Alumina NanoFibers Obtained by pH-Swing Method

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Introduction. Recently, fibrillar aluminas are attracting great attention because they could offer, as catalyst supports, high capacity of hydrodemetallization of petroleum residue, since this fraction contains large asphaltene molecules that should diffuse and react within the large pores. So far, pH-swing method, which involves variations of pH within a set of acid and basic values [1,2], has been scarcely applied to control pore size distribution and morphology of aluminas. The method is simple and involves conventional soluble Al-salts. In this work, a series of bohemite-phase aluminas were synthesized by a pH-swing method. Preparation variables, which included: Number of swings, Al-source and pH-values, were studied in order to affect the textural properties and obtain fibrillar particles.

Experimental. Fibrillar aluminas were prepared by a pH-swing method, which is based on the exponential U-shaped solubility curve of hydroxylated aluminas, and described elsewhere [1]. In this procedure, shown in Fig. 1, a portion of acid Al-salt solution is added to a portion of alkaline NaAlO₂ solution and kept at either acid pH or basic pH, for a given time and temperature. Repeating this cycle several times (number of swings) by adding alternating portions of either solution, it is possible to vary the textural properties of the product. All textural properties were derived from the adsorption isotherm of N₂ at 77 K. Transmission Electron Microscopy (TEM) was used to examine particle shape. X-ray diffraction was used to identify alumina structures.

Results and Discussion. In order to optimize pH-swing procedure, we found
that pure boehmite phase can be obtained when using pH 2 to 8. When basic pH above 8 was used, a mixture of boehmite and bayerite was obtained. Average pore size of pH-swing aluminas can be widely varied simply by changing the number of swings (see Fig. 2 and Table 1). For instance, pore size distributions of aluminas obtained with, 2-8 swings have pore size ranging 90 to 180 Å. Notwithstanding, pore size population becomes very spread out, specially when Al-source is sulfate and above 6-swings, the pore size distribution is narrow and practically the same. However, after 6- or 8- swings, sulfate-derived aluminas show very wide pore distributions, while those of NO₃⁻ or Cl⁻ -derived ones maintain considerably narrow distributions. Aluminas obtained after 4-swings showed a pseudomorph bundle of fibrils aligned in parallel fashion. All aluminas obtained with 6- or 8-swings (regardless of the Al-source) showed fibrilar particles (see Fig. 3) of about 50-60 Å thick. These fibrils stack randomly, resulting in a structure with low contact area between the fibrils with large porosity. The fibrils array exhibits strong resistance to sintering, even at 720 °C. Thus, after calcining at 720 °C, boehmite transforms into γ-Al₂O₃ with total pore volume and SSA of samples containing high fibrils concentration (e.g. SO₄²⁻-source, 8-swings) being 1.0 cm³/g and 214 m²/g, respectively. Other methods to obtain alumina nanofibers require the assistance of poly(ethylene oxide) surfactants [3] or the use of Al-alcoxides [4].

Table 1 Effect of the number of pH swings in the textural properties of sulfate-source aluminas.

<table>
<thead>
<tr>
<th>Number of swings between pH 2-8</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>6</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>SSA (m²/g)</td>
<td>197</td>
<td>218</td>
<td>240</td>
<td>246</td>
<td>247</td>
</tr>
<tr>
<td>PV (cm³/g)</td>
<td>0.44</td>
<td>0.61</td>
<td>0.81</td>
<td>0.93</td>
<td>1.1</td>
</tr>
<tr>
<td>PS (Å)</td>
<td>90</td>
<td>112</td>
<td>135</td>
<td>151</td>
<td>177</td>
</tr>
</tbody>
</table>

SSA: specific area, PV: pore volume, PS: Avg. Pore size

Fig. 3. TEM micrograph from sulfate-derived alumina obtained after 8-swings and calcined at 720°C

References