

## MMA Modified Inorganic/Organic Hybrid Membranes by Sol-Gel Technology

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The inorganic/organic hybrid membranes modified by MMA were deposited on the porous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrates (pore size, 2  $\mu$ m) by the sol-gel technology. It was found that the introduction of MMA can not only improve the membrane formation properties, but also increase the selectivity of O<sub>2</sub>/N<sub>2</sub> and O<sub>2</sub>/CO<sub>2</sub>. On the other hand, the modified hybrid membranes have more dense structure.

In the past decade, the design of inorganic/organic hybrids has been focused on the sol-gel materials, exhibiting the properties associated with both the organic moieties and the inorganic framework. In these materials, a very fine-scale morphology can be produced, that is becoming particularly interested for preparing inorganic/organic hybrid membranes with thermal and chemical stability as well as high permselectivity.<sup>1-3</sup> Phenyl group modified silica membranes for separating O<sub>2</sub>/N<sub>2</sub>, and O<sub>2</sub>/CO<sub>2</sub> have been developed, in which the selectivity was associated with the chemical affinity between gas molecule and membrane pore surface induced by phenyl group.<sup>4</sup> During preparation of these membranes, the roughness of the used substrate surface was highly qualified, the crack problem can only be avoided under optimized preparation condition, and the membrane structure could be more tailored by modifying the precursors. More recently, molecularly defined or covalently bonded hybrid networks have been shown to be more dense, interpenetrated hybrid network, without remarkable shrinkage, when thermally treated, having highly optical, mechanical properties. To form covalent linkage between organic and inorganic phase, the precursors containing non-hydrolyzable silicon-carbon bond, or hydrolyzable alkoxy-silicon bond or polymerizable organic monomer are usually involved. When the organoalkoxy silane contains olefinic moieties (allyl, vinyl or methacryl), conditions exist to break C=C bonds, and co-polymerized, simultaneously with the condensation of SiO<sub>2</sub>, TiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> networks derived from metal alkoxides.

In this paper, MMA organic moiety was attempted to be introduced into the phenyl group modified silica membrane system using 3-(trimethoxysilyl)propyl methacrylate (TSM) as a coupling agent. Its effects on the microstructure and gas selectivity of the membranes have been developed by the DTA and TGA, FTIR, SEM and gas separation tests.

The organic/inorganic hybrid membranes were prepared from both organic polymer phase and silica based hybrid phase. The organic polymer phase was obtained from in situ polymerization of MMA and TSM. During the synthesis, the mixture solution of MMA (5 mL, refined), acetone (15 mL), TSM (0.5 mL), and benzoyl peroxide (BPO, 0.038 g, refined) as well as hydrochloric acid solution (0.2 g, 0.01 M) was stirred at 62 °C for 2.5 h to pre-polymerize. The silica based hybrid phase was derived from hydrolysis and condensation of tetraethyl orthosilicate (TEOS), phenyltrimethoxysilane (PTMOS), and TSM<sup>4</sup>. In

the synthesis, TEOS and PTMOS were separately dissolved in ethanol, then pre-hydrolyzed at 40 °C for 2 h using a mixing solution of 0.01 M HCl and ethanol as catalyst, and then the two sols were blended and stirred at 40 °C for 3 h (TEOS:PTMOS:TSM = 5:5:1(volume)). Then the silica based hybrid phase was introduced to the organic polymer phase (MMA/Si = 4:6, molar), and stirred for about 5 h at 62 °C. Thus the MMA modified organic/inorganic hybrid sol was obtained for the following gel layer formation. Before the layer formation, an intermediate  $\alpha$ -alumina layer was first deposited on the as-received alumina substrate using boehmite sol due to its surface roughness and scattered pore size distribution.<sup>5</sup> And then the gel layers were deposited on the alumina intermediate layer by spinning-coating at rate of 6000 r/min at room temperature. After being dried at room temperature for 6 h and at 40 °C for 6 h, the gel layer was then finally fired at 120 °C for 2 h at a heating rate of 1 °C/min in air. In the last, the MMA modified organic/inorganic hybrid membranes were worked out.

For the synthesis of the hybrid sol, several precursors were involved, the effect of parameter on the characteristics of the resulted hybrid sol is more complicated, which are critical for the membrane formation. In our case, the pre-hydrolysis of TEOS and PTMOS was conducted in the solvent of ethanol. But in the pre-polymerization of organic phase, acetone was accepted as the solvent as the oligomer of MMA has better solvability in acetone than in ethanol, so that the phase separation can be avoided and the homogeneous sol was confirmed. In the reference 4, it was reported that only when the ratio of PTMOS/TEOS is large than 0.58, the crack can be avoided during the processing. From the experiments, it was found that when the MMA was introduced, the crack can be easily removed in a larger scale ratio. And from the SEM picture of the membrane surface (shown in Figure 1), it can be observed that the introduction of MMA is also helpful to improve the surface roughness. In addition, the time of co-reaction between the polymer phase and silica-based hybrid phase was controlled strictly to keep viscosity of the sol within the range of 46.5 to 200 m·Pa·s, which was most suitable for the hybrid layer formation.

Microscope-IR (Nicolet, magna-IR 750, Nic-Tlan) spectrum was recorded on the resulted hybrid membranes. The strongest bands originate from absorption of -Si-O-Si- at 1093 cm<sup>-1</sup> and C=O stretching at 1731 cm<sup>-1</sup>.<sup>6</sup> The absorption from the unreacted vinyl groups in TSM at 1636 cm<sup>-1</sup> could be negligible. This indicated that all of the C=O bonds in the TSM took part in the condensation. So it maybe be proposed that the covalent bond was created between the hybrid phase and the organic polymer phase via the C=O bonds in the TSM.

From the SEM images of the cross section, it can be estimated that the membrane thickness is also about 2  $\mu$ m, and pores larger than 100nm as well as defects cannot be observable from the membrane surface SEM images. The thermal analy-

sis, such as, TGA & DTA (DuPont 2100, General V4.1), recorded on the dried hybrid gel powders at 40°C under air atmosphere at a heating rate of 10°C/min, indicated that the –C–C– train in the hybrid layer was stable below 194.64°C.

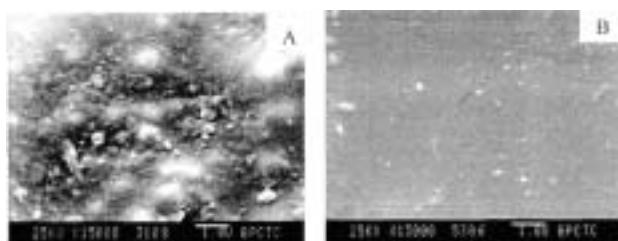


Figure 1. Surface SEM pictures of the hybrid membranes. A: without MMA, B: with MMA.

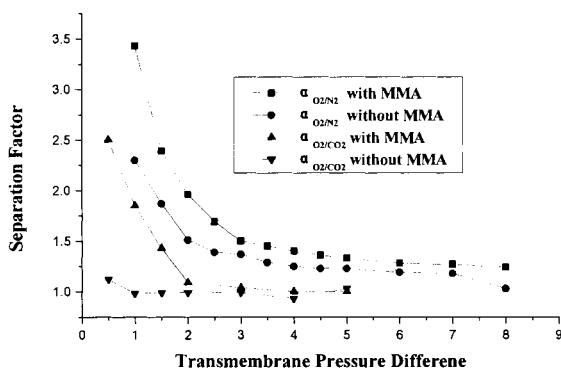


Figure 2. Effects of the MMA introduction on separation factor.

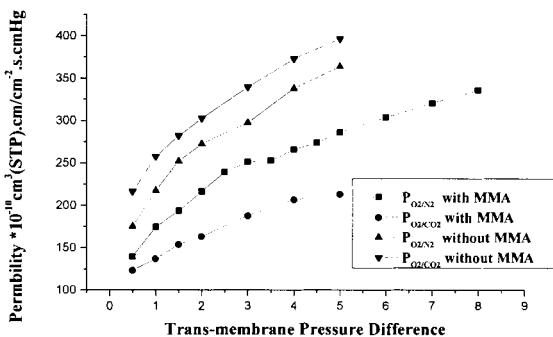


Figure 3. Effects of introduction of MMA on the permeability.

The gas selectivity and permeability of hybrid membranes were investigated on the binary combinations among O<sub>2</sub>, N<sub>2</sub> and CO<sub>2</sub> by the designed instrument in laboratory. For the common porous silica ceramic membrane, the ideal Knudsen separation factor is almost equal to 1 due to their almost equal molecular weight. The separation factor ( $\alpha$ ) was calculated as follow:  $\alpha_{ij} = (y_i/y_j)/(x_i/x_j)$ , where  $y_i$ ,  $y_j$  are the mole fraction of the permeate stream, and  $x_i$ ,  $x_j$  are the mole fraction of the feed stream, which were analyzed by gas chromatography.

The results showed that the addition of MMA increased the separation factor  $\alpha_{O_2/N_2}$ ,  $\alpha_{CO_2/O_2}$ , but decreased the permeability (shown in Figure 2 and Figure 3). It may indicate that the introduction of MMA helped to reduce the affinity of CO<sub>2</sub> molecule and the membrane surface, and to enhance the ones of O<sub>2</sub> molecule and the membrane surface. From permeability test, it also proved that the addition of –C–C– train to the silicate network densified the membrane structure further more.

From the preliminary gas separation test, it seemed that the gas transport mechanism through the membrane pore was governed mainly by the Knudsen diffusion and surface diffusion at pressure below  $2 \times 10^{-5}$  Pa and the Knudsen diffusion and laminar flow at pressure above  $5 \times 10^{-5}$  Pa. Of course more work should be done to confirm the details of the gas transport mechanism.

In summary, the addition of MMA helped to improve the membrane formation properties and the surface roughness of the membranes. It was also helpful to increase the selectivity of O<sub>2</sub>/N<sub>2</sub> and O<sub>2</sub>/CO<sub>2</sub>. However, the introduction of MMA reduced the permeability and densified the membrane structure further more.

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