

Supporting Information

A novel method for the synthesis of well-crystallized β -AlF₃ with high surface area derived from γ -Al₂O₃

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I. Experimental Details

1. Materials synthesis

HS- β -AlF₃: The high surface area β -AlF₃ (HS- β -AlF₃) were prepared by a solid-template method and the detailed process is as follows. 5 g of γ -Al₂O₃ (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 1h and dried at 120 °C. The resulting solid was calcined for 3h at 400 °C under N₂ atmosphere. The above process was repeated for 3 times to obtain a carbon-filled γ -Al₂O₃. The resulting sample was denoted as C@Al₂O₃. The C@Al₂O₃ was loaded in a fixed bed reactor and exposed in a gaseous HF flow (HF/N₂ = 4, total flow rate = 30 ml min⁻¹) for 10 h at different temperatures. The resulting sample was denoted as C@AlF₃. Finally, the C@AlF₃ was mixed with 4.8 ml 5 wt % KNO₃ aqueous solution and dried at 120 °C for 2h. 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 β -AlF₃: conventional β -AlF₃ was prepared by thermal decomposition of α -AlF₃·3H₂O according to the process reported in reference.^{S1} 5 g of α -AlF₃·3H₂O (A.R., Sinopharm Chemical Reagent Co.) was loaded in a tube furnace and heated at 400 °C for 2h.

α -AlF₃: α -AlF₃ was obtained by direct fluorination of Al₂O₃ under HF atmosphere. 5 g of γ -Al₂O₃ was loaded in a fix bed reactor and exposed in a gaseous HF flow (HF/N₂ = 4, total flow rate = 30 ml min⁻¹) for 10 h at 250 °C. The resulting surface area of α -AlF₃ is 15 m² g⁻¹.

2. Characterization

Surface areas of the samples were determined by the modified BET method from the N₂ 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 α radiation, in the 2 θ 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^{S2} 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⁻¹ in air (50 ml min⁻¹). Ammonia temperature-programmed desorption (NH₃-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⁻¹). Then it was cooled down to 50 °C. A flow of NH₃ (20 ml min⁻¹) was then introduced for 10 min. The gaseous or physisorbed NH₃ was removed by purging Ar flow (30 ml min⁻¹) at 80 °C for 1 h. Then the sample was heated to 700 °C with a ramp of 10 °C min⁻¹. The desorbed NH₃ was monitored continuously via a TCD detector. The total amount of NH₃ 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⁻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⁻¹ with 64 scans and at a resolution of 4 cm⁻¹.

II. Supporting Tables and Figures.

Table S1 Physicochemical property for various forms of AlF_3 .

Sample	Structure type	Structural features	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	$n\text{NH}_3$ ($\mu\text{mol g}^{-1}$)	Ref.
$\alpha\text{-AlF}_3$	VF_3 (LT)	3D network	3	–	S3
$\beta\text{-AlF}_3$	HTB	Hexagonal channels	31	380	S4
HS- AlF_3	Amorphous	Mesoporous	200	900	S5
$\kappa\text{-AlF}_3$	TTB	Tetra/pentagonal channels	19	–	S6
$\theta\text{-AlF}_3$	Own type	3D network	64	240	S7
$\eta\text{-AlF}_3$	Pyrochlore	Channels	2	160	S7
HS- $\beta\text{-AlF}_3$	HTB	Propous	104	876	This work

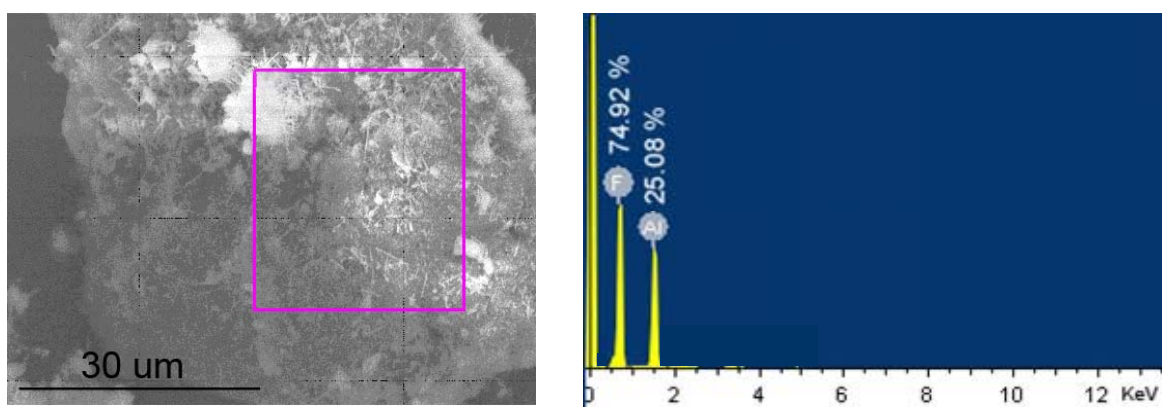


Figure S1 SEM image and EDX analysis for HS- $\beta\text{-AlF}_3$.

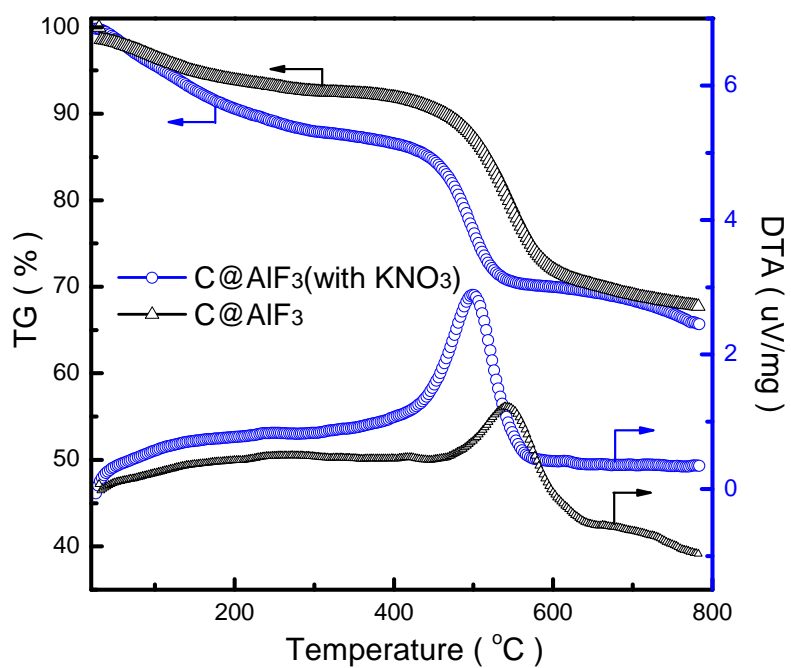


Figure S2 TG/DTA curves of C@AlF₃ with and without addition of KNO₃.

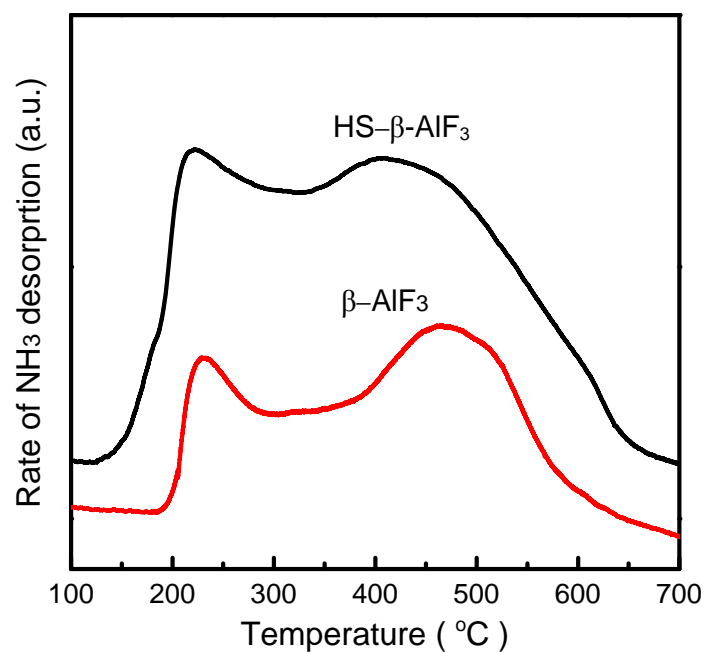


Figure S4 NH₃-TPD profiles of β-AlF₃ samples.

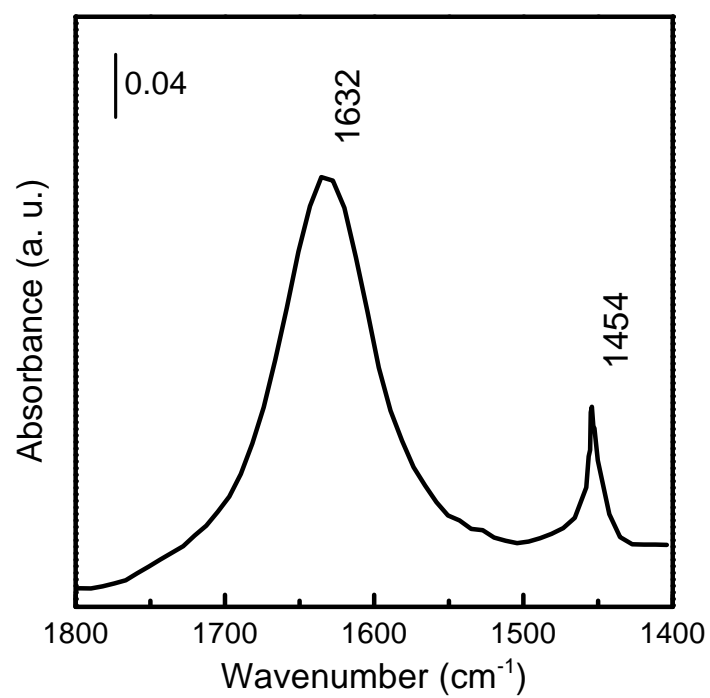


Figure S3 FTIR spectrum of pyridine adsorption on HS- β -AlF₃.

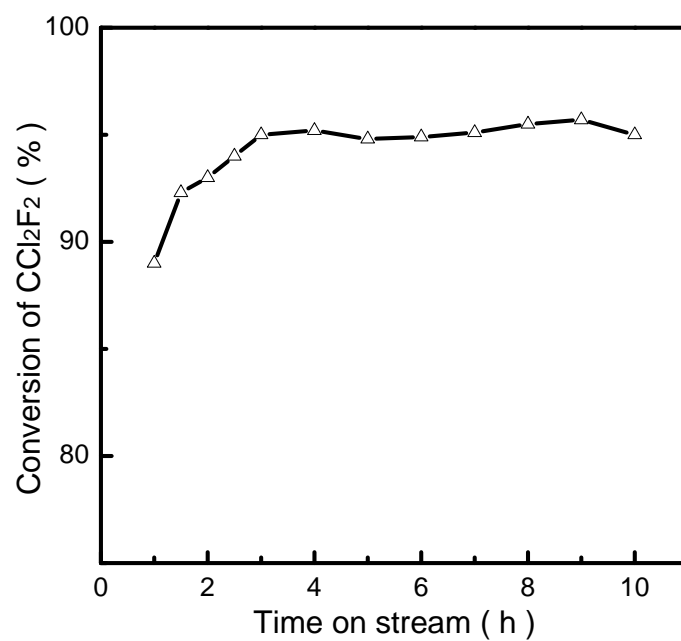


Figure S5 Dismutation of CCl₂F₂ over HS- β -AlF₃ at 300 °C.

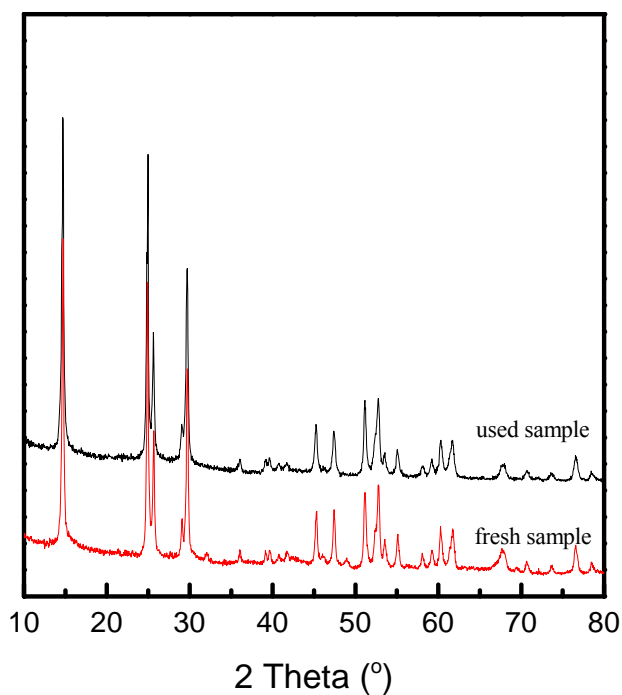


Figure S6 XRD patterns of fresh and used AlF₃ catalysts.

III. References

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