論　文　の　要　旨

題　目　　Development of functionalized organosilica membranes with high NH_3 permselectivity and their application to green NH_3 production

（NH_3 選択透過性を有するオルガノシリカ膜の開発とグリーン NH_3 製造への応用）

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Ammonia (NH_3) plays a vital role in population growth, agricultural production and even the development of human society, which has made it one of the most in-demand chemicals in the world. Since the advent of Haber-Bosch process at the beginning of the last century, NH_3 has been mass-produced as a revolutionary product for artificial nitrogen fixation, and its annual output has exceeded 230 million metric tons. However, the harsh NH_3 production conditions such as high temperature (400-500 °C) and intense pressure (20-50 MPa) via Haber-Bosch process bring many problems including high energy consumption, high pollution, and high cost, especially in NH_3 separation process by a condenser. The gas membrane separation technology, which has the advantages of low energy consumption, environmental friendliness, and continuous operation, would be expected to be used for NH_3 separation in NH_3 synthesis process.

Firstly, based on the Lewis acid-base interaction between NH_3 and transition metal, a strategy was proposed to improve NH_3 affinity through the coordination of transition metal with aminosilica structure. Notably, Ni-doped bis[3-(trimethoxysilyl)propyl] amine (BTPA) showed the highest NH_3 adsorption amount (1.77 mmol g^{-1}) compared with Fe, Co, Cu, and Ag-doped BTPA by metal-induced coordination and hydrogen bonds and/or van der Waals interactions caused by *N-H*, *N=O*, and *Si-OH* groups via characterizations and molecular simulations. Furthermore, after optimizing the amount of nickel doping (Ni/*N-H* molar ratios of 0, 0.125, 0.25, 0.50, and 1.00), 0.50 Ni-BTPA membrane showed a superior NH_3 separation performance, i.e., NH_3 permeance of ~2.8×10^{-6} mol m^{-2} s^{-1} Pa^{-1} with ideal NH_3/H_2 selectivity of 11 and NH_3/N_2 selectivity of 102 at 200 °C. It was ascribed to the sufficient molecular sieving owing to the enlarged pore size by metal coordination as well as high NH_3 adsorption-diffusion due to improved NH_3 affinity by doped nickel.

Additionally, based on the Brønsted acid-base interaction between NH_3 and acidic groups, the organosilica precursor with sulfonic acid group would be expectantly used to fabricate NH_3 separation membranes. In the first stage, the (3-mercaptopropyl)trimethoxysilane (MPTMS) containing mercaptan group (*-SH*) was used and further oxidized to sulfonic acid groups by H_2O_2 to improve NH_3 adsorption amount (~1.41 mmol g^{-1}). Owing to the enhanced acid-base interactions including intensified acidity and more acidic sites, oxidized MPTMS membrane showed an excellent NH_3/H_2 selectivity of 6 and NH_3/N_2 selectivity of 18 with an NH_3 permeance of ~1.4×10^{-7} mol m^{-2} s^{-1} Pa^{-1} at 300 °C. For another, 3-(trihydroxysilyl)-1-propanesulfonic acid (TPS) which contains $-SO_3H$ groups in the chemical structure was used to fabricate TPS-derived membrane by directly coating TPS solutions, that was diluted to 0.1 wt% with ethanol, on SiO_2-ZrO_2 intermediate layer. Owing to the inherently stronger proton-acidic $-SO_3H$ groups in TPS, TPS-EtOH membranes showed a superior NH_3 permeance of ~2.6 and ~1.8×10^{-7} mol m^{-2} s^{-1} Pa^{-1} with an excellent NH_3/H_2 selectivity of 7 and 165, and NH_3/N_2 selectivity of 266 and 18700 at 300 and 50 °C, respectively.

Finally, a green NH_3 production system was proposed and carried out, namely reactor combined with membrane separator with recycle flow, which enables the temperature of reactor and membrane separator controlled independently. The Ru (10 wt%)/Cs/MgO catalyst and two types of membranes (Aquivion/ceramic composite and oxidized MPTMS membranes have different permeation properties and NH_3 selectivity) were used to produce NH_3 and selectively extract the synthesized NH_3 from feed side to permeate side, respectively. For recycle membrane reactor, NH_3 mole fraction of permeate side can be greatly increased to 0.1-0.45, which is ten to forty times higher than 0.01 of equilibrium state without using membrane separator. A mathematical model with one-dimension, isothermal, and plug-flow was proposed and successfully applied to simulate recycle membrane reactor, which is beneficial to understand NH_3 mole fraction, recovery, and recycle parameters as a function of membrane length, membrane performance, feed pressure, and feed flow rate, respectively.

In this dissertation, three types of organosilica membranes were fabricated for selective NH_3 separation over a wide temperature range (50-300 °C) and a recycle membrane reactor process was developed for green NH_3 production with efficient and low energy consumption.