論 文 の 要 旨

題 目 Development of metal-coordinated aminosilica networks for highly permeable and selective membrane separation

(金属配位アミノシリカ膜の開発と高透過性・高選択性分離)

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Membrane processes and technology are considered energy efficient for the separation of gas and liquid systems. Over the past decades, organosilica membranes have attracted high attention due to high thermal and chemical stability with no swelling, high flux, high separation performance, and adjustable pore sizes. The primary goal of this dissertation was to fabricate and optimize a hybrid thin film of metal-coordinated aminosilica membranes based on sol-gel processing followed by coordination reaction and investigate their performance in the separation of gas and liquid mixtures via pervaporation. The best performance of metal coordinated-organosilica based membranes was achieved by optimizing four parameters including the affinity of transition metal as Lewis-acid molecules, the affinity of the ligand as Lewis-base molecules, the mole ratio of metal/amine groups, and the existence of metal in a different phase to facilitate the transport of permeating molecules. At each step of optimization, the fixed variable was selected and applied, and the investigation proceeded to the next step.

In the first stage of modification of metal coordinated-organosilica membranes, the effect of metal doping was evaluated using a single gas permeation system. Values for surface area and pore volume of the metal-doped bis[3-(trimethoxysilyl) propyl] amine (BTPA) at metal/amine mole ratio of 0.25 mol mol^{-1} were both expanded by increasing metal coordination affinity on the order of Ni-BTPA (214 m^2 g^{-1}) > Cu-BTPA (75.7 m^2 g^{-1}) > Ag-BTPA (20.1 m^2 g^{-1}) > BTPA (2.36 m^2 g^{-1}). In line with material characterization, gas permeation was also increased in the same order, which corresponds to a higher affinity for metal coordination. Ni-BTPA membrane with the highest affinity for coordination achieved high levels of both permeance of N_2 and N_2/SF_6 at 3.75×10^{-7} mol m^{-2} s^{-1} Pa^{-1} and 1,900, respectively. In the second stage, the optimization of coordination was examined by employing the incorporation of different amounts of nickel dopant (mole ratio of nickel/amine) into BTPA structure that ranged from 0.125 to 0.50

mol mol^{-1}. Higher nickel content increased the rigidity and resulted in a porous membrane structure with a high specific surface area that beneficially showed high performance for the pervaporation organic mixture of methanol/toluene on the order of Ni-BTPA 0.50 > Ni-BTPA 0.25 > Ni-BTPA 0.125 > BTPA. Ni-BTPA 0.50 has been found to exhibit superior performance with a high level of flux at 2.8 kg m^{-2} h^{-1} and a separation factor higher than 900 in a 10 wt% methanol feed solution at 50 °C. In that work, Ni-BTPA 0.50 shows an attractive performance due to the balance between the formation of microporosity that was induced by nickel-amine coordination and the excessive amount of nickel ions that facilitated the fast transport of methanol while restraining the transport of toluene.

To prove the concept of metal-coordinated aminosilica membranes, in the third investigation, the affinity of amine-functionalized organosilica as a ligand was evaluated via different types of precursors. Nickel doping restructured the aminosilica network via a coordination bond, which then increased both the rigidity of the organic chain and the surface area or resultant material on the order of nickel doped bis [3-(trimethoxysilyl) propyl] amine (Ni-BTPA) > nickel-doped 3-aminopropyl triethoxy silane (Ni-APTES) > nickel-doped trimethoxy[3-(methyl amino) propyl silane (Ni-MAPTS). The prepared hybrid nickel-composite membranes were used for the pervaporation of various types of organic mixtures with methanol 10 wt% at 50 °C in the feed solution. Ni-BTPA with the strongest affinity for coordination recorded the highest separation performance for the flux that reached as high as 1.42 kg m^{-2} h^{-1} with an optimum separation factor for methanol/toluene of 5,000. The enhancement for both membrane flux and the separation factor verifies the balance between higher levels of interconnected micropores from nickel-amine coordination and the existence of uncoordinated nickel acting as active sites for the diffusion of methanol.

Based on the previous investigation, two phases of metal can facilitate a specific transport of components while the coordinated network generates a high flux of membrane. In the fourth evaluation, we examine the fabrication of silver-doped BTPA for facilitating the transport of H_2. The evolution of silver in two phases as silver ions and nanoparticles successfully modify the membrane structure from dense into microporous, and silver-modified aminosilica membranes showed hydrogen permeance of 1.46 10^{-6} mol m^{-2} s^{-1} Pa^{-1} with excellent H_2/C_3H_8 selectivity of 1,500. Based on this result, it is

evident that the proposed modification via the two-phase structural evolution of silver reorganized the organosilica framework and improve the separation performance of the membranes.