Supporting Information

A novel method for the synthesis of well-crystallized $\beta$-AlF$_3$
with high surface area derived from $\gamma$-Al$_2$O$_3$

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I. Experimental Details

1. Materials synthesis

$HS$-$\beta$-AlF$_3$: The high surface area $\beta$-AlF$_3$ ($HS$-$\beta$-AlF$_3$) were prepared by a solid-template method and the detailed process is as follows. 5 g of $\gamma$-Al$_2$O$_3$ (A.R., Sinopharm Chemical Reagent Co., 20-40 meshes) was mixed with 4.5 ml of 25 wt% sucrose aqueous solution by incipient-wetness impregnation for 1 h and dried at 120 °C. The resulting solid was calcined for 3 h at 400 °C under N$_2$ atmosphere. The above process was repeated for 3 times to obtain a carbon-filled $\gamma$-Al$_2$O$_3$. The resulting sample was denoted as C@Al$_2$O$_3$. The C@Al$_2$O$_3$ was loaded in a fixed bed reactor and exposed in a gaseous HF flow (HF/N$_2$ = 4, total flow rate = 30 ml min$^{-1}$) for 10 h at different temperatures. The resulting sample was denoted as C@AlF$_3$. Finally, the C@AlF$_3$ was mixed with 4.8 ml 5 wt % KNO$_3$ aqueous solution and dried at 120 °C for 2 h. Then the mixture was thermally treated in a tube furnace at 425 °C for 8 h in a oxygen flow (60 ml min$^{-1}$) in order to remove the carbon. Finally, the obtained solid was washed with plenty of deionized water to remove K$^+$ ions, followed by dried at 120 °C for 8 h.

Conventional $\beta$-AlF$_3$: conventional $\beta$-AlF$_3$ was prepared by thermal decomposition of $\alpha$-AlF$_3$·3H$_2$O according to the process reported in reference. $^{S1}$ 5 g of $\alpha$-AlF$_3$·3H$_2$O (A.R., Sinopharm Chemical Reagent Co.) was loaded in a tube furnace and heated at 400 °C for 2 h.

$\alpha$-AlF$_3$: $\alpha$-AlF$_3$ was obtained by direct fluorination of Al$_2$O$_3$ under HF atmosphere. 5 g of $\gamma$-Al$_2$O$_3$ was loaded in a fix bed reactor and exposed in a gaseous HF flow (HF/N$_2$ = 4, total flow rate = 30 ml min$^{-1}$) for 10 h at 250 °C. The resulting surface area of $\alpha$-AlF$_3$ is 15 m$^2$ g$^{-1}$.

2. Characterization

Surface areas of the samples were determined by the modified BET method from the N$_2$ sorption isotherms at 77 K on an Autosorb-1 apparatus. The samples were treated at 373 K for 4 h under vacuum before measurement.

X-ray diffraction patterns were collected on a PANalytical X’Pert PROMPD powder diffractometer operating at 40 kV and 40 mA using Cu-K$\alpha$ radiation, in the 2$\theta$ range from 10 to 80° with a scan rate of 0.3° min$^{-1}$. Phase
composition and cell parameter were calculated by the Rietveld method\textsuperscript{22} using MID-JADE 6.5 software. Raman spectra were collected on a Renishaw RM1000 confocal microscope with exciting wavelength of 514.5 nm under ambient conditions.

Scanning electron microscopy (SEM) image of the sample was obtained on a Hitachi S-4800 microscope equipped with an energy dispersion X-ray (EDX) attachment. High resolution transmission electron microscopy (HRTEM) of the sample was obtained on a JEOL JEM 2100F equipment with a field emissive gun, operating at 200 kV and with a point resolution of 0.24 nm.

TG-DSC experiment of the sample was performed using a Netzsch STA 449C instrument. The experiments were carried out to a maximum temperature of about 800 °C with a heating rate of 10 °C min\textsuperscript{-1} in air (50 ml min\textsuperscript{-1}). Ammonia temperature-programmed desorption (NH\textsubscript{3}-TPD) was conducted on a home-made apparatus. 100 mg of catalyst was loaded in a quartz tubular reactor (i. d. = 6 mm) and was heated from room temperature to 300 °C and kept for 30 min in a flow of Ar (30 ml min\textsuperscript{-1}). Then it was cooled down to 50 °C. A flow of NH\textsubscript{3} (20 ml min\textsuperscript{-1}) was then introduced for 10 min. The gaseous or physisorbed NH\textsubscript{3} was removed by purging Ar flow (30 ml min\textsuperscript{-1}) at 80 °C for 1 h. Then the sample was heated to 700 °C with a ramp of 10 °C min\textsuperscript{-1}. The desorbed NH\textsubscript{3} was monitored continuously via a TCD detector. The total amount of NH\textsubscript{3} desorbed was determined by a reaction with an excess of dilute HCl and back titration with NaOH solution. The mixture indicator contains a mixture of 0.1% brom-cresol green ethanol solution and 0.2% methyl red ethanol solution with a weight ratio of 3 : 1.

Fourier transformation Infrared (FTIR) spectra of pyridine adsorption on the catalysts were recorded on a Nicolet NEXUS 670 spectrometer in the range 1800–1400 cm\textsuperscript{-1}. A self-supported pellet of catalyst was dried in a hot air oven for 1 h at 100 °C, then it was brought in contact with pyridine directly. The sample was kept in a hot air oven at 120 °C for 1 h to remove physisorbed pyridine. After cooling the sample to room temperature, the IR spectrum was recorded in the spectral range 1800–1400 cm\textsuperscript{-1} with 64 scans and at a resolution of 4 cm\textsuperscript{-1}.

II. Supporting Tables and Figures.
Table S1 Physicochemical property for various forms of AlF₃.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Structure type</th>
<th>Structural features</th>
<th>$S_{\text{BET}}$ (m² g⁻¹)</th>
<th>nNH₃ (μmol g⁻¹)</th>
<th>Ref.</th>
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<tbody>
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<td>$\alpha$-AlF₃</td>
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<td>–</td>
<td>S3</td>
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<td>Hexagonal channels</td>
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<td>S4</td>
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<tr>
<td>$\kappa$-AlF₃</td>
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<td>–</td>
<td>S6</td>
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<tr>
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<td>240</td>
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<td>HS-$\beta$-AlF₃</td>
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<td>876</td>
<td>This work</td>
</tr>
</tbody>
</table>

Figure S1 SEM image and EDX analysis for HS-$\beta$-AlF₃.
Figure S2 TG/DTA curves of C@AlF₃ with and without addition of KNO₃.

Figure S4 NH₃-TPD profiles of β-AlF₃ samples.
Figure S3 FTIR spectrum of pyridine adsorption on HS-β-AlF₃.

Figure S5 Dismutation of CCl₂F₂ over HS-β-AlF₃ at 300 °C.
Figure S6 XRD patterns of fresh and used AlF₃ catalysts.

III. References