Thermally Stable Aluminas for High Temperature Applications

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Thermal decomposition of the ammonium analogue of the mineral dawsonite, $NH_4Al(OH)_2CO_3.H_2O$, yields high surface area γ-alumina. The surface area can remain as high as 145 m^2/g after calcination at 1000 °C. $NH_4Al(OH)_2CO_3.H_2O$ can also be used as precursor for alumina-based binary or mixed oxides. Treatment of $NH_4Al(OH)_2CO_3.H_2O$ with appropriate amounts of $Ba(OH)_2$ and $La(NO_3)_3$ led to the formation of layered aluminate structure on subsequent heating. Highly thermally stable materials with surface areas of up to 25 m^2/g after sintering at 1400 °C were obtained.

Aluminas are widely used as catalyst supports. γ-Al_2O_3 being the most common support in chemical and petrochemical industries. It also has applications at high temperatures such as catalytic combustion and automotive emission control. γ- Al_2O_3 is a high surface area metastable phase formed most commonly by decomposition of $Al(OH)_3$. Raising the temperature to about 1100 °C leads to a phase transformation of the solid to give the α-alumina structure. Thermal transformations that occur due to transition from γ-alumina into less reactive low surface area α-alumina can be inhibited by addition of a suitable additive. Foreign ions incorporated into γ-alumina can obstruct aluminium diffusion and thereby stabilise the crystal lattice of γ-alumina towards sintering. There has been extensive interest in the effect of additives to alumina, for example the addition of barium or lanthanum oxides to alumina leads to the formation of layered β-alumina structure,[1,4] the sintering of oxides is significantly suppressed and a higher surface area is maintained at high temperatures. Polycrystalline barium β-hexaaluminate is known to maintain relatively larger surface areas at higher temperatures than α- and γ-Al_2O_3.

β-Alumina such as $BaO.6Al_2O_3$ and La_2O_3 .$11Al_2O_3$ are commonly prepared by hydrolysis of mixed metal alkoxides, followed by sintering at high temperatures.[3,4] This paper reports a new synthesis technique for γ- and β-Aluminas with high surface area from the ammonium analogue of the mineral dawsonite, $NH_4Al(OH)_2CO_3.H_2O$.

In conventional techniques, when aluminium ions are reacted with OH^-, the resulting precipitate can be one of a number of well-known hydrated aluminas. Depending on the working conditions, boehmite, pseudo-boehmite, or one of the trihydrates can be formed. Upon calcination, the hydrated alumina decomposes to activated γ-alumina. When ammonium bicarbonate is used as a precipitant, a different crystalline phase is formed under certain conditions. This crystalline phase has been identified by its distinct X-ray diffraction pattern as $NH_4Al(OH)_2CO_3$, the ammonium analogue of dawsonite, $NaAl(OH)_2CO_3$.

The infra-red spectrum of $NH_4Al(OH)_2CO_3.H_2O$ features C-O stretching modes in the 1300-1500 cm^{-1} range and O-H and N-H stretching modes consistent with OH^- and NH_4^+ respectively. The thermal gravimetric analysis (TGA) shows a total weight loss of 66.2% up to 300 °C, slightly lower than the predicted value of 67.5%. After heating to 300 °C, the sample displayed neither CO_3^{2-}, nor NH_4^+ bands in the infra-red spectrum, indicating complete decomposition to Al_2O_3. A very small weight loss observed as the temperature was increased to 800 °C was due to the elimination of surface OH. No evidence was found for the formation of AlOOH as an intermediate during heating.

Although there are references in the literature on $NH_4Al(OH)_2CO_3$,[5-6] there is little information regarding its textural properties or its potential as a catalyst, catalyst support or alumina-based materials precursor.

Decomposition of $NH_4Al(OH)_2CO_3$ prepared in this study led to a very high surface area Al_2O_3. Surface areas up to 450 m^2/g were obtained after calcination at 700 °C. Analysis of N_2 adsorption isotherms reveals a complete absence of micropores. The product was amorphous to X-rays after calcination at 700 °C, but selected area electron diffraction indicated the formation of γ-Al_2O_3 with micro-crystallinity. TEM studies showed small equiaxial particles with an average size of 7 nm (Figure. 1). Alumina obtained by this technique appears to be highly thermally stable. The surface area can remain as high as 145 m^2/g after calcination at 1000 °C for 2 h.

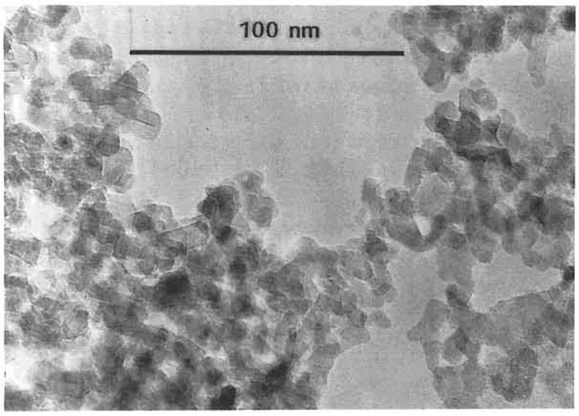

Figure 1. Transmission electron micrograph of γ-Al_2O_3 calcined 1000 °C.

Using $(NH_4)Al(OH)_2CO_3$ as a starting material, β-alumina can be prepared by adding appropriate amounts of $Ba(OH)_2$ or $La(NO_3)_3$ to a stirred slurry of $(NH_4)Al(OH)_2CO_3$ in water. The resulting solid is then separated and sintered.

BaO-Al_2O_3 system : The X-ray diffraction patterns of 20 wt% BaO/Al_2O_3 sintered at elevated temperatures show mainly $BaAl_2O_4$ and γ-Al_2O_3 up to 1100 °C,. At 1200 °C, $BaO.6Al_2O_3$ phase appeared and became dominant and finally at the sintering temperature of 1400 °C, the conversion of $BaAl_2O_4$ and γ-Al_2O_3

to $BaO.6Al_2O_3$ was complete. The sample heated to 1400 °C consisted of single phase $BaO.6Al_2O_3$ and with no diffraction lines characteristic of $BaAl_2O_4$. Noticeably no α-Al_2O_3 formation was found at any temperature. A transmission electron micrograph of the β- alumina phase is shown in Figure 2, with the distance between the broad white fringes in the thinner parts of the crystal approximately 11 Å. It is noted that the c-axis of the β-Al_2O_3 is about 22 Å. A surface area of 22 m²/g was obtained after calcination at 1400 °C for 4 h.

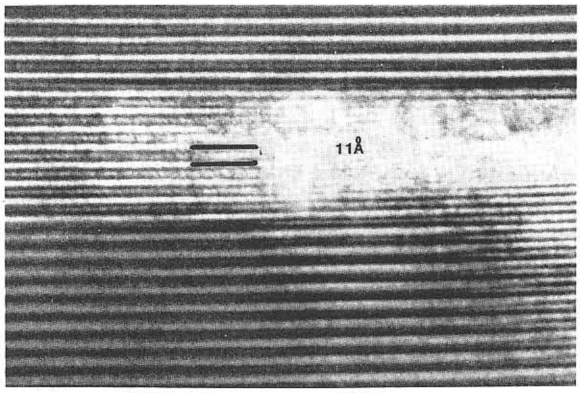

Figure 2. Transmission electron micrograph of β-Al_2O_3 calcined 1400 °C.

La_2O_3-Al_2O_3 system: The XRD of 22.5 wt%La_2O_3/Al_2O_3 calcined at high temperatures shows the existence of some $LaAlO_3$ at 1200 °C. The conversion to β-phase was completed at 1400 °C. This composition is commonly reported in the literature as La_2O_3 $.11Al_2O_3$.[4] The addition of La_2O_3 to Al_2O_3 leads to the formation of La-β-alumina which is effective in maintaining the surface area of alumina. A surface area of 20 m²/g was obtained from the $La_2O_3.11Al_2O_3$ calcined at 1400 °C for 4 h.

Figure 3 shows the surface area as a function of sintering temperature for Al_2O_3, $BaO.6Al_2O_3$ and $La_2O_3.11Al_2O_3$

All samples showed a sharp fall in surface area from 1100 °C to 1200 °C. This decrease in surface area is due to the transformation from the metastable Al_2O_3 into the equilibrium α-Al_2O_3. However in the presence of BaO and La_2O_3, further decrease at higher temperatures for $BaO.6Al_2O_3$ was suppressed by the formation of the β- phase. A surface area of 25 m²/g was obtained after sintering at 1400 °C for 4 h.

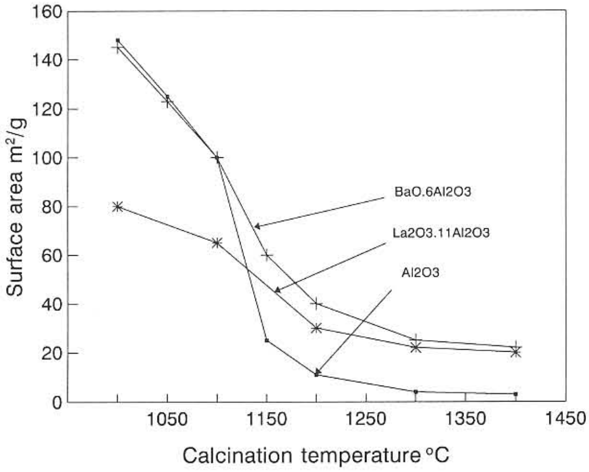

Figure 3. Surface area of γ-Al_2O_3 and β-Al_2O_3 as a function of calcination temperature

The need for a thermally stable support material is increasing for high temperature catalytic processes. $NH_4Al(OH)_2CO_3.H_2O$ was found to be a suitable precursor for high surface area aluminas. From this precursor, β-Al_2O_3 with a similar surface area to that obtained from alkoxide hydrolysis can be prepared. This technique is relatively simple and requires no organic solvents or expensive materials.

References

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