초청강연 I

Microporous Ceramic Membrane and Its Gas Separation Performance

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I. Introduction

Separation with synthetic membrane have become increasingly important processes in many fields. In the most application of membrane process, polymer membrane is used. the main advantage of polymers as a material for membrane preparation is the relative simplicity of this film formation which enables one to obtain rather high permeability rates. However, polymeric membranes have several limitations, such as high temperature instability, swelling and decomposition in organic solvent, et.al.. These limitations can be overcome by inorganic membrane. At the present time, commercially available inorganic membranes have pore diameters ranging 5nm to 50mm, and the predominant flow regime in such membrane is Knudsen diffusion. Since the Knudsen permeability is directly proportional to the molecular velocity, gases can be separated due to their molecular masses. However, this separation mechanism is only of important for light gases such as H2 and He. Other separation mechanisms like surface diffusion, active diffusion can play an important role only with very small pore diameters(2nm) and give rise to large permselectivities. Therefore, preparation of inorganic membrane with nano-sized pore have been attracting more and more attention.

Several approaches are known for preparation of porous inorganic membrane: sol-gel process phase separation and leaching, anodic oxidation, pyrolysis of a polymer precursor et. al.. Among them the sol-gel process seems to be the most adapted for the preparation of microporous membrane. In this paper, silica-alumina composite membrane was prepared by sol-gel method and the gas permeation characteristics through such membrane was examined.

II. Experimental

2.1 Membrane Preparation

The alumina substrate was provided by Dept. of Material Science and Technology at Tsinghua University, which is a composite material including a g-alumina top layer and a a-alumina support layer. Such substrates was further composited by silica through sol-gel method in our laboratory. The silica sols were prepared by combining tetraethylothosilicate(TEOS), ethanol and water according to the selected mole ratio of water to silicon. A small amount of nitric acid was added to catalyzed the hydrolysis. The mixture was heated for 5 hrs, cooled and then allowed to age for certain time. The effect of hydrolysis conditions coupled with the nature of drying control chemical agent(DCCA) on the sol and the resulting membrane property were investigated. The operating conditions of coating, drying, and cacinating were also studied.

Permeability of different gases through both alumina substrate and silica/alumina composite membrane were measured. The plate membrane with diameter of 50 mm was used. For pure gas peameation the gas flow rate through the membrane was measured with a soap-film flow meter. Separation performance for binary gas mixture was also measured. The composition on feed mixture was controlled by adjusting the flow rate of each component, and a gas chromatography was used to analyze the composition of gas mixture of feed inlet, feed outlet and permeate outlet. In order to further explore the gas transport mechanism through membrane, counter-diffusion measurements were also performed.

III. Experimental results and discussion

3.1 Pure gas permeation

The pure gas permeability's of hydrogen, nitrogen, ethylene and propane were measured, and the experimental results shown that the modification by silica decreased the permeability's of all gas studied. For alumina substrate, the permeability of different gases were in the range of 10-5뭆10-6 mol/m2뭗s뭗Pa, and the gas flux through it linearly increase with the increase of pressure difference.

This behavior can be interpreted by laminar flow mechanism. The gas permeability through silica modified membrane were about 25 to 30 times smaller than that through alumina substrate. Such decrease of permeability is apparently because the modification with silica decrease the pore size of membrane. Among the four gases tested, permeability of hydrogen was the highest. The permeability's of ethylene and propane were almost same, and both of them were higher than that of nitrogen. It seems that gas transport mechanism through silica modified membrane includes Knudsen diffusion, laminar flow, and perhaps also surface diffusion for ethylene and propane.

3.2 Separation of gas mixture

The separation performance of alumina substrate and silica modified membrane were also examined. The experimental results shown that the alumina substrate did not show any separation ability, i.e. under certain pressure difference, the compositions of feed and permeate were same. This indicate that the pore size of alumina membrane is so large that the gas transport through it is meanly through laminar flow mechanism, and therefore don't have any separation effect. The silica modified membrane sown quite good separation performance. At lower pressure difference, the permeability ration of H2/N2 was close to that expected for Knudsen diffusion. The permeability ratio for H2/C2H4 and H2/C3H8 were relative lower, and this result was consistent with the results of pure gas permeation. The relative lower separation effect for H2/C2H4 and H2/C3H8 is probably because that the ethylene and propane possess relative strong absorption ability, and their transport through membrane was enhanced by surface diffusion.

The experimental results also shown that the permeability ratio decreased with the increase of pressure difference across the membrane. Gas transport mechanism membrane includes Knudsen diffusion, laminar flow, and maybe also surface diffusion. The larger the pressure difference across membrane, the more obvious the contribution of laminar flow, and therefore the lower the permeability ratio.

3.3 Counter-diffusion

In order to eliminate the influence of laminar flow, counter-diffusion measurements were performed. in this case, two pure gases counterdiffuse in an isothermal, isobaric

system. For H2/N2 system, the permeability ratio measured during counter-diffusion experiment was equal to the idea Knudsen diffusion separation. Similar to the results of binary gas mixture separation, permeability ratio for H2/C2H4 system was still lower than that of H2/N2 system even though the molecular mass of nitrogen and ethylene were same. This phenomenon can be attributed to the relative strong adsorption ability of ethylene.

VI. Conclusions

In this paper, supported silica membrane was prepared by sol-gel method, and the gas transport characteristic through such membrane was studied. The experimental results show that the supported silica membrane possess quite good separation performance, and the permeability ratio of hydrogen/nitrogen is close to that expected for Knudsen diffusion. The permeability ratio of hydrogen/ethylene and hydrogen/propane are lower than idea Knudsen value, and this phenomena can be attributed to the relative strong adsorption ability of ethylene and propane.