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研究課題名（和文）Design and development of organosilica/polymer interpenetrating networks derived membranes for high-efficient, robust carbon dioxide capture

研究課題名（英文）Design and development of organosilica/polymer interpenetrating networks derived membranes for high-efficient, robust carbon dioxide capture

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研究成果の概要（和文）：相互貫入デュアルネットワーク構造を備えた一連のポリマー-シリカハイブリッド材料/膜を開発しました。アミン含有親水性ポリマーを選択して最初の柔軟なネットワークを形成し、ブリッジタイプの親水性有機シリカ前駆体を採用して2番目の剛直なネットワークを形成しました。構造の安定性、マイクロ相分離、およびガス分離特性に関するデュアルモードハイブリッドネットワーク構造の形成に対するポリマータイプ、有機シリカ源、および触媒種の影響を体系的に研究しました。

研究成果の学術的意義や社会的意義

The construction and development of advanced membranes that can simultaneously demonstrate high permeance and selectivity and robustness, is significantly important for high-performance CO₂ separations in potentially industrial applications (e.g. CO₂ removal from flue gas).

研究成果の概要（英文）：We developed a series of polymer-silica hybrid materials/membranes with interpenetrating dual-network structure. The amine-containing hydrophilic polymers were selected to form the first flexible network while bridged type, hydrophilic organosilica precursors were adopted to form the second rigid network. Effects of polymer type, organosilica source, and catalysis species on the formation of dual-mode hybrid network structure regarding structure stability, microphase separation, and gas separation properties were systematically studied. 1,2-bis(triethoxysilyl)ethane (BTESE) and polyethylenimine (PEI) were found to be very suitable to fabricate robust dual-network structure for CO₂ separation with excellent molecular sieving effect. These studies have been presented in several academic conferences and relative research manuscripts have been published in Industrial & Engineering Chemistry Research.

研究分野：membrane technology

キーワード：organosilica dual-network gas separation carbon capture

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様式 C-19、F-19-1、Z-19 (共通)

1. 研究開始当初の背景

The ever-increasing rate of *greenhouse gas emissions* in the atmosphere, particularly CO₂ generated from the combustion of fossil fuels, has led to *serious global climate concerns*. Therefore, efficient CO₂ capture technologies such as absorption/adsorption of CO₂ sorbents, cryogenic separation, and membrane separation, have been developed experimentally and industrially over the past few decades. *Membrane technology* shows great potential and is attracting growing attention because of the inherent advantages of *energy-efficiency*, ease of operation and scale-up, and a small footprint (*Science* 2011, 332, 674–676; *Chem. Rev.* 2013, 114, 1413–1492). Various materials including polymer, inorganic and the composite materials thereof have been adopted for the fabrication of membranes for CO₂ capture. However, it is still challengeable to well tune the membrane *pore size and/or chemistry* for high-performance CO₂/N₂ separation due to their *similar kinetic diameters* (CO₂, 3.3 Å; N₂, 3.64 Å). To overcome this limitation, various CO₂-philic moieties or molecules have been introduced to the membrane matrix to significantly improve CO₂ sorption performance considering the conjugation effect of solubility and diffusivity of the penetrating molecules that decides the gas separation performance (as schematically shown in Fig.1). However, the membrane performance is still restricted by a *trade-off between permeance and selectivity*, where high selectivity of a membrane can only be obtained by sacrificing permeability and vice versa (*Science*, 2017, 356, 6343: eaab0530). Therefore, the construction and development of advanced membranes that can *simultaneously* demonstrate *high permeance and selectivity and robustness*, is significantly important for high-performance CO₂ separations in potentially industrial applications (e.g. CO₂ removal from flue gas).

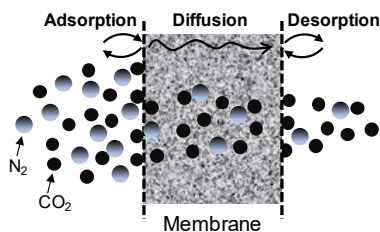


Fig. 1 Illustration of CO₂ separation through a membrane.

2. 研究の目的

Conventional amine-containing polymeric membranes show advantages of high-processibility, low-cost, and high selective permeation of CO₂, however, suffer from low resistance to high temperature and high pressure. On the contrary, amorphous silica-based membranes could exceed such limitations of polymeric membranes. Therefore, the purpose of this proposal is to develop a novel organosilica/polymer hybrid membrane with the interpenetrating networks (IPNs) that are expected to overcome the limitations from each individual network (Fig. 2a and c). The main objectives include the following:

- (i) *Design and synthesis* of organosilica/polymer interpenetrating networks (IPNs) derived membranes;
- (ii) *Exploration and optimization* of the microstructure of organosilica/polymer IPNs derived membranes;
- (iii) *Investigation and modeling* of gases, particularly CO₂, transport behaviors across IPNs derived membranes.

3. 研究の方法

Generally, CO₂ separation performance is mainly decided by the microstructure of membranes and the chemistry of materials employed such as amine density and affinity to CO₂. Hence, to develop high-performance CO₂ separation membranes, both the selection of membrane materials selection and the processing approaches should be well considered in this proposal. The main points for this proposal involve the following:

(i) Design and synthesis/selection of materials

Based on our previous studies, membranes with *too strong affinity* to CO₂ (high heat of adsorption) may *restrict CO₂ diffusion/desorption processes*, particularly at lower temperatures, within the membrane matrix and in turn *reduce* CO₂ permeation efficiency and *raise* the activation energies of permeation (*Sep. Purif. Technol.* 2017, 178, 232–241, 178, 232-241; *J. Membr. Sci.* 2017, 541, 447–456). Therefore, in this proposal, polymers with different amine densities and chemistry will be selected to form a diffusion-dominant polymer network (Fig. 2b). In addition, organosilica precursors with different linking -R- groups will be considered to adjust the

compatibility between organosilica derived network and polymer network.

(ii) Fabrication of membranes and optimization of the microstructures

The fabrication of organosilica/polymer IPNs derived membranes will follow a typical *sol-gel method* as reported in our previous studies (*ACS Appl. Mater. Interfaces* 2019, 11, 7164–7173). Generally, the organosilica network (A type) can be generated via the *hydrolysis and condensation* reactions (Fig. 2b) in the presence of selected linear or branched polymers (B type network). The organosilica/polymer IPNs would be then formed due to the *interpenetration* of A type and B type networks based on a careful selection of organosilica precursors and polymers. The microstructure of the achieved IPNs derived membranes can be primarily adjusted by the materials selected and the mass ratio thereof. In addition, layered IPNs derived membranes with different affinities to CO₂ in each layer will be also designed to investigate the effect of driving force (chemical potential) distribution within IPNs derived membranes on CO₂ permeation behaviors.

(iii) Investigation of gas permeation properties through IPNs derived membranes

The chemical and physical structures of achieved IPNs will be evaluated by Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), small angle X-ray diffraction (SAXRD), positron annihilation lifetime spectroscopy (PALS) etc. The formation of IPNs microstructure will be probed by the measures of element distribution, texture analysis etc. Both single gases with various kinetic diameters (He, H₂, Ar, CO₂, N₂, CH₄, CF₄, SF₆ etc.) and binary gas mixtures (CO₂/H₂ and CO₂/N₂ etc.) permeation tests will be conducted on the IPNs derived membranes at various of temperatures to probe the separation performance. Gas permeation mechanisms within these membranes will be studied and modeling of gas transport behaviors will be carefully performed.

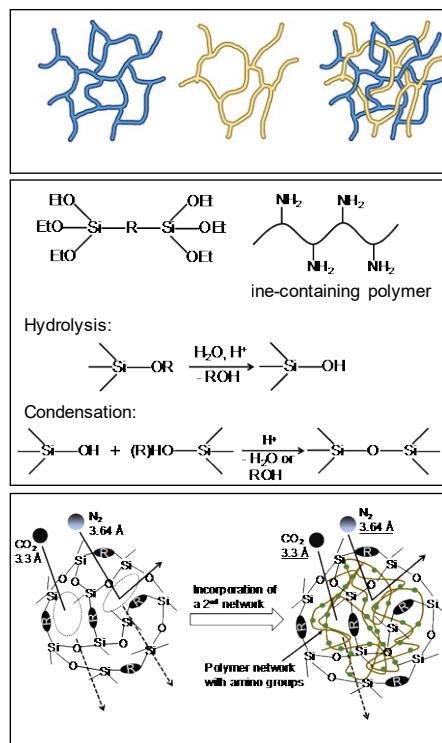


Fig.2 (a) Illustration of the structure of interpenetrating networks. (b) Chemical structures of organosilica precursors and amine-containing polymers together with the mechanism for the formation of organosilica network via hydrolysis and condensation reactions. (c) Illustration of the individual organosilica network and organosilica/polymer IPNs for CO_2/N_2 separation.

4. 研究成果

In this project, we developed a series of polymer-silica hybrid materials/membranes with interpenetrating dual-network structure. The amine-containing hydrophilic polymers were selected to form the first flexible network while bridged type, hydrophilic organosilica precursors were adopted to form the second rigid network. Effects of polymer type, organosilica source, and catalysis species on the formation of dual-mode hybrid network structure regarding structure stability, microphase separation, and gas separation properties were systematically studied. 1,2-bis(trimethoxysilyl)ethane (BTESE) and polyethylenimine (PEI) were found to be very suitable to fabricate robust dual-network structure for CO_2 separation with excellent molecular sieving effect. In addition, the mixing ratio of PEI/BTESE played an important role in the stability of the dual-network structure and gas permeation properties. These studies have been presented in several academic conferences and relative research manuscripts have been published in Industrial & Engineering Chemistry Research (<https://doi.org/10.1021/acs.iecr.1c00872>).

5. 主な発表論文等

〔雑誌論文〕 計1件（うち査読付論文 1件/うち国際共著 1件/うちオープンアクセス 0件）

1. 著者名 Keita Nakahiro, Liang Yu, Hiroki Nagasawa, Toshinori Tsuru, and Masakoto Kanezashi	4. 巻 60
2. 論文標題 Pore Structure Controllability and CO2 Permeation Properties of Silica-Derived Membranes with a Dual-Network Structure	5. 発行年 2021年
3. 雑誌名 Industrial & Engineering Chemistry Research	6. 最初と最後の頁 1c00872
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acs.iecr.1c00872	査読の有無 有
オープンアクセス オープンアクセスではない、又はオープンアクセスが困難	国際共著 該当する

〔学会発表〕 計2件（うち招待講演 0件/うち国際学会 0件）

1. 発表者名 1.中廣恵大, Liang Yu, 金指正言, 長澤寛規, 都留稔了
2. 発表標題 相互侵入網目構造を有するアミノシリカ膜の作製とCO2透過特性
3. 学会等名 日本膜学会第41年会
4. 発表年 2019年

1. 発表者名 2.中廣恵大, Liang Yu, 金指正言, 長澤寛規, 都留稔了
2. 発表標題 Dual-Network構造を有するシリカ系膜の細孔構造制御とCO2透過特性
3. 学会等名 化学工学会第51回秋季大会
4. 発表年 2020年

〔図書〕 計0件

〔産業財産権〕

〔その他〕

6. 研究組織

氏名 (ローマ字氏名) (研究者番号)	所属研究機関・部局・職 (機関番号)	備考
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7. 科研費を使用して開催した国際研究集会

〔国際研究集会〕 計0件

8 . 本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関
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