

## Plasma-Fluorination Synthesis of High Surface Area Aluminum Trifluoride from a Zeolite Precursor

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The metastable phases of aluminum trifluoride ( $\beta$ -,  $\eta$ -,  $\theta$ -,  $\kappa$ -AlF<sub>3</sub>) are well-known halogen exchange catalysts.<sup>1–3</sup> These polymorphs are typically synthesized using *chimie douce* techniques, but the surface areas are low (<65 m<sup>2</sup>/g) relative to oxide catalysts.<sup>3,4</sup> Active AlF<sub>3</sub> catalysts have also been prepared via the low-temperature fluorination of high surface area  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with HF, NH<sub>4</sub>F, SF<sub>4</sub>, hydrofluorocarbons, or chlorofluorocarbons.<sup>2,5–11</sup> However, as fluorination proceeds, the specific surface areas of treated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> drop significantly, eventually reaching dimensions that are equivalent to or smaller than traditionally prepared AlF<sub>3</sub>.<sup>4,12</sup> Considering that heterogeneous reaction rates scale with surface area, new synthetic routes to high surface area AlF<sub>3</sub> are currently being sought. In this communication, we describe a novel method for converting zeolites to high surface area AlF<sub>3</sub> via a plasma-assisted fluorination reaction with nitrogen trifluoride.

The low-temperature, perfluorocompound (PFC) plasma fluorination of oxides is routine in semiconductor processing, but the scope of this technique remains generally unexplored, especially in the context of materials synthesis. We have investigated the heterogeneous reaction of a cold NF<sub>3</sub> plasma with various aluminum-containing powders, including  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> (kaolinite), and H<sub>1.3</sub>[Al<sub>1.3</sub>Si<sub>22.7</sub>O<sub>48</sub>] (zeolite H-SSZ-32; structure type: MTT) for the preparation of AlF<sub>3</sub>. The main goals of this investigation were to determine if a metastable form of AlF<sub>3</sub> could be prepared in a PFC plasma, and to correlate the structural characteristics of the precursors with the properties of the fluoride products.

Alumina precursors were selected because there is precedent in the literature for the conversion of alumina to aluminum fluoride in a PFC plasma,<sup>13</sup> but no metastable phases of AlF<sub>3</sub> were observed. While there was no preexisting evidence that plasma fluorination of aluminosilicates would yield AlF<sub>3</sub>, we speculated that the aluminum oxide fraction would undergo a

**Table 1.** Average Volume Per Al Atom, Specific Surface Areas, and Phases Identified by Powder X-ray Diffraction

precursor	vol/Al atom (Å <sup>3</sup> /Al)	surface area <sup>a</sup> (m <sup>2</sup> /g)	surface area of fluorinated products <sup>a</sup> (m <sup>2</sup> /g)	phases identified <sup>b</sup>
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	21.2	6	6	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> , $\alpha$ -AlF <sub>3</sub>
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	23.0	90	15	$\alpha$ -AlF <sub>3</sub> , $\gamma$ -Al <sub>2</sub> O <sub>3</sub>
Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	82.4	18	32	$\alpha$ -AlF <sub>3</sub> , $\beta$ -AlF <sub>3</sub>
H-SSZ-32	4254	100	190	n/a

<sup>a</sup> BET isotherm (N<sub>2</sub> Adsorption) using Quantachrome Autosorb-1.

<sup>b</sup> Compared to JCPDS-ICDD (1999). Siemens D5000, Cu K $\alpha$ .

metathesis reaction, forming AlF<sub>3</sub> and NO<sub>x(g)</sub>, and the silicate fraction would readily decompose and volatilize as SiF<sub>x(g)</sub> and NO<sub>x(g)</sub>. NF<sub>3</sub> was used as a fluorinating agent because carbon-containing PFCs produced residual fluorocarbon polymers on the solid products.

We were intrigued by the possibility that the density of aluminum cations in the precursors would affect the properties and phase of AlF<sub>3</sub> products, so we chose a series of aluminas and aluminosilicates that encompasses a wide range of aluminum cation densities: from 21.2 Å<sup>3</sup>/Al to 4254 Å<sup>3</sup>/Al. Table 1 lists the average volume per aluminum atom, based on crystallographic data (JCPDS-ICDD, 1999), for each of the precursors. We also anticipated that under sufficiently mild reaction conditions, high surface areas could be transferred from precursors to their fluoride products. Therefore,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> aerogel and high surface area zeolites seemed to be logical choices for precursors to high surface area AlF<sub>3</sub>.

Plasma reactions were carried out in an inductively coupled tubular reactor that has been described previously.<sup>14</sup> The temperature of the reactor exterior, measured using a thermocouple, did not exceed 180 °C. The gaseous products were monitored continuously at the reactor exit by a Spectra Satellite quadrupole mass spectrometer.

For each fluorination reaction, 200 mg of powdered precursor was weighed into an alumina boat, which was placed inside the reaction chamber prior to evacuation. The power was set at 150–250 W and the chamber pressure was maintained at 250 mTorr. The NF<sub>3</sub> (Advanced Specialty Gases, 99.9%) flow rate was 10 sccm for all reactions. The reactions ran until an endpoint was detected with the mass spectrometer, typically 10–20 min. Endpoints were marked by the disappearance of oxygen-containing and/or silicon-containing species in the effluent. The identities of the products were determined by powder X-ray diffraction and the surface areas were determined from N<sub>2</sub> adsorption isotherms. The results are given in Table 1.

Plasma fluorination of  $\alpha$ - and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> gave  $\alpha$ -AlF<sub>3</sub>, the thermodynamically stable and catalytically inactive phase of aluminum trifluoride,<sup>2</sup> and unreacted starting material. Fluorination of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> did not affect the specific surface area, while fluorination of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> decreased the measured surface area from 90 m<sup>2</sup>/g to 15 m<sup>2</sup>/g. The plasma fluorination of  $\alpha$ - and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> did not yield the desired metastable phases with high surface areas.

The plasma fluorination of Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> gave a material that is comparable to traditionally prepared AlF<sub>3</sub>. The powder X-ray diffraction pattern showed reflections from both  $\alpha$ -AlF<sub>3</sub>, which has a distorted ReO<sub>3</sub> structure,<sup>15</sup> and  $\beta$ -AlF<sub>3</sub>, which is metastable and structurally related to the hexagonal tungsten bronzes.<sup>16</sup>

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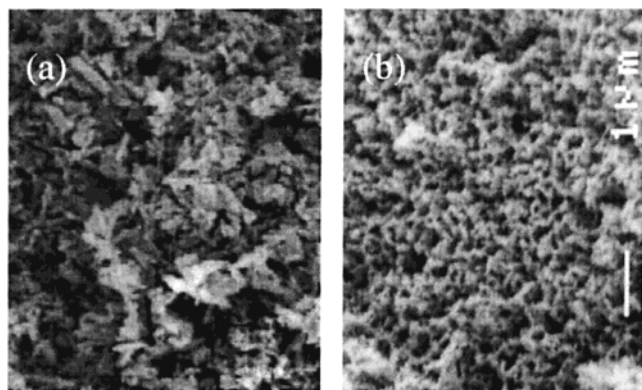
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**Figure 1.** (a) SEM image of H-SSZ-32. (b) SEM image of  $\text{AlF}_3$  derived from H-SSZ-32.

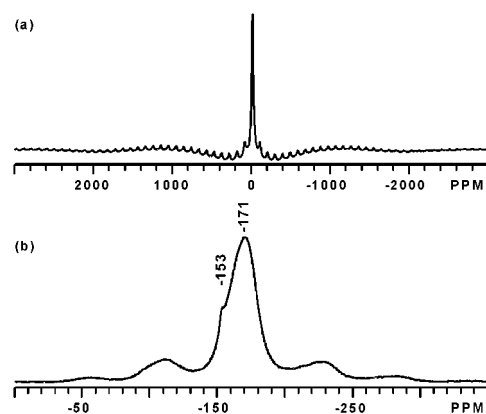
Interestingly, the BET surface area of the fluorinated  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$  ( $32 \text{ m}^2/\text{g}$ ) was greater than the starting material ( $18 \text{ m}^2/\text{g}$ ), suggesting that the crystallites fracture as the silicate layers are volatilized and the aluminum oxide layers are fluorinated. Mass balance calculations, which have been used to determine the degree of fluorination in thermal reactions, showed that 75% of the precursor was converted to  $\text{AlF}_3$ .

Under the same conditions, the zeolite H-SSZ-32 was converted to a flocculent, hygroscopic powder with a BET surface area of  $190 \text{ m}^2/\text{g}$ , which is extraordinarily high. Mass balance calculations indicated that conversion to  $\text{AlF}_3$  was quantitative. With such a large surface area, one would expect significant Scherrer broadening. Indeed, the material is nearly amorphous by XRD. However, broad reflections at  $2\theta = 25^\circ$  and  $53^\circ$ , characteristic of  $\alpha$ - or  $\beta$ - $\text{AlF}_3$ , were present. The associated  $d$  spacings,  $d = 3.6$  and  $1.8 \text{ \AA}$ , correspond to planes and half-planes established by corner-sharing octahedra, bridged by  $\text{Al}-\text{F}-\text{Al}$  bonds.

The H-SSZ-32 starting material and aluminum fluoride product were further examined using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) to assess the morphological and compositional changes associated with decomposition/fluorination. Both samples were coated with 20 nm of carbon and examined using a JEOL 6300 SEM-EDX. Figure 1a shows an SEM image of the H-SSZ-32 starting material. The zeolite is rather dense with well-defined crystallites, when compared to the porous  $\text{AlF}_3$  product, shown in Figure 1b. The plasma-synthesized  $\text{AlF}_3$  displays a significant void volume (micropores) undoubtedly a consequence of the selective removal of the silicate. EDX analysis showed that the material was composed of aluminum and fluorine; silicon and nitrogen were below detection limits. Trace amounts of oxygen, likely a product of surface hydration, were detected. Chemical analysis, using ICP-OES and a fluoride selective electrode, gave an Al:F ratio of 1:2.90(7), which does not preclude the possibility of surface hydroxylation.

Solid-state NMR<sup>11,17</sup> was used to probe the local environments of Al and F in the high surface area product of the plasma reaction with H-SSZ-32. The  $^{27}\text{Al}$  MAS spectrum (Figure 2a, acquired at 93.8 MHz using a Chemagnetics 3.2 mm double tuned probe) shows a single resonance at  $-18.1$  ppm consistent with aluminum in an octahedral  $\text{AlF}_6$  environment. The presence of a large sideband manifold spreading over more than 10 000 ppm, due to the satellite transitions, indicates that the aluminum sites in this material have a larger quadrupole coupling constant (QCC)

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**Figure 2.** (a)  $^{27}\text{Al}$  MAS NMR spectrum of the fluorinated H-SSZ-32 sample ( $\nu_r = 9 \text{ kHz}$ ). (b)  $^{19}\text{F}$  MAS NMR spectrum of the same sample collected with a rotor synchronized spin-echo sequence with a spin-evolution time of  $97.7 \mu\text{s}$  ( $\nu_r = 20 \text{ kHz}$ ).

compared with the aluminum sites in  $\alpha$ - $\text{AlF}_3$  ( $0.23 \pm 0.02 \text{ MHz}$ ) and  $\beta$ - $\text{AlF}_3$  ( $0.8 \pm 0.1 \text{ MHz}$ ).<sup>11</sup> No clear discontinuities are observed in the sideband manifold, indicating a distribution of QCCs. Simulations of the sideband pattern suggest that the QCCs are as large as 1.4 MHz. The larger QCC is indicative of a more distorted aluminum environment for H-SSZ-32-derived  $\text{AlF}_3$  compared with  $\alpha$ - or  $\beta$ - $\text{AlF}_3$ . The higher intensity first-order spinning sidebands, in comparison to the higher order sidebands, may be indicative of trace amounts of  $\alpha$ - $\text{AlF}_3$ .

The  $^{19}\text{F}$  MAS NMR spectrum (Figure 2b, acquired at 338.7 MHz and collected using a Hahn echo sequence) shows two discrete resonances at  $-171$  and  $-153$  ppm. The chemical shift of the larger resonance at  $-171$  ppm is identical to that of  $\alpha$ - and  $\beta$ - $\text{AlF}_3$  and is indicative of  $\text{Al}-\text{F}-\text{Al}$  linkages.  $^{19}\text{F}/^{27}\text{Al}$  TRAPDOR NMR<sup>18</sup> experiments showed that the weak resonance at  $-153$  ppm is not due to fluorine coordinated to aluminum, and is consistent with a silicon oxyfluoride environment,<sup>19</sup> indicating a small ( $<0.5\%$ ) fluorinated zeolite residue.

In conclusion, we have developed a method for converting zeolitic materials to  $\text{AlF}_3$  with an unusually high surface area. The high surface area and distorted Al environments observed for zeolite-derived  $\text{AlF}_3$  can be attributed to the low spatial density of Al atoms in the zeolite, as precursors with higher Al densities yield stable, low surface area products. The “cold” plasma environment is also an important feature of this synthesis, as it does not provide sufficient thermal energy to allow crystallite sintering and defect reparation, which would lower the total surface energy of the product. The  $\text{AlF}_6$  octahedra in the amorphous material are greatly distorted, even in comparison with the catalytically active, crystalline  $\beta$ -phase, suggesting that this material may display interesting catalytic properties for a variety of halogen exchange, halogenation, and dismutation reactions.

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