

# Improved $\gamma$ -alumina support based pseudo-boehmite shaped by micro-extrusion process for oxygen carrier support application

Noemie van Garderen<sup>a,b,\*</sup>, Frank J. Clemens<sup>a</sup>, Christos G. Aneziris<sup>b</sup>, Thomas Graule<sup>a,b</sup>

<sup>a</sup>Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for High Performance Ceramics, Ueberlandstrasse 129, 8600 Dübendorf, Switzerland

<sup>b</sup>Technical University Bergakademie Freiberg, Institute for Ceramic, Glass- and Construction Materials, Agricolastraße 17, 09596 Freiberg, Germany

Received 8 December 2011; received in revised form 22 March 2012; accepted 23 March 2012

Available online 1 April 2012

## Abstract

$\gamma$ -Alumina extrudates for chemical-looping combustion in fluidized bed reactors were shaped by varying acetic acid concentrations between 0.07 and 3.76 M. Influence of pseudo-boehmite peptization on structural properties, microstructure, chemical phases and attrition resistance was determined. With addition of acetic acid, the  $d_{90}$  of boehmite agglomerates after 1 h kneading decreased from 134 to 40  $\mu\text{m}$  at pH 4. Due to this, the extrusion diameter was reduced from 1500 to 200  $\mu\text{m}$ , as well as median pore radii (from 30.1 to 5.3 nm). Porosity was about 70%. Addition of more than 1.87 M acid lead to a slight increase in mesopore sizes caused by some pore blocking caused by the formation of aluminium acetate salts. A small micropore surface was determined with  $t$ -layer model from Harkins and Jura. Higher attrition resistance was observed for samples peptized with lower acid concentration because of the closer contact between particles after decomposition.

© 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

**Keywords:** A. Extrusion; Peptization; Microstructure; Attrition resistance

## 1. Introduction

Supports for oxygen carriers or catalysts are frequently made from transition aluminas, such as the  $\gamma$  structure. They can be synthesized by extrusion of pasty alumina hydroxide and calcination in air between 550 and 850 °C to dehydrate boehmite (or gibbsite) and to crystallise its amorphous phase. Boehmite is obtained from decomposition of gibbsite or hydrargillite, precipitation of aluminium solutions with a basic or acidic reactant or by sol–gel from aluminium alcoholates [1].

As explained by Fauchadour et al. [2] and Paglia et al. [3], boehmite is used as a precursor for  $\gamma$ -alumina catalyst supports in petroleum, chemical and medicine industries due to its adequate surface chemistry, porosity and thermal stability. However, care has to be taken in the preparation process to obtain adequate properties and avoid stability problems of the

final product [4]. Pseudo-boehmite (PB) is composed of an amorphous phase that will lead to a high specific surface  $\gamma$ -alumina material [5] and a low crystallised  $\gamma$  structure.

Dispersion of boehmite and PB in water are generally done at low pH. Different techniques allow the formation of a paste: either via sol–gel route [6,7] or by peptization [8]. The sol–gel technique is based on Yoldas discovery in the late seventies [6,9]. He explained that hydrolysis and condensation of aluminium hydroxides could lead to a monolithic gel. Chandrass and Balasubramanian showed the possibility to extrude alumina sol with a diameter of 350  $\mu\text{m}$  [7]. Peptization of aluminium hydroxide is made by addition of an acid solution to disperse the large particles/agglomerates and plasticize the feedstock [10]. In the peptization route, two reactions can occur, either hydrogen ions of acetic acid can react to the hydroxo groups of the particles to form aquo groups or boehmite –ol groups can form free hydroxo groups. Lamberov et al. mentioned that peptization leads to the breaking down of primary particles on (0 1 0) planes and to a partial dissolution of the hydroxide leading to water soluble basic aluminium salts between primary particles [11]. Formation of aluminium ionic micelles is obtained when high enough acid content is added to

\* Corresponding author at: Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for High Performance Ceramics, Ueberlandstrasse 129, 8600 Dübendorf, Switzerland. Tel.: +41 58 765 41 59; fax: +41 58 765 41 50.

E-mail address: [vangarderennoemie@yahoo.fr](mailto:vangarderennoemie@yahoo.fr) (N. van Garderen).

the particles. In case the ratio is too low, no dispersion of the particles will occur. It is known that precipitation made at temperatures from room temperature to 150 °C leads to the most labile structures because of the presence of weak bonds such as van der Waals interactions and coagulation contacts between primary particles and water. Lamberov et al. studied the effect of peptizing agent at 160 °C and at room temperature [11]. They found a lower mechanical resistance for samples prepared at high temperature and high pH. Water necessary to extrude pseudo-boehmite is influenced by the specific surface area of the powder and its crystallite size. Indeed, a powder with high specific surface area would need a high volume of water, which would lead to a large pore volume after drying [12]. Several patents and publications deal with extrusion of alumina with HNO<sub>3</sub> as a peptizing agent and NH<sub>4</sub>OH as a surfactant [13,14]. Hille et al. studied the influence of nitric acid on boehmite and mentioned the change in rheological properties in boehmite hydrogel caused by the formation of basic aluminium nitrates, which can enhance redispersion or desaggregation until the obtention of boehmite hydrosol [15]. Use of acetic acid was already reported in several works [10,11,16,17]. Recently, Tregubenko compared the use of acetic, oxalic and citric acids on PB and advised the use of oxalic acid because the obtained aluminium salt decomposes in a narrow temperature range [16]. However, the use of acetic acid leads to a narrower mesopore size distribution [16]. Parameters, such as solid/liquid ratio, acid/AlO(OH) molar ratio and a mixing time from 5 to 60 min can influence the plasticity of the feedstocks [12]. Pseudo-boehmite pastes can also be extruded with addition of organic or inorganic binder or with other materials, e.g. alumina powders, to adapt the packing density of the feedstock [17–21]. Peptization is followed by thermal treatment, which can lead to the formation of basic aluminium salts that are decomposing during calcination and form a new aluminium oxide phase [10].

A bimodal porosity is usually suitable because smaller pores (micro- or mesopores) enhance the specific surface area and macropores increase transport and diffusion of the gas inside the porous structure. The pore size is grouped by IUPAC into three categories; the first one, called micropore corresponds to pores with a radius smaller than 1 nm. The second one, mesopore, has a size between 1 and 25 nm. Finally the third one, macropore, is composed of pores larger than 25 nm in radius [22]. During dehydration, slit-shape pores are created due to the loss of water in alumina hydrate larger crystals [11,20]. Levin et al. mentioned the presence of a bimodal pore size distribution, a smaller one (~5 nm) from the ordered packing of primary particles and a bigger one from secondary aggregates formed by unordered packing (between 20 and 100 nm) [10]. They stipulated that increase in nitric acid content leads to a decrease in pores larger than 500 nm in radius due to the formation of basic aluminium salts, which will decrease the total pore volume. An increase in pore sizes of about 5–15 nm was observed and assumed to be caused by a significant deaggregation of the secondary structure of aluminium hydroxide and an increase in basic

salts, leading to a blocking of the pores. However, according to Levin et al., this has no significant influence on pores smaller than 5 nm in radius because the acid diffuses from macropores to mesopores, and does not affect the micropores [10].

$\gamma$ -Alumina is known as having a relatively good attrition resistance. Attrition has been defined as “the unwanted breakdown of particles within a process” (this includes both abrasion and fragmentation) by the British Standard (BS 2955:1958) [23]. Vaux and Fellers considered that in fluidized bed reactors, sufficient strength and attrition resistance of the bed material are important to survive transport, during the filling of the reactor (thermal shock when injection of new particles) and during operation (bubbling, grid jets splashing of ejected particles), which will result in a particle–particle and particle–reactor wall impact [24]. A too low attrition resistance of the bed material can lead to a change in material properties (particle size distribution, surface area, packing density).

Granulates with a size between 100 and 500  $\mu\text{m}$  are required for fluidized bed reactors. A precipitated pseudo-boehmite was chosen for this work because it leads to higher porosity than boehmite. The powder was peptized with acetic acid during a high shear mixing process. This permits the stabilization of the material into a plastic paste. The salts are then decomposed during calcination. The drawback with pseudo-boehmite is that it does not peptize as easily as alkoxide based boehmite and therefore different acetic acid contents from 0.07 to 3.76 M were evaluated. This study aims to understand the influence of acetic acid molar concentration and more specifically of pH on pseudo-boehmite based extrudates in terms of extrudability, pore network (micro, meso and macro-porosities) and attrition resistance.

## 2. Experimental procedure

### 2.1. Raw material

Pseudo-boehmite G-250 (BASF, USA) with an agglomerate size  $d_{50}$  of 60  $\mu\text{m}$  (given by the supplier), based on the conversion of bauxite into gibbsite by the Bayer process, followed by an acid/base dissolution and precipitation, was selected for this study. To investigate the primary particle size, the specific surface area was measured as 295  $\text{m}^2/\text{g}$  by Brunauer–Emmett–Teller model (BET). Considering spherical particles, the  $d_{\text{BET}}$  was calculated as 9 nm and agglomeration factor close to 6900. For redispersion, deionised water and acetic acid (peptizing agent) were used (Fig. 1).

### 2.2. Processing

The humidity of pseudo-boehmite powder was measured at 130 °C before the mixing step to achieve the same liquid content in the batches. Liquid content is defined as the combination of powder humidity, water and acid added to the batch. The kneading time and number of revolution per

Download English Version:

<https://daneshyari.com/en/article/1461933>

Download Persian Version:

<https://daneshyari.com/article/1461933>

[Daneshyari.com](https://daneshyari.com)