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# High-aluminum fly ash recycling for fabrication of cost-effective ceramic membrane supports

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ABSTRACT

In order to effectively utilize the industrial solid waste and produce high value-added products, a series of porous ceramic membrane supports made of waste fly ash and calcium carbonate mixtures were fabricated by in-situ reaction sintering method. The ceramic membrane supports with 15, 20, 25 wt % $CaCO_3$ sintered at the range of 1200–1350 °C show the high open porosity over 30% and are further investigated. The investigated ceramic membrane supports give the main phase of anorthite, some of which contain a minor mullite phase. The pore sizes of ceramic membrane supports increase with increasing of the amount of $CaCO_3$ and sintering temperature. The flexural strengths of ceramic membrane supports increase with sintering temperature. They are higher than 30 MPa and meet the requirement of application. This work provides a potential route to develop cost-effective ceramic membrane supports with controllable pore size, high porosity and good strength.


## 1. Introduction

Waste fly ash, one of main industrial solid wastes, is a by-product of incineration of coal in thermal power plants. The undealt fly ash produces serious environmental pollution and so is classified as a hazardous residue. It is of environmental concern that the huge amount of fly ash is disposed in landfills and surface impoundments or its re-use in construction materials. Furthermore, the production rate of fly ash is greater than the consumption rate. Therefore, more extensive application of fly ash need be further developed so as to better dispose and utilize solid waste resources [1–3].

Membrane technology has been proven to be highly effective for many separation processes, including purification of water and air, resource recovery, food industries, environment and other industries [4–6]. The applications of ceramic membranes have increased due to its excellent chemical thermal and mechanical stability and higher separation efficiency compared to the polymeric membrane [7,8]. Commercialized ceramic membranes are usually manufactured from alumina. Alumina ceramic membranes are too expensive due to the expensive raw material and high sintering temperature, especially when used in some environmental separation processes such as wastewater treatment and high-temperature dust removal [9]. Hence, recently there has been significant emphasis toward the development of low cost ceramic membranes (or membrane supports) using mineral materials or solid wastes [10–13]. Fly ash-based ceramic membrane is a good alternative for alumina ceramic membrane, which not only avoided environmental pollution of fly ash but also produced high value-added products. Jedidi et al. elaborated the new porous tubular microfiltration membrane from mineral coal fly ash, with the average pore diameter of 0.25 μm, and applied to waste water treatment [14,15]. Mullite ceramic membranes have also been fabricated using fly ash and some minerals as raw materials [9,16,17].

Generally the separation membranes possess an asymmetric structure consisting thick support and very thin top-layer membrane to increase the permeation fluxes. The support as a key

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component of asymmetric ceramic membrane provided mechanical strength and flow transport for top-layer membrane [18]. High porosity and good permeability are in demand for ceramic membrane supports, which can be realized by powder-processing route with addition of some pore-forming agents such as sawdust, starch or organic particulates [13,19–21]. The pore-forming in situ technique exploiting the decomposition of starting powders is a better way to prepare ceramics supports, in favor of maintaining well-distributed pores and high mechanical strength. When using aluminum hydroxide or some carbonates as raw materials of porous supports, more pores create in situ by their thermal decomposition into the corresponding oxide. Chen et al. [9] fabricated a porous mullite ceramic membrane support using $Al(OH)_3$ as raw materials. Bouzerara et al. and Zhou et al. respectively reported porous supports from kaolin and dolomite [22,23].

This work aim to develop low-cost ceramic membrane supports from fly ash and calcium carbonate, in which in situ decomposition of calcium carbonate forms pore. It is very meaningful for reducing ceramic membrane cost and widening application field of fly ash. In order to prepare the high-quality ceramic membrane support, the effect of $CaCO_3$ contents in starting materials and sintering temperature on porosity microstructure, phase composition, pore size and flexural strength was investigated and discussed in details.

## 2. Experimental

### 2.1. Staring materials and samples preparation

Industrial waste fly ash was obtained from Ningbo heat and power plant (Zhejiang province, China). The calcium carbonate of commercial grade was purchased from Sinopharm Group Co. LTD, China. The fly ash and calcium carbonate powders were milled using variable frequency planet-type grinding mill. The resulted fly ash and $CaCO_3$ powders, with different weight percentage of $CaCO_3$ from 0% to 30%, were wet-mixed well by grinding in a mortar for half an hour using ethanol as medium. The green disks with 20 mm in diameter and rectangular bars with the dimensions 40 mm × 5 mm × 3 mm were prepared by uniaxial cold-pressing the mixture under 200 MPa using 5 wt% PVA solution as organic binder. The disks samples with various $CaCO_3$ contents were sintered at different temperature in range of 1200–1350 °C with an interval of 50 °C for 2 h. The heating and cooling rates were 3 °C $min^{-1}$ and 5 °C $min^{-1}$ respectively. The obtained ceramic membrane supports were denoted as FC-x support (x = 0, 10, 15, 20, 25, 30, $CaCO_3$ weight percentage).

### 2.2. Characterization methods

The particle size distributions of fly ash and $CaCO_3$ were detected by a laser particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd., UK) using water as dispersing medium. The element composition of the fly ash was determined by quantitative X-ray fluorescence (XRF) spectrum analysis (Axios-Advanced, PANalytical Corporation, Netherlands). Phase compositions of starting materials and ceramic membrane supports were analyzed using an X-ray diffractometer (DX-2700, China) with Cu Kα radiation at a wavelength of λ = 0.154 nm, generated by 30 mA and 40 kV voltage. The scanning speed was 10°/min from 10°–80° with a step size of 0.03°. The sintering shrinkage behavior was measured using a high-temperature dilatometer (Netzsch DIL 402C, Germany) with heating rate of 10 °C/min in air. Open porosity was measured by the Archimedes method with water as liquid medium. The average and standard deviation in open porosity were measured with three specimens testing.

The microstructures of ceramic membrane supports were observed by scanning electron microscopy (SEM, S-4800, Hitachi, Janpan) at an accelerating voltage of 5 kV. A pore size analysis instrument (PSDA-20, Nanjing Gaoqian function materials Co. Ltd., China) was applied to determine the pore size distribution, average and maximum pore size. The pore diameter D was calculated according to the Washburn equation:

$$D = -\frac{4\gamma \cos\theta}{\Delta P}$$

Where $\gamma$ is surface tension of GQ-16 (16 dyn/cm) and $\theta$ is contact angle between the wetting liquid and the pore surface, $\Delta P$ is the trans-membrane pressure.

The ceramic membrane supports with diameters of 17–21 mm and thicknesses of 1.4–1.6 mm were used to a biaxial flexural strength test. Flexural strength was measured using the universal materials testing machine (AGS-X, Shimadzu Corporation Ltd., Janpan) and five specimens were tested to obtain the average flexural strength and standard deviation. The biaxial flexural strengths were given according to the equation:

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

Where $S$ is the flexural strength (MPa), $P$ is the maximum load (N), $a$ is the radius of three-ball support circle (mm), $\nu$ is the Poisson's ratio, and $t$ is the thickness of the disks.

## 3. Results and discussions

### 3.1. Raw material characterization

In this study, the low-cost ceramic membrane supports were fabricated from industrial waste fly ash and cost-effective $CaCO_3$. The chemical composition of the fly ash given in weight percentage (wt %) is listed in Table 1. The fly ash mainly consists of alumina and silica, whereas the main impurities are CaO, $Fe_2O_3$ and $TiO_2$. Beside, there are small amount of other elements existing in fly ash, such as Mg, P, Sr and Pb etc. The $CaCO_3$ is an analytical-grade product of 99.0%, only containing a trace of alkali and alkali-earth metal oxides.

XRD patterns of fly ash and $CaCO_3$ are showed in Fig. 1. The main crystalline phase of fly ash is mullite (PDF#15-0776), accompanied with some quartz (PDF#46-1045). The amorphous phase also exists due to a broad characteristic diffraction peak between 20°–30°. All peaks in XRD pattern of $CaCO_3$ attributes to rhombohedral calcite phase (PDF#05-0586) and no accidental peak appears.

The particle size distributions of ball-milled fly ash and $CaCO_3$, measured by a laser particle size analyzer, are shown in Fig. 2. The particle sizes of fly ash and $CaCO_3$ present the multi-peaks distribution. The particle size of fly ash keeps in range of 0.3–6 μm while the particle size of $CaCO_3$ distributes within 0.3–30 μm. The median particle size (D50) of fly ash and $CaCO_3$ are 2.53 μm and 9.15 μm, respectively. The D50 value of fly ash is small, around 28% of that of $CaCO_3$, and so it is highly reactive. The larger $CaCO_3$ particles provide the large pore and high permeation flux after high-temperature decomposition.

### 3.2. Variation of porosity on $CaCO_3$ content

The effect of $CaCO_3$ contents and sintering temperature on porosities of ceramic membrane supports was illustrated in Fig. 3. The open porosity of samples sintered at 1200 °C increases from 31% to