Note

Preparation of fine sized boehmite

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Preparation of boehmite of fine particle size (< 6 μm) was attempted by three different routes. Flash calcination of gibbsite at about 325°C for 2 h gave the desired material. However, the other two methods, dehydration of pseudoboehmite (at 110°C) and hydrothermal neutralisation of aluminate with acid gave boehmite of larger particle size (11 and 17 μm, D50).

Pseudoboehmite, AlO(OH) · 1.7 H2O, boehmite, AlO(OH) and aluminatrihydrates are employed as precursors in the preparation of catalysts, catalyst supports and adsorbents1-5. These precursors are essentially of very small particle size (~ 6 μm). In the preparation of FCC catalyst6 aluminium hydroxide and oxyhydroxides are used to trap the unwanted metallic impurity nickel. Boehmite is a very important precursor capable of being generated by dehydroxylation of any one of the three crystalline polymorphs (gibbsite, bayerite and nordstrandite) of alumina trihydrate or dehydration of pseudoboehmite. In the current study, the preparation of microstructured boehmite was examined making use of the gibbsite and pseudoboehmite. To achieve the objective, hydrothermal synthesis of boehmite prepared by pH adjustment of sodium aluminate has also been examined.

Well crystallised gibbsitic grains of fine particle size may well be envisaged as micro-reactors, wherein steam is generated during heating and attains high partial pressures of water, simulating locally and transiently conditions of flash drying initially. Dehydroxylation to boehmite gets initiated at ~180°C according to the following equation:

\[ \text{Al(OH)}_3 \rightarrow \text{AlO(OH)} + \text{H}_2\text{O} \] \hspace{1cm} \text{(1)}

Formation of γ-alumina occurs at temperature above 450°C. Contemporaneous to the above reaction (1), if any impurity of alumina exists, it can also get converted into boehmite by the reaction at high partial pressure of water:

\[ \text{Al}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{AlO(OH)} \] \hspace{1cm} \text{(2)}

Thus, heating finely powdered gibbsite at 325°C is expected to result in microstructured boehmite and the current investigation examines such possibility.

The second alternative route examines the dehydration of the pseudoboehmite gel prepared by using alum and sodium aluminate at ~60°C maintaining the pH in the range of 7 to 7.5. In a third approach, sodium aluminate was neutralised with sulphuric acid at ~95°C and the resulting product was examined for the nature and size.

Materials and Methods—Commercial gibbsite of two different particle sizes (D50 ~ 5.7 μm and ~17 μm) were procured. Sodium aluminate and sulphuric acid were of LR grade.

Gibbsite (~ 10 g) was taken in crucibles (SiO2 and Pt) and placed in a muffle furnace (of the following dimensions: length, 35 cm; breadth, 12 cm; height, 13 cm) maintained at 325°C. Periodically samples were withdrawn (by opening the front door of the muffle furnace) and the nature and the particle size of the products were determined. Some experiments were conducted at higher temperatures (approx. 525°C).

Pseudoboehmite was dehydrated at ~150°C for about two hours and the resulting samples were examined for their nature and particle size.

Sodium aluminate and H2SO4 solutions were reacted to different pH values while following the titration curve. The resulting products were digested at 95°C for 2 h, washed and dried at 110°C for 2 h. Dry samples were characterised for their nature and size.

The XRD characterisation of the nature of the products was made by employing Siemens D-500 Kristaloflex diffractometer using Ni filtered CuKα radiation. Particle size distribution measurements were made using Coulter Counter Multisizer II.

Results and discussion—The starting gibbsite showed 0.4% moisture, loss on ignition by heating in a muffle at 900°C for 2 h is 34.04%. TGA showed a loss of 34.7%, DSC showed an endotherm at ~325°C, FTIR showed hydargillitic (Al-OH) frequencies at 3524 and 3488 cm⁻¹. Gibbsite with particle size (D50) of 5.74 μm has shown the anticipated thermal behaviour when heated at ~325°C, this is presented in Fig. 1. Prominent gibbsitic7 peak intensities are observed

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(scan at RT, curve a) at 18.4, 20.2 and 20.6° (2θ) with the raw material as such. Dehydration for 30 min resulted in the decrease in the peak intensity of gibbsite at 20.6° (2θ) on the one hand and the appearance of new peaks of boehmite (at 14.1 and 28.8° (2θ) on the other. As the dehydroxylation continued further, the gibbositic peaks disappeared, whereas the intensities of boehmitic peaks continuously increased. At 90 min both the gibbositic peaks vanished. Between the period of 120 and 150 min, the boehmitic peaks remained unaltered in intensity (and area) and hence suggesting the completion of the formation of this transitional alumina. This time domain is a large and favourable operational window for the preparation of boehmite. However, the third hour product indicated a small reduction in the peak intensity of boehmite. These findings have suggested that boehmite formation was complete in about two hours.

Table 1 shows the particle size (D_{50}) observed with the products formed during the dehydroxylation for different periods. Gibbsite with a D_{50} value of 5.74 μ has been dehydroxylated into boehmite of 5.35-5.66 μ size indicating the absence of sintering during the process. This has demonstrated that thermal treatment at ~325°C for 105 ± 25 min results in microstructured boehmite as anticipated. However, at higher temperatures (~525°C) in about 15 min amorphous alumina was formed. When the same exercise was repeated with gibbsite of higher (~17 μ) particle size (D_{50}), the X-ray diffraction patterns of the heated products were nearly similar but the particle size of the resulting boehmite remained the same as that of the starting gibbsite (as revealed by Coulter Counter measurements).

**Pseudoboehmite dehydration**—Pseudoboehmite possesses fractional structural water, i.e., for every molecule of AlO(OH), the structural water present amounts of 1.7 ± 0.2 molecules. The XRD fingerprints^{2} of this material are:

<table>
<thead>
<tr>
<th>2θ (°)</th>
<th>d (Å)</th>
<th>2θ (°)</th>
<th>d (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.08</td>
<td>6.28</td>
<td>28.4</td>
<td>3.14</td>
</tr>
<tr>
<td>38.4</td>
<td>2.34</td>
<td>49.1</td>
<td>1.86</td>
</tr>
</tbody>
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The particle size of the wet gel was 9 ± 3 μ. This could be size reduced to about 5 ± 1 μ by colloid milling. The wet gel as such or after colloid milling was dried (at 110°C) and products of particle size of 10-12 μ were obtained. This clearly suggests that thermal sintering occurred during drying. Hence, this route is not suitable if particle size of <6 μ are needed.

**Hydrothermal precipitation**—The occurrence of an arrest in pH titration curve (Fig. 2) suggests that there are two possible aluminous species formed during the neutralisation. AlO_2-neutralisation by H^{+} will proceed through several intermediates. The pH of zero charge of the final material is ~9.2 from Fig. 2 and the same value is reported^{8} in literature for boehmite. This suggests that the product formed during the hydrothermal precipitation is boehmite. XRD finding (Fig. 3) indeed substantiates the same. FTIR studies have shown the appearance of the hydrargillitic frequencies at 3524 and 3488 cm^{-1} indicating the formation of boehmite. These bands disappeared on heating at temperature above 525°C in 10 min. (This is because boehmite became γ-alumina).
TGA also showed about 34.1% loss on ignition. Literature also shows\textsuperscript{9,10} the formation of boehmite as an intermediate in the pH range of 6-8. Aluminium hydroxide was neutralised in the presence of fulvic acid in the study. However, in the present investigation, aluminate was neutralised with sulphuric acid.

Boehmite has been identified as the major phase in all the eight cases of hydrothermal precipitations (Fig. 3). In some precipitations, however, gibbsite was present as impurity ($\leq 10\%$). Small quantity of gibbsite formation under our experimental conditions is anticipated (aquation of aluminate leads to gibbsite formation and addition of 5% acid solution necessarily involves unintended aquation). However, the products upon drying at...
325°C turned into boehmite (Fig. 3). The particle size of boehmite samples obtained by this route was \( \sim 17 \mu \) \((D_{50})\) and hence the products are unacceptable.

In conclusion the ideal route for preparation of fine sized boehmite \(<6 \mu\) is to flash calcine gibbsite at \( \sim 325^\circ\)C for 2 h. The current investigation has clearly demonstrated a simple procedure for preparing microstructured boehmite.

References
1 Stiles A B, Catalyst supports and supported catalysts, theoretical and applied concepts, (Butterworths, Boston), 1987, 11.