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Continuous Supercritical Hydrothermal Synthesis of Boehmite Nanoparticles: influence of morphology on adsorbed water.

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1. Introduction

The last decade has been marked by an explosion of research on nanotechnologies. In particular, inorganic nanoparticles are of interest in broad domains ranging from electronics to pharmaceuticals. These fields require high performance crystallized materials with controlled structures, compositions, particle sizes and morphologies as well as surface properties.

Boehmite nanoparticles (an aluminium oxyhydroxide, γ -AlOOH) have been the first synthesized using the continuous supercritical hydrothermal synthesis reported by Adschiri *et al.* in 1992¹. Since then, plenty of research exhibited the optimization of sizes, morphologies and surfaces of boehmite nanoparticles through simple modifications of process parameters (temperature, pressure or residence time) or precursor solution (concentration, pH, and modifier). For instance, Adschiri *et al.* have reported rhombic plate particles at low temperature and concentration while at high temperature or high concentration, particles were hexagonal plates¹. Furthermore, by adjusting other parameters, they obtained sword-like and football-like particles. Morphology and size modifications influence the bulk and surface properties. Especially, it has been shown an excess of water in nanoboehmite synthesized by traditional hydrothermal techniques (previously referred as pseudo-boehmite). Herein, adsorbed water involved on various boehmite morphologies synthesized by the continuous supercritical hydrothermal synthesis were characterized by XRD, HRTEM, XPS and TGA.

2. Materials and Methods

The flow synthesis was carried out in a custom-designed reactor used to avoid clogging problems. It is composed of a 0.74 m of 4.78 mm internal diameter stainless steel pipe. The set-up consisted of a HPLC pump, two ceramic band heaters and a back pressure regulator.

The reactor is pressurized to 25 MPa at room temperature using distilled water and then set to 400 °C the reaction temperature. The reactant is fed by a flow rate of 2.2 to 9.4 mL.min⁻¹ depending on the targeted residence time t , defined by: $t = \frac{V\rho}{F}$ with V , the reactor volume (m³), F , the mass flow rate (kg.s⁻¹) and ρ , the solution density at the reaction conditions (kg.m⁻³). In this study, the targeted time has been modified between 14 and 60 s. At the outlet of the reactor, the chemical reaction is quenched thermally downstream with an ice bath. Inside the cooling system, a stainless steel fritted filter (5 μ m porous size) is placed to collect the produced nanoparticles. Sometimes, the highly dispersed and smallest particles passed through the filter to be recovered as a colloidal solution.

The starting solution consists of an aluminium nitrate nonahydrate Al(NO₃)₃·9H₂O (> 98% purity) dissolved in distilled water. The concentration of this solution was modified between 5.10⁻³ mol.L⁻¹ and 1.10⁻¹ mol.L⁻¹ resulting in pH variation. For a fixed precursor concentration, pH value was also modified from 2.2 to 12 by adding droplets of HNO₃ or NaOH solutions.

3. Results and discussion

Well-crystallized boehmite has been synthesized no matter of conditions except at high pH of 9.3 where Bayerite β -Al(OH)₃, a more hydrated phase, was also formed and at a pH of 12 where no particle was recovered. It has been exhibited that simple modifications of the continuous process allow to synthesize various shapes of boehmite from hexagonal plates to rodlike morphologies observed by HRTEM analysis. Therefore, crystal structure was modified and investigated by powder X-ray diffraction. The crystallite size along [100], [010] and [001] which characterized the morphology were calculated using the Debye-Scherrer equation².

Evolution of pH and concentrations have almost the same impact on particle morphology evolution. Indeed, nitrate anions are mainly adsorbed on the OH-containing facets such as (010) and (001), inhibiting the growth along these facets and leading to the preferential growth of boehmite along the [100] direction². Furthermore, these anions were adsorbed as a hydroxyl nitrate such as Al₂O₂(OH)NO₃ on the boehmite surface which might let less possible adsorbed sites for water⁴. This has been exhibited with XPS analysis. In fact, the oxygen O_{1s} peak showed three peaks at approximately 530.7 eV, 531.8 eV and 532.5 eV which correspond to Al-O-Al structure, structural hydroxyls and adsorbed water at the surface, respectively. Oxygen atoms involved in H-O-H bonds corresponding to the surface adsorbed water decreased from 20.4 at.% to 17.6 at.% by changing the precursor concentration from 5.10⁻³ mol.L⁻¹ to 1.10⁻¹ mol.L⁻¹.

TGA showed 3 or 4 steps which correspond to the loss of physisorbed water, sometimes chemisorbed water (0-2 wt.%), the dehydroxylation to form γ -Al₂O₃ (13-14 wt.%) and finally the dehydration of transition alumina (loss of residual hydroxyl groups, 1-2 wt.%). These characterizations did not show drastic variations depending on the samples.

4. Conclusions

To conclude, we successfully synthesized various morphologies of boehmite particles using the continuous supercritical hydrothermal synthesis through simple modifications of process parameters and feed solutions. These boehmite particles were morphologically studied using XRD and HRTEM. As reported, nanobohmite often contained a high quantity of adsorbed water which has motivated our research. Indeed, adsorbed water and structural hydroxyls were analyzed using XPS. A modification of the content of water as a function of the boehmite morphologies is proved. Finally, as TGA results underlined, the boehmite synthesized using this supercritical technique did not reveal a major excess of water compared to the 30 wt.% of pseudobohmite synthesized using Yoldas process⁵.

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