Structure-Property Relationships in Solid AlF$_3$ Lewis Acids

N. Weiher, A. Makarowicz, A. M. Beesley, E. Kemnitz, S. L. M. Schroeder

$^1$ Molecular Materials Centre, School of Chemical Engineering and Analytical Science & School of Chemistry, The University of Manchester, Manchester, UK; $^2$ Institut für Chemie, Humboldt-Universität zu Berlin, Germany

Introduction

Recently discovered [1,2] high-surface area (HS) aluminium fluoride materials exhibit a Lewis acidity comparable to that of SbF$_5$, making them potential candidates for heterogeneous synthesis reactions or catalyst supports. The molecular structure underpinning their high Lewis acidity is currently not completely understood. Studies of their structure are also required because there is uncertainty about how the reaction conditions during the preparation — namely the fluorinating agent and temperature — influence the strength and stability of Lewis acidity in the final material. Elucidating the underlying structure-property relationships is of vital importance in order to tailor these promising new materials to the specific needs of applications. We have now carried out X-ray absorption near-edge structure (XANES) measurements at the Al K- and the F K-edges to analyse the local electronic structure by comparison with spectroscopic signatures from structural motifs in a number of reference compounds, particularly α-AlF$_3$ and β-AlF$_3$. The results are supported by an extended X-ray absorption fine-structure (EXAFS) analysis of the Al K-edge.

Methods and Materials

The synthesis of the materials proceeds via a sol-gel route [1,2] based on aluminium alkohalates, Al(OR)$_3$. Treatment with HF leads to a a partially fluorinated precursor material [3], in which the presence of residual OR ligands leads to a distorted network of corner-sharing [AlF$_6$(OR)$_3$] units. Careful fluorination of this precursor by a mild fluorination agent (e.g. CHF$_2$Cl) leads to the highly Lewis acidic materials. Using stronger fluorinating agents (e.g. F$_2$) or higher temperatures leads to the formation of more crystalline materials with lower acidity. The reference compounds α-AlF$_3$ and β-AlF$_3$ were obtained by standard synthesis procedures reported in the literature. Their phase purity was confirmed by powder X-ray diffraction (XRD).

Results & Discussion

Al K-edge (Fig. 1) and F K-edge (Fig. 2) XANES measurements reveal that the local coordination around the Lewis acidic Al$^{3+}$ species as well as around the fluoride atoms changes significantly when the synthesis conditions are varied. The Al K-edge spectra allow for a distinction of two categories of materials: (i) samples with long-range order (α-AlF$_3$, β-AlF$_3$ and the heat-treated precursor material) and (ii) samples with no long-range order (precursor, HS AlF$_3$). These categories correlate closely with the Lewis acidity of the materials. Mild fluorination of the precursor material leads to HS AlF$_3$ with high Lewis acidity and surface areas around 309 m$^2$/g. Heat-treatment leads to a more crystalline sample with no Lewis acidity. The XANES signature of the heat-treated precursor is similar to that of β-AlF$_3$. The EXAFS analysis shows that the precursor as well as the highly Lewis acidic HS AlF$_3$ materials have a significantly lower Al-F coordination than the heat-treated precursor and the crystalline reference compounds. These results suggest that the presence of distorted [AlF$_6$] units and/or undercoordination of the Al$^{3+}$ by F is required to obtain high Lewis acidity. Currently, additional ab initio analyses of the XANES patterns are performed. We have already derived a molecular orbital model for the analysis of F K-edge data (not shown here) for the local electronic structure around the fluorides [(4), which also rationalises the similarity between the heat-treated precursor and β-AlF$_3$ as well as that between precursor and HS AlF$_3$.

References