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Reversible olefin complexation by silver ions in dry poly(vinyl methyl ketone) membrane and its application to olefin/paraffin separations

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Rapid and reversible olefin coordination to silver ions in $AgBF_4$–poly(vinyl methyl ketone) membrane has been characterized using FTIR and UV spectroscopy.

Olefin/paraffin separation by facilitated transport membrane using silver salts as carriers has been considered as a promising alternative to the conventional energy intensive distillation process.[1,2] The basis for the separation is the ability of silver ions to react reversibly with olefins forming silver–olefin complexes.[1–4] In general, facilitated transport phenomena have been mostly observed in supported liquid membranes and ion exchange membranes.[5] However, such membranes show facilitated olefin transport only in the presence of water, which is a serious drawback for practical application.[5] A solution to this problem is the development of dry polymer membranes in which silver ions can interact with olefins even in the absence of water.[6] Despite the extensive research on facilitated olefin transport phenomena in the water-free state, only a few dry polymer membranes have been developed. Accordingly, very little information has been obtained about phenomena occurring on the solid polymer membrane such as reversible interactions of silver salts with olefins and/or the polymer matrix, which is of pivotal importance in the development of high performance dry polymer membranes.[7]

It is well known that silver–olefin complexes are extremely unstable and lose olefin easily upon exposure to air.[8] Therefore, in order to characterize reversible olefin coordination to silver ions in a solid polymer membrane, the polymer matrix should contain some functional group(s) to stabilize the silver–olefin complexes to a certain extent. In addition, appropriate equipment should be used for the spectroscopic measurements in an inert or olefin atmosphere. Antonio and Tsou suggested that the stability of silver–olefin complexes could be enhanced by weak interaction between silver ions and oxygen atoms.[9] Among various oxygen-containing polymers, poly(vinyl methyl ketone) (PVMK) was chosen since it has a relatively simple structure and contains carbonyl functional groups the absorption peaks of which can be clearly seen by IR spectroscopy. A pressure cell is employed for the spectroscopic characterization of reversible interactions of silver salts with olefins and/or the polymer matrix in an inert or olefin atmosphere.[10]

We report the direct spectroscopic observation of rapid and reversible coordination of olefins to silver ions in dry PVMK membranes and of the interaction of silver ions with carbonyl groups in PVMK using FTIR and UV spectroscopy. We also report that the facilitated transport membrane consisting of $AgBF_4$ and PVMK exhibits excellent performance for olefin/paraffin separation.

All the samples for spectroscopic characterization[11] and permeation tests[12] were prepared in a dry box under argon to avoid contact with water. Spectroscopic characterization was carried out using a pressure cell equipped with two CaF_2 or quartz windows[10] and permeation tests were performed in a stainless steel separation module described elsewhere.[13]

The series of IR spectra in Fig. 1 demonstrate the solid state interaction of $AgBF_4$ with PVMK and reversible olefin coordination to silver ions dissolved in the solid $AgBF_4$–PVMK membranes. The peak at 1709 cm^{-1} in Fig. 1(a), associated with the C=O stretching frequency of uncoordinated PVMK, shifts to a lower frequency upon incorporation of $AgBF_4$, demonstrating the coordination of carbonyl groups to silver ions. The membrane with a molar ratio $AgBF_4:PVMK = 1:4$ shows a strong carbonyl absorption peak at 1681 cm^{-1} and a shoulder peak at *ca.* 1709 cm^{-1} which are assigned to coordinated and free carbonyl groups, respectively [Fig. 1(b)]. However, the membrane with a molar ratio of 1:2 shows a single absorption band implying that the maximum coordination number of silver ion by carbonyl groups is approximately two.

When the membrane ($AgBF_4:PVMK = 1:2$) was exposed to 30 psig of propylene and then purged with N_2, a new IR absorption peak at 1586 cm^{-1} appeared [Fig. 1(d)]. This new peak represents the C = C stretching vibration of coordinated propylene (*cf.* $\nu_{C=C}$ of free hex-1-ene = 1640 cm^{-1}).[7] It is interesting that the peak at 1586 cm^{-1} remains even after outgassing at 10^{-5} Torr for 4 h at room temperature. However, exposure of the propylene coordinated membrane to 30 psig of buta-1,3-diene and subsequent treatment with N_2 gives a new peak at 1558 cm^{-1} with concomitant disappearance of the peak at 1586 cm^{-1}. The peak at 1558 cm^{-1} can be assigned to the C=C stretching frequency of coordinated buta-1,3-diene [Fig. 1(e)]. The peak at 1558 cm^{-1} is replaced by a peak at 1586 cm^{-1} upon introduction of propylene into the gas cell containing the buta-1,3-diene-coordinated $AgBF_4$–PVMK

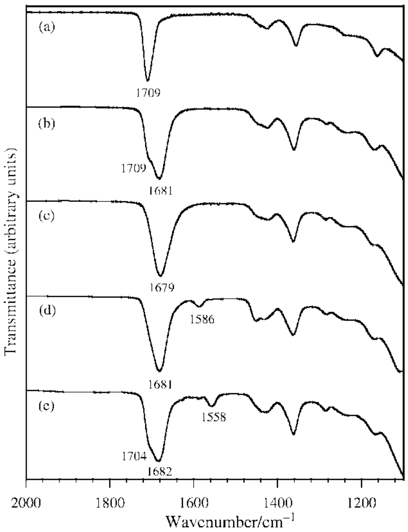

Fig. 1 IR spectra for the solid state interactions of $AgBF_4$ with PVMK and olefins: (a) PVMK, (b) $AgBF_4:PVMK = 1:4$, (c) $AgBF_4:PVMK = 1:2$, (d) propylene-coordinated membrane, (e) buta-1,3-diene-coordinated membrane.

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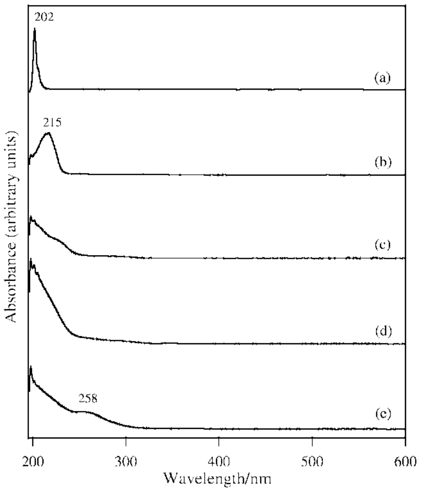

Fig. 2 UV spectra of olefin coordinated $AgBF_4$–PVMK membranes: (a) propylene, (b) buta-1,3-diene, (c) $AgBF_4$–PVMK ($AgBF_4$: PVMK = 1 : 2), (d) propylene-coordinated membrane, (e) buta-1,3-diene-coordinated membrane.

membrane. These results strongly indicate that the coordinated olefins are not rigidly held to silver ions in the membranes. Therefore, olefins can diffuse from the feed stream across the membrane to the permeate side thereby resulting in selective separation of olefins from the olefin/paraffin mixture.

The coordination of olefins to silver ions in the $AgBF_4$–PVMK membrane results in some significant changes in the absorption band of the coordinated carbonyl groups. As shown in Fig. 1(e), the IR spectrum of the buta-1,3-diene-coordinated membrane shows two carbonyl stretching bands at 1682 and *ca.* 1704 cm^{-1}. The shoulder peak at *ca.* 1704 cm^{-1} can be tentatively assigned to free carbonyl groups of PVMK, and this result strongly suggests that olefins and carbonyl groups compete with each other for coordination to silver ions.

Reversible olefin coordination was also observed by spectral changes in the UV absorption as shown in Fig. 2. Fig. 2(d) shows a strong and broad absorption band at 220–230 nm for propylene coordinated $AgBF_4$–PVMK ($AgBF_4$: PVMK = 1 : 2). When the propylene coordinated membrane was exposed to buta-1,3-diene atmosphere followed by an N_2 purge, the absorption band at 220–230 nm disappeared and a new band appeared at *ca.* 258 nm associated with coordinated buta-1,3-diene [Fig. 2(e)]. This result again indicates that co-ordinated propylene is labile enough to be readily replaced by other olefins. In the same manner, the absorption band of coordinated propylene at 220–230 nm reappeared when propylene was introduced into the cell containing the buta-1,3-diene coordinated membrane.

The separation of an olefin/paraffin mixture (1 : 1, v/v) was performed to evaluate the facilitated transport effect of silver ions in PVMK. Fig. 3 shows the effect of the molar ratio of $AgBF_4$/PVMK on the selectivity for olefins over paraffins. The selectivity for propylene (ethylene) over propane (ethane) increases with increasing molar ratio of $AgBF_4$: PVMK up to 1 : 1 and then decreases with further increases in the molar ratio. Such a selectivity dependence on the molar ratio of $AgBF_4$: PVMK implies that the coordination environment of silver ions in PVMK has a significant effect on the facilitated transport of olefins. The higher selectivity for ethylene/ethane in comparison with that for propylene/propane can be ascribed to the difference in diffusion rates of the mixture gas and/or to the difference in affinities for the olefins to silver ions in the membrane.

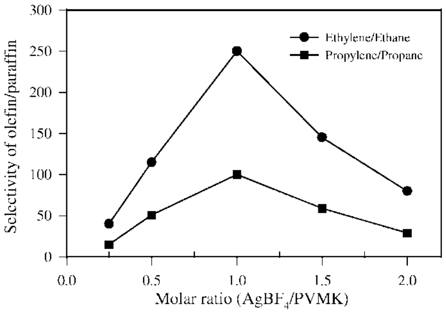

Fig. 3 Effect of molar ratio of $AgBF_4$/PVMK on the selectivity for olefins over paraffin selectivity.

XPS analysis of $AgBF_4$–PVMK membranes is under way to characterize the chemical states of silver, carbon and oxygen atoms in $AgBF_4$–PVMK membranes.

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