

Pressureless sintering and gas flux properties of porous ceramic membranes for gas applications



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ARTICLE INFO

Article history:

Received 29 April 2017

Received in revised form 17 September 2017

Accepted 2 October 2017

Available online 5 October 2017

Keywords:

Porosity

Pore formers

Kaolin

Physico-mechanical properties

Gas separation

Gas flux

ABSTRACT

The preparation and characterization of kaolin based ceramic membranes using styrofoam (STY) and sawdust (SD) as pore formers have been prepared by mechano-chemical synthesis using pressureless sintering technique with porogen content between (0–20) wt% by die pressing. Pellets were fired at 1150 °C and soaking time of 4 h. The membranes cast as circular disks were subjected to characterization studies to evaluate the effect of the sintering temperature and pore former content on porosity, density, water absorption and mechanical strength. Obtained membranes show effective porosity with maximum at about 43 and 47% respectively for membranes formulated with styrofoam and sawdust porogens but with a slightly low mechanical strength that does not exceed 19 MPa. The resultant ceramic bodies show a fine porous structure which is mainly caused by the volatilization of the porogens. The fabricated membrane exhibited high N₂ gas flux, hence, these membranes can be considered as efficient for potential application for gas separation by reason of the results shown in the gas flux tests.

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Introduction

The use of traditional ceramics, using raw materials instead of industrial chemicals is becoming very interesting mainly due to the lower price of the raw materials available. Nigeria and Ghana are amongst countries in the world that have abundantly available raw materials, such as kaolin, calcium carbonates (CaCO₃), feldspar and quartz. Some studies have already been published on the continent for ascribing value to these native raw materials, for the production of advanced ceramics [1–12] and ceramic membranes [13–15,41]. In particular, in the membrane field, the possibility of replacing the more expensive starting materials by cheaper raw materials is significantly important from the economic and energy perspectives. In fact, the price of alumina, usually employed as starting material for membrane fabrication, is at least 100 times greater than that of kaolin. The other important advantage is the possibility of reducing the sintering temperature

when alumina are replaced by other cheap raw materials. To add to this, several materials are usually employed for the preparation of ceramics membranes, such as alumina, zirconia and titania. However, natural raw materials, such as kaolin (chemical structure: Al₂O₃·2SiO₂·2H₂O) [16–18] are gaining relevance for preparing porous ceramics membranes [19–24] and it has been used in this work as a starting material.

In general, ceramic membranes have been widely investigated for energy and environmental applications due to its unique advantages such as high thermal, chemical and mechanical stability, environmental friendliness, and low energy-consumption [25]. These inorganic membranes have the afore-mentioned properties as have been buttressed by several researchers [26–29], in addition to a longer life-time, ease of cleaning, a low thermal conductivity and a low dielectric constant [30,31]. Furthermore, these membranes are found to be able to resist highly corrosive acidic and alkali media as well as to withstand high pressure applications. It is pertinent to note that single-channel or multi-channel tubular multi-layer ceramic membranes have practical value due to their low permeation resistance, high permeation flux and good mechanical performance, which are necessary during many practical industrial separation applications [32,33]. In recent studies [4,6], the potentials of fabricating porous ceramics bodies from

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kaolin using different pore formers was investigated in addition to the impact of dehydroxylation on the structural integrity of kaolin based ceramics.

Therefore, the objective of this study is to fabricate dense ceramic membranes with clay/sawdust and styrofoam mixture with varying ratios by weight. The physical and mechanical properties of the kaolin based ceramic membranes and gas flux test results are also presented. We prepared asymmetric kaolin based membranes for its potential in gas applications using sawdust and styrofoam as the porogens in order to improve the pore structure and connectivity. The physical and mechanical properties of fabricated membranes was investigated. The corrosion resistance of the sintered membranes has been characterized in terms of percentage mass loss. The membranes were tested for nitrogen gas flow for potential gas permeability applications.

Experimental procedures

Raw materials

Natural kaolin types: Kankara and Kibi (KK and KB) which were beneficiated, and milled sawdust and styrofoam (SD and STY) powders were used as starting materials. The raw kaolin were obtained from Kankara and Kibi regions in Nigeria and Ghana respectively, while the sawdust and styrofoam powders were used as pore formers. The raw materials were mixed in a ball mill at 50 rpm for 30 min. The particle size distribution of KK and KB and SD and STY materials were determined by the Light Laser Beam Scattering (LLBS) technique. The Zeta potential of the kaolin used were investigated to confirm the rheological properties of the paste that facilitate the forming of the membranes [6].

The surface morphology of the raw materials were carried out on an ultra-high vacuum and high resolution FEI XI-30 scanning electron microscopy equipped with an EVEX EDS and operated at 15 kV. Samples were metalized with gold/platinum coating prior to the analysis. Images were acquired using a Gatan MiniCL imaging system at various magnifications. Fourier Transform Infrared (FTIR) spectroscopy data was collected on a PerkinElmer Spectrum two FT-IR spectrometer equipped with UATR sampling accessory. The change in functional group of the kaolin was verified in the range of $400\text{--}4000\text{ cm}^{-1}$. Samples were grinded and mixed with dried KBr using ceramic porcelain mortar and loaded into a sample holder mounted in the instrument. Instrumentation for attenuated total reflection FTIR (ATR-FTIR) was used to verify the functional group of the porogens (SD and STY) using FTIR (Shimadzu IR Affinity). The spectra were collected in the range from $650\text{ to }4000\text{ cm}^{-1}$.

X-ray powder diffraction (XRD) patterns of the kaolin were collected on a Bruker AXS-D8 Advance Bragg-Brentano diffractometer operating a copper tube ($\lambda = 1.5418\text{ \AA}$) at 40 kV and 30 mA. The goniometer is equipped with a high resolution setup (0.3° divergence slit, 2.5° incident and diffracted beam Soller slits, 6 mm receiving slit) and a curved-crystal graphite analyser, providing a narrow and symmetrical instrumental profile over the investigated angular range. The instrumental resolution function was characterised with the NIST SRM 1976b (Al_2O_3) standard [39]. All reflection profiles were simultaneously fitted with symmetrical pseudo-Voigt functions whose width and shape were constrained according to the Caglioti et al. formulae [40]. The XRD patterns of all specimens were recorded in the $10\text{--}70^\circ 2\theta$ range with a step size of 0.017° and a counting time of 14 s per step.

Membrane fabrication

Porous membranes were fabricated from kaolin: Kankara and Kibi kaolin (KK and KB) and sawdust and styrofoam (SD and STY)

mixtures. The average particle size of SD and STY was investigated and STY was at huge variance to SD [6]. The selected composition of powders used for the plastic paste preparation was based on a fixed 20 wt% of the plasticizer (KB), and a 5 wt% step-wise variation of KK, SD and STY powders. This variation has been reported in a recent study carried out by our group with emphasis on the pore formers (SD and STY) used in this study [6]. The powder mixture was aged with a progressive addition of water to obtain a plastic paste with good homogeneity and to allow the shaping. Subsequently, the paste was left for 6 h under a high humidity to improve its rheological property. The paste was transferred into a die and lightly pressed (0.05 kPa) for 10 s. Subsequently, the desired asymmetric membrane configuration in disc shape was pressed for 5 min at 3.5 Mpa. The membranes were sintered at a temperature of 1150°C for 4 h. As was highlighted, a pressureless sintering technique was adopted which uses two different sintering temperature. The first sintering temperature should guarantee a relative density higher than 75% of theoretical sample density. This will remove supercritical pores from the body. The sample will then be cooled down and held at the second sintering temperature until densification is completed. The sintering process for the ceramic fabrication was run in two steps; firstly, sintering temperature was setup at 500°C at a rate of $2^\circ\text{C}/\text{min}$ and held for 2 h so that the pore formers (SD and STY) would be burned off. Then the sintering temperature was increased up to 1150°C at a faster ramping rate of $5^\circ\text{C}/\text{min}$ and held for 4 h. Finally, temperature was reduced to room temperature at a rate of $5^\circ\text{C}/\text{min}$. After sintering, the compact and porous ceramic membranes were polished on both sides using silicon carbide abrasive paper to obtain ceramic membranes with uniform surface and considerably free from defects. These membranes were washed with deionized water in an ultrasonic for 15 min to remove the loose particles adhered on the surface of membranes. This temperature (1150°C) was found to be appropriate since at lower sintering temperatures we did not obtain the adequate mechanical strength (results not shown).

For the mechanical properties testing of the membrane, the kaolin and pore former mixture was completely filled into a rectangular mold and pressed to the same level to ensure compactness and dimensional homogeneity using a hydraulic pressing machine with pressure corresponding to 3.5 Mpa. The as-prepared green body samples were removed from the mold and dried at room temperature on boards for three (3) days after which they were further dried at 150°C for 24 h in a hot air oven to remove moisture. The dried batch-formulated green bodies were sintered at 1150°C for 4 h in an electric muffle furnace at a heating rate of $5^\circ\text{C}/\text{min}$ after the systematic pore former oxidation process which was set at 500°C at a rate of $2^\circ\text{C}/\text{min}$ and held for 2 h.

To investigate the topography of the membranes, scanning electron microscopy analysis was conducted to study the morphological features of the various layers of the ceramic membranes using an ultra-high vacuum and high resolution FEI, XI-30 scanning electron microscope. Samples were metalized with gold/platinum coating prior to the analysis. Images were acquired at magnifications of $200\times$ and $500\times$ for sintered samples. The morphology of the lightly pressed membranes was examined by scanning electron microscopy. The fracture surface of membrane was dried and then imaged using a FEI, Inspect S50 instrument with an accelerating voltage of 15 kV. The samples were viewed perpendicular to the fractured surface. Furthermore, polished sections of the sintered membranes were imaged to provide additional qualitative data on the pore geometry and interconnectivity. Fine polishing of the ceramic membrane surfaces was conducted using graded ferric oxide suspensions in water. It was done on a rotating wheel with a layer of fluid on the surface of the polishing cloth using automatic wheels (Finchley polishing tool, UK).

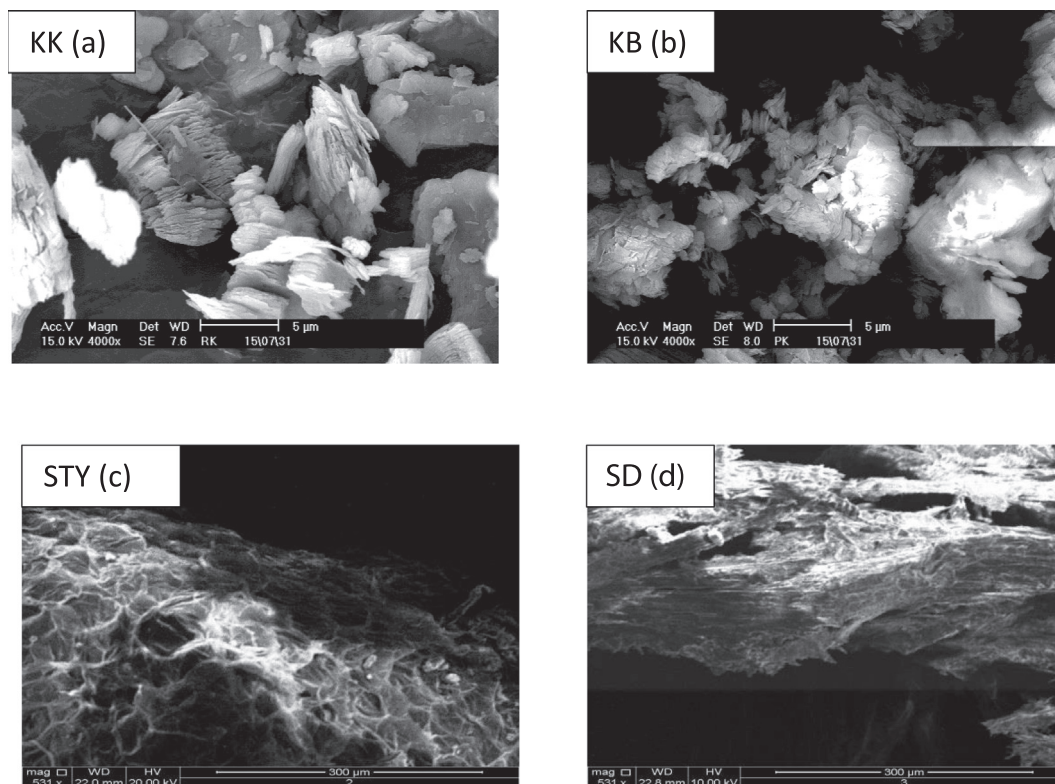


Fig. 1. SEM images of the raw materials, a) Kankara kaolin; b) Kibi kaolin; c) styrofoam; d) sawdust.

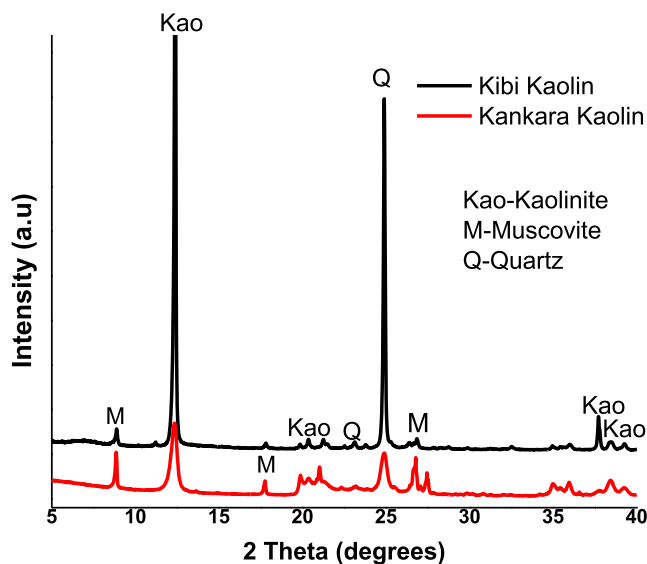


Fig. 2. XRD spectrum of the kaolin powders.

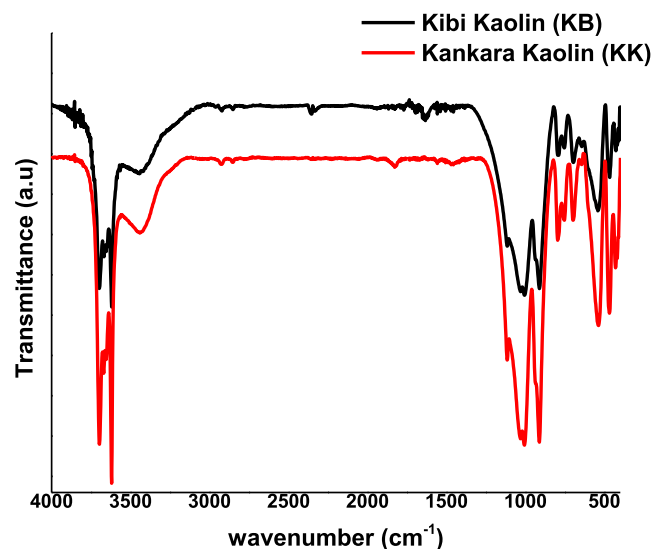


Fig. 3. FTIR spectrum of kaolin (KK & KB).

Chemical stability of the membranes was determined by subjecting the membrane separately into acid (pH 4) and alkali (pH 12) solutions. The pH of the solution was adjusted using HCl solution and NaOH pellets. The stability was measured in terms of mass loss after corrosion. For this, the membrane was placed in acid and alkali solutions for one week at an atmospheric condition.

Apparent porosity, density, water absorption, flexural properties and compressive strength, were determined according to the formulae as proposed [34] and adopted in our previous work [3]. Data on flexion resistance properties of the membranes have been obtained by the three-point static bending test. At least five spec-

imens of each formulation were tested for the physical and mechanical properties of membranes.

Gas flux tests

Gas flux through the asymmetric discs was conducted using an in-house-built rig [41]. The discs were assembled in a quartz tube, sealed and tested, and re-sealed and tested until nitrogen leaks were no longer detected at room temperature. The gas flux through the porous membrane samples was tested using N₂ as carrier gas. For this experimentation, the membranes were sintered at 1150 °C

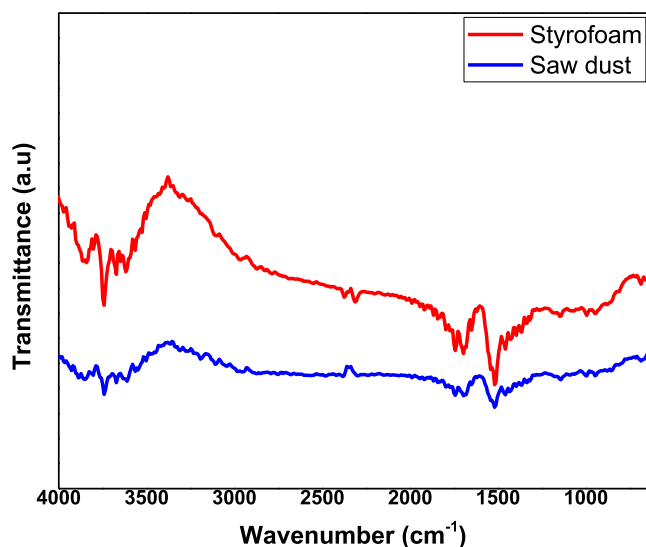


Fig. 4. FTIR spectrum of pore formers (SD & STY).

for 4 h in a muffle furnace at 5 °C/min. The mass flow controller was connected to the end of the quartz tube where the membrane was placed for the tests. The gas flow rate was measured at the out flow of the tube connected to valves for the control of inlet and outlet. The pressure supplied was varied as the flux of gas was measured at the gas exit.

Results and discussion

Morphology of raw materials

The SEM images of the raw materials used are shown in Fig. 1. Fig. 1a & b shows that KK has larger particle sizes than KB and both kaolin have lamellar or platelet shaped particles. Average particle size proportions of KK and KB are 5 μm . Fig. 1c & d show images of the porogens and it is observed that styrofoam portrays the typical elliptical shape while the finger-like morphology, which is typical of raw sawdust is visible.

Structural identification of kaolin

The kaolin (KK and KB) structure is confirmed as shown in Fig. 2. It is confirmed that kaolinite (K), quartz (Q) and muscovite (M) are the main crystalline minerals existing in this clay.

Functional group identification of raw materials

The results of FTIR spectroscopy of the starting kaolin (Fig. 3) show the KK and KB characteristic bands: Si–O (at around 426, 466, 696, 1004, and 1110 cm^{-1}), Si–O–Al (at around 534, 754, and 786 cm^{-1}), Al–OH (at around 910 and 928 cm^{-1}) and OH (at around 3692, 3668, 3650, and 3618 cm^{-1}).

The ATR-FTIR spectroscopy was used to characterize the pore formers. Fig. 4 presents the spectra of sawdust and styrofoam. Sawdust has a specific absorption band at 1033 cm^{-1} (cellulose C–O stretch). Styrofoam showed a specific band at 696 cm^{-1} (C–H out-of-plane deformation). In addition, The spectrum for the sawdust shows a broad band around 3400–3600 cm^{-1} , corre-

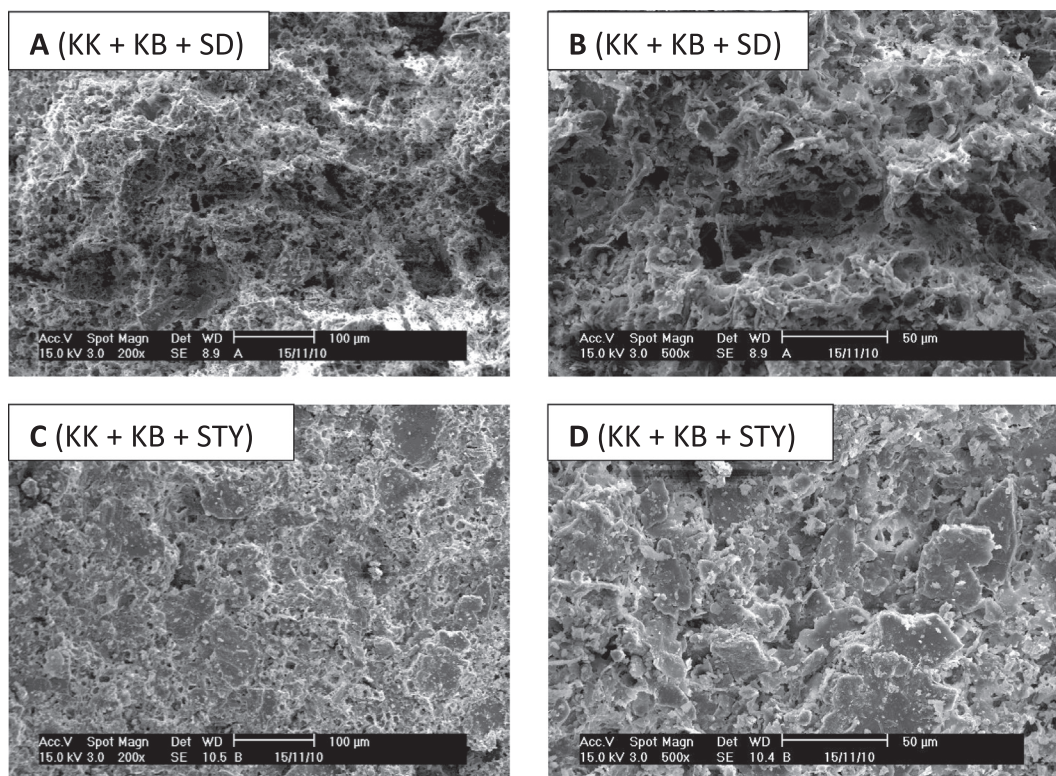


Fig. 5. SEM micrographs of membrane sintered for 4 h at 1150 °C, respectively: A and C: 200 $\times$; B and D: 500 $\times$.

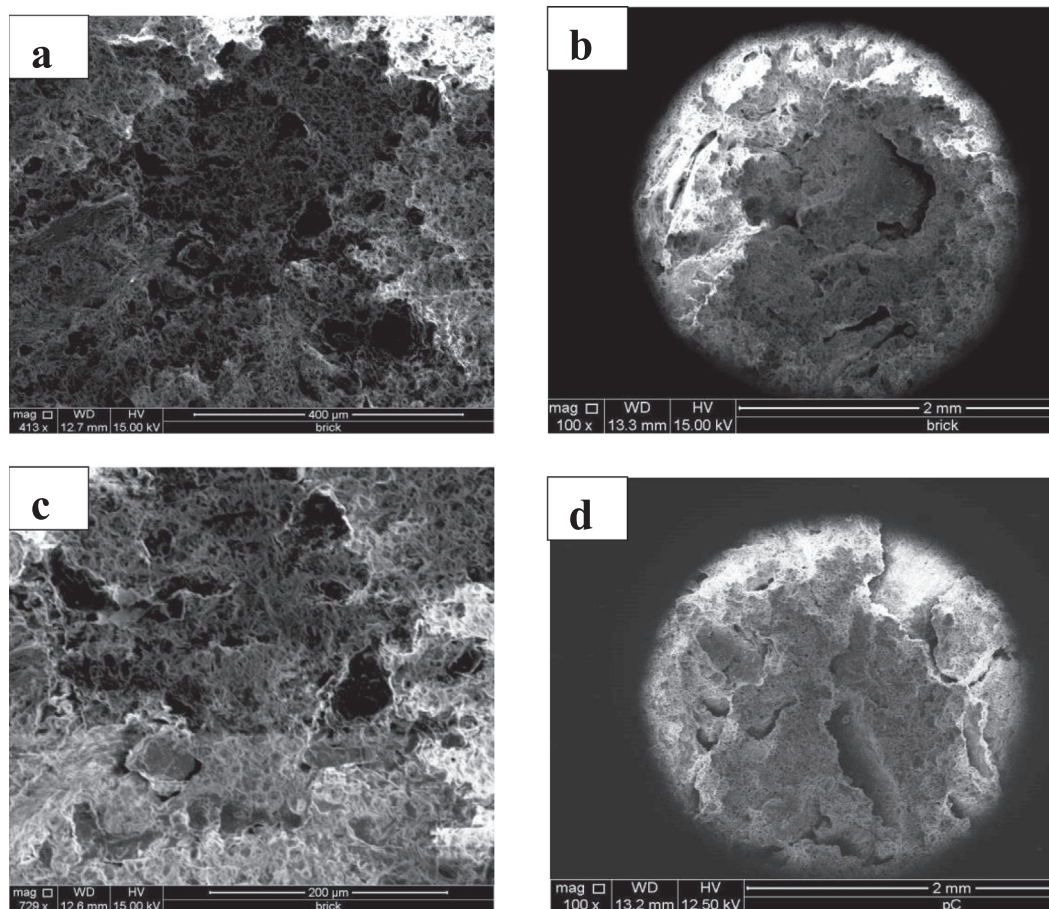


Fig. 6. SEM micrographs of polished sections of membrane (a & c) and images of lightly pressed membranes (b & d).

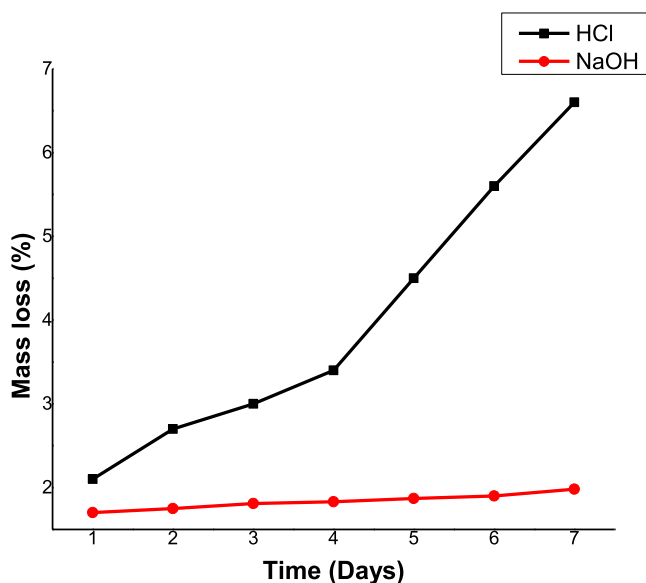


Fig. 7. Weight loss of support sintered at 1150 °C in the acidic (HCl) and alkaline (NaOH) solutions as a function of time.

sponding to the axial OH deformation. Signals around 2930 cm^{-1} , characterizes symmetric and asymmetric vibrations of $-\text{CH}_2-$ groups. A band near 1600 cm^{-1} , related to the stretching of C—C bonds of aromatic groups, a band near the region of 1230 cm^{-1} ,

related to the vibration of the aromatic lignin ring, and the bands between 1000 cm^{-1} and 1050 cm^{-1} , assigned to the stretching of C—O groups of lignin, cellulose or hemicelluloses or C—O—C group of cellulose and hemicelluloses, are also observed. Styrofoam (polystyrene) typically shows bands around $3030\text{--}3080\text{ cm}^{-1}$ attributed to aromatic CH stretching vibration.

Membrane morphology

The SEM images reported in Fig. 5 show the morphology of the membranes prepared from KK + KB + 20 wt% SD and STY sintered at 1150 °C for 4 h, respectively. The two membranes have a very similar surface morphology. This confirms the highly porous structure with a homogeneous pore distribution (even though the presence of large pores is to be noted). The pores are randomly shaped. It was seen that both macropores and micropores were interconnected. From images A–D, some cracking or intervening pore walls were also seen due to the fraction of pore formers embedded. It can be observed that the images show the porosities that have been embedded into the membranes by virtue of the combustible pore formers (large dark holes in the images).

Ceramic membranes for gas applications should have a high porosity ratio (percentage of porous volume to total volume), a narrow pore size range, and an accepted mechanical strength, as well as a high chemical stability. The regularity of porous texture is realized by the pore formers, which would dissociate into CO_2 gas under sintering conditions. The path taken by the released CO_2 gas creates the porous texture of the ceramic membrane and contributes to the membrane porosity during the sintering process.

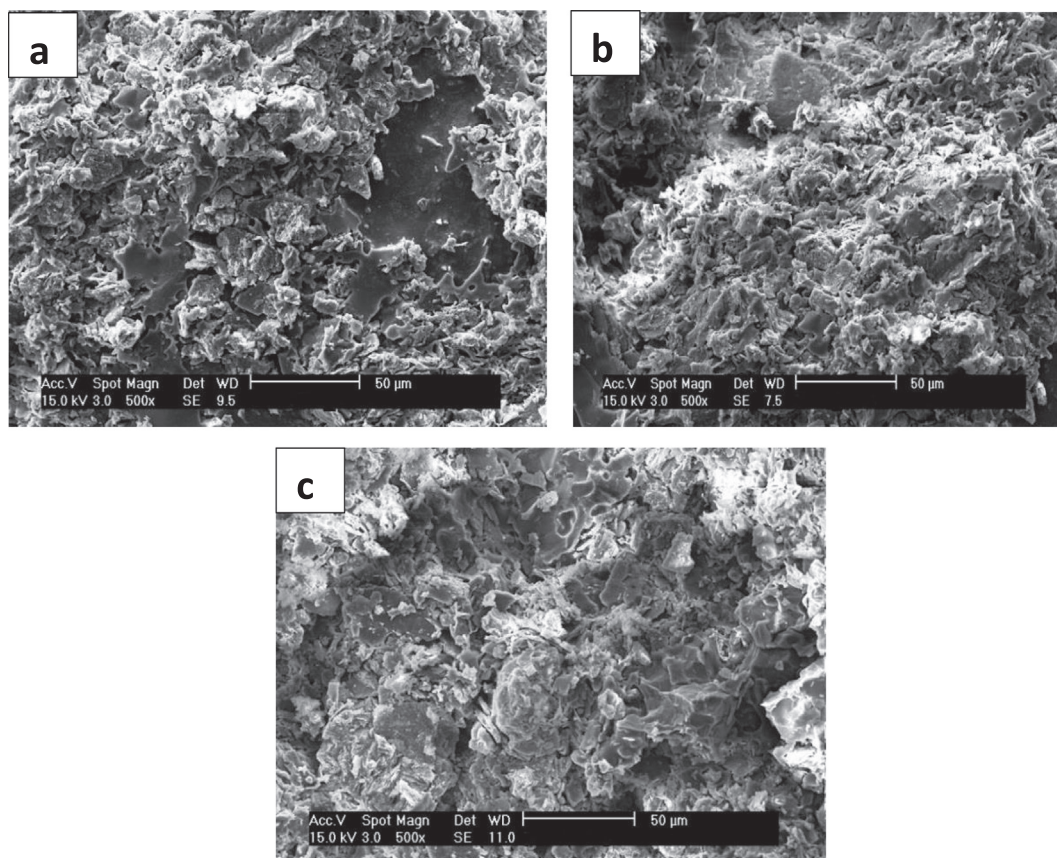


Fig. 8. SEM micrographs of the membrane before and after corrosion: (a) un-corroded; (b) pH 4, HCl corrosion (c) pH 12, NaOH corrosion.

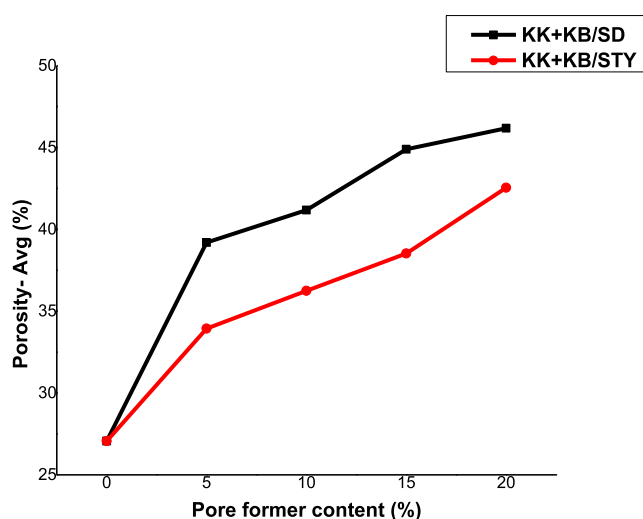


Fig. 9. Porosity of membranes with varying weight of pore formers.

The porosity should result in an increase in gas flux as it will be explained in Section “porosity and gas flux characteristics of membranes”. The main remarks that can be drawn from these results is that the pressureless sintering allows a systematic increase in voids and subsequent densification of the membranes.

Also, to allow for a better view of the porous network, Fig. 6a & c, show the SEM images of the polished sections of fabricated membranes. It was observed that the porous network of interconnected pores were quite visible. It can also be noticed that

a continuous porous structure was created. The addition of the pore generators (SD and STY) increases porosity and pore size as well as pore connectivity, owed to the increase in the amount of interconnected pores created by pore former burnout. Surface images of the pre-pressed asymmetric discs are shown in Fig. 6b & d. It is noticed that light/weak pressure in pressing the ceramic compact may compromise the mechanical integrity of membranes owing to the noticeable fractured surfaces.

Mass loss on corrosion

The chemical corrosion resistance, of the membranes sintered at 1150 °C, was evaluated by the mass loss after being immersed into HCl (pH = 4) and NaOH solutions (pH = 12) at room temperature for 7 days. The weight loss due to the corrosion of acids and alkali attack is shown in Fig. 7. It can be seen that the membranes shows a better alkali corrosion resistance since its mass loss is much lower than those of the membranes after acid corrosion. This can be explained by the high alkali content of the ceramic compacts under consideration which is in line with results reported elsewhere [35]. Therefore, the observed results in weight loss during corrosion tests suggest that the prepared membranes have good chemical corrosion resistance and it is suitable for applications involving acidic and basic media. This finding is also in agreement to other membrane support materials such as cordierite [29] and titania (TiO₂) [36], both of which exhibited good strong alkali corrosion resistance but poor strong acid corrosion resistance.

Fig. 8 shows the SEM of the membranes before and after corrosion at different conditions (un-corroded and after 7th day of immersion). It is noted that different morphologies are observed depending on the parameters (corrosion media and corrosion

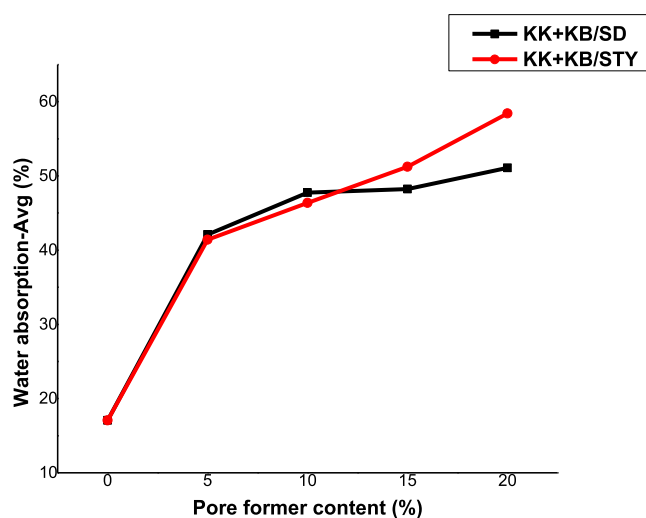
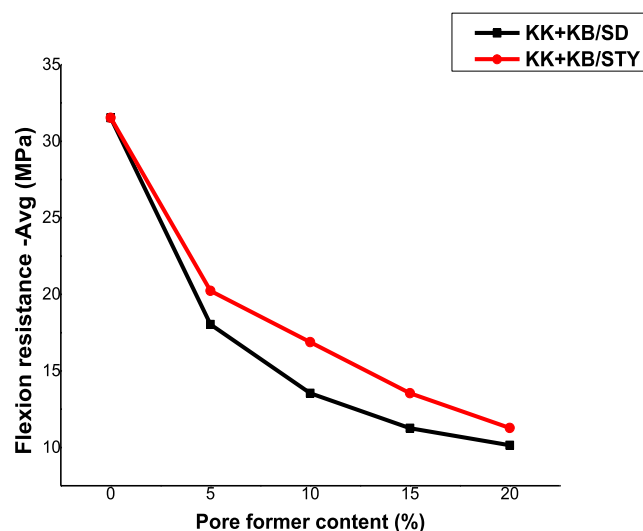
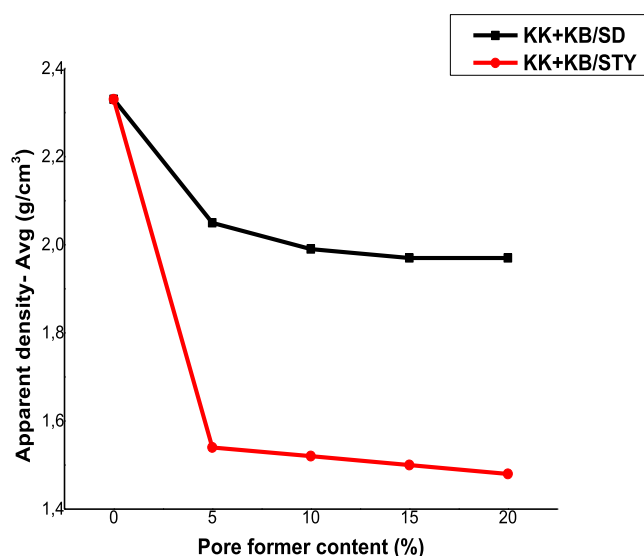
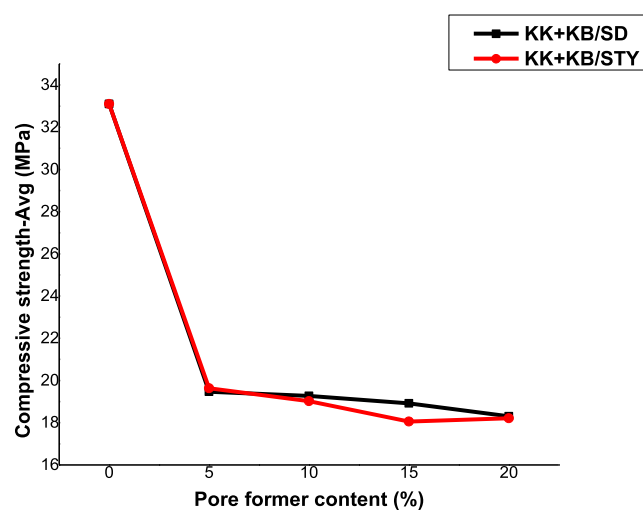
Table 1

Values of porosity and standard deviation for ceramic membranes.

Sample code	% P ₁	% P ₂	% P ₃	% P ₄	% P ₅	% P _{avg}	SD
0% CNS	27.03	27.03	27.17	27.03	27.04	27.06	0.06
5% SD	39.30	39.23	39.22	39.27	38.98	39.2	0.16
10% SD	41.24	41.20	41.02	41.17	41.22	41.17	0.08
15% SD	44.88	44.92	44.94	44.80	44.91	44.89	0.05
20% SD	46.16	46.13	46.17	46.20	46.19	46.17	0.03
5% STY	33.91	33.94	33.92	33.92	33.96	33.93	0.02
10% STY	36.25	36.28	36.24	36.16	36.27	36.24	0.04
15% STY	38.54	38.55	38.59	38.57	38.40	38.53	0.07
20% STY	42.57	42.54	42.56	42.60	42.43	42.54	0.06

% P₁₋₅ = Percentage porosities of the 5 samples for each batch formulation.

SD = Standard Deviation; CNS = Control sample.

**Fig. 10.** Water absorption of membranes with varying weight of pore formers.**Fig. 12.** Flexural strength of membranes with varying weight of pore formers.**Fig. 11.** Apparent density of membranes with varying weight of pore formers.**Fig. 13.** Compressive strength of membranes with varying weight of pore formers.

time). For the acid and alkaline-corroded samples, some small white ball-like particles were observed distributed on the sintered aluminosilicate grains. Especially, surface marking and cleavages were also observed on the surfaces. After strong acid corrosion, the microstructure of the sample remains slightly unchanged (see Fig. 8b), when compared with that of the un-corroded sample

(Fig. 8a). The sintered aluminosilicate grains become slightly smooth and rounded, indicating some degree of acidic corrosion. However, from Fig. 8c, it can be seen that, after strong alkali corrosion, the microstructure is different from that of the un-corroded sample. It is noticed that the sintered grains become finer. This was due to initial corrosion of the sintering necks and some very fine grains were removed from the membrane surfaces as a result of scouring by the NaOH solution.

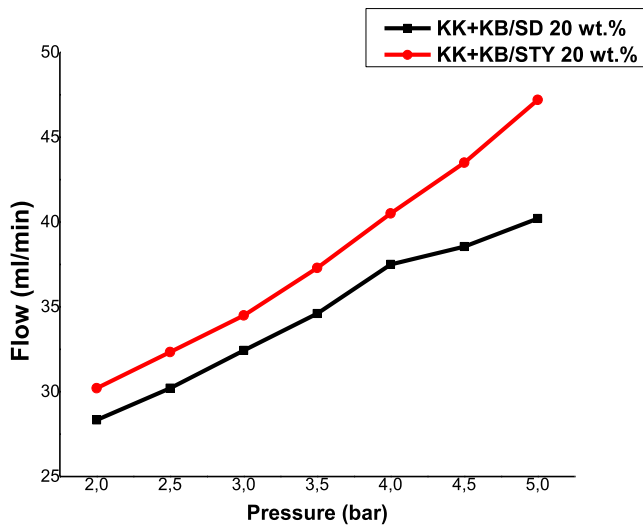


Fig. 14. Flow evolution with pressure for membranes heated at 1150 °C.

Fig. 9 and Table 1 shows the variation of membrane porosity with varying pore former addition. In this study, statistical averages are shown only for porosity data (see Table 1). The membrane porosity increases from $39.30 \pm 0.16\%$ through $46.17 \pm 0.16\%$ for sawdust addition whereas for styrofoam addition, porosity increases from $33.93 \pm 0.02\%$ through $42.54 \pm 0.06\%$ when pore former content varies from 5% to 20%. This is due to the fact that with increase in pore former content, porosity of the structure increases due to the creation of voids which are attributed to the decomposition of the pore formers during sintering. During the sintering process, the variation of apparent porosity is dominated by two factors: (1) the amount of surface pores which influences the variation of both volume and mass; and (2) the amount of pores in the walls which only affects the mass. For low pore former addition, the volume of the samples may remain relatively unaltered and accordingly, it may be dominated by continuous pores in the walls of ceramic membranes. When the pore former content increases, the relative density decreases gradually and accordingly, the apparent porosity increases. As a consequence, more porous structures are generated. But for the samples with 20 wt% of pore formers (SD and STY), the porosity was dominated by the surface voids and hence recorded porosities at this condition were highest.

The water absorption rate, which is the weight of the moisture in the pores as a fraction of the weight of the sintered membranes is an effective index of the quality of porous ceramic membranes. Fig. 10 shows the effect of increase in pore former content on the average values of water absorption of the sintered ceramic membranes. The plots show a similar trend, which is an increasing water absorption tendency with increasing pore former content. The values of water absorption were $51.07 \pm 0.02\%$ and $58.43 \pm 0.03\%$ for 20 wt% of SD and STY porogens respectively.

The membranes' apparent density as shown in Fig. 11 decreases from $2.05 \pm 0.02 \text{ g/cm}^3$ to $1.97 \pm 0.02 \text{ g/cm}^3$ and $1.54 \pm 0.03 \text{ g/cm}^3$ to $1.48 \pm 0.03 \text{ g/cm}^3$ when pore former content varies from 5% to 20% for sawdust and styrofoam pore formers respectively, thereby reducing the densification of the porous membrane structures. A reduction in membrane densification during sintering is in line with the inclusion of voids in the membrane structure and hence, an inverse relationship between apparent density and porosity is confirmed.

The flexural strength of the prepared membranes was performed using the three point bending strength method. The flexural strength of the membranes at different pore former content is

presented in Fig. 12. It can be seen that the flexural strength decreases (18.04 MPa at 5% to $10.14 \pm 0.03 \text{ MPa}$ at 20% for SD and $22.23 \pm 0.05 \text{ MPa}$ at 5% to $11.27 \pm 0.03 \text{ MPa}$ at 20% for STY) with increasing pore former content for membranes prepared with sawdust and styrofoam as porogens respectively. The decrease in flexural strength is attributed to the reduced densification of the membrane compact with increasing pore former content. This result can be reasoned along with trends found in literature [37,38]. The bending strength shows a linear variation against the content of porogens. The resulting mechanical strength is primarily a function of the amount of pore former content, the reduced densification, creation of voids and increased porosity.

Fig. 13 shows that the compressive strength is higher for the control sample (0% pore former content) in comparison to samples with pore formers due to higher porosity in the latter samples. Higher porosity implies fewer load bearing capacity. Therefore, the strength decreases at higher pore former content. However, the value of compressive strength, $18.31 \pm 0.02 \text{ Mpa}$ and $18.21 \pm 0.02 \text{ Mpa}$ obtained at maximum pore former content (20%) for membranes prepared with sawdust and styrofoam as pore formers respectively, is considered to be within tolerable limits. Usually, densification and grain size are the dominant factors controlling the mechanical strength, since most of the pores were inter-granular. The substantial decrease in strengths of samples corresponds to a parallel decrease in density, which means an increase in porosity ratio.

Fig. 14 shows the flow evolution with pressure for membranes (20wt.% of pore formers) heated at 1150 °C. A near linear evolution of the flow vs. pressure can be noted. At a maximum pressure of 5 bar, the flow evolution is 40.20 ml/min and 47.20 ml/min at 1150 °C for membranes prepared with sawdust and styrofoam porogens respectively. The outcome could be directly related to the bigger pore size generated by the high sintering temperature. It is known that pore nucleation or cavitation precedes pore growth in ceramics at high temperature. This result confirms that the pore size is more important for the gas flux than the total pore volume. High sintering temperature normally closes the porosity and also induces the pore coalescence which engages a bigger pore size. Usually, average pore diameter of the membrane increases with high sintering temperature and an increase in membrane gas flux. Similar trends are reported in literature [38] for the other type of clay based inorganic membrane fabrication.

Conclusions

The gas flux properties of kaolin based ceramic membranes have been examined by using a pressureless sintering technique. Membranes with batch formulation of KK + KB with 5–20 vol% of SD and STY were pressurelessly sintered at a temperature of 1150 °C for 4 h in air atmosphere. The prepared membranes sintered at 1150 °C offer tolerable mechanical properties, chemical stability, and good porosity. The porosity of the membranes can be well controlled by adjusting the content of SD and STY and sintering temperatures. Porosity alterations while the content of the pore former changed were noticed and fine and relatively uniform pores were observed on membrane surfaces. It was noticed that bending strength is not only influenced by the porosity but also by the amount of densification ascribed to the influence of pore former decomposition during sintering. This study indicates that ceramic membrane can be fabricated with higher contents of kaolin (80%) and pore formers. The obtained gas flux values show an increase of gas flow in relation to increase of gas pressure. These results provide significant opportunities to develop ceramic membranes with flexible pore sizes for gas applications.

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