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研究課題名（和文）Ultra-thin metal oxide films for gas separation

研究課題名（英文）Ultra-thin metal oxide films for gas separation

研究代表者

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研究成果の概要（和文）：現在の研究プロジェクトは効果的なＣＯ２分離二重膜の開発に専念した。二重膜には支持層としてポリジメチルシロキサンを、またガス分離層として二酸化チタンを架橋したフタル酸を用い、その結果、ＣＯ２および窒素ガスについての高選択的な分離性能を実証した。
ガス分離のメカニズムは、フタル酸に大きく占めるカルボキシル基に起因し、その材料選択は理論計算（密度汎関数理論）を用いて決定した。この計算によると、フタル酸／二酸化チタンの複合層におけるＣＯ２親和サイトを創りだすことに成功している。これらの部位は窒素に比べてＣＯ２ガスの高い親和性を有す。これを基に私たちは分子レベルの特性を材料特性に発展させることができた。

研究成果の概要（英文）：Current research project was devoted to the development of the double layer composite membrane for efficient separation of carbon dioxide. Polydimethylsiloxane was used as a support layer and phthalic acid incorporated titanium dioxide as a selective layer. Developed membranes demonstrated unique gas separation performance with high selectivity separation of carbon dioxide and nitrogen.
The mechanism of gases separation was attributed to the abundance of the carboxylic groups originated from the incorporated acids. The mechanism of material selectivity was verified using theoretical calculations (density functional theory). According to the calculations we have succeeded to create CO2-philic sites in the composite phthalic acid/titanium dioxide layer. These sites exhibit much higher attractive force for carbon dioxide gas compared to nitrogen. As a result we have in fact achieved the translation of the molecular level property (chemical affinity) to the material (high selectivity).

研究分野：　Materials chemistry

キーワード：　carbon dioxide　gas separation　laminate membrane　titanium dioxide　composite materials　nanomembrane　molecular imprinting　carbon-neutral energy

１．研究開始当初の背景

Prevention of the carbon dioxide emission into atmosphere requires proper carbon capture and storage solutions introduced in the points of massive CO_2 emissions such as coal-burning power plants or certain type of chemical plants. Development of reliable and economically reasonable CO_2 capture technology are crucial for the global environment in order to decrease the total concentration of the greenhouse gases in atmosphere. CO_2 gas separation with the usage of membranes is a promising, yet not used widely, method for industrial carbon capture that has potential to reduce capture costs to the economically feasible values.

Organic polymers represent the most investigated class of materials for the membrane preparation, however despite the good results achieved in the separation of CO_2 from other gases, polymers are lacking other necessary features for the membrane utilization. The most important of such features is the high gas permeability of the materials which is needed to maintain high gas fluxes leading to ability to capture (separate) huge amounts of CO_2 from the flue gas of the conventional power plants. Moreover, the trade-off relation between the permeability and selectivity of the organic polymer materials, settles the fundamental limitation for having highly permeable and selective materials in the same time.

２．研究の目的

The idea of current research was the separation of the main functions of gas filtration membrane in double layer design employing ultra-thin inorganic separating layer. In order to tune the selectivity of the membranes molecular imprinting and molecular templating as main methods were utilized.

Research target: Development of novel self-supporting gas separation membranes with nano-scale thickness of separation layer able to overcome the performance (selectivity and permeability) of organic polymer membranes.

３．研究の方法

1. Application of the ultra-thin dense, inorganic, metal oxide films as gas selective separation layer.
2. Utilization of the double layer structure with separated functions where “selectivity” relies on the nano-thin separating layer, supported by highly permeable and robust polydimethyl-siloxane (PDMS) layer responsible for membrane physical durability.
3. Employment of the free-standing giant nanomembrane fabrication approach, necessary for precise architecture of the films of nanoscale thickness.
4. Achievement of selectivity by introduction of gas selective compounds into the dense, ultrathin metal oxide film with initial high gas barrier (Fig.1).
5. Molecular imprinting and molecular templating used for the selectivity tuning in the ultra-thin metal oxide film.

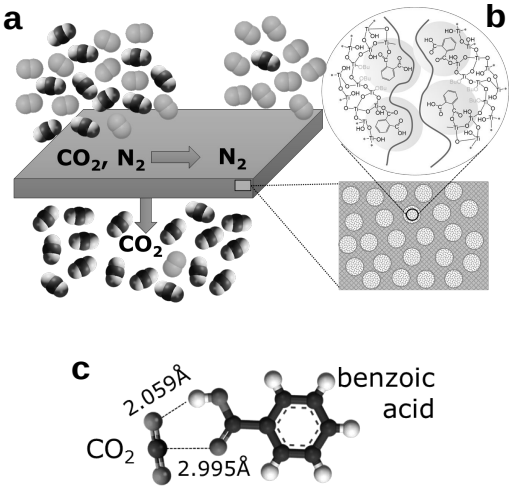

Fig. 1 Schematic illustration of the proposed gas separation membrane (**a**) suggests modification of the inorganic oxide material CO_2/N_2 selectivity (**b**) by addition of the CO_2-philic molecule (e.g. benzoic acid) to the separation layer which possess site with CO2 affinity (**c**).

４．研究成果

Current research project was devoted to the development of the double layer composite membrane for efficient separation of carbon dioxide. Polydimethylsiloxane was used as a support layer and phthalic acid (PA) was incorporated titanium dioxide (TiO_2) to form a selective layer. Developed membranes demonstrated unique gas separation performance with higher selectivity separation of carbon dioxide and nitrogen.

Metal oxides (MO) composite layers were fabricated using sol-gel method from alkoxide precursors. TiO_2 layer was modified

by incorporation of phthalic acid in matrix resulting in CO_2 selective material. Fig. 2a shows the structure of PA incorporated in TiO_2, Fig.2b shows the SEM image of the typical double layer membrane. Uniform inorganic layer with intended nanoscale thickness were successfully fabricated.

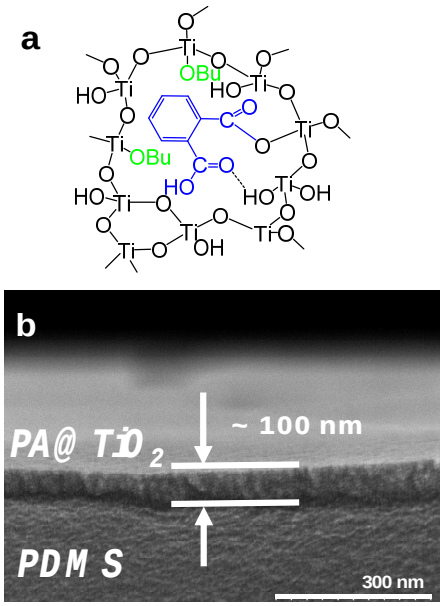

Fig. 2 (**a**) Chemical structure of the CO_2 selective site in the composite PA@TiO_2 layer (**b**) SEM image of the fabricated double layer PA@TiO_2/PDMS membrane.

Nitrogen and carbon dioxide separation performance of the fabricated membranes overcome the parent PDMS and reference TiO_2/PDMS membranes, evidencing successful transfer of CO_2 philicity from molecular level to material. Fig. 3 demonstrates long time performance of PA@ TiO_2/PDMS membrane for the separation of the CO_2 and N_2. Gas separation was measured using mixed 1:1 CO_2 and N_2.

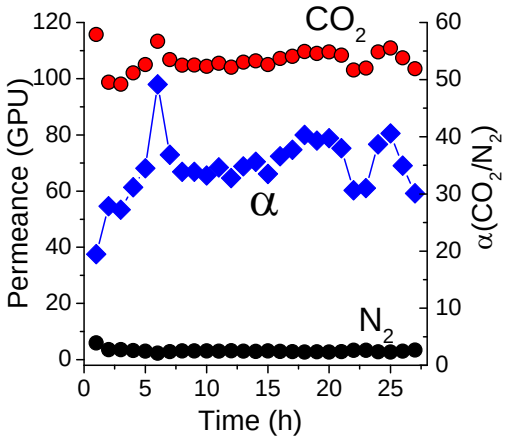

Fig.3 Gas separation performance of the double layer membrane.

Selectivity of composite membranes were more than $\alpha(CO_2/N_2)$ >30 that is significantly higher compared to PDMS alone ($\alpha(CO_2/N_2)$ = 11.6 at 25°C).

Figure 4 shows the comparison of the developed membranes (point 2) with state-of-art gas separation materials. In order to evaluate the selectivity and permeability of the PA@TiO_2 layer alone, the resistance model was used and the result is shown as point 3 in the Fig. 4. It is seen that the results for composite layer is lying below the upper bound, however with exceptionally high selectivity ($\alpha(CO_2/N_2)$ > 150) that is far higher than that reported for majority of organic polymers.

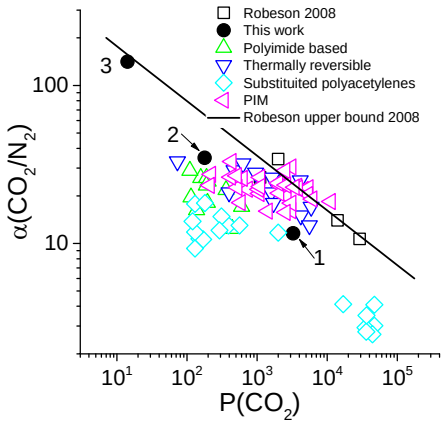

Fig.4 Gas separation performance of the double layer membrane (point 2) with reference PDMS (point 1) and several conventional organic polymer materials. Point 3 represents the performance of the selectivity layer alone, calculated using the resistance model.

The mechanism of gases separation was attributed to the abundance of the carboxylic groups originated from the incorporated acids. The mechanism of material selectivity was verified using theoretical calculations (density functional theory).

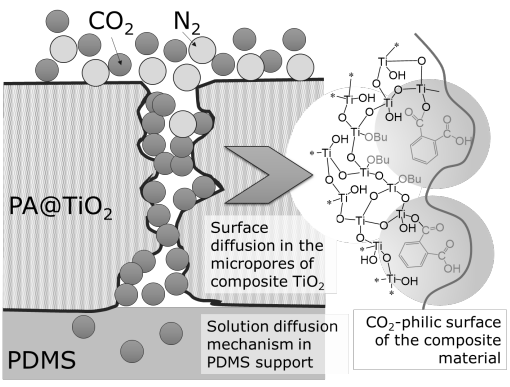

Fig. 5 Mechanism of gas separation in double layer membrane: TiO_2 film enriched with carboxylic acids provides preferential surface diffusion of CO_2 in the pores.

Plausibly, we have succeeded to create CO_2-philic sites in the composite phthalic acid/titanium dioxide layer. These sites exhibit much higher attractive force for carbon dioxide gas compared to nitrogen and provide the surface diffusion mechanism of gases separation (Fig. 5). As a result we have in fact achieved the translation of the molecular level property (chemical affinity) to the material (high selectivity).

５．主な発表論文等
（研究代表者、研究分担者及び連携研究者には下線）

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