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Preparation of microfiltration membrane supports using coarse alumina grains coated by nano TiO_2 as raw materials

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Abstract

To increase the mixing uniformity of coarse alumina grains with a small amount of nano TiO_2 particles, TiO_2 particles were prepared on the surface of coarse Al_2O_3 grains by in-situ hydrolysis of $TiCl_4$. The coated coarse Al_2O_3 powder was used to prepare microfiltration membranes supports. The effects of TiO_2 content and sintering temperatures on the bending strength, porosity and pore size distribution of the obtained supports were studied. The results show that the melted nano TiO_2 grains locate mainly at the neck of Al_2O_3 grains, which increases the bending strength of the support by increases the neck area. However, the bending strength is weakened if the TiO_2 content is excessive. No aggregated nano TiO_2 grainsare found. The resulting supports sintered at 1650 °C for 2 h yields a bending strength of 55.4 MPa, a porosity of 38% with a mean pore size of 8.0 μm.

Keywords: Alumina; Nano TiO_2; Microfiltration membrane; Support; Sintering aid

1. Introduction

Ceramic membranes have been gaining more and more attention in industrial applications due to their excellent thermal, chemical and mechanical stability.[1–4] Generally, ceramic membranes have an asymmetric structure consisting of macro-porous support and several porous thin layers of decreasing pore size till the final one responsible for the separation function. An excellent microfiltration membrane support should possess high mechanical strength, high permeability, and narrow pore size distribution, which mainly depend on the raw materials, sintering temperature and fabrication methods.[5] To achieve the high permeability, coarse alumina powder is generally chosen for the commercialized ceramic microfiltration membrane support. However, the poor sintering ability of coarse alumina grains results in high cost of this kind of support because no sufficient mechanical strength could be achieved unless the sintering temperature reaches 1700 °C, or even higher.[6] Some raw materials with low melting aptitude can be used to prepare the ceramic support.[6–8] However, alumina support still remains the more popular one due to its good bending strength and excellent acid/alkali resistance.[8] Various sintering aids, such as TiO_2,[4,7] boehmite,[9] kaolin,[10] and clay,[11] were added to decrease the sintering temperature of alumina supports.

TiO_2 is a good sintering aid for alumina supports since it reacts with the alumina during the sintering process to form Al_2TiO_5.[12,13] The amount of Al_2TiO_5 plays an important role in determining the mechanical strength of the supports. However, too much Al_2TiO_5 formed in the Al_2O_3/TiO_2 composite would lead to lower the strength of the supports[13,14] due to the decomposition of Al_2TiO_5 during the cooling process. Therefore, the added amount of TiO_2 should be optimized according to the

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bending strength and the porosity obtained. The manner such a few amount of TiO_2 is distributed uniformly represents the key to obtain a support with a high performance. If the size of TiO_2 particles is similar to the main powder, a small amount of TiO_2 can then be mixed uniformly with Al_2O_3 by traditional ball milling method. Otherwise, the fine-grained TiO_2 just fills the holes formed by the packing of coarse Al_2O_3 grains. The reaction upon sintering yielding to Al_2TiO_5 formation in the holes has indeed less effect on the bending strength of the porous ceramic. In our laboratory, TiO_2 coating was prepared on the membrane surface and the pore wall to obtain the hydrophilic surface by homogenous precipitation method.[15] The TiO_2 coating distributes uniformly on alumina grain surfaces. The thickness of the nano coating is about 20–50 nm. The uniform mixing of fine nano grains with coarse grains may be realized following this method.

In the present work, coarse alumina grains (d_{50} = 29 μm) coated by nano TiO_2 were prepared by in situ hydrolysis using $TiCl_4$ as raw material. The obtained alumina powder coated with nano TiO_2 grains was then used to prepare microfiltration membrane supports. The effects of TiO_2 content and sintering temperatures on the bending strength, porosity and pore size distribution of the supports were studied.

2. Experimental

2.1. Preparation of membrane supports

Al_2O_3 powder, denoted W40 hereafter (purity of 99.5%, purchased from Henan White-dove Group, China) was purchased without further treatment prior to the preparation of ceramic microfiltration membrane supports. The mean particle size of W40 was 29 μm measured by laser scattering particle size analyzer (Bettersize2000, Dandong, China). $TiCl_4$ and absolute ethanol (AR graded) were purchased from Sino Chemical Reagent Co. Ltd., China.

$TiCl_4$ solutions were prepared by dissolving $TiCl_4$ into absolute ethanol in an ice–water bath under vigorous stirring. W40 alumina powder was immersed into 20 g/L–100 g/L $TiCl_4$ solutions for 2 h. W40 alumina powder was then filtered and dried in a fumehood to obtain the TiO_2 coating formed by hydrolysis of $TiCl_4$ upon humidity present in air. The TiO_2-coated W40 alumina powder was calcined at 800 °C for 2 h. The content of nano TiO_2 was calculated according to the weight difference of the alumina powder before and after the treatment with $TiCl_4$. The content of nano TiO_2 was 0.3%, 0.6%, 0.8%, 1.2% and 1.6% after the treatment with the 20 g/L, 35 g/L, 50 g/L, 75 g/L and 100 g/L $TiCl_4$ alcoholic solutions, respectively.

To prepare the macroporous ceramic support, the alumina powder coated by nano TiO_2 was dry mixed with corn starch (d_{50} = 14.8 μm, Sinopharm Chemical Reagent Co. Ltd., China) in a ball mill at 150 rpm for 2 h to avoid the breakage of alumina grains. The mass ratio of powder:zirconia ball:water was 1:1:2. And then, polyvinyl alcohol (PVA, 1750 ± 50) solution of 20 wt% of the alumina powder quality was added. The obtained suspensions were dried overnight in an oven at 70 °C. The mixtures were molded into rectangular shapes of 40 × 10 × 10 mm

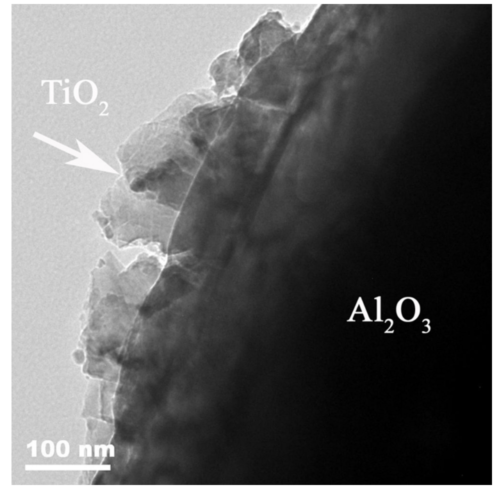

Fig. 1. TEM image of W40 alumina grains coated by nano TiO_2 (1.2 wt%, sintered at 800 °C for 2 h).

($L \times h \times w$) by dry pressing under the pressure of 2–10 MPa. The samples were calcined in a muffle furnace at a heating rate of 3 °C/min to 1500–1650 °C for 1–4 h.

2.2. Characterization of membrane supports

The particles coated by nano TiO_2 were observed using a Transmission Electronic Microscope (TEM, JEOL-2010, Japan). The sample was prepared by mashing the alumina grains coated by nano TiO_2 in the mortar until the grains were suitable for TEM observation.

The pore size distribution and the porosity of the sintered compacts were measured by Mercury Intrusion Porosimetry (Autopore IV9500, Micromeritics, USA).

The bending strength was measured by the three-point bending method at room temperature using a universal material testing machine (WDW-30, Xi'an Letry Machine Testing Co. Ltd., China), with a span length of 20 mm and loading speed of 0.2 mm/min. Five samples were measured and the data were averaged as the bending strength.

Fracture surfaces of the sintered ceramic supports were observed by means of Field Emitting Scanning Electron Microscope (FE-SEM, JSM-6700F, JEOL, Japan).

3. Results and discussion

3.1. Characterization of W40 alumina grains coated by nano TiO_2

Fig. 1 shows the TEM image of W40 alumina grain treated by 75 g/L $TiCl_4$ solution, then sintered at 800 °C for 2 h. It can be seen that nano TiO_2 particles distribute on the alumina grains' surface. The particle size of TiO_2 is less than 70 nm, which is about 0.24 wt% of the particle size of W40 alumina grain (~29 μm). It is implied that the addition of nano TiO_2 particles has less effect on the particle packing of W40 grains. $TiCl_4$ solution can wet W40 alumina grain completely. After hydrolysis and calcination, adsorbed $TiCl_4$ changes in situ into