Enhancement of the Permeabilities of Ethylene and Propylene Gases in the Nafion–Ag Composite

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Gas permeabilities of ethylene and propylene in Nafion have been enhanced 2—3 times by ion-exchanging with Ag^+ into the ionic domain of the membrane at 0—75 °C; the temperature programmed desorption spectra of C_3H_6 for the silver composite demonstrate clearly two peaks, one of which belongs to Ag–alkene complexes.

In 1974, Standard Oil Co.[1] developed the polypropylene–silver ion microcomposite membranes for ethylene and propylene separation by using Ag^+ as a carrier in the membrane. Nafion–palladium and –silver microcomposite membranes were also developed by Torikai *et al.*[2,3] for the separation of hydrogen and oxygen, respectively. In this communication, our interest is focused on the mechanism of permeability enhancement due to the Ag^+ ion supported in the Nafion membrane.

A membrane of Nafion 417 (du Pont) with the equivalent

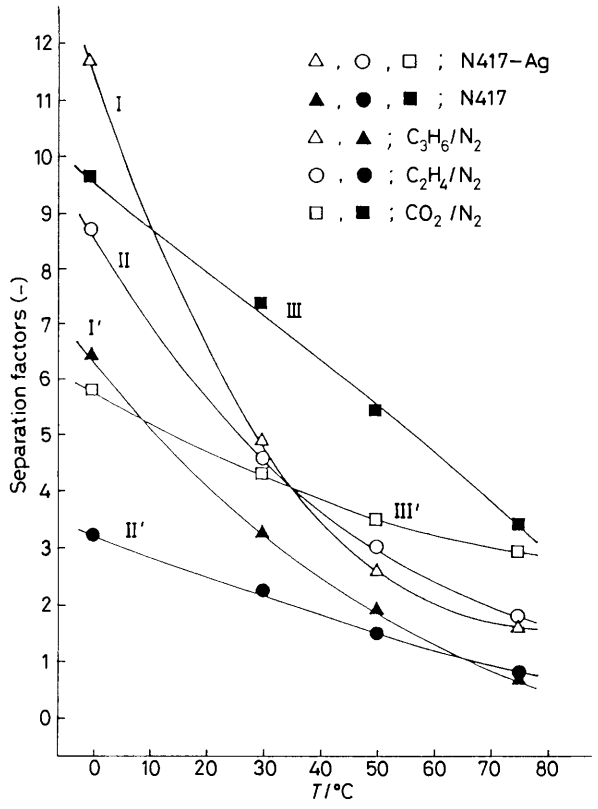

Figure 1. Comparison of the separation factors of C_3H_6/N_2, C_2H_4/N_2, and CO_2/N_2 for Nafion and the silver ion supported membranes.

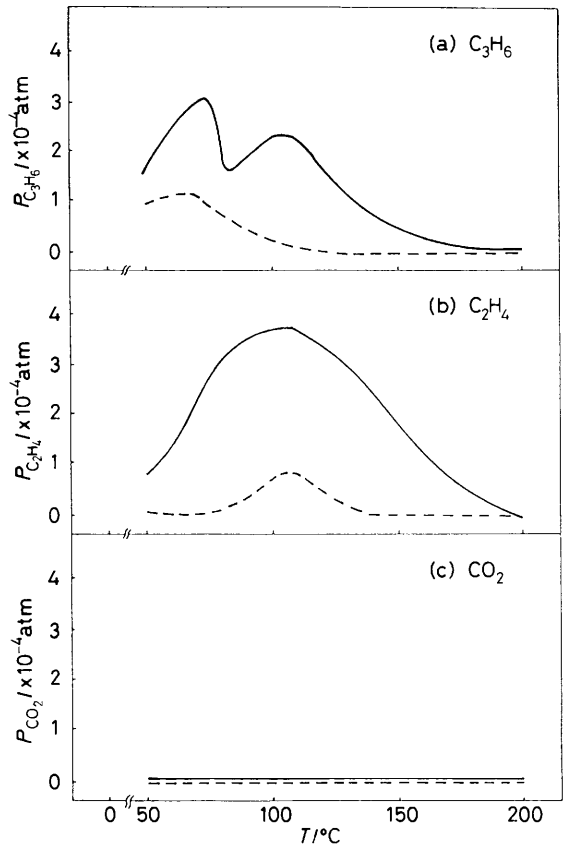

Figure 2. Comparison of the TPD spectra of C_3H_6, C_2H_4, and CO_2 for Nafion and the silver ion supported membranes. (—— = N417–Ag; - - - - = N417.)

weight of 1100 equiv./g and 0.043 cm thick was used. An acid-form membrane was used as a reference and it was ion-exchanged with silver ions by immersing it in an aqueous solution of $AgNO_3$ (0.1 M) for 7 days at room temperature. The loading amount of Ag^+ was found to be 6.8 mg of Ag per cm^2 of membrane by titration with KSCN (0.1 M) solution using an iron alum as an indicator.[4] Based on the loading amount of Ag^+, the percentage of Ag^+ ion exchanged was calculated to be 115%, suggesting a 15% excess somewhere in the membrane, such as the ionic domain. The water content of the membranes used was evaluated as the weight difference from the dry membrane which was prepared by drying them at 100 °C *in vacuo* for 12 h, and the evaluated values were ranged between 2—3.5% of water per gram of dry membrane through all the experiments. No serious change of water content was, therefore, observed even after exposing the membranes to permeation gases.

Figure 1 illustrates the C_3H_6/N_2, C_2H_4/N_2, and CO_2/N_2 separation factors for the Nafion (N417, see curves I,' II', and III) and silver supported Nafion (N417–Ag, see curves I, II, and III') membranes. N417–Ag provided a much larger separation factor for propylene and ethylene than N417, whereas for CO_2 it was reduced in value by 20 to 30%. This enhancement for C_3H_6- and C_2H_4-gases has been seen as a pumping effect of silver ion to form silver–alkene complexes (Ag–alkene$^+$) which work as carriers in the membrane.[1]

Figure 2 illustrates the temperature programmed desorption (TPD) spectra of C_3H_6 and C_2H_4. After N417 or N417–Ag were packed into a Pyrex glass tube, they were exposed to the C_3H_6, C_2H_4, or CO_2 gas stream for 13 h at 50 °C and then for 2 h while decreasing gradually the temperature to room temperature. The membranes were then exposed to a He stream, and the temperature was increased linearly at 2 °C min^{-1} by using a temperature programmed controller.

The TPD spectra of C_3H_6 [Figure 2(a)] and C_2H_4 [Figure 2(b)] clearly show extraordinary differences between N417 and N417–Ag, in contrast to CO_2 [Figure 2(c)] which has no desorption components, except a small amount of water. The differential thermal analysis (DTA) was separately conducted and gave an exothermic spectrum for N417–Ag containing C_2H_4 or C_3H_6, in contrast to N417–Ag which showed an endothermic spectrum. The exothermic spectrum may suggest the decomposition of the Ag^+–alkene complex.

On N417–Ag, C_3H_6 clearly demonstrates two peaks, one of which is for Nafion only (peak temperature, T_m 73 °C) and the other may be attributed to the Ag–propylene complex (T_m 98 °C). C_2H_4 demonstrates a large desorbed peak resulting from the Ag–ethylene complex formed in the ionic domain of the membrane, in contrast to Nafion in which only a small amount was desorbed. It has been evaluated independently that the amounts of alkene dissolved in N417–Ag increases in proportion to the amount of supported Ag^+. These results strongly suggest that the silver ion (Ag^+) works as a carrier, transporting into the membrane, similar to the liquid phase systems developed by Standard Oil Co.

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