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Novel extrudates based on the multiscale packing of alumina particles and boehmite or aluminophosphate binders

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ABSTRACT

Porous extrudates consisting of a packing of model spherical alumina particles with different median diameters (1.7 μm and 19 μm) were prepared. Peptized boehmite and aluminophosphate binders were used in order to ensure the cohesion of the materials. Combined effect of the multiscale packing of porous alumina particles contributed to generate supports with low binder content and good mechanical strength. The resulted microstructure is very attractive for porous materials such as catalyst supports and adsorbents and can be easily controlled by selecting relevant filler particles.

1. Introduction

The packing of particles has long been a subject of interest and widely reported on the literature [1–7]. The multiscale packing is a useful concept to have significant effects on most powder processing operations and on the resulting product quality. The formulation of the high-performance concretes and the ceramics fabrication, are examples of different practical domains where the multiscale packing is often applied.

The high-performance concretes are constituted by a packing of particles of at least four different grading classes, which can range from the centimeter to the micron, and bounded by the cement. Maximum packing density is obtained by a hierarchical organization where the fine particles can fit into the residual space formed by the large particle packing. It results from the optimized packing, besides a low-cost, a better flow, and an ideal compression resistance [8,9].

The packing formed by a bimodal powder mixture is commonly used on ceramics fabrication to get a higher green packing density and minimal shrinkage so that the microstructure of the resulting ceramics is improved. Differently from the high-performance concretes, micrometer and sub-micrometer particle sizes are generally preferred in the ceramics fabrication [10–12].

In the present work, we have been interested to apply the multiscale packing concept on the preparation of a novel porous alumina material. Catalyst supports and adsorbents are some foreseen applications for these materials.

Traditional alumina supports are prepared by extrusion of a paste made from kneading of boehmite or pseudo-boehmite, water and a peptizing agent as nitric acid [13–20]. Depending on the boehmite peptization capacity and on the acid solution concentration, some micrometric aggregates can stay occluded inside the mesoporous matrix. The resulting microstructure is constituted of nanometric aggregates of crystallites and micrometric agglomerates of these aggregates which generate, respectively, inter-aggregate and inter-agglomerate spaces, responsible for the mesoporosity and macroporosity. These traditional materials include no more than one micrometric class of particles.

The aim of this study was to prepare extrudates having a microstructure formed by the packing of fine and large porous alumina particles, where the voids between the large particles are filled by the fines, and the remaining inter-particle voids are partly occupied by a binder. The novel supports reported in this paper were prepared from a mixing of at least two kinds of porous micrometric alumina with a binder matrix to ensure the cohesion of the particle packing. Traditional peptized boehmite (AlOOH) and aluminophosphate (AlPO) binders [21–27] were used. The main difference between the two binders is their behavior during calcination: while peptized boehmite is transformed into porous alumina, the aluminophosphate evolves towards dense alpha-cristobalite-like and tridymite-like phases (non-porous). The resulting extrudate microstructure and the textural and mechanical properties were analyzed.

2. Experimental

2.1. Preparation of alumina extrudates

Fine and large alumina particles were used to prepare extrudates having a microstructure based on ordered multiscale packing. In this work, we used spherical particles because the packing of spheres leads to the highest density arrangements as traditionally reported in the

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literature [1–7]. In addition, the alumina powders were chosen in order to respect a medium size ratio between the large and fine fractions of at least 10 and thus promote a high packing density [1,2,5,7]. Fine alumina particles were prepared by spray-drying of a boehmite sol following internal conditions (IFPEN), while the large particles were commercially available (Sasol). Fig. 1 shows the morphology (SEM) and the particle size distribution (laser diffraction) of each alumina powder used. The textural properties and the packing density of the individual alumina particles and of the binary mixture constituted of fine (20 wt.%) and large (80 wt.%) fractions are summarized in Table 1.

The packing cohesion was ensured by a binding matrix that could be formed by a peptized boehmite with nitric acid (HNO_3, 60%), or by an aluminophosphate generated from the reaction between a boehmite powder and orthophosphoric acid (H_3PO_4, 85%) as reported by Lee et al. [21]. These binding matrices were formed "in situ" during the kneading step.

The amount of boehmite introduced was determined to guarantee that all inter-particle voids of the alumina packing could be filled by the binder paste. We considered that the binder volume (V_b) should be equal to the inter-particle volume (V_v) as indicated in expression (1), where ε denotes the inter-particle porosity ($\varepsilon = 1 -$ packing density) and V_p the volume of alumina particles. Then, the mass of binder (M_b) is calculated by expression (2), where ρ_{bp} is the density of the binder paste.

$$V_b = V_v = \frac{\varepsilon V_p}{1-\varepsilon} \quad (1)$$

$$M_b = V_b \rho_{bp} \quad (2)$$

The formulations presented in this paper were performed using a constant proportion of boehmite (24 wt.%) independently to the binding matrix type. This proportion was determined considering a packing of only large alumina particles (packing density = 0.65, $\varepsilon = 0.35$) assembled by a peptized boehmite binder matrix (HNO_3/AlOOH molar ratio = 0.03; $\rho_{binder\ paste} = 1.4\ g\ cm^{-3}$).

First, a paste was prepared by mixing the alumina particles, the boehmite powder (Pural SB3 — Sasol) and the acid solution (HNO_3 or H_3PO_4) at room temperature in a laboratory kneading machine (Brabender 50 EHT). Alumina (76 wt.%) powder and boehmite (24 wt.%) powder were first poured into the mixing chamber, and then the solid components were pre-mixed for 2 min at a constant rotor speed of 10 rpm. Thereafter, the acid solution was added at a constant flow in order to introduce all the solution in about 5 min, and then, the mixing was performed for 30 min at a rotor speed of 16 rpm. If a neutralization step was carried out, at the end of the mixing period with the nitric acid, an ammoniac solution was introduced to the paste and the kneading was followed for about 5 min at a rotor speed of 16 rpm. Usually, a basic solution is employed in order to modulate the rheological behavior of the paste and the textural properties of the supports [20].

The amount of water introduced with the acid solution was controlled according to the formulation and to the monitored torque measurements to get an extrudable paste. Here, we characterize the paste composition through the mass ratio of solids to liquid "*S*/*L*", wherein *S* represents the mass of alumina and boehmite powder, and *L* leads with the mass of all liquids.

Cylindrical extrudates were then created by extruding the paste through a die of 3 mm diameter and of 6 mm length by using a laboratory extruder machine (MTS Extruder). They were dried in a ventilated oven at 80 °C for 12 h, followed by calcination in a muffle furnace at 600 °C for 2 h in air with a heating rate of 3 °C min^{-1}. The resulting extrudates were then broken into pieces of 3 to 6 mm length, as it is the case for catalyst supports. Table 2 summarizes the formulations reported in this paper.

2.2. Characterization

Pore size distribution of the calcined extrudates was performed through mercury porosimetry (Autopore IV, Micromeritics). The mesopore volume was determined in a pore size range from 3.6 to 50 nm, and the macropore volume from 50 to 7000 nm. BET surface area measurements were obtained from N_2 adsorption isotherms conducted at −196 °C using an ASAP 2420 (Micromeritics) instrument.

Microstructures of polished and finished extrudates were observed by scanning electron microscopy (SEM) (JEOL JSM 6340F). Materials presenting the aluminophosphate binding matrix were analyzed by SEM associated to EDS (energy dispersive X-ray spectroscopy) in order to distinguish the phosphorous localization.

Side crushing strength (SCS) of the resulting extrudates was determined using a VINCI mechanical test machine at a constant crosshead speed of 0.5 mm min^{-1} until failure occurred. The measurements were

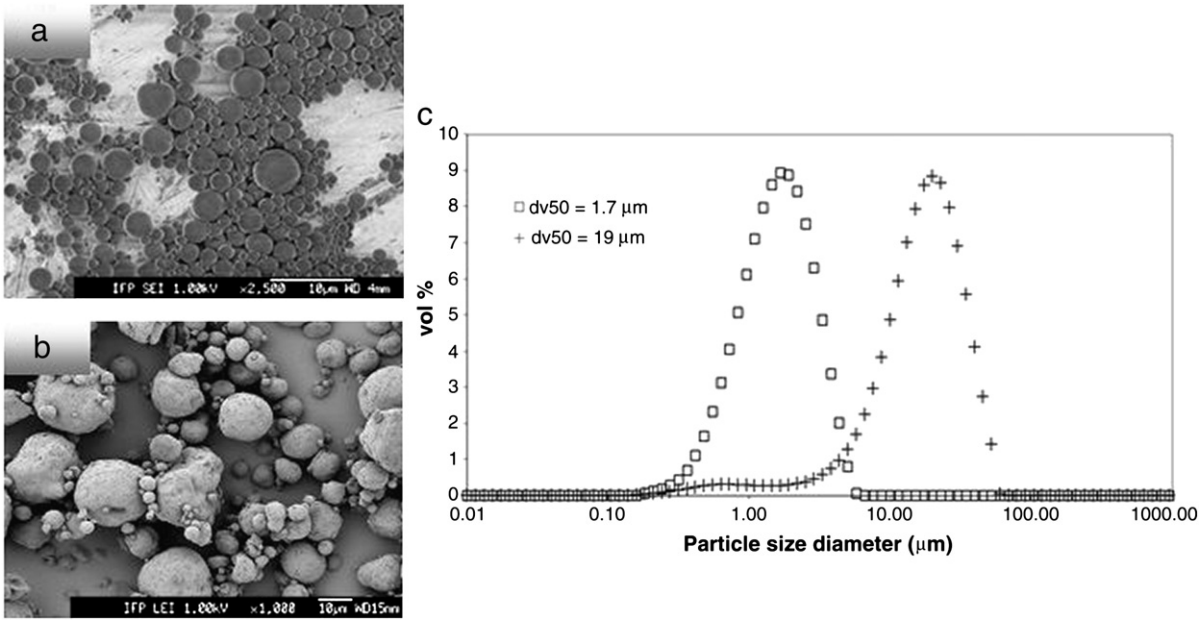

Fig. 1. SEM images of (a) fine (dv_{50} = 1.7 µm) and (b) large (dv_{50} = 19 µm) alumina particles and their particle size distribution (c).