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1-Methyl-3-octylimidazolium tetrafluoroborate/AgO nanoparticles composite membranes for facilitated gas transport

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Abstract−AgO nanoparticles (NPs) were generated in ionic liquid 1-methyl-3-octylimidazolium tetrafluoroborate ($Moim^+BF_4^-$). The formation of Ag NPs was attributable to the favorable interaction between the surface of particles and counteranions of ionic liquid. The generated AgO nanoparticles in $Moim^+BF_4^-$ were confirmed by TEM, and the average size was 40 nm. Coordinative interactions of AgO NPs with $Moim^+BF_4^-$ were investigated by FT-Raman spectroscopy. The prepared $Moim^+BF_4^-$/Ag NPs composites were utilized for CO_2 separation membrane, and consequently, CO_2 separation performance for composite membranes was improved compared with neat $Moim^+BF_4^-$. The ideal selectivity for CO_2/N_2 was 23.4 with a CO_2 permeance of 18.7 GPU was observed, while the neat $Moim^+BF_4^-$ membrane showed a selectivity of 15.9 and a CO_2 permeance of 12.7 GPU.

Keywords: Membrane, Facilitated Transport, Composite, Ionic Liquid, AgO

INTRODUCTION

CO_2 emission in the atmosphere is mainly from coal-fired power plants. Especially, it causes global warming associated with climate change, and the topic that our world faces is arguably one of the most important environmental issues [1-3]. Furthermore, because the world's main sources of energy are coal, oil and natural gas, CO_2 capture and separation has been essential. Carbon dioxide is often observed as an impurity in natural gas, including methane. So it can lead to degradation of natural gas due to the presence of carbon dioxide [4-7]. Thre are several technologies for the separation of CO_2 from light gases, such as cryogenic separation, adsorption, absorption and membrane separation [8-10]. Among these, conventional absorption with amine-based has been the most promising and used to scrub the CO_2 from gas streams [11-13]. However, it has drawbacks such as high cost and energy inefficiency since it demands a high temperature to regenerate the adsorbed gas and experiences degradation of the solvent [14]. Therefore, microporous metal-organic frameworks (MOFs) including the high flux, well-defined pore sizes, thermal stability, their versatility in chemical compositions and crystal structures have been recently proposed as promising novel separator for CO_2 capture [15-17]. To increase the interaction strength between CO_2 molecules and the MOFs with metal or metal oxide corners connected by organic linkers, unsaturated metal centers can help increase the CO_2 capacity for MOFs. Besides high CO_2 capacities, many MOFs must have high CO_2/N_2 and CO_2/CH_4 selectivities which are essential for CO_2 separation from flue gas and natural gas. Several research groups, including Thallapally, Denayer, Carreon, Rosi, and others have developed a variety of MOFs [18-22]. However, because most MOFs have been designed with very large pore sizes or channels to achieve maximum loadings, it has a lack of selectivity, which is required for gas separation applications. The cost of bulk synthesis and the stability toward water vapor have been also challenging problems. As another alternative, ionic liquids have been of interest as reusable adsorbent [23,24]. Especially, it is known that the solubility of carbon dioxide in imidazolium-based room-temperature ionic liquids is relatively high. Furthermore, to increase the CO_2 solubility and gas separation performance in ionic liquids, a carrier that can be reversibly complexed with CO_2 has been introduced for facilitated CO_2 transport. For example, separation performance was reported for 1-butyl-3-methyl imidazolium tetrafluoroborate ($BMIM^+BF_4^-$)/copper nanoparticles (Cu NPs). [25] Imidazolium cations with an amine group and the surface of Cu NPs partially polarized by BF_4^- anions cause an increase in copper-CO_2 complexation, enhancing the solubility of CO_2 [25]. This improved separation performance resulted in a CO_2 permeance of 25 GPU ($1\ GPU=1\times10^{-6}\ cm^3\ (STP)/(cm^2\cdot s\cdot cm\ Hg)$) and the ideal selectivity of 11 for CO_2/N_2. Very recently, we reported that dissociated silver(II) oxide particles in ionic liquids ($BMIM^+BF_4^-$) have an strong affinity for CO_2 because of the oxide layer and imidazolium cations, resulting in silver(II) oxide as a carrier used to selectively remove CO_2 [26]. Accordingly in a series of studies, 1-methyl-3-octylimidazolium tetrafluoroborate ($Moim^+BF_4^-$) with more free ions than $BMIM^+BF_4^-$ was chosen for facilitated CO_2 transport. The longer the alkyl chain in the imidazolium cations was expected to stabilize the metal oxide nanoparticles for a long time. Also, if the length of the alkyl chain is short, such as $BMIM^+BF_4^-$, both cations and anions in ionic liquids could tend to be aggregated each other because of hydrogen bonding. Thus, $Moim^+BF_4^-$ originally known as more free ions was expected to show high CO_2 solubility, resulting in the improvement of CO_2 separation performance with AgO particles.

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EXPERIMENTAL SECTION

1. Materials

1-Methyl-3-octylimidazolium tetrafluoroborate (Moim$^+$BF$_4^-$) was purchased from C-tri Co., Ltd. AgO was purchased from Sigma-Aldrich Chemical Co. Ethyl alcohol (greater than 94.0%) was purchased from Daejung Chemicals & Metals. All initial solvents and materials were used as received.

2. Membrane Preparation

The membranes were prepared using Moim$^+$BF$_4^-$, silver(II) oxide and ethanol. First, silver(II) oxide was sonicated to disperse in ethanol for 5 min. Then, Moim$^+$BF$_4^-$ was added to the mixtures of silver(II) oxide and ethanol. The solution was heated at 60 °C for 24 h to evaporate the ethanol. The final solution was coated onto a polysulfone support (Toray Inc., Ltd., Tokyo, Japan) and then cast using a RK control coater (Model 101, Control Coater RK Print-Coat Instruments Ltd., UK). The best performance of Moim$^+$BF$_4^-$/silver(II) oxide was observed at 1/0.001 (weight ratio).

3. Gas Separation Performance

Gas permeance values were measured with a bubble flow meter at upstream 2 kgf·cm^{-2} and atmospheric downstream pressure. Gas permeance is expressed as units of GPU (1 GPU=1×10^{-6} cm^3 (STP)/(cm^2 s cmHg)). Selectivity was defined as ideal selectivity (CO$_2$ permeance/N$_2$ permeance).

4. Characterization

A sonifier (Branson 450, Branson Ultrasonics Corporation, Danbury CT, USA) with a standard tip was used. Thermogravimetric analysis (TGA) was obtained by using a Universal V4.5A TA. The TEM images were obtained with a JEOL JEM-3000 operating at 300 kV. Raman spectra were taken by a Horiba Jobin Yvon Labram Aramis with a diode laser beam at an excitation radiation wavelength of 785 nm. The spectral resolution was approximately 0.5 cm^{-1}. The frequency of the Raman lines was calibrated by using the c-Si wafer at 521 cm^{-1}.

RESULTS AND DISCUSSION

1. Thermal Analysis

Fig. 1 shows the thermal decomposition characteristics of the Moim$^+$BF$_4^-$/AgO composite. The small weight loss between 80-280 °C appeared due to the loss of the adsorbed water or the residual ethanol solvent. The major weight loss occurred in the temperature range of 280-465 °C. In the neat Moim$^+$BF$_4^-$ and Moim$^+$BF$_4^-$/AgO composite, thermal decomposition showed a similar thermal stability. Also, in the Moim$^+$BF$_4^-$/AgO composite, decomposition temperature range was smaller than neat Moim$^+$BF$_4^-$. The little enhancement of thermal stability in Moim$^+$BF$_4^-$/AgO was attributable to the dispersion of AgO particles into ionic liquids.

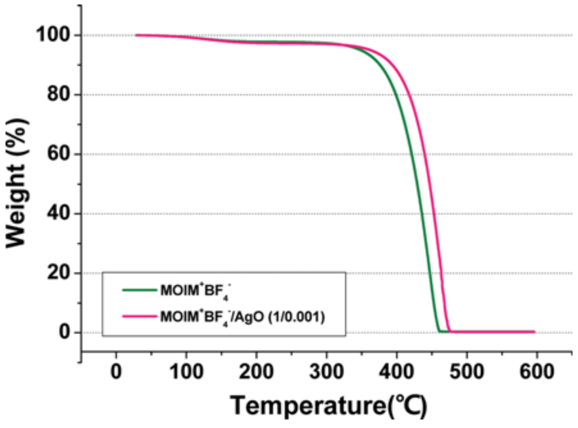

Fig. 1. TGA curves of Moim$^+$BF$_4^-$ and Moim$^+$BF$_4^-$/AgO composite.

2. FT-Raman Spectroscopy

Coordinative interactions of dissociated AgO particles with Moim$^+$BF$_4^-$ were investigated by FT-Raman spectroscopy. The Raman spectra in the regions of the BF$_4^-$ stretching bands for the Moim$^+$BF$_4^-$/AgO (1/0.001) are shown in Fig. 2. The BF$_4^-$ bands at 765, 770 and 774 cm^{-1} were assigned to free ions, ion pairs and ion aggregates, respectively [25]. As the silver oxide is finely dispersed in the ionic liquid, the distance of interaction between silver oxide and an ionic liquid is kept constant. Thus, main peak of free ions 765 cm^{-1} was unchanged and broadening of Raman line shapes only differed.

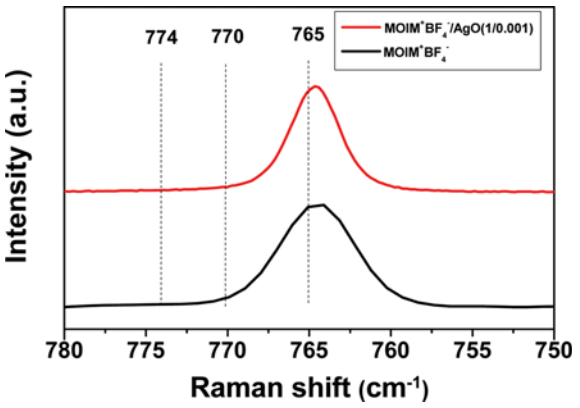

Fig. 2. FT-Raman spectra of neat Moim$^+$BF$_4^-$ and Moim$^+$BF$_4^-$/AgO in the BF$_4^-$ stretching region.

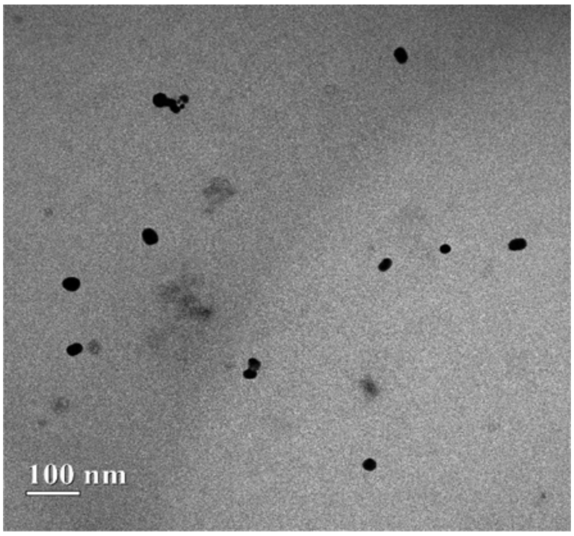

Fig. 3. Transmission electron micrograph of the dissociated AgO particles by the ionic liquid. Weight ratio of Moim$^+$BF$_4^-$/AgO =1/0.001.

Table 1. Permeance and selectivity of neat Moim$^+$BF$_4^-$ and Moim$^+$BF$_4^-$/AgO (1/0.001, weight ratio)

	Permeance (GPU)		Selectivity
	N_2	CO_2	CO_2/N_2
Neat Moim$^+$BF$_4^-$ [27]	1.8	20.3	11.8
Neat Moim$^+$BF$_4^-$	0.8	12.7	15.9
Moim$^+$BF$_4^-$/AgO	0.8	18.7	23.4

*Finger-like shaped polysulfone support (Woongjin Chemical Co., Ltd.) was used in our previous report [27]. However in this study, the sponge-like shaped polysulfone support (Toray Chemical Korea Inc.) was used. Compared to previous finger-like support, the gas permeation performance showed relatively low value because of conformational differences.

3. AgO Particles in Moim$^+$BF$_4^-$

The TEM image of ionic liquids composite with AgO nanoparticles is shown as Fig. 3, revealing a particle size of approximately 40±10 nm. The TEM images show AgO aggregates were very well dissociated as nanoparticles in ionic liquids Moim$^+$BF$_4^-$.

4. Separation Performance

The dissociated AgO particles in the ionic liquid Moim$^+$BF$_4^-$ were applied to CO_2 separation. The separation performance for CO_2 permeance and selectivity (CO_2/N_2) is shown in Table 1. Neat Moim$^+$BF$_4^-$ and Moim$^+$BF$_4^-$/AgO composite membranes were investigated. It is known to exist as more free imidazolium in the ionic liquids Moim$^+$BF$_4^-$ unlike BMIM$^+$BF$_4^-$. Thus, it was expected that the generated AgO particles could cause the CO_2 solubility to be enhanced by the increased oxide layer. Consequently, CO_2 separation performance for Moim$^+$BF$_4^-$/AgO composite membranes was improved compared with neat Moim$^+$BF$_4^-$ as shown in Table 1. The ideal selectivity for CO_2/N_2 was 23.4 with a CO_2 permeance of 18.7 GPU was observed, while the neat Moim$^+$BF$_4^-$ membrane showed a selectivity of 15.9 and a CO_2 permeance of 12.7 GPU.

CONCLUSION

We have succeeded in stabilizing AgO nanoparticles by employing an ionic liquid Moim$^+$BF$_4^-$. Furthermore, because an ionic liquid Moim$^+$BF$_4^-$ has a longer alkyl chain in the imidazolium cations, the ionic liquid Moim$^+$BF$_4^-$/AgO composite membrane could show high facilitated transport between more free ions Moim$^+$BF$_4^-$ and CO_2, improving CO_2 separation performance with the effect of AgO nanoparticles capable of increasing CO_2 solubility. As a result, the ionic liquid Moim$^+$BF$_4^-$/AgO composite membrane showed increased CO_2 separation performance in both CO_2/N_2 selectivity and CO_2 permeance by both facilitated CO_2 transport and enhanced CO_2 solubility. Moreover, it was expected that such a facile nanoparticles synthetic strategy could be further applied into specific applications.

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