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COMMUNICATION

A novel method for the synthesis of well-crystallized β-AlF_3 with high surface area derived from γ-Al_2O_3†

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Well-crystallized β-AlF_3 with high surface area was synthesized by a carbon template method. Porous γ-Al_2O_3 was filled with carbon and transformed into AlF_3 by fluorination. After removing the carbon template by thermal combustion, the resulting β-AlF_3 had a surface area of 114 m^2 g^{-1}. Temperatures for fluorination and thermal combustion were crucial for the phase composition of the resulting sample. The high surface area β-AlF_3 was very active for dismutation of CF_2Cl_2 due to its large amount of surface acid sites.

Aluminum fluoride (AlF_3) has many properties and applications such as electrolysis, electrical conductivity and fluoro-aluminate glasses. Moreover, AlF_3 is of great interest in heterogeneous catalysis as the well-known halogen exchange catalyst, which plays an important role in the synthesis of hydrofluorocarbons (HFCs) as Freon-alternatives and novel fluorinated organic compounds applied in pharmaceuticals.[1,2]

AlF_3 could be synthesized through the fluorination of high surface area γ-Al_2O_3 with HF, NH_4F, SF_4, hydro-fluorocarbons, or chlorofluorocarbons.[3] However, the resulting AlF_3 usually has a low surface area of 10–60 m^2 g^{-1}.

Recently, new methods have been developed to synthesize AlF_3 with high surface area, such as the NF_3 plasma-etching treatment of aluminum-rich zeolites reported by Delattre *et al.*,[4] resulting in a surface area of 190 m^2 g^{-1}. Kemnitz *et al.*[5] employed a sol–gel method to synthesize amorphous AlF_3 with a high surface area of 200 m^2 g^{-1} (HS-AlF_3). Wolfgang *et al.*[6] reported that Al_2O_3 reacting with HF solution and consecutive thermal decomposition resulted in β-AlF_3 with a surface area of 120 m^2 g^{-1}. However, by these methods, either the synthetic procedure is complicated or corrosive HF solution, explosive NF_3 and costly metal-alkoxide Al(O*i*Pr)$_3$ are used. In particular, as halogen exchange reactions usually take place in a temperature range of 200 to 400 °C,[7] amorphous AlF_3 may undergo phase transition under rigorous reaction conditions. Therefore, well crystallized AlF_3 is more thermally stable, and thus desirable for catalysis purpose.

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In spite of AlF_3 existing in crystalline forms of α, β, η, θ, κ,[8] the β-phase posses significant catalytic activity for halogen exchange and strong Lewis acid sites[9] compared to the α-phase. For heterogeneous Cl/F exchange reaction, catalysts with strong Lewis acid sites are required.[1,10] More importantly, the reactivity is generally correlated to the amount of surface acid sites on the AlF_3, and thus high surface area AlF_3 is more advantageous in the reactions.

In this work, we report a novel method for converting γ-Al_2O_3 to high surface area β-AlF_3 (hereafter denoted as HS-β-AlF_3) by the gas-solid fluorination reaction with gaseous HF. The prepara-tion process could be described as the following equations:

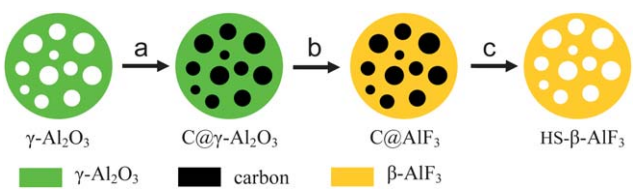
$$\gamma\text{-}Al_2O_3 + C_{12}H_{22}O_{11} \xrightarrow{N_2,400^\circ C} C@\gamma\text{-}Al_2O_3 + H_2O \quad (1)$$

$$C@\gamma\text{-}Al_2O_3 + HF \rightarrow C@AlF_3 + H_2O \quad (2)$$

$$C@AlF_3 + O_2 \rightarrow \beta\text{-}AlF_3 + CO_2 \quad (3)$$

Firstly, solid γ-Al_2O_3 was immersed in an aqueous sucrose ($C_{12}H_{22}O_{11}$) solution and the dried mixture was thermally treated under N_2 flow at 400 °C to obtain a γ-Al_2O_3 with carbon filled in the pores (denoted as C@γ-Al_2O_3), as shown in eqn (1). Then the C@γ-Al_2O_3 was fluorinated with gaseous HF at 250 °C to obtain C@AlF_3 [eqn (2)]. Finally, the carbon template was removed by combustion under oxygen flow to obtain well crystalline β-AlF_3 [eqn (3)]. The process is demonstrated in Scheme 1.

Fig. 1 shows the N_2 adsorption–desorption isotherms and XRD patterns of the samples during the preparation procedure. From Fig. 1a, it can be seen that after carbon filling into the pores of γ-Al_2O_3, the surface area of γ-Al_2O_3 dramatically declines from 347 to 77 m^2 g^{-1}, due to the blocking of pores by carbon particles. The C@AlF_3 has similar surface area to the C@Al_2O_3, indicating the



Scheme 1 Schematic diagram for the synthesis of HS-β-AlF_3. a: filling carbon hard template; b: fluorination with gaseous HF; c: combustion of carbon template in oxygen atmosphere.

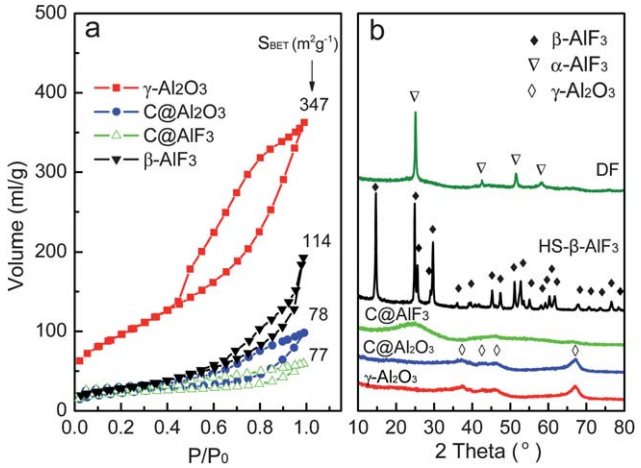


Fig. 1 a) N_2 adsorption–desorption isotherms, BET areas and b) XRD patterns of samples represented in the synthesis procedure. DF means the direct fluorination of γ-Al_2O_3 with HF.

maintenance of the sample structure. When the carbon template is removed, the resulting HS-β-AlF_3 has a surface area of 114 m^2 g^{-1}. Also, as can be seen from Fig. 1b, the γ-Al_2O_3 crystallite phase remains unchanged after filling of carbon template (C@Al_2O_3). After fluorination, the sample is amorphous (C@AlF_3). When the carbon is removed under a thermal treatment in oxygen at 425 °C for 8 h, well crystallized HS-β-AlF_3 is obtained, which exhibits the hexagonal tungsten bronze type structure.[8,11] This implies that during the thermal treatment, amorphous AlF_3 formed in fluorination stage transforms to β-AlF_3. However, direct fluorination of γ-Al_2O_3 at 250 °C results in the formation of α-AlF_3, which has a surface area of only 15 m^2 g^{-1}.

In order to further describe the preparation process for HS-β-AlF_3, Raman spectroscopy was also conducted and the results are shown in the ESI (Fig. S1†). Concerning the strong fluorescence and the fact that γ-Al_2O_3 and AlF_3 has no visible Raman signals, the Raman spectra are not very informative. However, distinct bands at 1360 and 1600 cm^{-1} which are characteristic of carbon[12] are found in the spectra for C@Al_2O_3 and C@AlF_3. This confirms that carbon is present in γ-Al_2O_3, which is in agreement with the N_2 adsorption–desorption isotherms in Fig. 1a.

Fig. 2 shows the representative SEM and TEM images of the HS-β-AlF_3 sample fluorinated at 250 °C. As can be seen in Fig. 2a, the synthesized material is disordered and flocculated. Also, EDX analysis of the selected area (Fig. S2†) shows that the sample contains

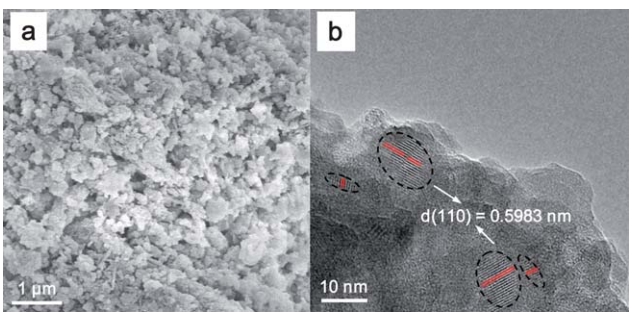


Fig. 2 a) SEM and b) TEM images of synthesized HS-β-AlF_3.

25.08% Al and 74.92% F, which is very close to an Al/F ratio of 3, indicating that the Al_2O_3 is completely fluorinated to form AlF_3. The TEM image (Fig. 2b) also shows the interplane distance of the β-AlF_3 (110) crystal face (0.5983 nm), which further confirms the formation of β-AlF_3.

Since the fluorination process is crucial for the resulting AlF_3, the effect of fluorination temperature on the final phase composition of the sample has been investigated. As can be seen in Fig. 3a, the C@Al_2O_3 cannot be completely fluorinated at 200 °C as the diffraction peaks of γ-Al_2O_3 are still present in the pattern. When the fluorination temperature is higher than 275 °C, however, diffraction peaks due to α-AlF_3 appear. Fig. 3b shows the XRD patterns of the template-removed samples with different fluorination temperatures. It can be seen that the C@Al_2O_3 cannot be completely fluorinated at 200 °C because the weak diffraction peaks of γ-Al_2O_3 remain. When fluorinated at 250 °C, only diffraction peaks due to β-AlF_3 are observed, implying the complete fluorination of γ-Al_2O_3 to β-AlF_3. When the fluorination temperature is higher than 250 °C, it is found that the peak intensity at 14.8° assigned to β-AlF_3 (110) plane decreases while that at 24.9° assigned to (002) plane of β-AlF_3 and (100) plane of α-AlF_3 significantly increases, suggesting the formation of α-AlF_3. Therefore, the fluorination temperature of 250 °C seems appropriate for the formation of β-AlF_3.

Table 1 summarizes the phase composition, average crystallite size, F/Al ratio and surface area of the samples fluorinated at different temperatures, determined by XRD, EDX and BET techniques, respectively. When the fluorination temperature is low (200 °C), the sample contains unfluorinated γ-Al_2O_3, which is also confirmed by EDX analysis which shows that the F/Al ratio is 1.92. At high fluorination temperature (≥250 °C), the sample is completely transformed to AlF_3, as the F/Al ratio is very close to 3 : 1. However, the content of α-AlF_3 in the sample increases with increasing temperature, and the sample fluorinated at 350 °C contains only α-AlF_3.

As for the surface area, it can be seen that it declines dramatically with increasing fluorination temperature. This is due to the fact that γ-Al_2O_3 could be readily fluorinated to form thermostable α-AlF_3 at high temperature because of their high lattice energies,[5,9] and the crystallite size gradually increases with fluorination temperature, which results in the decline of surface area. On the other hand, the decline in surface area implies that some pore structure may be destroyed during high temperature fluorination.

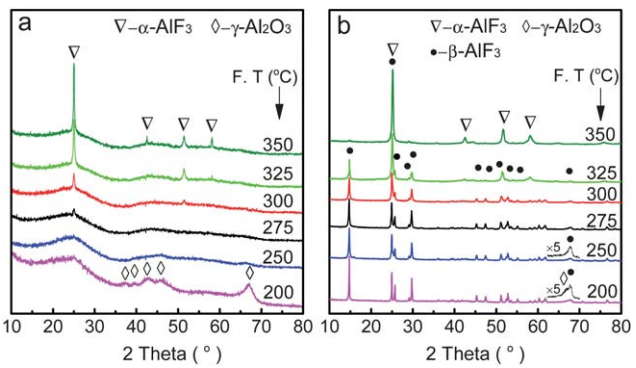


Fig. 3 XRD patterns of samples with different fluorination temperatures. a) fluorination process of C@Al_2O_3; b) samples after removal of carbon template. FT means the fluorination temperature.

Table 1 Properties of samples with different fluorination temperatures

Fluorination T/°C	Phase composition (wt%)	Average crystallite size/nm	F/Al molar ratio	Surface area/m^2 g^{-1}
200	β-AlF_3	77.2	1.92 : 1	136
	γ-Al_2O_3	n.d		
250	β-AlF_3 (100)	48.5	2.98 : 1	114
275	β-AlF_3 (96.3)	41.0	2.99 : 1	85
	α-AlF_3 (3.7)	10.0		
300	β-AlF_3 (85.2)	33.5	3.02 : 1	72
	α-AlF_3 (14.8)	15.1		
325	β-AlF_3 (58.1)	18.4	3.01 : 1	65
	α-AlF_3 (41.9)	22.3		
350	α-AlF_3 (100)	31.2	2.99 : 1	22

It was reported that amorphous AlF_3 could be transformed to β-AlF_3 at 350–475 °C, while the transformation of β-AlF_3 to α-AlF_3 will take place in the temperature range of 475–650 °C.[13] Therefore, the choice of the temperature for removal of carbon template in the present synthesis is essential to obtain the desired β-AlF_3. It should be noted that the complete combustion of carbon requires a temperature of 500 °C confirmed in our experiment, at which the resulting sample is α-AlF_3. By the addition of KNO_3 in the C@AlF_3, the carbon template could be efficiently combusted at 425 °C. The promoting effect of KNO_3 in soot combustion has been widely reported.[14] Also, our TG-DTA experiment shows that the addition of KNO_3 has lowered the carbon combustion temperature by 50 °C (Fig. S3†) compared to that without KNO_3. The lowered combustion temperature could effectively inhibit the phase transformation of β-AlF_3, which is also a key factor in obtaining the HS-β-AlF_3.

The acidic properties of the prepared HS-β-AlF_3 have been characterized by FTIR spectroscopy of pyridine adsorption and NH_3-temperature programmed desorption (NH_3-TPD), and more importantly by its catalytic properties. After pyridine adsorption, the FTIR spectrum (Fig. S4†) of the HS-β-AlF_3 shows intense bands at 1454 and 1632 cm^{-1}, which indicates Lewis acid sites.[15] The NH_3-TPD profile of HS-β-AlF_3 is shown in Fig. 4. It shows two distinct desorption peaks at about 220 and 460 °C. The amount of surface acidic sites of the HS-β-AlF_3 is calculated to be 876 μmol $g^{-1}_{cat.}$ This is among the highest values reported in the literature (Table S1†). For comparison, a conventional β-AlF_3 prepared by thermal treating

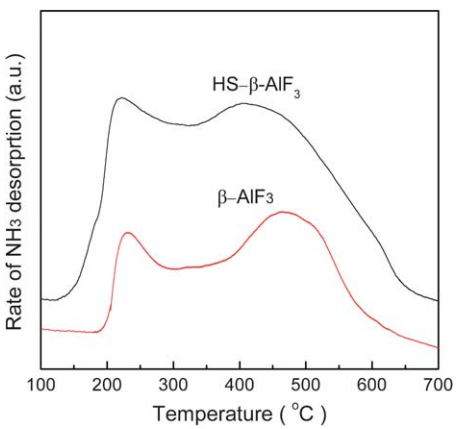


Fig. 4 NH_3-TPD profiles of β-AlF_3 samples.

Table 2 Dismutation of CF_2Cl_2 over AlF_3 catalysts

Sample	Surface area/m^2 g^{-1}	CF_2Cl_2 conversion (%)			
		300 °C	250 °C	200 °C	150 °C
α-AlF_3	15	54	16	10	2
β-AlF_3	41	89	78	25	11
HS-β-AlF_3	114	95	85	52	31

$AlF_3 \cdot 3H_2O$ according to ref. 16 resulted in a surface area of 41 m^2 g^{-1} and surface acidic sites of 421 μmol $g^{-1}_{cat.}$

The HS-β-AlF_3 has also been tested for catalytic CCl_2F_2 dismutation [eqn (4)].

$$5CCl_2F_2 \rightarrow 3CClF_3 + CCl_3F + CCl_4 \quad (4)$$

Table 2 lists the catalytic activity of various AlF_3 samples for the reaction. It can be seen that the HS-β-AlF_3 is much more active than the α-AlF_3 and low surface area β-AlF_3 at low reaction temperature, which is due to the higher amount of surface acidic sites. In addition, the synthesized HS-β-AlF_3 shows good stability during the reaction, with 95% conversion of CF_2Cl_2 in a reaction period of 10 h at 300 °C (Fig. S5†). A comparison of the fresh and the used samples by XRD revealed that there is no phase transition during the reaction (Fig. S6†). Also, the used catalyst has a surface area of 108 m^2 g^{-1}, suggesting that the catalyst structure remains unchanged.

To summarize, well crystallized HS-β-AlF_3 is prepared by a solid-template method, derived from the fluorination of carbon filled γ-Al_2O_3 and thermal removal of the carbon template. The resulting HS-β-AlF_3 has large amount of surface acidic sites due to its high surface area, which is beneficial for halogen exchange reaction such as dismutation of CF_2Cl_2 or $CHFCl_2$. The synthesized HS-β-AlF_3 is thermally stable, which could be applied to high temperature reactions. More importantly, other metal fluorides with high surface area such as MgF_2 may also be prepared in a similar way.

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