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Environment-oriented low-cost porous mullite ceramic membrane supports fabricated from coal gangue and bauxite

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HIGHLIGHTS

- Coal gangue was recycled to fabricate low-cost porous mullite membrane supports.
- A unique volume-expansion occurred due to a mullitization-crystal-growth process.
- A porous structure consists of glassy particles and embedded mullite crystals.

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ABSTRACT

Porous mullite ceramic supports for filtration membrane were successfully fabricated via recycling of coal gangue and bauxite at sintering temperatures from 1100 to 1500 °C with corn starch as pore-forming agent. The dynamic sintering behaviors, phase evolution, shrinkage, porosity and pore size, gas permeation flux, microstructure and mechanical property were systematically studied. A unique volume-expansion stage was observed at increased temperatures from 1276 to 1481 °C caused by a mullitization-crystal-growth process. During this stage, open porosity increases and pore size distributions broaden, which result in a maximum of nitrogen gas flux at 1400 °C. The X-ray diffraction results reveal that secondary mullitization took place from 1100 °C and the major phase is mullite with a content of ~84.7 wt.% at 1400 °C. SEM images show that the as-fabricated mullite supports have a porous microstructure composed of sintered glassy particles embedded with inter-locked mullite crystals, which grew gradually with increasing temperature from rod-like into blocky-like morphologies. To obtain mullite membrane supports with sufficient porosity and acceptable mechanical strength, the relationship between porosity and mechanical strength was investigated, which was fitted using a parabolic equation.

1. Introduction

Coal gangue, an industrial solid waste, is one of the by-products during coal mining. The production ratio of coal gangue varies from ~10% to 15% of raw coal, which mainly depends on mining and geological conditions [1,2]. Currently most of waste coal gangue is piled on land, which can cause serious environmental impacts, especially the atmospheric pollution caused from spontaneous combustion and water pollution from leaching and release of heavy metal ions [3–5]. Therefore, the comprehensive utilization of coal gangue is quite necessary. Many approaches on reusing of coal gangue have been reported so far. Most of coal gangue after processing is used for traditional construction materials, such as cement [6] and brick [7]. The coal gangue with high content of carbon is mixed with other types of coal for mine-mouth power generation, which has indicated its techno-economic feasibility of mine-mouth power plants [8]. In general, the major mineralogical phase composition of coal gangue is quartz and feldspar [9,10], with main chemical composition of SiO_2, Al_2O_3, Fe_2O_3 and some other minor oxide such as K_2O and TiO_2. Compared with other industrial wastes and minerals such as coal fly ash, kaolin, andalusite and sillimanite, particularly, the content of SiO_2 in coal gangue is generally as high as ~70%, so it can be considered as a potential low-cost silicon source in industry. There are some studies on the fabrication of glasses and ceramics by reusing of coal gangue. Yang et al. prepared a $CaO–Al_2O_3–SiO_2$

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glass ceramic from coal gangue [11], and β-SiC/Al_2O_3 ceramics have been fabricated from kaolinite gangue and anthracite by Han et al. [12].

Porous ceramic separation membranes have been widely studied for energy and environmental applications due to its unique advantages especially such as high thermal, chemical and mechanical stability, environment friendliness and low energy-consumption [13]. However, because porous ceramic separation membranes require a much higher cost than polymeric counterparts, their applications have been limited in some traditional industry such as food, beverage and pharmaceutical. Also, limited types of membrane materials (such as Al_2O_3, ZrO_2, TiO_2 and their composite oxides) hinder their further applications [14–16]. With increased needs of some environmental separation applications such as strong acidic/alkaline media separation, massive waste liquid pre-treatment and low-cost catalysis-separation supports, it is of great importance to develop low-cost fabrication and application techniques for ceramic membranes.

Among ceramic membrane materials, porous mullite (from $3Al_2O_3{\cdot}2SiO_2$ to $2Al_2O_3{\cdot}SiO_2$) has been attracting more and more attentions as membrane supports because of its unique advantages such as good chemical durability, low thermal expansion coefficient, good mechanical property and abundant Si- and Al-sources [17]. In order to further reduce cost, many researchers have been devoted to fabrication of porous mullite using various cheap raw materials such as fly ash [18,19], kaolin [20–23], andalusite [24] and sillimanite [25–27]. However, to the best of our knowledge, there are few reports on recycling of industrial solid waste coal gangue in fabrication of porous mullite ceramic membrane, which is an important route to decrease membrane processing cost. This method will be expected to be an effective way to reuse coal gangue not only to give a new and facile insight for solving its environment problems but also to endow a possibility of high-valued recycling.

In this study, in order to recycle coal gangue, porous mullite ceramic membrane supports were fabricated using coal gangue and bauxite. The properties of porous mullite ceramic membrane supports were characterized and discussed, including dynamic sintering behaviors, phase evolution, shrinkage, porosity and pore size, gas permeation flux, microstructure and mechanical property. Corn starch powder was added as pore-forming agent to produce sufficient porosity with acceptable mechanical property.

2. Experimental procedures

2.1. Sample preparation

Industrial coal gangue (after 800 °C calcination, Xiamen, Fujian Province, China) and calcined bauxite (after 1200 °C calcination, Gongyi, Henan Province, China) powders were used as the materials for the preparation of porous mullite membrane supports. Commercial corn starch ($(C_6H_{10}O_5)_n$, Beijing Gusong Economic and Trade Co., Ltd., China, D_{50} = 16.84 μm) was used as pore-forming agent.

Based on the composition of 3:2 mullite ($3Al_2O_3{\cdot}2SiO_2$), a batch of coal gangue and bauxite powders was weighed and then wet-mixed using zirconia-ball-milling at a constant rotation speed of 500 rpm for 10 h at room temperature, and subsequently dried at 90 °C for 1 day. On one hand, the powder mixture was mixed with organic binder PVA-1750 (5 wt.% solution) in an alumina mortar, and then uniaxially pressed into pellets (~1.0 g each sample) with diameter of 20 mm at 190 MPa to obtain the green samples without pore-forming agent. On the other hand, the powder mixture was mixed with organic binder PVA-1750 (5 wt.% solution) and various contents of corn starch in an alumina mortar, and then uniaxially pressed into pellets (~1.0 g each sample) with diameter of 20 mm at 190 MPa to obtain the green samples with pore-forming agent. Afterwards, the green pellets were placed in a muffle furnace (KSL-1700X, Hefei Kejing Materials Technology Co. Ltd., China) and sintered at temperatures from 1100 to 1500 °C for 2 h. The heating rates were 1 °C up to 450 °C, 2 °C up to 600 °C, and 3 °C up to final temperature. A holding time of 0.5 h was carried out at 450 and 600 °C to remove the added organic binder and inherent structural water, respectively.

2.2. Characterization

The chemical compositions of calcined coal gangue and bauxite were characterized by quantitative X-ray fluorescence spectrum analysis (Axios-Advanced, PANalytical Corporation, Netherlands). The particle size distributions of coal gangue and bauxite were determined by a laser particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd., UK) using water as dispersing medium. X-ray diffraction (XRD, X'Pert Pro, PANalytical Corporation, Netherlands) was used to characterize the phase compositions of the starting materials and the phase assemblage of the mullite ceramic membrane supports sintered from 1100 to 1400 °C for 2 h. Reference intensity ratio (RIR)-quantitative analysis was employed to determine the phase contents.

The morphology of the raw materials (coal gangue and bauxite) and the fracture surfaces of the mullite ceramic membrane supports were observed using scanning electronic microscope (SEM, S-4800, Hitachi Ltd., Japan). Before SEM observation, some of the samples were etched with 15 vol.% HF solution for 30 min and then dried at 90 °C for 10 h. The dynamic sintering shrinkage behavior of the green rectangular bar of the mullite ceramic membrane support was measured between room temperature and 1500 °C in a horizontal dilatometer (Netzsch DIL 402 C, Netzsch-Gerätebau GmbH, Germany) at a heating rate of 10 °C min^{-1}. The linear shrinkage percents in diameter direction of the sintered pellets were measured using a vernier caliper. Open porosity and bulk density were measured in water medium according to the Archimedes' principle. Pore size distribution and nitrogen gas permeation flux of the mullite ceramic membrane supports sintered at various temperatures were measured by a pore size distribution analyzer (PSDA-20, Nanjing Gaoqian function materials Co. Ltd., China). The pore diameter was calculated from the Washburn's equation according to bubble-point method:

$$d = \frac{4\gamma\cos\theta}{\Delta P} \quad (1)$$

where d is the pore diameter, γ is the surface tension of wetting liquid, θ is the contact angle between the wetting liquid and the testing material, and ΔP is the applied pressure difference [28].

Biaxial flexural strength (BFS) tests were performed using a universal testing machine (AGS-X, Shimadzu Corporation Ltd., Japan) according to ISO6872 on disc specimens (diameter: 15–17 mm; thickness: 0.70–0.85 mm). A crosshead speed of 0.1 mm min^{-1} and a preload of 5 N were utilized along with a test jig (lab-designed) with a support radius of 5 mm [29,30]. Finally, biaxial flexural strengths were calculated from the recorded maximum loads at fracture using the following equation given by Timmoschenko and Woinowsky-Kreiger [31],

$$\mathrm{SS(MPa)} = \frac{P}{t^2}\left\{(1+\nu)\left[0.485\ln\left(\frac{a}{t}\right)+0.52\right]+0.48\right\} \quad (2)$$

where SS is the flexural strength (MPa), P is the maximum load (N), r is the radius of three-ball support circle (mm), ν is Poisson's ratio (here ν = 0.257 for mullite-based materials), and t is the