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LITERATURE STUDY ON THE SCREENING OF AI-MOFS POROUS MATERIAL FOR DIMETHYL ETHER (DME) GAS PURIFICATION

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Abstract

Renewable dimethyl ether (DME) gas is expected to replace LPG due to the high demand for domestic fuel gas and the shortage of LPG supply. DME properties are closely identical to that of LPG. DME gas can be produced directly and indirectly from various sources, including coal, natural gas, and other readily available biomass. The synthetic DME gas produces by-product gases, mainly CO₂. Thus, purification of DME is needed. Al-MOF is proposed to be one of many candidates for CO₂ gas absorption. A literature review was conducted in this study to screen some potential Al-MOF based on scientific peer-reviewed articles published in the last decade. The data were gathered by developing research questions using PICO(S) analysis. Particularly, this study highlights the effect of ligands on pore sizes, the effect of the amine group on absorption capacity, and the thermal stability of Al-MOF. This preliminary study finds several potential Al-MOFs suitable for the task. Based on this study, the NH2-MIL-53(Al) and NH2-MIL-101(Al) are highlighted as having the potency to be used in the DME purification process. However, further studies, including evidence-based gas separation experiments, are compulsory and need to be performed before this Al-MOF is applied to the DME purification process on a bigger scale.

Keywords: Aluminum; CO2; Separation; DME; MOF

1. INTRODUCTION

The Indonesian Ministry of Energy and Mineral Resources (ESDM) targets to replace the consumption of liquid petroleum gas (LPG) with dimethyl ether (DME) (ESDM, 2020). This is due to the increasing demand for LPG supply, which reaches 7 tons per year, of which 70% is imported and expected to rise by 17.4 tons by 2050 (Yuliarita et al., 2020; Murti et al., 2021). The DME is currently one of the alternative fuels to replace LPG (Anggarani et al., 2014), targeted to reduce the increasing dependence on LPG imports in Indonesia (Ramadhani et al., 2020). It is a better option for fuel gas, as it emits less CO and NOx in the exhaust gases and has physical properties similar to LPG. Consequently, it can be used as an LPG substitute (Saravanan et al., 2017; Panigrahy and Mishra, 2018). DME can be produced from various sources of natural gas, coal, or other biomass abundantly available in nature (Seddon, 2011; Yuliarita et al., 2020).

DME is an organic gas (C_2H_6O) with a boiling point of -24°C, close to LPG's -30°C. It is a gas at room

temperature (Kurnia'Arifushidqi et al., 2021). It has a very high critical temperature (400°K) and can be liquefied at room temperature. Its density in the liquid phase is close to LPG (Murti et al., 2021). It has a molecular weight of 46.684 g mol⁻¹, a critical pressure of 54 bar, a critical temperature of 401°K, a boiling point of 249°K at 1 atm, a density of 0.663 g.cm⁻³ at 298°K, a viscosity of 0.15 cP or 0.15 kg.m.s⁻¹, equivalent to the viscosity of propane and butane (LPG), and surface tension of 11.731 dyne.cm⁻¹ (Mohan et al., 2017). The DME has a diameter of around 0.62 nm (Omojola et al., 2020).

 $CO + 2H_2 \rightleftharpoons CH_3OH \qquad \Delta H^\circ = -90.6 \text{ kJ/mol} \quad (eq. 1)$ $2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O \Delta H^\circ = -23.5 \text{ kJ/mol} \quad (eq. 2)$

Direct synthesis of DME: $3CO + 3H_2 \rightleftharpoons CH_3OCH_3 + CO_2$

The DME synthesis process consists of the conversion of natural gas hydrocarbons into synthetic

gases (CO, CO₂, and H₂O), and the second stage can be completed either indirectly via methanol synthesis or directly (Mevawala et al., 2017; Kurnia'Arifushidqi et al., 2021; Merkouri et al., 2022). The dehydration of methanol produced from syngas is the foundation of the industry's well-developed DME production process. In the first phase, syngas is turned into methanol (eq. 1), which is then transformed into DME (eq. 2) in a subsequent reactor (Mota, 2021). However, DME products still mix with impurities such as CO₂. So, it needs purification, for example gas adsorption using porous materials.

Porous materials such as silica, zeolite, and metalorganic frameworks (MOFs) can be explored as candidates for the purification of DME gas, particularly by separating the CO₂ by-products. However, MOFs are more promising because Post-synthetic Modification (PSM) is easier for their ligands and metal ions, so the gas adsorption ability can be enhanced as desired (Yin et al., 2022). Metal-organic frameworks (MOFs), a type of solid-state material, have emerged as modular and functional porous materials with the potential to address a wide range of long-term energy and environmental concerns regarding sustainability (Alezi et al., 2015; Wang et al., 2017; Towsif Abtab et al., 2018). MOFs have some structural advantages over standard porous materials like activated carbons and zeolites, like high porosity, large surface area, variable pore size and geometry, and functionalized pore surface (Li et al., 2019; Lin et al., 2020; Kumari et al., 2021). Their structure can be modified according to the expected applications (Fan et al., 2021).

MOFs are one of many synthetic porous materials consisting of metal ions linked together by organic linking ligands with strong bonds that has a high surface area (Tian et al., 2016; Gulati and Kakkar, 2018; Adegoke and Maxakato, 2021). MOFs have a specific surface area of 1000 to 10.000 m².g⁻¹, far exceeding that of most commonly used porous materials such as zeolite and carbon (J. Li et al., 2019; Fan et al., 2021; Elsayed et al., 2021). Nevertheless, most MOFs are made from divalent cations, which can produce MOFs with high crystallinity, but the instability of the divalent cations of the MOFs can limit their application, especially if they are used as an adsorbent (Wu et al., 2020). Therefore, one way to overcome this problem is to choose a larger metal cation charge because, from a thermodynamic point of view, a higher cation charge will lead to a stronger metal-ligand bond, which is the main determining factor for the thermal stability of the MOFs (Wu et al., 2020).

Aluminum has higher positive charge than divalent metals (Wu et al., 2020). The Al-MOF production process is relatively easy and has a high yield, which can be carried out by solvothermal or hydrothermal methods (Adegoke & Maxakato, 2021). It can be prepared at relatively low temperatures and raw material costs (J. Li et al., 2021; Z. Liu et al., 2021). In addition, the availability of aluminum in Indonesia is abundant (Kementerian ESDM RI - Booklet, 2020). It can also be obtained from the recycling process to be sustainable for MOFs (Joshi et al., 2019). The aluminum recycling process can usually be done by casting using sand-casting to produce new recycled aluminum material (Fasya & Iskandar, 2015). The Al-MOFs types have high porosity, like the CAU-10-NH₂ used for acetylene absorption (C_2H_2), a nonpolar organic compound almost the same size as DME. It absorbs 4.3 mmol cm⁻³ at a pressure of 1 bar and 298°K and even enhances to 4.1 mmol cm⁻³ at 0.5 bar or reaches 95%. The amine group of the ligand influences the absorption capacity (Zhang et al., 2022).

A systematic review was conducted to reveal the material characteristics of Al-MOFs that have the potential to purify DME. Furthermore, the results of this study are expected to provide added value for aluminum processing and provide scientific references to the government's policy plan to convert LPG to DME commercially for low-emission gas fuels.

This study gathered the data by developing research questions using PICO(S) analysis (Table 1.) to combine previous research findings with specific criteria specifications.

Table 1. PICO(S) analysis					
PICO(S)	Analysis				
Population	Al-MOFs				
Intervention	CO ₂ absorption or separation to Al- MOF				
Comparison	DME absorption to Al-MOF				
Outcome	Ligands, absorption capacity, conditions, pore sizes				
Study type	Oualitative				

Preferred Reporting Items for Systematic Review and Meta-analyses Statement (PRISMA) guidelines were also used to conduct the study. Indonesian and English keywords were used for the literature searches on international database sources such as ScienceDirect, ACS Publications, Proquest, SpringerLink, Royal Chemistry Society, and Wiley Online Library with keywords: "CO₂ Absorption" or "CO₂ Separation" or "CO₂ Purification" and "Porous Materials" and "Al-MOF".

The inclusion studies of abstract and full-text selection was done using the Rayyan AI application. To be considered for inclusion, the study had to meet the following criteria: 1) Recent studies (within the last ten years; 2) Primary research article; 3) Metal-Organic Frameworks studies; 4) Pore size, absorption capacity, ligands, conditions, regeneration, yields, and pore sizes.

Data was collected and inputted in a table from each study. The following information was included in the table: pore size, absorption capacity, ligands, conditions, regeneration, yields, and pore sizes. The data were then tabulated in the form of a PRISMA diagram chart (Figure 1).

In order to find as much relevant research as feasible for a systematic review, it is important to map

out the sensitivity and precision of the studies (Table 2) as follow:

Sensitivity:
$$\frac{A}{A+B}$$
; Precision: $\frac{A}{A+C}$

 Table 2. The sensitivity and precision of screening

 study

	Study	
	Unidentified	
Relevant	A (n=22)	B (n=1354)
Irrelevant	C (n=58)	D (n=0)

Sensitivity: $\frac{A}{A+B} = \frac{22}{22+1354} = 1.59\%$ Precision: $\frac{A}{A+C} = \frac{22}{22+58} = 27.5\%$ Note:

- Identified Relevant (A): appropriate study outcomes/population and outcome.
- Unidentified Relevant (B): not selected/limited access/fee access.
- Irrelevant Identified (C): studies under 10 years old and or wrong outcome
- Irrelevant Unidentified (D): not population

The primary data were then evaluated for completeness using these criteria: ligands, absorption capacity, conditions, and pore sizes (Table 3). Moreover, following the Scopus standards, the validity of the journal's quality was evaluated using the primary data completeness of outcomes (Table 4.).

Table 3. Identification of primary data for inclusion studies based on completeness of outcomes (*)

Outcomes	Complete	Incomplete
(n=22)	9	13
%	40.9	59.1

*J	Ligands,	Absorption	Capacity,	Conditions,	Pore Sizes

Table 4. The	Scopus s	tandards	s of prin	hary data
Casmus				

Standard	Q1	Q2	Q3	Q4
n=22	17	4	0	1

All these parameters were used to identify and discuss the possible candidates of Al-MOFs for CO_2 separation, based on: (1) the effect of ligands on pore sizes, (2) the effect of the amine group of the ligand on the absorption capacity, (3) the thermal stability of Al-MOF.

2. RESULTS AND DISCUSSION

2.1 Data Collection of Inclusion Study

The PICO(S) method was performed prior to the search of studies by database journals with the goal of identifying the research criteria to be used. Based on



Figure 1. PRISMA diagram chart

selected keywords, 1492 papers from the last ten years (2012-2022) from ScienceDirect, ACS, Proquest, SpringerLink, ACS Publications, RSC Publications, and Wiley Online Publications were obtained. Among those 1492 papers, only 138 papers have related content (based on title and abstract) with the objective of this review. Moreover, 58 articles were also excluded because the authors do not have an open access permit. Thus, the exclusion resulted in 80 articles for full-text screening. Based on the information availability of ligand's type, absorption capacity, adsorption conditions, and pore sizes in each paper, only 22 papers are included in this review.

2.2 Data Processing

Based on Table 5, the increasing sensitivity of study inclusion will reduce precision. Consequently, the resulting studies will have many irrelevant studies. Therefore, higher-quality inclusion investigations can be achieved by maximizing sensitivity while retaining the precision of search studies (Higgins et al., 2022). In this systematic review, the results of primary data are concluded based on completeness, with findings that the Scopus standard of the Al-MOFs characteristics from primary data sets are presented in the Table 6.

n = 138					In	clusio	on=22
	Primary	· · · · ·	Valid	ity (*))	Outcome	
Sensitivity	Precision	Data (n=22)	Q1	Q2	Q3	Q4	(n=9)
1.59%	27.5%	100%	17	4	0	1	40.9%

	Table 6. Detail information of selected Al-MOFs (*)								
No	Al-MOFs	Ligands	Absorption Capacity (mmol/g)	Condition (K/Bar)	Pore Size (nm)	Regeneration (**)	Yield	Ref	
1	Al-PMOF(Co)	Porphine- 5,10,15,20- tetrakis (benzoic acid)	3.32	273/1	0.5-1	NI	41 %	(Shang et al., 2022)	
2	Al-FUM	Fumaric acid	2.1	303/1	NI	75-83 %	NI	(Coelho et al., 2016)	
3	MIL-96(Al)	Benzene tricarboxylic acid	2	303/1	NI	20%	NI	(Benoit et al., 2013)	
		•	3.84	303/1-10	0.9	NI	NI	(Abedini et al., 2014)	
	MIL-53(Al)	MIL-53(Al)	Benzene dicarboxylic acid	2.36	298/1	1.42	9x	NI	(Panda et al., 2020)
				2.3	303/1	NI	86-99.6%	NI	(Ferreira et al., 2015)
4				2.16	298/1	0.7-1	NI	48- 91	(Sun et al., 2022)
			2.10	298/1	1.41	8x	NI	(Panda et al., 2020)	
			2.02	298/5	0.7- 0.8	NI	NI	(Ahmadi Feijani et al., 2015)	
		14	14.3	303/10	NI	NI	NI	(X. Y. Chen et al., 2012)	
	NH2-MIL-	2-aminobenz	4.3	303/3.5	NI	NI	NI	(D. Li et al., 2021)	
5	53(Al)	ene-1,4-dica rboxylic acid	3.75	303/1-10	0.83	NI	NI	(Abedini et al., 2014)	
			2.65	298/5	NI	13x	NI	(Zhu et al., 2016)	
			2.33	308/10	NI	NI	NI	(Tien-Binh et al.,	

		• • • •						
		-		<u>.</u>			-	2015)
								(Sabetghad
			1.86	298/9	NI	NI	NI	am et al.,
		-		÷	· · · · ·			2016)
								(Ahmadi
			1.85	298/5	NI	NI	NI	Feijani et
		-		÷	· · ·			al., 2015)
								(Rodenas,
								van Dalen,
			1.56	308/3	NI	NI	NI	García-Pér
								ez, et al.,
		-		·	· · · ·			2014a)
			1.23	298/5	NI	NI	NI	(Feijani et
		-		· ·	· · ·			al., 2015)
								(Rodenas,
			1.06	200/2	NI	NI	NI	Van Dalen,
			1.06	308/3	IN1	111	111	Garcia-Per
								2014_{2}
		• • •		29815-	· · · ·			(Babar et
			2.9	348 15/1	NI	NI	NI	al 2021)
		-		010.10/1	· · ·		÷	(Rodenas
								van Dalen.
		2-aminobenz	1.70	308/3	NI	NI	NI	Serra-
	NH ₂ -MIL-	ene-1.4-dica						Crespo, et
6	101(AI)	rboxylic acid						al., 2014b)
		-		-	· · ·		·	(Rodenas,
								van Dalen,
			1.11	308/3	NI	NI	NI	Serra-
								Crespo, et
								al., 2014b)
		Benzene	2 2 4	373/1	NI	NI	NI	(Dong et
7	MIL-68(Al)	dicarboxylic		0,0,1				al., 2016)
		acid	0.87	308/3	NI	II NI		(Seoane et
				,			95	al., 2013)
0	CALL 10 NUL	5- aminoiconht	2 5	200/1	NI	NI	NI	(Zhang et
8	CAU-10-NH2	ammoisopht balic acid	2.5	298/1	INI	INI	111	al., -2022)
		m bonzono						
9	САЦ-10-Н	dicarboxylat	2	298/1	0.48-	NI	NI	(Zhang et
,	CH0-10-11	e uicai boxyiat	2	270/1	0.6	141	111	al., 2022)
		č	13.17	273/9.5	1.57	NI	NI	
		-	12.76	273/9.5	1.56	NI	NI	-
		-	3.24	273/1	1.53	NI	NI	-
		Benzene	3.15	273/1	1.57	NI	NI	
	MIL-53 (Al)-	dicarboxylic	3.02	273/1	1.56	NI	NI	(Abid et al.,
10	Mn	acid	2.92	273/1	1.54	NI	NI	2021)
		-	2.84	298/1	1,53	NI	NI	-
		-	2.83	298/1	1.57	NI	NI	-
		-	2.67	298/1	1.56	NI	NI	-
		-	2.58	298/1	1.54	NI	NI	-
643								

(*) sorted in order of high to low absorption capacity; (**) in percentage or in cycles NI = No information

2.3 Discussion

2.3.1 Effect of ligands on pore sizes

The size of DME is around 6 Å (Omojola et al., 2020). However, the main target for DME purification is the separation of CO₂, which traps CO₂ in the pore. Herein, the pore sizes of Al-MOFs are screened based on the similarity to the size diameter of CO₂, which

ranges from 3.3 Å (Ahmadi et al., 2015; Feijani et al., 2015). The pore size used to trap CO_2 is between 3-5 Å. Hence, codes A and I can be recommended for CO_2 gas absorption (Table 7).

Moreover, the pore size can be altered by modifying the ligands. A rigid or flexible ligand as a linker unit governs the framework stability. Aliphatic linkers are more flexible than the aromatic ones. Thus, Al-MOFs formed by aliphatic linkers are commonly less stable and tend to collapse due to desolvation, although in some cases, interpenetration may form by the flexible aliphatic linkers and hold the structure stronger. Thus, the code B (Table 7) is unfavorable for Al-MOFs candidates.

Table	7. Some candida	ates of Al-MOF fo	or DME	purification	(based on	CO ₂ se	paratior	1 ability))
									-

CODE Al-MOFs		Al-MOFs	Ligands	Absorption Capacity (mmol/g)	Condition (K/Bar)	Pore Size (nm)	
_	Α	Al-PMOF(Co)	Porphine-5,10,15,20- tetrakis (benzoic acid)	3.32	273/1	0.5-1	
_	В	Al-FUM	Fumaric acid	2.1	303/1	NI	
_	С	MIL-96(Al)	Benzene tricarboxylic acid	2	303/1	NI	
				3.84	303/1-10	0.9	
				2.36	298/1	1.42	
		MIL-53(AI)	Benzene dicarboxylic acid	2.3	303/1	NI	
	D	MIL-55(AI)	Denzene ultar boxyne aciu	2.16	298/1	0.7-1	
				2.10	298/1	1.41	
_				2.02	298/5	0.7-0.8	
				14.3	303/10	NI	
		NH ₂ -MIL-	2-aminobenzene-1,4-dicarb	4.3	303/3.5	NI	
	Е	53(Al)	oxylic acid	3.75	303/1-10	0.83	
				2.65	298/5	NI	
_		-		2.33	308/10	NI	
	F	NH2-MIL- 101(Al)	2-aminobenzene-1,4-dicarb oxylic acid	2.9	298.15- 348.15/1	NI	
-	G	MIL-68(Al)	Benzene dicarboxylic acid	2.24	373/1	NI	
-	Н	CAU-10-NH ₂	5-aminoisophthalic acid	2.5	298/1	NI	
	Ι	CAU-10-H	<i>m</i> - benzene dicarboxylate	2	298/1	0.48-0.6	
-		MIL-53 (Al)- Mn Benze		13.17	273/9.5	1.57	
					12.76	273/9.5	1.56
				3.24	273/1	1,53	
				3.15	273/1	1.57	
			Benzene dicarboxylic acid	3.02	273/1	1.56	
	J		5	2.92	273/1	1.54	
				2.84	298/1	1,53	
				2.83	298/1	1.57	
				2.67	298/1	1.56	
				2.58	298/1	1.54	
-		(*) sorted by higher a NI = No information	absorption capacity. 1	2.00	270/1	1.01	
нс).	o ⊥	отон	0 NH ₂ 0			
	\uparrow	_OH			и но Ц	L	
	ö		H ₂ N 2-amin	obenzene-1,4-dicar	boxylic	$\bigcirc \neg \bigcirc$	
	Fumar	ic acid	5-aminoisophthalic acid	acid			
	0	он	OH	OH	но	J& E	
F	HO L		HO		Por tetra	phine-5,10,15,20- akis (benzoic acid)	

p-benzene dicarboxylic acid *m*-benzene dicarboxylic acid

Benzene tricarboxylic acid

Figure 2. Some organic precursors used in the Al-MOFs as the linkers

2.3.2 Effect of amine group on absorption capacity

As shown in Table 7, the Al-MOF codes A, C, D, E, F, G, H, I, and J are possible for CO_2 separation. Another factor is introduced to gain a more selective adsorbent for DME purification, namely the absorption capacity. Only a few candidates mentioned in Table 7 fulfill this criterion, summarized in Table 8 (Codes E, F, and H).

Figure 3 indicates that an amine group, as part of the ligand, enhances CO₂ separation. This is because the amine groups can form hydrogen bond with the oxygen of the CO₂ molecule $(-NH^{\delta+\dots-\delta}O=C=O^{\delta-\dots+\delta}HN-$). Each amine group on the ligand can bind two CO₂ $(0=C=0^{\delta-\dots+\delta}H-N-H^{\delta+\dots-\delta}O=C=0)$ molecules depending on the structure of the ligand and the crystal packing (Figure 4: Figure 5). In other words, the CO₂ molecules are absorbed in the pores due to the additional interaction of the amine group, which eventually enhances the CO₂ absorption capacity. Not only the amine group, when utilizing specific organic linkers, variations of active sites in the pore may also be modified, for example, hydroxyl (-OH) groups. The high electronegativity effect of the O atom of the hydroxyl group (compared to the N atom of amine) may increase the intermolecular interaction between the hydroxyl and CO_2 , and as a result, more CO_2 molecules can be adsorbed. In addition. intramolecular interactions may also occur between organic linkers and inorganic units (Figure 6) and enrich the host-guest interaction within the MOF pores.



Packing density (g/mL) Figure 3. MOFs of amine group shows improved performance (Zhang et al., 2022)



Figure 4. The amine group from the ligan may hold up to two CO₂ molecules



Figure 5. Other possible molecular interactions (Colorado-Peralta et al., 2022)



NH₂-MIL-53(AI)
Figure 6. The intermolecular interaction between the linker and inorganic units of NH₂-MIL-53 (Serra-Crespo et al., 2012)

	CODE	Al-MOFs	Ligands	Absorption Capacity (mmol/g)	Condition (K/Bar)	Pore Size (nm)
				14.3	303/10	NI
		NH ₂ -MIL- 2-aminobenzene-1,4-dica	2-aminobenzene-1,4-dicarboxylic	4.3	303/3.5	NI
	Ε	53(Al)	acid	3.75	303/1-10	0.83
				2.65	298/5	NI
_				2.33	308/10	NI
	F	NH2-MIL- 101(Al)	2-aminobenzene-1,4-dicarboxylic acid	2.9	298.15- 348.15/1	NI
_	Н	CAU-10-NH ₂	5-aminoisophthalic acid	2.5	298/1	NI

Table 8. Some candidates of Al-MOF for DME purification (based on the CO₂ separation ability)

NI = No information

2.3.3 Thermal stability of Al-MOF

The reported Al-MOF, both with and without utilizing amine-based ligand, frequently shows good thermal stability. In many cases, the decompositions of Al-MOF are reaching temperature of around 300-400 °C (573-673K) or above. This was supported by the TGA analysis of some Al-MOF as shown in Figure 7 and Figure 8. This considerably high stability is due to the fact that most Al-MOF forms 3D polymeric networks and uses rigid bridging ligand. This thermal stability enhances the properties and strongness of Al-MOF to be used as multi-cycles adsorbent in practical use.



(Babar *et al.*, 2021)

Based on the thermal properties criteria, there are two Al-MOFs proposed for the candidate in the DME purifications (Table 9), based on pore size, CO₂ absorption capacity, and thermal stability, namely the NH₂-MIL-53(Al) and NH2-MIL-101(Al). The CAU-10-NH₂ (code H) may need to be considered. However, the thermal analysis of the compound was not found in the paper yet. Preparing the three mentioned Al-MOFs is considerably easy and results in good yield. Moreover, the precursor availability for making the three mentioned Al-MOFs is sustainable. However, further studies, such as computational studies, including evidence-based DME/CO₂ gas separation experiments, are compulsory and need to be performed before this Al-MOF can be applied in the DME purification process on a bigger scale.

Table 9. The proposed candidates of Al-MO)Fs for	DME
C		

Al- MOFs	Ligand s	CO2 absorptio n capacity (mmol/g)	Condition (K/Bar)	Pore Size (nm)
NH2- MIL- 53(Al)	NH2- BDC	3.75	303/1-10	0.83
NH2- MIL- 101(Al)	NH2- BDC	2.9	298.15- 348.15/1	NI

NI = No information

3. CONCLUSION

This study highlights NH₂-MIL-53(Al) and NH₂-MIL-101(Al) as possible alternatives for DME purification based on pore size, CO₂ absorption capacity, and thermal stability. Further investigations, such as computational studies, are needed before the proposed Al-MOF can be applied practically.

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