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Microporous alumina substrate with porosity >70% by gelcasting

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Abstract

Microporous alumina membrane substrate in tubular and planar configurations have been prepared by gelcasting of alumina powder slurry using high amount of urea–formaldehyde as gelling agent followed by humidity controlled drying, binder removal and sintering of the gelled bodies. Porosity of the substrate samples sintered at 1350 °C was more than 70% as measured by mercury porosimeter. More than 51% porosity could be retained even after sintering of the samples at 1450 °C. Average pores size of the membrane substrate samples sintered at temperature in the range from 1250 to 1550 °C varied between 0.42 and 0.56 with a maximum at 1350 °C. More uniform pores were observed in sample sintered at 1450 °C. Urea-formaldehyde polymer present in the gelcast body acts as template for micropores.

Keywords: B. Porosity; Alumina; Gelcasting; Membrane substrate

1. Introduction

Microporous alumina membranes are used for separation of microbes from drinking water, concentration of fruit juices in food industry and filtration of beverages for their clarification and sterilization [1]. They also find application as substrate for nanofiltration, ultra filtration and reverse osmosis membranes [1–5]. These membrane substrates in planar form were usually prepared by methods such as powder pressing, slip casting or tape casting followed by partial sintering of powders of appropriate particle size and size distribution [6–10]. Membrane substrates in tubular form find more use and are fabricated by extrusion and centrifugal casting [11–12]. It is well known that permeate flux of a membrane is directly proportional to its porosity [7]. Literature shows that porosity of membrane substrates prepared by the above methods is <50%. The pores are unstable at higher sintering temperatures and lower sintering temperature leads only to partial sintering which does not provide adequate strength during rigorous use [2–12].

Gelcasting is a novel slurry based process for preparation of near-net-shape ceramic components. In this process, in situ polymerization of organic monomer and cross linking agent is used for setting of concentrated ceramic powder slurry cast in a mould [13–15]. Acrylamide monomers are widely used for gelcasting of aqueous ceramic powder suspensions. Recently, the process has been extensively studied for the preparation of porous ceramics and ceramic foams [16–20]. The gelcasting process has also been used for preparation of porous alumina and yttria stabilized zirconia supports for ceramic membranes [21–23]. Open porosity of membrane substrate fabricated by gelcasting is also less than 50%.

Prabhakaran et al. reported a gelcasting process for near-net-shape dense alumina bodies using urea–formaldehyde [24]. In this process, concentrated alumina suspensions prepared in acidic aqueous medium is set by acid catalyzed in situ polymerization of methylol urea (prepared from urea and formaldehyde) and urea. Amount of urea–formaldehyde used is less than 10 wt.% of alumina. Urea–formaldehyde system has also been used for fabrication of tubular alumina substrate with porosity ∼42% by a freeform gelcasting technique [25]. We have noticed that urea–formaldehyde system produce strong gels even at high polymer to alumina powder ratio (even polymer content >40 wt.%). Also, being a thermosetting

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polymer urea–formaldehyde would decompose without deformation of the gelcast body on binder removal even if it is present in high amount. The urea–formaldehyde polymer, in high amount, is expected to acts as template for micropores. In the present work, effort has been made for gelcasting of alumina using the highest amount of urea–formaldehyde possible with a view to prepare alumina membrane substrate with maximum porosity [26]. Microporous substrates in planar and tubular forms with porosity greater than 70% have been achieved by the present technique which has not been reported earlier.

2. Experimental procedures

A16SG alumina powder (ACC Alcoa India) of average particle size 0.34 μm and surface area 10.4 m^2/g was used. The urea and formaldehyde solution (37%, w/v) used were reagent grade (S.D. fine chemicals, India). Distilled water was used for preparation of dispersions and reagent grade HNO_3 (Merck, India) and NaOH (Merck, India) were used for pH adjustment.

The gelcasting flowchart for preparation of porous alumina substrate is shown in Fig. 1. Urea and formaldehyde solution were mixed in the molar ratio 1:4, the pH was adjusted to 8.5 using NaOH solution and then the solution was aged for 24 h to form methylol urea monomers [24,25]. A 23 vol.% alumina slurry was prepared in the methylol urea solution and pH of the slurry was adjusted to 2 using dilute HNO_3. The slurry was ball milled for 6 h in a polyethylene container using zirconia grinding media. The slurry was then supplemented with additional urea to make the mole ratio of urea and formaldehyde 1:2 and then cast in the form of circular disc of diameter 30 mm and thickness 3 mm in an open glass mold. The slurry, after necessary gelation was removed from the mold and dried at 75% relative humidity at 30 °C. Tubes having 150 mm length, 2 mm thickness and 18 mm inner diameter were also fabricated by casting the slurry in between two concentric pipes. Viscosity of the slurry was measured using Brook field viscometer (RVT Model) using small sample adapter (SC4-21/13R) of coaxial cylinder geometry.

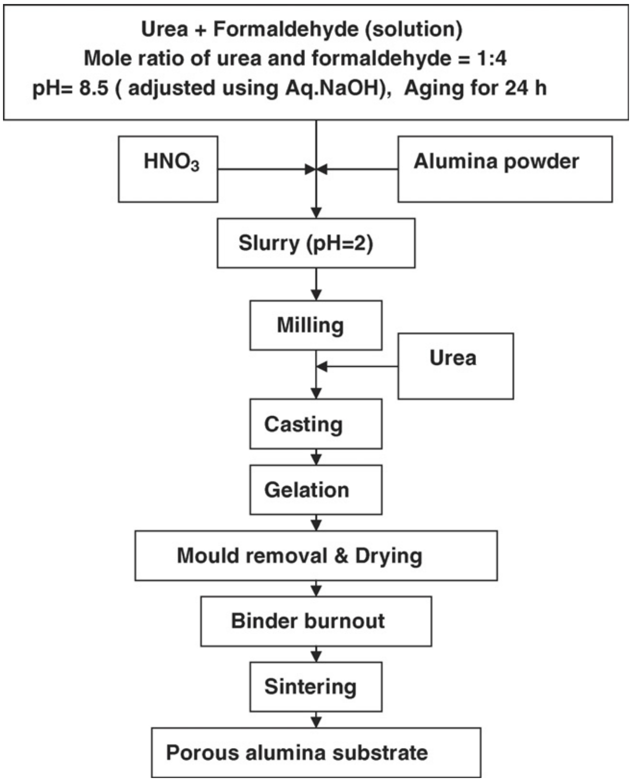

Fig. 1. Flow chart for preparation of microporous alumina substrate.

Polymer content in the dried sample was estimated by thermo gravimetric analysis (Hi Res TGA 2950, TA Instruments). Polymer removal from the dried gelcast discs and tubes were carried out by heating at a rate of 5 °C/h up to 300 °C and then 60 °C/h up to 600 °C. After binder removal, the substrate samples were sintered at various temperatures from 1250 to 1550 °C for 2 h with a heating rate of 300 °C/h up to the sintering temperatures. Porosity and pore size of the sintered samples were measured using mercury porosimeter (Thermo Finnigan, Pascal 440). Microstructure of fractured surface of the sintered samples was observed using a scanning electron microscope (LEO 1455).

3. Results and discussion

Urea reacts with formaldehyde at pH 8.5 to form methylol urea derivatives [24,27]. Alumina powder disperses well in acidic (pH 2) methylol urea solution and the slurry (23 vol.%) showed shear thinning flow characteristics. Viscosity of the slurry measured at shear rate in the range 4.65–93 s^{-1} is in the range from 200 to 76 mPa s. Fig. 2 shows viscosity versus shear rate plot of the slurry. Upon addition of urea to the above slurry, the methylol urea reacts with urea to form urea–formaldehyde polymer which transform the slurry in to a thick gel [24,27]. Gelation of the slurry was observed within 15 min after casting. The gel obtained had sufficient strength that the discs and tubes cast from the slurry could easily be removed from the mold without any deformation immediately after gelation. The cylindrical samples showed linear shrinkage of 11.83% during drying. However, no cracks or deformation was observed during drying under the humid conditions.

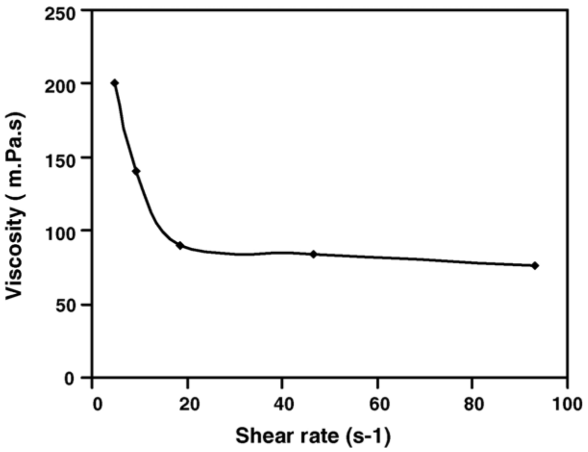

Fig. 2. Viscosity vs. shear rate plot of gelcasting slurry.

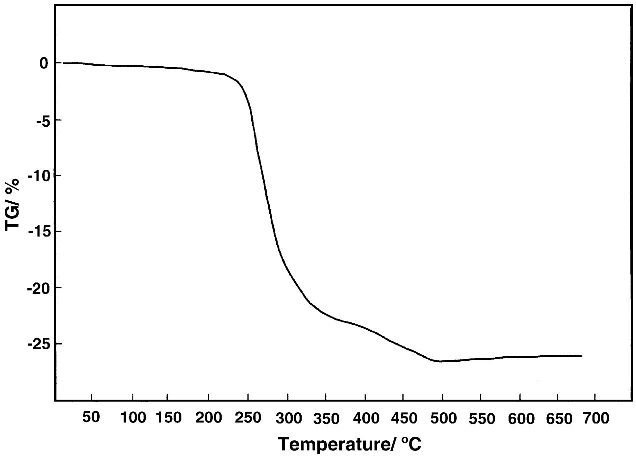

Fig. 3. TGA plot of the gelcast sample.

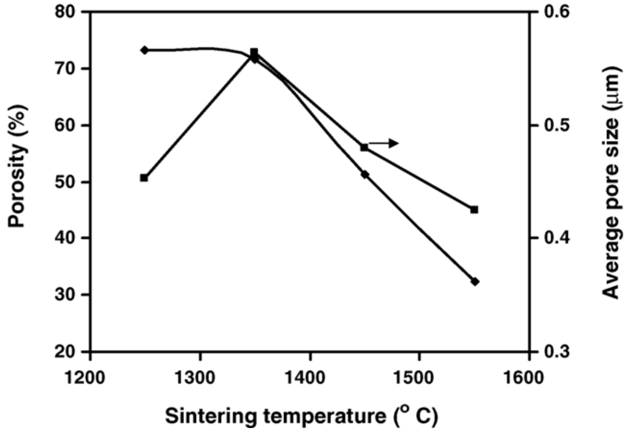

Fig. 5. Porosity and average pore size of alumina membrane substrate samples sintered at various temperatures.

Fig. 3 is the TGA plot of the gelcast sample. TGA analysis showed urea–formaldehyde polymer content of 26.5 wt.% in the dried gelcast sample. More than 70% of the polymer present in the gelcast sample was removed at temperature below 300 °C. Therefore, a slow heating rate of 5 °C/h was used in this temperature range to avoid crack and deformation. However, samples prepared from slurries of alumina loading lower than 23 vol.% (polymer content >27 wt.%) showed deformation during binder removal. The binder removed samples on sintering undergoes near isotropic shrinkage. The shrinkage observed in the thickness direction for cylindrical disc samples sintered at various temperatures is shown in Fig. 4. The samples sintered at temperature in the range from 1250 to 1550 °C showed linear shrinkage in the range 6.6–28.23% in the thickness direction. Corresponding diametrical shrinkage observed was in the range 5.35–27.02%.

Fig. 5 shows porosity and average pore size of the alumina substrate samples sintered at various temperatures. It is observed that porosity decreased from 73.1 to 71.6% when the sintering temperature was increased from 1250 to 1350 °C. Further increase in sintering temperature to 1450 °C decreased the porosity rapidly to 51.4%. A porosity of 32.4% is retained even after sintering at 1550 °C. However, average pore size first showed an increase from 0.45 to 0.56 μm when the sintering temperature increased from 1250 to 1350 °C and then decreased with increase in sintering temperature. The average pore size observed at 1450 and 1550 °C were 0.48 and 0.42 μm, respectively.

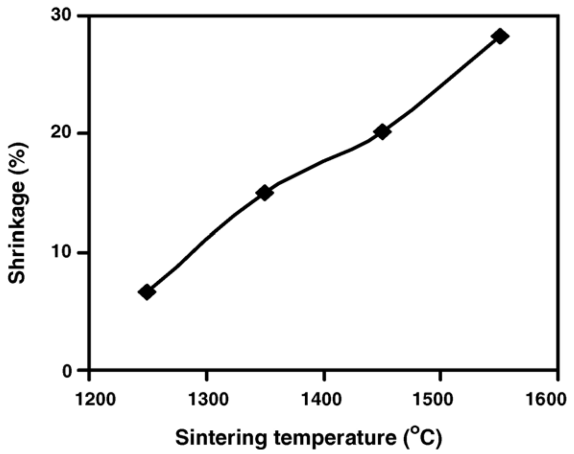

Fig. 4. Sintering shrinkage of gelcast alumina substrate samples.

Fig. 6 shows pore size distribution diagram of the alumina substrate samples sintered at various temperatures. For sample

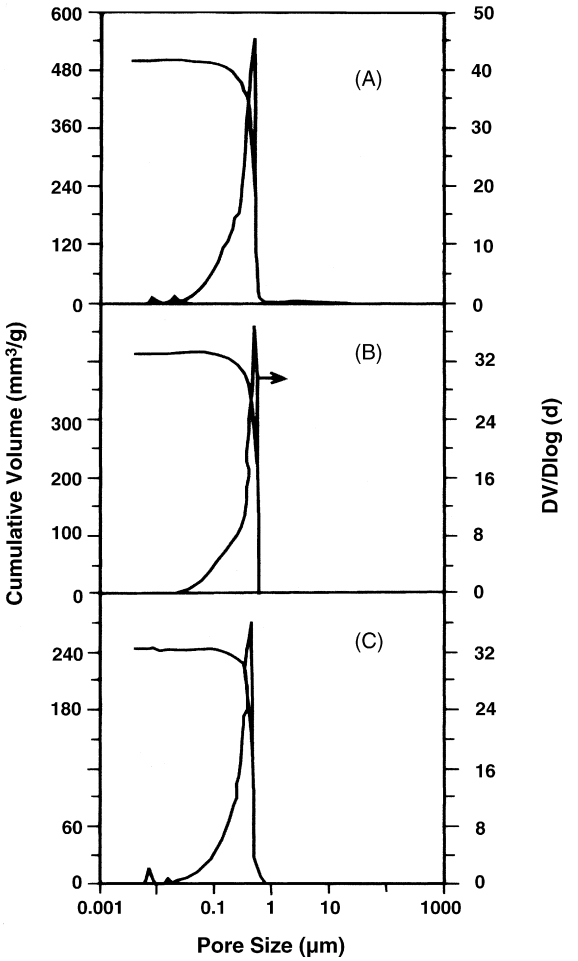

Fig. 6. Pore size distribution of alumina membrane substrate samples sintered at various temperatures (A) 1250 °C, (B) 1350 °C and (C) 1450 °C.

sintered at 1250 °C, 64.6% pores have size in the range 0.25–0.5 μm, 27.3% have size in the range 0.5–0.75 μm and remaining are below 0.25 μm. When sintering temperature increased to 1350 °C percentage of pores in the size range 0.25–0.5 μm decreased to 39.4 and the percentage of pores in the size range 0.5–0.75 μm increased to 55.7. Further increase in sintering temperature to 1450 °C decreased the percentage of pores in the size range 0.5–0.75 μm to 5.5 and 86. 7% of the pores became in the size range 0.25–0.5 μm. That is, more uniform pores were observed in samples sintered at 1450 °C. Microstructure study also reveals uniform pore structure in sample sintered at 1450 °C. The pore size distribution data is given in Table 1. Fig. 7 shows SEM microstructure of fractured surface of microporous alumina membrane substrate samples sintered at various temperatures.

Though an increase in pore size at sintering temperature in the range 1300–1350 °C was observed by Das et al. no explanation has been given for the observation [6]. A possible explanation for pore size increase observed in the temperature range 1250–1350 °C in the present work is diagrammatically shown in Fig. 8. The gelcast body after binder removal showed density of 25.4% TD. Alumina particles in the binder removed gelcast body are expected to be loosely packed. It is believed that on heat treatment at temperature in the range from 1250 to 1350 °C particles segregate to form clusters through neck formation resulting in widening of pores. Sintering of the samples continued with further increase in temperature resulted

Table 1
Pore size distribution data of alumina substrate samples sintered at various temperatures

Pore size range (μm)	Volume (%)
Sintered at 1250 °C	
1.5–1	0.09
0.75–0.5	27.32
0.5–0.25	64.57
0.25–0.1	6.56
0.1–0.075	0.55
0.075–0.05	0.36
0.05–0.025	0.09
0.025–0.01	0.27
0.01–0.0075	0.18
Sintered at 1350 °C	
0.75–0.5	55.66
0.5–0.25	39.44
0.25–0.1	4.43
0.1–0.075	0.35
0.075–0.0.05	0.12
Sintered at 1450 °C	
1–0.75	0.13
0.75–0.5	5.53
0.5–0.25	86.56
0.25–0.1	6.85
0.025–0.01	0.26
0.01–0.0075	0.66

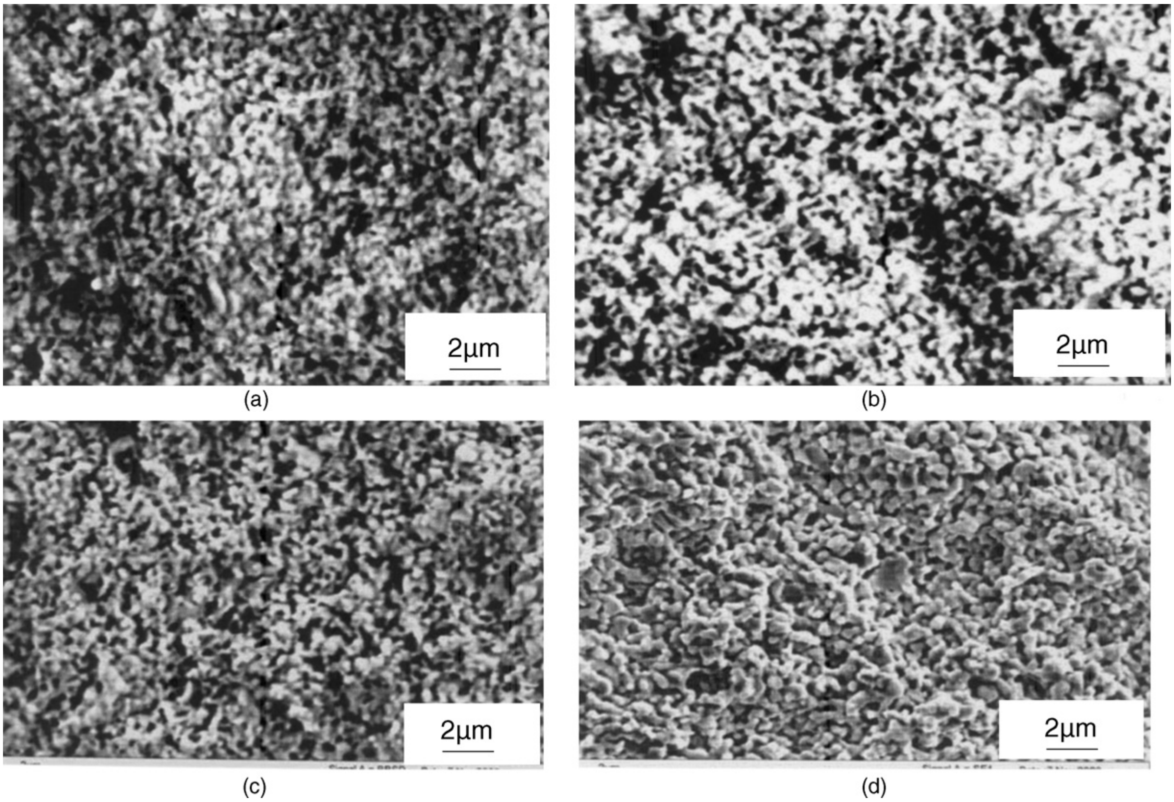

Fig. 7. SEM photograph of fractured surface of alumina membrane substrate samples sintered at various temperatures (a) 1250 °C, (b) 1350 °C, (c) 1450 °C and (d) 1550 °C.

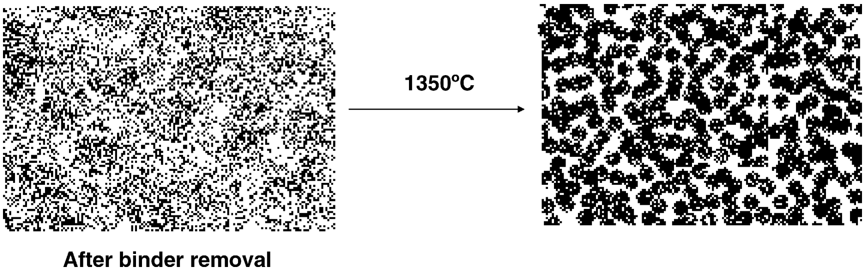

Fig. 8. Diagrammatic representation of the proposed mechanism of pore size increase in the temperature range from 1250 to 1350 °C.

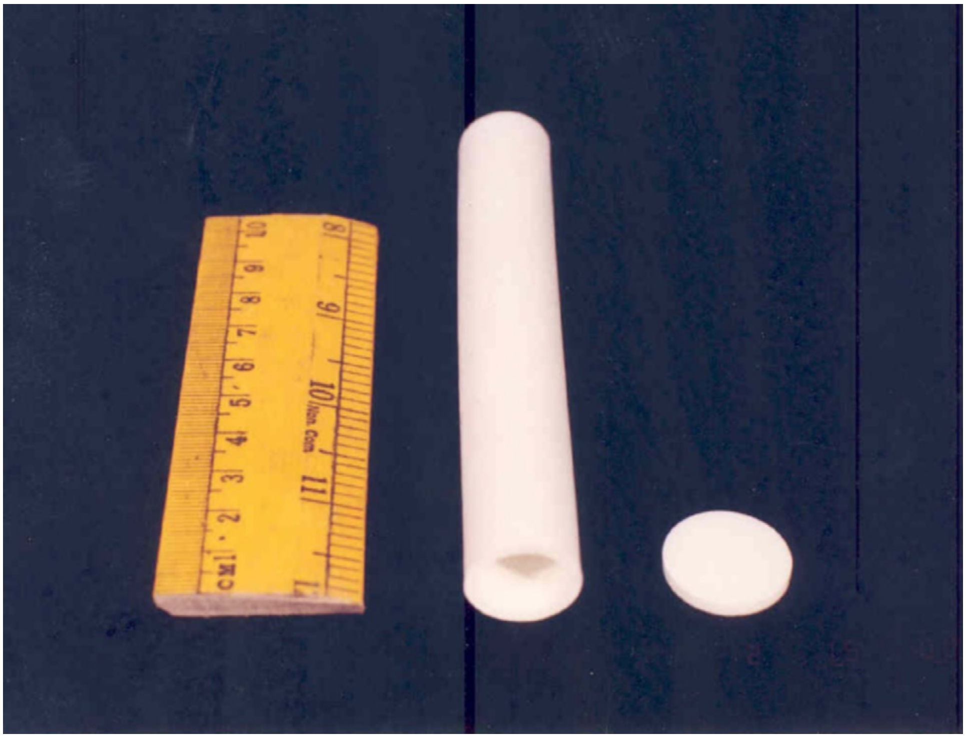

Fig. 9. Photograph of alumina membrane substrate in tubular and planar configuration prepared by gelcasting (sintered at 1350 °C, porosity 71.6%).

in pore shrinkage and elimination of some of the pores. Therefore, pore size and porosity decreases above 1350 °C.

Preparation of membranes substrate by usual methods gives porosity 40–50% and in most of the cases pores were unstable at temperature above 1250 °C. It is worthy to note in the present method that more than 70% porosity is retained at 1350 °C. The porosity of the substrate sample sintered at 1450 °C in this method is much higher than that reported for membrane substrates sintered at 1250 °C. Fig. 9 shows photograph of membrane substrate in tubular and planar configurations fabricated by the present method.

4. Conclusions

The present work demonstrate the possibility of fabrication of microporous alumina membrane substrate in tubular and planar configurations with porosity >70% and average pore size <0.5 μm by gelcasting. Urea–formaldehyde used in high amount acts as template for micro pores. Most of the pores are stable up to 1350 °C. The membrane substrate sintered at 1450 °C has more uniform sized pores.

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