

報告番号	甲 第 14185 号
------	-------------

主 論 文 の 要 旨

論文題目 **Study on Crystal Design and Growth of Metal-organic Frameworks toward Gas Separation and Membrane Fabrication**
(ガス分離と膜作製に向けた金属有機構造体の結晶設計と成長に関する研究)

氏 名 王 晓光

論 文 内 容 の 要 旨

Gas is used extensively as an energy source in industry and our daily lives. The combustion of fossil fuels and industrial production release massive gas mixture and the separation of gas is not only occupying a very important position in industrial production but also has a significant impact on the ecological environment. For example, the capture of carbon dioxide (CO₂) in flue gases can contribute to achieving carbon neutrality, the removal of traces of acetylene in ethylene to purify ethylene, and the separation of atmospheric air into its primary components, typically nitrogen and oxygen. Microporous and mesoporous materials are widely used in gas adsorption separation and membrane separations due to their large internal space, uniform pore channels, and permanent porosity, such as activated carbons, zeolites, mesoporous silicas, and so on. In the past few years, Metal-organic frameworks (MOFs), a class of

newly developed crystalline hybrid porous materials, have been a very rapid development not only in the synthesis of novel structures but also potential applications in a variety of fields. There are two main approaches to the application of MOFs for gas separation. One approach is to introduce functionalized reactive groups and active metal sites to improve the selectivity of gas adsorptive separation. Besides, the sieving of molecules through the channels of MOF membranes is another effective separation method. However, so far the design of MOFs for gas selective adsorption main focus on inserting open metal site to improve the bonding between frameworks and molecules, while the way of introducing functionalized ligands is more diverse. Thus, the design of MOFs with porous structures and functional groups which can coordinate with gas molecules in the pore channels of MOFs to achieve separation is worth exploring. What's more, the researches on MOFs membranes for gas separation are still limited compared to the number of reported MOFs. Crystal growth rate control, pore size adjustment, crystal growth into dense membranes, and structure orientation control are still not well clarified. Therefore, it needs further research on the fabrication of MOF membranes for gas separation and the synthesis of MOFs for selective adsorption.

In this thesis, the structural diversity of MOFs and MOFs containing functional groups for gas selective adsorption are summarized. Methods for the preparation of MOF membranes on porous substrates for gas separation and orientation control of MOF membranes are described. This thesis also has focused on the construction of SIFSIX (SIFSIX, hexafluorosilicate (SiF_6^{2-}) pillared MOFs containing reactive functional groups for trapping O_2 from the air and interaction sites for $\text{C}_2\text{H}_2/\text{C}_2\text{H}_4$ separation. Through the rational design of metal ions and organic ligands, as well as adjustment of solvent and post-treatment method, the stable three-dimensional (3D)

porous MOF crystals with internal nanospace to accommodate the guest molecules were obtained. This thesis also studies the fabrication of MOF membranes for H₂ purification, CO₂/CH₄, and CO₂/N₂ separation. The method for preparing dense membranes was developed through chemical modifications for porous substrates. What's more, a new concept of preparing bilayer membranes by adjusting the pore size and growth rate of the crystals to separate CO₂ was also established. This thesis will contribute to a deeper understanding of the design of the crystal structure of MOFs for selective adsorption and the growth of MOFs crystals into membranes on substrates for gas separation. This thesis is composed of six chapters as follows.

Chapter 1 describes the background and purpose of this thesis. First, the structure, development, and applications of MOFs are overviewed. Next, the secondary building units (SBUs) of MOFs, the influence of the conditions of synthesis on the structure, and the effects of post-treatment on the structure toward gases capture and separation are introduced. MOF crystals growth to form membrane and crystal orientation control are also described for the gas separations.

Chapter 2 describes that a series of MOFs based on 9,10-Di(4-pyridyl)anthracene (dpa) and two MOFs based on 9,10-epidioxidoanthracene (epo) were synthesized by self-assembly with metallic hexafluorosilicate. Interestingly, Co²⁺, Ni²⁺, Cd²⁺ or Zn²⁺ with 9,10-Di(4-pyridyl)anthracene show different 1D, 2D and 3D topologies using same solvent. Compounds [Zn(dpa)₂(SiF₆)] is a 3D structure that can maintain stability after removal of the solvent, it exhibits the property of trapping oxygen under photoirradiation and releasing oxygen after heating. We also directly synthesized compounds [Zn(epo)₂(SiF₆)] to determine the structure of [Zn(dpa)₂(SiF₆)] after photoirradiation. Our works indicate that [Zn(dpa)₂(SiF₆)] can selectively capture

oxygen from the air and can release O₂ through the reverse reaction upon application of heat. It has the potential application for the separation of oxygen in air.

Chapter 3 describes the synthesis of a series of 3D SIFSIX pillared MOFs using different metals and 4,4'-bipyridine or 1,2-bis(4-pyridyl)ethane. Due to the tendency of crystallization of SIFSIX pillared MOFs into 2D non-porous structures in an aqueous environment, it has been a challenge to synthesize those MOFs with 3D coordination networks. Based on the study of Chapter 2, the same method is applied to the synthesis of SIFSIX-1-M (Ni, Co, Cd) and SIFSIX-7-M (Ni, Co, Cd) using the organic linkers 4,4'-bipyridine and 1,2-bis(4-pyridyl)ethane, respectively. Among them, SIFSIX-1-Ni, SIFSIX-1-Co, and SIFSIX-7-Ni show excellent adsorption selectivities for CO₂ from a CO₂/N₂ gas mixture and C₂H₂ from a C₂H₂/C₂H₄ gas mixture respectively.

Chapter 4 describes the efficient fabrication method for the membrane of a metal-organic framework (MOF) (Kgm-OEt) which is one kind of kagomé-type MOF with a two-dimensional (2D) sheet structure having one-dimensional (1D) channels suitable for separation of H₂ from other larger gases. Kgm-OEt seed layer was created on an Al₂O₃ substrate using layer-by-layer (LBL) growth, then a membrane was fabricated by the secondary growth. The membrane on a 3-aminopropyltriethoxysilane (APTEs)-treated substrate obtained in this method was continuous and defect-free with the crystal orientation suitable for gas transportation, while the membrane grown on a bare substrate was loosely packed with the unfavorable crystal orientation. Kgm-OEt membrane also shows better H₂/CO₂ separation performance than polymer membranes.

Chapter 5 describes the fabrication of the heterobilayer membrane strategy using two isostructural MOFs. First, a MOF Kgm-OPr with fast nucleation rate was fabricated as a seed layer on an Al₂O₃ substrate, then the layer of Kgm-OMe or Kgm-H, which is

isostructural to Kgm-OPr, was prepared on the Kgm-OPr seed layer through secondary growth. In this way, the high-quality membranes which selectively permeate CO₂ over N₂, CH₄, and C₂H₄ were obtained, although all three MOFs did not form dense membranes when they were used alone. Our result would contribute to the expansion of the family of MOFs applicable to membranes for molecular separation.

Chapter 6 describes the conclusions of this thesis, including the synthesis of MOF crystals for the selective adsorption for gas and the fabrication of MOF membranes for gas separation.