide ligands. Mild fluorination of this compound leads to the desired highly amorphous product which can reach the Lewis acidity of gas phase AlF₃. In contrast to the well-known Lewis acid ACF (aluminium chloro fluoride), it is insensitive to moisture and can be stored in air without loss of acidity. Their ease of use makes these materials potential candidates for industrial applications where high Lewis acidity is a desired characteristic.

The origin of the high Lewis acidity of this material is not understood on a molecular basis. Such knowledge is necessary to be able to tweak the synthesis procedures in order to fine-tune the acidity. High Lewis acidity can be a consequence of electronic or geometric properties. It can be altered by changing the electrophilicity of the acid site or by creating open structures easily accessible for reactants.

In this study, we elucidate the origin of the Lewis acidity of high surface AlF₃ materials by systematically investigating the electronic and geometric structure of selected samples. A combined approach of Al K- and F K-edge X-ray absorption spectroscopy (XAS) gives an extensive insight in the molecular origin of Lewis acidity in high surface AlF₃ materials.
EXPERIMENTAL

The synthesis route leading to high surface AlF$_3$ is described in [6,7]. In short, aluminium isopropoxide (Al(i-OPr)$_3$) is treated with anhydrous HF to form a precursor with the formula AlF$_{3-x}$(OiPr)$_x$. Treating this precursor with mild fluorination agents like CCl$_2$F$_2$ leads to the desired high surface area AlF$_3$.

Al K-edge XAS data were recorded at station 3.4 of the SRS Daresbury Laboratory. A double-crystal YB66 monochromator was used with the second crystal being detuned to 80% of the maximum of the Bragg peak. Higher harmonics were rejected using a C/Si bilayer mirror, the beam was focused using a Cr coated toroidal mirror. Samples were mounted on a multi-sample stage using carbon sticky tape, introduced in the HV chamber and measured at 298 K at a pressure of 10$^{-6}$ mbar. Spectra were acquired using the total electron-yield (TEY) and fluorescence-yield (FY) detection modes. A 13-element solid state detector was used for measuring the fluorescent photons, the TEY signal was recorded as the drain current from the sample holder. Spectra were recorded between 1500 and 1850 eV, corresponding to a maximum k-value of 9. Typical data acquisition times were one hour per spectrum. F K-edge XAS data were recorded at station 5U.1 of the SRS Daresbury Laboratory. Undulator radiation was monochromatized using an SX700 type monochromator with a plane grating of 1200 lines/mm. The incident beam current was measured using a gold grid; the XAS signal was recorded in TEY mode by measuring the collector and drain currents. Samples were mounted using carbon sticky tape. All measurements were performed at 298 K after evacuating the chamber to <10$^{-5}$ mbar. Data reduction and analysis was performed using the IFEFFIT library [8] and its front ends ATHENA and ARTEMIS [9]. Theoretical backscattering paths were calculated using FEFF6 [10].

RESULTS AND DISCUSSION

All investigated materials show the same energy position of the Al K-edge (1570 eV; Figure 1) suggesting that the aluminium atom is present in the formal oxidation state 3+. At higher energies (1580-1620 eV) only α-, β-AlF$_3$ and the heat-treated precursor show intense features, all other materials are characterized by weak, low-frequency EXAFS oscillations. The XANES signatures allow for the distinction between two groups of materials: (i) precursor and high surface AlF$_3$ and (ii) heat-treated precursor and reference materials.

This is supported by the modeling of the Al K-edge EXAFS region (Figure 2, Table 1). Data of precursor, heat-treated precursor and AlF$_3$ (309 m$^2$/g) were fitted simultaneously in k-weightings of 1, 2 and 3 using an Al-F backscattering contribution. While E$_{0,F}$, R$_F$ and $\sigma^2$ are almost identical for all samples, the Al-F coordination number parallels intensity variations of the Al K-edge white line (Table 1). Notably the heat-treated precursor exhibits the highest value (6.0) followed by precursor (5.8) and high surface AlF$_3$ (5.3).

Elemental analysis shows that the precursor contains significant amounts of isopropoxide ligands. The coordination number of 5.8 therefore represents a distorted octahedral environment of F and isopropoxide ligands alike. Modeling the presence of isopropoxide in the precursor by including an Al-O shell failed due to the close proximity of F and O in the periodic table. Such a fit would also violate Nyquists’ theorem and has been discarded.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Precursor</th>
<th>Precursor</th>
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<tr>
<td></td>
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FIGURE 1. Al K-edge XANES data of high surface AlF$_3$, precursor and precursor after heat treatment in N$_2$.
The identical energy positions of the Al K-absorption edge suggest that the oxidation state and electronic structure of aluminium in the various samples remains unchanged. In the case of precursor and high surface AlF3 the absence of any multiple scattering contributions suggests a structure of strongly disordered [AlF6] building blocks which is further supported by the low Al-F coordination number found for the active high surface AlF3 material. Heat-treatment of the precursor forms a non-acidic material that exhibits a similar XANES pattern than that of β-AlF3. F K-edge XANES data and XRD patterns (not shown) confirm the above-mentioned distinction between disordered and ordered materials. Recent ab initio studies [11-13] predict under-coordinated Al atoms (e.g. [AlF5] units) at the surface of active AlF3 modifications. Evidence exists that these low-coordinated sites do interact with Lewis bases [14]. Together with our XAS results this suggests that the high Lewis acidity of these novel AlF3 modifications are caused by disorder of the local [AlF6] building blocks.

CONCLUSION

The origin of high Lewis acidity in novel high surface AlF3 modifications has been investigated using a combined Al K- and F K-edge XAS study. In line with ab initio predictions our results suggest that the preservation of local disorder throughout the synthesis is crucial to obtain a high acidity as under-coordinated Al atoms are the active sites in these materials. By controlling the amount and structure of the under-coordinated sites the genesis of tailored materials with specific acidities will be feasible making high surface AlF3 a potential target for industrial applications.

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REFERENCES