

## Ionic Liquid/Silver Nanoparticles Composite Membrane for Separation of Olefin/Paraffin Mixtures

Sang Wook Kang<sup>1</sup>, Kookheon Char<sup>1</sup>, Dong Hoon Lee<sup>2</sup> and Yong Soo Kang<sup>2\*</sup>

<sup>1</sup> Seoul National University, School of Chemical and Biological  
Engineering, Seoul, South Korea

<sup>2</sup> Hanyang University, Department of Chemical Engineering, Seoul,  
South Korea

e-mail : kangys@hanyang.ac.kr

### Introduction

Silver nanoparticles have attracted considerable interest because of their unique characteristics. They are electrically conductive, they can function as catalysts, and they exhibit a surface enhanced Raman effect as well as an anti-bacterial effect. [1-3] For example, a low temperature study of the reaction of elemental O<sub>2</sub> on the surface of Ag nanoparticles revealed that the adsorbed oxygen species at 80 K was predominantly O<sub>2</sub><sup>-</sup>, indicating electron transfer from the surface to O<sub>2</sub>. [4] In addition, aqueous silver nanoclusters have been found to be capable of transferring electrons to suitable acceptors such as *p*-benzoquinone(*p*-BQ). [5] *p*-Benzoquinone induced partially positive charges on the surface of silver nanoparticles which amplified reversible interactions 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] It is important to note that an olefin carrier should interact or react with olefin molecules *reversibly*. When carriers are incorporated into a membrane the *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 silver nanoparticles may have partially positive charge depending on the presence of suitable electron acceptors. Consequently, the surface becomes more chemically active to reversible interaction with olefin molecules. Therefore, the partially positively charged surface of silver nanoparticles can be utilized as a new olefin carrier for facilitated olefin transport. In present, we report a new method to create a partial positive charge on the surface of silver nanoparticles by employing ionic liquids. We demonstrate this method with specific application as a new olefin carrier for facilitated olefin transport.

Ionic liquids (ILs) have many advantages as compared to common organic solvents

including high polarity, ionic conductivity, thermal stability and low vapor pressure. [7-9] Thus, the highly charged nature of ILs is expected to polarize the surface of silver nanoparticles. In this study, the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ( $\text{BMIM}^+\text{BF}_4^-$ ) was employed to tailor the surface properties of silver nanoparticles. Nanocomposites comprised of silver nanoparticles dispersed in  $\text{BMIM}^+\text{BF}_4^-$  were treated to induce partially positive charge on the surface of the silver particles. Application of these partially polarized surfaces as new carriers for facilitated olefin transport in olefin/paraffin separation membranes is explored.

### Experimental Section

**Materials.** Silver nanopowder (70 nm, 99.5%) was purchased from Aldrich Chemical. The ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ( $\text{BMIM}^+\text{BF}_4^-$ ) was purchased from C-TRI. All chemicals were used as received without further purification.

**Characterization.** Raman spectra were collected for the  $\text{BMIM}^+\text{BF}_4^-/\text{Ag}$  composite films at room temperature using a Perkin-Elmer System 2000 NIR FT-Raman with a resolution of  $1\text{ cm}^{-1}$ . This spectrometer is equipped with a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser operating at 1064 nm. The spectroscopic data were obtained using a pressure cell with  $\text{CaF}_2$  windows. X-ray Photoelectron Spectroscopy (XPS) data were acquired using a Perkin-Elmer 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.

**Separation performance.** After the Ag powder was incorporated into  $\text{BMIM}^+\text{BF}_4^-$ , the solution was stirred for 1 hour until homogeneous phase was observed. Separation membranes were prepared by coating  $\text{BMIM}^+\text{BF}_4^-/\text{Ag}$  nanocomposite dispersions onto a polyester microporous membrane support (Osmonics Inc., average pore size of  $0.1\text{ }\mu\text{m}$ ) using an RK Control Coater (Model 101, Control Coater RK Print-Coat instruments LTD, UK). The weight of  $\text{BMIM}^+\text{BF}_4^-$  in the IL/Ag nanocomposite membranes was fixed at 1g while the mass of Ag nanopowder in the membrane was varied. The coated membrane was directly equipped with permeation cell since the ionic liquid didn't have the 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 at the steady-state. Gas flow rates or gas permeances were measured with a mass flow meter at an upstream pressure of psig and atmospheric downstream pressure. The upstream pressure of psig is 40 psig. Gas permeance is expressed in units of GPU, where  $1\text{ GPU} = 1 \times 10^{-6}\text{ cm}^3(\text{STP})/(\text{cm}^2\text{ sec cmHg})$ . 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, MA) equipped with a TCD detector and a unibead 2S 60/80 packed column.

## Results and Discussion

### Separation Performance

Figure 1 shows pure gas permeances of propylene and propane through the BMIM<sup>+</sup>BF<sub>4</sub><sup>-</sup>/Ag nanocomposite membrane. The presence of the silver nanoparticles in BMIM<sup>+</sup>BF<sub>4</sub><sup>-</sup> resulted in the increase in propylene permeance while the propane permeance remained nearly constant. In particular, the propylene permeance increased initially markedly with the increasing weight ratio of the silver nanoparticles up to a ratio of 0.7. This increase indicates facilitated olefin transport due to the interactions of propylene with the partially positively charged surface of silver nanoparticles. The maximum propylene permeance was obtained up to 7.8 GPU at a weight ratio of 0.7. The ideal separation factor, defined as the ratio of propylene flux to that of propane, had a maximum value of 780, also at a weight ratio of 0.7. At weight ratios higher than 0.7, the propylene permeance decreased with the increase in silver metal content, presumably due to aggregation of the silver nanoparticles which results in the loss of carrier activity. As was confirmed previously by XPS and theoretical *ab initio* calculations, the carrier activity is a consequence of the reversible interactions of propylene with partially positively charged surface of the silver nanoparticles induced by the ionic liquid. However, no separation performance for propylene/propane mixtures was achieved through metallic silver nanoparticles dispersed 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.

### Conclusion

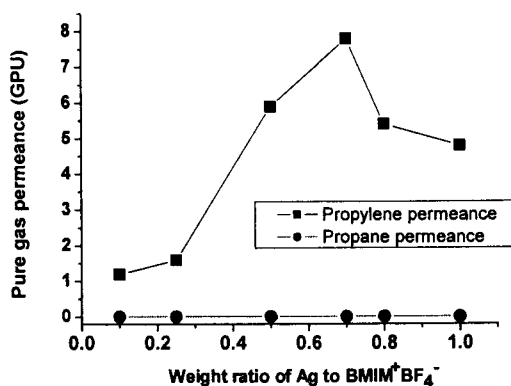
A new application of silver nanoparticles was explored for use in membranes to separate propylene/propane mixtures. The ionic liquid BMIM<sup>+</sup>BF<sub>4</sub><sup>-</sup> was employed to make the surface of the silver nanoparticles active in propylene complexation as a new olefin carrier, allowing for facilitated olefin transport. This is mostly due to the formation of a partial positive charge on the silver metal surface due to the interactions with BF<sub>4</sub><sup>-</sup>. The existence of a slightly positive charge on the surface of the Ag nanoparticles was confirmed by Raman spectroscopy. As a result, the performance of the nanocomposite membranes in separating propylene/propane mixtures and membrane long-term operational stability up to 100 hrs were markedly improved. For practical applications, potential side reactions of metallic silver with sulfur compounds and acetylene should be carefully treated.

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**Figure 1.** Permeances of propylene and propane: BMIM<sup>+</sup>BF<sub>4</sub><sup>-</sup> membrane with varying Ag content.