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Waste-to-resource preparation of a porous ceramic membrane support featuring elongated mullite whiskers with enhanced porosity and permeance

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Abstract

Different from traditional particle packing structure, a porous structure of ceramic membrane support was fabricated, featuring elongated mullite whiskers with enhanced porosity, permeance and sufficient mechanical strength. The effect of additives (MoO_3 and AlF_3) and sintering procedure on open porosity, mechanical properties, pore size distribution, micro-structure, phase structure, and permeance of the membrane supports was characterized in detail. The introduction of MoO_3 and AlF_3 promoted formation of a porous whisker-interlocked structure, which effectively improved open porosity and permeance. A mullite membrane support containing 5 wt.% MoO_3 and 4 wt.% AlF_3 exhibited an open porosity as high as $48.6 \pm 0.5\%$, a mechanical strength of 81.2 ± 3.2 MPa at 1200 °C, and the value of permeance was higher than the membrane without any additives. Such enhancements in porosity and permeance, with sufficient mechanical strength, were a result of tortuosity decrease due to a porous structure of interlocked mullite whiskers.

Keywords: Ceramic membrane support; Porosity; Mechanical strength; Mullite whiskers; Permeance

1. Introduction

Porous ceramic separation membranes are used in industrial fields due to their unique advantages, such as excellent temperature stability, good pressure resistance, good chemical stability, long life and good antifouling properties.[1] However, commercial porous ceramic membranes still cannot fulfill increasing environmental requirements at a large scale such as separation in strong alkaline media and massive liquid waste treatment due to the limited types of membrane materials[2] (such as Al_2O_3, ZrO_2, SiO_2, TiO_2 and their composites). Besides, high cost, associated with starting materials and formation/sintering processes, makes extensive applications of ceramic membranes still limited.[3,4] As a result, the preparation and potential applications of porous mineral-based ceramic membranes (kaolin,[5] bauxite,[6] sepiolite clay,[7] industrial solid waste coal fly ash,[8] etc) have attracted more attention due to the low cost of abundant raw materials available worldwide. For example coal fly ash emerges as a by-product from the combustion of raw coal in thermal power plants.[9] Without suitable treatment, fly ash may be a source of dust which adversely affects our environment. Therefore, it is necessary to utilize this waste not only to decrease environmental pollution but to produce high added-value products from it. Especially fly ash containing Al_2O_3 and SiO_2 is suitable for the fabrication of dense mullite-based ceramics, as has been proven in.[10,11] Recently a study has been made on the conversion of coal fly ash to mullite ($3Al_2O_3{\cdot}2SiO_2$) for the preparation porous ceramic membranes.[12]

As a structural material, porous mineral-based mullite is expected to be a promising candidate for ceramic membrane supports especially because of its excellent high temperature resistance, good corrosion resistance, abundant natural Al and

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Si-sources, low cost, and environment friendliness.[13] These properties are especially important for porous mullite, which is used as filter membrane for treatment of great volumes of liquid/gas effluents, which requires the use of porous support with higher porosity and good mechanical strength in order to maintain a lower pressure drop across the filter membrane and to withstand the pressure gradient imposed during practical separation applications.

Traditionally, the open porosity of a ceramic membrane is limited by the intergranular packing effect of the starting powder or precursor, mainly depending on its morphology and particle size distribution. It is well known that porosity can be effectively controlled by varying sintering conditions such as sintering temperature and dwelling time.[14] High temperature partial sintering is required to produce sintering necks, endowing porous ceramic membrane with sufficient strength, while degrading open porosity to some extent. Normally, an improvement in open porosity, which is required to endow a low fluid resistance, is achieved with addition of pore-forming agents such as graphite powder or some organic compounds,[15,16] which burn out or decompose completely during heating. However, the pores produced in this way are usually believed to deteriorate the mechanical reliability.[17] It is usually hard and thus of great importance to find a way to produce high porosity without alteration of mechanical strength of ceramic membrane supports, which are expected to withstand large pressure gradient imposed during practical separation applications. Apart from high mechanical strength, a proper ceramic membrane support should have high permeability.[18]

Recently, mullite whiskers have been widely investigated as candidates for reinforcement of ceramic-based composites due to their high aspect ratio and high strength.[19] Several approaches, such as addition of AlF_3[11,19,20] to starting material mixtures, are developed to produce mullite-whisker-reinforced composites. In order to further enhance mullite phase content at low temperatures, some sintering aids (such as V_2O_5,[21] MgO,[22] TiO_2[12] and WO_3[23]) are used during fabrication of low-cost porous mullite. However, there are few reports with MoO_3 as sintering additive. Since Mo and W are in the same subgroup of the element periodic table, associated with the lower melting point of MoO3 (795 °C), it is expected that addition of MoO_3 accelerates the growth of mullite crystals and thus enhances mullite content at lower temperatures.

Different from traditional particle packing structure processed by partial sintering, in this work, with MoO_3 and AlF_3 as additives, a highly porous structure of inter-locked mullite whiskers is realized in mullite membrane support made from waste coal fly ash and bauxite. The present study aims at elaborating a new type of porous structure for ceramic membrane support with enhanced porosity and permeance, but without significant degradation of mechanical property. The effect of additives and sintering parameters on the main properties of porous mullite membrane supports is studied in detail, mainly including porosity, mechanical properties, pore size distribution, micro-structure (SEM and phase compositions) and permeance.

2. Experimental procedures

2.1. Starting materials for membrane support

Coal fly ash (Ningbo, Zhejiang Province, China) and nature bauxite (Yangquan, Shanxi Province, China) were used as the starting materials. AlF_3 (98–102%, Guangfu Fine Chemical Reagent Ltd., Tianjin, China) and MoO_3 (Sinopharm Chemical Reagent Co., Ltd) were used as crystallization catalyst and mineralizer, respectively.

Based on mullite stoichiometric composition ($3Al_2O_3{\cdot}2SiO_2$), a series of MoO_3–AlF_3 doped and undoped mullite membrane supports were prepared by adding various weight percents (wt.%) of AlF_3 (x wt.%) and MoO_3 (y wt.%) into the powder mixture of fly ash and bauxite. All samples are labeled as AxMy. A stands for AlF_3, M for MoO_3, and the numbers following them represent their mass percentage in the samples (e.g. A0M0 for the sample without addition of AlF_3 and MoO_3, A4M5 for the sample with addition of 4 wt.% of AlF_3 and 5 wt.% of MoO_3).

2.2. Fabrication of membrane support

The raw materials with different compositions were wet-ball-milled in distilled water for 12 h using a planetary ball-milling machine (SFM-1, Hefei Kejing Materials Technology Co., Ltd) at a milling speed of 400 rpm. After complete drying, the milled powders were uniformly mixed with organic binder PVA-1750 (5.0 wt.% solution) in an alumina mortar and then uniaxially pressed into cylindrical pellets (20 mm in diameter and 1–2 mm in thickness) at a pressure of 190 MPa. The green disc-shape membrane supports were placed in a closed alumina crucible and sintered in an electrically heated muffle furnace in air at final temperatures ranging from 1100 °C to 1500 °C for 2 h.

2.3. Characterization and test

Particular emphasis is placed on characterization of membrane properties of the supports: open porosity, pore size distribution, mechanical strength, gas and water permeances. A detailed microstructural analysis was performed to understand the formation process and the reinforcement of this mullite membrane support.

The particle size distribution of fly ash and bauxite was determined by a laser particle size analyzer (Mastersizer 2000, Malvern Instruments Ltd., UK). Chemical compositions of the raw materials (coal fly ash and natural bauxite) were examined by X-ray fluorescence spectrometry (WDXRF, PANalytical Corporation, The Netherlands).

Open porosity was determined by the Archimedes method[24] with water as the liquid medium. Pore size distribution was measured by a pore size distribution analyzer (PSDA-20, Nanjing Gaoqian function materials Co. Ltd., China) based on a gas–liquid displacement method. The pore diameter can be