論文の要旨

題　目 Development of organosilica membranes for separation of light hydrocarbons
（軽炭化水素分離のためのオルガノシリカ膜の開発）

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Propylene (C_3H_6) plays a vital role in industrial applications due to the fact that it is widely used for the production of downstream chemicals which are closely related to our daily life. The annual production of C_3H_6 is approximately to 100 million tons in the world in 2016 and is expected to grow with a rate of 3.6% by 2025. To obtain the high-purity C_3H_6, the separation of C_3H_6 from other ingredients such as propane (C_3H_8) is inevitable and now has been conducted in the cryogenic distillation process. Nevertheless, the cryogenic distillation process consumes substantial energy due to the quite similar physical properties of C_3H_6 and C_3H_8 molecules. The intensive energy required for this process is estimated equally to the annual energy expenditure of Singapore. For this reason, even minor optimization of the purification process would have significant impact on the energy saving for processing the C_3H_6 and C_3H_8 mixtures. Consequently, it is urgent to exploit new separation techniques with lower energy consumption.

Membrane separation techniques provided substantial prospects in propylene/propane separation considering the advantages of low energy consumption and investment cost, which was proposed to replace or to combine with the conventional cryogenic distillation process. Over the past decade, organosilica membranes have been attracted much attention due to the impressive features, for instance, the superior molecular sieving properties and excellent hydrothermal stability. The objective of this dissertation was to exploit the organosilica membranes for advanced propylene/propane separation.

Sol-gel-derived organosilica membranes with different linking groups consisting of 2 carbon atoms (ethane, ethylene, and acetylene) were fabricated using bis(triethoxysilyl)ethane (BTESE), bis(triethoxysilyl)ethylene (BTESEthy), and bis(triethoxysilyl)acetylene (BTESA).

No research group has ever proposed tailoring the microstructure and permeation properties of bridged organosilica membranes as a way to control the bond angles. In this study, however, the author found that increases in the Si-O-Si and Si-C-C bond angles contributed to the formation of a loose and uniform structure, which was suggested by the blue shift of Si-O-Si and Si-C-C bonds in the FT-IR spectra. BTESA membranes featured a more open and accessible pore structure, which was suitable for the separation of C_3H_6/C_3H_8. BTESA membranes showed high permeance for C_3H_6 ($1.0\text{-}2.0\times10^{-7}$ mol m^{-2} s^{-1} Pa^{-1}) together with an ideal selectivity (11-14) for C_3H_6/C_3H_8.

The author proposed an effective strategy to finely engineer the pore subnano-environment of BTESA membranes for highly selective propylene/propane separation via controlling the calcination temperatures. Measurement of the surface energy, the ^{29}Si-NMR spectra, and the gas sorption isotherms clearly indicated that low-temperature calcined BTESA materials with a greater number of silanol groups showed an enhanced affinity to propylene molecules. BTESA membranes calcined at 150 °C featured a promisingly high C_3H_6/C_3H_8 selectivity of 52 and a C_3H_6 permeance of 1.7×10^{-8} mol m^{-2} s^{-1} Pa^{-1} at 50 °C. These values were approximate to those reported for ZIF-8 membranes and higher than the standards for commercialization. The high level of C_3H_6/C_3H_8 separation performance was believed to be accounted by the synergetic effects of both controlled pore size and enhanced affinity to propylene molecules.

In addition, the pore sizes of organosilica membranes were finely tuned via the co-condensation of BTESA and bis(triethoxysilyl)benzene (BTESB). The evolution of the network structure indicated that the incorporated BTESB decreased the membrane pore size, which was determined by a modified gas translation (GT) model according to the steric effect of the phenyl groups. The incorporation of BTESB to BTESA finely tuned the membrane structure and endowed the resultant composite membrane with improved separation properties. The relationship between membrane pore size and C_3H_6/C_3H_8 separation performance was examined in detail. Membranes with pores that were either too large or too small were not suitable for highly efficient separation.

This dissertation dedicated to the development of organosilica membranes for C_3H_6/C_3H_8 separation. The network structure and surface chemistry have been clearly illustrated via a series of characterizations. To promote the C_3H_6/C_3H_8 separation properties, the geometrical microstructures of these membranes were also tailored via control of the bond angles, calcinations temperatures, and pore sizes. The present research highlights the fabrication of novel organosilica membranes, which may pave the way for advanced C_3H_6/C_3H_8 separation applications. However, some aspects must be paid attention to for future directions of C_3H_6/C_3H_8 separation using organosilica membranes. Firstly, no successful trial was achieved for industrial application of ornosilica membranes with respect to the C_3H_6/C_3H_8 separation. New manufacture strategy of scalable organosilica membranes must be further exploited for the practical separation of C_3H_6 and C_3H_8 mixtures. The low-cost support such as the hollow fiber can also be applied. Secondly, the amorphous structure of organosilica membranes always generates a formation of network with pore size distribution rather than the network with a uniform pore size. As a result, the utilization efficiency of the useful pores for C_3H_6/C_3H_8 separation are limited to a relative low level. The template method using the surfactant contributed to the formation of the uniform pores of organosilica materials. Yet, the pore sizes of these material are intrinsically too large for the C_3H_6/C_3H_8 separation. Hence, the effective decrease of the pore size to a molecular scale is the key to obtain novel organosilica membranes with both superior C_3H_6 permeance and C_3H_6/C_3H_8 selectivity simultaneously. Last but not the least, the assessments of the affinity between C_3H_6 or C_3H_8 molecules and organosilica membranes are currently conducted through qualitatively measuring the single-component adsorption isotherms, which is far from the real conditions of binary separations of C_3H_6/C_3H_8 mixtures. The binary gas sorption properties or a measurement of breakthrough may provide us more useful information for better understanding the separation mechanism of C_3H_6/C_3H_8 through organosilica membranes.