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研究課題名(和文) MOF-based polycrystalline nanomembranes directly grown on microporous polymeric supports for advanced post-combustion CO₂ separation研究課題名(英文) MOF-based polycrystalline nanomembranes directly grown on microporous polymeric supports for advanced post-combustion CO₂ separation

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研究成果の概要(和文)：結晶性材料は、選択的なCO₂ガス分離のために複合膜に組み込まれました。プルシアブルー(PB)結晶は様々な多孔質支持体上に直接膜の形で成長しました。PB選択層を備えた複合膜は、サイズふるい効果を示しました。結果として窒素とCO₂分離機能の強化が観察されました。別の方法で、フッ素化金属有機構造体(MOF)とPebax-1567高分子に組み込まれました。MOFとポリマーの適切な組み合わせにより、低濃度(空気など)のCO₂回収を実現できることが分かりました。MOFの高いCO₂吸着選択性を利用して、高いCO₂透過選択性を備えた分離膜を実現する方法が概念化されました。

研究成果の学術的意義や社会的意義

本研究では、二酸化炭素を効率的に回収するための膜を開発しました。低濃度混合物からCO₂を分離するためにガス分離膜を使用するという前例を生み出します。メンブレンに選択的金属有機構造体を適切に組み込むことで、低濃度混合物からの効率的な捕捉が可能になります。気候変動は喫緊の課題であり、その解決が求められています。本研究の発展、ガス分離の分野での重要な波及効果が期待され、また、建築物の空気浄化や農業などの環境管理にも重要な役割を果たすことも期待されます。

研究成果の概要(英文)：Crystalline materials were incorporated in the composite membranes for the selective CO₂ gas separation. Prussian blue (PB) crystal was grown in form of membrane directly on the variety of organic and inorganic porous supports. Composite membrane with PB selective layer demonstrated the characteristic size sieving effect. As a result, enhanced separation of CO₂ from nitrogen was observed. Using the different approach, fluorinated metal organic framework material (NbOFFIVE-1-Ni) was incorporated in the Pebax-1567 polymer matrix as a part of separation membrane. It was found that proper combination of MOF and CO₂-philic polymer can deliver unique CO₂ capture from low concentration feed. It was conceptualized how the high CO₂ sorption selectivity of hybrid microporous MOFs can be utilized to achieve the separation membrane with high CO₂ permeation selectivity. Based on the results membrane-based CO₂ separation from air can be considered.

研究分野：二酸化炭素ガス分離膜

キーワード：thin-film composite metal-organic network CO₂/N₂ separation selective interface CO₂ philicity transport phenomena ultramicroporous MOF mixed matrix membranes

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1 . 研究開始当初の背景

Humans are currently living in the era of climate change – global phenomena that is manifested by increased temperatures, thawing of sea and land ice, sea rise and extreme weather events such as heatwaves, anomalous precipitation, and droughts. All these transformations are threatening socio-economic stability in very near future. Emissions of CO₂ – main greenhouse gas (GHG), as well as others, should be drastically decreased and further removed from atmosphere to in a process called negative emissions. However, to be accepted on large scale, methods of CO₂ capture economically feasible with the cost below 40\$/ton of captured CO₂ in industrial processes. Among the available methods CO₂ capture using membranes is expected to achieve relatively low-cost needed for large scale applications. However, this is only possible, when membranes have high CO₂ permeances (>1000 GPU, GPU = 7.5×10⁻¹² m³(STP)m⁻²s⁻¹Pa⁻¹) and relevant CO₂/N₂ selectivity (>40). Unfortunately, organic polymer membranes, widely utilized for several decades for specific gas separations applications, have limited ability to achieve the performance needed for industrial CO₂ capture, mainly due to the well documented trade-off between target gas permeability and selectivity. Therefore, hybrid membranes are attracting lots of scientific efforts as they offer new separation mechanisms and as a result potential for more efficient separation. Metal organic frameworks (MOFs) are particularly studied class of materials, promising breakthroughs in many applications, especially for gas capture and storage [5]. Recently, a highly selective CO₂ adsorption was demonstrated in a number of ultramicroporous MOFs (SIFSIX-3-Zn, SIFSIX-3-Ni, SIFSIX-3-Cu, TIFSIX-1-Ni, NBOFFIVE-1-Ni, AIOFFIVE-1-Ni etc.) making them a good candidate for solid adsorption applications where CO₂ capture can be realized via pressure- or temperature- swing adsorption (PSA or TSA). While sorption amount is usually driven by pore volume, selectivity is more often related to pore geometry and chemical nature. Mentioned above ultramicroporous MOFs have both proper pore size and pore chemical properties, ideal for CO₂ and N₂ separation (kinetic diameters 3.3Å and 3.64Å respectively). Additional advantage of these materials is fine tuning of the pore size via isorecticular chemistry (e.g. by changing the coordination metal). Current proposals' key question was whether the high and selective CO₂ sorption in MOFs (*known*) could be translated into similarly selective permeation of CO₂ through the membrane containing the MOF (*unknown*), (*Fig. 1*). Positive answer to this question could make a significant contribution into so much needed CO₂ capture technology.

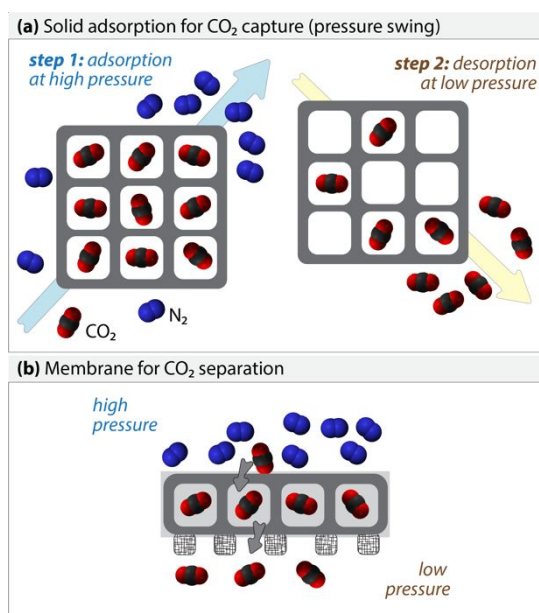


Figure 1: Two approaches aimed to separate/capture CO₂ with the aid of porous materials: (a) solid adsorption that can be enabled via pressure swing (step-like operation) and (b) membrane separation (continuous operation).

2 . 研究の目的

Microporous materials (in particular MOFs) are rarely used in pure form of membranes for gas separation due to number of reasons, such as inability to fabricate them in form of membranes, poor mechanical stability and susceptibility to defect formation. Mixed matrix membranes (MMM) with MOFs as fillers are therefore used more commonly but they often fail to provide sufficient improvement of gas separation. Among the reasons are incompatibility of fillers with matrix material, formation of leaky or block-interfaces, formation of defect and transport mainly governed by the polymer matrix and diminished interaction of gas with MOF fillers. The purpose of this proposal was to find the ways how the highly selective ultramicroporous MOFs can be effectively used to enhance the target separation performance.

The first approach in this proposal was to use interfacial deposition method to grow the crystalline later directly on the organic polymer porous supports. It is believed that well controlled growth achieved via precise chemical modification of support surface, can prevent aggregation of crystals in the pores and simultaneously provide good adhesion of MOF layer to porous support. Such membranes would realize an effective gas interaction with the MOF component leading to improved CO₂ separation. For practical use MOF layer should be embedded in a thin film composite structure additionally coated with the caulking layer which is essential to cure the inevitable defects in crystalline selective layer. In this work, asymmetric polyacrylonitrile (PAN) was used as a primary choice of porous support, Prussian blue was used to fabricate the selective polycrystalline layer with polydimethylsiloxane (PDMS) used as caulking layer.

3 . 研究の方法

Specific difference of this method of direct deposition of crystalline layer on porous support from conventional approaches was to carefully consider the factors necessary for uniform and controlled crystal growth on porous support. Membrane fabrication procedure schematically depicted in *Fig. 2*, “Route 1” relies on four factors: 1) proper porous support (chemical nature, structure and surface porosity); 2) chemical modification of interface; 3) controlled diffusion of components separated by the porous support membrane enabling interface reaction; 4) proper growth geometry where interface for the reaction is placed in the face-down position enabling only attached (rooted) crystal particles on the support. To minimize the defects formation in crystal layer, the method excludes the significant physical influence during manipulations. Polydimethylsiloxane was additionally used as caulking layer to ensure the membrane durability, by curing minor, unavoidable defects that occur during the membrane handling.

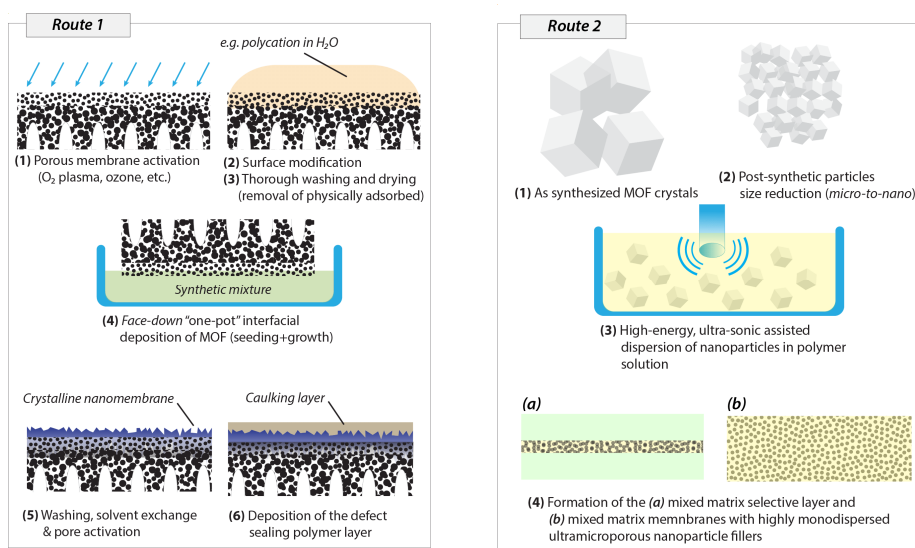


Figure 2: Two membrane fabrication routes adopted in this proposal: Route 1 – interfacial deposition of the crystalline layer directly on the porous support; Route 2 – formation of the quasi-MOF layer in the mixed matrix membrane (including MOF particles size reduction and subsequent dispersion in the polymer).

4 . 研究成果

Route 1 was applied to grow of the classical crystalline material Prussian blue (PB) on the variety of porous supports. The unique properties of the crystal formation reaction enabled to satisfy all necessary conditions for the membrane fabrication. Namely, deposition of the amine-polycations on the porous support was used for the modification purpose.

The presence of amine allowed the controlled reduction of the non-reactive potassium ferricyanide to reactive ferricyanide (tracked by specific spectral changes, *Fig.3a*) which, when combined with ferrous chloride formed the uniform crystalline layer on the surface of the porous supports of different nature as shown in *Fig. 3b* (e.g. anodized alumina polysulfone, polycarbonate etc.).

To test these membranes for the gas separation and verify whether one can utilize the PB crystalline porous layer for separation the influence of the minor defect should be eliminated. For this, common approach for the thin film composite membranes formation was used and additional polymer layer was deposited on the top of PB. This, so called caulking layer was fabricated using highly gas permeable polymer – polydimethylsiloxane (PDMS) (*Fig. 3c*). The properties of the PDMS are well known and once the thicknesses are carefully defined, conventional resistance in series model was used to calculate the performance of the PB layer separately from the composite membrane properties.

The results for four small gases permeation rates (permeances) as a function of the gas kinetic diameters in PB/PDMS membrane compared to the PDMS alone are shown in *Fig. 4a*. Drastic decrease of the permeances – due to the presence of the crystalline PB layer was observed. The fact that permeance decrease is correlating with the size of the gas molecules, namely – the higher the molecular size, the higher is the decrease in permeance confirmed that gas passes through the certain form of molecular sieve which is likely formed in PB layer. The same effect is observed for the selectivity of different gas pairs separation which is given in *Fig.4b*. The selectivity became higher in the membrane containing crystal layer and the factor of improvement is highest for the gas pair which has the largest difference in kinetic diameters – namely hydrogen vs. nitrogen where 16-fold increase in selectivity was observed.

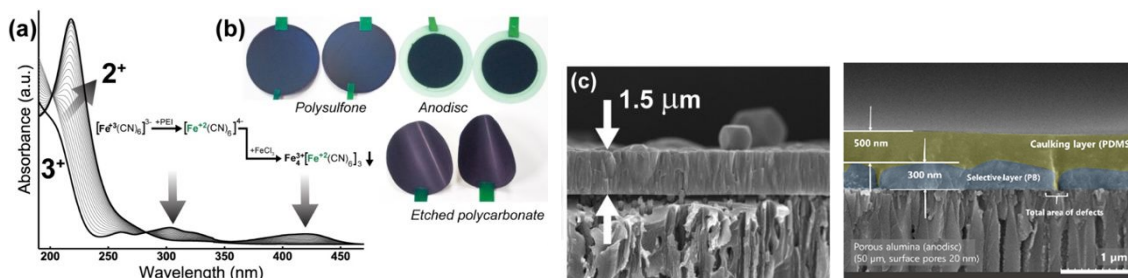


Figure 3: Membrane fabrication via *Route 1* – interfacial deposition of the crystalline layer directly on the porous support. (a) Spectral changes taking place in the 0.5 mM aqueous solution of $K_3Fe(CN)_6$ after the addition of the **branched PEI** (molar ratio Fe:N = 1:5) which demonstrate the reduction of the ferricyanide to ferrocyanide ($[Fe^{3+}(CN)_6]^{3-} \rightarrow [Fe^{2+}(CN)_6]^{4-}$). (b) SEM image of the PB crystalline membrane deposited on porous polycarbonate support. (c) composite membrane with PB selective layer and PDMS used as a caulking layer, allowing the gas transport testing in the crystalline membrane with the use of resistance in series model.

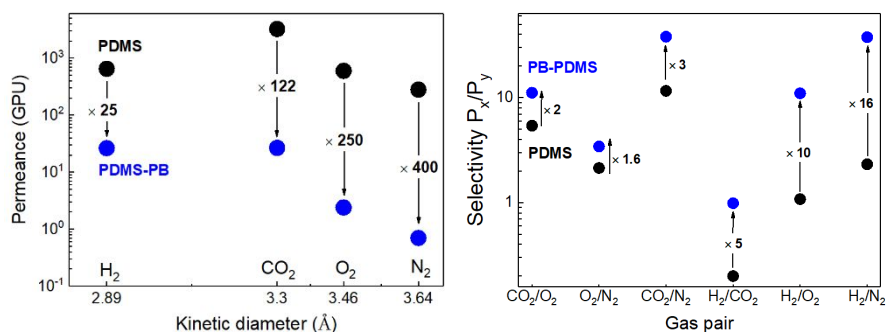


Figure 4: Results of the gases permeation tests in the composite membranes with the selective PB-based crystalline layer directly deposited on the porous support and further caulked with PDMS: (a) permeances of four small gases compared to the reference sample – PDMS alone; (b) ideal selectivity of the composite membrane compared to the PDMS shows drastic changes more pronounced towards small gases: evidence of the added size-sieving in the crystalline layer.

The existing challenge of the majority of CO₂ selective MOFs (e.g. SIFSIX-m-Me) is that they cannot be simply fabricated on the porous substrates, using the Route 1. Moreover, most of the MOFs (e.g. SIFSIX-3-Zn) are not stable in the ambient conditions and quickly degrade/change crystal structure if left in normal atmosphere in the presence of humidity. To overcome these limitations and proceed to the membrane fabrication, the approach was modified in order to create the quasi layer in the composite membrane that is rich with the MOF material using the Route 2 in Fig. 2. Among the variety of MOFs, hydrolytically stable NbOFFIVE-1-Ni ultramicroporous material was selected (structure shown in Fig. 5a) to demonstrate the concept. Additional problem for the utilization of MOF as fillers in the membranes is that the large particle sizes of raw synthesized material (hundreds of micros, Fig. 5b). Planetary ball milling was used to downsize the particle sizes from microscale to nanoscale and was confirmed by particle size distribution measurements and electron microscopy (Fig. 5c shows particles after milling process). The reduction of the particle sizes enabled the formation of the highly durable and uniform mixed matrix membranes with peculiar micro-structure (Fig. 5d and 5e) where the MOFs are present in form of quasi layers, are well dispersed and do not form visible defects or leaky interfaces. These membranes with different amount of MOF loading were used for the gas separation tests.

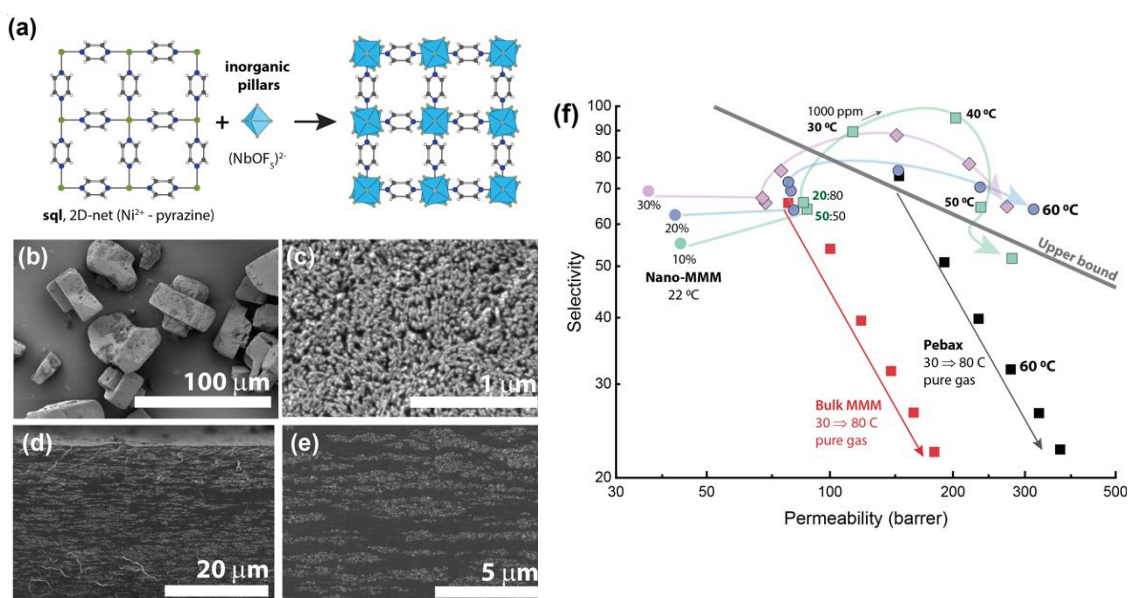


Figure 5: Summary for the mixed matrix membranes containing quasi layers of the ultra CO₂ selective NbOFFIVE-1-Ni MOF in CO₂ selective polymer Pebax-1657: **(a)** Structure of the NbOFFIVE-1-Ni **(b)** microparticles of the material obtained in the hydrothermal synthesis are too large for the membrane fabrication; **(c)** MOF nanoparticles produced by the scalable post-processing of raw material using the planetary ball milling **(d)** example of the mixed matrix membrane containing 20 wt% of the MOF nanofillers demonstrates peculiar and uniform morphology (“wagyu”-like). **(e)** magnified view of the membrane cross section; **(f)** combined CO₂/N₂ separation performance of the different membranes at different conditions prove the significant impact of the MOF properties on the CO₂ separation from the low concentration mixture.

Surprisingly, these membranes demonstrated much better performance with mixed gases rather than pure gases was supplied for separation (Fig. 5f). In particular, the best separation was achieved when low concentration (1000 ppm) CO₂ gas was used for the test. Moreover, the MOF MMMs manifested the superior performance at elevated temperatures, increasing both CO₂ permeability and CO₂/N₂ selectivity. As a result, at some point all membranes containing from 10 to 30% of MOF nanofillers exceeded the performance of matrix polymer (Pebax-1657) as well as the upper bound of performance of organic polymers (grey line in Fig. 5f). All these results are very important from the point of view of practical applications. Namely, the superior performance with the low concentration mixtures open the path for these membranes to be used for application of membranes in the direct air capture applications.

In summary, in this proposal it was indeed showed that the ultrasensitive CO₂ adsorption in hybrid ultramicroporous MOFs can be used also for the selective transport and as a result – separation of gases in the membranes with the microporous layers or fillers.

5. 主な発表論文等

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〔図書〕 計0件

〔産業財産権〕

〔その他〕

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6. 研究組織

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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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