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# A simple aqueous phase synthesis of high surface area aluminum fluoride and its bulk and surface structure

Wolfgang Kleist, Carmen Haeßner, Oksana Storcheva, Klaus Köhler \*

Technische Universität München, Department of Chemistry, Lichtenbergstr. 4, D-85747 Garching, Germany

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Dedicated to Professor Dr. Dr. h.c. mult. Wolfgang A. Herrmann.

#### Abstract

A simple novel synthesis route to aluminum fluoride, AlF<sub>3</sub>, from aqueous phase is reported. Al<sub>2</sub>O<sub>3</sub> is dissolved in aqueous hydrofluoric acid, HF, and re-precipitated as AlF<sub>3</sub> · 3H<sub>2</sub>O. Thermal decomposition results in thermally stable AlF<sub>3</sub> with high specific surface areas between 120 and 60 m<sup>2</sup>/g depending on treatment temperatures (up to 450 °C). Bulk and surface structures of the resulting amorphous and crystalline materials were characterized by X-ray powder diffraction, infrared and solid state NMR spectroscopy (<sup>27</sup>Al, MAS), nitrogen physisorption and adsorption of paramagnetic probe molecules (vanadium complexes). © 2006 Elsevier B.V. All rights reserved.

Keywords: Aluminum fluoride synthesis; High surface area; Surface structure

#### 1. Introduction

Metal oxides have found broad interest and applications in material chemistry and in particular in heterogeneous catalysis [1]. In catalysis, the oxides are active themselves (bulk catalysts) or the active phase is supported on the surface of oxides such as Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, and MgO. Synthesis routes for high surface area oxides are well known and their surface structure and catalytic properties have been investigated in detail for many decades and are well understood. Recent studies have demonstrated that several fluoride materials, like magnesium [2], aluminum [3] or calcium [4] fluoride, are interesting inorganic materials for applications in material science and catalysis. However, the knowledge about surface structure and simple synthesis routes to materials with high specific surface areas ( $\ge 100 \text{ m}^2/\text{g}$ ) is limited up to now. Aluminum fluoride, AlF<sub>3</sub>, represents an interesting type of material for applications in heterogeneous catalysis (as bulk and support) due to surface properties which are expected to be different from those of metal oxides. Only few investigations were reported about synthesis and characterization of polycrystalline or amorphous aluminum fluoride materials with high specific surface areas and about their stability towards air or moisture at elevated temperatures. It is generally assumed that aluminum trifluoride prepared conventionally by precipitation in aqueous media exhibits surface areas in the range from 10 to few ten m<sup>2</sup>/g only because of the high lattice energy, which forces the formation of regular crystalline structures.

Accordingly, most synthetic strategies for aluminum fluoride with high specific surface areas focus on the use of anhydrous hydrogen fluoride [5] or aluminum precursors like AlMe<sub>3</sub> [6] or AlCl<sub>3</sub> [7], which require special working conditions and experimental setup. In this work, we present a simple preparation method for high surface AlF<sub>3</sub> in aqueous phase under mild conditions. The resulting material was investigated using a variety of analytical

<sup>\*</sup> Corresponding author. Tel.: +49 89 289 13233; fax: +49 89 289 13183. *E-mail address:* klaus.koehler@ch.tum.de (K. Köhler).

methods (XRD, solid state MAS-NMR, IR, EPR) to elucidate the bulk and surface structure (crystalline structure, surface groups, specific surface area) of  $AlF_3$  as a function of the calcination temperature and its stability towards air and moisture under these conditions.

# 2. Experimental

# 2.1. Synthesis of aluminum fluoride (AlF<sub>3</sub>)

In a flask made of perfluoroalkoxy polymer (PFA), 9.18 g of  $Al_2O_3$  (90 mmol) is suspended in 150 mL of water. Twenty-four milliliters of hydrofluoric acid (40%; 540 mmol HF) is added dropwise under vigorous stirring at room temperature and subsequently the solid oxide is dissolved completely. The resulting clear solution is stirred for three days at room temperature. During this period, a white solid precipitates which is separated from the solvent by centrifugation (6000 rpm, 10 min). The resulting white aluminum fluoride is washed 3 times with 5–10 mL of water and dried at 70 °C overnight. Subsequently, the material is treated in a muffle furnace for 4 h at the desired calcination temperature.

## 2.2. Characterization

X-ray powder diffraction measurements were performed on a Philips X' Pert-1-System-Diffractometer. The Spectra were taken in the range of  $10-75^{\circ}$  (2 $\Theta$ ).

IR spectra were recorded on a FTS 575C spectrometer (BIO-RAD), using the potassium bromide (KBr) pellet technique (loading: 0.3 wt%) in the range of 4000–400 cm<sup>-1</sup>.

Specific surface areas were determined by N<sub>2</sub> physisorption at a temperature of 77 K using a Micromeritics ASAP 2010. All samples were degassed at 150 or 250 °C in vacuum for 3 h. The specific surface area is derived from measurements in the range of  $p/p_0 = 0.06-0.20$  according to the Brunauer–Emmett–Teller method (BET). The required area for one molecule of N<sub>2</sub> is assumed to be  $n_m = 0.162 \text{ nm}^2$ .

Solid state <sup>27</sup>Al MAS-NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer equipped with a standard 4 mm probehead allowing spinning frequencies of 9000 kHz and operation at 130.318 MHz for <sup>27</sup>Al. Typically 10000 scans were collected, the chemical shift was referenced to  $Al(NO_3)_3$  as external standard (-0.5427 ppm).

EPR spectra of the immobilized vanadium complexes were recorded on a JEOL JES-RE2X EPR spectrometer at X-band frequency at temperatures of 298 K. The spectra were measured at a microwave frequency of 9.05 GHz with a microwave power of 5 mW, with modulation amplitude of 0.4 mT, sweep time 4 min, sweep width 100 mT, time constant 0.1 s, and a modulation frequency of 100 kHz.

#### 3. Results and discussion

#### 3.1. Synthesis of high surface area aluminum fluoride

Different approaches have been applied for the synthesis of high surface aluminum fluoride. Aluminum fluoride can be obtained from thermal decomposition of fluoroaluminate salts like HAlF<sub>4</sub> [8] or  $(NH_4)_3AlF_6$  [9], or dehydration of aluminum fluoride hydrates  $(AlF_3 \cdot 3H_2O)$  [10], which leads to impurities of the resulting fluoride (partial decomposition) or causes remarkable reduction of the specific surface area. As an alternative, preparation methods have been developed which involve either the use of anhydrous hydrogen fluoride [5] or of air sensitive precursors like AlMe<sub>3</sub> [6] or AlCl<sub>3</sub> [7].

In contrast to the routes described above, aluminum fluoride can be obtained from a simple reaction in aqueous medium (Scheme 1). Addition of 40% hydrofluoric acid to a suspension of Al<sub>2</sub>O<sub>3</sub> in water causes dissolution of the formation oxide by of fluoroaluminates e.g.  $(AlF_4^{-}, AlF_6^{3-})$  without additional heating. After some time, precipitation of aluminum fluoride from the clear solution can be observed. After a reaction period of 3 days, AlF<sub>3</sub> can be separated from the solution by centrifugation and dried at 70 °C. For investigations of the bulk and surface structure as a function of the calcination temperature, the raw material was calcined at 200 and 450 °C, respectively. The resulting samples were investigated by X-ray powder diffraction, nuclear magnetic resonance and infrared spectroscopy to elucidate their structure.

# 3.2. Bulk structure

X-ray powder diffraction measurements (Fig. 1) were performed to investigate the bulk structure of the material and its stability towards elevated temperatures. Reflections of the pre-dried sample (70 °C) can be assigned to a highly crystalline aluminum fluoride trihydrate (AlF<sub>3</sub> · 3H<sub>2</sub>O). The water of crystallization is removed by thermal treatment at 200 °C, resulting in an amorphous, water-free AlF<sub>3</sub> which starts to crystallize at higher temperatures (450 °C). The X-ray diffraction measurements indicate that the bulk material consists of trigonal  $\alpha$ -AlF<sub>3</sub>. No crystalline oxide or hydroxide species were detected after calcination in air.

Solid-state NMR was used to probe the local environment of Al in the high surface area product. A <sup>27</sup>Al MAS NMR spectrum of AlF<sub>3</sub> after thermal treatment at 200 °C is shown in Fig. 2. The <sup>27</sup>Al chemical shift of the sample is found in the range observed for bulk aluminum fluoride at -16 ppm (Fig. 2). The resonance is assigned to octahedral AlF<sub>6</sub> environments in amorphous AlF<sub>3</sub>. No

$$Al_2O_3 + 6 HF_{(aq)} \xrightarrow{H_2O} 2 AlF_3 + 3 H_2O$$
  
Scheme 1.



Fig. 1. X-ray powder diffraction patterns of aluminum fluoride after thermal treatment at 70 (a), 200 (b) and 450  $^{\circ}{\rm C}$  (c).



Fig. 2. <sup>27</sup>Al MAS NMR spectrum of AlF<sub>3</sub>.

contributions from  $Al_2O_3$  (octahedral or tetrahedral aluminum sites) could be found.

#### 3.3. Surface properties

IR spectroscopy was applied to characterize the surface of aluminum fluoride. While the XRD investigations provided only information on bulk crystalline material, IR spectroscopy can elucidate if the surface of the fluoride is stable towards air (oxidation) or moisture (formation of surface OH groups). The IR spectra shown in Fig. 3 demonstrate that Al–F vibrations dominate after thermal treatment in air. The signal arising from the Al–F vibration is shifted from 616 cm<sup>-1</sup> in the case of hydrate material (70 °C) to 667 cm<sup>-1</sup> after removal of the water of crystalli-



Fig. 3. IR spectra of aluminum fluoride (0.3% in KBr) after thermal treatment at 70 (a), 200 (b) and 450 °C (c).

zation. The observed values are in accordance with Al–F vibrations reported in the literature for AlF<sub>3</sub> [11]. A strong, clearly separated signal at 870 cm<sup>-1</sup>, which can be assigned to Al–O vibrations from hydroxyl groups, appears in the spectrum of AlF<sub>3</sub> · 3H<sub>2</sub>O. However, the intensity of this band clearly decreases after removal of the water at elevated temperatures. In the spectra of water free AlF<sub>3</sub>, the signal of Al–O vibration can only be identified as a shoulder of the Al–F band. Absorption bands at >3000 cm<sup>-1</sup> and at 1600 cm<sup>-1</sup> arise from water. As expected, the intensity of these signals decreases remarkably at higher calcination temperatures.

The paramagnetic vanadium(IV) complex bisacetylacetonatooxovanadium(IV),  $[VO(acac)_2]$ , has been used as a probe for investigations of the AlF<sub>3</sub> surface (Fig. 4). The



Fig. 4. X-band EPR spectrum of the complex  $VO(acac)_2$  immobilized on  $AlF_3$  by equilibrium adsorption (recorded at r.t.).

Table 1

Specific surface area of AlF<sub>3</sub> materials after thermal treatment at different temperatures

Entry	Calcination temperature (°C)	Specific surface area (m <sup>2</sup> /g)
1	200	120
2	450	60

generation of well defined molecularly dispersed complexes is feasible by equilibrium adsorption from solution. The driving force for the adsorption from aqueous solution is assumed to be surface complex formation rather than electrostatic forces. The resulting surface complexes are isolated mononuclear vanadium(IV) complexes of defined structure. This can be deduced from the well resolved EPR spectra and their parameter ( $g_{\parallel} = 1.932$ ,  $A_{\parallel} =$  $0.0185 \text{ cm}^{-1}$ ,  $\Delta B_{pp\parallel} = 2.7 \text{ mT}$ ,  $g\perp = 1.984$ ,  $A\perp =$  $0.0075 \text{ cm}^{-1}$ ,  $\Delta B_{pp\perp} = 2.7 \text{ mT}$ ; nuclear spin of <sup>51</sup>V: 7/2), which are typical for one unpaired electron in a  $3d_{xy}$  orbital ( $3d^1$ , S = 1/2). In fact, electron nuclear double resonance techniques (ENDOR, HYSCORE; not shown) clearly prove that the complex [VO(acac)<sub>2</sub>] is bound to the aluminum fluoride surface via a Al–F–V bond, i.e. by axial coordination of a surface fluoride ion to the transition metal atom. Details about these investigations will be published elsewhere in due time.

The specific surface area of  $AlF_3$  after thermal treatment determined by nitrogen physisorption measurements is given in Table 1.

## 3.4. Concluding remarks

Simple preparation of aluminum fluoride material in aqueous phase at room temperature is feasible using alumina,  $Al_2O_3$ , as Al precursor and hydrofluoric acid (40%) as fluoride source. The resulting  $AlF_3$  material exhibits a high stability towards air or moisture at elevated temperatures. The presence of hydroxyl groups or F–OH exchange reactions could be observed only to a minor extent at the surface. Thus, the material can represent a promising alternative to conventional support materials in heterogeneous catalysis since its specific surface area is higher than 50 m<sup>2</sup>/g even after calcination at 450 °C.

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