Novel Application of Partially Positively Charged Silver Nanoparticles for Facilitated Transport in Olefin/Paraffin Separation Membranes

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The interactions between BF_4^- ions (from the ionic liquid $BMIM^+BF_4^-$) and the surfaces of silver nanoparticles caused the Ag surfaces to be partially positively charged, resulting in increased activity in silver−olefin complexation. The surface positive charge was confirmed by the increase in binding energy of the $d_{5/2}$ orbital of the silver nanoparticles from 368.26 to 369.12 eV as the silver content increased. The surface positive charge and consequent enhancement in olefin complexation ability were exploited through the use of silver nanoparticles as a new type of olefin carrier for facilitated transport. As a result, membranes containing $BMIM^+BF_4^-$/Ag nanoparticles demonstrated a mixed-gas selectivity of 17 for a 50/50 (vol %) propylene/propane mixture and showed stable performance for 100 h.

Introduction

Silver nanoparticles have attracted considerable interest because of their unique characteristics. They are electrically conductive, can function as catalysts, and exhibit a surface-enhanced Raman effect as well as an antibacterial effect.[1–3] For example, a low-temperature study of the reaction of elemental O_2 on the surface of Ag nanoparticles revealed that the adsorbed oxygen species at 80 K was predominantly O_2^-, indicating that electron transfer from the surface to O_2 occurred.[4] In addition, aqueous silver nanoclusters have been found to be capable of transferring electrons to suitable acceptors, such as *p*-benzoquinone.[5] *p*-Benzoquinone induced partial positive charges on the surfaces of silver nanoparticles, which amplified reversible interactions of the nanoparticles with olefins such as propylene.[6] Such interactions were utilized to develop carriers for facilitated olefin transport in membranes and contactors used for separation of olefin/paraffin mixtures.[6–17] It is important to note that an olefin carrier should interact or react with olefin molecules *reversibly*. When carriers are incorporated into a membrane, these reversible interactions or reactions result in carrier-mediated transport in addition to Fickian transport. The resulting combination of processes is known as facilitated transport.

It is now understood that the surface of a silver nanoparticle may have a partial positive charge if suitable electron acceptors are present. Consequently, the surface becomes more chemically active toward reversible interactions with olefin molecules. Therefore, the partially positively charged surface of a silver nanoparticle can be utilized as a new olefin carrier for facilitated olefin transport. In the present work, we report a new method for creating partial positive charges on the surfaces of silver nanoparticles that involves the use of ionic liquids (ILs). We demonstrate this method with a specific application of silver nanoparticles as olefin carriers for facilitated olefin transport.

Ionic liquids have many advantages compared with common organic solvents, including high polarity, ionic conductivity, thermal stability, and low vapor pressure.[18–31] Of

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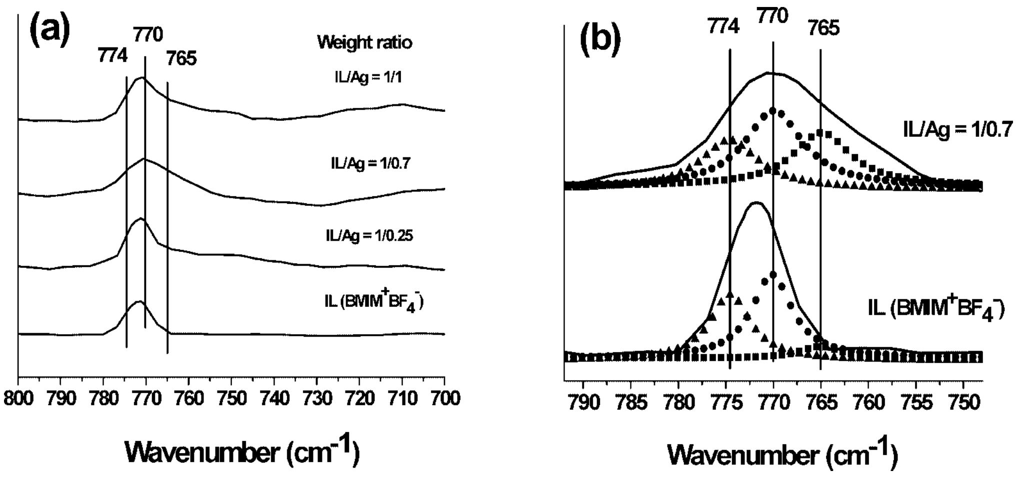

Figure 1. (a) FT-Raman spectra in the BF_4^- stretching region for $BMIM^+BF_4^-$/Ag nanocomposites having various weights of Ag per gram of $BMIM^+BF_4^-$. (b) Deconvoluted FT-Raman spectra for pure $BMIM^+BF_4^-$ (bottom) and the 1/0.7 (w/w) $BMIM^+BF_4^-$/Ag composite (top). Squares, circles, and triangles indicate free ions, ion pairs, and ion aggregates of BF_4^-, respectively.

particular interest here is the highly charged nature of ILs, which would be expected to polarize the surface of silver nanoparticles. In this study, the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIM^+BF_4^-$) was employed to tailor the surface properties of silver nanoparticles. Nanocomposites composed of silver nanoparticles dispersed in $BMIM^+BF_4^-$ were treated in order to induce partial positive charges on the surfaces of the silver particles. Application of these partially charged surfaces as new carriers for facilitated olefin transport in olefin/paraffin separation membranes was then explored.

Experimental Procedures

Materials. Silver nanopowder (70 nm, 99.5%) was purchased from Aldrich Chemical. The ionic liquid $BMIM^+BF_4^-$ was purchased from C-TRI. All chemicals were used as received without further purification.

Characterization. Raman spectra were collected for the $BMIM^+BF_4^-$/Ag composite films at room temperature using a PerkinElmer System 2000 NIR FT-Raman spectrometer with a resolution of 1 cm^{-1}. This spectrometer was equipped with a neodymium-doped yttrium−aluminum−garnet (Nd:YAG) laser operating at 1064 nm. Spectroscopic data were obtained using a pressure cell with CaF_2 windows. X-ray photoelectron spectroscopy (XPS) data were acquired using a PerkinElmer Physical Electronics PHI 5400 X-ray photoelectron spectrometer. This system was equipped with a Mg X-ray source operated at 300 W (15 kV, 20 mA). The carbon (C 1s) line at 285.0 eV was used as the reference in our determinations of the binding energies of the silver nanoparticles.

Separation Performance. After the Ag powder was incorporated into $BMIM^+BF_4^-$, the solution was stirred for 1 h until a homogeneous phase was observed. Separation membranes were prepared by coating $BMIM^+BF_4^-$/Ag nanocomposite dispersions onto a polyester microporous membrane support having an average pore size of 0.1 μm (Osmonics Inc.) using an RK Control Coater (model 101, RK Print Coat Instruments Ltd.). The weight of $BMIM^+BF_4^-$ in the IL/Ag nanocomposite membranes was fixed at 1 g, and the weight of Ag nanopowder in the membrane was varied. The coated membrane was directly equipped with a permeation cell because the ionic liquid did not have an organic solvent. The flow rates of mixed gas and sweep gas (helium) were controlled using mass-flow controllers. The all-gas flow rates represented by gas permeance were determined using a mass-flow meter in its steady state. Gas flow rates and gas permeances were measured using a mass flow meter at an upstream pressure of 40 psig and at atmospheric pressure downstream. Gas permeance was expressed in units of GPU, where 1 GPU = 1×10^{-6} cm^3 (STP) cm^{-2} s^{-1} $(cm\ Hg)^{-1}$. The effectiveness of the IL/Ag nanocomposite membranes in separating a mixed gas [50/50 (vol %) propylene/propane] was evaluated using a gas chromatograph (Hewlett-Packard G1530A) equipped with a TCD detector and a Unibead 2S 60/80 packed column.

Results and Discussion

Interactions between Ag nanoparticles and BF_4^- ions in $BMIM^+BF_4^-$/Ag nanocomposites were investigated using FT-Raman spectroscopy. Raman spectra in the region of the BF_4^- stretching bands are shown in Figure 1a for $BMIM^+BF_4^-$/Ag nanocomposites with increasing amounts of Ag. Note that the peaks for free ions, ion pairs, and higher-order ion aggregates of BF_4^- appear at 765, 770, and 774 cm^{-1}, respectively.[32] The intensity of the peak at 765 cm^{-1}, which corresponds to free BF_4^- anions, was found to increase upon the addition of the Ag nanoparticles, with a concomitant decrease in the intensity of the peak at 774 cm^{-1}, which corresponds to ion aggregates. The deconvoluted spectra in Figure 1b reveal that the fraction of free ions increased from 0.07 in pristine $BMIM^+BF_4^-$ to 0.29 in the 1/0.7 (w/w) $BMIM^+BF_4^-$/Ag nanocomposite. The fraction of ion aggregates, however, decreased from 0.41 in neat $BMIM^+BF_4^-$ to 0.28 in the 1/0.7 (w/w) $BMIM^+BF_4^-$/Ag nanocomposite. These results from the Raman spectra suggest the following interaction scheme (see Scheme 1): (1) pristine $BMIM^+BF_4^-$ exists mostly as ion pairs and ion aggregates, and (2) free BF_4^- ions are formed in the $BMIM^+BF_4^-$/Ag nanocomposites. In this scheme, the BF_4^-/Ag nanoparticle interaction

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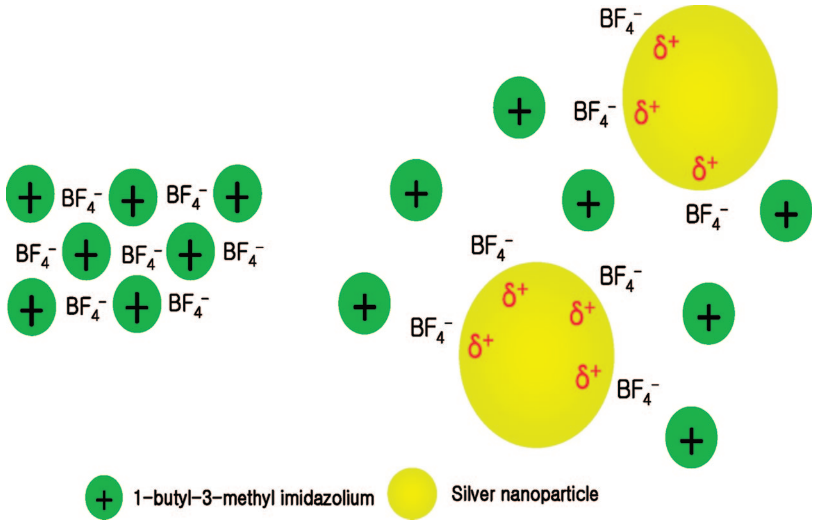
Scheme 1. Complexation between Silver Nanoparticles and $BMIM^+BF_4^-$



results in a reduction of the interaction between BF_4^- and $BMIM^+$ and, consequently, an increase in the free-anion concentration. It was therefore thought that the favored interactions between Ag and BF_4^- caused the surface of the Ag nanoparticle to have a slight positive polarization.

X-ray photoelectron spectroscopy was used to observe changes in the chemical environment around the silver nanoparticles in the $BMIM^+BF_4^-$/Ag nanocomposites and also to confirm the formation of partial positive charges on the surfaces of the nanoparticles. The binding energy of the $d_{5/2}$ orbital of silver nanoparticles in the 1/0.7 (w/w) $BMIM^+BF_4^-$/Ag nanocomposite increased gradually from 368.26 to 369.12 eV, as shown in Figure 2. This indicates that the binding energy of valence electrons in the silver atoms increased as a result the energetically favorable interactions between the silver atoms and BF_4^- and thus that the surfaces of the silver nanoparticles were partially positively charged. Therefore, it was expected that the surfaces of the silver nanoparticles would be active in forming complexes with olefin molecules.

Figure 3 shows pure-gas permeances of propylene and propane through the $BMIM^+BF_4^-$/Ag nanocomposite membrane. The presence of the silver nanoparticles in the membrane resulted in an increase in propylene permeance, but the propane permeance remained nearly constant. In particular, the propylene permeance initially increased markedly as the Ag/IL weight ratio increased, up to a ratio of 0.7. This increase indicates facilitated olefin transport due to the interactions of propylene with the partially positively charged surfaces of the silver nanoparticles. The maximum propylene permeance of 7.8 GPU was obtained at a weight ratio of 0.7. The ideal separation factor, defined as the ratio of propylene flux to propane flux, had a maximum value of 780, also at a weight ratio of 0.7. At weight ratios greater than 0.7, the propylene permeance decreased as the silver metal content increased, presumably as a result of aggregation of the silver nanoparticles, which results in the loss of carrier activity. As confirmed previously by XPS and ab initio calculations,[6] the carrier activity is a consequence of reversible interactions of propylene with silver nanoparticle

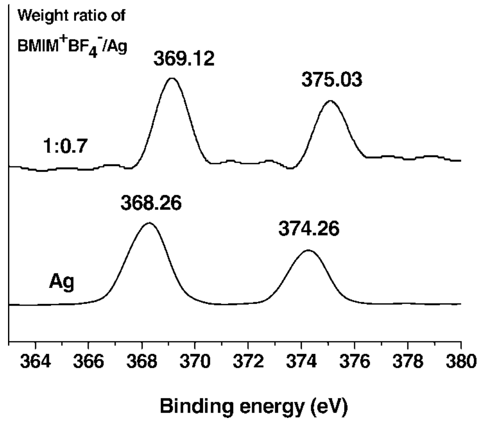


Figure 2. Change in binding energy of Ag with increasing Ag content in $BMIM^+BF_4^-$/Ag nanocomposites.

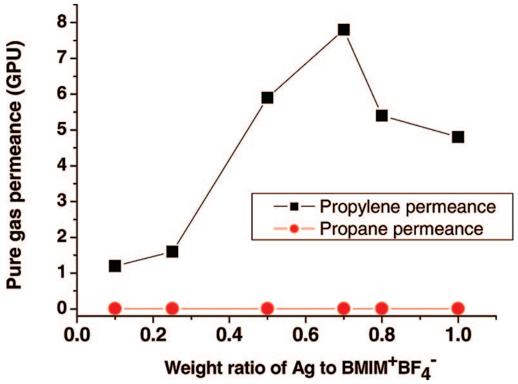


Figure 3. Permeances of propylene (black squares) and propane (red circles) in $BMIM^+BF_4^-$ membranes with varying Ag content.

Table 1. Propylene/Propane Mixed-Gas Permeances and Selectivities of Neat $BMIM^+BF_4^-$ and 1/0.7 (w/w) $BMIM^+BF_4^-$/Ag Composite Membranes

membrane	mixed-gas permeance (GPU)	mixed-gas selectivity
$BMIM^+BF_4^-$	0.5	0.9
1/0.7 (w/w) $BMIM^+BF_4^-$/Ag	2.7	17

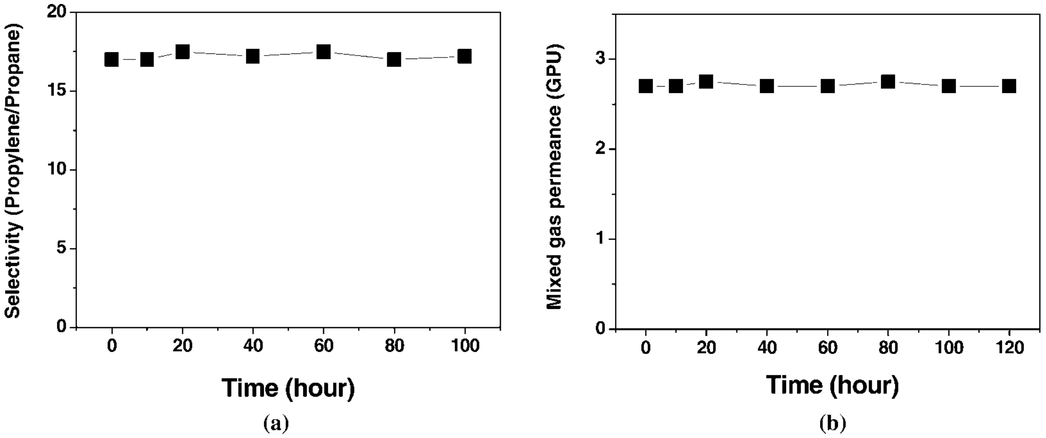


Figure 4. Separation performance: (a) propylene/propane selectivity and (b) mixed-gas permeance as a function of time.

surfaces bearing partial positive charge induced by the ionic liquid. Indeed, no separation performance for propylene/propane mixtures was achieved through dispersion of metallic silver nanoparticles in an inert polymer such as poly(ethylene-*co*-propylene), suggesting that the ionic liquid plays an important role in making the surface of the silver nanoparticles partially positively charged.[6]

The separation performance of the $BMIM^+BF_4^-$/Ag nanocomposite membranes with respect to propylene/propane mixtures was evaluated, and the results are summarized in Table 1. The mixed-gas selectivity for propylene over propane, defined as the ratio of the propylene concentration in the permeate to that in the feed, was only about 0.9 for the neat $BMIM^+BF_4^-$ membrane, which had a permeance of 0.5 GPU.[33] However, the addition of silver nanoparticles significantly improved the separation performance: the selectivity of the 1/0.7 (w/w) $BMIM^+BF_4^-$/Ag nanocomposite membrane was found to be 17, and the mixed-gas permeance was 2.7 GPU. The differences in mixed-gas selectivity and ideal separation factor may arise from the plasticization effect of propylene.[34,35] The improvement in both gas permeance and selectivity may be due to the facilitated olefin transport originating from the carrier activity of Ag nanoparticle surfaces bearing partial positive charge induced by the ionic liquid. The stability of the long-term separation performance of the $BMIM^+BF_4^-$/Ag nanocomposite membrane was also tested, and stable separation performance over 100 h of continuous operation was observed, as shown in Figure 4.

Conclusions

A new application of silver nanoparticles for use in membranes to separate propylene/propane mixtures was explored. The ionic liquid $BMIM^+BF_4^-$ was employed to make the surfaces of the silver nanoparticles active in propylene complexation, enabling them to serve as olefin carriers contributing to facilitated olefin transport. This enhanced complexation activity was mostly due to the formation of partial positive charge on the silver metal surface due to interactions with BF_4^-. The existence of a slight positive charge on the surfaces of the Ag nanoparticles was confirmed by XPS. As a result, the performance of the nanocomposite membranes in separating propylene/propane mixtures and the long-term membrane operational stability (observed to last up to 100 h) were markedly improved. For practical applications, potential side reactions of metallic silver with sulfur compounds and acetylene should be treated carefully.

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