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Processing alumina spheres by a colloidal route using silica-polystyrene hybrid nanoparticles

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ABSTRACT

Colloidal granulation of alumina is an original shaping process leading to spherical granules directly in suspension from a diluted system. It is based on a heterocoagulation mechanism where silica added in small amount acts as a binding agent. The role of a submicronic latex of polystyrene was investigated, free, or as a hybrid object covered by silica nanoparticles synthesized by a Pickering emulsion polymerization method. Latex particles were not able to form primary agglomerates despite a high negative zêta potential. An addition of latex in combination with silica improved the state and homogeneity of the final microstructure which could be attributed to a decrease of the internal strains during the processing. Hybrid nanoparticles, by combining the binding agent (silica) and the organic phase, were able to form primary agglomerates, and to finally obtain alumina spheres exhibiting both a spherical morphology and a greater homogeneous microstructure.

1. Introduction

Colloidal processing of ceramics is a concept appeared in the 80's in order to improve the reliability of the ceramics shaping processes [1], through the manipulation of the interparticle forces in powder suspensions. The nature and intensity of the interparticle forces make possible the control of the suspension stability, from dispersed colloids repelling each other on close approach thanks to the presence of a steric or an electrostatic barrier, towards an agglomerated state of the suspension where the attractive forces of Van der Waals predominate [2]. The internal structure of the suspension directly determines its rheological properties, which behaves either as an easily pourable liquid or as a stiff paste by changing the interparticle forces from repulsive to attractive [3,4].

Most of the colloidal processes are based on the use of highly concentrated ceramic suspensions in order to reach the highest green density and finally the greatest properties after sintering through the obtention of a homogeneous and dense microstructure. However, a new process of powder granulation was proposed several years ago in our group to elaborate ceramic spheres directly in suspension at low solid concentration (typically 3%vol.) [5,6]. This previous work showed that a mixture of alumina (400 nm) and of silica (25 nm) powders presents a common pH range for which the zeta potential of the two powders is of opposite polarity (positive for alumina and negative for silica). Thus nanometric silica adsorbs on the submicronic alumina surface causing particles agglomeration and suspension flocculation [7,8]. Formation of "primary agglomerates" with a size close to 2–3 μm constitutes the first step of the process. When such "primary agglomerates" are mixed under a continuous rotational movement, they form a powder bed immersed into water, in which they are in permanent contact. As the alumina surface is not entirely covered by silica nanoparticles, opposite charges exist locally induce mutual attraction between agglomerates and ensure their combination provided that collisions occur during the rotational movement. This second step leads to "secondary agglomerates" which exhibit a typical size of 1 mm very close to that of the final sphere. The mutual friction between the objects and friction in contact with the bottle wall promotes a spherical morphology and smoothens the surface while keeping the agglomerates cohesion. This process can be considered as a "wet granulation by colloidal method" using a diluted suspension.

Few processes are able to lead to spherical final products close to 1 mm in diameter especially when starting from a water-based

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suspension [9,10]. Classical granulation techniques are spray drying [11,12], freeze-granulation [13–16], the "oil drop" technique from sol-gel [17,18], or coagulation techniques with alginate for example [19,20]. However if there are a lot of techniques allowing the formation of spheres with a diameter ranging from 50 to 500 μm, the granulation of millimetric spheres still remains challenging. Another great interest of heterocoagulation is the use of very simple equipment. Moreover little energy is necessary for water removal, which is accomplished at room temperature under a controlled moisture. However, although the size distribution of the spheres appears as almost monomodal, a major drawback lies in the presence of large internal defects in the objects. These defects are detrimental to the mechanical strength of the spheres once they have been dried and consolidated by firing. The potential use of these millimetric spheres is expected in some deagglomeration processes in the field of ceramic suspensions. To explain the formation of such defects, it has been suggested that during drying, finer grains migrate with the liquid, which redistributes within the internal porosity when moving toward the surface before evaporation. Then, cracks occur because capillary forces exceed the cohesive strength of the body itself. In classical ceramic processing problems caused by the drying step are generally avoided by adapting the formulation and using organic additives (binders and plasticizers) [21,22]. Some works were thus conducted on the colloidal granulation of titania with a mixed system of a polyanion, the poly(sodium 4-styrenesulfonate), and a polycation, the chitosan [23]. The reaction of condensation between the two polyelectrolytes led to in situ formation of filaments acting as a binding agent, favoring the coalescence step, and at the same time preventing the formation of cracks within the granules, by allowing the migration of the grains due to the capillary forces during the drying stage [24,25].

More recent work in our group was dedicated to a completely new subject: synthesis of organic-inorganic hybrid materials for ceramic applications [26]. Such nano-objects have attracted a lot of interest from all the scientific community in recent years, and became rapidly a multidisciplinary field of research, where chemists, material scientists, physicists, and biologists converge for the development of new designed and smart structures [27–29]. The combination of organic properties (plasticity, deformability, shaping and structural properties, lightness, optical properties, biocompatibility) and inorganic properties (mechanical properties, density, cost, structural, optical, and electronic properties, biocompatibility) make the development of hybrid nanostructures a very exciting approach in the research of new materials and new applications [30–32]. In this context Pickering emulsion polymerization was investigated and succeeded in the synthesis of silica-polystyrene hybrid particles, where polystyrene latex with a diameter around 400 nm were homogeneously decorated by silica nanoparticles (25 nm) [26].

This work proposes to study the role of submicronic polystyrene particles for the heterocoagulation of alumina, with the aim of improving the drying step of such granules by introducing an organic phase which is supposed to provide plasticity, and as a consequence, leading to a decrease of the internal strains and to a more homogeneous structure during this critical step. A latex of polystyrene, and silica-polystyrene hybrid particles, were synthesized in our lab. They were added into a diluted suspension of alumina in order to study their ability to form primary agglomerates, through the measurement of zêta potential and sedimentation tests. Then some compositions were chosen to conduct the colloidal granulation, and lead to the formation of the granules in suspension. The size of the granules, their morphology, their internal structure, their density and their mechanical properties were compared to those obtained with silica only.

2. Experimental

2.1. Raw materials

A high purity (99.9%) **alumina powder** (AKP30, Sumitomo, Japan) was used (d_{50} = 400 nm, 7 $m^2\ g^{-1}$). Then three different binding agents were used:

- commercial **silica** nanoparticles dispersed in an alkaline medium (Ludox TM50, Grace Davison USA, d_{50} = 25 nm, 140 $m^2\ g^{-1}$).
- a **latex of polystyrene** synthesized by an emulsion polymerization technique as described in a previous paper [26]. In summary, the protocol of this synthesis was based on an emulsion of styrene (10 wt.% in water) prepared with poly (ethylene glycol) methyl ether methacrylate (PEGMA, Mn = 2080 g mol^{-1}, 0.10 wt.% in water) and heated at 70 °C. After degassing with N_2, the initiator sodium persulfate NaPS (0.75 wt.% relatively to styrene) was introduced into the reactor and the reaction of polymerization started. The reaction was maintained during six hours under a nitrogen flow and a magnetic stirring. After the synthesis, the particles were dialyzed during five days, in order to remove free ions and non-reacted materials from the liquid medium.
- **silica-latex hybrid nanoparticles** synthesized by an emulsion polymerization technique. The same protocol as the one detailed above for the latex of polystyrene was followed, by adding silica (Ludox TM50) with PEGMA in the styrene emulsion, in order to create a Pickering emulsion, and promotes the anchoring of silica nanoparticles at the polystyrene surface and form hybrid structures [26]. A non-ionic initiator 2,2′-azobis(2-methylpropionitrile) (AIBN) was used instead of NaPS in order to improve the particle coverage by silica, as demonstrated in the mechanisms proposed in a previous paper [26].

All the reagents were provided by Aldrich and used without further purification.

2.2. Elaboration of spheres, drying and sintering

10 mL of a suspension of alumina at 3.0 vol.% in deionized water was introduced into a glass container of 30 mL and dispersed with an ultrasonic horn (no deflocculant was used, pH of the suspension = 6.5, sonication time 2 min, Pulse on 3 s/Pulse off 1 s). Then different amounts of a binding agent presented in the last section were added into the alumina suspension. The low concentration of the alumina was necessary to conserve a low viscosity after the addition of the binding agent necessary for the granulation process [5].

The mixture was stirred under a controlled speed (40 rpm, ie 0,3 m s^{-1}) with a stirrer named "rollers rock'n roll" (Bioblock, France) which creates a sinusoidal wave, inducing the formation of primary agglomerates, and the growth of spheres. The maximum duration of stirring was 7 days.

Once formed, the sphere cohesion was sufficiently high so that they could be transferred into a large dish, where the excess of liquid could be removed. The spheres were then let for drying during 48 h at ambient temperature. Then they were sintered at 1500 °C (3.3 °C/min, 3 h, Nabertherm LHT 04/17).

2.3. Characterization methods

Zêta potential measurements were conducted as a function of the pH on the raw materials dispersed at 1.0 wt.% in deionized water with an ESA analyser (Acoustosizer II S flow through system,

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