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Chemical stability of olefin carrier based on silver cations and metallic silver nanoparticles against the formation of silver acetylide for facilitated transport membranes



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ABSTRACT

Facilitated transport membranes containing silver cations and metallic Ag nanoparticles (NPs) as an olefin carrier have high olefin permeability and selectivity over propane. Silver ions are known to readily react with acetylene in aqueous conditions to produce silver acetylide, which can explosively decompose at temperatures over 160 °C, and therefore its formation should be avoided. In this regard, we examined whether silver acetylide from olefin carriers such as free silver cations and surface-activated Ag NPs by 7,7,8,8-tetracyanoquinodimethane (TCNQ) is formed upon exposure to acetylene, which is present as a minor impurity in many petrochemical feeds. The results showed that silver acetylide was not formed from the activated Ag NPs under the current experimental conditions, while free silver cations of polymer electrolyte produced silver acetylide by reacting with acetylene. Therefore, it is concluded that the activated Ag NPs showed superior chemical stability, compared to free silver cations.

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1. Introduction

The separation technology of olefin from propane among the petrochemical mixtures is an important process in the petrochemical industry. The large initial and operational expenses required for the separation of ethylene/ethane and propylene/propane mixtures via low-temperature distillation (−40 °C and 150 trays) have led to the increased demand for an energy-saving separation process [1–4].

In principle, membrane-based technology has many advantages over the conventional separation process; however, common polymeric membrane materials have not yet exhibited high-separation performance for olefin/paraffin mixtures such as propylene/propane and ethylene/ethane. During the last several years, facilitated transport membranes containing silver salts dissolved in a solid polymeric matrix have shown high separation performance for propylene/propane mixtures, including mixed-gas selectivity of propylene over propane over 50, and gas permeance over 5 gpu [5]. This high selectivity arises from carrier-mediated transport due to the reversible complexation of silver cations with olefins such as ethylene and propylene, but not with paraffins such as ethane and propane.

In particular, facilitated transport membranes of silver polymer electrolytes containing AgNO₃ and AgBF₄, dissolved in a polar

polymeric solvent such as poly(ethylene oxide) (PEO), poly(2-ethyl-2-oxazoline) (POZ) and poly(N-vinyl pyrrolidone) (PVP) showed an ideal separation factor of over 100 [6–8]. Typically, polymer electrolyte membranes of POZ or PVP with AgBF₄ or AgCF₃SO₃ have resulted in the very high selectivity as shown in Fig. 1(a) [9].

Recently, Ag NPs chemically activated by an electron acceptor such as *p*-benzoquinone (*p*-BQ), 1-methyl-3-butyl imidazolium tetrafluoroborate (BMIM⁺BF₄[−]) or 7,7,8,8-tetracyanoquinodimethane (TCNQ) have been demonstrated to function as effective olefin carriers, providing the high gas selectivity as shown in Fig. 1(b–d) [10–12]. In particular, the PVP/Ag NPs/TCNQ composite membrane showed the mixed gas selectivity up to 50 and has maintained its separation performance up to longer than 130 h as shown at Fig. 1(d) [12]. These results suggest the possibility of using facilitated transport membranes for the separation of olefin/paraffin mixtures in practical applications. However we care for the chemical stability of olefin carriers such as silver cations or metallic silver nanoparticles for facilitated transport membranes against acetylene. This is because acetylene, a minor impurity commonly present in most feed streams, may react with silver cations or metallic silver nanoparticles to form silver acetylide, which is known for thermal, mechanical, and chemical instability [13].

In this regard, the formation of silver acetylide is carefully examined to investigate the chemical stability of various olefin carriers including silver cations and surface-activated metallic Ag NPs against acetylene. The formation of silver acetylide was

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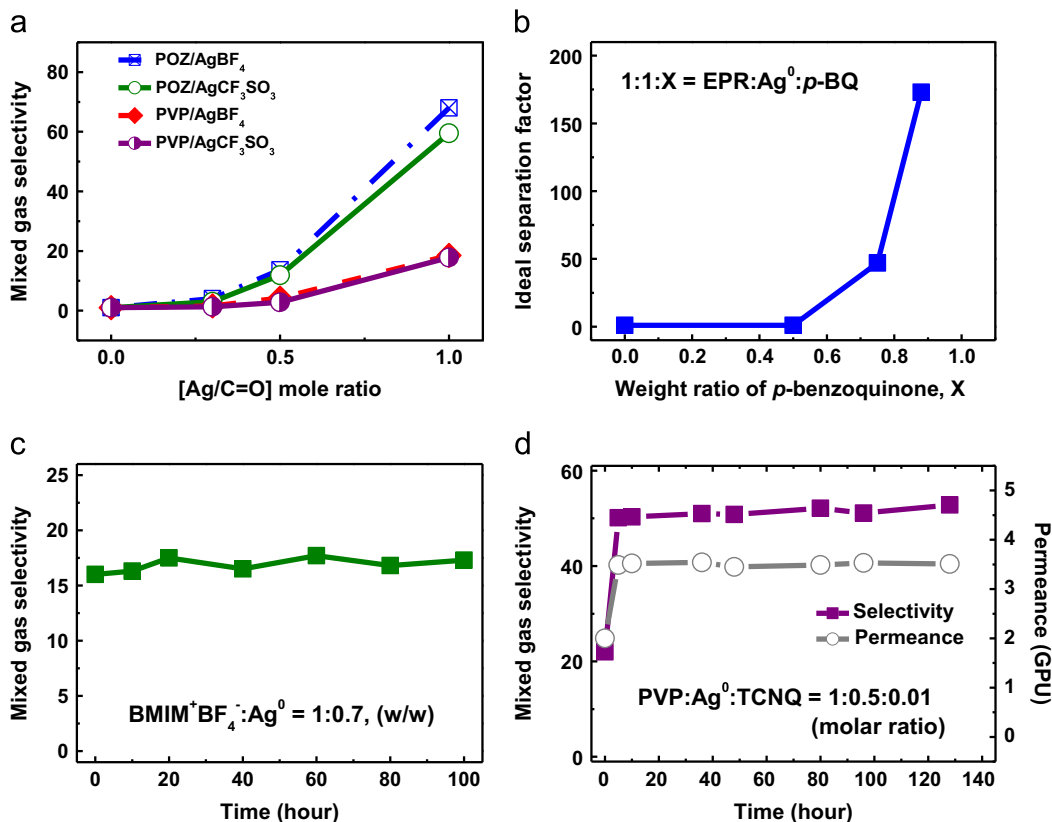


Fig. 1. The separation performance of membranes comprising (a) polymer/Ag salts [9], (b) poly(ethylene-co-propylene) (EPR)/Ag NPs/p-benzoquinone [10], (c) 1-methyl-3-butyl imidazolium tetrafluoroborate (BMIM⁺BF₄⁻)/Ag NPs (1/0.7 w/w) [11] and (d) PVP/Ag NPs/TCNQ (1/0.5/0.01, mole ratio) for separation of propylene/propane (50/50) mixtures [12].

confirmed *via* surface-enhanced Raman spectroscopy (SERS), thermogravimetric analysis (TGA) and transmission electron microscopy (TEM). In particular, SERS has been proven a powerful tool in the detection and study of metal acetylide and polyynes [14,15].

2. Experimental section

2.1. Synthesis of silver acetylide

Silver nitrate (AgNO₃) (purity 99%, Aldrich) (0.5 g) was dissolved in demineralized water, (7.2 ml) and 5.6 ml of 30% aqueous ammoniacal solution (Aldrich) was added to the solution. After stirring for 30 min, acetylene gas (purity > 99%) was bubbled into the solution [13]. The resulting gray precipitate was washed with demineralized water several times. CAUTION! *The gray precipitate is explosive and sensitive to heat and shock. It must be handled in a moistened condition or submersed in water.*

2.2. Synthesis of silver nanoparticles

2.2.1. Chemical method

Silver tetrafluoroborate (AgBF₄) (purity > 98.0%, TCI) (0.877 g) and poly(vinyl pyrrolidone) (PVP) (Mw. 40,000, Aldrich) (0.45 g) were dissolved in ethanol (purity > 95.0%, Samchun chemical) (20 ml). The mixture was stirred at 75 °C for 24 h. The color of the solution changed from invisible to dark brown [12]. The diameter and morphology of the Ag NPs formed *via* the chemical method were characterized with TEM.

2.2.2. Physical method

(EOWL, electrical explosion of wires in liquid method); A silver wire (0.2 mm in diameter) was installed in the cylinder filled with distilled water and ethanol. The capacitor was charged to 300 V, and the current flowed through the wire when the spark-gap switch was closed (Fig. S1 in Supplementary information). High-temperature plasma was generated by the electrical energy deposited in the wire, and was condensed by the basic fluids [16–18]. The Ag NPs 10–40 nm in diameter produced *via* the EOWL method were characterized *via* TEM.

2.3. Surface activation via TCNQ

0.01 M ratio of 7,7,8,8-tetracyanoquinodimethane (TCNQ) (Aldrich) was added to the chemically- and physically-synthesized Ag NPs dispersed in ethanol solution. The mixture solutions were stirred at 60 °C for 6 h. The solutions changed color to dark green.

2.4. Membrane fabrication

2.4.1. Polymer electrolyte membrane

Polymer electrolyte membrane was prepared by dissolving AgBF₄ in ethanol solution containing 20 wt% PVP (Mw. 40,000). The solution was then coated onto a commercial micro-porous polysulfone membrane support with an average surface pore size of 0.1 μm (Woongjin Chemical Co., Ltd.) using a RK Control coater (Model 101, Control Coater RK Print-Coat Instruments Ltd., UK). The membrane was dried under dark ambient condition for 24 h.

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