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Low-cost porous mullite ceramic membrane supports fabricated from kyanite by casting and reaction sintering

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Abstract

Porous mullite supports are firstly fabricated by casting and reaction sintering based on kyanite with $Al(OH)_3$ as porogenic agent. The effects of composition and sintering temperature on phase evolution, microstructure, apparent porosity, pore size distribution, linear shrinkage, gas permeation flux and mechanical property of supports are systematically investigated. Results show that the mullitization of kyanite generates needle-like mullite crystals, which form skeleton structures and improve the apparent porosity and strength of supports. $Al(OH)_3$ addition not only promotes the formation of needle-like mullite but also enhances the apparent porosity of supports. Temperature promotes the development of mullite, from 1450 to 1500 °C, the amount and size of needle-like mullite crystals increase, ≥1500 °C, they reveal columnar morphology. The support prepared with kyanite+40 wt%$Al(OH)_3$ sintered at 1500–1550 °C exhibits high apparent porosity, good gas permeation flux, excellent mechanical performance and interlocked network structure composed of well development needle-like mullite.

Keywords: Porous support; Needle-like mullite; Pore size distribution; Gas permeation flux

1. Introduction

Due to their unique advantages such as high separation efficiency [1–3], excellent thermal and chemical stability [4–6], environment friendliness and low energy consumption [7,8], ceramic separation membranes have been widely used in fields of gas storage/separation [9], water purification [10,11], food and beverage processing [12], and molecular separation systems in the petrochemical and chemical industry.

Ceramic separation membrane can be seen as a kind of gradient porous material, which generally consists of several thin separation layers on a porous support. As a key part of the ceramic membrane, the support is required to provide mechanical strength and flow transport to the thin top-layer membrane [10]. The mechanical strength and transport properties (e.g. permeability) of the support greatly depend on the apparent porosity, pore size and pore size distribution, which are mainly determined by the starting materials, sintering processes and fabrication methods [13,14]. In the past decades, most of researches have focused on the preparation of porous ceramic supports with materials such as Al_2O_3, ZrO_2, SiC or their composites. However, both expensive starting materials and high cost of formation/sintering processes restrict their extensive applications in industrial fields [15].

In recent years, in order to reduce the fabrication cost, some researchers have been devoted to develop porous mineral-based ceramic membrane supports [16], which have attracted more attention due to their low cost, species diversity and novel additional properties [17]. Among these porous mineral-based materials, porous mullite ceramics have advantages such as good chemical and thermal durability, low expansion coefficient and excellent mechanical properties, all of these characteristics make them used as ceramic membrane supports,

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catalyst supports and refractory bricks [18,19]. Various mineral materials can be used for the preparation of porous mullite ceramics, such as kaolin [20], bauxite [21,22], and coal gangue [7], et al. However, to the best of our knowledge, there are no reports on natural mineral kyanite as the main starting material in fabrication of porous mullite ceramic membrane supports. Kyanite belongs to Al_2O_3–SiO_2 system, its chemical formula is $Al_2O_3 \cdot SiO_2$, the crystal structure is closely related to the mullite structure, therefore, it is easily to generate mullite at high temperature, and the mullitization process accompanies 16–18 vol% expansion, making it be widely used as expanding agent in the refractory field [23].

In order to enhance the porosity of supports, it is generally prepared by adding pore-forming agents such as corn starch [2], graphite [21], they are burned out completely during heating, or by leaching out the excess silica from fired clays with solutions such as NaOH, acid and caustic potash [1]. However, these methods are high cost and have some dangers. Recently, reports have shown that the aluminum hydroxide ($Al(OH)_3$) is suitable for preparing porous ceramics, the in situ decomposition of $Al(OH)_3$ produces *ca* 60 vol% contraction and leaves pores around the α-Al_2O_3 [24,25]. Meanwhile, the new formed α-Al_2O_3 has high activity, which not only contributes to the formation of secondary mullite by reacting with the silica, but also improves the porosity by consuming the glassy phase. In addition, the ceramic supports are generally prepared by dry-pressing or extrusion, which are difficult to prepare supports with high apparent porosity and high complexity shapes, but the casting method in this study can solve these problems [26,27].

In this paper, low-cost porous mullite ceramic membrane supports are prepared by casting and reaction sintering using natural mineral kyanite as the raw material, $Al(OH)_3$ as the porogenic agent. The effects of composition and sintering temperature on phase evolution, microstructure and properties (including apparent porosity, pore size distribution, linear shrinkage as well as the mechanical strength) of supports are investigated.

2. Experimental procedures

2.1. Sample preparation

The raw material used to prepare porous mullite ceramic membrane supports was commercial kyanite powder (Nanyang Kyanite Company, China) with solid density of 3.5 g/cm^3, $Al(OH)_3$ was used as the porogenic agent (Gibbsite, China aluminum Co., Ltd., China), calcium aluminate cement (CA) (Secar 71, Lafarge, France) was selected as the binder, their characteristics are shown in Table 1.

For the present study, the mass ratio of kyanite + $Al(OH)_3$ to CA was 97:3, and four batches of different $Al(OH)_3$ contents were selected to be 0, 20, 40, and 60 wt% relative to the kyanite powder. The starting materials were weighed in terms of these mass ratios and dry-mixed for 4 h in a polyurethane bottle with zirconia balls, then put them into a mechanical mixer, and mixed with 40 vol% water for 5 min, the suspensions were immediately cast into strip molds and cured in a humid atmosphere at 40 °C for 24 h. After demoulding, the green samples were dried at 110 °C for 24 h, and then sintered at different temperatures (1450, 1500, 1550 and 1600 °C) for 3 h.

2.2. Characterization

Apparent porosity was measured by Archimedes method in distilled water. Linear shrinkage was determined by the following equation:

$$\text{Shrinkage} = \frac{l_b - l_a}{l_a} \times 100\% \quad (1)$$

where l_a and l_b are length of samples before and after sintering, respectively. Room temperature flexural strength was determined by the three-point bending method in a universal materials testing machine (HT-8391, Hongta Co, China), the value was calculated according to the following expression (ISO9693-1999):

$$\sigma = \frac{3F \times L}{2b \times h^2} \quad (2)$$

where σ is the fracture strength (Pa), F is the fracture load (N), L is the span length (m), b and h are the width and height of samples (m), respectively. All experiments were carried out on a series of at least 5 bars to report an average strength for each series. Pore size distribution was examined by mercury intrusion porosimetry (PM-60GT, Quantachrome instruments, America). Nitrogen gas fluxes of samples at different pressures were measured in the experimental device reported by Nandi et al [28]. Phase compositions were conducted using Philips X-ray diffractometer (XRD) with Cu Kα radiation ($\lambda = 1.5406$ Å) in the 2θ range of 10–80 °C for a period of 3°/min in the step scan mode. Here, XRD quantitative analysis based on the normalized reference intensity ratio (RIR) method was adopted to calculate the content of mullite phase. Microstructure and composition of samples were investigated by scanning electron microscopy (SEM, JEOL JSM-5610LV) equipped with an energy dispersive spectrometry (EDS, INCA2000).

Table 1
Chemical compositions and average particle size of the starting materials.

Materials	Chemical compositions, wt%									d_{50}, μm
	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	Others	
Kyanite	53.41	39.74	0.33	1.7	1.07	0.14	0.64	0.2	2.77	74
$Al(OH)_3$	66.8	0.05	0.05		0.15	0.03	0.01	0.03	32.88	84
CA Cement	69.05				28.44				2.51	21

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