Effect of coating steps on uniformity and gas permeability of mesoporous layers in ceramic membranes

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Porous silica, silica-cobalt, silica-zirconia and zirconia membranes were synthesized by the sol-gel method. Multi-step coating (two, six, and ten steps) was used to reduce the defectiveness of the mesoporous layer. Scanning electron microscopy (SEM) images indicated that an increase in the number of coating steps improved the mesoporous layer quality. The results obtained from gas permeability tests with nitrogen and argon, however, indicated a reduction in the gas permeability with increasing coating steps. The reduction in gas permeability from two to six coating steps was more pronounced than from six- to ten- coating steps. It was found that six-step coating was economically justified in obtaining a uniform mesoporous layer. The results of pore radius calculations by Knudsen flow mechanism revealed that the pores in the silica, silica-cobalt, and zirconia membranes were in the mesoporous range. The sols with a mean particle size more than 100 nm are not recommended for synthesis of mesoporous layer free of defects. Furthermore, the type of acid used as a catalyst is also important in obtaining a layer without defectiveness.

Keywords: *ceramic membrane; sol-gel; coating steps; defectiveness; gas permeability*

1. Introduction

Membrane separation is an energy efficient, simple, and easy to control separation process [1]. A typical membrane consists of four components that include the feed, the membrane, the permeate phase, and the retentive phase [2]. The most important component in any membrane process is the membrane itself. To increase the efficiency of membrane process, it is necessary to improve the membrane properties using an appropriate preparation method [3]. Both organic and inorganic membranes are classified based on their shapes, structures, and materials that they are made of. Inorganic membranes include ceramic, zeolite, and metal membranes [4]. Many investigations have focused on the ceramic membranes due to their mechanical, chemical, and thermal stability as well as their regenerative characteristics [5]. The use of ceramic membranes in pervaporation processes has been recommended by many investigators [6–11].

Ceramic membranes are generally manufactured as composite structures. The first layer of a

ceramic membrane is typically made of α -alumina or macroporous layer containing pores with diameter greater than 200 nm [7, 12]. This layer is used in ultrafiltration and macrofiltration processes [13]. The next layer, typically referred to as the mesoporous layer, has pores with diameters in the 10 nm to 200 nm range. Membranes consisting of the combination of the first and the second layers are used in ultrafiltration, nanofiltration, and in gas separation processes. The third layer, commonly referred to as the separation layer, is microporous [14, 15]. The combination of these three layers is used in gas separation (e.g. separation of hydrogen from gas mixtures) and pervaporation (e.g. dehydration of organic liquids) [16, 17]. To improve the separation process, it is essential that the latest or third layer of the composite membrane was uniform and free of any damages [9]. The particle size distribution of the last layer is conditioned by the pore diameter of previous layer so that the difference between particle size and pore diameter is slight. For example, when the particle size of the sol is less than 2 nm and the pore diameter of the previous layer is greater than 50 nm, the next layer cannot be formed in a uniform or continuous

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manner, i.e. the small particles of the next layer will merge into the large pores. Therefore, the next layer cannot be formed in a continuous manner [18, 19].

Two main methods are used in the construction of ceramic membranes: sol-gel method and chemical vapor deposition (CVD) [18]. The sol-gel method is simple and more energy efficient as compared with CVD. The sol-gel is also more attractive due to its excellent processability and its potential to precisely control pore size and pore structure. The sol-gel method can be applied during colloidal and polymeric routes. In the colloidal route, a metal salt is mixed with water to form a sol. This sol is subsequently coated on a membrane support where a colloidal gel is formed. There are different options to choose metal salt and colloidal sol. Mesoporous layer can be made of γ -alumina, colloidal silica or silica containing other components such as zirconia, cobalt and titania into silica. The type of mesoporous layer depends on the application of the membrane. γ -alumina and colloidal silica are not suitable as a mesoporous layer in aqueous media because of their poor stability. Incorporation of silica into titanium enhances the silica stability in acid and aqueous media. Also, incorporation of silica into zirconia increases silica stability in alkaline media and hydrophilicity of membrane. Cobalt salt and its incorporation into silica causes an increase in hydrophilicity [20–23].

In the polymeric route, metal-organic precursors are mixed with an organic solvent to form a sol which is then coated on a membrane support to form a polymeric gel. The pore diameter of the mesoporous layer is about 4 nm to 30 nm and the pore diameter is smaller than 4 nm for the microporous layer. The colloidal sol is, therefore, appropriate as a mesoporous layer. The polymeric sol, on the other hand, is appropriate as the last or the separation layer [21, 24–26]. The uniform mesoporous layer contributes to the formation of a uniform microporous layer. An increase in the uniformity and a decrease in the defectiveness of the mesoporous layer would lead to the formation of a less defective compact microporous layer with the less defectiveness. When the mesoporous layer is free of any damages, the number of coating steps required to deposit the microporous layer is reduced leading

to less energy being consumed during deposition of the microporous layer.

In this investigation, a uniform mesoporous layer has been overlaid on a macroporous layer to fabricate a support free of damages for the ceramic composite membrane. The mesoporous layer uniformity and gas permeability have been assessed for different number of coating steps and different sols. Uniformity of the layer was improved by an increase in the number of coating steps at the expense of higher energy and material consumption indicating that the number of coating steps and the quality of the mesoporous layer should be optimized. Gas permeability has been used as a measure to compare the uniformity of the layers when different number of coating steps was applied. Such membrane can be used for dehydration of alkaline and organic solutions.

2. Experimental

2.1. Chemicals

The chemicals used in this investigation include LUDOX or colloidal sol of silica (30 wt.% suspension in H₂O, Aldrich), tetraethyl orthosilicate or TEOS (Sigma Aldrich), ethanol or ETOH (Merck), cobalt(II) nitrate (Sigma Aldrich), nitric acid (65 wt.%, Merck), hexanol (Sigma Aldrich), cyclohexane (Sigma Aldrich), zirconium(IV) isopropoxide solution (70 wt.% in 1-propanol, Sigma-Aldrich), hydrochloric acid (37 wt.%, Merck), acetylacetone (Sigma Aldrich), polyvinyl alcohol or PVA (average $M_w = 31,000$ to $50,000$, 87 % to 89 % hydrolyzed, Sigma Aldrich), porous mullite disc (diameter of 2 cm and thickness 5 mm, Ceram Co., Iran), high purity argon and nitrogen gases (99.995 %, Oxygen Sabalan Co., Iran) and distilled water.

2.2. Equipment

An ultrasonic bath (model C12, Lainate, Italy) was used for sol mixing and an oven (model UF6250, Memmert, Germany) was used for drying the mesoporous layers. Mesoporous layers were sintered in a controllable furnace (model BEF1250, Azarkoureh, Iran).

2.3. Sol synthesis procedure

Five colloidal sols were prepared for depositing the mesoporous layer on the mullite substrate. The preparation procedures of these sols are described as follows.

First sol (sol L)

The first sol was of LUDOX or colloidal silica sol diluted by distilled water to 5 % and labeled as L.

Second sol (sol C)

10 g of TEOS was added to 50 g ETOH. 6.98 g of cobalt nitrate was dissolved in the TEOS and ETOH solution. After 12 hours, 2 g of nitric acid diluted in 500 g of water was added to the sol. After additional 12 hours, this sol was prepared and was ready to be deposited on the substrate. This sol was labeled as C.

Third sol (sol Z)

3.52 g of ETOH was added to 50 g of TEOS and mixed. 0.5 g of nitric acid diluted in 50 g of water was then added to the ETOH and TEOS solution. 6.48 g of zirconium isopropoxide and 50 g of ETOH were then added to this solution followed by the addition of a solution of 25 g of ETOH in 50 g of water. After 12 hours, 500 g of water and 3 g of nitric acid were added to this solution and boiled for 10 hours to allow all organic compounds to be evaporated. This sol was labeled as Z.

Fourth sol (sol Z')

28.53 g of hexanol diluted in 50 g of distilled water was added to 25 g of cyclohexane using an ultrasonic bath. 30 g of zirconium isopropoxide was then added to this solution and mixed in the ultrasonic bath at 25 °C for an additional 15 minutes. 8.4 g of hydrochloric acid was next added to this solution. The final molar ratio of the solution was: $\text{Zr:H}_2\text{O:HCl} \rightarrow 1 : 3 : 5$

The fourth sol was labeled as Z'.

Fifth sol (sol Z'')

The precursor of the fifth sol was zirconium isopropoxide. Firstly, 18.54 g of acetylacetone was gradually added to 60 g of zirconium isopropoxide and mixed in an ultrasonic bath at 25 °C for 15 minutes. 10 g of water was then added to the mixture and mixed in the ultrasonic bath at 25 °C

for an additional one hour. The final molar ratio of the solution was: $\text{Zr:H}_2\text{O:AcAc} \rightarrow 1 : 3 : 1$

The fifth sol was labeled as Z''.

2.4. Dip-coating

A 12.5 wt.% PVA was prepared by dissolution of PVA in water. The PVA solution was added to each sol at a ratio of 1: 4. The dip-coating was carried out for all discs. The discs were first preheated at 200 °C. Each disc was subsequently placed in contact with the respective sol for 30 seconds. The drying process was carried out in an oven at 100 °C for one hour. Sintering took place in a furnace at 500 °C with 2 °C/min temperature ramp.

For each of the prepared sols, six mullite discs were selected as the support to coat the mesoporous layer. Each pair of discs was coated in 2, 6, and 10 coating steps. For example, two of the six discs coated in two steps with LUDOX were labeled L2, another two discs coated in 6 steps were labeled L6, and the last couple of the discs coated in 10 steps was labeled L10. Preheating, dip-coating, drying, and sintering were performed for each coating step. One of the duplicate discs was used for the SEM analysis while the other was used in gas permeability tests.

2.5. Gas permeability tests

The defectiveness of membranes was assessed by performing a gas permeability test. The set up for the gas permeability tests is shown in Fig. 1. The disc-shaped membranes were placed in a stainless steel permeant cell with a mesoporous layer at the feed side. The gas flow at the feed side was controlled by an accurate pressure controller. A flow meter was used to measure the gas flow at the permeant side. Argon and nitrogen gases were used in this test.

2.6. Characterization

The particle size distribution of each sol was determined by DLS analysis (Malvern ZEN3600, England). The morphology of the mesoporous layers was examined by SEM images (Testcan Vega3 Lab6, Germany).

Fig. 1. Set up for gas permeability tests, 1: gas cylinder and pressure gauges, 2: pressure controller, 3: pressure gauge, 4: membrane, 5: flow indicator.

3. Results and discussion

3.1. Sol characterization

The particle size distributions in the prepared sols are shown in Fig. 2 to Fig. 6. In Fig. 2, a stable and narrow particle size distribution of LU-DOX with average particle size within the 12 nm to 20 nm range is shown. Fig. 3 indicates that the average particle size of sol C is within the 10 nm to 25 nm range with a stable and narrow particle size distribution.

Particle size distribution of sols Z, Z', and Z'' is shown in Fig. 4. A stable particle size distribution within the 250 nm to 350 nm range is observed for sol Z. This behavior is also observed for sols Z' and Z'' within the 100 nm to 180 nm and 30 nm to 35 nm ranges, respectively.

The transition from a liquid (solution or colloidal solution) into a solid is known as sol-gel process. The steps in the sol-gel process of silica consist of hydrolysis of silicon alkoxide, condensation, and forming the silica nanoparticles. Depending on the reaction conditions, these particles may further grow and form a sol that can be deposited on a substrate to form a film of desired shape. The hydrolysis reaction consists in replacing the alkoxide groups ($-OR$) with hydroxyl groups ($-OH$) and releasing the corresponding ROH alcohol molecules. Due to the immiscibility of alkoxide and water, a mutual solvent (such as an alcohol) is used as the homogenizing agent to facilitate the hydrolysis process [27].

Condensation reactions involve producing siloxane bonds ($Si-O-Si$) by silanol groups ($Si-OH$), and by-products - water and alcohol.

Types of precursors and solvents, molar ratios between reactants, use of modifying agents, pH, and synthesis temperature influence the microstructure and thus the properties of the resulting material.

The condensation reaction is followed by an inorganic polymerization process to produce nanoparticles. This process is strongly dependent on pH and modifying agents. Table 1 shows the formation conditions of nanoparticles in the prepared sols (except sol L). Reactants molar ratio (H_2O /precursor) of sol C is too high in comparison to the other sols. So, the hydrolysis and also condensation rate increase. Therefore, the formation of the nanoparticles is enhanced. Sol Z'' was prepared using acetylacetone (AcAc) as modifying ligand or using a microemulsion-based preparation. Due to the use of modifying agent, its preparation condition was different from those of two other sols of zirconia. While the parameters of the sol-gel process of the first and second zirconia sol were favorable, the modifying agent had an important effect on sol Z'' containing finer or smaller nanoparticles. Therefore, its particle size was smaller than sol Z and Z'. Because solubility of zirconium (IV) isopropoxide in hexanol is higher than that of ethanol, hydrolysis reaction of sol Z' was facilitated and so condensation reaction and nanoparticle formation was easier. Therefore, sol Z' involves finer particles than sol Z. According to DLS analysis, it can be concluded that the molar ratio of reactants (H_2O /precursor), pH of sol, and modifying agent have an important effect on forming finer particles [27].

The SEM images of sol L coated in two, six, and ten steps are shown in Fig. 5 indicating that the quality of layer L6 is better than that of L2 and the quality of layer L10 is better than that of L6. Defectiveness of the L10 was reduced.

The SEM images of sol C coated in two, six, and ten steps are shown in Fig. 6 indicating that the quality of C6 has improved in comparison with C2. Fig. 7 and Fig. 8 illustrate the SEM images of sols Z and Z' coated in two, six, and ten steps, respectively. The characteristics of these two sols are similar. An increase in the coating steps resulted in increased defectiveness of the Z and Z' sol layers. The defectiveness is due to the increase in the

Table 1. Formation conditions of nanoparticles in prepared sols.

	Sol C	Sol Z	Sol Z'	Sol Z''
Precursor	Tetraethyl orthosilicate and cobalt nitrate	Tetraethyl orthosilicate and zirconium (IV) isopropoxide solution	Zirconium (IV) isopropoxide	Zirconium (IV) isopropoxide
Molar ratios of reactants (H ₂ O/precursor)	50 (TEOS) 71.94 (cobalt nitrate)	10 (TEOS) 77 (zirconium (IV) isopropoxide)	3	3
Molar ratios of (alcohol/precursor)	5 (TEOS) 7.19 (cobalt nitrate)	7.65 (zirconium (IV) isopropoxide) 14.20 (TEOS)	0.951	–
pH	<1	<1	<1	≈ 6
Synthesis temperature [°C]	25	25	25	25
Solvents	ETOH, water	ETOH, water	Hexanol, water	Water
Modifying agents	–	–	–	acetylacetone

number of sintering processes. The defectiveness of layers Z2 is less than that of Z6 and Z10 and this holds true for Z'2, Z'6 and Z'10. The SEM images of sol Z'' coated in two, six, and ten steps are shown in Fig. 9. Behavior of sol Z'' is similar to the sols L and C. Also, the SEM images of sols L, C, and Z'' reveal that when the coating steps were repeated, the defectiveness of the mesoporous layer decreased. The membranes made of zirconia by sol-gel method are normally in the metastable tetragonal phase that may be transformed to the stable monoclinic phase at calcination temperatures of 500 °C and higher [26, 28]. During the transformation, various defects usually appear on the membrane layer due to a change in the lattice dimension and the stress developed in the membrane. Increasing the number of sintering process steps results in a change in the lattice dimension that causes stress in the lattice leading to the defectiveness of sol Z and Z' layers. In case of sol Z'', however, the flexibility of sol Z'' is higher than that of sols Z and Z' due to a higher pH and use of modifying agent (acetylacetone) [27, 29] and consequently, the lattice resists and phase transformation does not cause stress in the layer. Comparison of the SEM images for all the sols with two coating steps indicates

that the layer of sol Z' has the best quality. When coating is repeated six times, the mesoporous layer quality is improved for all the sols with sol C layer showing the best quality. For ten-step coating, the quality of all mesoporous layers would improve and the defectiveness would decrease.

Fig. 2. Particle size distribution of sol L.

3.2. Gas permeability tests

Scanning electron microscope (SEM) analysis only shows the morphological quality of the samples. The defectiveness and uniformity of the mesoporous layers have been studied by gas permeability test with various gases of different particle sizes.

Fig. 3. Particle size distribution of sol C.

Fig. 4. Particle size distribution of sol Z(—), sol Z'(--), sol Z''(···).

Fig. 5. SEM images of mesoporous layer coated in 2, 6, and 10 steps by sol L.

Fig. 6. SEM images of mesoporous layer coated in 2, 6, and 10 steps by sol C.

Fig. 7. SEM images of mesoporous layer coated in 2, 6, and 10 steps by sol Z.

Fig. 8. SEM images of mesoporous layer coated in 2, 6, and 10 steps by sol Z'.

Fig. 9. SEM images of mesoporous layer deposited in 2, 6, and 10 steps by sol Z''.

In other words, using of various gases provides accurate investigation of the defectiveness of the fabricated layer. Gas permeability has been investigated and compared in different coating steps including two, six and ten steps. Gas permeability for the disc membranes was measured with nitrogen and argon at pressures of 0.05 MPa, 0.1 MPa and 0.15 MPa at 25 °C.

The nitrogen and argon gas permeability through the layers deposited from the colloidal sols are shown in Fig. 10 and Fig. 11, respectively. A comparison of nitrogen permeability through different layers with the same number of coating steps is presented in Fig. 12. The following results were obtained from the gas permeability tests:

1. An increase in the number of coating steps led to a decrease in gas permeability. The quality and conformity of the mesoporous layer has improved with increasing the number of coating steps resulting in less defectiveness and lower gas permeability. It should be noted that an increase in coating steps means longer sintering process in a furnace at 500 °C and an increase in energy consumption and costs.
2. With only two steps of coating, the gas permeability of nitrogen and argon through sol Z'' is ranked the highest. The gas permeation, however, decreased with an increase in the number of coating steps. It is deduced

that the composition of this sol cannot form a uniform and continuous layer with two steps of coating. Because of high pH of sol Z'' or consumption of a weak acid (acetic acid) as a catalyst during the synthesis of the sol and the use of modifying agent (acetylacetone), its structure may be flexible. The defectiveness of the layer decreased during the consecutive sintering processes. The particle size distribution of sol Z'' is also narrower than those of the other sols made of zirconium isopropoxide as precursor. This issue is very important in forming a uniform layer.

3. With two steps of coating, the gas permeability through sol Z' was lower than those of all other sols. With increasing the number of coating steps, however, sol Z' no longer had the lowest permeability among the sols. It can be deduced that the uniformity of this sol obtained in two steps of coating is better than that of Z'6 and Z'10. As mentioned earlier, phase transformation occurred during consecutive sintering processes resulting in the defectiveness of the coated layer. An increase in the number of coating steps beyond 2 has not significantly affected the gas permeation and layer uniformity.
4. The behavior of sol Z is similar to that of sol Z'. Sol Z makes a uniform layer with two coating steps. An increase in the coating steps did not have a significant effect on gas permeation. Consecutive sintering process caused defectiveness and reduced uniformity of the given layer. Low pH of these two sols (Z and Z') and particle size larger than 100 nm reduced the uniformity of the resulting layers from these sols.
5. Sols L and C showed a similar behavior. The amount of organic compounds in both sols is quite low. According to Fig. 10a, Fig. 10b, Fig. 11a, and Fig. 11b, an increase in the coating steps led to an improvement in the quality of the layer.
6. Gas permeability for sols L, C, and Z'' deposited in six steps of coating was lower

than for other sols with two steps of coating. Sols with the mean particle size greater than 100 nm cannot form a layer free of defects even in six steps of coating. The changes resulting from increased number of coating steps from six to ten were not as significant as those resulting from increased number of coating steps from two to six. Consequently, due to increased energy consumption with each additional coating step, it is difficult to justify increasing the coating steps from six to ten.

Fig. 10. Nitrogen permeability tests at pressures of 0.05 MPa, 0.1 MPa and 0.15 MPa at 25 °C through: 10 (a) sol L, 10 (b) sol C, 10 (c) sol Z, 10 (d) sol Z', and 10 (e) sol Z''.

3.3. Calculation of pore radius from gas permeability

Pores in ceramic membranes can be classified according to their size, as macropores (>1000 Å), mesopores (1000 Å to 50 Å) and micropores (<50 Å). Assuming that pores in membranes are composed of a bundle of capillary tubes, transport of gases through the capillary tubes can be described based on the kinetic theory of gases. Three types of mechanisms have been proposed for gas transport through capillaries, namely: (1) Knudsen flow (2), slip flow, and (3) viscous flow. Knudsen mode of gas transport is important when the mean

Fig. 11. Argon permeability tests at pressures of 0.05 MPa, 0.1 MPa and 0.15 MPa at 25 °C through: 11 (a) sol L, 11 (b) sol C, 11 (c) sol Z, 11 (d) sol Z' and 11 (e) sol Z''.

Fig. 12. Nitrogen permeability tests for layers obtained in two, six, and ten coating steps.

free path of gas molecules is much greater than the pore size of the membrane, i.e. $(r_p/\lambda) < 0.05$. In such situation, the collisions of the molecules with the pore wall are more frequent than the collisions among the molecules. This mechanism is often predominant in macroporous and mesoporous membranes and is described by the Knudsen equation for diffusive flow of molecules in a capillary tube in this regime [12]:

$$J_k = -D_k \left(\frac{dc}{dz} \right) \quad (1)$$

or

$$J_k = -\frac{D_k}{RT} \left(\frac{dp}{dz} \right) \quad (2)$$

where D_k is the Knudsen diffusion coefficient. It is dependent on the mean molecular speed, u and pore radius, r_p and is given by [12]:

$$D_k = \frac{2}{3} u r_p \quad (3)$$

An expression for the mean molecular speed can be obtained from the kinetic theory of gases [12]:

$$u = \left(\frac{8RT}{\pi M} \right)^{1/2} \quad (4)$$

where R and T are the gas constant and temperature, respectively, and M is the molecular weight of the gaseous species. Substituting equation 3 and equation 4 into equation 2 and then integrating, the permeation rate based on the Knudsen diffusion mechanism can be obtained for a single capillary tube [12]:

$$J_k = \left(\frac{32}{9MRT\pi} \right)^{1/2} r_p \frac{p_h - p_l}{l} \quad (5)$$

where p_h and p_l are the pressures before and after the membrane, respectively, and l is the thickness of the membrane. Equation 5 provides an expression to obtain the pore radius from the slope of measured gas flux versus the pressure gradient. The results are presented in Fig. 13 and the calculated results for pore radius are reported in Table 2. The smallest pore radius has been obtained in ten steps of coating by each sol. In two-step coating, the pore radius of the layer which was coated by sol Z' is smaller than those of the other sols. The comparison between gas fluxes for all the sols obtained in two and six steps of coating indicates that the mesoporous layer coated in two steps is defective. By increasing the coating steps up to six, pore radius for all the sols is decreased with the pore radius of sols L, C and Z'' being smaller than that of Z and Z'. On the other hand, gas permeability of these sols suggests that the coated layer of the sols can be free of any defects and that ten-step coating

Fig. 13. N₂ flux versus pressure gradient for different sols at 25 °C: 13 (a) sol L, 13 (b) sol C, 13 (c) sol Z, 13 (d) sol Z', 13 (e) sol Z''.

provides similar results as compared with six-step coating.

As it is shown in Table 2, pore radii after each coating are smaller, but not in case of Z'. An explanation for this is that the quantity of water in the sol-gel solution influences strongly the hydrolysis and condensation kinetics. An increase in water content leads to a corresponding increase in hydrolysis and condensation rate. At low molar ratio of H₂O/precursor, a matrix with a more open structure is produced due to incomplete hydrolysis and, consequently, less cross linking in the sol-gel material and the fracture in the developed layer. On the other hand, an increase in alcohol content can intensify the hydrolysis rate. In case of sol Z', alcohol and water contents are low. Therefore, partial hydrolysis occurs and nanoparticles are formed slowly. As a consequence, the uniform layer can't be formed by two or six-step coating. In practice, gas permeability fluxes of two and six-step coatings are almost similar. Gas permeability is also dependent on pore radius. Finally, it can be expected that pore radius is similar in the two coatings.

Table 2. Pore radius of sol coated on the support [nm].

Steps of coating	Sol L	Sol C	Sol Z	Sol Z'	Sol Z''
2	240	198	173	99	990
6	74	74	99	99	74
10	49	49	49	74	49

4. Conclusions

The uniformity of mesoporous layer made of silica, silica-cobalt, silica-zirconia and zirconia sols was assessed. The TEOS, zirconium (IV) isopropoxide, and cobalt nitrate solution were used as precursors to prepare the sols. After depositing the mesoporous layers on the mullite support through different number of coating steps, the SEM analysis indicated that an increase in the number of coating steps improved the mesoporous layer quality. The results obtained from gas permeability tests using nitrogen and argon gases indicated that two-step coating was not sufficient to form a uniform layer. In contrast, the layer with six steps of coating led to a uniform mesoporous layer. When the coating steps were increased to ten, the reduction in gas permeation was not significant. In terms of energy and economic considerations, therefore, ten-step coating was not beneficial as the six-step coating was sufficient to form a uniform mesoporous layer free of defects. This implied that the probability of formation of polymeric or microporous layer without the defects was high. The quality of layers made of the five sols indicated that sols L, C and Z'' were more appropriate for mesoporous layers due to their particle size distribution. The results of pore radius calculations by the Knudsen flow mechanism revealed that the pores were in the mesoporous range. Pore radius of sols L, C and Z'' was smaller than those of the other two sols obtained in six-step coating. For sols L, C and Z'', therefore, it can be expected that the polymeric sols have not penetrated into the mesoporous layers. It was found that the pH of the sol and the use of modifying agent (acetylacetone) in case of zirconia sols and as well as molar ratio of reactants (H₂O/precursor) were important factors to make a layer free of defectiveness.

References

- [1] KUJAWSKA A., KNOZOWSKA K., KUJAWA J., KUJAWSKI W., *Sep. Purif. Technol.*, 159 (2016), 68.
- [2] ALVENTOSA-DELARA E., BARREDO-DOMAS S., ALCAINA-MIRANDA M.I., IBORRA-CLAR M.I., *J. Hazard. Mater.*, 209 (2012), 492.
- [3] LAU W.J., ISMAIL A.F., MISDAN N., KASSIM M.A., *Desalination*, 287 (2012), 190.
- [4] NATH K., *Membrane separation processes*, P.H.I. Learning Pvt. Ltd., Delhi, 2017.
- [5] SCOTT K., HUGHES R., *Industrial membrane separation technology*, Springer Science and Business Media, Dordrecht, 2012.
- [6] KUMER R.V., GHOSHAL A.K., PUGAZHENTHI G., *J. Membrane Sci.*, 490 (2015), 92.
- [7] GOEI R., LIM T.T., *Ceram. Int.*, 40 (2014), 6747.
- [8] CHANG Q., ZHOU J.E., WANG Y., LIANG J., ZHANG X., CERNEAUX S., WANG X., ZHU Z., DONG Y., *J. Membrane Sci.*, 456 (2014), 128.
- [9] TAFRISHI R., TAHERI-NASSAJ E., SADIGHZADEH A., ESKANDARI M.J., *Mater. Sci.-Poland*, 33 (2015), 792.
- [10] MA Y., LIU F., SUN X., ZHENG J., *J. Chin. Ceram. Soc.*, 3 (2010), 227.
- [11] JIN T., MA Y., MATSUDA W., MASUDA Y., NAKAJIMA M., NINOMIYA K., HIRAOKA T., FUKUNAGA J.Y., DAIKO Y., YAZAWA T., *Desalination*, 280 (2011), 139.
- [12] LI, K., *Ceramic membranes for separation and reaction*, John Wiley & Sons, West Sussex, 2007.
- [13] ALVENTOSA-DELARA E., BARREDO-DOMAS S., ZURIAGA-AGUSTI E., ALCAINA-MIRANDA M.I., IBORRA-CLAR M.I., *Sep. Purif. Technol.*, 129 (2014), 96.
- [14] MCCOOL B.A., HILL N., DICARLO J., DESISTO W.J., *J. Membrane Sci.*, 218 (2003), 55.
- [15] ELMA M., YACOU C., WANG D.K., SMART S., DINIZ DA COSTA J.C., *Water Sui.*, 4 (2012), 629.
- [16] ISMAIL A.F., KHULBE K.C., MATSUURA T., *Gas Separation Membranes*, Springer, Switzerland, 2015.
- [17] SHI G.M., CHUNG T.S., *J. Membrane Sci.*, 448 (2013), 34.
- [18] CIRIMIINNA R., FIDALGO A., PANDARUS V., BELAND F., ILHARCO L.M., PAGLIARO M., *Chem. Rev.*, 113 (2013) 6592.
- [19] GRAF C., VOSSEN D.L., IMHOF A., VAN BLAADEREN A., *Langmuir*, 19 (2003), 6693.
- [20] TSURU T., *J. Sol-Gel Sci. Technol.*, 46 (2008), 349.
- [21] WANG J., TSURU T., *J. Membrane Sci.*, 369 (2011), 13.
- [22] SEKULIĆ, J., TEN ELSHOF J.E., BLANK D.H., *J. Membrane Sci.*, 254 (2005), 267.
- [23] WEI Q., DING Y. L., NIE Z. R., LIU X. G., LI Q. Y., *J. Membrane Sci.*, 466 (2014), 114.
- [24] KREITER R., RIETKERK M.D., CASTRICUM H.L., VAN VEEN H.M., TEN ELSHOF J.E., VENTE J.F., *Chem. Sus. Chem.*, 2 (2009), 158.
- [25] ASAEDA M., YAMASAKI S., *J. Sep. Purif. Technol.*, 25 (2001), 151.
- [26] AGOUDJIL N., KERMADI S., LARBOT A., *Desalination*, 223 (2008), 417.
- [27] MILEA C.A., BOGATU C., DUTA A., *Bull. Transylv. Univ. Braşov*, 4 (2011), 53.
- [28] TOPUZ B., ÇİFTÇIOĞLU M., *J. Sol-Gel Sci. Technol.*, 56 (2010), 287.
- [29] QIANYAO S., CHUNMING X., *Pet. Sci. Technol.*, 4 (2007), 80.

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