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Enhanced Thermal Stability of a Silica/Stainless Steel Composite Membrane via the Soaking-Rolling Method

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1. Introduction

Concerning the application of the inorganic composite membranes to high temperature process such as the catalytic dehydrogenation of hydrocarbons, important aspects to consider in the application include the improvement of the thermal stability and good permeability. Drioli et al. [1] and Li et al. [2] emphasized that thermally stable substrates should be needed to maintain high permeability and selectivity of a top coated layer. Our previous work [3] showed that the failure of the stainless steel supported composite membranes in the presence of hydrogen at high temperature was attributed to the reduction of reducible metal oxides such as iron oxide.

In this study, the thermal stability of the sol-gel derived silica composite membranes was observed, when the porous stainless steel was used as a support. The reason why the stainless steel supported membranes are unstable at high temperature was discussed. In order to improve the thermal stability of the stainless steel supported silica membranes, new technique of the soaking-rolling method was introduced.

2. Experimental

2.1. Preparation of a silica/SUS membrane by dip-coating method

Disks of 316L stainless steel (SUS) used as a porous substrate were purchased from Matt Metallurgical. The stainless steel support has a thickness of 1mm, a surface area of $5cm^{2}$, and an average pore size of 0.5 ㎛. The support as purchased has wide pore size distribution, rough surface and too many macropores above 10 ㎛ to be used directly.

Some modifications of the porous stainless steel substrate were needed using boehmite sol and colloidal silica sols, so that the pore size and surface roughness of the substrate could be gradually reduced. The first modification of the stainless steel support was conducted by dip-coating the support into silica (500nm) sol. The second modification of the support with boehmite sol was carried out to reduce the pore size of the support into the region of Knudsen diffusion, followed by drying process of the modified support at room temperature and calcination at 650℃ with ramping rate of 1℃/min. The silica top layer was synthesized by dip-coating procedure with polymeric silica sol. The top layer was dried at same temperature as modification procedure with γ-Al_2O_3 and calcined at 500℃ with ramping rate of 1℃/min.

2.2. Preparation of a silica/SUS membrane by the soaking-rolling method

The porous stainless steel support was modified by silica xerogels with particle size of 500nm or 100nm obtained by drying colloidal silica sols with a rotary evaporator. The silica xerogel was pressed into the macropores of one side of the stainless steel by a press under 10MPa. The modified stainless steel was calcined at 650℃ with ramping rate of 1℃/min. The second modification of the stainless steel support was conducted by the soaking-rolling method with boehmite sol. The back side of the support loaded on the O-ring sealed-cell was vacuumed by a rotary vacuum pump. Boehmite sol was poured onto the front side of the support maintaining vacuum of the back side of the support so that the boehmite sol could penetrate into inner pores of the support. After the soaking process, the boehmite sol on the front side of the support was rolled out with an urethane rolling pin in order to remove the boehmite sol on the surface of the stainless steel support. The modified support was dried overnight at 25℃ and calcined at 650℃. The preparation of top layer using polymeric silica sol was carried out by the same manner as the support modification with boehmite sol, and the silica top layer was dried at 25℃ and calcined at 500℃.

3. Results and Discussion

To investigate the thermal stability of SiO_2(polymeric)/γ-Al_2O_3/SiO_2(500nm) /SUS membrane prepared by dip-coating method, the single gas permeation test was conducted with permeation time changing the feed gas in turns of nitrogen, hydrogen and nitrogen at 350℃. Because we can estimate the thermal stability of the composite membrane in the presence of hydrogen by comparing the nitrogen permeance measured before hydrogen permeation test with that measured after hydrogen permeation test.

That is, when the composite membrane is failed in the presence of hydrogen at high temperature, the nitrogen permeance after hydrogen permeation test becomes higher than that before hydrogen permeation test [3]. Fig. 1 shows the variation of permeance of the silica composite membrane prepared by dip-coating method. As shown in Fig. 1, nitrogen permeance before hydrogen permeation test was about 6.8×10^{-9} mol•m^{-2}•s^{-1}•Pa^{-1}. After changing the feed gas into hydrogen, hydrogen permeance increased rapidly for 30 min and reached steady state. The ratio of hydrogen permeance to nitrogen permeance measured before hydrogen gas test is about 56. However, when nitrogen permeance was measured directly after hydrogen permeation test, unexpected increase in nitrogen permeance was observed and the ratio of hydrogen permeance to nitrogen permeance measured after hydrogen permeation test was about 4.0. According to our previous work [3], the failure of the stainless steel supported composite membranes in the presence of hydrogen at high temperature is attributed to the reduction of reducible metal oxides such as iron oxide formed on the surface of the stainless steel support. That is, the stainless steel support can contribute to the failure of the composite membranes due to surface oxide layers.

The thermal stability of SiO_2(polymeric)/γ-Al_2O_3/SiO_2(500nm)/SUS membrane prepared by the soaking-rolling method was also observed by single gas permeation test with permeation time changing the feed gas in turns of nitrogen, hydrogen and nitrogen at 350℃. As shown in Fig. 2, the nitrogen permeance measured before hydrogen permeation test was about 5.7×10^{-9} mol•m^{-2}•s^{-1}•Pa^{-1}. After changing the feed gas into hydrogen, the hydrogen permeance reached steady state at 6.7×10^{-8} mol•m^{-2}•s^{-1}•Pa^{-1} in 10 min. Differently from the permeation result of the silica membrane prepared by dip-coating method shown in Fig. 1, the nitrogen permeance was rapidly decreased after changing hydrogen feed gas into nitrogen. The nitrogen permeance measured directly after hydrogen permeation test was almost consistent with that measured before hydrogen permeation test. Fig. 3 presents the surface of the silica composite membrane prepared by the soaking-rolling method. Interestingly, the islands of stainless steel still appeared in the micrograph of the surface of the silica composite membrane prepared by the soaking-rolling method despite several coating procedure. The improvement of the thermal stability of the stainless steel supported membrane is attributed to the minimization of the interface between coating materialsand stainless steel induced by the soaking-rolling method, and colloidal silica particles, included even in top layer, as a barrier of propagation of the cracks derived from the remaining interface between the coating layer and the wall of stainless steel.

References

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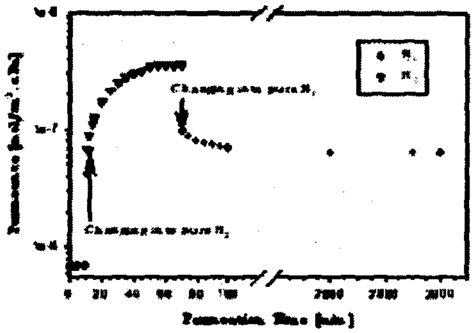

Fig. 1. The variation of permeance of the SUS supported silica membrane prepared by dip-coating method at 350℃

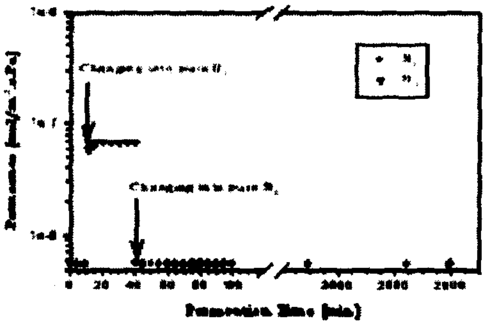

Fig. 2. The variation of permeance of the SUS supported silica membrane prepared by the soaking-rolling method at 350℃

Fig. 3. Topograph of the SUS supported silica composite membrane prepared by the soaking-rolling method