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Sintering and characterization of magnesium oxide macroporous membranes

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Abstract

This paper describes a method for obtaining a magnesium oxide macroporous structure with a homogeneous pore size using a reproducible technique. The proposed method used MgO nanoparticles synthesized by a sol-gel/nanotemplating technique as a starting material. The MgO nanopowder was pressed to form a pellet and sintered. The studied parameters were the pressure employed to make the pellets and the sintering temperature. The samples were characterized by scanning electron microscopy, nitrogen adsorption analyzed using BET and BJH analyses, X-ray diffraction and mercury intrusion porosimetry. MgO nanoparticles with crystallite sizes of approximately 9 nm were synthesized and used to make sintered membranes with 50–150 nm macroporous diameters, total pore areas above 8 m^2/g and open porosities above 42% for the pressure of 173.4 MPa and sintering temperatures of 1173 and 1273 K.

Keywords: A. Sol-gel; Magnesium oxide; Nanoparticles; Sintered membrane; Macroporous

1. Introduction

The search for cheaper processes to separate oxygen from the air has been triggered by environmental concerns related to the reforming of methane to produce the synthesis gas and combustion using pure oxygen [1,2]. These processes may require the removal of nitrogen from the flue gas to make the CO_2 capture more efficient. Mixed ionic/electronic conductive ceramics have emerged as good candidates; however, these materials must be thin to improve the flux [2], therefore, they are prone to failure by fracture. One proposed solution is the use of a ceramic membrane to support the conducting thin ceramic [3]. The ceramic membrane must have high temperature thermal stability, good mechanical resistance, good chemical stability, long life and good defouling properties [4]. Magnesium oxide has some these properties and is relatively cheap; therefore, it is an excellent material candidate for use as a porous support for thin film oxygen transport membranes used to purify oxygen in industrial processes [5,6]. Indeed, it has already been used as the support membrane for $La_{0.2}$ $Sr_{0.8}$ Co O_{3-x} and $Ce_{0.9}$ $Gd_{0.1}$ $O_{1.95-\delta}$ conductive membranes [7,8].

Porous magnesium oxide support membranes have already been made from the mixtures of MgO powder and an organic material that was eliminated before the sintering process at temperatures above 1250 °C [7,5,6], which are typical of ceramic sintering. Hong et al. [7] and Ramachandran et al. [5] used the exotemplate method [9,4,10] to restrain the sintering coalescence at the very high process temperatures. Hong et al. [7] reported a porosity range from 28% to 55% and pore diameters from 0.7 μm to 2.4 μm for membranes made from a mixture of carbon black and commercial MgO powder, pressed and sintered at 1873 K. Smaller pore sizes were obtained by Ramachandran et al. [5] with similar porosity. They were able to get pore sizes from about 75 nm up to 315 nm, with open porosity of 46.8% for the sintering temperature of 1250 °C. Their porous distribution was clearly bimodal for their lower temperature and changed to a monomodal distribution when the temperature was above 1350 °C. Lipińska-Chwalek [6] used commercial MgO powder to prepare their sintered membranes. They did not report the MgO powder size and used as a binder a mixture of methylhydroxypropylcellulose, hydroxypropylmethylcellulose and water for most membranes, except for a few membranes that they also added bohemite. Their sintering temperatures ranged from 1300 to 1700 °C. Their membranes had a porosity of 36% measured by optical, confocal and scanning electron microscopies. They

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observed that the fracture stress was around 45 MPa and almost independent of the sintering temperature, however the room temperature elastic modulus increased for higher sintering temperature.

The recent researches on producing MgO membranes have used commercial MgO powder sizes, however, if MgO nanoparticles are used, the sintering may be performed at much lower temperatures as observed by Kleiman and Chaim [11,12]. The coalescence kinetics will be controlled by both time and the initial size of the nanoparticles [12]. Nonetheless, the present authors do not know of any previous study on the sintering of nanoparticles to produce a ceramic MgO support membrane.

This paper reports the use of MgO nanoparticles produced by a modified sol-gel method [13] to fabricate sintered MgO membranes with very small pores. Membrane disks were made at two pressures for green densification and four temperatures for sintering. The sintering time was kept constant. The sintered membranes were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), textural analysis by nitrogen adsorption (BET) and mercury intrusion porosimetry (MIP).

2. Materials and methods

MgO nanoparticles were prepared by a modified sol-gel method that employed polyvinyl alcohol (PVA) as a gelling agent and template of the nanoporous structure [13]. Five grams of PVA were dissolved in 50 mL of water and heated at 373 K for approximately 3 h. Then 5 g of $Mg(NO_3)_2 \cdot 6H_2O$, 98% purity ISOFAR, dissolved in 50 mL of water was slowly added to the PVA solution under constant stirring. The system was maintained at the same temperature until it reached rubbery consistency. This final material was calcined at 473 K for one hour followed by a second heat treatment at 873 K for another hour to burn up the polymer residues. The resulting material was a very porous white aggregate of MgO nanoparticles that was easily reduced to a powder. The crystallite size measured by XRD was in the range of 7–11 nm, which was consistent with the previous research [13].

The membrane was a disk made by compressing the MgO powder without additives in a cylindrical steel matrix with 12.92 mm diameter. Two different pressures were used to obtain the green disks: 173.4 (P1) and 260.1 (P2) MPa. The pressure was maintained for 60 s. The disks were sintered in a tubular furnace under an air atmosphere. Four temperatures were employed: 1173 (T1), 1273 (T2), 1373 (T3) and 1473 (T4) K. The temperature was kept constant within 5 K. The samples were slowly placed inside the hot furnace, heat treated for 1 h and then slowly removed from the furnace to avoid thermal shock.

The sintered samples were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), nitrogen adsorption at liquid nitrogen temperature using the Brunauer–Emmett–Teller (BET) technique and mercury intrusion porosimetry (MIP). The sintered disks were either polished or fractured before taking SEM images obtained from secondary electrons using a Jeol JSM-6390LV microscope. Phase identification and crystallite size determination were conducted using X-ray diffraction with a Siemens D-5000 instrument, Cu Kα radiation, a Ni filter, and Bragg–Bretano geometry. Rietveld analyses of the diffraction patterns using the fundamental parameters approach were least-squares fitted using TOPAS 3 software [14]. The surface area and porosity were measured using a gas sorption analyzer (Micromeritics ASAP 2010). The samples were dried at 573 K and weighted before the measurement. High-pressure mercury intrusion porosimetry (Micromeritics AutoPore IV 9500) was performed according to ASTM Standard D4404 [15,16]. The material was previously dried at 373 K for one hour. Thrice distilled mercury was used, and the pressure was gradually increased to 413.5 MPa.

3. Results and discussion

Table 1 shows the diameter of the disks after sintering. The 2.9% diameter reduction observed at the lowest sintering temperature shows that sintering had started. As the temperature was increased, the disk diameter was reduced due to the densification of the particles (Table 2).

Fig. 1 shows the fractured surface of a disk pressed at the lowest pressure, 173.4 MPa, and sintered at 1273 K. The pores showed open and fully interconnected microstructure, which was consistent with a process between the initial and the intermediate stages of the sintering process [17]. The particle size range was between 200 and 600 nm.

Fig. 2 shows the polished surface cross-section of a disk pressed at 173.4 MPa and sintered at 1473 K, which was the highest temperature used. The sintering process seemed to be in the intermediate stage; however, the pore structure was still open and interconnected. Similar results were also obtained by Kleiman and Chaim [11] who studied the annealing of cold isostatically pressed compacts between 600 °C and 900 °C. They observed particle growth that was consistent with surface diffusion, a porous microstructure and sintering that occurred at temperatures one third of the melting point for MgO. However, they did not characterize the porosity, which is important for membrane applications.

X-ray diffraction showed that the sintered disks were essentially made of MgO; however, a very small amount of MgO_2 was also observed, usually less than 2% mass. Table 3 summarizes the experimental data from the X-ray diffraction, BET analysis and mercury intrusion porosimetry. The lattice parameter of the MgO increased as the sintering temperature was increased. This result suggested that the lower sintering

Table 1
Diameter (mm) of the sintered disks as a function of sintering temperature and compressing pressure.

Pressure (MPa)	Sintering temperature (K)			
	1173 (T1)	1273 (T2)	1373 (T3)	1473 (T4)
173.4 (P1)	12.54	12.18	11.52	10.88
260.1 (P2)	12.54	12.22	11.64	11.06