Journal of the European Ceramic Society xxx (2017) xxx–xxx

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Full length article

Highly permeable macroporous cordierite ceramics with controlled microstructure produced by particle-stabilized emulsions with a reactive thermal treatment

Yu Ma[a], Jinhong Li[a,*], Xiang Wang[a], Lijie Liu[b], Changhong Wang[c]

[a] *Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials, School of Materials Science and Technology, China University of Geosciences, Beijing, 100083, China*
[b] *National Academy of Innovation Strategy, Beijing, 100038, China*
[c] *School of Earth Sciences and Resources, China University of Geosciences, Beijing, 100083, China*

ARTICLE INFO

Article history:
Received 28 November 2016
Received in revised form 16 March 2017
Accepted 18 March 2017
Available online xxx

Keywords:
Hierarchical microstructures
Emulsions
Reactive sintering
High permeability
Cordierite

ABSTRACT

Macroporous cordierite ceramics, comprising hierarchical microstructures, are produced by a method of particle-stabilized emulsions, combined with a followed reactive thermal treatment. The microstructure is tailored by altering sintering temperature and solid content in the emulsion templates. Pore throats generate in-situ by introducing magnesite in templates, in contrast to conventional methods, which use either surfactants or depending on thin film contact. Moreover, microstructural evolution of samples is studied by DTA/TG, XRD, and SEM analyses. The results of analyses show that the formation of much more pore throats is closely related to the release of gas from the raw materials and volume shrinkage. The optimal process conditions are a temperature of 1300 °C and a solid content of 30 vol.%. The as-prepared sample displays a nitrogen permeability of $\sim 1.8 \times 10^{-11}$ m^2. The method shows great promise for producing many other highly permeable ceramics using pore former agents in the emulsion templates.

1. Introduction

Porous membranes are found extensively in many applications, such as catalyst supports, heat exchangers, water treatment, oil servicing industry, insulators, and so on. These applications require porous materials with high permeability and a significant compressive strength. Moreover, porous ceramic membranes have attracted extensive attentions because their resistance to high temperature or corrosive environments and high mechanical strength. Construction of macroporous ceramics is considered an effective solution to improve the permeability of membrane elements. In general, macroporous ceramics can be obtained by three main processing techniques: replica technique, sacrificial template method, and direct-foaming technique. [1–6] However, the use of these methods makes it difficult to control the porosity and morphology of the structure to meet specific industrial requirements. Thus, methods that enable tailoring of porous structures are of particular interest.

Recently, the use of emulsions as templates has been extensively researched and developed into a versatile method that enables the deliberate design of the porous structure. [7–11] In this context, Schluter et al. prepared monolithic hybrid ceramics with macroscopic structure using a surfactant assisted emulsion-based syntheses route composed of controllable micro and macropore distributions with mesoscopic cell windows .[12] Ge et al. synthesized macroporous silicon carbide ceramics using a suspension emulsions to obtain ceramics with an average pore size varying between 10.77 µm and 26.40 µm. [13] In spite of the success of these methods, more efforts are required to further improve this technology of pore-formation. Firstly, the film separating the emulsion droplets should be thin enough to form pore throats, which determines the mechanical strength of the ceramics. Secondly, the introduction of a surfactant to the emulsion for generating open porous structure complicates the process. Thirdly, the requirements for modification of starting materials are demanding, in terms of requirement of pure chemical reagents or polymer gels, that limit the extensive applications of the method. [7,9,10,12,14–17] In spite of these limitations, particle-stabilized emulsions are expected to have potential applications for fabrication of macroporous ceramics, primarily due to their facile preparation processes and wide choice of staring materials. [6,18,19] Even the stability of the particle-stabilized emulsions can

---

* Corresponding author.
E-mail address: jinhong@cugb.edu.cn (J. Li).

http://dx.doi.org/10.1016/j.jeurceramsoc.2017.03.035
0955-2219/

Please cite this article in press as: Y. Ma, et al., Highly permeable macroporous cordierite ceramics with controlled microstructure produced by particle-stabilized emulsions with a reactive thermal treatment, *J Eur Ceram Soc* (2017), http://dx.doi.org/10.1016/j.jeurceramsoc.2017.03.035

be increased by the formation of 3D networks of particles (flocculation). [20] which do not easily rupture during drying and sintering.

Ceramic membranes are commonly fabricated using inorganic materials such as silicon carbide, silicon nitride, mullite, alumina and cordierite, with silicon carbide, alumina and cordierite being the three commonly explored. [21–24] It is known that cordierite, as one of the phases of the ternary MgO-SiO_2-Al_2O_3, can be synthesized from a variety of raw minerals such as talc, kaolin, magnesite, coal gangue, and bauxite. [25,26] Cordierite is commonly prepared by the reaction of some of these mineral mixtures, compromising of other additives, within the range of 1200–1350 °C with some impurities in the minerals as fluxes in some cases. [27] Additionally, the sintering temperature is lower than commercially available alumina ($\geq$1700 °C) and silicon carbide ($\geq$2000 °C), due to its low melting temperature (1460 °C). [26] Therefore, talc raw materials were introduced here to prepare stable cordierite emulsion precursors, compromising of alumina and silica.

A facile method of particle-stabilized emulsions, combined with a followed reactive thermal treatment, was employed in this paper, to produce macroporous cordierite ceramics. Till date, there are very few literature reports for producing highly permeable macroporous ceramics using this method. Pore throats that generated in-situ were controlled in numbers and sizes by varying the sintering temperatures and cell film thickness. This is in contrast to the conventional methods using surfactants or depending on thin film contact. The thickness of closed-cell film that separated the droplets in the particle-stabilized emulsion templates was tailored by altering the solid contents (vol.%). Furthermore, the as-produced macroporous ceramics with a wide range of pore and pore throat size would be highly advantageous in many applications, such as thermal insulation and heat exchangers, as well as in catalyst supports or low-weight structures. The synthetic method uses a series of techniques, making it promising for large-scale highly permeable porous structures production.

2. Experimental

2.1. Raw materials

Commercially available talc raw mineral from Liaoning Province, China (2500 mesh, Jinhua Jincai Chemical Co., Ltd. Zhejiang Province, China), alumina (AR (analytical reagent), d_{50} = 300 nm, Xuancheng Jingrui New Material Co., Ltd. Anhui Province, China), silica (AR, d_{50} = 500 nm, Shenzhen Crystal Materials Chemical Co., Ltd. Guangdong Province, China) were used as starting materials as received, without further purification. It is worth mentioning that this kind of talc from Liaoning Province is frequently associated with magnesite, as a result of paragenesis. In the experiment, as shown in Fig. 1, the raw material for talc contains a certain amount of magnesite (~18 wt.%), which is used as pore throat former here. Calcite mineral (6000 mesh) was purchased from Changzhou Fengshuo Chemical Co., Ltd. Jiangsu Province, China, to prepare gehlenite. The short amphiphile propyl gallate ($C_{10}H_{12}O_5$) (AR), ammonium polyacrylate salt 40 wt.% in water and carboxymethyl cellulose sodium salt (CMC) (AR) were purchased from Adamas Reagent Co., Ltd. Sodium hexametaphosphate (AR) was purchased from Beijing Yili Fine Chemicals Co., Ltd. The other chemical reagents, water, ammonia (4 M), hydrochloric acid (2 M), and ethanol, were deionized. The chemical compositions of talc and calcite raw minerals were analyzed by X-ray fluorescence spectroscopy (XRF, Rigaku ZSX Primus) as shown in Table 1.

A fine powder of talc raw minerals was obtained by subjecting the initial material to fine grinding in a machine (Beijing Gospel Powder & Technology Co., Ltd.) for 1 h using alumina milling bottle, alumina balls (41.5–42 μm) and 1.0 wt.% sodium hexametaphosphate as dispersant with a grain size of 760 nm approaching the size of the alumina and silica powders, which is conducive to prepare particle-stabilized emulsions.

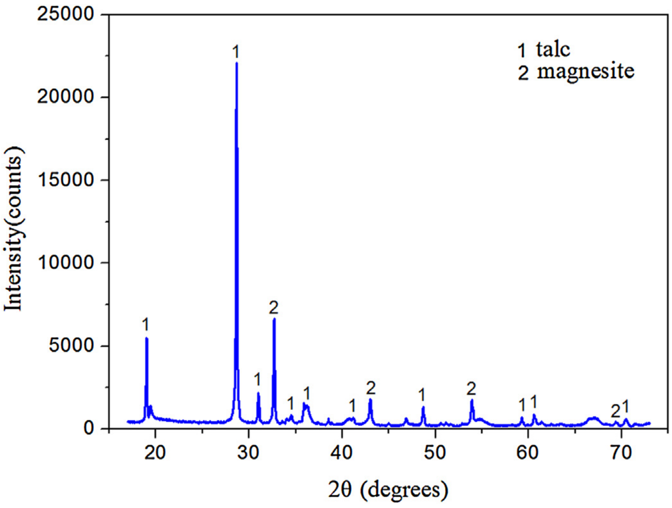

Fig. 1. XRD results of talc raw minerals.

2.2. Preparation procedure

All the powders, in appropriate stoichiometric amounts (talc 34.07 wt.%, alumina 33.32 wt.%, silica 32.36 wt.%) were blended together to obtain cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) and ball milled for 48 h, using Al_2O_3 balls to obtain a homogeneous suspension, after adding the dispersant of ammonium polyacrylate salt (1.0 wt.%) and binder of CMC (0.5 wt.%). [17] pH of the suspension was adjusted to 11 with ammonia and hydrochloric acid, in which the zeta potential was the lowest. A stable suspension is expected when the electrostatic repulsion between particles in a suspension is strong enough with the lowest zeta potential. [28] The zeta potential of the suspension was measured by a zeta probe (ZS90, Malvern Instruments Ltd., UK). The average particle size of the ball-milled particles in the suspension was measured by laser particle-size analyzer (Zetazizer Nano ZS90, Malvern Instruments Ltd., UK) and found to be 557 nm. Then the suspended particles were modified in-situ using 1.5 wt.% of short amphiphilic molecules. [29] The pH was readjusted to 11 under vigorous and continuous stirring (1000–1200 rpm) with an electric mixer. The proportions of the reagents mentioned above referred to the amounts of particles. The emulsification process was carried out using a household mixer (HR1613, Philips) at full speed of 16000 rpm for 5 min, after adding 300 vol.% (to the suspension) of octane as the oil phase. Finally, the emulsions were transferred to a culture vessel and dried under ambient conditions. After about a week, the dried samples were sintered at different temperatures ranging between, 1200 °C and 1350 °C, at a heating rate of 5 °C/min for 2 h.

To study the pore throat forming mechanism of cordierite ceramic, mullite (alumina 70.15 wt.%, silica 29.85 wt.%) and gehlenite (calcite 34.07 wt.%, alumina 33.32 wt.%, silica 32.61 wt.%) ceramics were prepared in the same way using the raw materials. The mullite and gehlenite were sintered at 1400 °C and 1300 °C respectively, at a heating rate of 5 °C/min for 2 h.

2.3. Characterization methods

XRD (D8 ADVANCE, Bruker, Germany) analyses were carried out on the grinding ceramic powder and as-received talc raw mineral. Thermal analysis (DTA/TG, SDT Q600, TA Instruments, America) was conducted at a constant heating rate of 10 °C/min from 400 °C

Please cite this article in press as: Y. Ma, et al., Highly permeable macroporous cordierite ceramics with controlled microstructure produced by particle-stabilized emulsions with a reactive thermal treatment, J Eur Ceram Soc (2017), http://dx.doi.org/10.1016/j.jeurceramsoc.2017.03.035