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## 科学研究費助成事業 研究成果報告書



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研究課題名（和文）A novel core@shell structured dual faceted MOF-based sorbent for mega scale CO<sub>2</sub> capture研究課題名（英文）A novel core@shell structured dual faceted MOF-based sorbent for mega scale CO<sub>2</sub> capture

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研究成果の概要（和文）：裸の -CD-MOFの大きな孔径は、効率的なCO<sub>2</sub>収着には不向きである。これは、細孔径が大きくなるにつれてファンデルワールス力が減少するため、その結果、収着挙動が不利になる。本研究では、最適なCO<sub>2</sub>収着を達成するために合成パラメータを最適化し、MOFの気孔率を調整することを目的とした。最適化されたK-CD MOFは、273Kで4.1mmol/gのCO<sub>2</sub>収着を達成しました。合成パラメータを調整することで、より大きな孔を狭めることができましたが、申請者は、K-CD MOFのはるかに大きな表面はまだ未開拓であると信じています。

研究成果の学術的意義や社会的意義

The project resulted a CO<sub>2</sub> sorbent with high surface area and high sorption capacity, using green and sustainable precursor materials. It could advance the field of carbon capture and contribute to sustainable solutions for mitigating CO<sub>2</sub> emissions and promoting environmentally friendly practices.

研究成果の概要（英文）：The large pore size of bare -CD-MOFs is not conducive to efficient CO<sub>2</sub> sorption. This is due to the decrease in Van der Waals forces as the pore size increases, resulting in less favorable sorption behavior. This study aimed to optimize synthesis parameters to achieve optimum CO<sub>2</sub> sorption and tune the porosity of the MOFs. The optimized K-CD MOF achieved a CO<sub>2</sub> sorption of 4.1 mmol/g at 273 K. While applicant made progress in narrowing the larger pores by regulating synthesis parameters, applicant still believes that the much larger surface of K-CD MOF is yet to be explored.

研究分野：Material development for mitigating CO<sub>2</sub> emissionキーワード：Metal Organic Framework Cyclodextrin ligands Regenerable CO<sub>2</sub> sorbent Direct Air Capture P  
EI activation

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## 1. 研究開始当初の背景

Global warming has emerged as a critical issue in the 21<sup>st</sup> century, and the primary culprit behind this phenomenon is the emission of anthropogenic greenhouse gases (GHGs), particularly CO<sub>2</sub>. The applicant's previous research primarily focused on harnessing GHGs for green hydrogen energy production<sup>1</sup>. However, the applicant now acknowledges that addressing global warming requires a dual approach: reducing GHG emissions and capturing anthropogenic GHGs for value-added applications.

While considerable efforts have been made to explore materials like activated carbon, polymers, MOFs, and zeolites for CO<sub>2</sub> capture, their common implementation is hampered by challenges related to cost, stability, efficiency, and regeneration. Consequently, the establishment of an economically viable and portable CO<sub>2</sub> sorption device remains undeveloped.

Recognizing the need for a breakthrough, the applicant proposes a paradigm shift in CO<sub>2</sub> capture technology by advocating the development of highly fictionalized materials specifically designed for direct CO<sub>2</sub> capture applications, with their exceptional properties and tailored sorption capabilities, hold the potential to simplify the sorption process significantly. By using intensively fictionalized materials, the efficiency of conventional CO<sub>2</sub> capture technology can be dramatically improved, overcoming the limitations of existing approaches.

In conjunction with this concept, the applicant emphasizes the importance of integrating state-of-the-art, cost-effective Direct Air Capture (DAC) technology on a large scale. Combining intensively fictionalized materials with DAC technology will revolutionize CO<sub>2</sub> capture, making it more efficient, practical, and accessible for widespread implementation.

1. J Taiwan Inst Chem E, 61, 247–260

## 2. 研究の目的

The project aims to propose an efficient sorbent for capturing CO<sub>2</sub> using MOFs that can be regenerated, with the intention of contributing to the development of a portable CO<sub>2</sub> capture device. The specific objectives of the project are as follows: i) optimizing the structure of cyclodextrin (CD)-based MOFs to have suitable surface characteristics for effective CO<sub>2</sub> sorption, ii) applying a coating of graphene oxide (GO) and polymer onto the MOFs, and iii) evaluating the sorption and regeneration capabilities of the CO<sub>2</sub> sorbent.

MOFs are generally a porous and crystalline material, possess exceptional internal surface areas of approximately 7800 m<sup>2</sup>/g.<sup>2</sup> Moreover, the surface properties of the MOF pores can be easily adjusted due to their modular design, allowing for the incorporation of different chemical moieties, such as amines, to achieve desired chemical features. These advantageous characteristics make MOFs highly promising for CO<sub>2</sub> capture research.

2. Kenji Sumida et al. 2016, Chem. Rev. 2012, 112, 724–781

### 3. 研究の方法

The research was conducted in two stages:

#### **Stage 1:** CD MOF Synthesis, Parameter Optimization, and CO<sub>2</sub> Capture Studies

The objective of this stage was to develop a well-structured CD MOF with a surface area of approximately 2000 m<sup>2</sup>/g. The Vapor Diffusion Crystallization method was utilized in a newly designed diffusion chamber, enabling the synthesis of a large quantity of MOF. Pretreatment with high power probe sonicator (VCX 750) eases the homogenous synthesis. The synthesis parameters were optimized to investigate the proper coordination between the CD ligand and the metal, resulting in the formation of three-dimensional body-centered-cubic MOF structures with optimal CO<sub>2</sub> sorption properties. The thermal and chemical stability of the prepared materials was assessed using techniques such as TGA, powder XRD, SEM, and surface characteristic analysis (BET). The CO<sub>2</sub> sorption capacity was studied using a BET sorption device.

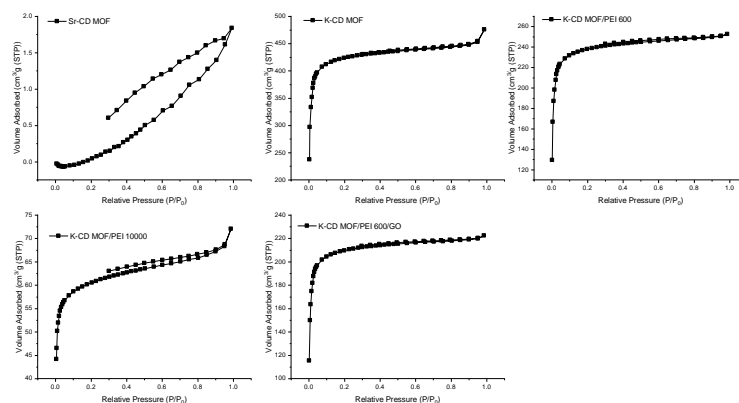
#### **Stage 2:** GO-PEI Coating on CD MOF and CO<sub>2</sub> Capture

The objective of this stage was to apply a protective GO-PEI coating on the CD MOF. GO was used to create a molecular-sieving channel within the PEI structure. The polarized center of GO, with its hydroxy, carbonyl, and carboxy groups, facilitates the generation of hydrogen bonding. Different molecular weights of PEI (ranging from 600 to 10000) were experimented with to investigate their diffusion into the CD MOF materials. All the characterization and evaluation methods employed in Stage 1 were also utilized in Stage 2.

### 4. 研究成果

$\gamma$ -cyclodextrins ( $\gamma$ -CD) are cyclic oligosaccharides composed of eight D-glucopyranose units, primarily derived from biomass. They are characterized by a high density of hydroxyl groups per unit area. Given their unique chemical composition,  $\gamma$ -CDs are considered suitable organic small molecules for the synthesis of carbon-based materials. In this study, CD-MOF crystals were synthesized using a simple reaction diffusion method. Two different metals and various methanol diffusion methods (i. vapor diffusion at 45 °C and ii. Addition of methanol at controlled flow) and rates were analyzed to optimize parameters for achieving the highest CO<sub>2</sub> adsorption capacity.

Irrespective of the time-consuming vapor diffusion, the addition of methanol at a rate of 25 mL/h yielded the highest BET surface area of 1717 m<sup>2</sup>/g, consequently exhibiting the highest CO<sub>2</sub> sorption capacity among the investigated materials. Conversely, the Sr-based MOFs displayed an inability to absorb gases of larger size, such as N<sub>2</sub>. This limitation can be attributed to the small diameter of the solvent-accessible voids in Sr-CD MOF. As a result, Sr-CD MOF did not consider for further investigation.



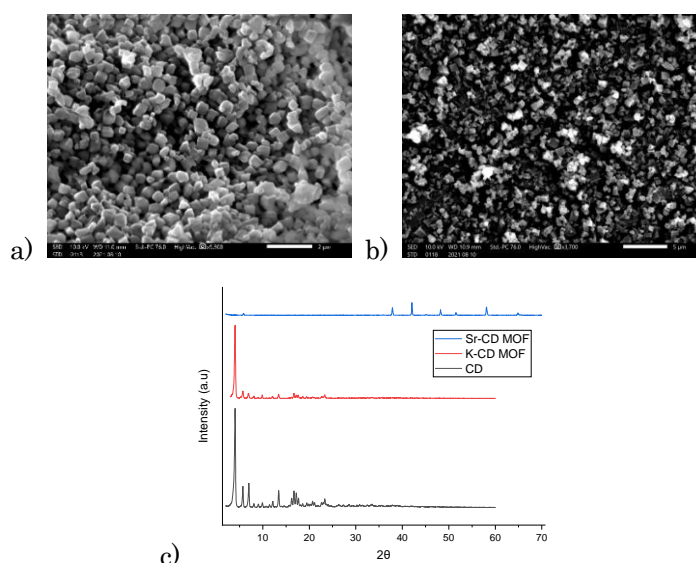
**Fig. 1** N<sub>2</sub> adsorption-desorption isotherms for the CD-based MOFs at 77 K.

The mesoporous feature of K-CD MOF was confirmed by Type IV Brunauer–Emmett–Teller (BET)sorption isotherms shown in Fig. 1. The BET analysis indicated the synthesis of PEI and GO incorporation with CD-MOF results in the blockage of pores and hence, decreased the pore availability from 1717 m<sup>2</sup>g<sup>-1</sup> in CD-MOF to the level of 240 m<sup>2</sup>g<sup>-1</sup> in K-CD MOF/PEI 10000 (Table 1). At the same time, the presence of GO slightly improved the BET surface area to 1388 m<sup>2</sup>g<sup>-1</sup> from 966 m<sup>2</sup>g<sup>-1</sup> that might be due to the additional porous contribution from GO.

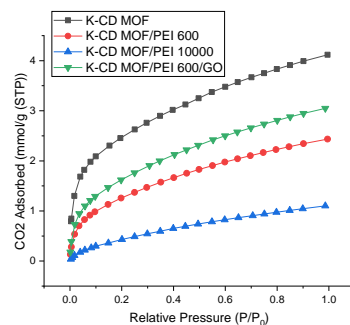
**Table 1** BET areas and CO<sub>2</sub> sorption capacity of MOFs

Sample	Surface Area (m <sup>2</sup> /g)	CO <sub>2</sub> sorption capacity (mmol/g)
Sr-CD MOF	--	--
K-CD MOF	1717.1	4.1
K-CD MOF/PEI 600	966.3	2.4
K-CD MOF/PEI 10000	240.1	1.1
K-CD MOF/PEI 600/GO	1388.084	3.0

The cubical morphology of CD-MOF crystals was observed by scanning electron microscopy (SEM) in Fig. 2a. In addition, XRD patterns in Fig. 2c confirmed the crystal structure of K-CD-MOF by the typical γ-CD-MOF peaks at 2θ values of 4° and 17°.



**Fig.2** SEM images of a) K-CD MOF, b) Sr-CD MOF, and their c) XRD patterns.



**Fig. 3** CO<sub>2</sub> adsorption isotherms of the K-CD MOFs at 273 K.

The large pore size of bare  $\gamma$ -CD-MOFs is not conducive to efficient CO<sub>2</sub> sorption. This is due to the decrease in Van der Waals forces as the pore size increases, resulting in less favorable sorption behavior. This study aimed to optimize synthesis parameters to achieve optimum CO<sub>2</sub> sorption and tune the porosity of the MOFs. As shown in Fig 3, the optimized K-CD MOF achieved a CO<sub>2</sub> sorption capacity of 4.1 mmol/g at 273 K. To further enhance CO<sub>2</sub> sorption, the use of PEI as an amino functional group promoter was considered. However, contrary to expectations, impregnation with large polymeric PEI molecules reduced or blocked the pores of the K-CD MOF, resulting in lower CO<sub>2</sub> sorption. The introduction of PEI 600 reduced the CO<sub>2</sub> sorption capacity of K-CD-MOF to 2.4 mmol/g at 1.0 atm. This capacity significantly declined to 1.1 mmol/g when coordinated with PEI 10000.

In addition to different sizes of PEI molecules, GO was also experimented with in combination with the best PEI-CD MOF. The presence of GO slightly improved the sorption capacity, which may be attributed to the capture of CO<sub>2</sub> in the pores of GO. However, the sorption capacity was still much lower than that of the original K-CD MOF. Future direction:

This work has successfully demonstrated the potential to tune the porosity of K-CD MOF through the optimization of synthesis parameters. While applicant made progress in narrowing the larger pores by regulating synthesis parameters, applicant still believes that the much larger surface of K-CD MOF is yet to be explored. Enhancing the Van der Waals attraction forces between CO<sub>2</sub> and the MOF surfaces, further improvements are necessary. Applicant's findings suggest that the utilization of PEI and GO for functionalization did not yield the desired outcomes. Therefore, more effective functionalization methods and focus on alternative materials and approaches for optimizing the large surface area of K-CD MOF. By addressing these challenges, we can further advance the field and develop a highly efficient CO<sub>2</sub> sorbents based on K-CD MOF.

5 . 主な発表論文等

〔雑誌論文〕 計0件

〔学会発表〕 計0件

〔図書〕 計0件

〔産業財産権〕

〔その他〕

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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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