ELECTRON-MICROSCOPIC INVESTIGATION OF CHROMIUM HYDROXIDE IN THE PROCESS OF PRECIPITATION

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The structure, activity, and selectivity of heterogeneous catalysts depend substantially upon the conditions of their production, beginning with the earliest steps [1]. In catalysts produced by precipitation, the basic textural characteristics evidently are already laid down in the process of precipitation. In this work we undertook an attempt to investigate in detail the process of precipitation and formation of a chromium hydroxide precipitate by electron microscopy, since an x-ray diffraction study gives no information on the structure of the hydroxide, in view of the amorphous nature of Cr(OH)₃.

EXPERIMENTAL

Cr(OH)₃ was prepared by precipitation from a 10% solution of Cr(NO₃)₃ with a 6% ammonia solution at a temperature of 20° and constant pH during the entire precipitation process. Three samples were obtained, precipitated at pH 7.5, 8.3, and 9.5. The electron-microscopic investigation was conducted by the aqueous suspension method on the "Tesla" BS-413 electron microscope with resolving power 6-8 Å. Preliminary experiments established that no crystals are formed from a solution of Cr(NO₃)₃, the concentration of which is ten times as great as in the experiment on precipitation, when a drop is applied on the mesh-specimen holder. Figures 1-3 present electron micrographs of the Cr(OH)₃ precipitates obtained at pH 7.5, 8.3, and 9.5, 2 min after the beginning of precipitation. A statistical analysis of the photograph indicates that with increasing pH of precipitation, the number of finer crystals increases, and the maximum of the distribution curve is shifted in the direction of finer particles (Fig. 4). It is characteristic that the particles that precipitate in the first 2 min possess a distinctly rectangular shape (see Figs. 1-3). There is an abrupt change in the shape of the particles, forming hexahedra, 4 min after the beginning of precipitation (Fig. 5). The further course of the process of precipitation is accompanied by a decrease in the number and dimensions of the crystals and by the appearance of an amorphous phase (Fig. 6). During aging of the precipitate, a crystalline phase again appears, and the picture resembles that which was observed at the beginning of the precipitation (see Figs. 7 and 5). Such a change in the structure of the precipitate during the precipitation process is characteristic of all the investigated pH values.

Table 1 presents changes in the size of the crystals at various stages of precipitation and aging of samples produced at various pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>2 min</th>
<th>4 min</th>
<th>30 min</th>
<th>2 h</th>
<th>1 day after aging</th>
<th>2 days after aging</th>
<th>3 days after aging</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5</td>
<td>170-230</td>
<td>-</td>
<td>250-1400</td>
<td>300-1900</td>
<td>300-1900</td>
<td>300-1900</td>
<td>-</td>
</tr>
<tr>
<td>8.3</td>
<td>200-2900 300-1300 200-1500</td>
<td>-</td>
<td>200-1500</td>
<td>150-600 120-600</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9.5</td>
<td>130-1300 200-1300</td>
<td>-</td>
<td>60-200 200-700 200-700 140-1000</td>
<td>-</td>
<td>-</td>
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</tr>
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</table>

DISCUSSION OF RESULTS

The decrease in the size of the crystals that precipitate in the first moment of precipitation, at higher pH of precipitation, is naturally explained by a change in the conditions of supersaturation of the solution.
Fig. 1. Electron micrograph of Cr(OH)$_3$ suspension, precipitated at pH 7.5, 2 min after the beginning of precipitation.

Fig. 3. Electron micrograph of Cr(OH)$_3$ suspension, precipitated at pH 9.5, 2 min after the beginning of precipitation.

Fig. 2. Electron micrograph of Cr(OH)$_3$ suspension, precipitated at pH 8.3, 2 min after the beginning of precipitation.

Fig. 4. Distribution curves of Cr(OH)$_3$ particles according to size as a function of the pH for preparations 2 min after the beginning of precipitation: 1) pH 7.5; 2) pH 8.3; 3) pH 9.5.

Fig. 5. Electron micrograph of Cr(OH)$_3$ suspension, precipitated at pH 8.3, 4 min after the beginning of precipitation.

Fig. 6. Electron micrograph of Cr(OH)$_3$ suspension, precipitated at pH 8.3, 2 h after the beginning of precipitation.

Fig. 7. Electron micrograph of Cr(OH)$_3$ suspension, precipitated at pH 8.8, after 3 days of aging.

with respect to the concentration of Cr$^{3+}$ ions. At a higher pH, the supersaturation is greater and, consequently, the size of the crystals that precipitate is smaller. The apparent contradiction with the data of [2], in which Ni(OH)$_2$ particles became larger when the precipitation pH was increased, is due to the appreciable formation of ammonia complexes of nickel at high pH, which greatly reduces the supersaturation of the solution.

It is considerably more difficult to explain the processes related to the formation of crystals during the first minutes of precipitation by a change in their form, disappearance of the crystals, and the appearance of an amorphous phase and secondary appearance of crystals during aging. An examination of Table 1 data shows that the size of the crystals formed during aging either differs little from the size of the crystals that precipitated during the first minutes of precipitation (pH 7.5 and 9.5) or is considerably smaller (pH 8.3). From this it follows that the crystals formed during aging were produced not from primary crystals that precipitated at the beginning of the precipitation process, since in the latter case they should have been substantially larger on account of the process of growth during precipitation and aging, but from an amorphous phase, which in turn was formed from the primary crystals.

The occurrence of such complex processes during precipitation may evidently be understood if we consider the process of precipitation of chromium hydroxide as a polymerization of aquo ions of chromium.