



Preparation and characterization of Ag⁺ ion-exchanged zeolite-Matrimid[®]5218 mixed matrix membrane for CO₂/CH₄ separation

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ABSTRACT

In this work, the zeolite-Y was ion-exchanged by introducing silver cations into the framework of micro-sized nano-porous sodium zeolite-Y using a liquid-phase ion exchanged method. The Ag⁺ ion-exchanged zeolite, was then embedded into the Matrimid[®]5218 matrix to form novel mixed matrix membranes (MMMs). The particles and MMMs were characterized by ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS), N₂ adsorption-desorption isotherm, X-ray diffraction (XRD), Fourier transform infrared (FTIR) and scanning electron microscopy (SEM). Furthermore, the effects of filler content (0–20 wt%) on pure and mixed gas experiments, feed pressure (2–20 bar) and operating temperature (35–75 °C) on CO₂/CH₄ transport properties of Matrimid/AgY MMMs were considered. Characterization results confirmed an appropriate ion-exchange treatment of the zeolites. The SEM results confirmed the superior interfacial adhesion between polymer and zeolites, particularly in the case of Matrimid/AgY membranes. This is due to the proper silverous zeolite/Matrimid functional groups' interactions. The gas permeation results showed that the CO₂ permeability increased about 123%, from 8.34 Barrer for pure Matrimid to 18.62 Barrer for Matrimid/AgY (15 wt%). The CO₂/CH₄ selectivity was improved about 66%, from 36.3 for Matrimid to 60.1 for Matrimid/AgY (15 wt%). The privileged gas separation performance of Matrimid/AgY (15 wt%) was the result of a combined effect of facilitated transport mechanism of Ag⁺ ions as well as the intrinsic surface diffusion mechanism of Y-type zeolite. In order to survey the possibility of using the developed MMMs in industry, the CO₂-induced plasticization effect and mixed gas experiment were accomplished. It was deduced that the fabricated MMMs could maintain the superior performance in actual operating conditions.

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1. Introduction

Zeolites have attracted much attention because they have a wide range of structure, various chemical composition and physicochemical properties [1,2]. Zeolites are widely used as catalysts, adsorbents and ion-exchange systems [1,3,4]. The molecular transport through the zeolites experiences three steps: first is the molecular adsorbing in zeolite pores, second is the diffusing within the pore surfaces, and third is desorbing from zeolite [3,5]. Typically, gas molecules are physically adsorbed in zeolites through a nonactivated, exothermic and reversible process [2,3].

It must be noted that penetrants are adsorbed into zeolite pores due to the intermolecular attractive forces. The heat of adsorption is superior for gas molecules with larger dipole moments [3,6]. Thus, the strong interaction between quadrupole moments of CO₂ molecules with oxygen atom of hydroxyl group of zeolites causes more CO₂ adsorption in comparison with lighter gases such as CH₄, N₂ and H₂. In other words, CO₂ has superior heat of adsorption on FAU, LTA, CHA, and MOR zeolites in various forms [3,4].

Currently, zeolites are extensively incorporated into various polymer matrixes in order to prepare a new type of membranes known as mixed matrix membranes (MMMs) [1]. The pioneering work on preparing zeolitic MMMs for gas separation was referred

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to the work of Paul and Kemp [7], which incorporated the 5A zeolite into polydimethylsiloxane (PDMS) matrix. They surveyed the delayed diffusion time-lag effect on CO₂/CH₄ gas permeation properties. Their results revealed that although the diffusion time lag was enhanced, the steady state permeation rate was slightly affected. Ahmad et al. [8] prepared Matrimid®9725/zeolite 4A MMMs for CO₂/N₂ separation. The morphological observations revealed that a homogeneous pattern achieved at 20 wt% loading. Furthermore, the gas permeation results indicated that CO₂ permeability increased when the filler loading increased. The Matrimid/zeolite 4A (30 wt%) membrane, presented the CO₂ permeability and CO₂/N₂ selectivity of 48.34 Barrer and 23.35, respectively. Dorosti et al. [9], embedded the ZSM-5 zeolite (0–20 wt% filler loadings) into polysulfone/Matrimid®5218 blend membranes with different polymers ratio (from 100% PSF, 70/30 (PSF/PI), 50/50, 30/70 and 100% PI). Their results exhibited that the PSF/PI (50/50) membrane with 10 wt% filler loading was the best-yield MMM with the acceptable permselectivity. In another work, Huang et al. [10] prepared MMMs composed of 0–30 wt% β -zeolite embedded in Matrimid®5218 for CO₂/CH₄ separation. Their results indicated that with 10 and 30 wt% filler loadings, CO₂ permeability was respectively enhanced about 45% and 152%. Although, the CO₂/CH₄ selectivity at 10 wt% filler loading was unchanged, while the CO₂/CH₄ selectivity at 30 wt% filler loading was reduced considerably (about 45%). They also claimed that these behaviors were attributed to presence of β -zeolite and its uniform distribution in polymer matrix. Yong et al. [11] incorporated various types of zeolites (4A and 13X) into Matrimid®5218 matrix using 2,4,6-triaminopyrimidine (TAP) to form interfacial void-free zeolite filled MMMs. The results showed that the PI/13X/TAP membrane had the higher CO₂ permeability with a little expense in CO₂/CH₄ selectivity, compared with the PI/TAP membrane. On the other hand, an opposite behavior was achieved for PI/4A/TAP MMM. For PI/13X (43 wt%)/TAP (21 wt%) MMM, the CO₂ permeability increased from 0.194 to 0.640 Barrer and the CO₂/CH₄ selectivity enhanced from 84 to 133, respectively, in comparison with PI/TAP membrane. Moreover, for PI/zeolite4A (43 wt%)/TAP (21 wt%) MMM, the CO₂ permeability decreased from 0.194 to 0.185 Barrer, while the CO₂/CH₄ selectivity increased from 84 to 617. They ascribed the results to the higher pore sizes of zeolite 13X (7.4 Å) compared with zeolite 4A (3.8 Å), which this provides zeolite 13X with an easier passage for the gas molecules.

The filler size, pore size and loading adjustment are the three important factors, which have crucial impacts on performance of MMMs. The permeability of the MMM increases with increasing particle size/pore size. In addition, at higher filler loadings, the permeability enhancement is much more evident with increase in particle size [1,2]. Hence, it can be said that using a lower filler loadings of larger pore-size zeolites for preparing MMMs would significantly compensate the negative effects of polymer chain rigidification and partial pore blockage, which usually, occurred at higher filler loadings of smaller zeolites. Although, facilitating the gas molecule transport through the larger pores of zeolites can be coinciding with the selectivity decrease [11–14].

In recent years, many researches have been accomplished on ion-exchange treatment of zeolites with mono- or di-positive ions, such as Ag⁺, Cu⁺ and Co²⁺ without creating any alteration of the crystalline network, to change the physical and chemical adsorption properties of penetrants in the zeolites [15]. Hasegawa et al. [16] synthesized several FAU-type zeolite membranes with various Si/Al ratios and investigated the CO₂, CH₄ and N₂ permeances through the membranes. Their results indicated that the gas permeances were in the order of CO₂ > N₂ > CH₄. They also showed that the strong adsorption rate of CO₂ into the NaY zeolite, in comparison with CH₄ and N₂, as well as the smaller kinetic diame-

ter of CO₂ (3.3 Å) in comparison with CH₄ (3.8 Å) and N₂ (3.64 Å), were the two key factors which influenced the results, dramatically. Furthermore, their results revealed that the gas permeation rates are associated with zeolite pore size, even though the pores are larger than the gas molecule sizes. In similar work, Kusakabe et al. [17] synthesized a Y-type zeolite membrane on a porous α -alumina support for CO₂/N₂ separation and reported that the CO₂ permeance was in the order of 10⁻⁷ mol/m²/s/Pa. Besides, they surveyed the CO₂ separation properties of ion-exchanged NaY zeolite membranes with alkali (K, Rb, Cs) and alkali-earth (Mg, Ca, Ba) cations. Their results showed that although the CO₂ permeances did not experience the considerable changes, the selectivities of ion-exchanged membranes were higher than that of NaY-type zeolite membrane [16,18–20]. Qi et al. [21] fabricated polydimethylsiloxane (PDMS) based MMMs by incorporating Ag⁺ ion-exchanged Y-type zeolite for desulfurization of gasoline. Their results indicated that the ion-exchanged zeolite had a superior total flux with almost no decrease in the selectivity, in comparison with the neat NaY zeolite. They also claimed that these trends were the result of the continuous complexation/decomplexation reaction between Ag⁺ ions and organo-sulfurs and accordingly varying the local concentration. In another works, Lin et al. [22] prepared novel MMMs composed of polyimide (PI), NaY zeolites, and ion-exchanged AgY and CeY zeolites for desulfurization of transportation fuels. Their results indicated that MMMs with 40 wt% of filler content possess superior physical properties. Moreover, the adsorption capacity for AgY/PI and CeY/PI MMMs were greater than that of NaY/PI MMM. The trend of adsorption/desorption behavior of MMMs with different functional zeolites, may be attributed to their various binding force/binding mode with sulfur compounds. Li et al. [23] fabricated novel MMMs by embedding 0–50 wt% of pure/Ag⁺ ion-exchanged NaA zeolite into polyethersulfone (PES) matrix. The SEM results demonstrated that the filler distribution and filler/polymer interface was similar before and after the ion-exchange treatment. In other words, it is possible to rule out the change of interfacial properties, as an important factor, which affects the gas permeabilities, after the Ag⁺ ion-exchange treatment. Their gas permeation results revealed that with increase in filler loadings, CO₂ permeability decreased, while the CO₂/CH₄ selectivity increased. This was attributed to the polymer chain rigidification and partial pore blockage of the zeolites. Indeed, the partial pore blockage of modified zeolite was predictable, since the AgA pore size is smaller than that of NaA (3.8 Å), because the Ag⁺ ionic radius is larger than Na⁺ ionic radius (1.15 Å > 1.02 Å). On the other hand, the CO₂ permeability of AgA zeolite/PES is higher than that of NaA zeolite/PES MMMs, while the opposite behavior achieved for CH₄ permeability. This trend was ascribed to the reversible reaction between silver ion and CO₂ molecules. In other words, a reversible reaction occurs between the transient metal ions and O₂, CO, CO₂ and unsaturated hydrocarbon molecules to form π -complexation bonds [24–27].

In this study, we prepared a new silver ion-exchange zeolite by introducing Ag⁺ into the framework of NaY zeolite through a cation exchange reaction. In order to enjoy the benefits of combination the facilitated transport mechanism of Ag⁺ ion as well as the intrinsic surface diffusion mechanism of Y-type zeolite, the ion-exchanged zeolites were incorporated into the glassy polyimide, Matrimid®5218, for CO₂/CH₄ separation. The particles and MMMs were characterized by UV-vis DRS, BET, XRD, FTIR and SEM. Furthermore, the effects of filler content (0–20 wt%) on pure and mixed gas experiments, feed pressure (2–20 bar) and operating temperature (35–75 °C) on CO₂/CH₄ transport properties of Matrimid/AgY membranes were investigated. Finally, a comparison was performed between the performances of pure and ion-exchanged zeolite filled MMMs.

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