

Functionalization of MOFs for Enhancing Carbon Dioxide Adsorption Ability under Atmospheric Conditions

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(大気条件下における二酸化炭素吸着能向上に向けた MOF の機能化)

区 分 : 甲

論 文 内 容 の 要 旨

Since the Industrial Revolution, the consumption of fossil fuels and human activities have led to continuously rising atmospheric carbon dioxide (CO₂) concentration, now far exceeding those of 200 years ago and driving unprecedented global climate change. As one of the greenhouse gases, CO₂ is the principal contributor to global warming, and its accumulation has already resulted in severe and widespread environmental impacts, including accelerated glacier melting, extreme weather events, ecosystem degradation, and disruptions to global hydrological and carbon cycles. Current atmospheric CO₂ concentration has surpassed 440 ppm and is projected to exceed 500 ppm by the 2050s under current energy demand scenarios. Although renewable and clean energy technologies are increasingly applied, they cannot resolve the cumulative effect of CO₂ already emitted into the atmosphere, making effective CO₂ capture and removal technologies indispensable components of global climate mitigation efforts.

This thesis focused on direct air capture (DAC) of CO₂ under atmospheric conditions and investigates the functional enhancement of metal-organic frameworks (MOFs), as a material for this purpose. This thesis consists of the following three chapters; Chapter 1: A Review of Recent Porous Materials for Efficient Direct Air Capture of CO₂, Chapter 2: An Efficient Synthesis of Novel Amine Modified BDC Linker for Functionalization of MIL-101(Cr) and Chapter 3: Enhancement of CO₂ Adsorption Ability by Amine Appending of Amine Functionalized MIL-101(Cr).

Chapter 1: A Review of Recent Porous Materials for Efficient Direct Air Capture of CO₂

Conventional industrial CO₂ capture relies on amine-based chemisorption, which is effective at high CO₂ concentrations but limited by high regeneration energy, thermal instability, and poor moisture tolerance. Direct air capture (DAC) has therefore emerged as a promising approach to remove CO₂ from ambient air, requiring adsorbents with high CO₂ selectivity, good stability under humid conditions, and low regeneration energy. Among various porous materials explored for DAC, metal-organic frameworks (MOFs) have attracted significant attention due to their high surface areas, well-defined pore structures, and tunable chemical functionalities. Through functionalization of the framework and open metal site engineering, MOFs enable enhanced CO₂ affinity at low concentrations, making them a promising platform for DAC.

Chapter 2: An Efficient Synthesis of Novel Amine Modified BDC Linker for Functionalization of MIL-101(Cr)

A concise and reproducible synthetic route for amine-functionalized terephthalate (BDC) linkers is developed, and their incorporation into MIL-101(Cr) (1), a metal-organic framework (MOF) with an appropriate pore structure and framework, is systematically examined. Amino-alkyl side chains with controlled lengths were covalently introduced onto the linker (1,4-benzenedicarboxylic acid: H₂BDC). Because the modified H₂BDC (H₂L) formed MOF with poor crystallinity, a mixed-linker (solid-solution) strategy was employed, enabling the formation of highly crystalline MIL-101(Cr) by tuning the ratio of pristine and modified H₂BDC. Structural characterization confirms retention of the MIL-101 framework and successful incorporation of H₂L. While amine functionalization of the framework enhances water affinity, CO₂ uptake under DAC-relevant conditions shows no significant improvement, likely due to pore blocking and amine passivation. This study provides a robust synthetic basis and practical insights for further optimization of MIL-101(Cr)-based CO₂ capture materials.

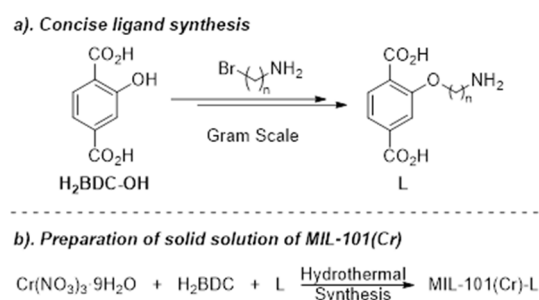


Figure 1. a. Synthesis of modified ligand; b. Synthesis of solid solution

Chapter 3: Enhancement of CO₂ Adsorption Ability by Amine Appending of Amine Functionalized MIL-101(Cr)

The enhancement of CO₂ adsorption in amine-functionalized MIL-101(Cr) was investigated by post-synthetic amine appending. Small amine molecules were introduced into solid-solution MIL-101(Cr) frameworks to increase CO₂ affinity while preserving structural integrity. Aminoguanidine shows limited improvement in CO₂ uptake due to amine passivation and restricted accessibility. In contrast, appending 1,4-butyldiamine (BDA) significantly enhanced CO₂ adsorption, especially in the low-pressure region relevant to direct air capture. The BDA-appended MIL-101(Cr) with 50% of H₂L1 (1-50%L1_BDA0.9) exhibits markedly improved CO₂ uptake compared with pristine and non-appended materials, despite a reduction in surface area. Spectroscopic and thermal analyses indicate reversible amine-CO₂ adduct formation through CO₂ adsorption/desorption, and cyclic tests confirm stable low-pressure CO₂ adsorption. These results demonstrate the effectiveness of diamine appending in large-pore MIL-101(Cr) systems for improving CO₂ adsorption ability.

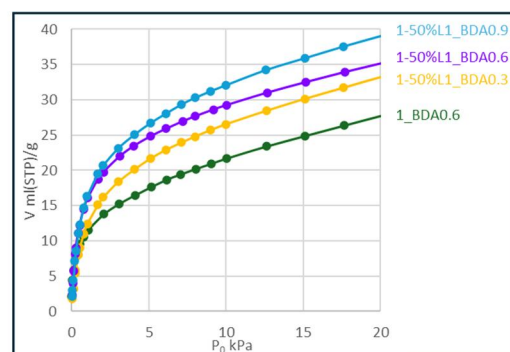


Figure 2. CO₂ Adsorption of amine-appended 1-50%L1 in low-pressure