

Facilitated Olefin Transport by Reversible Olefin Coordination to Silver Ions in a Dry Cellulose Acetate Membrane

Jae Hee Ryu,^[a] Hyunjoo Lee,^[b] Yong Jin Kim,^[b] Yong Soo Kang,^[a] and Hoon Sik Kim*^[a, b]

Abstract: The highly selective dry complex membrane AgBF₄–cellulose acetate (CA) was prepared and tested for the separation of ethylene/ethane and propylene/propane mixtures. The maximum selectivity for olefin over paraffin was found to be 280 for the ethylene/ethane mixture and 200 for the propylene/propane mixture. Solid-state interactions of AgBF₄ with cellulose acetate (CA) and/or olefins have been investigated by using FT-IR, UV, and X-ray photoelectron spectroscopy (XPS). FT-IR and XPS studies clearly show that the

silver ions are coordinated by carbonyl oxygen atoms among three different types of oxygen atoms present in CA—two in the acetate group and one in the ether linkage. Upon incorporation of AgBF₄ into CA, the carbonyl stretching frequency of the free cellulose acetate at 1750 cm⁻¹ shifts to a lower frequency by about 41 cm⁻¹. The binding energy cor-

responding to a carbonyl oxygen atom in the O 1s XPS spectrum shifts to a more positive binding energy by the incorporation of AgBF₄. Reversible olefin coordination to silver ions has been observed by FT-IR and UV studies. Treatment of the AgBF₄–CA membrane placed in a gas cell with propylene produces a propylene-coordinated membrane in which coordinated propylene is easily replaced by other olefins such as 1,3-butadiene.

Keywords: cellulose acetate • facilitated transport • IR spectroscopy • membranes • silver

Introduction

Olefin/paraffin separation is one of the most important processes in the petrochemical industry.^[1] The conventional method for separating olefin/paraffin mixtures is highly energy-intensive low-temperature distillation.^[2, 3] Among a number of alternative separation processes, separation by facilitated transport membranes in which silver salts are used as carriers has attracted much interest because of the low energy consumption, compact apparatus, and simple operation.^[3, 4] The basis for the separation is the ability of a silver ion to react reversibly with olefin by forming silver–olefin complexes.^[1, 3–8] There have been many reports on the facilitated transport of olefins by using various membranes such as supported liquid membranes and ion-exchange membranes;^[9] however, those membranes exhibit high ole-

fin/paraffin selectivity only in the presence of water, requiring costly and undesirable humidification and dehumidification steps in the practical applications.^[9] A solution to this problem is the development of dry polymer membranes such as a Ag salt/poly(ethylene oxide) membrane in which the silver ion can reversibly interact with olefin even in the absence of water.^[10] Many investigators have studied facilitated transport phenomena in water free state, but only a limited number of reactive dry polymer membranes with high olefin/paraffin selectivity have been developed.

Accordingly, very little information is provided about the phenomena occurring on the solid polymer membrane.^[11–13] The following three interactions should be considered in the investigation of the phenomena on the solid polymer membrane for facilitated olefin transport: silver salt/polymer, silver salt/olefin, and olefin/silver salt/polymer interactions. Since the degree of each interaction seems to be strongly dependent on the type of donor atom present in the polymer atoms, the choice of the polymer material with an appropriate functional group would be one of the most important factors in determining the performance of the membrane. For this reason, we have been interested in polymer materials that contain various types of donor atoms to elucidate the favorable coordination site of silver ions.

We report here the spectroscopic characterization of the solid-state interaction between AgBF₄ and cellulose acetate (CA), which contains various types of oxygen donor atoms,

[a] Dr. H. S. Kim, J. H. Ryu, Dr. Y. S. Kang
Center for Facilitated Transport Membrane
Korea Institute of Science and Technology
P.O. Box 131, Cheongryang
Seoul 130-650 (Korea)
Fax: (+82)2-958-5859
E-mail: khs@kist.re.kr

[b] Dr. H. S. Kim, H. Lee, Y. J. Kim
CFC Alternatives Research Center
Korea Institute of Science and Technology
P.O. Box 131, Cheongryang
Seoul 130-650 (Korea)

and the reversible coordination of olefins to silver ions in dry CA by using FT-IR, UV, and X-ray photoelectron spectroscopy. We also report that the facilitated transport membrane consisting of AgBF_4 and CA exhibits the highest selectivity for propylene over propane and ethylene over ethane reported to date.

Results and Discussion

Figure 1 shows the IR spectra of the AgBF_4 -CA membranes for various molar ratios of AgBF_4/CA (1:1 to 3:1). The peak at 1750 cm^{-1} in Figure 1 a, associated with the C=O stretching

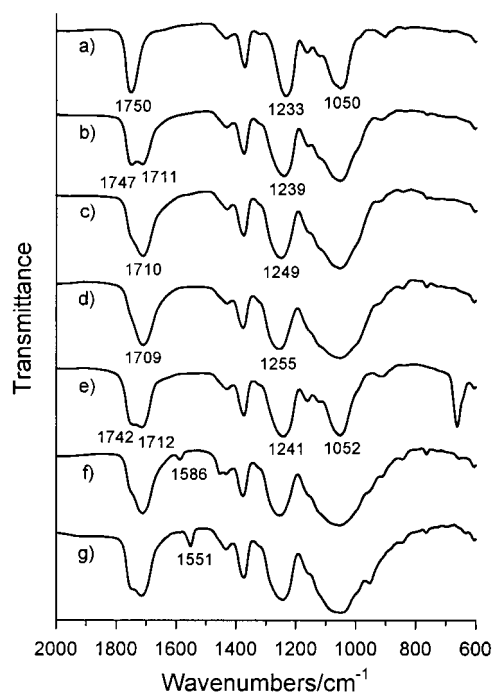


Figure 1. IR spectra of AgBF_4 -CA membranes containing different molar ratios of AgBF_4/CA as well as those of olefin-coordinated membranes ($\text{AgBF}_4/\text{CA} = 3:1$): a) CA, b) $\text{AgBF}_4/\text{CA} = 1:1$, c) $\text{AgBF}_4/\text{CA} = 2:1$, d) $\text{AgBF}_4/\text{CA} = 3:1$, e) $\text{AgSbF}_6/\text{CA} = 1:1$, f) propylene-coordinated AgBF_4 -CA membrane, g) 1,3-butadiene-coordinated AgBF_4 -CA membrane.

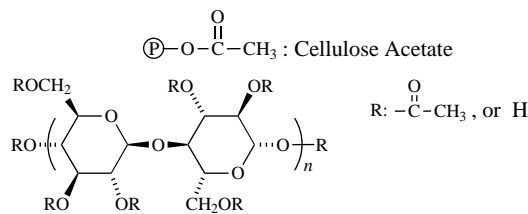
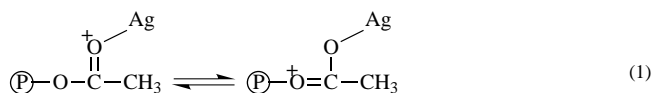
frequency of uncoordinated cellulose acetate, shifts to a lower frequency by the incorporation of AgBF_4 . This result indicates that the carbonyl groups coordinate to silver ions

Abstract in Korean:

AgBF_4 와 CA로 이루어진 촉진수송분리막을 에텐/에탄 및 프로펜/프로판 혼합기체의 분리에서 사용한 결과 각각 280 및 200의 뛰어난 선택성을 보여주었다.

FT-IR, UV 및 XPS와 같은 분광학적 방법을 사용하여 은이온과 CA 및 올레핀과의 상호작용을 연구한 결과 은이온은 카보닐기 및 올레핀과 가역적으로 반응하며 은이온에 결합된 올레핀은 다른 종류의 올레핀과 쉽게 치환됨을 알 수 있었다.

through electron donation from oxygen atoms to the vacant 5s orbital of the silver ion. The degree of shift of the carbonyl absorption band increases with increasing molar ratio of AgBF_4/CA . At a higher molar ratio of AgBF_4/CA , carbonyl groups have more chances to interact with silver ions, which leads to a reduction of C=O bond order. Such an interaction between silver ions and carbonyl groups has been well described in the dense membrane consisting of AgBF_4 and poly(vinyl methyl ketone).^[8] The two carbonyl absorption bands observed in the molar ratio range from 1:1 to 2:1 can be assigned to free and coordinated carbonyl groups, respectively. Interestingly, the peak centered at 1233 cm^{-1} corresponding to a C-O single-bond stretching band of the acetate group continuously shifts to a higher frequency with increasing molar ratio of AgBF_4/CA . The peak shift to a higher frequency implies that AgBF_4 is not directly coordinated to the oxygen atom of the C-O single bond, and the shift can be ascribed to the increased C-O bond strength resulting from the resonance structures shown in Equation (1).



Due to the overlap of BF_4^{-1} and C-O absorptions in the range $1000\text{--}1100\text{ cm}^{-1}$, the interaction between silver ions and oxygen atoms in ether linkages has been investigated by using a AgSbF_6 -CA film ($\text{AgSbF}_6/\text{CA} = 1:1$). Unlike in AgSbF_6 -poly(ethylene oxide), the C-O absorption frequency in the ether linkage of free CA, which is centered at 1050 cm^{-1} , remains unchanged upon incorporation of AgSbF_6 into CA, indicating that there is no interaction between silver ions and oxygen atoms in ether linkages (Figure 1 a, e).^[14]

Figure 1 also demonstrates the rapid and reversible olefin coordination to silver ions dissolved in the solid AgBF_4 -CA membrane. When the membrane ($\text{AgBF}_4/\text{CA} = 3:1$) was exposed to propylene (2 atm) for a couple of seconds and then purged with N_2 , a new IR absorption peak appeared at 1586 cm^{-1} (Figure 1 f). This new peak, which is at lower frequency than the C=C stretching of free propylene, represents the C=C stretching vibration of coordinated propylene. Interestingly, the peak at 1586 cm^{-1} remains even after degassing at 10^{-5} Torr for 4 h at room temperature. However, exposure of the propylene-coordinated membrane to 1,3-butadiene (2 atm) followed by a N_2 purge gives a new peak at 1551 cm^{-1} with the concomitant disappearance of the peak at 1586 cm^{-1} . The peak at 1551 cm^{-1} can be assigned to the C=C stretching frequency of coordinated 1,3-butadiene (Figure 1g). This behavior indicates that the coordinated olefin is not rigidly bound to the AgBF_4 . Therefore, olefins

can diffuse from the feed stream across the membrane thereby resulting in selective separation of olefin from olefin/paraffin mixtures. Likewise, the absorption band at 1586 cm^{-1} reappeared when propylene was introduced into the gas cell containing the 1,3-butadiene-coordinated AgBF_4 -CA membrane. The coordination of olefins to silver ions also results in some significant changes in the carbonyl absorption band. The band at 1709 cm^{-1} , associated with carbonyl groups coordinated to silver ions, shifts to a higher frequency at 1740 cm^{-1} (Figure 1d). The appearance of the peak at 1740 cm^{-1} can be related to the formation of a silver ion/carbonyl oxygen/olefin complex.^[12] It is also conceivable that the olefin and carbonyl group compete with each other for the coordination to silver ions, because the frequency of 1740 cm^{-1} is close to 1750 cm^{-1} for the uncoordinated carbonyl group. A similar coordination profile has been observed in the THF solution containing AgBF_4 and cellulose acetate.

The reversible olefin coordination was also observed by the spectral changes in the UV absorption spectra (Figure 2). Figure 2d shows a strong and broad absorption band at 220–230 nm for propylene-coordinated AgBF_4 -CA ($\text{AgBF}_4/\text{CA} = 3:1$). When the propylene-coordinated membrane was

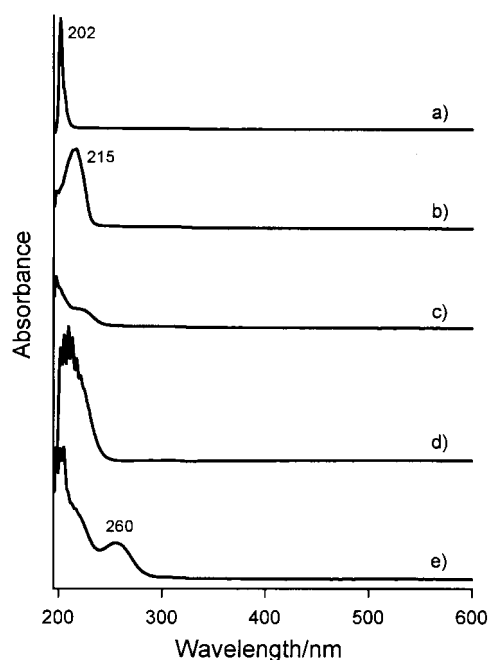


Figure 2. UV spectra showing the effects of olefin coordination on the AgBF_4 -CA membrane: a) propylene, b) 1,3-butadiene, c) AgBF_4 -CA membrane ($\text{AgBF}_4/\text{CA} = 3:1$), d) propylene-coordinated AgBF_4 -CA membrane, e) 1,3-butadiene-coordinated AgBF_4 -CA membrane.

exposed to a 1,3-butadiene atmosphere, followed by a N_2 purge, the absorption band at 220–230 nm disappeared and a new band appeared at around 260 nm for the coordinated 1,3-butadiene (Figure 2e). This result again indicates that coordinated propylene is labile enough to be easily replaced by another olefin. In the same manner, the absorption band of coordinated propylene at 220–230 nm reappeared when

propylene was introduced into the cell containing the 1,3-butadiene-coordinated membrane.

X-ray photoelectron spectroscopy (XPS) was applied to clearly identify the coordination site and chemical states of the silver ion in AgBF_4 -CA membranes with a varying molar ratio of AgBF_4/CA . The high-resolution Ag core spectra of these samples are shown in Figure 3. The Ag $3d_{5/2}$ core

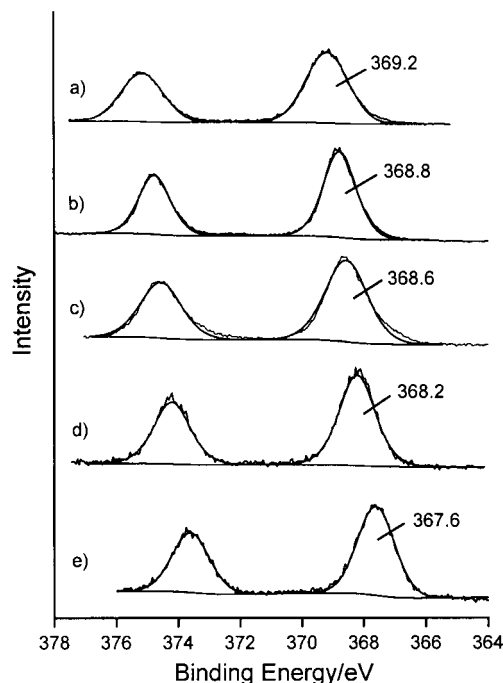


Figure 3. Ag $3d_{5/2}$ XPS spectra of AgBF_4 -CA membranes containing different molar ratios of AgBF_4/CA : a) AgBF_4 , b) $\text{AgBF}_4/\text{CA} = 6:1$, c) $\text{AgBF}_4/\text{CA} = 3:1$, d) $\text{AgBF}_4/\text{CA} = 1.5:1$, e) $\text{AgBF}_4/\text{CA} = 1:1$.

spectrum of uncoordinated AgBF_4 shows a single peak at 369.2 eV (Figure 3a). The incorporation of AgBF_4 into CA results in the decrease of silver binding energy, and the degree of shift to a lower binding energy increases with increasing amounts of CA. It is reasonable to assume that the increased electron density on silver atoms by the coordination of oxygen atoms in CA is responsible for the decrease in the binding energy of the silver atoms.

Cellulose acetate has three different types of oxygen atoms that can donate electrons to silver ions—two in acetate groups and one in the ether linkage [Eq. (1)].^[15, 16]

The O 1s XPS spectrum of CA can be fitted to three components as shown in Figure 4a. The peaks at 531.4 eV, 532.2 eV, and 532.8 eV correspond to the C=O in the acetate group (O1), the oxygen atom in the ether linkage (O2), and the oxygen atom of the C–O single bond in the acetate group (O3), respectively. Upon incorporation of AgBF_4 into CA, the intensities of components O1 and O3 decrease and two new peaks appear at about 533.2 eV and 534.1 eV. As the molar ratio of AgBF_4/CA increases, the peaks of the new components shift to more positive binding energy and the relative peak intensities of the new peaks increase. These results indicate that the two new peaks are associated with coordination of the O1 and O3 atoms in the acetate groups to silver

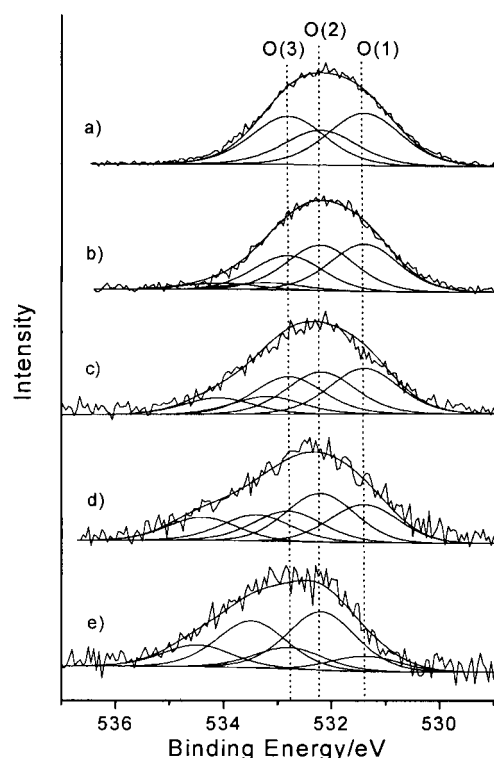


Figure 4. O 1s XPS spectra of AgBF_4 -CA membranes containing different molar ratios of AgBF_4/CA : a) CA, b) $\text{AgBF}_4/\text{CA} = 1:1$, c) $\text{AgBF}_4/\text{CA} = 1.5:1$, d) $\text{AgBF}_4/\text{CA} = 3:1$, e) $\text{AgBF}_4/\text{CA} = 6:1$.

ions. On the other hand, the intensity of the O2 component remains unchanged with the increasing amounts of AgBF_4 , implying that silver ions are not directly bonded to oxygen atoms in the ether linkage.

The separation of an olefin/paraffin mixture was performed to evaluate the facilitated transport effect of silver ions in the cellulose acetate membranes. Figure 5 shows the effect of

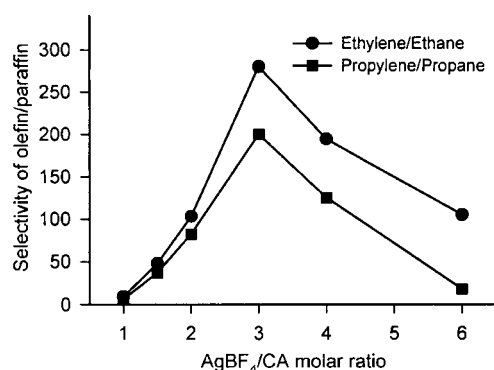


Figure 5. Effect of the molar ratio of AgBF_4/CA on the selectivity for olefin over paraffin.

increasing the molar ratio of AgBF_4/CA on the selectivity for olefin over paraffin. The selectivity for propylene over propane and ethylene over ethane increases with increasing molar ratio of AgBF_4/CA up to 3:1 and then gradually decreases with further increase in the molar ratio. The maximum selectivity at the molar ratio of $\text{AgBF}_4/\text{CA} = 3:1$ implies that the coordination environment of silver ions in the

cellulose acetate membrane has a significant effect on the facilitated transport of olefin. The monomer unit of cellulose acetate (acetyl content: 39.8 wt%) has approximately 4.9 carbonyl groups and thus, in principle, each silver ion in the membrane ($\text{AgBF}_4/\text{CA} = 3:1$) is coordinated by about 1.6 carbonyl groups. From this result and the spectroscopic data, it is likely that the silver ions in the AgBF_4 -CA membrane should be approximately twofold coordinated by carbonyl groups for the membrane to be highly selective in the facilitated transport of ethylene and propylene. Considering the maximum coordination number of four for a silver ion, it is interesting to note that the membrane with the molar ratio of AgBF_4/CA of 1:1 exhibits some selectivity for propylene over propane and for ethylene over ethane because there are 4.9 carbonyl groups around each silver ion in the membrane. This result implies that propylene or ethylene can coordinate to the fully coordinated silver ion by replacing carbonyl group(s). This is supported by a separate IR experiment in which the interaction of propylene with the fully coordinated silver ions in the membrane ($\text{AgBF}_4/\text{CA} = 1:1$) was studied; an absorption peak for the coordinated propylene occurs at 1586 cm^{-1} . The higher selectivity for ethylene/ethane over that for propylene/propane can be ascribed to the difference in diffusion rates of mixture gas and/or to the difference in affinities of olefins for silver ions in the membrane.

Experimental Section

All the samples were prepared in a dry box under argon and the spectroscopic measurements except the X-ray photoelectron spectra were performed by using a specially designed gas cell because silver-olefin and silver-polymer interactions are sensitive to moisture.^[17-19]

The dense membranes with different molar ratios of AgBF_4/CA were prepared as follows: AgBF_4 (Aldrich, 98%) was mixed with 10 wt% cellulose acetate (Aldrich, acetyl content: 39.8 wt%) in THF (Baker, 99+) solution. The solution was cast onto a glass plate and dried for 2 h in air and then vacuum-dried at 40°C for 6 h. The prepared membrane was placed between two $25 \times 3\text{ mm}$ KBr windows located in a specially designed gas cell. FT-IR spectra were recorded on a Mattson Infinity spectrophotometer equipped with a MCTA detector.

The XPS measurements were conducted with a VG Scientific ESCALAB 220 spectrometer equipped with a hemispherical energy analyzer. The nonmonochromatized $\text{Al}_{K\alpha}$ X-ray source ($h\nu = 1486.6\text{ eV}$) was operated at 12.5 kV and 16 mA. Before data acquisition, the membranes were degassed for 3 h at 298 K under a pressure of about 1.0×10^{-9} Torr to minimize the surface contamination.

The samples for UV spectra were prepared by coating 1 wt% AgBF_4 -CA solution in THF onto a $25 \times 3\text{ mm}$ quartz window. The coated quartz window was vacuum-dried for 2 h at room temperature. UV spectra were taken on a Scinco UV S-2100 spectrophotometer using the gas cell equipped with two $25 \times 3\text{ mm}$ quartz windows.

Separation measurements were performed with the dense membranes placed in a stainless steel separation module with an olefin/paraffin (50/50) mixture gas as described elsewhere.^[20] The flow rates of mixed gas and sweep gas (helium) were controlled by using mass flow controllers. The total feed pressure of mixed gas was set at 1.4 atm by back pressure regulators. Average fluxes of ethylene/ethane and of propylene/propane through the membranes at the molar ratio of $\text{AgBF}_4/\text{CA} = 4:1$ were 1.6×10^{-5} and $1.2 \times 10^{-5}\text{ cm}^3\text{ cm}^{-2}\text{ s}^{-1}\text{ cm Hg}^{-1}$, respectively at room temperature. The permeated gas was analyzed by using a Gaw-Mac gas chromatograph equipped with a TCD and unibead 2S 60/80 column.

Acknowledgement

The authors acknowledge the financial support from the Ministry of Science and Technology of Korea through the Creative Research Initiatives Program.

- [1] D. J. Safarik, R. B. Eldridge, *Ind. Eng. Chem. Res.* **1998**, *37*, 2571.
- [2] J. L. Humphrey, A. F. Seibet, *Chem. Eng.* **1992**, *99*, 86.
- [3] H. Jarvelin, J. R. Fair, *Ind. Eng. Chem. Res.* **1993**, *32*, 2201.
- [4] K. N. Trueblood, H. J. Lucas, *J. Am. Chem. Soc.* **1952**, *74*, 1338.
- [5] J.-S. Yang, G.-H. Hsiue, *J. Membr. Sci.* **1996**, *120*, 69.
- [6] a) D. Wang, K. Li, W. K. Teo, *J. Appl. Polym. Sci.* **1997**, *66*(5), 837; b) J.-S. Yang, G.-H. Hsiue, *J. Polym. Sci. Part B* **1997**, *35*(6), 909.
- [7] a) W. Featherstone, A. J. S. Sorrie, *J. Chem. Soc.* **1964**, 5235; b) C. A. Jull, R. S. Kominar, N. K. Mainland, H. W. Quinn, *Can. J. Chem.* **1966**, *44*, 2663; c) G. Bressan, R. Broggi, M. P. Lachi, A. L. Segre, *J. Organometal. Chem.* **1967**, *9*, 355.
- [8] H. S. Kim, J. H. Ryu, H. Kim, B. S. Ahn, Y. S. Kang, *Chem. Commun.* **2000**, 1261.
- [9] a) W. S. Ho, D. C. Dalrymple, *J. Membr. Sci.* **1994**, *91*, 13; b) J.-S. Yang, G.-H. Hsiue, *J. Membr. Sci.* **1996**, *111*, 27; c) T. Yamaguchi, C. Baertsch, C. A. Koval, R. D. Noble, C. N. Bowman, *J. Membr. Sci.* **1996**, *117*, 151.
- [10] S. Sunderrajan, B. D. Freeman, I. Pinnau, *In proceedings of the American Chemical Society Division of Polymeric Materials: Science and Engineering*, American Chemical Society, Washington DC, **1997**, *99*, pp. 267–268.
- [11] M. R. Antonio, D. T. Tsou, *Ind. Eng. Chem. Res.* **1993**, *32*, 273.
- [12] S. Sunderrajan, B. D. Freeman, C. K. Hall, *Ind. Eng. Chem. Res.* **1999**, *38*, 4051.
- [13] Y. H. Kim, J. H. Ryu, J. Y. Bae, Y. S. Kang, H. S. Kim, *Chem. Commun.* **2000**, 196.
- [14] The stretching frequency of the C–O single bond in the ether linkage of poly(ethylene oxide) (PEO) at 1113 cm⁻¹ shifts to a lower frequency of 1080 cm⁻¹ upon incorporation of AgSbF₆ (AgSbF₆/PEO = 1:1).
- [15] G. Beamson, D. Briggs, *High Resolution XPS of Organic Polymers—The Scienta ESCA300 Database*, Wiley, New York, **1992**, pp. 164–165.
- [16] C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, G. E. Muilenberg, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin Elmer Corporation, **1979**, p. 47.
- [17] a) C. D. M. Beverwijk, G. J. M. van der Kerk, A. J. Leusink, J. G. Noltes, *Organometal. Chem. Rev. A* **1970**, *5*, 215; b) W. O. Jones, *J. Chem. Soc.* **1954**, 1808.
- [18] H. W. Quinn, J. S. McIntyre, D. J. Peterson, *Can. J. Chem.* **1965**, *43*, 2896.
- [19] a) M. Wojciechowska, W. Gut, M. Grunwald-Wyspiansta, *Catal. Lett.* **1992**, *15*, 237; b) J. Haver, M. Wojciechowska, *J. Catal.* **1988**, *110*, 23.
- [20] S. Bai, S. Sridhar, A. A. Khan, *J. Membr. Sci.* **1998**, *147*, 131.

Received: July 26, 2000 [F2627]