Process conditions on the preparation of supported microporous SiO₂ membranes by sol–gel modification techniques

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Abstract

The formation process is described of supported microporous membranes, prepared by modification of α-alumina supports with colloidal silica sols. The sols were prepared by acid catalyzed hydrolysis of tetraethylorthosilicate (TEOS), using different molar ratios of H₂O/TEOS and of HNO₃/TEOS. Membrane composites with multiple separation layers were synthesized by a conventional dip-coating method, in which process multiple layers with interconnected pores were formed by sequentially dipping a support in sol solutions in descending order of sol size. Emphasis is given to the parameters of dipping process such as dipping time and the number of dipping procedures applied, and to the preparation conditions of silica sols, in order to identify the main factor governing performance of processed membranes. It has been found that the modification procedure using several sols with different sol size is effective for preparing a multiple separation layer through which a percolation system of pores is successfully formed. The proposed process has made it possible to prepare membranes with CO₂ permeation rates on the order of 10⁻³ cm³(STP) cm⁻² s⁻¹ cmHg⁻¹, which is one to two orders of magnitude higher than those previously possible by sol–gel techniques. The ideal CO₂/N₂ selectivities, determined from single-component gas permeation experiments, are 4.2 for high-quality membranes.

Keywords: Sol–gel process; Ceramic membranes; Dip-coating; Membrane preparation and structure

1. Introduction

Microporous ceramic membranes recently have been attracting a good deal of attention due to the important applications of such membranes in separation industries where their organic counterparts fail to function, such as in high-temperature gas separation [1–3] and reactor [4] applications. The development of ceramic membranes has been hampered by practical problems such as low fracture toughness and complicated processing steps until sol–gel process has been applied as a feasible way to prepare microporous membrane. The characteristics of sol–gel derived membranes are determined by a large number of sol–gel process parameters, and it is therefore important that the effects of these parameters are well understood to make sol–gel process a reliable and practical technology for membrane fabrication [5,6].

In the present paper the preparation is described of microporous silica membranes by sol–gel modification of macroporous alumina supports. These mem-
Brines are prepared by a conventional dip-coating process, which is basically a slip-casting process of a porous support with a silica sol solution [7,8]. The sol–gel process of silica has been shown quite attractive for preparation of inorganic membranes with ultra-fine pores less than 1 nm. Starting from a silicon alkoxide dissolved in an organic solvent, the alkoxide hydrolysis is performed with water under catalytic conditions. In an acid catalytic system, hydrolysis of the alkoxide groups takes place rapidly while the condensation reaction is slow. This type of reaction sequence leads to weak cross-linking of the condensed species which can interpenetrate and shrink greatly as the solvent is removed during gelation and, in turn, this leads to dense microporous gels [9]. Brinker et al. [10] have claimed that separation layers with a pore radius <1 nm are achievable with this technique.

A ceramic membrane usually consists of a thin top-layer responsible for separating components, and a porous support with single or multiple separation layers which can have different morphologies and microstructures. The basic idea behind this asymmetric structure is to minimize the overall hydraulic resistance of the permeate flow path through the membrane structure. In cases where the colloidal particles are very small in size compared to the pore size of the bulk of the support, these particles can significantly penetrate the support pores and the resulting permeability of the membrane/support composite will deteriorate. A practical solution is to form one or more intermediate layers having pore sizes between those of the membrane layer and the bulk support. In this study, we prepare several kinds of colloidal silica sols whose sizes are precisely controlled, and plan to improve the gas separation ability of the membrane by forming a percolation system of pores through the system. The membrane with a gradual change in structure through the system is formed by sequentially dipping a support in silica sol solutions in descending order of sol size [11,12]. The formation process of these modified membranes is discussed in this paper, where the focus is on process conditions such as preparation conditions of colloidal silica sols, dipping time, and the number of dip-coating procedures applied, in order to identify the main parameter governing the gas separation ability of the membrane. The characterization of the processed membranes is discussed based on results from single-component gas permeation experiments. The performance of the membrane in gas separation application is critically determined by the modification process as well as the synthesis process of dip solutions and this is why details of the preparation procedures are so important.

2. Experimental procedure

Porous supported silica membrane was synthesized by a sol–gel technique on the outer surface of α-alumina tube with an average pore size of 1.4 μm, porosity of 0.4, and an outer and inner diameter of 13 and 9 mm, respectively. Fig. 1 shows the finally determined sequence of steps in preparing supported silica membrane, the process of which is one of the pre-

![Diagram](image-url)

Fig. 1. Preparative procedure of supported silica membranes by sol–gel modification technique.
Comparison of reaction mixtures for preparing silica polymeric sols

<table>
<thead>
<tr>
<th>Sol</th>
<th>TEOS mol (mol ratio: X/TEOS)</th>
<th>H₂O mol (rH₂O)</th>
<th>HNO₃ (1 N) mol (rHNO₃)</th>
<th>Dₓ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.096 (1.0)</td>
<td>0.56 (5.8)</td>
<td>0.008 (0.083)</td>
<td>18.9</td>
</tr>
<tr>
<td>B</td>
<td>0.048 (1.0)</td>
<td>1.1 (22.9)</td>
<td>0.008 (0.17)</td>
<td>13.4</td>
</tr>
<tr>
<td>C</td>
<td>0.024 (1.0)</td>
<td>1.4 (58.3)</td>
<td>0.008 (0.33)</td>
<td>6.2</td>
</tr>
<tr>
<td>D</td>
<td>0.024 (1.0)</td>
<td>1.4 (58.3)</td>
<td>0.016 (0.67)</td>
<td>4.0</td>
</tr>
<tr>
<td>E</td>
<td>0.024 (1.0)</td>
<td>1.4 (58.3)</td>
<td>0.032 (1.33)</td>
<td>&lt;3.8</td>
</tr>
</tbody>
</table>
3. Results and discussion

As shown in the table, the size of silica sol shows a tendency to decrease with increasing \( r_W \) and/or \( r_H \). The concentration of TEOS also exerts an influence on the prepared sol size. When the same TEOS concentration and \( r_W \) were used, the size of prepared sol gradually decreased with increasing \( r_H \). The colloidal particles prepared from sol-E had an average size smaller than 3.8 nm, which is the lower limit measurable by the photon-correlation spectroscopy.

Fig. 2 demonstrates the effects of multiple modification procedure on the ideal \( \text{CO}_2/\text{N}_2 \) selectivity. The specimen was prepared by dipping the support with intermediate layer in the sol-B for 60 s, followed by drying and then calcining. It should be noted that the calcination was carried out after every dipping–drying step. It is found, as might be expected, that the selectivity reasonably increases with an increase in the number of modified layers, and that the permeation rate of \( \text{CO}_2 \) decreases accordingly. This result can be explained by the self-repairing of the defects existing in the previously formed separation layer. At the places, where defects are present, the resistance against liquid transport is much lower than that at the site of defect-free layer. During the next dipping procedure, sol solution is sucked faster into the previously formed layer at defect sites, due to this lower resistance, and hence initially preferential deposition of a gel layer takes place at these defects. Compared to the membrane after twice modification steps, the membrane after ten times modification steps increased the selectivity only by a factor of 1.2 and, on the other hand, reduced the \( \text{CO}_2 \) permeation rate by half. The influence of modification procedures applied more than five times is only very minor with respect to the selectivity under the conditions studied in this paper. The result shown in Fig. 2 implies that the remarkable increase in the selectivity would not be expected for the membrane prepared from a single sol-B. Fig. 2 also shows the selectivity of the membrane prepared by applying the calcination procedure after five times dipping–drying procedure. The selectivity was increased by a factor of 1.2 as compared with the case where the calcination procedure was applied after each dipping–drying procedure. This result probably implies that the calcination procedure applied after forming multiple layers of a single sol would effectively structure the interconnected pores, and consequently improve the selectivity.

In order to increase the selectivity, the membrane consisting of several layers with a different pore structure was prepared by applying the subsequent modification procedures. The concept behind this modification is a formation of separation layers with a gradual decrease in pore size to the feed side of the membrane. The modification procedure was carried out on the support, using the sol-B, C, and then D, in descending order of sol size. Fig. 3 shows the ideal \( \text{CO}_2/\text{N}_2 \) selectivity of the membrane with multiple separation layers. The specimen was prepared by applying dipping–drying–calcining procedure five times for each sol. The standard dipping time was 60 s. It is shown that the selectivity increases steadily with no significant decrease in the permeation rate for \( \text{CO}_2 \). The selectivity was increased from 1.2 to 1.8 when the sols-C and D were used for the modification. This result implies that the modification procedure using several sols with different sol sizes is effective for preparing a multiple separation layer through which a percolation system of pores is successfully formed. A still higher improvement of the selectivity would be expected by applying the calcination procedure after multiple dipping procedure for each sol, as demonstrated in Fig. 2.
Fig. 3. Ideal CO₂/N₂ selectivity of the membrane with multiple separation layers. The dipping-drying–calcining sequence was repeated five times for each sol. Dipping time was 60 s.

Fig. 4. Ideal CO₂/N₂ selectivity of the membrane prepared from (○) original sols and from (●) second sols. Finished top layer was deposited with sol-E or E'. Dipping time was 60 s.

Fig. 4 shows the ideal CO₂/N₂ selectivity of the membrane with an finished top-layer prepared from sol-E. Also shown are the results for the processed membranes with multiple separation layers. To investigate the effect of the preparation conditions of dipping solution on the gas separation ability, other supports were modified by using second sols. The second sol was prepared by increasing $n_4$ to 1.4 times of the original composition for each sol (referred to as B', C', D' and E'). The values of $r_w$ were the same as the original mixtures. The colloidal particles with mean diameter of 4.7 nm were obtained from the reaction mixture for sol-B'. In the other cases, the colloidal particles had sizes smaller than 3.8 nm. In all cases, the original sol-A was used to form an intermediate layer which reasonably plugged large pores in the alumina support. The dipping procedure with the standard dipping time of 60 s was repeated five times for each sol.

It may be noted that the selectivity for the membrane prepared using sol-B or sols-B and C was slightly increased, compared with the results in Fig. 3, since the calcination procedure was performed after applying five times dipping–drying procedures for each sol. As demonstrated in Fig. 3, the selectivity of the membrane after coating sol-D increases resulting from a successfully formed percolation system of pores. While in the case where the calcination procedure was performed after applying dipping–drying procedure five times for each sol, the selectivity of the membrane after coating sol-D (or sol-D') decreased, as shown in Fig. 4. This result was not satisfactorily explained. No significant difference has been observed in the selectivity between the membranes prepared from the original sols-B, C, and D and those from the second sols-B', C' and D'. The selectivity of the membrane with the finished top-layer (prepared from the sol-E) is as high as 4.2, the value of which is on almost the same level with that previously possible by sol–gel techniques [16]. On the other hand, the CO₂ permeation rate is on the order of $10^{-3}$ cm$^3$(STP) cm$^{-2}$ s$^{-1}$ cmHg$^{-1}$, which is one to two orders of magnitude higher than that of the conventional sol–gel derived membranes. This results again implies that it is of vital importance to optimize a gradual change in percolation system of pores through the membrane/support system for reasonably improving the selectivity of supported membranes. It is also demonstrated that the membrane with the finished top-layer synthesized from the original sol-E has a higher selectivity than that prepared using the second sol-E'.

In the dipping process, the dispersion medium is forced into the pores of the support and/or the previously formed separation layers by capillary action of the microporous matrices. Since the capillary pressure directly depends on the size of pores, it is important to
control the dipping time according to the sol size which strongly affects the pore size distribution. The influence of the change in dipping time on the selectivity is demonstrated in Fig. 5, where the dipping time ranges from 15 to 60 s. The membranes were prepared by using the second sols. The calcination procedure was carried out after applying dipping-drying procedure five times for each sol. As shown in the figure, no significant effect was observed in the case where the sol-B was used to form the first separation layer. It is shown, on the other hand, that the dipping time of 60 s for the sol-C and that of 15 s for the sol-D and -E are more effective for the higher selectivity. This results suggests that the selectivity has a possibility to be improved by controlling the dipping time so that optimal pore size and interconnected pore structure should be formed.

In the present paper we used several sols whose sizes are listed in Table 1. There is, in fact, a feasibility to use sols with other sizes. In that case it is necessary to investigate the optimal process conditions on preparing a gradual change in microstructure for a given combination of sol sizes.

4. Conclusions

The formation process has been investigated methodically of supported microporous membranes, prepared by modifications of porous α-alumina supports with colloidal silica sols. The processed membrane is composed of an intermediate layer with a moderate thickness and is followed by multiple separation layers. In the proposed process multiple layers with interconnected pores are formed by sequentially dipping a support in solutions of sol in descending order of sol size. It has been found from gas permeation experiments, that the modification procedure using several sols with different sol size is effective for preparing a multiple separation layer through which a percolation system of pores is successfully formed. It has also been demonstrated that the formation process of separation layer is strongly dependent on the preparation conditions of silica sols as well as on the membrane processing parameters such as dipping time, multiple modification, and calcination procedure.

The proposed dip-coating process should make it possible to prepare membranes with CO₂ permeation rate one to two orders of magnitude higher than those previously possible by sol–gel techniques, with undergoing no significant change in separation factor. The ideal CO₂/N₂ selectivities are as high as 4.2 for high-quality membranes. The combination of high permeation rates and separation factors make these membranes very attractive for gas separation applications and/or for incorporation in membrane reactors.

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References


