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Activated Ag ions and enhanced gas transport by incorporation of KIT-6 for facilitated olefin transport membranes

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ABSTRACT

Facilitated olefin transport membranes consisting of polymer/Ag salt/$Al(NO_3)_3$ have shown long-term stability, increasing the possibility of being used in practical applications. However, even though they show excellent separation performance over a long duration, the need for significant amounts of Ag salts acts as an obstacle, owing to relatively high cost of Ag. Thus, reduction in the amount of Ag salts in the membranes is required for practical applications in the industry. However, since the separation performance is directly related to the amount of Ag salts, it has been difficult to reduce the amount of Ag salts. In this study, we succeeded in preparing polymer/Ag salts/$Al(NO_3)_3$ membranes with 30% reduction in the amount of Ag salts by utilizing KIT-6, which is a porous material. When KIT-6 was incorporated into the polymer/Ag salts/$Al(NO_3)_3$ membrane, the separation performance for propylene/propane mixed gas increased with a propylene over propane selectivity of 20 and mixed gas permeance of 10 GPU. These values of selectivity and permeance amounted to 154% and 133% enhancement, respectively, compared to the performance without KIT-6. The enhanced separation performance is attributed to both the coordination of hydroxyl groups in KIT-6 with Ag ions and the porous properties of KIT-6, which leads to increased diffusivity. The coordination behavior of polymer/Ag salts/$Al(NO_3)_3$ containing KIT-6 was investigated by FT-IR, FT-Raman, and XPS analyses.

1. Introduction

The separation of olefin/paraffin mixtures such as ethylene/ethane and propylene/propane is a principal industrial process. Although cryogenic distillation has been used for such separation processes over the last few decades, this process demands a significant proportion of the total distillation energy and has to be operated at quite low temperatures and high pressures because of the similar sizes and properties of the olefin and paraffin components [1–2]. Therefore, comprehensive efforts to develop new olefin/paraffin separation processes have been pursued over the past years and several new technologies such as membrane and materials such as porous solid adsorbents have been developed [3–7]. Among the various separation technologies, facilitated transport membrane technologies involving olefin carriers such as Ag ions and copper nanoparticles have been of particular interest as a possible alternative to cryogenic distillation [8–9]. These membranes present various advantages including high energy efficiency, low operating costs [10]. Moreover, they contain the so-called olefin carriers, which are capable of reversibly interacting with specific olefin molecules, leading to high selectivity as well as permeance. When olefin/paraffin gas mixtures penetrate the facilitated-transport membranes, olefin molecules that interact with the carriers are more rapidly transported compared to the uncomplexed molecules by both the Fickian transport and carrier-mediated transport mechanisms [11–17]. Therefore, a large number of studies have been conducted on polymer electrolyte membranes utilizing Ag salts with low lattice energy such as $AgBF_4$, $AgClO_4$, and $AgCF_3SO_3$ [18]. These Ag salts are dissolved in polymer matrices such as poly(ethylene oxide) (PEO), poly(vinylpyrrolidone) (PVP), poly(2-ethyl-2-oxazoline) (POZ), poly(dimethyl siloxane) (PDMS), and poly(vinyl alcohol) (PVA) via coordination bonds. The use of polymer electrolyte membranes provides a very interesting strategy for improving the separation performance of olefin/paraffin mixtures [19–22]. However, it has been reported recently that facilitated transport membranes containing Ag ions have limited applications in practical processes, owing to their poor long-term stability. Ag ions, which are typically used as olefin carriers, are easily reduced to Ag nanoparticles, which results in deteriorated carrier activity [23]. Considering this, attempts have been made to improve the long-term stability of the olefin separation membranes by adding $Al(NO_3)_3$ to POZ/$AgBF_4$

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complex membranes. These membranes exhibited excellent long-term stability for more than 14 days, and the color of the membrane films remained white for more than three months, implying the stable state of the Ag ions [23]. Very recently, our group reported that when poly(ethylene oxide) (PEO), which is a permeable polymer, was used as the polymer matrix in facilitated transport membranes, the separation performance was enhanced. The selectivity and permeance in this system were measured to be about 10 and 20 GPU, respectively. In addition, the PEO/$AgBF_4$/Al$(NO_3)_3$ complex membranes showed significant stability of Ag ions for more than 10 days [24]. Such enhanced permeance of the membranes was attributed to the high permeability characteristics of PEO, which was a new polymer matrix. However, from the point of view of cost, Ag complexes still have limitations for practical applications. It is well known that the separation performance of the facilitated transport membranes is directly related to the Ag salt content.

In this study, facilitated olefin transport membranes containing reduced amount of Ag salt were prepared by utilizing KIT-6, a porous inorganic material, for enhancing the capacity of the olefin carrier. We investigated in detail the effect of KIT-6 on the previously reported PEO/$AgBF_4$/Al$(NO_3)_3$ membranes from the point of view of separation performance [24].

2. Experimental

2.1. Materials

Silver tetrafluoroborate ($AgBF_4$, 98%) was purchased from Tokyo Chemical Industry Co. Aluminum nitrate nonahydrate (Al$(NO_3)_3 \cdot 9H_2O$, 99%) was purchased from Aldrich Chemical Co. and PEO (Mw 9×10^5 g/mol) was purchased from ACROS Co. All the chemicals were used as-received.

2.2. Preparation of membranes

KIT-6 mesoporous silica material was prepared according to the method reported by Kleitz et al. [25]. Polymer electrolyte membranes containing PEO/$AgBF_4$/Al$(NO_3)_3$/KIT-6 active layer were prepared by the simple method of dissolving $AgBF_4$, Al$(NO_3)_3$, and KIT-6 in an aqueous solution containing 5 wt% PEO. The PEO/$AgBF_4$/Al$(NO_3)_3$ M ratio was fixed at 1:0.7:0.015 (2 g PEO/0.31 g $AgBF_4$/0.013 g Al$(NO_3)_3$) and KIT-6 silica (0.007 g) was incorporated into the membrane. The solution was then coated onto polysulfone microporous membrane supports (Toray Inc, Japan) using an RK Control Coater (Model K202, Control Coater RK Print-Coat Instruments Ltd, UK). The PEO/$AgBF_4$/Al$(NO_3)_3$/KIT-6 composite membrane that was prepared in this manner was completely dried in a vacuum oven for one day at room temperature. Scheme 1 shows a schematic illustration of the prepared membrane.

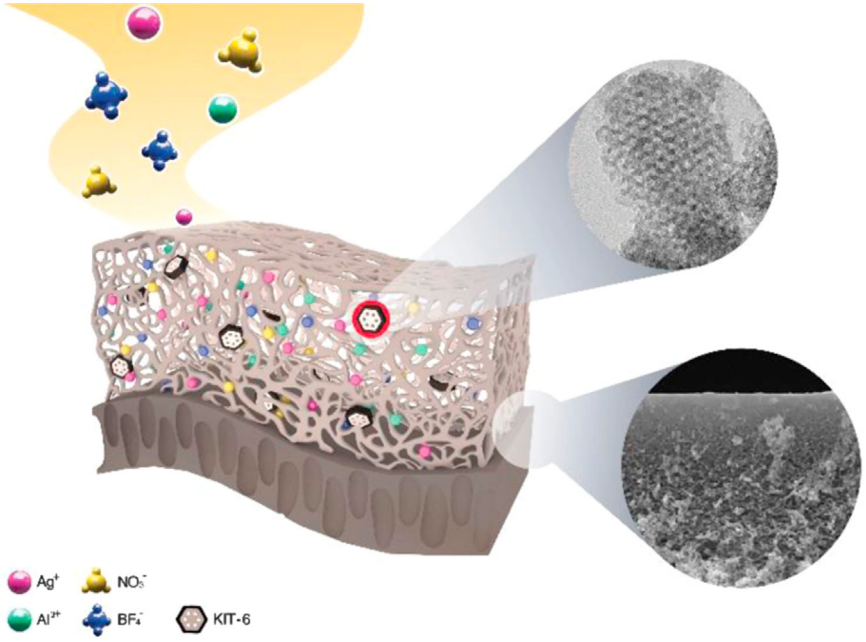
2.3. Gas separation experiments

The performance of the PEO/$AgBF_4$/Al$(NO_3)_3$/KIT-6 composite membrane in separating the mixed gas composed of propylene and propane (50:50 vol%) was investigated using gas chromatography (Young Lin 6500GC system). The flow rates of the mixed gas were controlled using a mass flow controller (MFC). Gas permeance values were measured with a bubble flow meter at various upstream pressures. The gas permeance is expressed in GPU, where 1 GPU $= 1 \times 10^{-6}$ cm^3 (STP)/(cm^2 s cmHg).

2.4. Characterization

The morphology of the KIT-6 porous silica was observed using transmission electron microscopy (TEM, FEI Cyrotecnai F20G2), operated at an accelerating voltage of 200 kV.

The thickness of the top selective layer was determined by scanning electron microscopy (SEM, JEOL JSM-5600LV). X-ray photoelectron spectroscopy (XPS) data were acquired using a K-alpha (Thermo Scientific Inc., U.K). This system was equipped with an Al Ka μ-focused monochromator (1486.6 eV) with variable spot size (30–400 μm in 5 μm steps). The carbon (C 1 s) line at 285.0 eV was used as a reference for determining the binding energies of the Ag ions. Weight loss was confirmed using thermogravimetric analysis (TGA, TGA Q50, TA Instrument) of the composite membranes under flowing N_2. IR measurements were performed on a Vertex 70 FT-IR spectrometer and 64 scans at a



Scheme 1. Schematic illustration of the PEO/$AgBF_4$/Al$(NO_3)_3$/KIT-6 composite membrane for facilitating olefin transport.