



## Original article

## Impact of inorganic waste fines on structure of mullite microspheres by reaction sintering

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## ABSTRACT

The impact of waste composition and morphology on the properties of the mullite microstructure were studied by reaction sintering two types of siliceous waste powders with calcined alum sludge. Stoichiometric mixtures of fly ash or rice husk ash with the alum sludge were shaped into mullite microspheres by droplet coagulation. The mullitization reaction was followed by HT-XRD with a distinct difference in onset temperature. The specific powder composition of fly ash (presence of primary mullite) shifted the onset temperature to higher values as compared to the rice husk ash mixture. After sintering at 1600 °C, the mullitization reaction resulted in the same yield for both samples. Although the mullite content in the microspheres was equal, distinct differences on the microstructure could be observed. Reaction sintering of the fly ash mixture resulted in lower total porosity with smaller pore sizes.

## 1. Introduction

During the last decades, mullite has received significant attention as a potential material for various applications. Its attractive properties such as good chemical stability, low thermal expansion coefficient ( $4.5 \times 10^{-6} \text{ °C}^{-1}$ ), and thermal shock resistance enables the use of mullite as catalyst support in high temperature combustion processes [1,2]. Shaping the catalyst support in the proper shape and size is key to unlock its excellent performance in processes. The choice of the size, shape and porous architecture are mainly driven by the type of reactor, all with their own demands concerning the support properties [3]. For example, fluidized bed reactors require spherical supports with a narrow size and shape distribution to prevent catalyst loss due to mechanical attrition [4]. One of the known methodologies to achieve such requirements in shaping ceramic microspheres with controlled properties is droplet coagulation [5–7]. Microspheres are shaped by the ionotropic gelation of sodium alginate with a multivalent cation, offering a wide range of process parameters (e.g. concentrations, alginate and cation type and powder properties) to control the microsphere properties.

Different types of synthesis (chemical, fused, reaction sintered) to prepare mullite were demonstrated in previous studies, varying in reaction mechanism and precursors [2]. Chemical mullite materials are prepared by heat treatment of organic and/or inorganic precursors (e.g. tetraethoxysilane and aluminum sec-butyrate) with consequently a low

mullitization temperature (below 1200 °C) [8]. Fused mullite is obtained by melting alumina and silica above 2000 °C, enabling the preparation of translucent materials [9]. Rodrigo et al. studied the reaction sintering of fine-grained powders to obtain dense mullite structures. Firing powder mixtures of silica and alumina at 1600 °C resulted in mullite with high purity [10]. During the past years, a wide range of starting materials was used to shape mullite materials, indicating also the potential use of inorganic waste powders as raw material [11,12]. Often the mullitization reaction is enabled by the incorporation of an inorganic waste powder in a primary material as for example fly ash in bauxite alumina [13]. In this way, the cost effectiveness of the mullite preparation can be controlled. Vieira et al. prepared mullite by smart mixing of alum sludge (anodization process) and slate waste resulting in mullite materials [14]. However, the impact of the properties of the waste resources on the mullite preparation and sintered materials were not elucidated. Nevertheless, the variations in chemical composition, morphology and waste impurities (e.g.  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ) can have a promoting or inhibiting effect on the sintering of mullite materials, with consequently an impact on the obtained porosity and microstructure [15,16].

This work stipulates the added value of mixing different fine-grained waste materials without the use of primary materials, in order to tune mullite materials with different properties and microstructures. In this study, calcined alum sludge is used as a substitute for commercial alumina. Alum sludge is generated as a byproduct of waste

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water treatment. It originates from the addition of an aluminum salt (e.g.  $\text{AlCl}_3$ ) to polluted surface water, enabling the coagulation of natural organic matter (NOM) into sludge [17]. This alum sludge contains colloidal aluminum hydroxides (36 wt% aluminum content) in the presence of process additives (e.g. flocculant) and additional impurities (e.g.  $\text{Al}_2(\text{SO}_4)_3$ , calcium) [18]. Previous work specified the need of pre-processing (calcination and washing), enabling the shaping of alum sludge into microspheres by droplet coagulation [18]. As mullite microspheres are based on the stoichiometric mixture (3:2) of  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ , silica rich waste powders were selected to add to the calcined alum sludge material. Both fly ash and rice husk ash are candidates as they contain high amounts of  $\text{SiO}_2$  in their matrix [19,20]. Substantial amounts of fly ash (FA) are generated by coal firing for power generation. Additionally, the depletion of fossil fuels for the power generation has stimulated the utilisation of biomass as a source of fuel. Hence, this generates a new type of inorganic ash. Among the various biomass resources, rice husk is one of the key residues for energy production [21]. The combustion of the rice hulls, in order to acquire energy, leads to the production of rice husk ash (RHA). These two types of  $\text{SiO}_2$  waste sources have been added to the alum sludge to investigate the ability to form mullite microspheres from 100% waste based resources as well as the consequences of the waste origin and composition on the microstructure of the mullite spheres.

The prime objective of this paper is to investigate the applicability of silica and alumina rich waste powders as precursors for the mullite preparation. Calcined alum sludge was mixed with two different silica waste fines (FA and RHA). Changes in mullitization reaction and mullite properties are expected originating from the differences in physical and chemical properties of the waste fines. Our aim is to study the extent of this impact of waste properties on the mullite preparation and consequently on the properties of the sintered microspheres. Furthermore, shaping microspheres by droplet coagulation incorporates a hetero-element (e.g. calcium) in the microstructure [6]. Hence, also the presence of the added calcium will be evaluated.

## 2. Materials and methods

### 2.1. Materials

Silpazz was supplied as rice husk ash (RHA) source (NK Enterprises, India). Fly ash (FA) was collected from the Tarong Power Station (Australia). Alum sludge (AS) was collected at the water treatment plant of “De Watergroep” (Kluizen, Belgium) and pre-processed as described in our previous paper [22]. Sodium alginate Br-W was provided by Brace GmbH (Alzenau, Germany). Additionally, calcium chloride (Sigma Aldrich, anhydrous powder  $\geq 97\%$  pure), isopropyl alcohol (VWR, 98%) and RO water ( $< 5 \mu\text{S}/\text{cm}$ ) were used.

### 2.2. Shaping microspheres

Prior to shaping the microspheres, a suspension containing 1 wt% sodium alginate and 30 wt% powder was prepared. Mixtures of the waste powders were made based on the chemical composition analyzed by XRF on the melt. The AS-FA (77.2% AS and 22.8% FA) and AS-RHA (83.7% AS and 16.3% RHA) suspensions were prepared by mixing stoichiometric amounts of respectively AS, FA and RHA with the sodium alginate solution in a planetary mixer. In addition, an AS suspension was prepared in order to distinguish the effect of the mullitization on the sintering process. The microspheres were shaped by gravitational droplet coagulation and denoted as AS/M, AS-FA/M and AS-RHA/M. During shaping, the suspension was pushed through a 600  $\mu\text{m}$  nozzle (Nordson EFD) and droplets were generated by gravitational force. The droplets fell in a coagulation bath containing 4 wt%  $\text{CaCl}_2$ , in order to induce the ionotropic coagulation. After 24 h, the wet microspheres were rinsed with tap and RO water to remove the excess of ions. Finally, the microspheres were washed with isopropyl alcohol

to reduce capillary forces during drying. The microspheres were dried at 105 °C for 24 h and sintered at varying temperatures between 1400–1600 °C with a heating rate of 2 °C/min under ambient air and pressure.

### 2.3. Characterization techniques

The chemical composition of the initial waste powders was examined by X-ray fluorescence (XRF) (HE XEPOS, Spectro Analytical Systems, Kleve, Germany). The powders were calcined at 1000 °C for 4 h in a muffle furnace prior to mixing in a platinum crucible with 100%  $\text{Li}_2\text{B}_4\text{O}_7$  flux in a flux:sample ratio of 10:1. The fusion of the sample was performed in an automatic fusion system (XrFuse 2, XRF Scientific, Brussels, Belgium), in which the sample was fused at 1250 °C during 11 min. An  $\text{NH}_4\text{I}$  tablet was added as release agent prior to pouring the fused sample in the pre-heated mold. Quantification of the elements was performed using a precalibrated software package for the quantitative analysis of geological fused bead materials.

The starting powders and sintered microspheres were characterized using X-ray diffraction (XRD) analysis (X'Pert Pro MPD diffractometer, PANalytical) with filtered  $\text{Cu K}\alpha$  irradiation. The analysis was executed in the 2 $\theta$  mode using a bracket sample holder with scanning speed of 0.04°/4 s continuous mode. The sintered microspheres were milled prior to the analysis.

The crystal phase changes in function of the temperature of thermal treatment were identified by high temperature X-ray diffraction analysis (HT-XRD, X'Pert Empyrean, PANalytical) with a high temperature chamber HTK 16 (Anton Paar) and applying  $\text{Co K}\alpha$  irradiation. The milled microspheres were placed on the platina sample holder and heated to 800 °C (10 °C/min). The sample was further heated to 1400 °C at a constant heating rate (10 °C/min) and XRD patterns were collected in steps of 100 °C. The measurements were conducted in dry air (50 ml/min).

Thermogravimetric analysis (TGA) was carried out using a STA 449 F3 Jupiter (Netzsch, Germany) in dry air (50 ml/min). The microspheres were analyzed from room temperature to 1500 °C (10 °C/min). The TGA device was coupled online with a quadrupole mass spectrometer TGA/STA-QMS 403 D Aeolus (Netzsch, Germany) with a heated capillary (200 °C).

To study the sintering behavior, pellets of crushed microspheres were analysed using a DIL 402 C dilatometer (Netzsch, Germany) in dry air (70 ml/min). The pellets were measured between room temperature and 1600 °C (10 °C/min).

The shape of the sintered microspheres was determined by optical microscopy using a Zeiss Discovery V12 stereomicroscope, equipped with a Plan Apo S 1.0 w FWD 60 mm objective. An Axiovision MRC digital camera connected to the microscope was used to generate images of the microspheres. Axiovision Rel. 4.8 software was employed to perform image processing as explained in earlier work [6].

The cross-section of the microspheres was investigated using a cold field emission scanning electron microscope (FEGSEM) of the type Nova Nano SEM 450 (FEI, USA) at 20 kV. The microspheres were encapsulated in epoxy resin, cut and polished prior to the analysis. Element mapping was performed by a Bruker XFlash Detector 5030 and a Bruker QUANTAX-200 EDS system. The total porosity was calculated on the cross-section using ImageJ. The outer surface of the microspheres was characterized at 5 kV.

The specific pore volume and pore size distribution was measured with mercury intrusion porosimetry (Pascal 140–240 series, Thermo Electron Corporation). The pore size was calculated using a surface tension of 480 Dynes/cm and a contact angle of 140°.

The side crushing strength (SCS) test on an Instron 5582 Universal testing machine was used to estimate the crushing strength of the sintered microspheres, following Couroyer et al. [23]. Ten spheres were crushed to calculate the average strength on a single shaped microsphere.

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