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Coordination structure of various ligands in crosslinked PVA to silver ions for facilitated olefin transport

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The most effective ligand among –OH, –O– and –CHO for facilitated olefin transport by silver ions in room temperature crosslinked poly(vinyl alcohol) membrane has been evaluated.

Separation of olefin/paraffin gas mixtures is one of the most energy intensive processes in the petrochemical industry because it is performed mainly by cryogenic distillation. Membrane processes have been considered to be an intriguing alternative to the cryogenic distillation.[1,2] In particular, solid-state facilitated transport membranes have recently demonstrated their promising applicability for separation of olefin/paraffin mixtures.[3–5] The basis of facilitated transport in solid state is the reversible interaction of olefins with silver ions dissolved in a polymer matrix to make silver cation–olefin complexes.[5]

Poly(vinyl alcohol) (PVA) is an interesting matrix for silver polymer electrolytes where silver cations are coordinated by hydroxy oxygens of PVA. In the case of crosslinked PVA membranes containing $AgNO_3$, facilitated olefin transport was observed only when the feed stream was saturated with water, but not in the dry state,[6] which causes critical problems for commercial applications. Thus, dry facilitated transport membranes in the solid state are demanding.

When PVA membranes are crosslinked by dialdehydes such as glutaraldehyde, three functional groups are available for coordination to silver ions: –OH, –O– and –CHO. Therefore it is interesting to investigate the effectiveness of each functional group on coordination behavior with silver ions as well as on facilitated olefin transport. $AgSbF_6$ was chosen as an olefin carrier, since (1) it possesses a low enough lattice energy to be readily dissolved in PVA matrix[7] and (2) the anion vibration mode of $AgSbF_6$ is not overlapped with the C–O stretching peak of PVA in the range of 1000–1200 cm^{-1} and thus IR spectroscopy can be readily applied to characterize the C–O stretching mode.[5] Here we investigate the most effective ligand of silver ions for solid state facilitated olefin transport membranes consisting of silver salt and room temperature crosslinked PVA.

In previous research,[6] PVA was commonly crosslinked by crosslinking agents such as formaldehyde, vinyl sulfone or toluene diisocyanate at a high temperature, *e.g.* 70 °C for three days. The heating step was necessary to ensure the crosslinking reaction of PVA. However, it was found that heat treatment of the polymer membranes containing silver salts produced the reduction of silver ion Ag(I) to metal Ag(0), and consequently deterioration of the membrane performance.[8,9] In this study, the crosslinking reaction was therefore carried out at room temperature with a catalyst HCl to avoid the possible reduction reaction.

PVA solution was prepared by dissolving 10 wt% PVA in deionized water with stirring at 70–80 °C and cooled at room temperature. After complete dissolution, HCl (0.15 wt% of the total PVA solution) and glutaraldehyde (GA, 50% in water, Aldrich) were successively added to the solution as catalyst and crosslinking agent, respectively. The predetermined amount of $AgSbF_6$ (98%, Aldrich) was added in the solution. Spectroscopic characterization and gas permeation tests were carried out as described in previous papers.[3,5]

Fig. 1 illustrates the FT-IR spectra of pure and crosslinked PVA containing different concentration of GA. With increasing GA content, the O–H stretching vibration band at 3350 cm^{-1} was decreased along with the band shift to a higher wavenumber at 3460 cm^{-1}. This result suggests that the hydrogen bonding becomes weaker in crosslinked PVA than in pure PVA because of the diminution in the number of OH groups. In addition, the hydroxy C–O stretching band at 1100 cm^{-1} in pure PVA disappears gradually and is replaced by two absorption bands at 1134 and 1001 cm^{-1}, which can be attributed to the ether C–O and the acetal ring C–O stretching bands, respectively. The appearance of the aldehyde C=O band at 1718 cm^{-1} above 2 : 1 mole ratio of [OH] to [GA] indicates that the aldehyde groups of GA do not completely react with OH groups, and the unreacted aldehyde groups are thus available for coordination with silver salts. Therefore, –OH, –O– and –CHO groups are present in PVA membranes crosslinked by glutaraldehyde.

The series of FT-IR spectra in Fig. 2 presents the *solid state* interaction of silver ion with polymer matrix as well as with propylene molecules. As can be seen in Fig. 2a, the aldehyde C=O band at 1718 cm^{-1} was hardly observed for [OH] : [GA] =

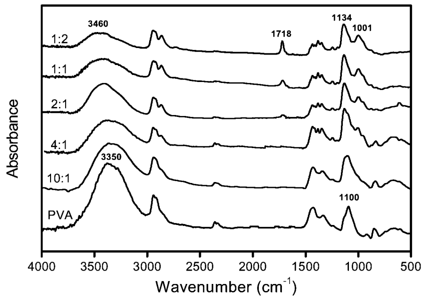

Fig. 1 FT-IR spectra of pure PVA and crosslinked PVA with GA as a function of [OH] : [GA] mole ratio.

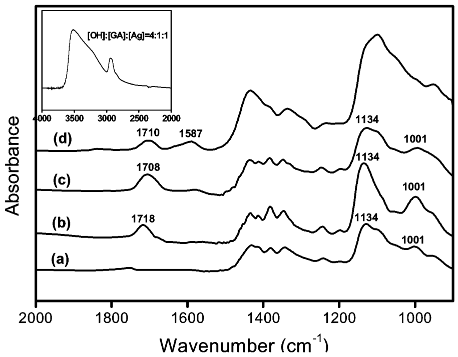

Fig. 2 FT-IR spectra changes of crosslinked PVA containing $AgSbF_6$ as well as those of propylene-coordinated membrane. (a) [OH] : [GA] : [Ag] = 4 : 1 : 0, (b) [OH] : [GA] : [Ag] = 1 : 1 : 0, (c) [OH] : [GA] : [Ag] = 4 : 1 : 1, (d) propylene coordinated [OH] : [GA] : [Ag] = 4 : 1 : 1. The inset is the spectra of (c) in a range of 1000 and 2000 cm^{-1}.

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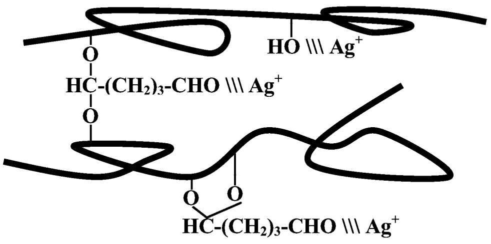
4 : 1, implying a sufficient crosslinking reaction between PVA and GA even at a room temperature. When the concentration of GA was raised to [OH] : [GA] = 1 : 1, the aldehyde C=O band at 1718 cm^{-1} appeared as seen in Fig. 2b. Upon incorporation of AgSbF$_6$, the aldehyde C=O band at 1718 cm^{-1} and the O–H band at 3350 cm^{-1} shift to the wavenumbers at 1708 and 3525 cm^{-1}, as shown in Fig. 2c and the inset figure, respectively. It demonstrates that the silver ions are coordinated by both aldehyde and hydroxy oxygens through an electron donation to the vacant 5s orbital of the silver ions. It should be noted that the aldehyde C=O band at 1708 cm^{-1} appears for [OH] : [GA] : [Ag] = 4 : 1 : 1 whereas it is not observed for [OH] : [GA] : [Ag] = 4 : 1 : 0 although [OH] : [GA] is fixed at 4 : 1. This implies that silver ions may play an important role in the crosslinking reaction, *i.e.*, the aldehyde groups of GA may coordinate to silver ions prior to the crosslinking reaction and the coordinated aldehyde groups may not actively involve in the crosslinking reaction.

It has been known that ether oxygens of poly(ethylene oxide) (PEO) coordinate to silver cations of AgBF$_4$, resulting in facilitated olefin transport.[4] In the case of PEO:AgSbF$_6$ polymer electrolytes, the frequency shift of the ether C–O from 1113 to 1080 cm^{-1} occurred (spectra not shown here), indicating the coordinative interaction between silver ion and ether oxygen. However, the ether C–O absorption band in the crosslinked PVA : AgSbF$_6$ remained invariant at 1134 cm^{-1}. No band shift for the acetal C–O band at 1001 cm^{-1} was observed either. Therefore, it is obvious that silver ions are not coordinated by either ether C–O or acetal C–O groups in the crosslinked PVA, but by aldehyde and hydroxy groups. As a result, the expected chemical structure of crosslinked PVA coordinating to silver ions is depicted as Scheme 1.

Complexation of silver cations by olefins is essential for facilitated olefin transport. When the crosslinked PVA membrane containing AgSbF$_6$ was exposed to propylene at 413.5 kPa for 30 min and then successively purged with N$_2$, a new IR absorption band at 1587 cm^{-1}appeared as provided in Fig. 2d. This new shoulder band represents the coordinated C=C stretching vibration of propylene to silver ion (ν_1 and ν_2 of C=C in free propylene are 1665 and 1640 cm^{-1}, respectively), demonstrating the complexation of silver ions by propylene molecules.

In PVA membranes crosslinked by glutaraldehyde, there are three functional groups such as –OH, –O– and –CHO, among which oxygens of only –OH and –CHO groups coordinate to silver ions. Thus it is interesting to investigate which group between –OH and –CHO is more effective to make olefin–silver cation complexes for facilitated olefin transport. The separation experiment of propylene/propane mixtures was thus carried out to evaluate the separation performance of uncrosslinked and crosslinked PVA membranes containing AgSbF$_6$. As a result it is found that the uncrosslinked PVA membranes containing AgSbF$_6$ exhibited almost no separation performance for olefin/paraffin mixtures (selectivity $\approx$ 1.0). This suggests that silver cations coordinated by hydroxy oxygens are not effective as an olefin carrier for facilitated transport.



Scheme 1

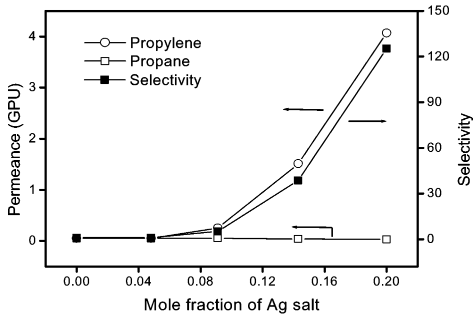


Fig. 3 Mixed gas permeance and selectivity of propylene/propane through crosslinked PVA containing AgSbF$_6$ as a function of silver mole fraction.

Fig. 3 shows the gas permeances and the selectivity of propylene/propane through crosslinked PVA membranes as a function of the silver concentration at 25 °C. The separation performance was very poor until the mole fraction of silver reached *ca.* 0.09 ([OH] : [Ag] = 10 : 1). However, it was increased thereafter in proportion to the silver concentration. When the mole fraction of silver was 0.2 ([OH] : [Ag] = 4 : 1), the propylene permeance and the selectivity were increased up to 4.1 GPU and 125, respectively. The observed facilitated olefin transport suggests that olefins make complexes with silver cations coordinated by oxygens most effectively from –CHO groups among –OH, –O– and –CHO.

In summary, the three different functional groups –OH, –O– and –CHO are available for coordination with silver cations in crosslinked PVA membranes. Among them, oxygens from –OH and –CHO groups coordinate to silver cations, but not those from –O– groups. In separation performance for propylene/propane mixtures, it is found that silver cations coordinated only by –CHO groups are very effective in facilitated olefin transport, resulting in high separation performance while those coordinated by –OH groups are not. Therefore, it is proposed that the most effective ligand of silver cations for facilitated olefin transport among –OH, –O– and –CHO is the aldehyde oxygen.

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9 In our system, after crosslinking PVA : AgSbF$_6$ membranes ([PVA-] : [GA] : [Ag] = 4 : 1 : 1) at 70 °C for two days, the mixed gas permeance and selectivity of propylene/propane were sharply decreased from *ca.* 4.1 to 0.1 GPU and *ca.* 125 to 1.1, respectively.