MECHANISM OF PREFERENTIAL CO₂ PERMEATION OF AMINE-CONTAINING POLYMERIC MEMBRANE

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Introduction

H₂ is industrially produced by steam reforming and following water-gas shift reaction of light hydrocarbons in Japan. This process emits CO₂ but can be carbon-free, if CO₂ in the off-gas is separated over H₂ after H₂ purification by pressure-swing adsorption. We have developed polymeric membranes containing various amines including poly(amidoamine)s (PAMAMs) for preferential CO₂ permeation over H₂ [1-4]. The PAMAM immobilized membranes show excellent CO₂ separation properties in the separation. However, the CO₂ permeability of the polymeric membranes should be elevated for implementation of the membrane, for example, from 5 (current) to 30 GPU in CO₂ capture at on-site H₂ station. Recently, we found that alkanolamines, such as (2-aminoethyl)ethanolamine (AEEA), exhibit higher CO₂ separation properties than PAMAM in the same polymeric matrices. Hydroxyl group adjacent to amino group forms hydrogen bonding to CO₂ in the interaction between amine and CO₂, which reduces the interaction and/or dissociation energy to facilitate CO₂ diffusion in the membrane. In this presentation, immobilization of various alkanolamines in poly(vinyl alcohol) (PVA) matrix was studied to formulate polymeric membranes, and the CO₂ separation performance was examined. The mechanism of preferential CO₂ permeation of the amine-containing PVA membranes will be discussed.

Experimental

PVA aqueous solution was blended with alkanolamines by various weight ratios. The resulting solution was cast onto a plastic dish. A self-standing and transparent membrane was obtained after evaporating the solvent. The membrane morphology was characterized by XRD, SAXS, SEM, NMR, and DSC. The CO₂ separation over H₂ was performed under various operation conditions, and the CO₂ separation performance was determined by gas chromatography.

Result and discussion

Figure 1 demonstrates an effect of relative humidity on CO₂ separation properties of AEEA-containing PVA membranes. The CO₂ permeance was improved by elevating relative humidity and reached 13 GPU with 15 in separation factor when the AEEA content was 50 wt%. A part of CO₂ turns to bicarbonate ion in the presence of humidity determined by ¹³C NMR, which would be the major migrating species through the membrane. Effective transformation of bicarbonate ion is a key for the CO₂ permeation. Poly(ethylene glycol) (PEG) has been used to immobilized various amines, and the resulting polymeric membranes are translucent due to phase separation on a couple of microns scale. The membranes lose the CO₂ separation properties by reducing the thickness caused by leakage of amines from the PEG matrix [3]. On the other hand, PVA shows better compatibility to the amines, thus CO₂ permeability could be further enhanced by reducing the membrane thickness.

References