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Engineering**www.elsevier.com/locate/procedia**Euromembrane Conference 2012****[P1.099]****Preparation and properties of organic-inorganic hybrid facilitated olefin separation membranes via sol-gel method**K. Kuraoka*, S. Matsuura, K. Ueda
*Kobe University, Japan***Introduction**

Separation of olefins through membranes has attracted much attention due to the energy intensiveness of the conventional distillation process. It has been known that the silver ion (Ag^+) based facilitated transport mechanism in the liquid membranes or ion-exchanged membranes for olefin separation is controlled by the diffusion of the olefin- Ag^+ complex through the membranes. Mainly, three types of facilitated Ag^+ membranes have been reported: supported liquid membranes, ion-exchange membranes, and salt/polymer blend membranes. Both the supported liquid membranes and ion-exchange membranes require that the feed gas be saturated with solvent, to maintain the selectivities of the membranes, and silver-polymer blend membranes can be used to separate olefins and paraffins without water; however, their applications are limited by the low thermal stability and low permeability. The disadvantage of these approaches is that the facilitated transport in the membranes will be greatly decreased with the loss of water from the membranes. Therefore, further research is needed to find novel olefin separation membranes without addition of water into the feed.

In this study, organic-inorganic hybrid facilitated olefin separation membranes were prepared by sol-gel method using silicon alkoxides and poly(sodium acrylate) (PANa) on porous alumina tubular supports, followed by Ag^+ exchange treatment.

Methods

Organic-inorganic hybrid layer of the membrane was prepared using sol-gel method. The composition of the sol was tetraethoxysilane (TEOS): H_2O : HNO_3 =1: 40: 0.2 (molar ratio). PANa, the amount of which is equal to 20 wt% of TEOS, was added to H_2O and the mixture was stirred several hours, then HNO_3 was added. After the mixture was stirred for several hours at room temperature, TEOS was added and the mixture was stirred at room temperature until a homogeneous sol was obtained. All the chemicals used were at commercial grades. A porous alumina tubular support with mean pore diameter of 0.1 μm , inner and outer diameters of 7.5mm and 10.5mm was used as substrate. The tubular support, with one end closed, was dipped and withdrawn at a speed of 1mm/s, then dried at room temperature for one hour. The dip-coating process was repeated two times. The coated tube was heated to 423K at a rate of 0.5K/min, and maintained at that temperature for 2 hours, then cooled to room temperature. This coating and heating procedures were repeated three times, then one ends of the membrane was sealed using epoxy resin and the other end was connected to a glass tube, which was prepared for ion exchange treatment and gas permeation measurement. Ag^+ exchange treatment was performed using 0.5 mol/L AgBF_4 solution. After ion exchange treatment, permeation of He , N_2 , C_2H_4 and C_2H_6 through the membranes were measured at 298, 323 and 373 K. The C_2H_4 selectivity was also measured using a gas mixture of 50% C_2H_4 -50% C_2H_6 .

Results and discussion

Fig.1 shows permeance of C_2H_4 and C_2H_6 through the membrane at 298, 323 and 473 K. The permeance of C_2H_4 was $1.6 \times 10^{-9} \text{ mol}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}\cdot\text{s}^{-1}$ at 298 K and $2.6 \times 10^{-9} \text{ mol}\cdot\text{m}^{-2}\cdot\text{Pa}^{-1}\cdot\text{s}^{-1}$ at

373 K. The permeance increased with increase of temperature. This thought to be due to promotion of decomplexation of C_2H_4 from Ag^+ sites in the membrane. Ratio of the permeance, C_2H_4/C_2H_6 through the membrane at 298, 323 and 473 K were shown in Fig. 2. These values were more than 30 (theoretical Knudsen value of $C_2H_4/C_2H_6=1.0$). The values at temperatures of 373 and 423 K showed that the organic-inorganic membranes did not lose their facilitated effect. This unique property is the contribution of nature of PANa and structure of organic-inorganic hybrid. PANa is known as water adsorbent. Thus it is difficult to release water at moderate temperature. One can speculate that this phenomenon was accelerated by organic-inorganic hybrid because of depression of molecular vibration of PANa by silica network in the hybrids.

The prepared membrane also indicates high C_2H_4 -selectivity using a gas mixture of 50% C_2H_4 -50% C_2H_6 .

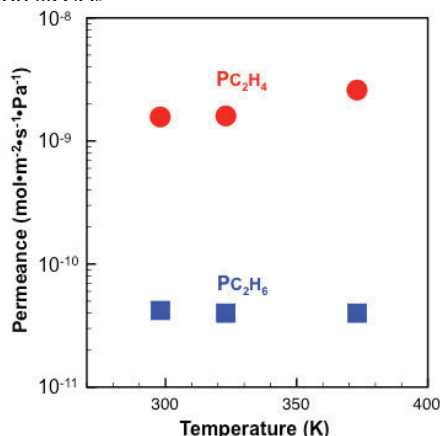


Fig. 1 Permeance of C_2H_4 and C_2H_6 through the membranes at 298, 323 and 473 K.

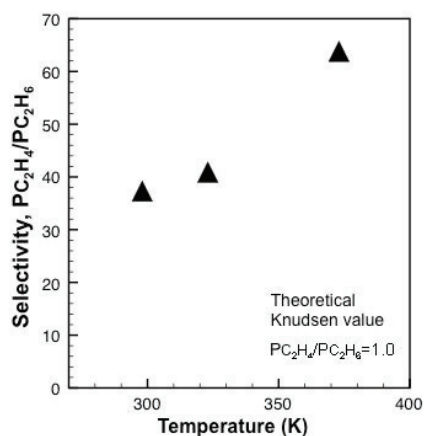


Fig. 2 Ration of permeance, C_2H_4/C_2H_6 through the membranes at 298, 323 and 473 K.

Conclusion

Organic-inorganic hybrid facilitated olefin separation membranes were prepared via sol-gel method and Ag^+ exchange treatment. The ratio of the permeance, C_2H_4/C_2H_6 through the membrane attained more than 30 and showed a dependence on temperature. Increase in the measurement temperature promoted the decomplexation of C_2H_4 from sites. The stable performance of the membrane at high temperature was due to water adsorption property of PANa and the depression of molecular vibration by silica network.

Keywords: Organic-inorganic hybrid, Olefin separation, Silver ions, Sol-gel method

