순수한 표면을 지닌 은 입자의 양극화와 촉진 수송 분리막에서의 올레핀 운반체로의 응용

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Polarization of Silver Nanoparticles having Pure Surface and Its Application as Olefin Carriers in Facilitated Transport Membranes

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1. Introduction

The separation of olefin/paraffin mixtures such as ethan/ethylene or propane/propylene is very important in petrochemical industry. At present, the olefin/paraffin separation process is carried out by cryogenic distillation process which requires high capital investment and huge operation cost[1]. In addition, the petroleum price is reaching almost $110/barrel. Therefore, the alternatives, energy saving technologies, has been demanded highly. Among them, facilitated olefin transport in solid state has been received tremendously because of its high selectivity and gas permenace[2]. The facilitated transport membranes comprise carriers which can interact with a *specific* solute *reversibly*, dissolved or dispersed in polymeric matrix. In facilitated transport membrane, carrier-mediated transport occurs in addition to general mass transport by Fickian diffusion, resulting in both selectivity and gas permenace.

In general silver cation is well known as specific interaction with olefin molecules, Π-complexation, and consequently can play a role as olefin carriers for facilitated olefin transport membranes[3]. Therefore, we prepared facilitated olefin transport membranes consisting of silver salt such as $AgNO_3$, $AgCF_3SO_3$ and $AgBF_4$ dissolved in poly (vinyl pyrrolidone) (PVP), poly (2-ethyl-2-oxazoline) (POZ) or poly (ethylene phthalate) (PEP) and membrane performance showed both high selectivity and gas permeance for separation of propylene/propane mixtures[2-3]. Recently, we were also found that partially charged surface of silver nanoparticles can react olefin molecules reversibly like silver cations. Partially positive charge on the surface of silver nanoparticles was derived by an electron acceptor such as *p*-benzoquinone[4].

Generally, commercial silver nanoparticles are surrounded by stabilizer such as capping agent or surfactants which might influence surface state of silver nanoparticles. In addition, electron acceptors could not easily approach to surface of silver nanoparticles. Thus, it is very important to utilize pure and clean silver nanopaticles without any contaminants on the surface of silver nanoparticles.

In this report, we utilzed silver nanoparticles prepared by plasma-ion method. Apart from commerical silver naoparticles, silver nanoparticles fabricated from plasma-ion method have pure and clean surface. We employed ionic liquid, $BMIM^+BF_4^-$, as dispersion medium as well as an electron acceptor to induce positive charge on the surface of silver nanoparticles. Through peculiar interaction between surface of silver nanoparticles and anions of ionic liquid, we explored its application as olefin carriers in facilitated transport membranes.

2. Experimental

Materials. Silver-sugar were purchased from P&I Co. 1-butyl-3-methyl imidazolium tetrafluoroborate was purchased from C-TRI. (Korea). All reagent were not used without further treatments.

Membrane Preparation and Membrane Performance Test. The silver nanoparticles/ionic liquid nanocomposite were fabricated by dissolving various weight ratio of silver-sugar into the ionic liquid. These complex solutions were dispersed onto a microporous polyester membrane support (GE Water & Process Technologies, average pore-size: 0.2 ㎛) by using a RK Control Coater (Model 101, Control Coater RK Print-Coat instruments LTD, UK). The experimental setup for membrane test is schematically shown in Figure 1.

3. Results and Discussion

The size of silver nanoparticle was measured by UV-vis spectroscopy. The maximum peak was appeared at 410 nm, To obtain concentration of silver nanoparticles, we measured ICP-AES spectrometer and result was 664.5 ppm. Interaction among silver nanoparticles, sugar and anion of ionic liquid were investigated using FT-IR. The free ether peak in surgar was not shifted in spite of deposition of silver nanoparticles. However, when Ag-sugar was dissolved into $BMIM^{+}BF_4^{-}$, the peak was migrated to 1284 cm^{-1}. This result is related with complexation between silver nanoparticles and ether oxygen. The membrane selectivity and gas permenace were shown at Table 1.

4. Conclusion

Partially positive charge on surface of silver nanoparticles could be induced by anion of ionic liquids. Partially charged silver nanoparticles in ionic liquid showed high separation performance of olefin/paraffin in spite of very low silver nanoparticle concentration. Interaction among silver nanoparticles, sugar, BF_4^{-} was confirmed by FT-IR

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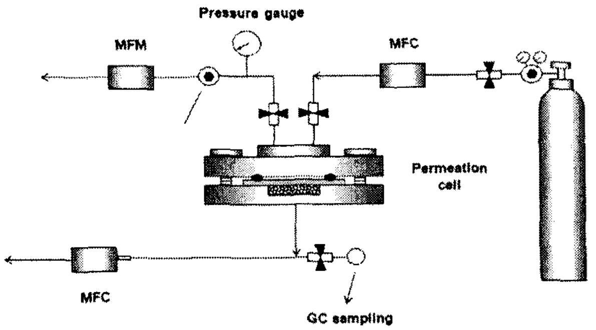

Figure 1. Scheme of experimental setup for membrane test

Membrane(weight ratio)	Selectivity	Gas Permeance(GPU)
$BMIM^+BF_4^-$/Ag-sugar (1/0.2)	14.37	2.57
$BMIM^+BF_4^-$/Ag-sugar (1/0.0.5)	12.87	3.14

Table 1. Propylene/Propane selectivity and mixed gas permenance of $BMIM^+BF_4^-$/Ag-sugar composite membrane