

On Understanding the Formation of Extrudable Pastes with Pseudoboehmite

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Introduction

Most catalysts used in the petrochemical and petroleum industries consist of metals supported on γ -alumina pellets or spheres. The γ -alumina is formed by calcination of pseudoboehmite (α -alumina monohydrate) at 500-550°C. In order to be activated to the more porous form, the majority of pellets and spheres form are initially formed by extrusion of a paste that is formed by mulling the monohydrate with water and, in many cases, with further addition of a peptizing agent (e. g. nitric acid). Mulling is done on several different industrial mixers (e.g. Eirich, Simpson or Littleford) which add “work” to the materials by different degrees of shear and grinding. During the mulling operation, a paste with sufficient plasticity is formed that is adequate for extrusion. Further mulling tends to decrease this plasticity. Generally, testing of the mixture is done by “feel” to qualitatively determine the apparent “cohesiveness” that leads to the proper plasticity. The endpoint is usually determined by the operators “feel”, based on experience. Less often, a test with a Carver press is used, generally only in scoping.

At Rutgers, over the last several years, we have been trying to develop suitable methods to detect and understand the chemical and physical changes that occur during the apparently simple mulling operation that leads to extrudability. We have been using a small granulator (Fukae Powtec) with 200-500 g batches and sampling every 15 min. The samples so collected have been subjected to a variety of characterization tests to try and understand what has happened at the alumina monohydrate surface- PXRD, FTIR, UV-VIS, Nitrogen Porosimetry (PSD, SA), and particle size distribution by light scattering and SEM. In addition, a Carver extrusion test has been applied in an attempt to correlate our observations with extrudability.

Materials and Methods

Catapal B was obtained from Chevron and directly from Sasol. Most mixing experiments have been done on a laboratory size (100-400 g charge) Fukae granulator; some experiments have been performed on an Eirich RO2 mixer (1000-3000g charge) at BASF catalysts.

Results and Discussion

Three phenomena are observed during the mulling of alumina monohydrate and provide a conceptual framework for further discussion:

- *Dispersion of alumina agglomerates.* Particle sizes measured by light scattering decrease by at least 30-50% over mixing times of up to 1 hr due to peptization. It is this dispersion that generates the needed pore volume and surface area.
- *Granulation.* During mulling, larger spheroidal particles (e.g. 1-5 mm) are formed and continue to enlarge. These “granules” seem to be a positive indicator of extrudability and may consist of a plastic hydrogel-like material formed by interaction of the alumina surface with water (the “binder” in granulation terminology)
- *Heat.* During mixing the temperature increases dramatically; in the small mixer, temperatures of 45-60°C are attained within 45-60 min; in the larger Eirich mixer, temperatures as high as 100°C are observed at high mixer speeds. The amount of heat generated increases with the amount of water added, suggesting that a chemical reaction is taking place, perhaps hydration of the surface.

Heat is also generated during extrusion, to a degree that requires cooling of the barrel. The cause of that heat may be friction, chemical reaction or may be due to compression in the barrel.

We have been studying this system by FTIR using Attenuated Total Reflectance (ATR). Using this method, we have been able to probe the 400-4000 cm^{-1} region allowing us to investigate the variation of modes directly related to the hydrogen bond interactions. Because of the overlapping between the chemisorbed H_2O stretching modes and the AlO-H stretching modes from the alumina interlayer making the deconvolution difficult, we have instead investigated the variation of the AlO-H bending mode of the alumina interlayer (bulk mode at 1070 cm^{-1}) which appears isolated from any other absorbance features. We have also access to the stretching mode of the hydrogen bond between the surface alumina crystallites and the water molecules (surface mode at 900 cm^{-1}). We have monitored the variation of both modes as a function of the mixing time between the catapal B and the water with or without nitric acid. The preliminary results show that without addition of water, the catapal B is hydrolyzed by the humidity of the air to about 50%: with increasing humidity, we observe an increase of the surface mode suggesting that only the surface of the crystallites is modified. However, when water is added to the catapal B and mixed, the area of the bulk mode increases indicating that the alumina interlayer exhibits stronger hydrogen bonding: the distance of the zig-zag interplane is decreasing. Adding nitric acid to the system has no effect on the surface mode suggesting that the H^+ proton is interacting with the surface of the crystallites. However, the bulk mode is affected for $c(\text{HNO}_3) > 1\%$ in such a way that the H-bonding interactions are lower. This behavior can be explained by the diffusion of HNO_3 in the alumina crystallites.

Significance

Understanding of the mechanisms involved in the formation of catalyst supports by extrusion, spray drying, spherulization, etc. could lead to improved mechanisms for controlling the quality of these products. In addition to the characterization methods mentioned above, we are now trying to understand the rheological characteristics of the alumina-water-peptizing agent system.

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