Synthesis of K–β-Al_2O_3 Powder by Hydrothermal Multicomponent Coprecipitation Method

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A precursor for K–β-Al_2O_3 powder has been synthesized by hydrothermal multicomponent coprecipitation method. The precursor for the synthesis was composed of the solid solution of $K_xNH_{4(1-x)}Al(OH)_2CO_3 (x = 0.1885)$. The effect of calcination temperature on the formation of K–β-Al_2O_3 phase was investigated. It is the first attempt to prepare K–β-Al_2O_3 powder by a kind of low-cost wet chemical process.

K–β-Al_2O_3, a kind of K^+ ion conductor with a chemical formula of $K_2O{\cdot}5.33Al_2O_3$ has been applied in many fields such as alkaline metal thermal electric convector (AMTEC),[1] anticorrosive agent for metal,[2] ion exchange precursor for hydronium β-Al_2O_3,[3] etc. Each application needs high performance of K–β-Al_2O_3 ceramics and K–β-Al_2O_3 powder with high quality. Up to now, K–β-Al_2O_3 is usually prepared via solid-state reaction,[4] which would to some extent restrict the improvement of the quality of these materials.

In this paper, we try to develop a new wet chemical process, coprecipitation technique to synthesize K–β-Al_2O_3, by which the homogeneity and reactivity of the products are expected to be remarkably improved over traditional solid-state reaction. Unfortunately, hydrate and salts of potassium are usually dissoluble in H_2O and not in normal organic solvents. Therefore, it's difficult to apply conventional coprecipitation technique to the fabrication of K–β-Al_2O_3. It's exciting to find a precursor, dawsonite-type compound, which is a mineral of formula $MAl(OH)_2CO_3$ (M = Na, K, NH_4) named after the Canadian geologist, J. W. Dawson.[5,6] Such compounds have been employed in the preparation of new ceramic materials made of alumina.[7–10] For example, in our laboratory, sodium-alumina powder was obtained by calcining the mixture composed of dawsonite and ammonium dawsonite at lower temperature previously.[10]

This work involves the synthesis of an appropriate solid solution or mixture of potassium and ammonium dawsonite by hydrothermal method which has comparable K/Al molar ratio to K–β-Al_2O_3. By calcining the precursor, K–β-Al_2O_3 powder can be obtained immediately.

Hydrothermal synthesis of dawsonites was achieved by the processes as reported in the previous work.[11] For a typical reaction, an appropriate amount of $Al(NO_3)_3{\cdot}6H_2O$ was mixed with supersaturated $KHCO_3$ solution very slowly in order to avoid the vigorous release of CO_2 in a Teflon-lined autoclave whose fill factor was 80%. After this reaction ended, an amount of NH_4NO_3 ($[K^+]/[NH_4^+] = 1$) was added to the solution as the source of NH_4^+ ion. The autoclave was maintained at 120 °C in an electric oven for 4, 8, 24, and 72 h to adjust the composition of the product and then cooled to room temperature. All the precipitates were centrifugated, repeatedly washed with deionized water and ethanol, and finally dried at 60 °C in air for 24 h. Thus, the desired precipitates were calcined at different temperatures for 5 min. The X-ray powder diffraction patterns were acquired from a Rigaku D/MAX-III A powder diffractometer with nickel-filtered Cu Kα ($\lambda = 1.5418$ Å) source. Differential thermal analysis/thermogravimetric analysis (DTA/TG) of the precursor was performed using a DTA/TG analyzer (Model ZRY-1P, SHANGPING, Shanghai, China) in air with a heating rate of 10 °C/min. The contents of K and Al in these products were tested by the ICP spectrophotometric technique.

In this work, composition of the precursor depends on the hydrothermal reaction time because all the precursors were synthesized with the same starting material and thus the reaction time was the only controlling parameter. Based on our previous investigation on dawsonites with single cations,[11] the following chemical reactions were expected in the hydrothermal reaction system,

$$Al^{3+} + 3HCO_3^- \rightarrow Al(OH)_3\downarrow + 3CO_2\uparrow \tag{1}$$

$$Al(OH)_3 \leftrightarrow AlO(OH)_2^- + H^+ \tag{2}$$

and the formation of a solid solution,

$$\begin{gathered} AlO(OH)_2^- + HCO_3^- + xK^+ + (1-x)NH_4^+ \rightarrow \\ K_x(NH_4)_{1-x}Al(OH)_2CO_3 + OH^- \end{gathered} \tag{3}$$

or a mixture of dawsonites,

$$\begin{gathered} AlO(OH)_2^- + HCO_3^- + xK^+ + (1-x)NH_4^+ \rightarrow \\ (1-x)NH_4Al(OH)_2CO_3 + xKAl(OH)_2CO_3 + OH^- \end{gathered} \tag{4}$$

Therefore, the ratio of K^+ and NH_4^+ in the products will be the result of competition between K^+ and NH_4^+ during combining with $AlO(OH)_2^-$ anions according to Eqs 3 or 4.

As known, both $KAl(OH)_2CO_3$ and $NH_4Al(OH)_2CO_3$ called potassium dawsonite and ammonium dawsonite respectively, have the same structure of space group.[12] There is only a little difference in the radius of K^+ (133 pm) and NH_4^+ (143 pm). Therefore, it is possible that the solid solution of $K_x(NH_4)_{1-x}Al(OH)_2CO_3$ would appear when both the cations exist in a hydrothermal system at the same time.

Figure 1 shows XRD spectra of the products hydrothermally synthesized for 4 and 24 h in comparison with the pristine dawsonites, $NH_4Al(OH)_2CO_3$ and $KAl(OH)_2CO_3$. It can be seen that all compounds displayed similar diffraction patterns, with only monotonous shift of the diffraction peaks of pristine dawsonites. Therefore, it is reasonably expected that the phase based on the solid solution of $K_x(NH_4)_{1-x}Al(OH)_2CO_3$ has been formed.

Table 1. The contents of K and Al in precursors synthesized at 120 °C for different reaction time

	K/wt %	Al/wt %	NH_4^+/wt %	Reaction Time/h
1	11.58	18.21	6.68	4
2	9.00	18.48	8.17	8
3	5.14	18.88	10.18	24
4	2.11	19.20	11.83	72

Table 1 lists the contents of K and Al in the products hydrothermally synthesized for different periods. Since there was no other phase identified besides the compound $K_x(NH_4)_{1-x}Al(OH)_2CO_3$, the content of NH_4^+ ion in the products can therefore be calculated simply based on the chemical formula of the solid solution and listed in Table 1. It was indicated that when the reaction time was extended to 24 h, the product revealed a solid solution of $K_x(NH_4)_{1-x}Al(OH)_2CO_3$, with $x = 0.1885$. The molar ratio of K/Al was 1:5.31 which is similar to the molar ratio in the K–β-Al_2O_3 with the molar ratio of K/Al 1:5.33. The as-synthesized solid solution precursor (Figure 1c) was crystalline. Therefore, this product can be selected as the precursor for K–β-Al_2O_3.

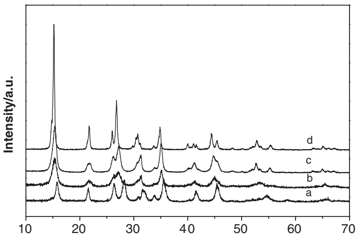

Figure 1. XRD spectra of the precursor hydrothermal synthesized at different time (a) pure $KAl(OH)_2CO_3$, (b) 4 h, (c) 24 h, (d) pure $NH_4Al(OH)_2CO_3$.

Figure 2 shows that the calcined products of the solid solution precursor were essentially amorphous when the calcination temperature is lower than 850 °C. Previous work[13] demonstrated that $KAlO_2$ and Al_2O_3 appeared when the potassium and ammonium dawsonite were heated between 600 and 700 °C, respectively. In our case, however, there was no presence of these two phases until the heating temperature was up to 850 °C, which may indicate that there was different thermal effect between the solid solution of $K_{0.1885}(NH_4)_{0.8115}Al(OH)_2CO_3 \cdot 0.33H_2O$ and the pristine dawsonite compounds. The formation of this kind of amorphous products was attributed to the slow release of NH_3 and CO_2 gases with the decomposition of the solid solution. Furthermore, very complex solid-state reaction might happen at 1050 °C, and potassium aluminates appeared. But it was not easy to confirm what kind of the phase was. Rising the calcining temperature to 1250°C, K–β-Al_2O_3 phase, i.e. $K_2O \cdot 5.33Al_2O_3$, was clearly detected as shown in Figure 2.

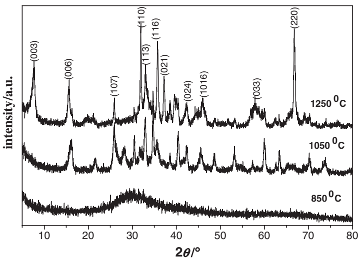

Figure 2. XRD spectra of the calcined powders.

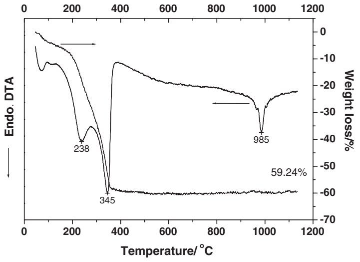

Figure 3. DTA/TG curves of the precursor hydrothermal synthesized at 120 °C for 24 h.

According to the DTA/TG curves (Figure 3) of the precursor, the first and second endothermic peaks at 238 °C and 345 °C were ascribable to the decomposition of $NH_4Al(OH)_2CO_3$ and $KAl(OH)_2CO_3$, respectively. At 985 °C, the endothermic peak was attributed to the solid state reaction between the complex decomposition products. As a result, $K_2O \cdot 5.33Al_2O_3$ powder with good crystallinity was obtained at 1250 °C.

In conclusion, a solid solution precursor for K–β-Al_2O_3 phase was successfully synthesized via hydrothermal multicomponent coprecipitation method. The precursor was confirmed as a kind of solid solution of $K_{0.1885}(NH_4)_{0.8115}Al(OH)_2CO_3 \cdot 0.33H_2O$. The K–$\beta$-$Al_2O_3$ phase has formed by the decomposition of the precursor at 1250 °C. Further studies will be aimed at producing a K–β-Al_2O_3 powder with higher crystallinity and well-developed crystal structure.

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