Preparation and characterization of high surface area $\alpha$-AlF$_3$

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High surface area $\alpha$-AlF$_3$ has been prepared by a carbon hard template method. Wherein $\gamma$-Al$_2$O$_3$ is immersed with sucrose aqueous solution and the dried mixture thermally treated under N$_2$ flow at 450 °C to obtain the C@$\gamma$-Al$_3$O$_4$. C@$\gamma$-Al$_3$O$_4$ can be completely transformed to C@$\alpha$-AlF$_3$ with hydrogen fluoride at 400 °C. After the carbon template in C@$\alpha$-AlF$_3$ is removed by high temperature combustion, a high surface area $\alpha$-AlF$_3$ (66 m$^2$ g$^{-1}$) is obtained. It is found that the fluorination process is crucial for the resulting $\alpha$-AlF$_3$. Although high fluorination temperature is favorable to the formation of $\alpha$-AlF$_3$, it also results in the decline of surface area.

Keywords: High surface area, Fluorination, Raman spectra, Crystal structure, Aluminium fluoride

Aluminum fluoride is an important inorganic material, which can be used as commodity chemical and as catalyst or support for the ozone-friendly alternatives to chlorofluorocarbons$^{1-4}$. It has been reported that the chemistry of the aluminum-fluorine system is very rich due to the existence of several crystal structure forms of AlF$_3$$^{5-10}$ viz., $\alpha$, $\beta$, $\gamma$, $\epsilon$, $\delta$, $\eta$, $\theta$, $\kappa$-AlF$_3$. The most common phases are $\alpha$-phase and $\beta$-phase, with the $\beta$-phase possessing significant catalytic activity and strong Lewis acid sites as compared to the $\alpha$-phase due to its high surface area. However, for some high temperature reactions, such as the fluorination of CF$_3$CH$_2$Cl to CF$_3$CH$_2$F$^{11}$ and the fluorination of CCl$_3$F$_2$ to produce CF$_4$, $\beta$-AlF$_3$ readily transforms to the more stable $\alpha$-AlF$_3$ during the reaction process, resulting in a dramatic decline in surface area and consequently the loss of reactivity. Therefore, the thermally stable $\alpha$-AlF$_3$ with high surface area is desirable.

The $\alpha$-AlF$_3$ can be synthesized through the fluorination of high surface area $\gamma$-Al$_2$O$_3$ with HF, hydrofluorocarbons or chlorofluorocarbon$^{12-14}$. However, the resulting AlF$_3$ has usually low surface area of 10-30 m$^2$ g$^{-1}$. For example, Skapin and Kemnitz$^{15}$ reported that the $\alpha$-AlF$_3$ prepared by direct fluorination of $\gamma$-alumina aerogels and xerogels under CHF$_3$ atmosphere at 480 °C, had a surface area of 22.1 m$^2$ g$^{-1}$. Recently, new methods have been developed to synthesize $\alpha$-AlF$_3$ with high surface area, such as $\alpha$-AlF$_3$ prepared by calcining the precursor $\beta$-AlF$_3$·3H$_2$O$^{16}$, resulting in a surface area of 123 m$^2$ g$^{-1}$. However, by this method, costly $\beta$-AlF$_3$·3H$_2$O is used.

In this work, we present a simple and novel preparation method for converting $\gamma$-Al$_2$O$_3$ to high surface area $\alpha$-AlF$_3$. The prepared $\alpha$-AlF$_3$ was characterized by XRD, BET, Raman, N$_2$ physisorption, SEM and EDX techniques. Also, the effects of preparation parameters during the synthesis on the resulting sample were investigated.

**Experimental**

High surface area $\alpha$-AlF$_3$ (hereafter denoted as HS-$\alpha$-AlF$_3$) was prepared by a solid-template method by the synthesis procedure comprising three consecutive steps, as shown in Scheme 1.

For a typical synthesis, 10 g of $\gamma$-alumina grains (AR, Sinopharm Chemical Reagent Co., Ltd; 20-40 mesh) were dried at 100 °C for 3 h under vacuum. Then, $\gamma$-Al$_2$O$_3$ was immersed in sucrose (C$_{12}$H$_{22}$O$_{11}$) aqueous solution (11 ml, 40 wt%), dried at 120 °C and calcined at 500 °C for 3 h in N$_2$ atmosphere. The impregnation, dry and calcination process was repeated for twice. However, for the fourth impregnation, the concentration of sucrose was 15 wt%. The resulting sample was denoted as C@$\gamma$-Al$_3$O$_4$ mid-complex and this synthesis step was demonstrated as step (a) in the scheme. Step (b) was

![Scheme 1](image-url)

**Notes**
the treatment of C@γ-Al₂O₃ with an anhydrous HF, which was carried out in a fixed bed reactor. The mixture of HF/N₂ (molar ratio = 4) was introduced to the sample at certain temperature for 10 h. The pre-fluorinated sample was denoted as C@α-AlF₃ mid-complex. Finally, 5 ml of 5 wt% KNO₃ solution was added to solid C@AlF₃ by incipient-wetness impregnation method. The carbon in the α-AlF₃ was removed by calcination at 425 °C for 8 h in oxygen. (Step c in Scheme 1). The obtained sample was washed with plenty of deionized water to remove K⁺ ions, followed by drying at 120 °C for 5 h.

Low surface area α-AlF₃ was prepared by direct fluorination of γ-Al₂O₃ under HF atmosphere. γ-Al₂O₃ (10 g) was loaded in a fix bed reactor and exposed to a gaseous HF flow (HF/N₂ = 4) for 10 h at 400 °C. The resulting surface area of α-AlF₃ was 17 m² g⁻¹.

Surface area of the sample was determined by the modified BET method from the N₂ sorption isotherms at -196 °C on an Autosorb-1 apparatus. The samples were heated at 100 °C for 4 h under vacuum before measurement. X-ray diffraction patterns were collected on a PANalytical X'Pert PROMPD powder diffractometer operated at 40 kV and 40 mA using Cu-Kα radiation in the 2θ range from 10 to 90° with a scan rate of 0.3° min⁻¹. The crystalline size was calculated by the Rietveld method 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) images of the sample were obtained with a Hitachi S-4800 microscope equipped with an energy dispersion X-ray (EDX) attachment.

**Results and discussion**

Figure 1 shows the XRD patterns and N₂ adsorption-desorption isotherms of the samples during preparation procedure. As can be seen from Fig. 1 (a), it is found that the γ-Al₂O₃ crystallite phase does not change after filling the carbon in the template (C@γ-Al₂O₃). When the C@γ-Al₂O₃ was fluorinated, the diffraction peaks of α-AlF₃ were clearly observed in the pattern, and the diffraction peaks of γ-Al₂O₃ disappear. This indicates that the C@γ-Al₂O₃ completely transforms into C@α-AlF₃ at 400 °C. When the carbon template was removed by the thermal treatment in oxygen at 425 °C, the well crystallized α-AlF₃ remains unchanged. Also, from Fig. 1(b), it can be seen that after filling carbon in the pores of γ-Al₂O₃ the surface area of γ-Al₂O₃ dramatically declines from 350 to 101 m² g⁻¹, due to the blocking of pores by carbon particles. However, when the C@γ-Al₂O₃ transforms into C@α-AlF₃, the further decline of the surface area indicates that micropores and mesopores of the C@γ-Al₂O₃ collapse during its transformation into α-AlF₃. It is also found that the N₂ adsorption-desorption isotherms of both C@γ-Al₂O₃ and C@α-AlF₃ exhibit type IV behavior, indicating maintenance of the sample structure. When the carbon template is removed, the resulting α-AlF₃ has a surface area of 66 m² g⁻¹. However, direct fluorination

**Fig. 1** – (a) XRD patterns of samples represented in the synthesis procedure, and, (b) N₂ adsorption-desorption isotherms. [DF: direct fluorination of γ-Al₂O₃ with HF; fluorination temperature: 400 °C; temperature for removal of carbon: 425 °C].
of $\gamma$-$\text{Al}_2\text{O}_3$ at 400 °C results in the formation of $\alpha$-$\text{AlF}_3$, which has a surface area of only 17 m$^2$ g$^{-1}$.

Figure 2 shows the XRD patterns of $\alpha$-$\text{AlF}_3$ samples fluorinated at different temperatures. As can be seen from Fig. 2, the C@$\gamma$-$\text{Al}_2\text{O}_3$ cannot be completely fluorinated at 350 or 380 °C, as shown by the weak diffraction peaks due to $\gamma$-$\text{Al}_2\text{O}_3$ remaining. At 400 °C only the diffraction peaks of $\alpha$-$\text{AlF}_3$ are observed, which indicates that $\gamma$-$\text{Al}_2\text{O}_3$ is completely fluorinated to $\alpha$-$\text{AlF}_3$. In addition, with increase in fluorination temperature from 350 to 450 °C, the intensities of diffraction peaks of $\alpha$-$\text{AlF}_3$ increase with increase in crystalline size from 17.7 nm at 350 °C to 27.9 nm at 450 °C, which consequently leads to a decline of surface area.

Table 1 lists the surface area, average crystallite size and F/Al ratio of the samples fluorinated at different temperatures, as determined by BET techniques, XRD, and EDX, respectively. As can be seen in Table 1, when the fluorination temperature is low (≤ 350 °C), the sample contains unfluorinated $\gamma$-$\text{Al}_2\text{O}_3$, which is confirmed by EDX analysis that the F/Al ratio is 1.92. At high fluorination temperature (≥ 400 °C ), the sample is completely transformed to $\alpha$-$\text{AlF}_3$, as the F/Al ratio is very close to 3:1. In addition, the crystallite size gradually increases with fluorination temperature, which results in the decline of surface area. On the other hand, direct removal of the carbon template in the sample usually needs a high temperature of 500 °C, which leads to a loss of surface area during the procedure. It is worth noting that the promoting effect of KNO$_3$ in soot combustion has been widely reported. Therefore, the addition of KNO$_3$ in the C@$\alpha$-$\text{AlF}_3$ can efficiently lower the combustion temperature of the carbon template to 425 °C.

Figure 3 shows the Raman spectroscopy of samples represented in the synthesis procedure. As can be seen from Fig. 3, the Raman bands of $\gamma$-$\text{Al}_2\text{O}_3$ and $\alpha$-$\text{AlF}_3$ are not observed. However, two distinct bands of carbon$^{18}$ at 1360 and 1600 cm$^{-1}$ are observed in the C@$\gamma$-$\text{Al}_2\text{O}_3$ and C@$\alpha$-$\text{AlF}_3$. This indicates that the carbon templates have been completely removed after thermal treatment.

In the present study, well crystallized $\alpha$-$\text{AlF}_3$ has been synthesized by a carbon hard template method. By this method, the resulting $\alpha$-$\text{AlF}_3$ has a higher surface area (66 m$^2$ g$^{-1}$) compared to that prepared by direct fluorination method (17 m$^2$ g$^{-1}$). In addition, the synthesized HS-$\alpha$-$\text{AlF}_3$ is thermally stable, and may find application in high temperature reactions.

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References