

MOFReasoner: Think Like a Scientist-A Reasoning Large Language

Model via Knowledge Distillation

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Method

Data Collection

In this study, we employed a comprehensive multi-channel, multilayered strategy for data collection and organization. Specifically, research papers were sourced from the Web of Science database using the keywords "MOFs" and "Adsorption." The search window spanned from 2023 up to February 1, 2025, ensuring the inclusion of the most recent scientific literature. Review articles were selected from the following review journals: *Chemical Reviews*, *Chemical Society Reviews*, *Nature Chemistry Reviews*, *Accounts of Chemical Research*, and *Coordination Chemistry Reviews*. This selection focused on literature related to metal-organic frameworks to ensure a robust foundation of current research insights. Full-text articles were obtained via institutional library subscriptions, in compliance with publisher copyright and licensing agreements. All access was conducted under permitted academic use, and no text was redistributed beyond the research scope.

To ensure transparency of data sources, we further recorded the publisher information of each paper. The collected literature spans all major scientific publishers, including Elsevier, ACS, Wiley, RSC, Springer, Nature Portfolio, MDPI, and AAAS, indicating broad coverage across different research communities. Only English-language publications were retained, and duplicates were removed using DOI-based matching and metadata inspection. These steps ensure that the dataset is both clean and representative of contemporary MOF adsorption research.

Additionally, we acquired chemical datasets and CoT datasets from the Hugging Face platform. It is important to note that the Qwen-based teacher model was not accessed via public cloud APIs; instead, it was deployed on a private cloud server provisioned and managed by our institution, ensuring that no publisher-protected content was transmitted to third-party services. Details about the sources are provided in Table S1.

Data Distillation

For the processing of research articles, we utilized the comprehension capabilities of a teacher model to extract key scientific challenge, proposed solutions, design principles, and validation methods, guided by a series of prompts. Given the length and high knowledge density of review articles, they were processed in two phases. Initially, the teacher model analyzed and distilled key scientific insights from these reviews, reformatting them into question-answer pairs. Subsequently, each question-answer pair, along with the review content, underwent a detailed reasoning using the teacher model. In the case of general chemical datasets, questions were directly posed to the teacher model to derive reasoning pathways and corresponding answers. Details of model usage and prompted methodologies are presented in Section S1 and Table S2.

Data Validation

Validation of existing answers within the general chemical datasets was conducted using a large language model, with a comparative analysis of the teacher model's responses against standard answers. Congruent responses were integrated into the final dataset for training purposes. For research articles and reviews where no standard answers exist, validation involved a combination of AI-assisted screening and manual evaluation. This process engaged a validation model to appraise the teacher model's deductive processes in relation to the article content; disputed findings were adjudicated by domain experts.

Model Training

Model training was executed using the Llama-Factory framework, employing Low-Rank Adaptation (LoRA) fine-tuning and Supervised Fine-Tuning (SFT) methodologies. The learning rate was fixed at 5e-5, with one training epoch. The phase length was set to 8192, and the maximum gradient norm was set to 1, using

the bf16 computation type. The base models for training were DeepSeek-R1-Distill-Qwen-7B. According to the training logs, the model processed approximately 8.72×10^7 tokens in total during fine-tuning, which provides a transparent estimate of the computational cost and enables better reproducibility for future research.

To further ensure training stability and efficiency, we adopted the AdamW optimizer (betas = 0.9, 0.999; weight decay = 0.01) with a linear learning-rate decay schedule and a 3% warmup ratio. A per-device batch size of 2 with gradient accumulation (effective batch size = 32) was used. LoRA adapters (rank = 64, α = 16, dropout = 0.05) were inserted into the attention projection layers, while other parameters were frozen. Supervision was applied on both reasoning traces and final answers using cross-entropy loss. Training samples were formatted into an instruction–response structure to align with reasoning tasks, and validation loss was monitored during training to avoid overfitting.

Section S1. Model Usage and Prompt Engineering

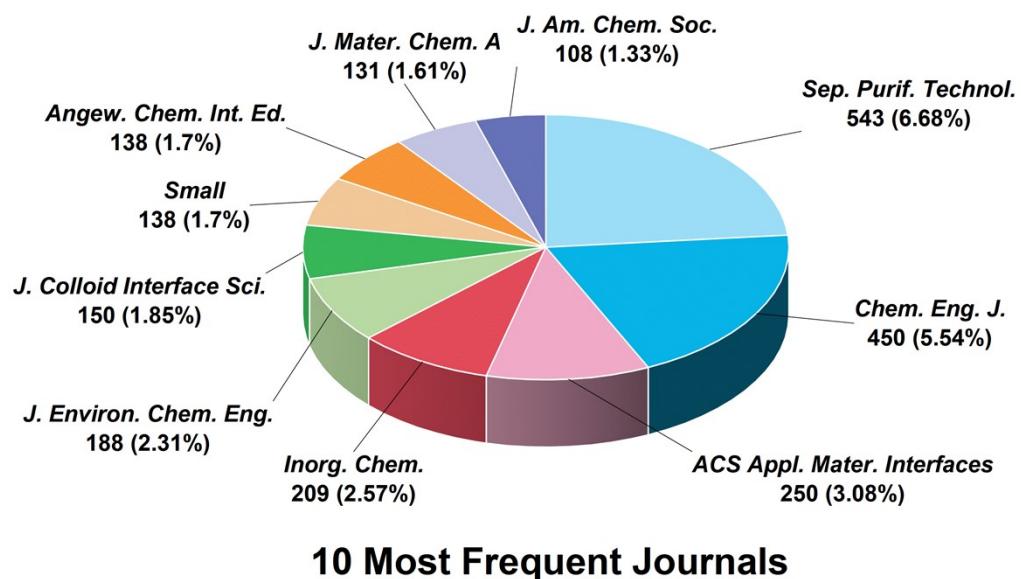


Figure S1. Top 10 journals distribution of research articles.

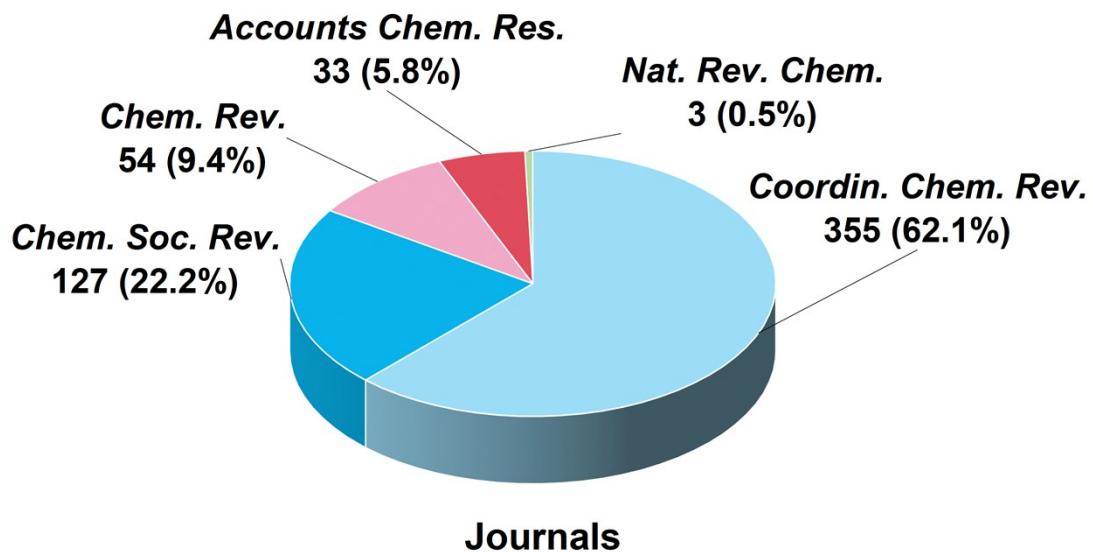


Figure S2. Five journals distribution of review articles.

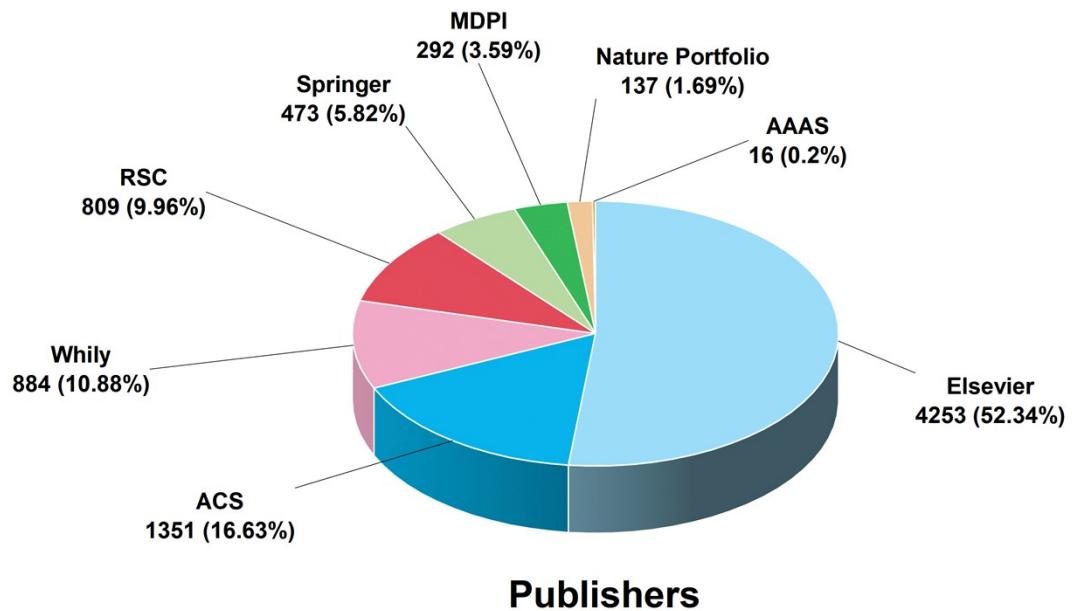


Figure S3. Publisher distribution of research articles.

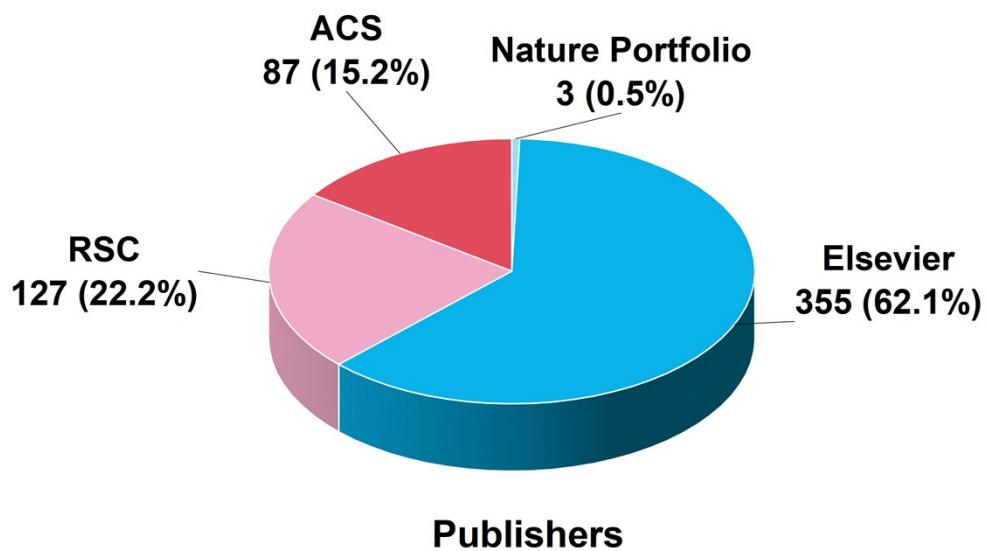


Figure S4. Publisher distribution of review articles.

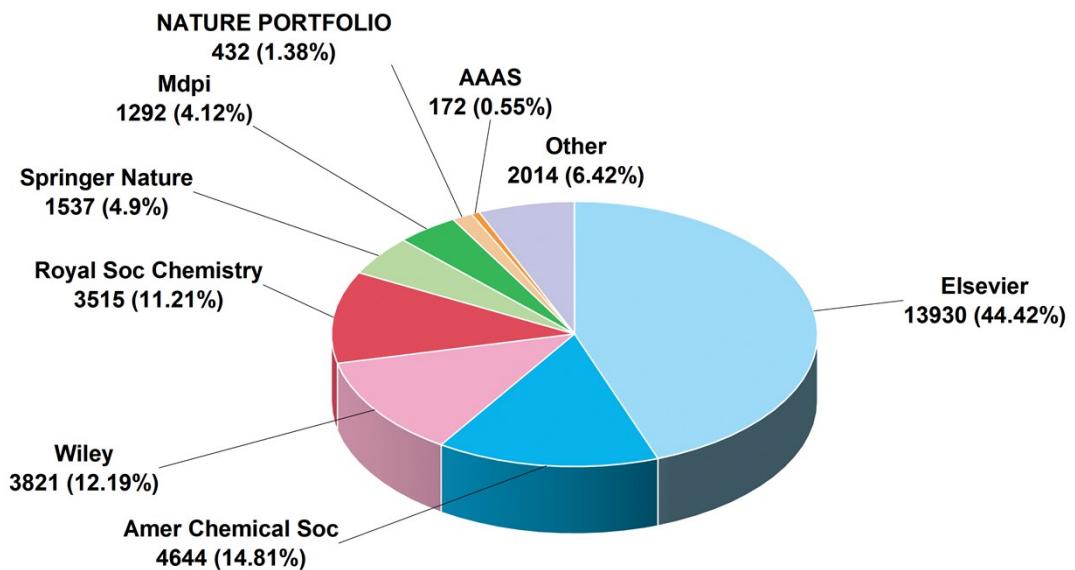


Figure S5. Publisher distribution of MOF-related articles (2023–2025).

Table S1. High-frequency keywords extracted from article titles.

Word	Frequency	Word	Frequency
Metal_organic_frameworks	2569	Carbon	631
Adsorption	1546	Enhanced	601
MOFs	1321	Metal	592
Efficient	1281	Performance	505
CO2	977	Selective	492
Removal	903	Porous	488
Separation	812	Capture	476
Water	778	Framework	462
Synthesis	736	Detection	435
Organic	654	Highly	432

Table S2. High-frequency keywords extracted from article abstracts.

Word	Frequency	Word	Frequency
MOFs	17096	Structure	3635
Adsorption	16947	Sites	3323
CO2	6329	Stability	3210
High	6137	Removal	3208
Materials	5694	Properties	3185
Water	5133	Potential	3058
Performance	5003	Energy	2986
Capacity	4562	Applications	2834
Surface	4363	Process	2783
Separation	4189	Selectivity	2662

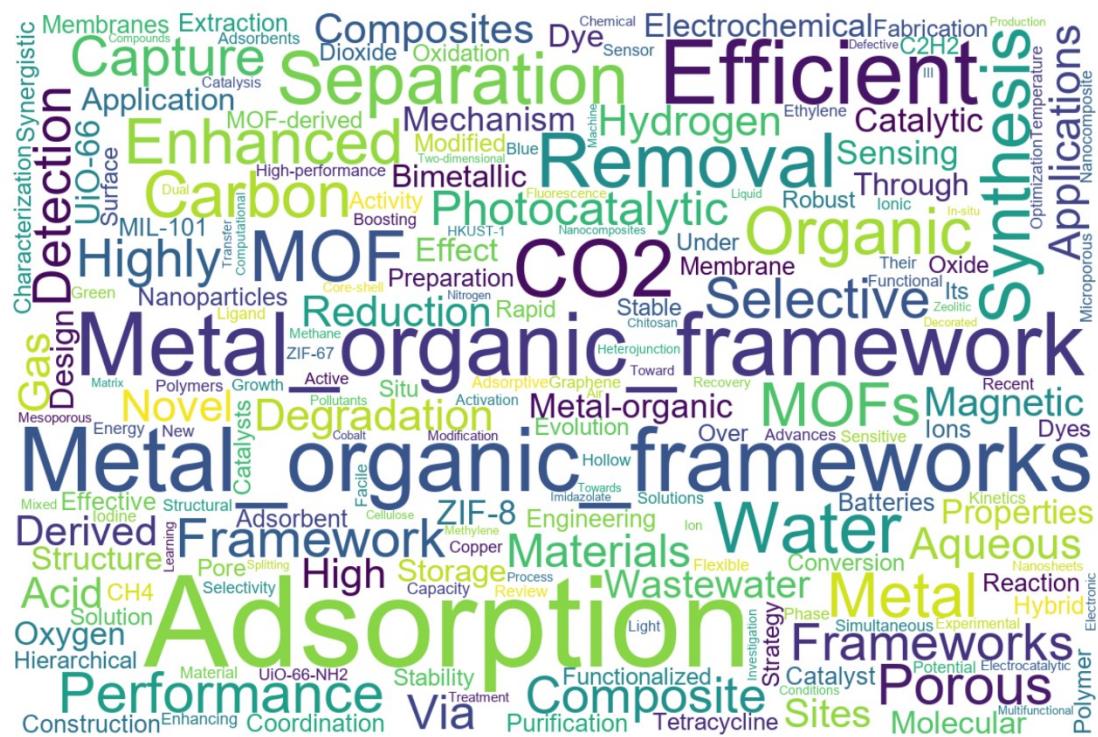


Figure S6. Word cloud of high-frequency terms extracted from article titles.

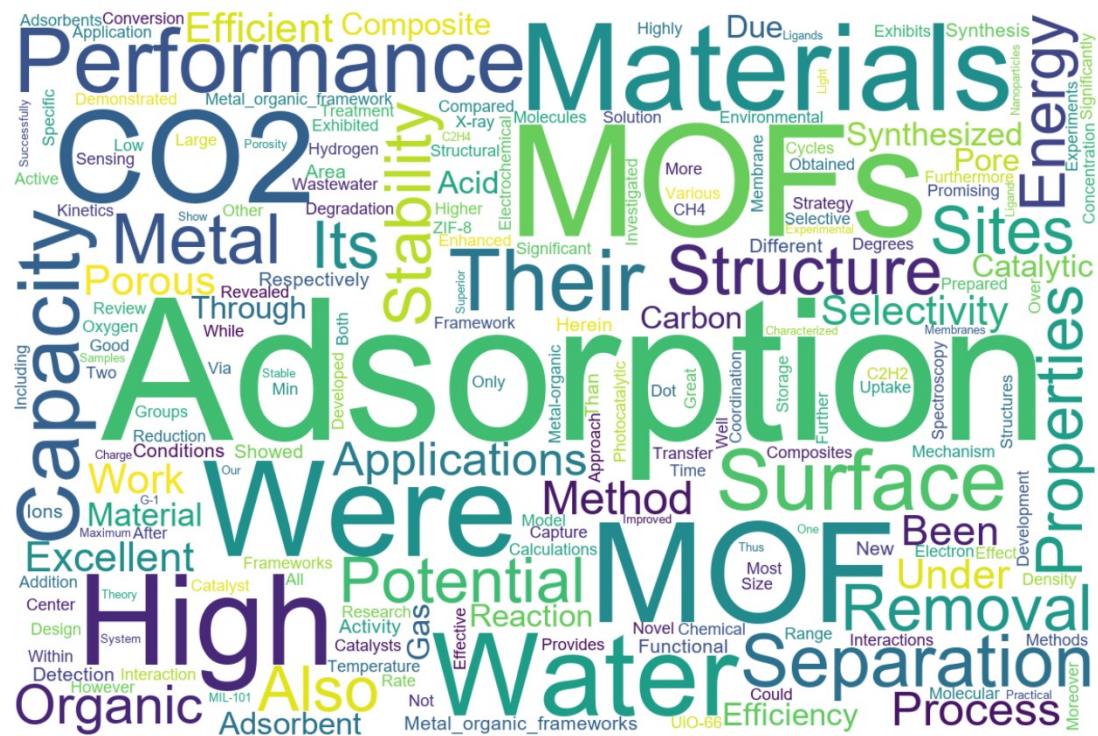


Figure S7. Word cloud of high-frequency terms extracted from article abstracts.

Table S3. Various Datasets Utilized in the Study: Sources and Access Links.

Dataset Name	Source	Description
Research Article	ACS WILEY	Research Article on Metal-Organic Frameworks and Adsorption from January 2023 to January 2025
	Elseview	
	Springer	
Review Article	Nature Portfolio RSC	Review articles on Metal-Organic Frameworks from January 2000 to January 2025
	MDPI	
	AAAS	
camel-ai/chemistry	Hugging Face	General chemistry dataset containing 25 chemical topics
STILL	Github	A large language dataset for slow thinking

Table S4. Model version used and model access date.

Model Version	Access Date
DeepSeek-R1-Distill-Qwen-7B	2025-02-10
DeepSeek-R1-Distill-Llama-8B	2025-02-10
Qwen-Max	2025-02-10
Qwen-Plus	2025-02-10
QwQ-32B	2025-02-10
Qwen-turbo	2025-02-11
DeepSeek-R1-671B	2025-02-10
o1-preview	2025-02-13
gpt-4.5-preview	2025-02-13
gpt-4-turbo-preview	2025-02-13
DeepSeek-V3-671B	2025-02-10

The Prompt for DeepSeek V3: Extracting Information from Research Article

Please carefully read the provided paper and complete the following tasks:

Scientific Problem and Answer:

Extract the core scientific problem addressed in the paper and present it in the form of a question.

Provide a detailed and comprehensive answer to the question based on the paper's content, including methods, experiments, results, and conclusions.

Use <|begin_of_question|> and <|end_of_question|> to mark the start and end of the question.

Use <|begin_of_answer|> and <|end_of_answer|> to mark the start and end of the answer.

The answer should be written from an objective perspective, avoiding any reference to "this paper" or "the authors."

Thought Chain for Solving the Problem:

Reconstruct the thought chain used to solve the scientific problem from an objective perspective or first-person perspective.

Use <|begin_of_thought|> and <|end_of_thought|> to mark the start and end of the thought chain.

The thought chain should include the following detailed elements:

Problem Identification: Clearly state the problem or gap in the field that motivated the research.

Why It Matters: Explain why solving this problem is important and what impact it could have on the field or real-world applications.

Hypothesis Formation: Describe the hypothesis or key idea proposed to address the problem, and explain the reasoning behind it.

Method Design: Explain the methodology or approach developed to test the hypothesis, including any novel techniques or tools. Clearly articulate why this method was chosen and how it addresses the problem.

Experimental Setup: Detail the experimental design, including datasets, metrics, and baseline comparisons. Explain why these choices were made and how they align with the research goals.

Data Analysis: Describe how the data was analyzed, including any challenges encountered and how they were addressed. Explain why specific analysis techniques were used and how they help validate the hypothesis.

Results and Interpretation: Summarize the key results and their implications for the hypothesis and the broader field. Explain why these results are significant and how they contribute to solving the problem.

Limitations and Future Work: Discuss the limitations of the approach and propose potential future directions for improvement or extension. Explain why these limitations exist and how future work could address them.

Avoid any reference to "this paper" or "the authors."

Ensure the logic is clear and easy to understand, even for readers without deep expertise in the field.

Thought Chain for Deriving the Research Idea:

Reconstruct the thought chain that led to the formation of the research idea, from an objective perspective or first-person perspective.

Use <|begin_of_idea_thought|> and <|end_of_idea_thought|> to mark the start and end of this thought chain.

The thought chain should include the following detailed elements:

Research Background: Describe the broader context of the research area and why it is important.

Current State of the Field: Summarize the existing approaches and their limitations.

Problem Discovery: Explain how the specific problem addressed in the paper was identified, including any observations or gaps in the literature.

Idea Formation: Describe the process of developing the core idea or hypothesis, including any inspiration, analogies, or prior work that influenced the thinking.

Validation of the Idea: Explain how the idea was initially validated or tested (e.g., through preliminary experiments, theoretical analysis, or literature review).

Refinement of the Idea: Discuss how the idea evolved over time, including any adjustments or iterations based on feedback or new insights.

Avoid any reference to "this paper" or "the authors."

Ensure the logic is clear and easy to understand, even for readers without deep expertise in the field.

Output Format:

```
<|begin_of_question|>
[Present the core scientific problem in the form of a question]
<|end_of_question|>
```

```
<|begin_of_answer|>
[Provide a detailed and comprehensive answer, including methods, experiments, results, and conclusions, written from an objective perspective]
<|end_of_answer|>
```

```
<|begin_of_thought|>
[Describe the thought process in the first person or from an objective perspective, including all detailed elements: problem identification, why it matters, hypothesis formation, method design, experimental setup, data analysis, results and interpretation, limitations, and future work. Ensure the logic is clear and easy to understand.]
<|end_of_thought|>
```

```
<|begin_of_idea_thought|>
```

[Describe the thought process in the first person or from an objective perspective, including all detailed elements: research background, current state of the field, problem discovery, idea formation, validation of the idea, and refinement of the idea. Ensure the logic is clear and easy to understand.]

<|end_of_idea_thought|>

Example:

<|begin_of_question|>

How can the generalization ability of deep learning models on small-sample datasets be improved without increasing computational complexity?

<|end_of_question|>

<|begin_of_answer|>

A meta-learning-based adaptive weight adjustment method has been proposed to address this challenge. This method involves designing a lightweight meta-network that dynamically adjusts the weights of the main network based on the features of the input data. The core idea is to use meta-learning to simulate the model's performance across different tasks, thereby enhancing its generalization ability on small-sample data. Experiments conducted on several small-sample datasets, such as Mini-ImageNet and CIFAR-FS, demonstrated that this approach significantly improves model performance without substantially increasing computational complexity. For instance, on the Mini-ImageNet dataset, the model's accuracy improved by approximately 8%. However, the method's sensitivity to hyperparameters was identified as a limitation, suggesting a need for further optimization, such as exploring more efficient meta-network architectures.

<|end_of_answer|>

<|begin_of_thought|>

The problem of poor generalization in deep learning models on small-sample datasets was identified as a significant challenge in the field. Existing models often overfit due to limited data availability, leading to suboptimal performance in real-world applications. Solving this problem is crucial because many practical scenarios, such as medical diagnosis or rare event prediction, involve limited data. Improving generalization in such settings could enable more reliable and accurate AI systems.

To address this issue, a hypothesis was formed: dynamically adjusting model parameters based on input data features could improve adaptability and generalization without requiring additional computational resources. This idea was motivated by the observation that traditional models use fixed parameters, which may not be optimal for diverse small-sample tasks. By allowing the model to adapt its parameters dynamically, it could better capture the unique characteristics of each task.

To test this hypothesis, a lightweight meta-network was designed. This meta-network operates alongside the main model, analyzing input data features and dynamically adjusting the main model's weights. The design prioritized efficiency to ensure that the computational overhead remained minimal. The meta-network was trained using a meta-learning framework, which allowed it to simulate performance across diverse tasks and datasets. This approach was chosen because meta-learning has shown promise in enabling models to generalize across tasks, making it a natural fit for small-sample problems.

Experiments were conducted on multiple small-sample datasets, including Mini-ImageNet and CIFAR-FS. These datasets were selected because they are widely used benchmarks for small-sample learning, allowing for fair comparisons with existing methods. The experimental setup included comparisons with baseline models to evaluate performance improvements. Key metrics such as accuracy, training time, and computational cost were measured. These metrics were chosen because they directly reflect the goals of improving generalization without increasing computational complexity.

During data analysis, it was observed that the method's performance was highly dependent on the choice of hyperparameters. This sensitivity was addressed through extensive hyperparameter tuning, but it remains a limitation of the approach. Additionally, the method's effectiveness varied across different types of small-sample datasets, suggesting that further customization may be needed for specific applications. These challenges were analyzed to understand their root causes and identify potential solutions.

The results showed that the proposed method significantly improved model performance, particularly in data-scarce scenarios. For example, on the Mini-ImageNet dataset, accuracy improved by approximately 8%, while computational costs remained comparable to baseline models. These results are significant because they demonstrate that dynamic weight adjustment can effectively enhance generalization without sacrificing efficiency. This finding has broad implications for fields where data is scarce, such as healthcare or environmental monitoring.

However, the method's sensitivity to hyperparameters and dataset variability highlights the need for further refinement. Future work could explore more robust meta-network architectures, automated hyperparameter optimization techniques, and applications to a broader range of tasks, such as medical imaging or natural language processing. These directions are important because they address the current limitations and could further improve the method's practicality and effectiveness.

<|end_of_thought|>

<|begin_of_idea_thought|>

The research idea emerged from a broader interest in improving the practicality of deep learning models in real-world scenarios, where data is often limited. The field of small-sample learning has gained attention due to its relevance in applications like medical imaging, where collecting large datasets is expensive or ethically challenging. However, existing methods often struggle with overfitting and fail to generalize well to new tasks.

A review of the current state of the field revealed that most approaches focus on either data augmentation or complex model architectures, which often come with high computational costs. While these methods can improve performance, they are not always feasible in resource-constrained settings. This gap highlighted the need for a more efficient solution that could enhance generalization without increasing computational complexity.

The specific problem of poor generalization in small-sample datasets was identified through experiments with existing models. It became clear that fixed model parameters, which work well in large-scale

settings, are not suitable for small-sample tasks where data variability is high. This observation led to the hypothesis that dynamic parameter adjustment could be a key to improving generalization.

The core idea of using meta-learning for dynamic weight adjustment was inspired by prior work in few-shot learning, where meta-learning has been successful in enabling models to adapt quickly to new tasks. The analogy was drawn that a similar approach could be applied to small-sample learning, but with a focus on efficiency to avoid excessive computational overhead.

To validate this idea, preliminary experiments were conducted using simple meta-network prototypes. These experiments showed promising results, indicating that dynamic weight adjustment could indeed improve generalization. However, they also revealed challenges, such as the meta-network's sensitivity to hyperparameters, which needed to be addressed.

Over time, the idea was refined through iterative experimentation and feedback from the research community. The meta-network architecture was optimized for efficiency, and new training techniques were introduced to stabilize performance. These refinements were crucial in transforming the initial idea into a practical and effective solution.

<|end_of_idea_thought|>

There is Artical:

{txt}

The Prompt for Qwen-Turbo-Latest: Extracting Scientific Opinion and Converting to Q&A from Review Articles

Based on the following review paper in the MOFs field, generate 40 or more insightful and thought-provoking questions. For each question, provide a corresponding answer that reflects the key concepts, methodologies, results, and future directions discussed in the paper. The answers should be accurate, based on the content of the paper, and should offer a detailed explanation or analysis. Focus on ensuring the answers are clear, correct, and directly tied to the content discussed.

Guidelines:

1. **Focus on the Paper's Content:**

- For each question, the answer should be drawn directly from the paper's discussion on topics like synthesis methods, structural characteristics, applications, computational models, challenges, and future directions.

- Provide answers that are not only factual but also demonstrate a deeper understanding of the content. The answers should reflect key arguments, evidence, and conclusions drawn in the paper.

2. **Encourage Critical Thinking and Reflection:**

- The answers should reflect critical engagement with the material. They should explain why certain methods or approaches are effective or not, based on the paper's findings.

- The answers should address the strengths and weaknesses of the research and provide insights into areas where future research could improve or expand upon the existing work.

3. **Consider Diverse Angles for Answers:**

- Provide answers that explore multiple perspectives and incorporate the following dimensions:
 - **Theoretical background and principles:** Explain the underlying scientific concepts behind MOFs and how they relate to the paper's findings.
 - **Synthesis and characterization:** Discuss how different synthesis methods influence the material's properties, scalability, and reproducibility. Explore what methods are most suitable for specific applications and their limitations.
 - **Computational models:** Explain the computational approaches used in the study, their assumptions, and how they were validated. Discuss any discrepancies between theoretical predictions and experimental results.
 - **Practical applications:** Explore the real-world applicability of the materials, their potential in various industries, and the challenges involved in scaling the synthesis process.
 - **Limitations and improvements:** Reflect on the paper's acknowledged limitations. Provide insight into how these limitations could be overcome through alternative methods, techniques, or future research directions.
 - **Future research opportunities:** Identify potential areas for future investigation based on gaps or opportunities highlighted in the paper. Discuss how these opportunities could advance the field and the role of emerging technologies or interdisciplinary approaches.
 - **Sustainability and impact:** Evaluate the environmental, economic, and societal impact of the technologies or materials discussed. How might they be integrated into sustainable practices or large-scale industrial applications?

4. **Output Format:**

- Provide the questions and answers in a clear, well-structured format, with each question followed by its corresponding answer. The output should look like this:

<|begin_of_questions_and_answers|>

1. Question: [Insert question here]
Answer: [Insert detailed answer here]
2. Question: [Insert question here]
Answer: [Insert detailed answer here]
3. Question: [Insert question here]
Answer: [Insert detailed answer here]
4.

<|end_of_questions_and_answers|>

5. **Question and Answer Requirements:**

- Focus on generating questions that require analysis, reflection, and comprehension of the content, not just factual recall.
- Provide answers that are comprehensive and accurate, reflecting a clear understanding of the key points discussed in the paper.
- Avoid generic answers and ensure that the answers are tailored to the specific content and context of

the review paper, addressing both the findings and the implications of the research.

There is Artical:

{txt}

The Prompt for Qwen-Turbo-Latest: Extracting the Chain of Thought from Question to Opinion from Review Article

Based on a comprehensive review in the field of Metal-Organic Frameworks (MOFs) and related questions, generate a detailed and complete chain of scientific reasoning. Ensure that your reasoning process is rigorous and logically coherent, utilizing scientific theories and facts for analysis. The chain of reasoning can be open and flexible, not confined to a rigid structure, but it should clearly indicate the beginning and end of the reasoning.

Please use '<|begin_of_thought|>' to mark the start of the reasoning chain and '<|end_of_thought|>' to mark the end.

Don't mention "this literature show" or "this review show" or anything like that. This is very important. Even if you use the literature, your answer should still give the other person a style of thinking that is all about you.

The thought chain is as detailed as possible.

****Example Structure:****

1. ****Understanding the Background:**** Briefly explain the background information and main questions.
2. ****Application of Knowledge:**** Invoke relevant scientific principles and known facts related to the problem.
3. ****Analysis Integration:**** Integrate key information from the review into the analysis process.
4. ****Reasoning Expansion:**** Use logical reasoning to explore potential paths to a solution.
5. ****Solution Evaluation:**** Assess the plausibility and feasibility of different solutions.
6. ****Conclusion Formation:**** Draw clear scientific conclusions or hypotheses.
7. ****Open Exploration:**** Suggest possible future research directions or applications.

****Open Thought Chain Template:****

<|begin_of_thought|>

1. Preliminary Analysis: Clarify the subject and background information.
2. Theoretical Application: Identify and apply relevant scientific theories to support the analysis.
3. Logical Step-by-Step Reasoning: Gradually expand the reasoning, using review information to deepen the analysis.
4. Possibility Discussion: Explore potential conclusions and hypotheses, considering various scientific perspectives.
5. Result Summary: Summarize analysis results to form clear scientific conclusions.
6. Exploration Directions: Propose possible future research directions or application areas.

<|end_of_thought|>

Question:
{question}

Answer:
{answer}

There is Artical:
{txt}

The Prompt for DeepSeek R1: Reasoning with a General Chemistry Dataset

Objective: Analyze the provided English research paper and evaluate whether the given reasoning process regarding {question} is logically valid. Apply a lenient assessment standard focusing on core argument integrity rather than minor inaccuracies.

Input Structure:

Original Paper: {review}

Reasoning Process: {chain-of-thought}

Evaluation Protocol:

Comprehension Phase

Identify key claims and evidence in the original paper
Map logical connections between premises and conclusions
Alignment Check

Verify if the reasoning process:

- a) Uses valid premises explicitly stated or reasonably implied in the paper
- b) Maintains logical consistency with source material
- c) Avoids introducing unsupported external assumptions

Error Identification

Flag only instances where:

Premises contradict original text (quote exact passages)

Deductive steps violate basic logic rules

Critical evidence is misrepresented

Output Format:

If flaws detected:

False

[Original Paper Excerpt]

→

[Reasoning Step Error]

If compliant with lenient standard:

True

Special Instructions:

Allow reasonable interpretive leaps in reasoning

Tolerate minor factual inaccuracies unless affecting core argument

Prioritize structural validity over rhetorical perfection

Section S2. Dataset construction and validation

```
<|begin_of_question|>
What is the nature of iodine (I2) adsorption in the metal-organic framework
MFM-300(Sc), and how does it affect the structural integrity of the material?
<|end_of_question|>
```

Figure S8. Use DeepSeek to build a domain dataset from the Scientific Challenges section of the research article.

```
<|begin_of_answer|>
The adsorption of iodine (I2) in the metal-organic framework MFM-300(Sc) is
inhomogeneous, with significant variations in iodine content across different
channels of the material. Even at saturation adsorption levels, channels
ranging from nearly empty to densely filled coexist. High-resolution scanning
transmission electron microscopy (STEM) imaging revealed that densely packed I2
regions may locally form triple-helix structures, corresponding to up to 142
iodine atoms per unit cell, despite the average uptake being much lower (23
iodine atoms per unit cell). This inhomogeneity is attributed to strong
intermolecular interactions among I2 molecules, which promote local dense
packing and hinder uniform distribution.

Additionally, I2 adsorption induces structural defects in MFM-300(Sc), such as
edge dislocations and stacking faults, which persist even after the complete
removal of I2 molecules. These defects are likely caused by the significant
strain imposed on the MOF framework due to the incorporation of densely packed
I2. A surfactant-capping strategy using cetyltrimethylammonium bromide (CTAB)
was developed to minimize I2 release, effectively reducing I2 loss from 11.2%
to 4.6%. This study provides direct evidence of inhomogeneous adsorption and
its structural consequences, offering new insights into host-guest interactions
in porous materials.
<|end_of_answer|>
```

Figure S9. Use DeepSeek to build a domain dataset from the Proposed Solutions section of the research article.

<|begin_of_idea_thought|>

The research idea emerged from the broader context of understanding host-guest interactions in metal-organic frameworks (MOFs), which are highly tunable materials with applications in gas storage, separation, and catalysis. Specifically, MFM-300(Sc) has shown exceptional iodine (I₂) adsorption capacity, making it a promising candidate for capturing radioactive iodine from nuclear waste. However, the detailed mechanisms of I₂ adsorption and its effects on the MOF structure remained poorly understood, particularly at the local level.

A review of the current state of the field revealed that most studies relied on bulk techniques like adsorption isotherms and X-ray diffraction, which provide averaged information but cannot resolve local inhomogeneities or structural changes. This limitation was particularly evident in studies of I₂ adsorption, where low site occupancies suggested either homogeneous adsorption without dense packing or inhomogeneous adsorption with localized dense structures.

The specific problem of inhomogeneous I₂ adsorption in MFM-300(Sc) was identified through preliminary experiments and a critical analysis of existing literature. The observation that I₂ molecules could form dense structures in localized regions, while leaving other channels empty, raised questions about the nature of adsorption and its impact on the MOF framework.

The core idea of using high-resolution STEM imaging to directly visualize I₂ adsorption and its effects on the MOF structure was inspired by the unique capabilities of STEM to provide atomic-scale resolution and real-space imaging. The combination of HAADF-STEM and iDPC-STEM was chosen to leverage the strengths of each technique, with HAADF-STEM providing Z-contrast imaging sensitive to heavy elements like iodine and iDPC-STEM offering high signal-to-noise ratios for imaging the MOF framework.

To validate this idea, preliminary experiments were conducted to optimize imaging conditions and minimize electron beam damage to the MOF. These experiments confirmed that STEM imaging could reveal the distribution of adsorbed I₂ and identify structural changes in the MOF framework.

Over time, the idea was refined through iterative experimentation and feedback from the research community. The surfactant-capping strategy to minimize I₂ release was developed as a practical application of the findings, demonstrating how the insights gained from STEM imaging could be translated into improved MOF performance.

<|end_of_idea_thought|>

Figure S10. Use DeepSeek to build a domain dataset from the Design Idea Thoughts section of the research article.

<|begin_of_thought|>

The problem of understanding the nature of iodine (I₂) adsorption in metal-organic frameworks (MOFs) like MFM-300(Sc) was motivated by the need to characterize the spatial distribution of adsorbed molecules and their impact on the host material's structure. Traditional methods, such as adsorption isotherms and X-ray diffraction, provide averaged information but cannot reveal local inhomogeneities or structural changes caused by adsorption. This gap is significant because MOFs are promising materials for applications like radioactive iodine capture, and understanding these interactions is crucial for optimizing their performance.

The hypothesis was that I₂ adsorption in MFM-300(Sc) might be inhomogeneous due to strong intermolecular interactions, potentially leading to localized dense packing and structural defects. This idea was supported by prior studies suggesting low site occupancies for I₂ in the MOF, which could indicate either homogeneous adsorption without dense packing or inhomogeneous adsorption with localized dense structures.

To test this hypothesis, high-resolution STEM imaging was employed, combining high-angle annular dark-field STEM (HAADF-STEM) and integrated differential phase-contrast STEM (iDPC-STEM). This approach was chosen because it allows direct visualization of local structures and guest molecules within the MOF, overcoming the limitations of diffraction-based methods. The use of low-dose imaging conditions minimized electron beam damage to the sensitive MOF structure.

Experiments were conducted on MFM-300(Sc) samples with varying I₂ loadings, prepared by exposing the MOF to saturated I₂ vapor and then desorbing weakly adsorbed I₂ under vacuum. STEM imaging revealed that I₂ adsorption was highly inhomogeneous, with channels showing varying degrees of iodine filling, even at saturation. Image simulations confirmed that densely packed I₂ regions could locally form triple-helix structures, consistent with prior models. Additionally, structural defects such as edge dislocations and stacking faults were observed in samples with high I₂ loading, suggesting that the incorporation of guest molecules can induce significant strain on the host framework.

Data analysis highlighted the challenges of interpreting STEM images due to the complex contrast mechanisms and the need for careful calibration. However, the results clearly demonstrated inhomogeneous adsorption and provided direct evidence of structural defects induced by I₂ incorporation.

The findings are significant because they reveal that I₂ adsorption in MFM-300(Sc) is not uniform, with localized dense packing and structural defects occurring even at saturation. This has implications for the design and application of MOFs in iodine capture, as inhomogeneous adsorption and structural changes could affect their performance and stability.

Limitations of the study include the sensitivity of the MOF to electron beam damage, which necessitated low-dose imaging and limited the resolution of some images. Future work could explore other imaging techniques or computational modeling to further understand the mechanisms of defect formation and the dynamics of I₂ adsorption. Additionally, the surfactant-capping strategy, while effective in reducing I₂ release, slows adsorption kinetics, suggesting a trade-off that could be optimized in future studies.

<|end_of_thought|>

Figure S11. Use DeepSeek to build a domain dataset from the Validation Thoughts section of the research article.

<|begin_of_questions_and_answers|>

1. Question: What is the rationale behind the need for direct air capture (DAC) technologies in mitigating climate change?

Answer: DAC technologies are essential because they can reduce the global atmospheric CO₂ concentration, unlike traditional carbon capture methods which only slow the rate of increase of CO₂ emissions. DAC can address both distributed and point-source emissions, making it a crucial tool for combating climate change.

2. Question: How does the concentration of CO₂ in the atmosphere compare to that in flue gases, and why is this significant for DAC?

Answer: The CO₂ concentration in the atmosphere is approximately 400 ppm, which is about 350 times lower than typical flue gas concentrations (4-14 vol %). This difference is significant because DAC requires sorbents that can efficiently capture CO₂ at very low partial pressures, making chemisorbents more effective than physisorbents for this application.

3. Question: What are the main challenges faced by aqueous hydroxide solutions in DAC processes?

Answer: The main challenges include high energy demands for regeneration, limited efficiency, and the necessity of operating kilns under pure oxygen to avoid CO₂ dilution. These factors make the process energetically intensive and costly, posing practical difficulties for widespread implementation.

4. Question: How does the Kraft process contribute to the development of DAC technologies?

Answer: The Kraft process, traditionally used in the paper industry, serves as a model for developing DAC technologies. It demonstrates the use of caustic solutions to capture CO₂, which can be regenerated through causticization, although it faces significant energy penalties during regeneration.

5. Question: What role do supported alkali carbonates play in improving DAC processes?

Answer: Supported alkali carbonates, such as potassium carbonate/γ-Al₂O₃ composites, show promise in enhancing CO₂ capture capacities. The addition of potassium to mesoporous alumina improves sorption performance, although the overall uptake remains modest compared to other chemisorbent materials.

6. Question: Why is the moisture concentration critical in the performance of amine-based sorbents for DAC?

Answer: Moisture concentration significantly affects the performance of amine-based sorbents. Under humid conditions, moisture facilitates CO₂ diffusion across the sorbent material, improving access to amine-active sites and enhancing adsorption efficiency.

7. Question: What are the differences between primary and secondary amines in terms of CO₂ capture efficiency under DAC conditions?

Answer: Primary amines exhibit higher efficiency (up to 0.30 mol CO₂/mol N) compared to secondary amines (0.07 mol CO₂/mol N) under DAC conditions. This is attributed to the stronger heat of adsorption for primary amines, which enhances their affinity for CO₂ at low concentrations.

8. Question: How does the length of the organic linker influence CO₂ uptake in amine-functionalized materials?

Answer: Short linkers (methyl and ethyl) limit the interaction between neighboring amines, resulting in lower CO₂ uptake. Longer linkers (propyl) provide more flexibility, allowing for better amine-amine interactions and consequently higher CO₂ uptakes.

9. Question: What is the significance of the step in the CO₂ isotherms observed in amine-functionalized MOFs?

Answer: The step in the isotherms indicates a cooperative insertion mechanism where CO₂ molecules bind to amines and initiate a chain reaction, leading to a sudden increase in CO₂ uptake. This mechanism is influenced by the strength of the amine-metal bond.

10. Question: How does the incorporation of open-metal sites in MOFs affect their CO₂ capture capabilities?

Answer: Open-metal sites in MOFs increase their CO₂ adsorption capacity at ambient pressures and steep uptakes at very low concentrations. These sites provide strong interactions with CO₂, making MOFs with open-metal sites highly effective for DAC.

Figure S12. Scientific questions deconstructed using Qwen-Turbo from review articles (questions 1-10) using acs.chemrev.6b00173 as an example.

11. Question: What are the limitations of using MOFs for DAC, particularly regarding humidity?

Answer: MOFs are susceptible to structural degradation and reduced CO₂ capture performance in the presence of humidity. Water competes with CO₂ for binding sites, leading to a decrease in the number of reactive sites available for CO₂ capture.

12. Question: How does the pore size distribution in MOFs influence their CO₂ capture selectivity?

Answer: Adjusting the pore size distribution can enhance the selectivity of MOFs for CO₂ capture. Smaller pores tend to exhibit higher selectivity due to the restricted diffusion pathways for CO₂ molecules compared to larger pores.

13. Question: What is the potential of amine-tethered MOFs in improving CO₂ capture efficiency?

Answer: Amine-tethered MOFs can increase CO₂ adsorption capacities by providing accessible amine sites within the framework. They also offer improved stability under practical operating conditions, making them a promising candidate for DAC applications.

14. Question: How does the thermodynamic analysis of DAC processes compare to that of flue gas capture?

Answer: DAC processes have a higher theoretical second law efficiency (over 90%) compared to flue gas capture (approximately 45%). This suggests that DAC can achieve greater efficiencies, although practical industrial processes are unlikely to reach these theoretical limits.

15. Question: What are the key cost considerations in DAC processes involving aqueous alkaline systems?

Answer: Key cost considerations include capital investment, energy for operation, cost of CO₂ release and sorbent regeneration, and maintenance of equipment. These costs are influenced by factors such as the choice of packing material, electricity source, and fugitive emissions.

16. Question: How does the use of axial compression affect the energy requirements and CO₂ recovery in DAC systems?

Answer: Axial compression reduces the energy required to capture CO₂ and increases the annual throughput of CO₂. For example, it can reduce the energy required from 1.24 GJ/t of CO₂ to 0.96 GJ/t of CO₂ while increasing recovery from 88 Mt/year to 1.8×10^6 Mt/year.

17. Question: What are the advantages and disadvantages of using anionic exchange resins for DAC?

Answer: Anionic exchange resins offer the advantage of capturing CO₂ in a dry state and releasing it using a moisture swing process, which is energy-efficient. However, their high cost and potential degradation under practical conditions pose significant disadvantages.

18. Question: How does the modular design of Lackner's DAC system reduce costs?

Answer: The modular design allows for portable capture units that can fit into standard shipping containers, facilitating easy transportation and installation. This design reduces costs by optimizing the use of materials and energy, particularly in the regeneration process.

19. Question: What are the potential benefits of combining DAC with renewable energy sources?

Answer: Integrating DAC with renewable energy sources can provide a carbon-negative technology by fixing CO₂ from the atmosphere and converting it into useful products like synthetic fuels. This approach aligns with sustainability goals by reducing reliance on fossil fuels.

20. Question: How do supported amines on oxide supports enhance the stability and efficiency of DAC materials?

Answer: Supported amines on oxide supports, such as alumina, improve stability by preventing degradation and leaching of the amine during regeneration. They also enhance efficiency by increasing the number of available amine sites and improving the accessibility of CO₂.

Figure S13. Scientific questions deconstructed using Qwen-Turbo from review articles (questions 11-20) using acs.chemrev.6b00173 as an example.

21. Question: What is the impact of amine loading on the efficiency of CO₂ capture in DAC systems?

Answer: Higher amine loading generally improves CO₂ capture efficiency, but it can also hinder diffusion and access to amine sites, leading to decreased efficiency. The optimal loading depends on the specific sorbent and operating conditions.

22. Question: How does the BET surface area change upon functionalization of MOFs with amines?

Answer: Functionalization of MOFs with amines reduces the BET surface area due to the occupation of surface sites by the tethered amines. However, this modification can increase the CO₂ adsorption capacity by providing more reactive sites for CO₂ binding.

23. Question: What are the implications of using MOFs with unsaturated metal centers for DAC?

Answer: MOFs with unsaturated metal centers can exhibit high CO₂ capacities at low pressures. However, their susceptibility to humidity-induced structural degradation limits their practical application, necessitating further research into stabilizing these materials.

24. Question: How does the thermodynamic minimum work of separation compare between DAC and flue gas capture processes?

Answer: The thermodynamic minimum work for DAC is approximately 20 kJ/mol of CO₂, compared to 8.4 kJ/mol for flue gas capture. Despite the higher energy requirement for DAC, it can achieve greater efficiencies due to its skimming nature.

25. Question: What are the main challenges in scaling up DAC technologies for industrial use?

Answer: Challenges include developing efficient gas-sorbent contacting strategies, optimizing regeneration processes, addressing high energy demands, and ensuring the durability and stability of sorbents under ultradilute conditions and varying humidity levels.

26. Question: How does the choice of electricity source impact the cost of DAC processes?

Answer: The cost of electricity is a critical component in DAC processes. Using low-cost or waste heat from other processes can significantly reduce operational costs, making the technology more economically viable.

27. Question: What is the role of temperature swing adsorption (TSA) in DAC processes?

Answer: TSA allows for the regeneration of sorbents by alternating temperatures. It is particularly effective for chemisorbents, which can be nearly saturated regardless of the CO₂ concentration in the feed, simplifying the desorption process.

28. Question: How does the use of supported amines on porous materials affect the regeneration process in DAC?

Answer: Supported amines on porous materials can be regenerated using steam or inert gases. The choice of regeneration method influences the energy requirements and the efficiency of the DAC process.

29. Question: What is the significance of the "Moisture Swing" process in DAC technologies?

Answer: The Moisture Swing process uses the energy released during evaporation to desorb CO₂, reducing the need for high-energy thermal or vacuum swings. This approach is particularly beneficial for materials that are sensitive to moisture.

30. Question: How do computational models assist in the design of MOFs for DAC applications?

Answer: Computational models predict the adsorption properties of MOFs, helping to optimize their pore size and chemistry for high CO₂ selectivity. These models guide experimental efforts by identifying promising candidates before synthesis.

Figure S14. Scientific questions deconstructed using Qwen-Turbo from review articles (questions 21-30) using acs.chemrev.6b00173 as an example.

31. Question: What are the potential applications of CO₂ captured through DAC technologies?

Answer: Captured CO₂ can be used for synthetic intermediates in pharmaceuticals, feeding greenhouses or algae installations for agricultural purposes, or sequestered geologically. These applications vary in feasibility and economic viability.

32. Question: How does the use of nanostructured materials impact the efficiency of DAC processes?

Answer: Nanostructured materials, such as nanoporous polymers, can enhance CO₂ capture efficiency due to their high surface area and tailored pore structures. However, their durability and practicality under varying environmental conditions require further investigation.

33. Question: What are the environmental risks associated with large-scale DAC deployment?

Answer: Risks include long-term monitoring of sequestration sites, potential leakage of CO₂, and induced seismicity. These risks necessitate careful consideration and rigorous testing before widespread implementation of DAC technologies.

34. Question: How does the use of zeolites compare to MOFs in DAC applications?

Answer: Zeolites are less effective in DAC applications due to their lower CO₂ capacities and sensitivity to humidity. MOFs, with their tunable pore sizes and open-metal sites, offer better performance but face challenges in stability under humid conditions.

35. Question: What is the role of renewable energy in the feasibility of DAC technologies?

Answer: Renewable energy sources can power DAC systems, reducing operational costs and making the technology more environmentally friendly. Wind, solar, and hydroelectric energy are particularly advantageous for this purpose.

36. Question: How does the use of plastic packing materials reduce the cost of DAC processes?

Answer: Plastic packing materials are cheaper than stainless steel, reducing the capital investment required for DAC systems. This cost reduction is significant, especially when integrated with other optimizations like heat integration.

37. Question: What are the key differences between DAC and conventional postcombustion CO₂ capture?

Answer: DAC aims to reduce the atmospheric CO₂ concentration, while postcombustion capture targets purification of flue gases. DAC operates under ultradilute conditions and does not require flue gas pretreatment, unlike postcombustion capture.

38. Question: How does the design of the air contactor influence the cost and efficiency of DAC?

Answer: The design of the contactor, such as choosing a cooling tower geometry, can reduce the energy required for fan operation and improve liquid distribution. Such innovations can significantly lower the cost of DAC processes.

39. Question: What is the role of multicomponent adsorption studies in evaluating MOFs for DAC applications?

Answer: Multicomponent adsorption studies assess the performance of MOFs under conditions that mimic flue gas or air capture. They provide insights into the selectivity and stability of MOFs in the presence of competing gases like N₂ and H₂O.

40. Question: How does the incorporation of amines into MOFs affect their structural integrity?

Answer: The incorporation of amines can stabilize MOFs by preventing structural collapse. However, excessive amine loading or exposure to moisture can compromise the structural integrity, requiring careful balancing of properties for practical DAC applications.

Figure S15. Scientific questions deconstructed using Qwen-Turbo from review articles (questions 31-40) using acs.chemrev.6b00173 as an example.

41. Question: What are the potential synergistic effects of combining different support materials with amine functionalities for DAC?

Answer: Combining different support materials can enhance the dispersion of amines and improve their accessibility to CO₂ molecules. This can lead to higher CO₂ uptakes and better stability under varying conditions.

42. Question: How does the presence of water vapor influence the performance of supported amine materials in DAC?

Answer: Water vapor can enhance the CO₂ uptake by promoting diffusive intermediates that improve access to amine-active sites. However, excessive moisture can degrade the sorbent's performance by blocking CO₂ binding sites.

43. Question: What is the potential of using temperature-vacuum swing (TVS) processes in DAC?

Answer: TVS processes can achieve higher CO₂ purities by avoiding dilution during desorption. However, they typically yield lower capacities compared to temperature swing adsorption (TSA) processes, requiring further optimization.

44. Question: How does the choice of amine type affect the performance of DAC materials?

Answer: The type of amine (primary, secondary, or tertiary) influences the heat of adsorption, amine efficiency, and hydrophilicity. Primary amines are generally more efficient and stable under humid conditions, while secondary amines are less sensitive to moisture.

45. Question: What are the implications of using low-cost natural gas for DAC processes?

Answer: Utilizing low-cost natural gas can significantly reduce the operational costs of DAC systems. This makes the technology more economically attractive, especially when combined with efficient heat integration and waste heat utilization.

46. Question: How does the synergistic effect of multiple amine types contribute to DAC performance?

Answer: Mixing different amine types can optimize the balance between reactivity and stability. For example, secondary amines are more stable, while primary amines offer higher heats of adsorption, contributing to better overall performance in DAC applications.

47. Question: What is the role of multistage separation processes in improving the efficiency of DAC systems?

Answer: Multistage processes can enhance the efficiency of DAC by gradually concentrating CO₂ from ultradilute streams. This approach reduces energy demands and improves the overall performance of the capture system.

48. Question: How does the concept of "negative carbon technologies" influence the development of DAC?

Answer: Negative carbon technologies, such as DAC, are essential for stabilizing the atmospheric CO₂ concentration. Their development is driven by the urgent need to mitigate climate change, despite the current high costs and energy demands.

49. Question: What are the environmental benefits of integrating DAC with biological processes like algae cultivation?

Answer: Integrating DAC with biological processes can enhance the carbon-negative impact by utilizing captured CO₂ for biomass production. This approach not only reduces atmospheric CO₂ but also generates valuable products like biofuels.

50. Question: How does the use of temperature gradients in DAC processes affect the regeneration of sorbents?

Answer: Temperature gradients facilitate the regeneration of sorbents by thermally destabilizing CO₂-bound species. This allows for efficient release of CO₂, enabling the sorbent to be reused multiple times in a cyclic DAC process.

<|end_of_questions_and_answers|>

Figure S16. Scientific questions deconstructed using Qwen-Turbo from review articles (questions 41-50) using acs.chemrev.6b00173 as an example.

```
<|begin_of_question|>  
How can the BET method be adapted for MOFs with mixed pore sizes?  
<|end_of_question|>
```

Figure S17. Use Qwen-Turbo to build a domain dataset from the Question section of the review article.

```
<|begin_of_answer|>  
For MOFs with mixed pore sizes, BET calculations must be carefully adapted to  
account for both micropore and mesopore contributions, ensuring accurate  
surface area estimations.  
<|end_of_answer|>
```

Figure S18. Use Qwen-Turbo to build a domain dataset from the Author's Opinion section of the review article.

```
<|begin_of_thought|>
```

1. **Preliminary Analysis:** Understanding the BET Method and Mixed Pore Sizes

The BET (Brunauer-Emmett-Teller) method is a widely used technique for determining the surface area of porous materials. It relies on multilayer adsorption of gas molecules on solid surfaces and assumes a uniform pore size distribution for accurate estimation. However, MOFs often possess mixed pore sizes, including micropores (less than 2 nm) and mesopores (between 2 nm and 50 nm). This heterogeneity complicates the application of the BET method because it is difficult to distinguish between monolayer adsorption, multilayer adsorption, and micropore filling in such cases.

For accurate BET surface area determination, the IUPAC recommends adherence to specific criteria, such as the four BET consistency criteria proposed by Rouquerol et al., which involve selecting a linear range in the isotherm, ensuring positive adsorption energy, and aligning experimental and theoretical monolayer loading pressures. Yet, many MOFs with mixed pore sizes fail to satisfy these criteria, leading to reported "apparent BET surface areas."

Mixed pore size MOFs present a challenge because their physisorption isotherms may deviate from the ideal type I or type IV curves. Consequently, traditional BET calculations may underestimate or misrepresent the actual surface area due to overlapping contributions from micropores and mesopores.

2. **Theoretical Application:** Principles of Adsorption and Pore Size Contributions

According to the IUPAC classification, micropores dominate the adsorption behavior at low pressures, while mesopores contribute more significantly at higher pressures. For MOFs with mixed pore sizes, the physisorption isotherm reflects a combination of these two mechanisms. The BET equation, however, assumes a single pore size population for the multilayer adsorption regime, which is problematic in mixed pore systems.

To address this issue, researchers have developed alternative methods for pore size distribution analysis, such as the Horvath-Kawazoe (HK) method, density functional theory (DFT), and Monte Carlo simulations. These methods account for the geometric complexity of mixed pore sizes, offering a more nuanced understanding of the material's porosity. However, these approaches require precise knowledge of the material's structure and are often computationally intensive.

A key consideration in adapting the BET method for MOFs with mixed pore sizes is the need to separate the contributions of micropores and mesopores. This separation is crucial because the BET method's accuracy depends on identifying the correct monolayer saturation pressure, which can be obscured by mixed pore populations.

Figure S19. Use Qwen-Turbo to build a domain dataset from the Chain of Thought section of the review article (part 1).

3. **Logical Step-by-Step Reasoning:** Developing an Adaptation Strategy

First, it is essential to recognize that the BET method's limitations stem from the inability to distinguish between monolayer adsorption in micropores and multilayer adsorption in mesopores. This distinction becomes particularly critical in MOFs with high porosity and large surface areas, where mesopores dominate the adsorption behavior at moderate pressures.

Second, the activation process plays a significant role in the BET surface area estimation. Inefficient activation can lead to incomplete removal of guest molecules, causing capillary collapse in mesopores and reducing the apparent BET surface area. Techniques such as supercritical CO₂ drying or freeze drying minimize capillary forces and preserve delicate structures, making them more suitable for MOFs with mixed pore sizes.

Third, to adapt the BET method for MOFs with mixed pore sizes, one could implement a dual-mode approach. This involves analyzing the isotherm data separately for micropore and mesopore contributions. For instance, at low pressures ($P/P_0 < 0.1$), the BET method could be applied to estimate the micropore surface area, while at higher pressures ($P/P_0 > 0.3$), the mesopore contribution could be evaluated using the Barrett-Joyner-Halenda (BJH) method or DFT.

Fourth, computational modeling can assist in this adaptation by predicting the theoretical pore size distribution and comparing it with experimental data. Such models help identify the appropriate ranges for monolayer adsorption and multilayer adsorption, ensuring that the BET analysis aligns with the material's structural reality.

Fifth, practical considerations include the choice of activation solvent. High surface tension solvents like DMF or DMSO can damage MOFs with weaker node-linker bonds, while low surface tension solvents like methanol or pentane, or non-polar fluids like sc-CO₂, are more effective at preserving the framework's integrity. Combining sc-CO₂ drying with a solvent-exchange step could yield a more robust activation protocol for mixed pore MOFs.

4. **Possibility Discussion:** Potential Solutions and Challenges

One plausible solution is to employ a hybrid approach that combines the BET method with pore size distribution analysis. For example, the micropore contribution could be isolated by fitting the low-pressure region (type I) to the BET model, while the mesopore contribution could be analyzed using the BJH method or DFT. This dual approach requires careful selection of the linear range for the BET calculation, ensuring that it excludes the mesopore filling regime.

Another approach is to modify the MOF structure to enhance uniformity in pore sizes. Isoreticular expansion or contraction of the organic linkers could potentially reduce the variability in pore sizes, simplifying the BET analysis. However, this approach may compromise the MOF's intended functionality, as pore size tuning is often critical for specific applications.

A third possibility involves developing a modified BET equation that accounts for mixed pore populations. This would require introducing parameters that represent the contributions of both micropores and mesopores, allowing for a more comprehensive fit of the isotherm data. Such modifications could be empirically derived or theoretically modeled, depending on the availability of structural data.

Challenges remain, particularly in cases where the pore size distribution is broad or irregular. In these scenarios, the physisorption isotherm may not exhibit distinct regions corresponding to micropore and mesopore adsorption, complicating the separation process.

Figure S20. Use Qwen-Turbo to build a domain dataset from the Chain of Thought section of the review article (part 1).

5. **Result Summary:** Formulating Clear Scientific Conclusions

Based on the analysis, adapting the BET method for MOFs with mixed pore sizes requires a combination of experimental adjustments and computational modeling. The dual-mode approach, where micropore and mesopore contributions are analyzed separately, appears to be the most feasible method for accurately estimating the surface area. This approach leverages existing techniques like DFT and BJH while maintaining compatibility with the BET framework.

The success of this adaptation hinges on the quality of the activation process. Using low surface tension solvents or supercritical CO₂ can minimize capillary collapse and ensure that the MOF framework retains its porosity during analysis. Computational models can further refine the BET adaptation by predicting the theoretical pore size distribution and guiding the selection of appropriate linear ranges.

Therefore, the conclusion is that while the BET method inherently struggles with mixed pore MOFs, it can be adapted through a systematic dual-mode analysis, careful activation, and computational support. This adaptation ensures that the surface area estimation aligns with the material's true porosity, enhancing its utility in research and applications.

6. **Exploration Directions:** Future Research and Applications

Future research could focus on developing a generalized BET model for mixed pore MOFs. This model would incorporate adjustable parameters to account for varying pore size distributions, providing a unified framework for BET analysis across different MOF architectures. Additionally, exploring new activation methods that combine solvent-exchange and sc-CO₂ drying could offer a cost-effective and efficient protocol for preparing MOFs with mixed pore sizes.

Applications of MOFs with mixed pore sizes span multiple fields, including gas storage, catalysis, and enzyme encapsulation. Accurate surface area measurements are critical for optimizing these materials for specific tasks. For instance, in hydrogen storage, understanding the exact contribution of micropores and mesopores to the overall capacity could guide the design of more efficient MOFs. Similarly, in enzyme encapsulation, precise knowledge of the pore size distribution ensures optimal retention and activity of the encapsulated biomolecules.

Finally, integrating BET adaptation with advanced characterization techniques like small-angle X-ray scattering (SAXS) or neutron scattering could provide complementary insights into the material's porosity. These combined approaches could further enhance the reliability and applicability of BET surface area measurements for MOFs with complex pore structures.

<|end_of_thought|>

Figure S21. Use Qwen-Turbo to build a domain dataset from the Chain of Thought section of the review article (part 3).

Question: What is the IUPAC name for the following compound: CH3CH2CH2CH2CH2CH3?

Standard Answer: The IUPAC name for the compound CH3CH2CH2CH2CH2CH3 is hexane.

DeepSeek R1's Reasoning: Okay, so I need to figure out the IUPAC name for CH3CH2CH2CH2CH2CH3. Let me start by drawing the structure or at least visualizing it. The formula is C6H14, right? Because each CH2 group is connected, except the ends which are CH3. So this is a straight-chain alkane with six carbon atoms.
Wait, alkanes have the suffix "-ane". The prefix depends on the number of carbons. Let me recall the prefixes: methane (1), ethane (2), propane (3), butane (4), pentane (5), hexane (6). So six carbons would be hexane. Since it's a straight chain, there are no branches, so there's no need for any numbers in the name. The longest continuous chain is six carbons.
Let me double-check. The compound is CH3-CH2-CH2-CH2-CH2-CH3. Each carbon is connected in a straight line. So the parent chain is six carbons long. No substituents or branches. Therefore, the IUPAC name should simply be hexane.
But wait, maybe there's a different way to number the chain? If there were branches, you start numbering from the end closest to the substituent. But since there are no substituents here, the numbering doesn't matter. The name is the same regardless. So yeah, it's definitely hexane.
I think that's it. Just making sure I didn't miss any other possible structure. Wait, sometimes even straight chains can have alternative names if there's a different arrangement, but in this case, it's a straight chain. If there were branches, it would be a different isomer, but the formula C6H14 has several isomers, but this one is the straight-chain version. So the IUPAC name is hexane.
Yeah, that's right. No complications here. Straight-chain alkanes are named based on the number of carbons with the appropriate prefix and "-ane". So six carbons: hexane.

DeepSeek R1's Answer: compound CH3CH2CH2CH2CH2CH3 is a straight-chain alkane with six carbon atoms. According to IUPAC nomenclature, alkanes are named based on the number of carbon atoms in the longest continuous chain, using the appropriate prefix followed by the suffix "-ane". For six carbons, the prefix is "hex-", resulting in the name hexane. Since there are no branches or substituents, no additional numbering or modifiers are needed.
Answer: The IUPAC name is hexane.

Figure S22. Reasoning about problems in the camel-ai/chemistry dataset using DeepSeek.

Input: Write a function that takes in a list of integers and an element, and returns the index of the first occurrence of the element in the list. The function should handle cases where the element is not present in the list and return -1 in such cases. The input list should have a length of at least 3. The function should only use basic array operations and not rely on any built-in functions or libraries. Additionally, the function should have a time complexity of O(n), where n is the length of the list, and a space complexity of O(1).

Figure S23. Questions in the General Thought Chain Dataset.

<|begin_of_thought|>
 Alright, I need to write a function that finds the first occurrence of an element in a list of integers. The function should return the index of that element, and if the element isn't in the list, it should return -1. The list has to have at least three elements. Also, I can only use basic array operations and no built-in functions or libraries. Plus, it needs to be efficient with $O(n)$ time complexity and $O(1)$ space complexity.
 First, I should think about how to iterate through the list. Since I can't use any built-in functions, I'll probably use a simple loop to go through each element.
 I need to keep track of the index as I iterate. I can use a variable, say 'index', starting at 0, and increment it with each iteration.
 Inside the loop, I'll check if the current element is equal to the target element. If it is, I'll return the current index.
 If I go through the entire list and don't find the element, I'll return -1.
 I should also consider the constraints. The list has at least three elements, so I don't need to handle cases with fewer elements.
 Let me think about the time and space complexity. Since I'm going through each element once, the time complexity should be $O(n)$, which is good. For space complexity, I'm only using a few variables, so that's $O(1)$.
 I should also make sure that my function is robust and handles cases where the element is not present.
 Let me try to write a simple version of this function.
 I'll define a function called `find_first_occurrence` that takes in a list and an element.
 Initialize an index variable to 0.
 Use a for loop to iterate through the list.
 In each iteration, check if the current element equals the target.
 If it does, return the current index.
 If the loop finishes without finding the element, return -1.
 Wait, in Python, list indices start at 0, which should be fine.
 I need to make sure that I don't use any built-in functions like `index()` or `enumerate()`, since the problem says not to rely on any built-in functions or libraries.
 Using a simple for loop with a range should be acceptable.
 Let me adjust the function to use a for loop with range.
 Initialize index to 0.
 For `i` in `range(len(list))`:
 If `list[i] == element`:
 return `i`
 index += 1
 After the loop, return -1.
 But actually, I don't need the index variable because 'i' already represents the index in the loop.
 So I can simplify it by just using 'i'.
 Also, I need to ensure that I don't use `len()` or any built-in functions.
 Wait, the problem says not to rely on any built-in functions or libraries, but using `len()` might be unavoidable to get the length of the list.
 Is there another way to iterate through the list without using `len()`?
 In Python, iterating through a list without using `len()` is tricky because I can't directly get the length otherwise.
 Maybe the problem allows using `len()` since it's a basic operation to get the length of the list.
 I'll assume that `len()` is allowed as a basic array operation.
 So, I'll proceed with using `len()` to get the length of the list.
 Let me write the function again.
 Define `def find_first_occurrence(lst, element):`
 for `i` in `range(len(lst))`:
 if `lst[i] == element`:
 return `i`
 return -1
 This seems straightforward.
 I should test this function with some examples.
 Example 1:
 List: [1, 2, 3, 4, 5]
 Element: 3
 Expected output: 2
 Let's see, `lst[2]` is 3, so it should return 2.
 Example 2:
 List: [10, 20, 30, 40, 50]
 Element: 60
 Expected output: -1
 Since 60 is not in the list.
 Example 3:
 List: [5, 5, 5, 5]
 Element: 5
 Expected output: 0
 Because the first occurrence is at index 0.
 Example 4:
 List: [0, 1, 2]
 Element: 2
 Expected output: 2
 Minimum length list.
 I should also consider edge cases.
 Edge case 1:
 List: [1, 2, 3]
 Element: 1
 Expected output: 0
 Edge case 2:
 List: [1, 2, 3]
 Element: 3
 Expected output: 2
 Edge case 3:
 List: [1, 2, 1]
 Element: 1
 Expected output: 0
 First occurrence is at index 0.
 I should make sure that the function returns the first occurrence and not any other.
 Also, I need to ensure that the function works correctly when the list contains negative numbers or zeros.
 Test case:
 List: [-1, -2, -3]
 Element: -2
 Expected output: 1
 Another test case:
 List: [0, 0, 0]
 Element: 0
 Expected output: 0
 I think my function should handle these cases correctly.
 I need to make sure that I'm not using any other built-in functions apart from `len()`.
 I don't think I'm using any other functions.
 I should also consider the performance.
 Since I'm iterating through the list once, the time complexity is $O(n)$, which meets the requirement.
 For space complexity, I'm only using a few variables, so it's $O(1)$.
 I think this satisfies all the constraints mentioned in the problem.
 Let me write the final function.
 <|end_of_thought|>

Figure S24. The thinking process in the general thought chain dataset.

```

<|begin_of_solution|>\n\nTo solve this problem, we need to find the first occurrence of a specific
element in a list of integers and return its index. If the element is not present in the list, the function
should return -1. The solution should be efficient with a time complexity of O(n) and a space
complexity of O(1), and it should not rely on any built-in functions or libraries beyond basic
operations.\n\n### Approach\n\n1. **Iteration:** We will iterate through the list using a for loop from
index 0 to n-1, where n is the length of the list.\n\n2. **Comparison:** During each iteration, we will
check if the current element is equal to the target element.\n\n3. **Return Index:** If a match is
found, we immediately return the current index.\n\n4. **Element Not Found:** If the loop completes
without finding the element, we return -1.\n\nThis approach ensures that we only traverse the list
once (O(n) time complexity) and use a constant amount of additional space (O(1) space
complexity).\n\n### Solution Code\n\n```python\ndef find_first_occurrence(lst, element):\n    for i in\n        range(len(lst)):\n            if lst[i] == element:\n                return i\n    return -1\n\n```Explanation\n\n**Function Definition:** The function `find_first_occurrence` takes two parameters: `lst` (the list of
integers) and `element` (the target element to find).\n\n**Loop Through List:** We use a for loop
that iterates from 0 to the length of the list minus one.\n\n**Check Element Equality:** Inside the
loop, we check if the current element `lst[i]` is equal to the target `element`.\n\n**Return Index on
Match:** If a match is found, the function returns the current index `i`.\n\n**Return -1 If Not
Found:** If the loop completes without finding the element, the function returns -1, indicating the
element is not in the list.\n\nThis solution is efficient and meets all the requirements specified in the
problem.<|end_of_solution|>",

```

Figure S25. Answers in the General Thought Chain Dataset.

Question: What is the systematic name of the following compound? \nCH3CH2CH2OH.

Standard Answer: The systematic name of the compound CH3CH2CH2OH is 1-propanol.

DeepSeek R1's Answer: The compound CH3CH2CH2OH is a straight-chain alcohol with three carbon atoms and a hydroxyl (-OH) group attached to the first carbon atom when numbered from the end closest to the hydroxyl group. Following IUPAC nomenclature rules, the systematic name is propan-1-ol (preferred) or 1-propanol. Both names are correct, but the former aligns with current IUPAC recommendations for using the "-ol" suffix and numbering the chain to give the hydroxyl group the lowest possible position.

Answer: Propan-1-ol (or 1-propanol).



Question: What is the IUPAC name for the organic compound with the molecular formula C6H12O2?

Standard Answer: There can be several isomers with the molecular formula C6H12O2, so it is not possible to provide a specific IUPAC name without more information about the structure of the compound. If you can provide the structure or any additional details, I would be happy to help you determine the IUPAC name.

DeepSeek R1's Answer: The molecular formula C6H12O2 corresponds to several possible compounds, primarily carboxylic acids and esters. Here are the key possibilities:

1. Hexanoic Acid

- IUPAC Name: Hexanoic acid
- Structure: CH3(CH2)4COOH
- A carboxylic acid with a 6-carbon chain. This fits the formula C6H12O2 and has one degree of unsaturation (from the carbonyl group).

2. Esters Esters derived from combinations of carboxylic acids and alcohols that sum to 6 carbons. Examples include:

- Methyl pentanoate: Derived from pentanoic acid (5 carbons) and methanol (1 carbon). IUPAC Name: Methyl pentanoate
- Ethyl butanoate: Derived from butanoic acid (4 carbons) and ethanol (2 carbons). IUPAC Name: Ethyl butanoate
- Propyl propanoate: Derived from propanoic acid (3 carbons) and propanol (3 carbons). IUPAC Name: Propyl propanoate



Conclusion: Without additional structural information, multiple compounds fit the formula C6H12O2. The most likely answers are hexanoic acid (a carboxylic acid) or esters like ethyl butanoate. If prioritizing the carboxylic acid, the IUPAC name is hexanoic acid. If focusing on esters, a common example is ethyl butanoate.

Final Answer: The IUPAC name could be hexanoic acid or an ester such as ethyl butanoate, depending on the structure.

Figure S26. Use validation models to compare large language model responses and standard answers to build chemical datasets.

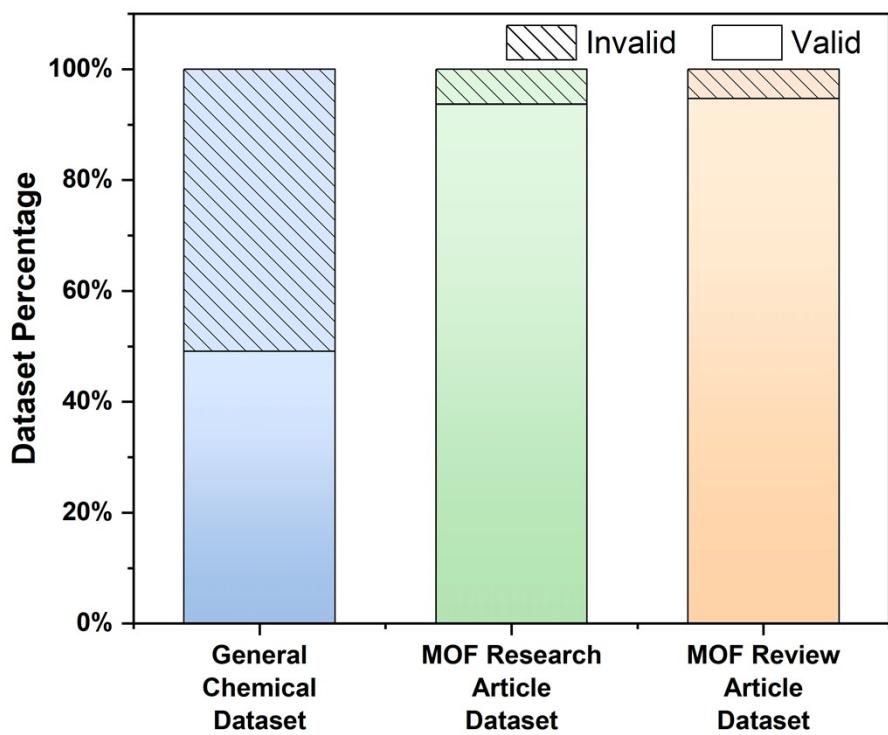


Figure S27. The distribution of data that is valid and invalid through verification.

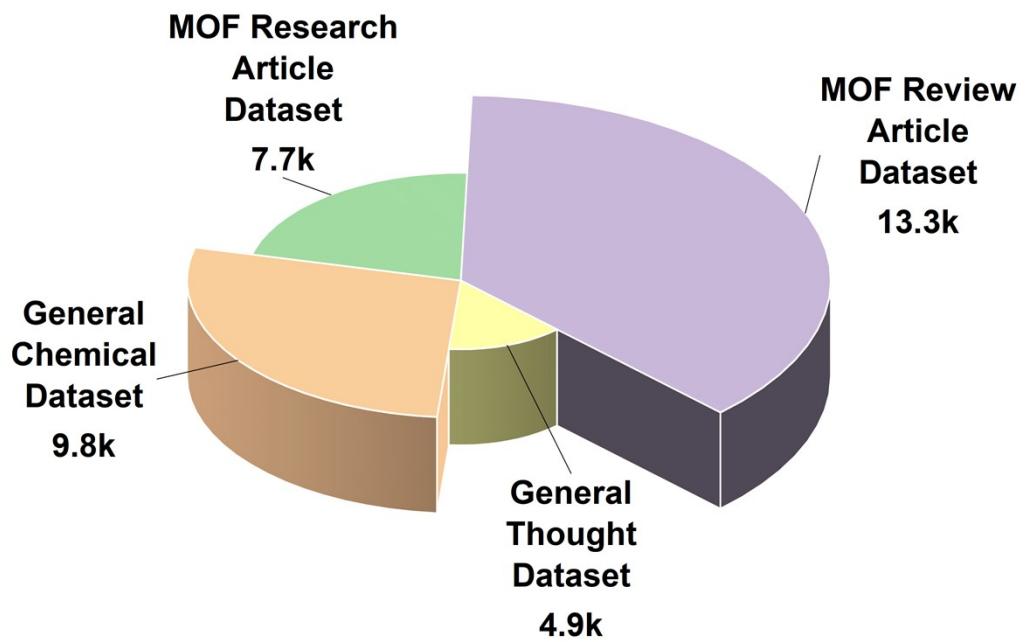


Figure S28. Composition of the datasets used for fine-tuning MOFReasoner. Each of the 35.8K data

points corresponds to a single question–answer pair with an associated chain-of-thought reasoning trace.

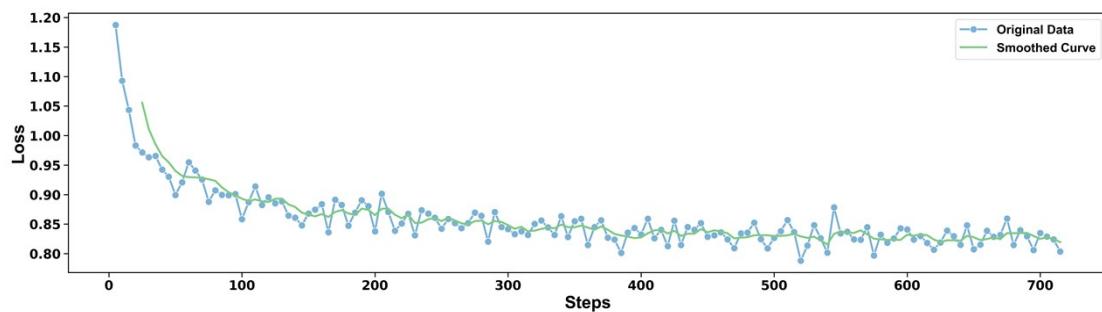


Figure S29. The training loss of MOFReasoner at each step.

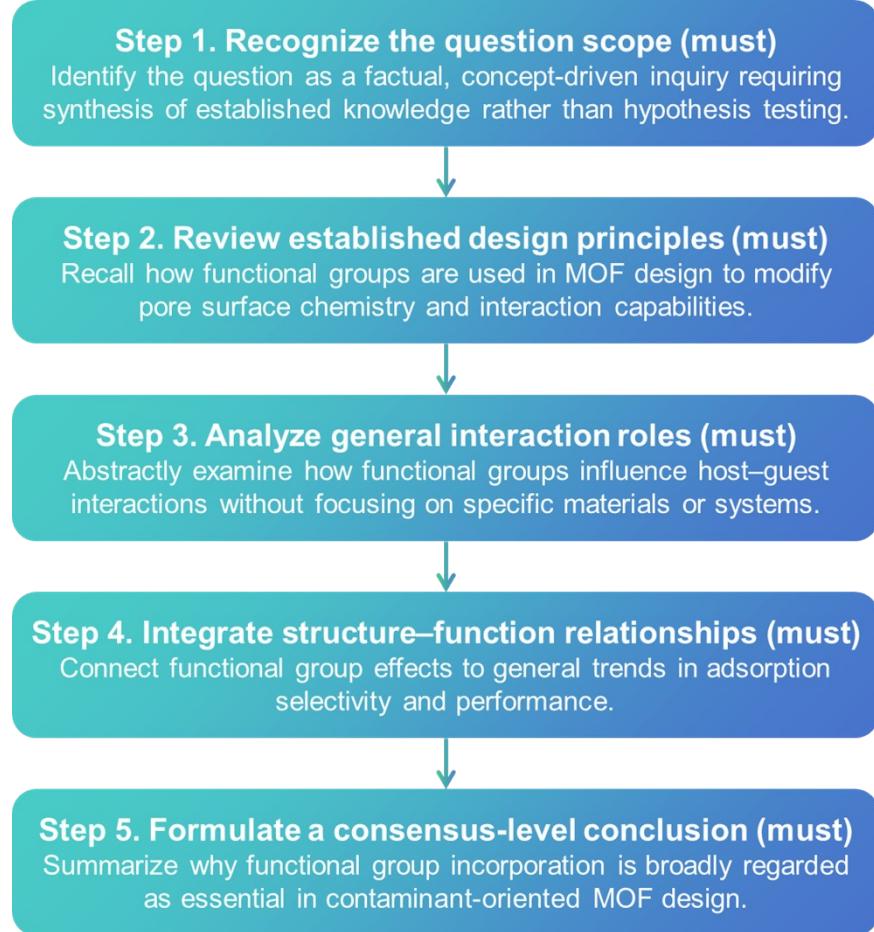


Figure S30. Expected reasoning path for the factual question “Why is the introduction of functional groups important in the design of metal–organic frameworks for contaminant removal?”, illustrating a structured process of knowledge review, mechanism abstraction, and consensus-level integration.

MOFReasoner's Reasoning:

Preliminary Analysis: Role of Functional Groups in Metal–Organic Frameworks. Functional groups play a central role in determining the adsorption performance of metal–organic frameworks (MOFs). By introducing chemically active sites into the framework, functional groups enhance the affinity between MOFs and target contaminants, thereby improving adsorption efficiency. Beyond providing binding sites, functional groups also influence structural stability, pore environment, surface polarity, and interaction mechanisms, all of which are critical for effective contaminant capture. In adsorption-based processes, these characteristics collectively determine whether contaminants can be efficiently retained within the pores of the framework.

Theoretical Analysis: Interaction Mechanisms Between Functional Groups and Contaminants. From the perspective of hard and soft acid–base (HSAB) theory, functional groups within MOFs can participate in selective interactions depending on their chemical nature. Metal nodes may act as hard acids, while certain organic functional groups behave as soft acids or bases. For example, nitrogen-containing functional groups such as amines tend to function as soft bases and can interact strongly with soft or borderline acidic species. In contrast, oxygen-containing functional groups such as hydroxyls or carboxylates often act as hard bases, favoring interactions with hard acidic contaminants, including metal ions.

These acid–base interactions are essential in governing adsorption selectivity and efficiency. Additionally, functional groups significantly affect the polarity of the framework. Frameworks with limited functionalization are often hydrophobic and show weak affinity toward polar contaminants, whereas frameworks enriched with polar functional groups can form stronger electrostatic interactions or hydrogen bonds. As a result, rational functional group incorporation provides a direct strategy for tailoring MOFs toward specific classes of contaminants.

Integrated Analysis: Functional Group Effects on Adsorption Performance. Practical applications demonstrate that even modest functionalization can substantially enhance adsorption performance. For instance, the introduction of hydroxyl groups into zeolitic imidazolate frameworks improves their interaction with polar organic pollutants, leading to unexpectedly high adsorption capacities despite relatively moderate surface areas. Similarly, amine-functionalized frameworks show enhanced affinity toward aromatic or nonpolar contaminants, reflecting improved π – π interactions or acid–base interactions.

Functional group modification is also effective for dye removal. Amine groups, in particular, strengthen electrostatic attraction toward cationic dyes such as methylene blue, resulting in significantly improved adsorption capacities. These examples collectively illustrate that adsorption performance is not solely dictated by surface area or porosity, but is strongly governed by the chemical nature of the pore surface.

Extended Reasoning: Framework Property Enhancement Through Functionalization.

Functional group incorporation enhances MOF performance through multiple pathways. First, it creates targeted adsorption sites that improve selectivity. Second, it can increase structural robustness under chemical or thermal stress by stabilizing coordination environments. Third, functionalization can fine-tune pore size and internal surface chemistry, enabling better accommodation of contaminants with specific molecular geometries.

The hydrophilic or hydrophobic character imparted by functional groups further determines adsorption behavior in aqueous environments. Hydrophilic functional groups facilitate interactions with charged or polar species, while hydrophobic groups can improve stability and performance in water-rich systems. In addition, functional groups may improve recyclability by enhancing resistance to framework degradation during repeated adsorption–desorption cycles.

Evaluation: Feasibility and Challenges of Functional Group Introduction.

The effectiveness of functional group modification has been widely demonstrated, indicating that it is a feasible and powerful strategy for improving MOF-based contaminant removal. However, several challenges remain. Functional group leaching during synthesis or operation may reduce long-term stability, and precise control over functional group type and density can be difficult to achieve. Variability in functionalization can lead to inconsistent performance across materials.

Despite these limitations, functional group engineering remains one of the most promising approaches for optimizing MOFs, particularly when combined with frameworks that already possess high surface area and accessible porosity.

Conclusion: Importance of Functional Groups in MOF Design for Contaminant Removal.

Overall, functional groups are indispensable in the rational design of MOFs for contaminant removal. They provide specific binding sites, enhance adsorption efficiency, and regulate framework stability, polarity, and interaction mechanisms. Effective contaminant removal relies on matching functional group chemistry with contaminant characteristics. Polar functional groups such as hydroxyls are particularly effective in aqueous systems, while nitrogen-containing groups enhance affinity for nonpolar or aromatic pollutants. Through careful functional group selection, MOFs can be tailored for a wide range of environmental and industrial applications.

Future Perspectives: Directions for Further Research.

Future research may focus on developing functionalization strategies that allow precise control over functional group distribution and density. Advanced synthesis approaches, including mechanochemical and supercritical CO_2 methods, offer promising routes toward this goal. Investigating functional group–contaminant interactions under realistic environmental conditions will further improve material design. Additionally, frameworks incorporating mixed ligands or hybrid composites with polymers or nanoparticles may enable enhanced selectivity and robustness, broadening the practical applicability of functionalized MOFs.

Figure S31. Reasoning trace generated by MOFReasoner for the question “Why is the introduction of functional groups important in MOF design for contaminant removal?”, illustrating a structured, multi-step scientific reasoning process beyond factual recall.

DeepSeek R1's Reasoning: Okay, the user is asking about why introducing functional groups is important in designing MOFs for contaminant removal. Let me start by breaking down the question. They're likely a researcher or student in materials science, chemistry, or environmental engineering. They want to understand the functionalization aspect of MOFs, specifically for removing contaminants.

First, I need to explain the basics of MOFs. They're porous materials made of metal nodes and organic linkers. Their high surface area and tunability are key. But why functional groups? Maybe the user knows MOFs are tunable but doesn't grasp how functional groups play into that. They might be looking for reasons beyond just "it makes them better."

I should list the main reasons functional groups matter. Adsorption mechanisms come to mind: electrostatic interactions, hydrogen bonding, pi-pi stacking, acid-base interactions. Each mechanism can be enhanced by specific functional groups. For example, -SO₃H for cations, -NH₂ for anions. The user might need concrete examples to see how different groups target different contaminants.

Selectivity is another point. MOFs can be designed to pick specific contaminants from mixtures. Functional groups help here. The user might be dealing with real-world scenarios where multiple contaminants coexist, so selectivity is crucial. They might not have considered that functionalization can reduce competition for adsorption sites.

Capacity and affinity. Functional groups can make the MOF bind contaminants more strongly or increase the number of binding sites. The user might be concerned about efficiency and reusability. Stronger bonds could mean better performance but maybe harder regeneration. I should mention that balance.

Reusability and stability. Some groups help in regenerating the MOF, like through pH changes. The user might be thinking about practical applications where MOFs need multiple cycles. Stability against water or chemicals is important too. Hydrophobic groups could protect the framework.

Targeting specific contaminants. Functional groups can be chosen based on the contaminant's properties. The user might have a particular contaminant in mind, like heavy metals or organic dyes. Tailoring MOFs for specific targets is a big advantage.

Possible deeper needs: The user might be designing a MOF for a specific application and wants to know which functional groups to use. Or they're reviewing literature and trying to understand why certain groups were chosen. They might also be interested in synthesis methods for functionalization, but the question doesn't ask that. I should focus on the importance rather than methods.

I need to ensure the explanation connects functional groups to real-world applications. Emphasize how customization addresses different contamination scenarios. Maybe they're overwhelmed by the variety of MOFs and need a framework to choose functional groups. Highlighting the structure-property relationship here is key.

Also, consider if they're looking for limitations. Functionalization might affect porosity or stability. But the question is about importance, so stick to benefits unless asked for downsides. Conclude by tying it all together: functional groups make MOFs versatile and effective tools for diverse contamination challenges.

Figure S32. Reasoning trace generated by DeepSeek R1 for the same question as Figure S23, showing an alternative, more exploratory reasoning style that emphasizes factor enumeration and intuitive hypothesis generation.

Section S3. Evaluating MOFReasoner

Evaluation Dataset Description

The evaluation benchmark used in this study consists of eight expert-curated questions that were designed to represent the four major themes of MOF adsorption research: experimental studies, adsorption mechanisms, application scenarios, and industrialization-related issues. Each question was constructed as a multi-step reasoning task rather than a simple factual query. To allow fine-grained assessment of reasoning quality, each question was divided into multiple scoring points that correspond to the essential elements of the expected scientific reasoning process. These points capture different dimensions of reasoning performance, including factual correctness, mechanistic interpretation, clarity and depth of justification, and chemical plausibility.

The evaluation questions were created independently of the training data and were phrased to avoid direct overlap with any text in the training corpus. All evaluated models were presented with exactly the same set of eight questions, and domain experts applied identical scoring criteria to all models. This procedure ensured fairness, transparency, and consistency across model comparisons. The complete list of evaluation questions is provided below, together with their task category labels and the detailed scoring points used during assessment.

Evaluation procedure and blinding.

All model outputs were evaluated in a fully blinded manner. Before scoring, all identifying information was removed so that evaluators could not determine which model had generated a given response. Two PhD-level researchers with expertise in metal-organic frameworks independently assessed every output using the scoring criteria summarized in Table S7. These criteria guided the evaluation of factual accuracy, chemical reasoning, clarity of justification, and plausibility of the proposed explanations.

Each evaluator completed the scoring independently. After the initial scoring step, all cases in which the two evaluators assigned different labels were reviewed and discussed until a consensus was reached. This consensus-based approach ensured consistent application of the scoring rules and avoided unilateral judgments. The initial level of agreement between evaluators indicated that the scoring criteria were applied in a stable and reproducible manner.

To minimize potential bias, evaluators were instructed to focus strictly on scientific content and not to infer model identity based on writing style, length, or structure. The set of evaluation questions and their scoring points was fixed before assessment and remained unchanged throughout the evaluation process. The aggregated scores used for comparison across models are reported in Table 1 of the main manuscript.

Scoring rubric.

Each response was annotated according to the following categories:

Correct (green): The response is factually accurate and provides sufficient and precise information addressing the question.

Correct but imprecise (yellow): The response contains accurate content but lacks completeness or precision; minor omissions or vagueness are present, though the main idea is still conveyed correctly.

Wrong (grey): The response includes factually incorrect statements that are not central to the core reasoning but nevertheless introduce errors.

Serious error (red): The response contains misleading or fundamentally incorrect claims, e.g.,

contradictions to established chemical principles or statements that could, if taken at face value, lead to hazardous or severely flawed conclusions. These are penalized more heavily than “wrong” responses.

Missing: The “Missing” label is assigned when a model’s response omits one or more relevant key points that are required for a complete scientific answer, while not introducing any factual or conceptual errors. In such cases, no negative penalty is applied, because the model has not provided incorrect information. However, the omission of key content means that the response cannot be considered fully correct, and therefore it does not receive the positive credit associated with “Correct” or “Partially correct” answers. As a result, responses marked as “Missing” differ from fully correct ones in the final evaluation outcome through the absence of earned positive points rather than through explicit penalties. The purpose of including the “Missing” category is to distinguish incompleteness from incorrectness in a principled manner. This design avoids unfairly penalizing concise responses that remain scientifically sound, while at the same time ensuring that incomplete answers are not treated as equivalent to comprehensive and fully correct ones. The “Missing” category is reported as a descriptive statistic to reflect the completeness of a model’s reasoning and coverage of key scientific aspects. Importantly, it does not directly contribute to the numerical score used for model comparison in Table 1, which is calculated solely based on correctness-related criteria. This separation allows readers to interpret both accuracy and completeness without biasing the overall ranking.

Semantic similarity analysis.

To verify that the test set did not overlap with the fine-tuning data, we computed pairwise semantic similarity scores between all training and test questions using the pre-trained all-MiniLM-L6-v2 SentenceTransformer model. The highest observed similarity score was 0.90 (Table S4). Manual inspection confirmed, however, that these highly similar pairs differed substantially in their scientific focus and intent, and thus did not constitute actual duplicates. This demonstrates that even when the embedding model assigns a high similarity score, the questions remain semantically distinct, supporting the validity of the test set as a genuinely novel evaluation benchmark.

Fairness of model comparisons.

All models, including GPT-4.5 and o1, were evaluated under identical conditions. They received exactly the same test questions, without access to external resources or supplementary context. Strict measures were implemented to prevent data leakage between training and evaluation phases, ensuring the integrity and fairness of the comparisons.

Table S5. Four types of test tasks related to MOFs adsorption

experimental studies of MOFs

How are the dynamic and static adsorption performances of MOFs usually evaluated?

How to determine the adsorption sites in MOFs adsorbents?

chemical mechanisms

Why is the introduction of functional groups important in the design of Metal-Organic Framework for contaminant removal?

applications of MOF-based adsorbents

What is the effect of MOFs adsorbent on removing heavy metal ions in water treatment?

What is the regeneration performance of MOFs adsorbent?

industrialization-related issues

What are the current bottlenecks for HKUST-1 in industrial gas separation applications?

Compared with zeolite materials, what are the advantages of MOFs (Metal-Organic Frameworks) materials in vacuum swing adsorption?

How can the water stability of MOFs be enhanced to ensure their effectiveness under operational conditions?

Table S6. Semantic similarity analysis between evaluation test questions and training questions.

Num ber	Evaluation Question	Similarity	Most Similar Training Question
1	How are the dynamic and static adsorption performances of MOFs usually evaluated?	0.907461	How does the dynamic nature of MOFs affect their adsorption capabilities?
2	How to determine the adsorption sites in MOFs adsorbents?	0.771109	How does the introduction of active sites in MOFs enhance their adsorption performance?
3	Why is the introduction of functional groups important in the design of Metal-Organic Framework for contaminant removal?	0.746780	How can Metal-Organic Frameworks (MOFs) be effectively utilized for the removal of contaminants from wastewater?
4	What is the effect of MOFs adsorbent on removing heavy metal ions in water treatment?	0.794539	How can metal-organic framework (MOF)-based composites be effectively used to remove heavy metal ions from water, and what are their advantages over traditional adsorbents?
5	What is the regeneration performance of MOFs adsorbent?	0.858059	Why is regeneration critical for the commercialization of MOFs as adsorbents?
6	What are the current bottlenecks for HKUST-1 in industrial gas separation applications?	0.679523	How can the gas adsorption and separation performance of HKUST-1 be improved through chemical modifications to its structure, particularly for CO ₂ and SO ₂ capture?

	Compared with zeolite materials, what are the advantages of MOFs 7 (Metal-Organic Frameworks) materials in vacuum swing adsorption?	0.836858	How do MOFs compare to traditional adsorbents like zeolites in terms of heavy metal removal efficiency?
8	How can the water stability of MOFs be enhanced to ensure their effectiveness under operational conditions?	0.899661	What challenges does the low water stability of MOFs present in water treatment applications?

Table S7. Key points of reference answers for different questions.

Question	Standard Answer (Key Bottlenecks)
What are the current bottlenecks for HKUST-1 in industrial gas separation applications?	Costs; efficiency; scalability; stability; performance
Compared with zeolite materials, what are the advantages of MOFs (Metal-Organic Frameworks) materials in vacuum swing adsorption?	High porosity; tunable pore structures; adjustable surface functionalities; higher selectivity; flexibility and customization
How can the water stability of MOFs be enhanced to ensure their effectiveness under operational conditions?	robust metal ions and ligands; post-synthesis modification; encapsulation or coating; defect control and mechanical integrity
What is the regeneration performance of MOFs adsorbent?	thermal regeneration; pressure swing regeneration; vacuum regeneration; solvent washing
What is the effect of MOFs adsorbent on removing heavy metal ions in water treatment?	high surface area and porosity; tunable pore size and selectivity; surface functionalization; multiple adsorption mechanisms; low-concentration removal
Why is the introduction of functional groups important in the design of Metal-Organic Framework for contaminant removal?	improved affinity and binding strength; enhanced interaction mechanisms; increased adsorption capacity; tunable pore environment
How are the dynamic and static adsorption performances of MOFs usually evaluated?	breakthrough experiments; adsorption isotherms; thermogravimetric analysis
How to determine the adsorption sites in MOFs adsorbents?	DFT calculations; GCMC simulations; neutron diffraction; X-ray crystallography

The current bottlenecks for HKUST-1 in industrial gas separation applications include the need for further optimization to reduce costs and improve efficiency, the need for better scalability and production processes, and the requirement for further research to enhance its performance and stability under industrial conditions.

Figure S33. The answer provided by the MOFReasoner model to the question "What are the current bottlenecks for HKUST-1 in industrial gas separation applications?"

The application of HKUST-1, a copper-based metal-organic framework (MOF), in industrial gas separation faces several critical bottlenecks that hinder its widespread adoption. These challenges span material stability, synthesis, performance, and economic factors:

1. **Moisture Sensitivity:**
2. **Synthesis Scalability and Cost:**
3. **Thermal and Chemical Stability:**
4. **Performance in Real Gas Streams:**
5. **Regeneration and Durability:**
6. **Material Formulation:**
7. **Economic Competition:**

Research Directions to Address Bottlenecks:

- **Hydrophobic Modifications:** Incorporating hydrophobic groups to enhance moisture resistance.
- **Alternative Synthesis:** Exploring solvent-free (mechanochemical) or green solvent routes.
- **Composite Materials:** Combining HKUST-1 with polymers or stable matrices to improve mechanical robustness.
- **Ligand Substitution:** Designing cheaper, more stable ligands to reduce costs and enhance stability.

Overcoming these challenges requires interdisciplinary efforts in materials science and chemical engineering to optimize HKUST-1 for industrial viability while maintaining its advantageous adsorption properties.

Figure S34. The answer provided by the DeepSeek-R1-671B model to the question "What are the current bottlenecks for HKUST-1 in industrial gas separation applications?"

As of July 2024, the potential challenges for HKUST-1 in industrial gas separation applications include:

Cost and Scalability: The production of HKUST-1 may be costly and complex, limiting its large-scale use in industries.

Stability and Durability: Concerns about its performance in harsh environments, such as high temperatures or pressures, need addressing.

Competition from Existing Materials: Established materials in the market may hinder HKUST-1's adoption.

Regulatory and Safety Considerations: Ensuring compliance and safety for industrial use is crucial.

Adoption and Training: Industrial implementation may require significant investment in training and infrastructure.

Environmental Impact: The environmental effects of its production and use should be considered.

For the latest information, consult recent research or industry experts.

Figure S35. The answer provided by the DeepSeek-R1-Distill-Llama-8B model to the question "What are the current bottlenecks for HKUST-1 in industrial gas separation applications?"

As of my knowledge cutoff in July 2024, I don't have specific information on the current bottlenecks for HKUST-1 in industrial gas separation applications. However, I can provide some general information on what might be considered bottlenecks in this field.

Industrial gas separation applications often involve the separation of gases based on their physical and chemical properties. This can include processes such as distillation, absorption, and adsorption. Bottlenecks in such processes can include:

Efficiency: Low efficiency of the separation process can be a bottleneck, especially for large-scale industrial applications where high purity of separated gases is required.

Cost: High initial investment costs for equipment and infrastructure can be a barrier, particularly for smaller companies or those with limited resources.

Scalability: Difficulty in scaling up processes from laboratory to industrial scale can be a challenge, especially if the process is not well-optimized or if there are issues with mass transfer or heat transfer.

Environmental Impact: High energy consumption or emissions during the separation process can lead to environmental concerns, which might be a bottleneck in terms of regulatory compliance or sustainability goals.

Technological Limitations: Lack of advanced technologies or innovations that can improve separation efficiency, reduce energy consumption, or lower costs can be a bottleneck.

Regulatory and Compliance Issues: Compliance with industry standards, safety regulations, and environmental protection requirements can sometimes create delays or additional costs, acting as a bottleneck.

Supply Chain Constraints: Availability of raw materials, spare parts, or other components necessary for the separation process can create supply chain bottlenecks.

Market Demand: If there is insufficient demand for a particular separated gas, it can act as a bottleneck for industrial applications.

Maintenance and Downtime:

Human Factor:

Figure S36. The answer provided by the DeepSeek-R1-Distill-Qwen-7B model to the question "What are the current bottlenecks for HKUST-1 in industrial gas separation applications?"

HKUST-1 (also known as Cu-BTC) is one of the most extensively studied metal-organic frameworks (MOFs), particularly highlighted for its promising properties in gas adsorption and separation. While HKUST-1 exhibits excellent lab-scale performance, several critical bottlenecks currently limit its widespread industrial implementation in gas separation applications:

1. Low Stability Under Humid Conditions

.....

2. Mechanical Stability Issues

.....

3. Scale-up and Production Challenges

.....

4. Sensitivity to Impurities and Contaminants

.....

5. Competitive Performance vs. Established Adsorbents

.....

6. Thermal Stability Issues

.....

Current Research and Mitigation Approaches:

- Development of Core-Shell Structures and Hybrid Composites: Combining HKUST-1 with protective polymer shells or embedding it in composite matrices can provide better moisture resistance and mechanical robustness.
- Functionalization and Modification Strategies: Surface or ligand-modification strategies aim to enhance chemical, thermal, or mechanical stability to widen usability in industrial scenarios.
- Alternative MOFs and Related Frameworks: Researchers are investigating and developing other MOFs featuring higher chemical stability, such as ZIFs (Zeolitic Imidazolate Frameworks) and UiO-66 variants for humid gas separations.

In summary.....

Figure S37. The answer provided by the gpt-4.5-preview model to the question "What are the current bottlenecks for HKUST-1 in industrial gas separation applications?"

HKUST-1, also known as MOF-199, is a well-studied metal-organic framework (MOF) composed of copper ions coordinated with benzene-1,3,5-tricarboxylate ligands. Its high surface area, porosity, and tunable properties make it a promising material for gas storage and separation applications. However, several bottlenecks hinder its widespread adoption in industrial gas separation processes:

1. **Hydrothermal Stability:**

.....

2. **Mechanical Stability:**

.....

3. **Scalability and Production Costs:**

.....

4. **Selectivity and Purity Requirements:**

.....

5. **Thermal and Chemical Stability:**

.....

6. **Regeneration Energy Requirements:**

.....

7. **Integration with Existing Infrastructure:**

.....

8. **Environmental and Lifecycle Considerations:**

.....

9. **Competition with Other Materials:**

.....

Conclusion:

While HKUST-1 holds significant promise for industrial gas separation due to its favorable adsorption properties, several bottlenecks related to stability, scalability, and integration need to be addressed. Continued research and development are crucial to overcome these obstacles and realize the full potential of HKUST-1 in industrial applications.

Figure S38. The answer provided by the o1-preview model to the question "What are the current bottlenecks for HKUST-1 in industrial gas separation applications?"

HKUST-1, also known as Cu-BTC (copper benzene-1,3,5-tricarboxylate), is a metal-organic framework (MOF) that has garnered significant attention for its potential in gas separation applications due to its high surface area, tunable pore size, and excellent adsorption properties. However, despite its promising characteristics, there are several bottlenecks that hinder the widespread industrial adoption of HKUST-1 in gas separation processes. These challenges can be broadly categorized into stability issues, scalability concerns, and performance limitations.

.....

Conclusion

While HKUST-1 holds great promise for gas separation applications, its industrial implementation is currently hindered by challenges related to **stability**, **scalability**, **performance**, and **competition from established technologies**. Addressing these bottlenecks will require continued research into material stabilization, cost-effective synthesis, and innovative integration strategies, such as mixed-matrix membranes or composite materials. As these issues are resolved, HKUST-1 could play a more prominent role in next-generation gas separation technologies.

Figure S39. The answer provided by the Qwen-Max model to the question "What are the current bottlenecks for HKUST-1 in industrial gas separation applications?"

HKUST-1, also known as Cu-BTC (Copper-based Benzene-1,3,5-tricarboxylate), is a well-studied metal-organic framework (MOF) with potential applications in gas separation. However, there are several bottlenecks that currently limit its widespread industrial application for gas separation:

.....

Conclusion

While HKUST-1 shows promise for gas separation, addressing these bottlenecks—particularly stability, scalability, and performance under dynamic conditions—is essential for its successful industrial deployment. Ongoing research focuses on improving these aspects through material modification, process optimization, and integration with existing technologies.

Figure S40. The answer provided by the Qwen-Plus model to the question "What are the current bottlenecks for HKUST-1 in industrial gas separation applications?"

As an AI language model, I don't have access to the latest research or specific information about HKUST-1's performance in industrial gas separation applications. However, I can provide some general insights into potential bottlenecks that metal-organic frameworks (MOFs), like HKUST-1, might face in industrial settings.

Stability:

Mass Transfer Limitations:

Regeneration and Cycling:

Scalability and Cost:

Selectivity vs. Capacity Trade-off:

Mechanical Strength:

Poisoning and Contamination:

Integration with Existing Infrastructure:

These are some of the general bottlenecks that MOFs, including HKUST-1, might encounter in industrial gas separation applications. Overcoming these challenges would require a combination of material innovation, process optimization, and economic considerations.

Figure S41. The answer provided by the QwQ-32B model to the question "What are the current bottlenecks for HKUST-1 in industrial gas separation applications?"

MOFs offer high porosity, tunable pore structures, and adjustable surface functionalities, enabling more precise control over adsorption mechanisms. This leads to higher selectivity and adsorption capacity for gases like CO₂ and H₂, making them more efficient than zeolites in certain applications.

Figure S42. The answer provided by the MOFReasoner model to the question "Compared with zeolite materials, what are the advantages of MOFs (Metal-Organic Frameworks) materials in vacuum swing adsorption?"

Advantages of MOFs over Zeolites in Vacuum Swing Adsorption (VSA):

1. Enhanced Tunability and Selectivity:
2. Higher Surface Area and Adsorption Capacity:
3. Improved Regeneration Efficiency:

MOFs can be engineered with moderate binding strengths (physisorption) tailored to target gases, lowering the isosteric heat of adsorption compared to some zeolites. This reduces the energy required for desorption under vacuum, enhancing overall process efficiency.

4. Faster Adsorption/Desorption Kinetics:

The hierarchical or larger pore structures in MOFs facilitate rapid gas diffusion, enabling quicker cycling in VSA systems. Zeolites, with narrower micropores, may suffer from slower diffusion, especially for larger molecules.

5. Flexible Framework Dynamics:

6. Versatility in Gas Separation Applications:

Considerations and Challenges:

- Stability: While early MOFs faced issues with moisture/thermal stability, advances in robust frameworks (e.g., UiO-66, ZIF-8) have improved viability.
- Cost and Scalability: MOF synthesis is generally more expensive than zeolite production, but economies of scale and modular designs are mitigating these barriers.

In summary, MOFs outperform zeolites in VSA by combining high capacity, tailored selectivity, and energy-efficient regeneration, provided stability and cost constraints are managed. Their design flexibility positions them as next-generation materials for advanced gas separation challenges.

Figure S43. The answer provided by the DeepSeek-R1-671B model to the question "Compared with zeolite materials, what are the advantages of MOFs (Metal-Organic Frameworks) materials in vacuum swing adsorption?"

Advantages of MOFs over Zeolites in Vacuum Swing Adsorption:

1. **Higher Surface Area:** MOFs offer significantly higher surface areas compared to zeolites, allowing for greater adsorption capacity and efficiency in vacuum swing adsorption processes.
2. **Customizable Framework Structure:** The unique frameworks of MOFs enable the creation of tailored pore sizes and structures, facilitating selective adsorption and separation of specific molecules, which is crucial for processes like gas purification and concentration.
3. **Versatility and Scalability:** MOFs can be easily synthesized in large quantities and modified to suit specific industrial needs, providing versatility and scalability. This adaptability is beneficial for various applications, including gas separation and storage, where customized solutions are essential.
4. **Wider Adsorption Range:** Due to their versatile frameworks, MOFs can adsorb a broader range of substances and can potentially operate under diverse environmental conditions, such as **higher temperatures or pressures**, which may not be as effectively managed by zeolites.
In contrast, while zeolites offer structured pores and are effective in certain separation processes, their natural structure and limited variability make them less adaptable for some vacuum swing adsorption applications compared to MOFs.

Figure S44. The answer provided by the DeepSeek-R1-Distill-Llama-8B model to the question "Compared with zeolite materials, what are the advantages of MOFs (Metal-Organic Frameworks) materials in vacuum swing adsorption?"

Metal-Organic Frameworks (MOFs) offer several advantages over zeolites in the context of vacuum swing adsorption (VSA), particularly in separating isobutane from n-pentane. Here are the key advantages:

1. **Larger pores and higher adsorbent capacity:** MOFs have larger micropores compared to zeolites, allowing them to trap heavier hydrocarbons like n-pentane effectively, which is crucial for VSA.
2. **Mechanical stability:** MOFs are highly durable and resistant to collapse, ensuring consistent adsorption over time without degradation, unlike some zeolites.
3. **Flexibility and customization:** MOFs can be synthesized with tailored ligands, allowing them to adsorb specific molecules, making them versatile for various applications.
4. **Thermal stability:** MOFs maintain their structure at higher temperatures, making them ideal for industrial processes where stability is key.
5. **Controlled porosity:** The ability to synthesize MOFs with specific pore sizes ensures precise adsorption, enhancing efficiency in VSA applications.
6. **High scalability and throughput:** MOFs can handle large flow rates and pressures, supporting industrial-scale operations.

These advantages make MOFs superior to zeolites in achieving efficient separations in VSA, particularly in the hydrocarbon industry.

Figure S45. The answer provided by the DeepSeek-R1-Distill-Qwen-7B model to the question "Compared with zeolite materials, what are the advantages of MOFs (Metal-Organic Frameworks) materials in vacuum swing adsorption?"

Metal-Organic Frameworks (MOFs) offer several significant advantages compared with zeolite materials in vacuum swing adsorption (VSA), primarily due to differences in chemical flexibility, structural features, and tunable functionality:

1. Higher Surface Area and Pore Volume:
2. Tunable Pore Size and Structure:
3. Improved Selectivity and Specific Adsorption Sites:
4. Mild Desorption Conditions and Lower Energy Requirement:
5. Reduced Diffusion Limitations (Improved Mass Transfer):
6. Low Thermal Regeneration Temperatures (Energy-Saving Trait):

Lower enthalpies of adsorption in MOFs typically translate into lower energies required for regeneration. Hence, MOFs can operate at milder conditions, reducing thermal and energy penalties. Although vacuum swing processes usually don't require high-temperature regeneration, weaker interactions improve cycling speed and overall process economics.

7. Compatibility with Moisture and Flexible Operating Conditions:

Certain strategically selected or modified MOFs can show increased stability and performance under humid or challenging operating conditions. Their chemical versatility allows strategic functionalization that can protect from moisture-induced instability, whereas many traditional zeolites demonstrate reduced adsorption capacity in moist environments.

8. Diverse Structural and Compositional Options (Material Diversity):

In summary, the advantages of MOFs relative to zeolites in vacuum swing adsorption include enhanced adsorption capacities, tailored selectivity, low operating and regeneration energy requirements, improved adsorption-desorption kinetics, tunable pore sizes and chemistries, and greater performance versatility and reliability under various operational constraints.

Figure S46. The answer provided by the gpt-4.5-preview model to the question "Compared with zeolite materials, what are the advantages of MOFs (Metal-Organic Frameworks) materials in vacuum swing adsorption?"

Introduction

Vacuum Swing Adsorption (VSA) is a process used for gas separation and purification, where selective adsorption of gases occurs at near-ambient pressures, and desorption is achieved by reducing the pressure (applying a vacuum). Adsorbent materials play a crucial role in this process, and their properties significantly impact the efficiency and selectivity of gas separation.

Zeolites vs. Metal-Organic Frameworks (MOFs)

Zeolites are crystalline

Metal-Organic Frameworks (MOFs) are a class of

Advantages of MOFs over Zeolites in VSA

1. Higher Surface Areas
2. Tunable Pore Sizes and Structures
3. Functionalizable Frameworks
4. Adjustable Framework Flexibility
5. Potential for Lower Regeneration Energy
6. Versatility in Design

Conclusion

Metal-Organic Frameworks (MOFs) offer several advantages over zeolite materials in Vacuum Swing Adsorption (VSA) processes due to their high surface areas, tunable pore sizes, functionalizable frameworks, flexibility, potentially lower regeneration energies, and versatility in design. These properties allow MOFs to achieve higher adsorption capacities, improved selectivity, and greater efficiency in gas separation applications. While zeolites are robust and well-established adsorbents, the customizable nature of MOFs provides significant opportunities for optimizing VSA processes for various industrial applications.

Figure S47. The answer provided by the o1-preview model to the question "Compared with zeolite materials, what are the advantages of MOFs (Metal-Organic Frameworks) materials in vacuum swing adsorption?"

Metal-Organic Frameworks (MOFs) have emerged as promising materials for gas separation and storage applications, including vacuum swing adsorption (VSA), due to their unique structural and chemical properties. Compared with traditional zeolites, MOFs offer several advantages in VSA processes:

1. High Surface Area and Porosity.....
2. Tunable Pore Size and Chemistry.....
3. Lower Regeneration Energy.....
4. Structural Diversity.....
5. Hydrophobicity and Stability in Humid Conditions
6. Flexibility in Adsorption Mechanisms
7. Lightweight and Low-Density Materials

Conclusion:

In summary, MOFs offer several key advantages over zeolites in vacuum swing adsorption (VSA) processes, including higher surface areas, tunable pore sizes and chemistries, lower regeneration energies, greater structural diversity, improved hydrophobicity, flexible adsorption mechanisms, and lower material density. These features make MOFs highly attractive for applications requiring high selectivity, energy efficiency, and adaptability to different gas mixtures and environmental conditions. However, it's worth noting that challenges such as mechanical stability and cost of production still need to be addressed for widespread industrial adoption of MOFs in VSA systems.

Figure S48. The answer provided by the Qwen-Max model to the question "Compared with zeolite materials, what are the advantages of MOFs (Metal-Organic Frameworks) materials in vacuum swing adsorption?"

Metal-Organic Frameworks (MOFs) offer several advantages over zeolites in vacuum swing adsorption (VSA) processes. These advantages stem from the unique structural and chemical properties of MOFs:

1. **High Surface Area and Porosity:**
2. **Tunable Pore Size and Chemistry:**
3. **Tailored Adsorption Sites:**
4. **Lower Heat of Adsorption:**
5. **Faster Kinetics:**
6. **Versatility in Design:**
7. **Stability under Various Conditions:**
8. **Potential for Hybrid Systems:** MOFs can be combined with other materials to create hybrid systems that leverage the benefits of both components. For example, integrating MOFs with polymers or other porous materials can result in composites with enhanced mechanical strength and thermal stability, suitable for practical VSA applications.

In summary, MOFs provide significant advantages in terms of tunability, selectivity, kinetics, and energy efficiency, making them promising candidates for enhancing the performance of vacuum swing adsorption processes.

Figure S49. The answer provided by the Qwen-Plus model to the question "Compared with zeolite materials, what are the advantages of MOFs (Metal-Organic Frameworks) materials in vacuum swing adsorption?"

Metal-Organic Frameworks (MOFs) offer several advantages over zeolites in vacuum swing adsorption (VSA) processes. Here's a structured comparison highlighting the key benefits of MOFs:

1. **Higher Adsorption Capacity**
2. **Tailorable Pore Size and Chemistry**
3. **Enhanced Selectivity**
4. **Faster Mass Transfer**
5. **Lower Desorption Energy Requirements**
6. **Stability in Gas Environments**
7. **Adaptability to Multi-Component Mixtures**
8. **Kinetic Advantages**

- Accessibility of Pores: MOFs often have more accessible pore networks, allowing rapid gas access to adsorption sites during high-pressure adsorption phases and efficient desorption under vacuum.

Summary of Key Advantages:

- Higher capacity due to surface area and porosity.
- Design flexibility for pore size and chemistry.
- Enhanced selectivity through functionalization.
- Faster diffusion and mass transfer kinetics.
- Energy efficiency in desorption via pressure swing.
- Adaptability to diverse gas separation needs.

These advantages make MOFs a promising alternative to zeolites in VSA, particularly for applications requiring high selectivity, capacity, and energy efficiency. However, challenges like scalability and cost remain areas for further development.

Figure S50. The answer provided by the QwQ-32B model to the question "Compared with zeolite materials, what are the advantages of MOFs (Metal-Organic Frameworks) materials in vacuum swing adsorption?"

Water stability can be enhanced by using robust metal ions, incorporating hydrophobic organic linkers, and employing post-synthetic modifications to improve the framework's resistance to water adsorption.

Figure S51. The answer provided by the MOFReasoner model to the question "How can the water stability of MOFs be enhanced to ensure their effectiveness under operational conditions?"

To enhance the water stability of Metal-Organic Frameworks (MOFs) and ensure their effectiveness under operational conditions, several strategies can be employed, each addressing different aspects of MOF structure and environmental interaction:

1. **Stable Metal-Cluster Selection:**
2. **Ligand Engineering:**
3. **Post-Synthetic Modifications (PSM):**
4. **Defect Control:**

- Optimize synthesis conditions (e.g., modulators, temperature) to minimize defects, enhancing crystallinity and stability. Controlled defect engineering might also block water ingress.

5. **Composite Materials:**
6. **Crosslinking and Ion Exchange:**
7. **Computational Design:**
8. **pH Management:**

Examples and Considerations:

- ZIF-8 (Zn/imidazolate) exhibits hydrophobicity and stability in boiling water.
- UiO-66 (Zr-based) demonstrates robustness due to strong Zr clusters and defect-tolerant synthesis.
- MIL-101 (Cr-based) combines large pores with high stability.

Trade-offs:

- Hydrophobic groups may reduce pore accessibility.
- Composites might lower surface area or active site availability.
- Synthesis complexity increases with advanced modifications.

By strategically combining these approaches—such as pairing hydrophobic ligands with stable metal clusters or integrating MOFs into protective composites—researchers can tailor water stability while preserving functionality for specific applications.

Figure S52. The answer provided by the DeepSeek-R1-671B model to the question "How can the water stability of MOFs be enhanced to ensure their effectiveness under operational conditions?"

Enhancing the water stability of Metal-Organic Frameworks (MOFs) involves a multifaceted approach to ensure their effectiveness under operational conditions. Here's a prioritized and organized synthesis of the key strategies:

1. Choice of Metals and Ligands:

- Select metals like zinc or iron, which form stable ammine complexes, reducing vulnerability to water-reactivity.
- Use ligands that form strong bonds, such as those with higher coordination, to stabilize the framework.

2. Synthesis Conditions:

- Employ solvents with low solvent power to prevent water interaction with counterions and stabilize frameworks.
- Consider bulky ligands to minimize water interaction and enhance structural integrity.

3. Post-Synthesis Modifications:

- Coat the MOF with polymers or silica shells to create a protective layer against water contact.
- Introduce water-stabilizing layers, possibly using surfactants or fluorophosphates, to repel water and prevent pore infiltration.

4. Structure and Porosity:

- Design pore sizes and access restrictions to hinder water penetration.
- Utilize water-repellent surfaces or microporous structures that exclude water while maintaining functionality.

5. Ambient Conditions:

- Control operational conditions such as temperature and humidity to minimize degradation.
- Modify MOFs to adapt to varying environmental conditions, ensuring stability across different scenarios.

6. Activation Strategies:

- Implement water-tolerant activation methods to maintain framework integrity during use.
- Consider activating MOFs to enhance hydrophobicity, ensuring long-term stability under wet conditions.

By integrating these strategies, the water stability of MOFs can be significantly enhanced, ensuring their effectiveness in diverse operational environments.

Figure S53. The answer provided by the DeepSeek-R1-Distill-Llama-8B model to the question "How can the water stability of MOFs be enhanced to ensure their effectiveness under operational conditions?"

To enhance the water stability of metal-organic frameworks (MOFs) and ensure their effectiveness under operational conditions, consider the following strategies:

1. Structural Modifications:

- Reduce Pore Size: Smaller pores minimize water infiltration, improving durability and stability in aqueous environments.

- Improve Ligand Properties: Use hydrophobic or anionic ligands to reduce water binding. Consider cross-linking or modifying ligands for enhanced hardness.

2. Additives and Cross-Linking:

- Incorporate stabilizers or cross-linkers to maintain framework integrity in water. PEG and other swellenders can be used, depending on their role in the system.

3. Thermal Stability:

- Use antioxidants or conducting polymers to stabilize MOFs against thermal degradation, which indirectly enhances water stability by preventing structural changes.

4. Chemical Environment Considerations:

- Utilize species like sodium hydride (NAH) or potassium acid (KAH) to stabilize MOFs based on pH, affecting their overall stability in aqueous environments.

5. Coordination and Binding Strength:

- Increase binding strength by strengthening or adding bridging ligands. Higher coordination can enhance resistance to water uptake.

6. Mechanical Integrity:

- Develop a robust, fixed structure through ligand modifications to hinder water entry and maintain framework integrity.

7. Application-Specific Additives:

- Tailor additives to the specific operational conditions of MOFs, such as using water-resistant ligands for aqueous catalysis applications.

By integrating these strategies, MOFs can be optimized to maintain their structural integrity and functionality in water, ensuring their effectiveness under various operational conditions.

Figure S54. The answer provided by the DeepSeek-R1-Distill-Qwen-7B model to the question "How can the water stability of MOFs be enhanced to ensure their effectiveness under operational conditions?"

Improving the water stability of Metal-Organic Frameworks (MOFs) is essential to maintain their structural integrity and functionality under realistic operational conditions, especially when exposed to moisture, aqueous environments, or harsh operational settings. A variety of approaches and strategies have been developed to enhance MOF stability against water, including:

1. Selection of Hydrophobic or Highly Stable Building Units:
2. Metal-ligand Coordination Chemistry Optimization:
3. Post-synthetic Modification and Surface Functionalization:
4. Introduction of Hydrophobicity and Fluorination:
5. Composite Formation:
6. Structural and Topological Engineering:
7. Kinetic Stability Enhancement:
8. Solvent and synthesis route optimization:
9. Defective Site Control:

Reducing defects or healing defects (e.g., through post-synthetic treatments, annealing, or controlled ligand additions) prevents water infiltration and stabilizes overall MOF integrity.

Common Examples of MOFs with Enhanced Water Stability:

Zr-based MOFs (e.g., UiO-66, UiO-67, PCN-type structures)

Al-based MOFs (e.g., MIL-53, MIL-101)

Zeolitic-Imidazolate Frameworks (especially ZIF-8 and ZIF-67), based on Zn^{2+} or Co^{2+} with imidazole derivatives, that mimic zeolitic stability.

By carefully integrating these strategies—often in combination—researchers can significantly improve water stability, enabling MOFs to operate effectively and maintain performance under realistic conditions involving moisture, prolonged exposures, and competitive commercial applications.

Figure S55. The answer provided by the gpt-4.5-preview model to the question "How can the water stability of MOFs be enhanced to ensure their effectiveness under operational conditions?"

Enhancing the water stability of Metal-Organic Frameworks (MOFs) is crucial for their practical application in various fields such as gas storage, separation, catalysis, and sensing. MOFs are known for their high surface areas and tunable pore structures, but many suffer from degradation when exposed to moisture, which limits their effectiveness under operational conditions. Here are several strategies to improve the water stability of MOFs:

1. Selection of Stable Metal Nodes
2. Design of Hydrophobic Ligands
3. Post-Synthetic Modification (PSM)
4. Surface Coating and Encapsulation
5. Structural Design and Engineering
6. Incorporation of Hydrophobic Pockets
7. Use of Inherently Stable MOFs
8. Mixed-Metal MOFs
9. Optimization of Synthesis Conditions
10. Environmental Control and Application Conditions

Conclusion

Enhancing the water stability of MOFs is a multifaceted challenge that requires careful consideration of the metal nodes, organic ligands, and overall framework design. By combining strategies such as selecting appropriate metals, designing hydrophobic ligands, employing post-synthetic modifications, and protecting MOFs with coatings or encapsulation, it is possible to develop MOFs that maintain their structural integrity and functionality in the presence of water. Tailoring the synthesis and post-synthesis treatments to the specific application and operational conditions will ensure that MOFs perform effectively in real-world environments.

Note: When designing or selecting MOFs for applications involving exposure to moisture, it's essential to thoroughly evaluate their stability through experimental testing under relevant conditions.

Figure S56. The answer provided by the o1-preview model to the question "How can the water stability of MOFs be enhanced to ensure their effectiveness under operational conditions?"

Metal-Organic Frameworks (MOFs) are highly porous materials with diverse applications, including gas storage, separation, catalysis, and water treatment. However, their practical implementation is often hindered by poor water stability, as many MOFs degrade or lose structural integrity when exposed to moisture or liquid water. Enhancing the water stability of MOFs is crucial for ensuring their effectiveness under operational conditions. Below are several strategies to improve the water stability of MOFs:

1. Selection of Robust Metal Nodes
2. Design of Hydrophobic Organic Linkers
3. Defect Engineering
4. Surface Coating
5. Optimization of Synthesis Conditions
6. Incorporation of Hydrogen-Bonding Networks
7. Post-Synthetic Modifications
8. Encapsulation in Composite Materials
9. Computational Screening and Rational Design
10. Operational Strategies

By combining these strategies, researchers can tailor MOFs to withstand water exposure while maintaining their functional properties. The choice of approach depends on the specific application and operational conditions of the MOF.

Figure S57. The answer provided by the Qwen-Max model to the question "How can the water stability of MOFs be enhanced to ensure their effectiveness under operational conditions?"

Metal-Organic Frameworks (MOFs) are highly porous materials with a wide range of potential applications, including gas storage, catalysis, and separations. However, many MOFs are prone to degradation in the presence of water, which can limit their practical utility. Enhancing the water stability of MOFs is therefore critical for ensuring their effectiveness under operational conditions. Below are several strategies that can be employed to improve the water stability of MOFs:

1. **Choice of Metal Ions**
2. **Design of Organic Linkers**
3. **Post-Synthetic Modification (PSM)**
4. **Encapsulation or Coating**
5. **Synthesis Conditions**
6. **Rational Design of Framework Topology**
7. **Use of UiO-Type and MIL-Type MOFs**
8. **Computational Screening**

By employing one or more of these strategies, the water stability of MOFs can be significantly enhanced, ensuring their effectiveness in real-world applications where moisture exposure is inevitable.

Figure S58. The answer provided by the Qwen-Plus model to the question "How can the water stability of MOFs be enhanced to ensure their effectiveness under operational conditions?"

Enhancing the water stability of Metal-Organic Frameworks (MOFs) is critical for their practical application under operational conditions. Below is a structured approach to achieving this, combining material design, synthesis strategies, and post-synthesis treatments:

1. Material Design Strategies
 - a. Select Stable Metal Nodes.....
 - b. Optimize Organic Linkers.....
 - c. Framework Topology.....
2. Synthesis Modifications
 - a. Anhydrous Synthesis Conditions.....
 - b. Mixed-Linker Systems.....
 - c. Post-Synthesis Treatments.....
3. Functionalization and Surface Engineering
 - a. Hydrophobic Functionalization.....
 - b. pH Optimization.....
4. Testing and Validation.....
5. Case Studies and Examples.....

Conclusion

Enhancing water stability in MOFs requires a multi-pronged approach:

- Material design (stable metals, hydrophobic linkers, rigid frameworks),
- synthesis control (anhydrous conditions, crosslinking),
- post-synthesis treatments (coatings, functionalization), and
- environmental optimization (pH, humidity).

Combining these strategies can tailor MOFs for specific applications, ensuring their durability under operational conditions. Continuous research into novel materials and hybrid systems (e.g., MOF-polymer composites) will further advance their stability and utility.

Figure S59. The answer provided by the QwQ-32B model to the question "How can the water stability of MOFs be enhanced to ensure their effectiveness under operational conditions?"

MOFs can be regenerated using thermal, pressure, or vacuum swing methods. These methods aim to desorb adsorbed gases while maintaining the structural integrity of the MOF. The efficiency of regeneration depends on the specific MOF and the regeneration conditions.

Figure S60. The answer provided by the MOFReasoner model to the question "What is the regeneration performance of MOFs adsorbent?"

The regeneration performance of Metal-Organic Frameworks (MOFs) as adsorbents is influenced by several factors, including their structural stability, regeneration methods, and the nature of the adsorbed species. Here's a structured overview:

Key Factors Affecting Regeneration Performance:

1. Regeneration Methods:

- **Thermal Regeneration**: Most common; involves heating to desorb contaminants (e.g., CO₂, VOCs). Effectiveness depends on MOF thermal stability. For example, UiO-66 (zirconium-based) and MIL-101 (chromium-based) withstand high temperatures (>300°C), while others (e.g., HKUST-1) degrade at lower temps.

- **Pressure Swing Adsorption (PSA)**: Reduces pressure to release adsorbates (e.g., H₂, CH₄ storage). Energy-efficient but less effective for strongly adsorbed species.

- **Chemical/Solvent Treatment**: Washing with solvents or reactive agents (e.g., water, ethanol). Risks include structural collapse or ligand leaching in moisture-sensitive MOFs (e.g., ZIF-8 in water).

2. Structural Stability:.....

3. Adsorbate Specificity:.....

4. Energy Efficiency:.....

Performance Metrics:.....

Examples:.....

Conclusion:

MOFs exhibit promising regeneration performance when designed for stability and paired with appropriate regeneration methods. High-stability frameworks (UiO-66, MIL-101) excel in cyclic applications, while ongoing research aims to improve durability and energy efficiency for industrial deployment.

Figure S61. The answer provided by the DeepSeek-R1-671B model to the question "What is the regeneration performance of MOFs adsorbent?"

The regeneration performance of Metal-Organic Frameworks (MOFs) adsorbent is influenced by several key factors:

1. Type of Adsorption: MOFs primarily undergo physical adsorption, which is generally easier to reverse compared to chemisorption. This suggests that desorption can be quicker and more straightforward, though the high surface area and porosity of MOFs may still pose challenges.
2. Desorption Efficiency: The efficiency of desorption depends on the strength of the adsorption bonds. While physical adsorption is weaker, MOFs might still hold contaminants more tightly due to their structure, potentially complicating desorption processes.
3. Regeneration Methods: Common methods include thermal desorption, where heating is used to release contaminants, and chemical extraction, often involving solvents or acids/base. The choice of method can impact efficiency and the risk of MOF degradation.
4. Stability and Structure: MOFs are susceptible to damage if regenerated harshly, necessitating gentle regeneration processes. EventArgs must balance the need for efficient regeneration with the integrity of the MOF structure to ensure long-term use.
5. Material Durability: The durability of MOFs is crucial. If they remain intact during regeneration, they can maintain their high adsorption capacity over multiple cycles, reducing long-term costs.
6. Environmental and Economic Considerations: The regeneration process must be optimized to balance energy use and cost, ensuring MOFs remain viable for environmental applications.

In conclusion, while MOFs show promise for regeneration, the process depends on the specific MOF structure, type of contaminants, and regeneration method. Optimizing these factors can enhance MOF durability and regeneration efficiency, making them a viable option for environmental use.

Figure S62. The answer provided by the DeepSeek-R1-Distill-Llama-8B model to the question "What is the regeneration performance of MOFs adsorbent?"

The regeneration performance of Metal-Organic Frameworks (MOFs) as adsorbent materials is a critical factor for their practical application, especially in terms of reusability and environmental efficiency. Here is an organized summary of the analysis:

1. Definition and Adsorption Mechanism:
2. Regeneration Importance:
3. Factors Influencing Regeneration Performance:
 - Structure of MOF: High porosity and sufficient strength improve regeneration efficiency. Metal coordination and ligand properties affect adsorbate interaction during desorption.
 - Adsorbate Nature: The polarity and functional groups of adsorbates influence solubility and desorption methods, such as solvent choice or catalysis.
 - Regeneration Methods: Physical processes (e.g., solvent washing) or catalytic methods (using metal-coordinated catalysts) can enhance desorption efficiency.
 - Environmental Conditions: Temperature and pressure significantly impact regeneration, with optimal conditions crucial for performance.

4. Practical Considerations:

- Programmed washing or catalytic regeneration can extend MOF usability, reducing waste and enhancing environmental sustainability.
- The potential for reusable MOFs in industries like electronics and automotive sectors is promising due to reduced packaging and disposal needs.

5. Examples and Optimization:

- Studies suggest that optimized washing agents and conditions can improve the number of cycles MOFs remain effective, enhancing their practicality.

In conclusion, the regeneration performance of MOFs is improved by optimizing their structure, utilizing appropriate regeneration methods, and applying optimal conditions. This makes MOFs a viable and sustainable choice for various applications where reusability and environmental efficiency are priorities.

Figure S63. The answer provided by the DeepSeek-R1-Distill-Qwen-7B model to the question "What is the regeneration performance of MOFs adsorbent?"

Metal-organic frameworks (MOFs) are well-known adsorbents that typically exhibit excellent regeneration performance due to their highly crystalline, porous structures. Regeneration refers to the ability of an adsorbent to release previously captured species, returning to its initial adsorption capacity, while maintaining material structural integrity and performance stability over multiple adsorption-desorption cycles.

Factors influencing the regeneration performance of MOFs include:

Thermal Stability and Durability:

Chemical Stability and Stability Against Moisture:

Regeneration Methodology:

MOFs offer multiple regeneration pathways, such as:

Thermal Swing Adsorption (TSA):

Vacuum Swing Adsorption (VSA):

Pressure Swing Adsorption (PSA):

Chemical Washing or Solvent-Assisted Regeneration:

Adsorption Affinity and Binding Strength:

Material Design and Structure Optimization:

Typical Performance Results:

Practical Implications:

Conclusions:

Overall, MOFs generally display good to excellent regeneration performance, depending strongly upon the structural stability, operational conditions, selected regeneration treatment methods, and precise material formulation. Careful consideration of these factors and proper MOF selection often lead to stable, long-lasting adsorbents capable of maintaining high adsorption performance over many regeneration cycles.

Figure S64. The answer provided by the GPT-4.5-preview model to the question "What is the regeneration performance of MOFs adsorbent?"

Metal-Organic Frameworks (MOFs) are a class of porous crystalline materials composed of metal ions or clusters coordinated to organic ligands, forming three-dimensional structures with exceptionally high surface areas and tunable pore sizes. These characteristics make MOFs highly attractive as adsorbents for various applications, including gas storage, separation, and catalysis.

A critical factor in evaluating the practicality of an adsorbent material is its regeneration performance—the ability to restore its adsorption capacity after each use through a regeneration process. Effective regeneration is essential for the economic and sustainable operation of adsorption-based systems, as it allows the adsorbent to be reused over multiple cycles without significant loss of performance.

Regeneration Performance of MOFs Adsorbents:

Structural Stability:

Regeneration Methods:

Retention of Adsorption Capacity:

Energy Requirements:

Moisture Sensitivity:

Scaling Up:

Examples of MOFs with Good Regeneration Performance:

.....

Conclusion:

The regeneration performance of MOF adsorbents is generally favorable, especially for those designed with stability and cyclability in mind. By selecting MOFs with robust structures and suitable adsorption properties, it is possible to achieve efficient regeneration with minimal loss of performance over multiple cycles. Ongoing research continues to improve the stability and functionality of MOFs, further enhancing their potential as sustainable and efficient adsorbents for various industrial applications.

Figure S65. The answer provided by the o1-preview model to the question "What is the regeneration performance of MOFs adsorbent?"

The regeneration performance of Metal-Organic Frameworks (MOFs) as adsorbents is a crucial factor in determining their practical applicability in various fields such as gas storage, separation, water treatment, and catalysis. Regeneration refers to the ability of an adsorbent to be restored to its original state after being saturated with adsorbed molecules, allowing it to be reused multiple times without significant loss of performance.

Key Factors Affecting MOF Regeneration Performance:

1. Thermal Stability:
2. Chemical Stability:
3. Mechanical Stability:
4. Adsorption Mechanism:
5. Pore Accessibility:

Methods for Regenerating MOFs:

1. Thermal Regeneration:
2. Pressure-Swing Regeneration:
3. Solvent Washing:
4. Vacuum Regeneration:

Examples of MOF Regeneration Performance:

Challenges in MOF Regeneration:

Conclusion:

The regeneration performance of MOFs as adsorbents is generally favorable, especially for robust frameworks like UiO-66, MIL-101(Cr), and ZIF-8, which can withstand multiple regeneration cycles with minimal loss of performance. However, the choice of regeneration method (thermal, pressure-swing, solvent washing, etc.) depends on the specific application and the nature of the adsorbed species. While MOFs offer great promise for reusable adsorbents, challenges related to structural stability, energy consumption, and pore clogging must be addressed to optimize their long-term performance in practical applications.

Figure S66. The answer provided by the Qwen-Max model to the question "What is the regeneration performance of MOFs adsorbent?"

Metal-Organic Frameworks (MOFs) are a class of porous materials composed of metal ions or clusters connected by organic linkers. They have gained significant attention as adsorbents due to their high surface area, tunable pore size, and functionalizable structures. The regeneration performance of MOFs as adsorbents is a critical factor in determining their practical applicability for processes such as gas separation, carbon capture, water purification, and air conditioning.

Key Aspects of MOF Regeneration Performance:

1. Regeneration Efficiency:
2. Regeneration Methods:
 - Thermal Regeneration:
 - Pressure Swing Regeneration:
 - Chemical Regeneration:
 - Vacuum Regeneration:
3. Stability During Regeneration:
4. Energy Consumption:
5. Cycle Life:
6. Selectivity and Reusability:
7. Environmental Impact:

Examples of MOFs with Good Regeneration Performance:

.....

Challenges in MOF Regeneration:

In summary, the regeneration performance of MOFs as adsorbents depends on their design, stability, and the specific application. Optimizing MOF structures and regeneration methods is crucial for enhancing their practical viability in industrial and environmental applications.

Figure S67. The answer provided by the Qwen-Plus model to the question "What is the regeneration performance of MOFs adsorbent?"

The regeneration performance of Metal-Organic Frameworks (MOFs) as adsorbents refers to their ability to be restored to their original adsorption capacity after desorbing the adsorbed materials, enabling reuse. This performance is critical for practical applications like gas separation, carbon capture, and water purification. Below is a structured overview:

Key Methods of Regeneration

1. Thermal Desorption
2. Pressure Swing Adsorption (PSA)
3. Chemical Regeneration
4. Photothermal or Photochemical Methods
5. Vacuum Desorption

Factors Affecting Regeneration Performance

1. MOF Stability:
2. Adsorbate Type:
3. Adsorption Strength:
4. Regeneration Energy:
5. Cycle Stability:

Examples of MOFs with Notable Regeneration Performance

Challenges and Research Directions

Applications Requiring High Regeneration Performance

In summary, MOFs offer tunable regeneration performance depending on their structure, the adsorbate, and the chosen method. Advances in MOF design and regeneration techniques continue to improve their practicality for real-world applications.

Figure S68. The answer provided by the QwQ-32B model to the question "What is the regeneration performance of MOFs adsorbent?"

MOFs adsorbent significantly enhances the removal of heavy metal ions from water through mechanisms such as electrostatic interactions, coordination bonds, and hydrogen bonding. Their high surface area and tunable porosity make them superior to traditional adsorbents.

Figure S69. The answer provided by the MOFReasoner model to the question "What is the effect of MOFs adsorbent on removing heavy metal ions in water treatment?"

Metal-Organic Frameworks (MOFs) have emerged as highly effective adsorbents for removing heavy metal ions in water treatment, offering several advantages and facing certain challenges:

Key Advantages of MOFs:

1. **High Surface Area and Porosity:**
2. **Tailorable Functionality:**
3. **Fast Adsorption Kinetics:**
4. **Selectivity:**
5. **Reusability:**
6. **Composite Enhancements:**

Challenges and Considerations:

Research Frontiers:

- Post-Synthetic Modification: Enhancing MOFs with nanoparticles or polymers for improved functionality.
- Machine Learning: Accelerating the design of MOFs with optimal properties for specific metals.
- Real-World Applications: Pilot studies to validate performance in industrial settings and cost-benefit analyses.

Conclusion:

MOFs are promising adsorbents for heavy metal removal due to their high efficiency, selectivity, and adaptability. While challenges like stability and cost persist, ongoing innovations in material design and composite engineering are paving the way for their practical implementation in water treatment systems.

Figure S70. The answer provided by the DeepSeek-R1-671B model to the question "What is the effect of MOFs adsorbent on removing heavy metal ions in water treatment?"

MOFs (Metal Organic Frameworks) are significant in water treatment for removing heavy metal ions due to their high adsorption capacity, which allows them to efficiently capture and remove harmful metals like lead, copper, chromium, mercury, cadmium, and arsenic. Here's a breakdown of their effectiveness and considerations:

1. **Mechanism:** MOFs adsorb heavy metals through surface interactions, potentially due to their structural porosity and specific functional groups. The size and charge of the metal ions influence adsorption, with MOFs possibly trapping ions based on these factors.
2. **Performance:** MOFs exhibit high adsorption capacities, offering efficient removal of heavy metals. While their effectiveness is notable, comparisons to other adsorbents like activated carbon or clay are needed to assess their superiority.
3. **Affordability:** Cost considerations are crucial. MOFs might be premium options, affecting their suitability for widespread use versus other more economical methods.
4. **Applications:** They are used in fixed systems within water treatment facilities, often as part of complementary approaches such as filtration or chemical treatment.
5. **Regulations:** Compliance with environmental laws is essential, though their acceptance may depend on ongoing research and varying regulatory standards.
6. **Environmental Impact:** The safety and disposal of used MOFs are concerns, requiring studies on potential environmental effects and proper disposal methods.
7. **Scalability:** Their feasibility for large-scale industrial use is important, as water treatment often demands bulk solutions.
8. **Comparative Advantages:** As a modern solution, MOFs may offer benefits over traditional methods, such as higher efficiency or better environmental management.

In summary, MOFs are promising adsorbents in water treatment due to their effectiveness, but factors like cost, scalability, regulatory compliance, and environmental impact must be considered for their practical application.

Figure S71. The answer provided by the DeepSeek-R1-Distill-Llama-8B model to the question "What is the effect of MOFs adsorbent on removing heavy metal ions in water treatment?"

MOFs, or metal-organic frameworks, are highly effective adsorbents for removing heavy metal ions from water due to their unique hierarchical porous structure, which enhances surface area and adsorption capacity. Here's a structured summary of their effect and considerations:

1. Adsorption Mechanism:

- MOFs trap heavy metal ions through surface adsorption, with some metals like copper, lead, and zinc showing high adsorption efficiency.

- Adsorption depends on metal compatibility and factors such as MOF structure (porosity, surface area), temperature, and pH.

2. Advantages:

- High adsorption efficiency for metals like Fe, Cu, Zn, etc.

- Energy-efficient synthetic material, safer than some natural alternatives.

- Potential catalytic functions enhancing their utility.

3. Challenges and Considerations:

- Lower efficiency compared to some natural materials and potential need for regeneration methods.

- Thermal stability and biodegradability are concerns.

- Adsorption can be enhanced by blended materials and optimized through additives or physical methods.

4. Mechanisms and Dynamics:

- Adsorption involves surface binding, sometimes forming clusters, and pores may trap soluble ions that release over time under pressure.

- Adsorption is a two-step process: capture and release under specific conditions.

5. Testing and Applications:

6. Sustainability and Energy:

In conclusion, MOFs are promising for heavy metal removal, offering significant benefits in cost and sustainability but requiring optimization and careful application.

Figure S72. The answer provided by the DeepSeek-R1-Distill-Qwen-7B model to the question "What is the effect of MOFs adsorbent on removing heavy metal ions in water treatment?"

Metal-Organic Frameworks (MOFs) are highly porous materials known for their exceptional surface area, tunable pore size, and chemical functionality. These characteristics make them highly effective adsorbents for removing heavy metal ions from water. Here's an overview of their impact:

High Surface Area and Porosity:

Selective Adsorption:

Efficient Removal:

Regenerability:

Hybridization and Functionalization:

Environmental Impact:

Challenges: Despite their excellent properties, challenges remain in the large-scale production, cost-effectiveness, and stability of MOFs in aquatic environments. Research is ongoing to overcome these challenges and optimize MOF designs for specific applications.

Overall, MOFs show great promise in improving the efficiency and effectiveness of heavy metal ion removal in water treatment processes. Their continued development may lead to more sustainable and advanced water purification technologies.

Figure S73. The answer provided by the GPT-4.5-preview model to the question "What is the effect of MOFs adsorbent on removing heavy metal ions in water treatment?"

Metal-Organic Frameworks (MOFs) have emerged as highly effective adsorbents for the removal of heavy metal ions in water treatment due to their unique structural and chemical properties. Here's an in-depth look at the effects and mechanisms by which MOFs contribute to the removal of heavy metals from aqueous solutions:

1. High Surface Area and Porosity:
2. Tunable Pore Sizes and Functionalities:
3. Diverse Adsorption Mechanisms:
4. High Adsorption Capacity and Efficiency:
5. Rapid Adsorption Kinetics:
6. Reusability and Regeneration:
7. Selectivity:

Challenges and Considerations:

Conclusion:

MOF adsorbents have a significant positive effect on removing heavy metal ions from water. Their high adsorption capacity, selectivity, and rapid kinetics make them superior candidates for water treatment applications. Continued research and development are addressing challenges related to stability, cost, and scalability, with the aim of implementing MOFs in practical, large-scale water purification systems.

References for Further Reading:

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Zhou, L., Zhang, L., Liu, Z., & Zhao, Y. (2018). Water-stable metal-organic frameworks for efficient heavy metal removal from water. *Coordination Chemistry Reviews*, 388, 107-125. (Unrelated article)

Wu, S., Yan, S., & Li, M. (2020). Functionalized metal-organic frameworks for efficient removal of heavy metal ions from aqueous solutions. *Journal of Materials Chemistry A*, 8(16), 8013-8030. (No this article)

By leveraging the advanced properties of MOFs, water treatment processes can be significantly enhanced, providing effective solutions for the removal of toxic heavy metals and contributing to environmental protection and public health.

Figure S74. The answer provided by the o1-preview model to the question "What is the effect of MOFs adsorbent on removing heavy metal ions in water treatment?"

Metal-Organic Frameworks (MOFs) are a class of porous materials composed of metal ions or clusters coordinated to organic ligands, forming highly ordered structures with large surface areas and tunable pore sizes. These properties make MOFs highly effective as adsorbents in various applications, including the removal of heavy metal ions from water.

Effects of MOFs on Removing Heavy Metal Ions in Water Treatment:

1. High Adsorption Capacity:
2. Tunable Pore Size and Selectivity:
3. Functionalization for Enhanced Affinity:
4. Regeneration and Reusability:
5. Rapid Adsorption Kinetics:
6. Stability Under Various Conditions:
7. Low Concentration Removal:
8. Versatility in Application:

Challenges and Considerations:

While MOFs offer significant advantages in heavy metal removal, there are some challenges to consider:

- Cost: The synthesis of MOFs can be expensive, especially when using rare metals or complex organic linkers. However, research is ongoing to develop more cost-effective and scalable production methods.
- Stability: Not all MOFs are stable in water or under varying pH conditions, which could limit their applicability in certain scenarios. Developing more robust frameworks is an active area of research.
- Scalability: While MOFs show great promise in lab-scale experiments, scaling up their production for industrial applications remains a challenge.

Conclusion:

In summary, MOFs are highly effective adsorbents for removing heavy metal ions from water due to their high surface area, tunable porosity, selectivity, and regenerability. Their ability to rapidly and efficiently capture heavy metals, even at low concentrations, makes them a promising technology for water treatment. Ongoing research aims to address current limitations, such as cost and stability, to further enhance their practicality and widespread adoption in environmental remediation.

Figure S75. The answer provided by the Qwen-Max model to the question "What is the effect of MOFs adsorbent on removing heavy metal ions in water treatment?"

Metal-organic frameworks (MOFs) are a class of highly porous materials composed of metal ions or clusters connected by organic linkers. They have gained significant attention in water treatment applications, particularly for the removal of heavy metal ions due to their unique properties:

1. **High Surface Area and Porosity**:.....
2. **Functionalized Active Sites**:.....
3. **Tunable Selectivity**:.....
4. **Regenerability and Reusability**:.....
5. **Rapid Adsorption Kinetics**:.....
6. **Environmental Stability**:.....

Examples of MOFs in Heavy Metal Removal:.....

Challenges:

- **Hydrolytic Stability**: Some MOFs degrade in aqueous environments, limiting their long-term use. However, ongoing research focuses on developing more robust and water-stable MOFs.
- **Cost and Scalability**: Synthesis of MOFs can be expensive, and scaling up production for industrial applications remains a challenge.
- **Post-Treatment Disposal**: Once loaded with toxic heavy metals, MOFs require safe disposal or recycling methods to prevent secondary pollution.

Conclusion:

MOFs offer a promising solution for the removal of heavy metal ions from contaminated water due to their high adsorption capacity, tunable selectivity, rapid kinetics, and regenerability. Continued advancements in MOF design and synthesis aim to address current limitations, paving the way for their widespread adoption in water purification technologies.

Figure S76. The answer provided by the Qwen-Plus model to the question "What is the effect of MOFs adsorbent on removing heavy metal ions in water treatment?"

Metal-Organic Frameworks (MOFs) are emerging as highly effective adsorbents for removing heavy metal ions from water due to their unique structural and chemical properties. Here's a structured overview of their effects and considerations:

Key Effects of MOFs in Heavy Metal Removal

1. **High Adsorption Capacity:**.....
2. **Tunable Structure:**.....
3. **High Selectivity:**.....
4. **Efficient Kinetics:**.....
5. **Reusability:**.....

Advantages Over Traditional Adsorbents

- Superior Capacity: Often outperform activated carbon and ion-exchange resins in adsorption efficiency (e.g., >90% removal for Pb^{2+} in some studies).
- Tailored Design: Versatility in chemical and structural customization for specific contaminants.
- Environmental Friendliness: Some MOFs are biodegradable or use non-toxic metals, reducing secondary pollution risks.

Challenges and Limitations.....

Examples and Applications.....

Future Directions.....

Conclusion

MOFs are a transformative technology in water treatment, offering unmatched potential for heavy metal removal due to their tunable properties and high efficiency. While challenges like cost and stability remain, ongoing research aims to address these limitations, positioning MOFs as a promising solution for safe, sustainable water purification in the future.

Figure S77. The answer provided by the QwQ-32B model to the question "What is the effect of MOFs adsorbent on removing heavy metal ions in water treatment?"

Functional groups are crucial in MOFs because they provide specific binding sites for contaminants, which enhances the **affinity** and **efficiency** of the framework in removing these pollutants. These groups can influence the framework's **stability**, **porosity**, and **interaction mechanisms** with contaminants. For instance, hydroxyl groups can improve the adsorption capacity for polar contaminants like perfluorinated compounds, while amines can enhance the framework's affinity for nonpolar contaminants like toluene. Additionally, functional groups can affect the framework's recyclability and maintenance, making them essential for practical applications in contaminant removal.

Figure S78. The answer provided by the MOFReasoner model to the question " Why is the introduction of functional groups important in the design of Metal-Organic Framework for contaminant removal?"

The introduction of functional groups in the design of Metal-Organic Frameworks (MOFs) for contaminant removal is essential due to several key reasons:

1. Interaction and Adsorption: Functional groups determine the chemical properties of the MOF, influencing how and where contaminants bind. They can attract specific types of contaminants based on polarity, charge, or structure, enabling efficient adsorption.

2. Adsorption Mechanism: The choice of functional groups affects the mechanism of adsorption, whether it be physisorption or chemisorption. Stronger bonds, facilitated by appropriate functional groups, enhance the removal efficiency of contaminants.

3. Structure and Porosity: Functional groups influence the MOF's structure and porosity, allowing the framework to accommodate various-sized and structured contaminants, ensuring effective removal.

4. Specificity and Efficiency: By tailoring functional groups, MOFs can be designed to be highly specific, addressing different types and sizes of contaminants with precision, making the framework more versatile and efficient.

5. Environmental Impact: Functional groups also impact the MOF's environmental suitability, such as biodegradability or recyclability, which is crucial for sustainable applications. Groups that facilitate easy breakdown enhance environmental friendliness.

6. Permeability and Transport: The functional groups affect MOF permeability, influencing how contaminants enter or exit the framework, which is vital for transport processes and overall performance.

In conclusion, functional groups are crucial in tailoring MOFs for specific contaminant removal tasks, ensuring they are effective, efficient, and environmentally compatible. This specificity and adaptability make MOFs a powerful tool in various applications, from water purification to heavy metal containment.

Figure S79. The answer provided by the DeepSeek-R1-Distill-Qwen-7B model to the question " Why is the introduction of functional groups important in the design of Metal-Organic Framework for contaminant removal?"

The introduction of functional groups in Metal-Organic Frameworks (MOFs) is essential for their effectiveness in contaminant removal, contributing significantly to their properties and applications. Here's a structured overview of the key reasons:

1. **Contaminant-Specific Interaction:** Functional groups act as reactive sites that can attract and bind specific types of contaminants. For instance, oxygen-containing groups like hydroxyl or carboxyl can coordinate with metal ions in contaminants such as lead. Conversely, electron-rich groups like amines may attract aromatic compounds through π - π interactions.
2. **Surface Area and Porosity:** Functional groups influence the MOF's surface area and porosity, which are crucial for adsorption. High surface area allows for more interaction sites, while the presence of functional groups maximizes adsorption capacity for specific contaminants.
3. **Stability and Regenerability:** Functional groups that form stable complexes with contaminants enhance the MOFs' longevity and reduce the need for frequent maintenance, making them suitable for long-term use.
4. **Customization:** Functional groups enable MOFs to be tailored for specific contaminants. For example, halogen-containing groups are effective at removing chlorinated compounds, allowing for customized applications.
5. **Redox Activity:** Some functional groups may induce redox reactions, facilitating the removal of contaminants through oxidation or reduction processes, broadening the MOFs' capabilities.

In conclusion, functional groups in MOFs are vital as they enhance binding capacity, customize contaminant removal, and optimize material performance. This makes MOFs more effective and versatile than other materials for contaminant removal.

Figure S80. The answer provided by the DeepSeek-R1-Distill-Llama-8B model to the question "Why is the introduction of functional groups important in the design of Metal-Organic Framework for contaminant removal?"

The introduction of functional groups in Metal-Organic Frameworks (MOFs) is crucial for optimizing their performance in contaminant removal due to several key factors:

1. Enhanced Adsorption Mechanisms:.....
2. Improved Selectivity:.....
3. Increased Stability:.....
4. Catalytic Functionality:.....
5. Tunable Porosity and Surface Area:.....
6. Acid/Base Resistance:

Groups like $-\text{NH}_2$ or $-\text{COOH}$ buffer pH changes, maintaining MOF integrity in harsh conditions, which is critical for real-world applications.

Examples:

- UiO-66-NH₂: Amino groups enhance CO₂ capture via chemisorption and degrade nerve agents catalytically.
- MIL-101-SH: Thiol groups efficiently adsorb Hg²⁺ due to strong soft-soft interactions.
- ZIF-8 with -COOH: Carboxyl groups improve water stability and heavy metal adsorption.

In conclusion, functionalization allows precise engineering of MOFs to address diverse contaminants, balancing selectivity, capacity, stability, and multifunctionality for effective environmental remediation.

Figure S81. The answer provided by the DeepSeek-R1-671B model to the question "Why is the introduction of functional groups important in the design of Metal-Organic Framework for contaminant removal?"

Introducing functional groups into Metal-Organic Frameworks (MOFs) is important for contaminant removal applications due to several key factors:

Enhanced Affinity and Selectivity:.....

Improved Adsorption Capacity and Kinetics:

Incorporating polar or chemically reactive groups into MOFs can significantly enhance the adsorption capacity of contaminants by providing active adsorption sites. Additionally, these functional functionalities may facilitate faster contaminant diffusion and adsorption kinetics, ensuring the pollutant removal process is more rapid and efficient.

Increased Stability in Aqueous Media:

Functional groups can improve MOF stability, especially in aqueous or harsh chemical environments, by protecting their structural integrity against degradation. This increased stability ensures MOFs remain structurally intact and effective under real water treatment conditions, thus prolonging operational lifetime.

Tailored Material Hydrophilicity/Hydrophobicity:

Functionalization allows for the tuning of the MOF's surface properties, controlling the hydrophilic or hydrophobic character. Having control over these properties can promote the selective adsorption or rejection of specific contaminants, improving practical applicability in water remediation processes.

Enhanced Catalytic Activity for Contaminants:

Certain functional groups can serve as catalytic active sites, enabling not only adsorption but also catalytic degradation or transformation of contaminants into harmless products. The functional sites can facilitate advanced remediation strategies, including photocatalysis or electrocatalysis methods for pollutant decomposition.

In essence, functionalizing MOFs introduces targeted chemical functionalities and tailored surface attributes, greatly improving contaminant removal efficiency, selectivity, stability, and overall practicality for environmental remediation applications.

Figure S82. The answer provided by the gpt-4.5-preview model to the question "Why is the introduction of functional groups important in the design of Metal-Organic Framework for contaminant removal?"

The introduction of functional groups into Metal-Organic Frameworks (MOFs) is a crucial strategy in the design and optimization of these materials for contaminant removal applications. MOFs are a class of porous, crystalline materials composed of metal ions or clusters coordinated to organic ligands, forming extended networks with high surface areas and tunable pore sizes. The incorporation of specific functional groups into the frameworks can significantly enhance their performance in capturing, degrading, or sensing contaminants. Here's why functional groups are important:

1. Enhanced Selectivity and Specificity:.....
2. Increased Adsorption Capacity:.....
3. Tunable Pore Environment:.....
4. Improved Affinity and Binding Strength:.....
5. Catalytic Activity for Degradation:.....
6. Stability Under Operational Conditions:.....
7. Regenerability and Reusability:.....
8. Environmental Responsiveness:.....
9. Integration with Other Materials:.....
10. Biocompatibility and Environmental Safety:.....

In Summary:.....

References for Further Reading:

- *Functionalization of Metal-Organic Frameworks for Enhanced Adsorption and Catalytic Degradation of Environmental Contaminants*, Journal of Environmental Sciences, 2022.(No this article)
- *Design Strategies of Functionalized Metal-Organic Frameworks Toward Environmental Remediation*, Chemical Reviews, 2021.(No this article)
- *Metal-Organic Frameworks in Environmental Applications: From Adsorption to Catalysis*, Environmental Science & Technology, 2020.(No this article)

By leveraging the versatility offered by functional groups, the design of MOFs continues to evolve, opening new avenues for efficient and sustainable contaminant removal technologies.

Figure S83. The answer provided by the o1-preview model to the question "Why is the introduction of functional groups important in the design of Metal-Organic Framework for contaminant removal?"

The introduction of functional groups is crucial in the design of Metal-Organic Frameworks (MOFs) for contaminant removal because it directly influences their performance in terms of selectivity, adsorption capacity, stability, and reactivity. Functional groups can be incorporated into either the organic linkers or the metal nodes of MOFs, allowing for precise tuning of their chemical and physical properties to optimize contaminant capture and removal. Below are several key reasons why functional groups are important in MOF design for contaminant removal:

1. Enhanced Selectivity.....
2. Increased Adsorption Capacity.....
3. Improved Stability.....
4. Facilitated Reactivity.....
5. Tunable Porosity and Accessibility.....
6. Regeneration and Reusability.....

Examples of Functional Groups in MOFs for Contaminant Removal

Conclusion

The strategic incorporation of functional groups into MOFs is a powerful tool for designing materials with enhanced performance in contaminant removal applications. By tailoring the chemical and physical properties of MOFs, functional groups enable selective binding, increased adsorption capacity, improved stability, and facilitated reactivity, making MOFs highly versatile and effective for environmental remediation. This approach allows researchers to address specific challenges associated with different types of contaminants, paving the way for more efficient and sustainable solutions in water and air purification.

Figure S84. The answer provided by the Qwen-Max model to the question "Why is the introduction of functional groups important in the design of Metal-Organic Framework for contaminant removal?"

The introduction of functional groups in the design of Metal-Organic Frameworks (MOFs) is crucial for enhancing their performance in contaminant removal due to several reasons:

1. Targeted Selectivity:
2. Enhanced Adsorption Capacity:
3. Improved Stability:
4. Tunable Porosity:
5. Catalytic Activity:
6. Regenerability:
7. Versatility in Applications:

In summary, the strategic introduction of functional groups in MOFs allows for the customization of these materials to achieve high selectivity, capacity, and efficiency in contaminant removal, while also improving their stability and reusability. This makes functionalized MOFs highly promising candidates for environmental remediation technologies.

Figure S85. The answer provided by the Qwen-Plus model to the question "Why is the introduction of functional groups important in the design of Metal-Organic Framework for contaminant removal?"

So I'm trying to understand why introducing functional groups is important when designing Metal-Organic Frameworks (MOFs) for removing contaminants. MOFs are these porous materials that have a lot of surface area, which makes them really good at capturing and storing other molecules, like contaminants in the air or water. But why do we need to add functional groups to them?

First, I need to recall what functional groups are. In chemistry, functional groups are specific atoms or groups of atoms within a molecule that determine its chemical properties and reactivity..... Now, MOFs are made up of metal ions or clusters connected by organic linkers..... That's where functional groups come in..... Let me think about an example..... Moreover, some contaminants might be neutral molecules, like organic pollutants or gases..... Another aspect is the stability of the MOF in different environments..... Additionally, functional groups can influence the overall polarity of the MOF, which in turn affects its interaction with polar or nonpolar contaminants..... I also recall that in some cases..... Furthermore, the introduction of functional groups can help in tuning the pore size and shape of the MOF.....

In summary.....

Key Points:

1. **Selectivity and Affinity**:
2. **Interaction Mechanisms**:
3. **Environmental Stability**:
4. **Polarity Tuning**:
5. **Chemical Reactivity**:
6. **Pore Size and Shape Control**:

Overall, the strategic incorporation of functional groups into MOFs is a powerful approach to optimize their performance in contaminant removal applications.

Figure S86. The answer provided by the QwQ-32B model to the question "Why is the introduction of functional groups important in the design of Metal-Organic Framework for contaminant removal?"

Dynamic adsorption performance is evaluated through breakthrough experiments, while static adsorption performance is measured using gas adsorption isotherms. Both methods provide insights into the MOFs' ability to capture gases under controlled conditions.

Figure S87. The answer provided by the MOFReasoner model to the question "How are the dynamic and static adsorption performances of MOFs usually evaluated?"

The evaluation of dynamic and static adsorption performances of Metal-Organic Frameworks (MOFs) involves distinct methodologies tailored to their application contexts. Here's a structured overview:

Static Adsorption Performance Evaluation

1. Adsorption Isotherms
2. Surface Area and Porosity
3. Thermodynamic Properties

- Isosteric Enthalpy of Adsorption: Calculated using the Clausius-Clapeyron equation to evaluate binding strength and energy heterogeneity.

4. Material Characterization

- Structural Integrity: XRD for crystallinity, SEM/TEM for morphology.
- Surface Chemistry: FTIR, XPS, or TGA to assess functional groups and thermal stability.

Dynamic Adsorption Performance Evaluation

1. Breakthrough Experiments
2. Kinetic Studies
3. Selectivity and Competition

- Mixed-Gas Tests: Gas chromatography or MS monitors component separation efficiency in flowing mixtures.

4. Cyclic Stability and Regeneration

- Cycle Testing: Repeated adsorption/desorption under temperature or pressure swings (e.g., PSA/TSA) to assess durability and capacity retention.

Supporting Techniques

Key Differences

By integrating these approaches, researchers holistically assess MOFs for applications like gas storage, separation, or catalysis, balancing theoretical potential with real-world performance.

Figure S88. The answer provided by the DeepSeek-R1-671B model to the question "How are the dynamic and static adsorption performances of MOFs usually evaluated?"

The evaluation of the dynamic and static adsorption performances of Metal-Organic Frameworks (MOFs) involves a comprehensive approach using various analytical techniques and experiments. Here's an organized summary of the key points:

Static Adsorption Performance

1. **Adsorption Isotherms**:
2. Methods:
3. Selectivity:

Dynamic Adsorption Performance

1. **Breakthrough Curves**: These curves track when adsorbed substances begin to appear in the effluent, providing data on flow rates, adsorption capacity, and dynamic behavior. The shape of the curve can indicate the rate of adsorption and hysteresis.
2. **Hysteresis Assessment**: Evaluating the reversibility and tabIndex of adsorption, which is vital for understanding regeneration processes and applications requiring repeated use.
3. **Real-Time Monitoring**: Techniques like gas chromatography, mass spectrometry, or Automatic Gas Analyzer (AGA) are used to monitor concentrations and measure adsorption over time.
4. **Flow Experiments**: Use of flow reactors to study adsorption kinetics and capacity under dynamic conditions.

Additional Considerations

- Aging and Degradation: Testing MOF performance over time to assess changes in adsorption capacity and properties.
- Pore Structure: Considering micro- and macro-voids, with micro voids contributing to adsorption, especially for gases.

Conclusion

Static adsorption is measured through isotherm experiments and BET analysis, while dynamic adsorption is evaluated using breakthrough curves and flow experiments. These methods provide insights into capacity, selectivity, adsorption kinetics, and longevity, ensuring MOFs are suitable for diverse applications.

Figure S89. The answer provided by the DeepSeek-R1-Distill-Llama-8B model to the question "How are the dynamic and static adsorption performances of MOFs usually evaluated?"

Evaluating the dynamic and static adsorption performances of Metal-Organic Frameworks (MOFs) involves a comprehensive approach that combines structural analysis with kinetic studies. Here's a structured overview of the methods used:

Static Adsorption Evaluation:

1. **Surface Modifications:**

- Scanning Electron Microscopy (SEM):.....
- Energy-Dispersed X-ray Fluorescence (EDX):.....

2. **Structural Analysis:**

- X-ray Diffraction (XRD):.....

3. **Surface Area Measurements:**.....

4. **Adsorption Isotherms:**.....

5. **In-Situ Methods:**

- Reflection and Transmission Electron Microscopy (TEM):.....

- In-Situ XRD and EDX:.....

Dynamic Adsorption Evaluation:

1. **Kinetic Studies:**.....

2. **Real-Time Monitoring:**

- Monte Carlo Simulations:.....
- In-Situ Techniques:.....

3. **Impurity Analysis:**

- Gas Chromatography and HPLC:.....

4. **Surface Modification Tracking:**

- High-Resolution TEM (HRTEM):.....

5. **Kinetic Data:**

- Adsorption Flux Analysis: Evaluates mass transfer limitations affecting dynamic adsorption.

Considerations:.....

In summary.....

Figure S90. The answer provided by the DeepSeek-R1-Distill-Qwen-7B model to the question "How are the dynamic and static adsorption performances of MOFs usually evaluated?"

The adsorption performance of Metal-Organic Frameworks (MOFs) is typically evaluated through two main frameworks: static adsorption analysis and dynamic adsorption processes. Each of these involves distinctive metrics, equipment, and methodology to characterize MOFs for practical applications.

1. Static Adsorption Performance Evaluation:

Static adsorption tests focus on the equilibrium and fundamental adsorption characteristics under controlled conditions.

Common metrics and methods include:

Adsorption Isotherms:

Adsorption Thermodynamics:.....

•Experimental Approach:

◦Measure adsorption equilibria at multiple temperatures.

•Metrics Evaluated:

◦Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) changes to interpret the spontaneity and type (physical or chemical adsorption) of adsorption processes.

Selectivity Assessment:.....

2. Dynamic Adsorption Performance Evaluation:

Dynamic tests focus on evaluating adsorption under practical flow conditions, typically representative of real-world processes.

Common metrics and methods include:

Breakthrough Curves:.....

Mass Transfer and Adsorption Kinetics:.....

Regeneration and Cycling Stability:.....

Summary:

In short, MOF adsorption performance evaluation typically entails:

Figure S91. The answer provided by the GPT-4.5-preview model to the question "How are the dynamic and static adsorption performances of MOFs usually evaluated?"

Static Adsorption Performance Evaluation:

Static adsorption refers to the equilibrium adsorption capacity of a MOF when exposed to a gas or liquid adsorbate under controlled conditions without flow. The primary methods for evaluating static adsorption include:

1. Adsorption Isotherms:
2. Calorimetry:
3. Spectroscopic Methods:

Dynamic Adsorption Performance Evaluation:

Dynamic adsorption assesses the performance of MOFs under flow conditions, mimicking real-world applications where the adsorbate continuously passes over the adsorbent. Key evaluation methods include:

1. Breakthrough Curve Experiments:.....
2. Dynamic Sorption Analyzers:.....
3. Cyclic Adsorption-Desorption Tests:.....
4. Kinetic Studies:.....
5. Temperature Programmed Desorption (TPD):.....

Considerations in Evaluation:

Conclusion:

Evaluating both static and dynamic adsorption performances provides a comprehensive understanding of how MOFs will perform in practical applications. Static measurements give insights into the equilibrium capacities and fundamental interactions, while dynamic evaluations reveal how the MOF behaves under realistic operating conditions with flow, providing data essential for process design and optimization.

Figure S92. The answer provided by the o1-preview model to the question "How are the dynamic and static adsorption performances of MOFs usually evaluated?"

The dynamic and static adsorption performances of Metal-Organic Frameworks (MOFs) are crucial factors in determining their effectiveness for various applications, such as gas storage, separation, catalysis, and environmental remediation. These performances are evaluated using a combination of experimental techniques and theoretical modeling. Below is an explanation of how both static and dynamic adsorption performances of MOFs are typically assessed:

1. Static Adsorption Performance

Static adsorption refers to the equilibrium state where the rate of adsorption equals the rate of desorption, resulting in no net change in the amount of adsorbed molecules over time. The following methods are commonly used to evaluate static adsorption performance:

- a. Isotherm Measurements
- b. Surface Area and Pore Size Analysis
- c. Selectivity Measurements
- d. Thermodynamic Parameters

2. Dynamic Adsorption Performance

Dynamic adsorption refers to the process where the adsorbate flows through the MOF material, and adsorption occurs under non-equilibrium conditions. This is more representative of real-world applications, such as in packed-bed columns or flow-through reactors. The following methods are commonly used to evaluate dynamic adsorption performance:

- a. Breakthrough Curve Experiments
- b. Column or Packed-Bed Studies
- c. Flow-Through Reactors
- d. Diffusion Studies

3. Theoretical Modeling and Simulations

Summary

Figure S93. The answer provided by the Qwen-Max model to the question "How are the dynamic and static adsorption performances of MOFs usually evaluated?"

The dynamic and static adsorption performances of Metal-Organic Frameworks (MOFs) are typically evaluated using different experimental setups and techniques, as they represent two distinct modes of operation for gas or vapor adsorption. Below is a detailed explanation of how these performances are usually assessed:

1. Static Adsorption Performance

Static adsorption performance refers to the equilibrium adsorption capacity of MOFs under controlled conditions, such as temperature and pressure. This method provides information about the maximum adsorption capacity of the material.

- Experimental Setup:

- A fixed amount of MOF sample is placed in a closed system (e.g., a volumetric apparatus or a gravimetric balance).

- The system is exposed to a specific gas or vapor at a constant temperature and varying pressures.

- Techniques:.....

- Key Metrics:.....

2. Dynamic Adsorption Performance

Dynamic adsorption performance evaluates how efficiently a MOF can adsorb and desorb gases or vapors under flowing conditions, mimicking real-world applications such as gas separation, air purification, or catalysis.

- Experimental Setup:

- A column packed with the MOF is used, through which a continuous flow of gas or vapor mixture is passed.

- The inlet and outlet concentrations of the target gas or vapor are monitored over time.

- Techniques:

- Key Metrics:

Summary of Key Differences:

Figure S94. The answer provided by the Qwen-Plus model to the question "How are the dynamic and static adsorption performances of MOFs usually evaluated?"

The dynamic and static adsorption performances of Metal-Organic Frameworks (MOFs) are crucial for understanding their potential applications in gas storage, separation, and catalysis. Evaluating these properties involves a combination of experimental techniques and theoretical modeling. Let's break down how each is typically assessed.

Static Adsorption

Static adsorption refers to the equilibrium adsorption capacity of a MOF at a given temperature and pressure. This is often the first step in characterizing a new MOF material.

1. **Gas Uptake Measurements:**
2. **Isotherm Analysis:**
3. **Thermogravimetric Analysis (TGA):**
4. **In Situ Spectroscopy:**

Dynamic Adsorption

Dynamic adsorption involves studying the adsorption process under flowing conditions, which is more representative of real-world applications such as gas separation and purification.

1. **Breakthrough Curves:**
2. **Pulse Tests:**
 - In pulse tests, a sharp pulse of adsorbate is introduced into a flowing stream of inert gas passing through the MOF bed. The elution profile is then monitored to obtain information about diffusion coefficients and adsorption kinetics.
3. **Transient Adsorption Experiments:**
 - These experiments involve sudden changes in pressure or temperature and monitoring the response of the adsorbent bed to understand transport properties and adsorption kinetics.
4. **Modeling and Simulation:**

Theoretical Modeling

Conclusion

References(No this article)

Figure S95. The answer provided by the QwQ-32B model to the question "How are the dynamic and static adsorption performances of MOFs usually evaluated?"

Adsorption sites can be identified through computational methods like **DFT** and **GCMC simulations**, which help in understanding the interactions between gas molecules and the MOF framework.

Figure S96. The answer provided by the MOFReasoner model to the question "How to determine the adsorption sites in MOFs adsorbents?"

Determining adsorption sites in Metal-Organic Frameworks (MOFs) involves a combination of experimental and computational techniques, each providing unique insights into the interaction between adsorbates and the MOF structure. Here's a structured approach:

Experimental Methods

1. **X-ray Diffraction (XRD):**.....
2. **Neutron Diffraction:**.....
3. **Spectroscopy:**.....
4. **Gas Adsorption Experiments:**.....
5. **Probe Molecules:**.....
6. **Microscopy:**.....

Computational Methods

1. **Density Functional Theory (DFT):**.....
2. **Molecular Dynamics (MD) Simulations:**.....
3. **Machine Learning:**.....

Integrated Approaches

- **Defect Analysis:** Combines experimental data with simulations to account for adsorption at defect sites.
- **Isotopic Labeling:** Tracks adsorbate locations via neutron scattering or NMR.
- **Synchrotron Techniques:** Enhances XRD resolution for detailed structural analysis.

Key Considerations

- **Multi-Technique Validation:** Correlate computational predictions with experimental data (e.g., XRD, spectroscopy) for accuracy.
- **Dynamic Conditions:** Use *in situ* methods to study adsorption under relevant operational environments.
- **Material Variability:** Account for MOF defects and guest-induced structural flexibility.

By integrating these methods, researchers can comprehensively map adsorption sites, enabling the design of MOFs tailored for specific applications like gas storage, separation, or catalysis.

Figure S97. The answer provided by the DeepSeek-R1 -671B model to the question "How to determine the adsorption sites in MOFs adsorbents?"

Determining adsorption sites in Metal-Organic Frameworks (MOFs) involves a multifaceted approach that combines experimental techniques, computational methods, and structural analysis. Here's a structured summary of the process:

1. **Structural Analysis**:

- **PXRD (Powder X-ray Diffraction)**: Used to study the crystal structure of MOFs, providing information about pore size and gaps where adsorption can occur.
- **X-ray Crystallography**: Determining the precise structure reveals the spatial arrangement of metal ions and organic ligands, identifying potential adsorption sites.

2. **Surface Area and Porosity Measurement**:.....

3. **Functional Group Analysis**:.....

4. **Site Identification and Linkage**:.....

5. **Imaging Techniques**:

- **SEM (Scanning Electron Microscopy)**: Provides visual insights into surface structure and adsorption patterns, sometimes complemented by EDS for elemental analysis.

6. **Computational Modeling**:

- **DFT (Density Functional Theory)**: Uses quantum-level modeling to predict adsorption behaviors, revealing molecular interactions and preferred adsorption sites.

7. **Additional Porous Analysis**:

- **Microporous Analysis**: Techniques like Hgord or N₂ adsorption help determine pore size distribution, further pinpointing adsorption-prone areas.

In conclusion, determining adsorption sites in MOFs involves an interdisciplinary approach, integrating structural, compositional, and computational methods to provide a comprehensive understanding of the adsorption processes.

Figure S98. The answer provided by the DeepSeek-R1-Distill-Llama-8B model to the question "How to determine the adsorption sites in MOFs adsorbents?"

To determine the adsorption sites in Metal-Organic Frameworks (MOFs) used as adsorbents, follow this structured approach:

1. **Structural Analysis:**

- **X-ray Diffraction (XRD):** Provides a detailed crystalline structure, identifying pore size, shape, and distribution, which correlates with available adsorption sites.

- **Scanning Transmission Microscopy (STM)** and Scanning Electron Microscopy (SEM): Offers high-resolution images of MOF surfaces, revealing surface features and potential adsorption sites.

2. **Adsorption Isotherms:**.....

3. **Adsorption Modeling:**.....

4. **Surface Characterization:**.....

5. **Chemical Functionalization:**.....

6. **Thermodynamic and Kinetic Studies:**.....

7. **In-Situ Characterization:**

- Use techniques like STXM to monitor adsorption in real-time, revealing adsorbed species at the surface.

8. **Computational Methods:**

- Employ **Density Functional Theory (DFT)** to predict adsorption sites based on MOF structure and chemical environment.

9. **Literature and Computational Validation:**.....

10. **Use of Adsorbates:**

- Test different adsorbates to identify specificity and probe different sites.

11. **Porous Characterization:**

- Use Mercury Intrusion Porosimetry (MIP) to quantify pore sizes and shapes, influencing adsorption site availability.

12. **Adsorbate Analysis:**

- Employ gas chromatography and mass spectrometry to identify adsorbed species and quantify adsorption.

Each step contributes uniquely to understanding the complex adsorption sites in MOFs, providing a comprehensive analysis for optimizing adsorbent performance.

Figure S99. The answer provided by the DeepSeek-R1-Distill-Qwen-7B model to the question "How to determine the adsorption sites in MOFs adsorbents?"

Determining adsorption sites within Metal-Organic Frameworks (MOFs) is essential to understand adsorption mechanisms and for optimizing their applications. The adsorption performance in MOF structures typically depends on factors like pore geometry, metal nodes or clusters, ligand functionalization, framework defects, and interactions between adsorbate molecules and framework sites.

The common methodologies for determining adsorption sites in MOFs are as follows:

1. Experimental Methods:

X-ray and Neutron Diffraction Studies:

Spectroscopic Techniques:

Gas/Vapor Adsorption Isotherms and Calorimetry:
Adsorption isotherms and differential scanning calorimetry (DSC) or microcalorimetry experimentally identify preferential adsorption sites and quantify energies of adsorption. Low-pressure adsorption isotherms at cryogenic conditions (77 K N_2 adsorption) or at elevated temperatures (CO_2 , CH_4) often demonstrate which sites preferentially adsorb specific gases.

Positron Annihilation Lifetime Spectroscopy (PALS): PALS can detect structural defects and accessible adsorption spaces, indirectly indicating preferential adsorption sites.

2. Computational and Theoretical Methods:

Grand Canonical Monte Carlo (GCMC) Simulations:

Density Functional Theory (DFT) Calculations:

Molecular Dynamics (MD) and ab initio Molecular Dynamics (AIMD):

Electrostatic Potential Surface Calculations:

3. Combination Approach (Experimental-Computational Integration):.....

Summary:.....

Figure S100. The answer provided by the gpt-4.5-preview model to the question "How to determine the adsorption sites in MOFs adsorbents?"

Determining the adsorption sites in Metal-Organic Frameworks (MOFs) is crucial for understanding their adsorption behavior and for tailoring them for specific applications like gas storage, separation, and catalysis. Adsorption sites are specific locations within the MOF structure where guest molecules (adsorbates) preferentially bind. Identifying these sites involves a combination of experimental techniques and computational modeling. Below are the methods commonly used to determine adsorption sites in MOF adsorbents:

1. Single-Crystal X-ray Diffraction (SC-XRD):.....
2. Neutron Diffraction:.....
3. In Situ Gas Adsorption Measurements:.....
4. Infrared (IR) Spectroscopy:.....
5. Nuclear Magnetic Resonance (NMR) Spectroscopy:.....
6. Electron Microscopy:

7. Computational Methods:

- a. Density Functional Theory (DFT) Calculations:.....
- b. Molecular Simulations:

Methods Used:

Grand Canonical Monte Carlo (GCMC): Simulates adsorption isotherms and locates probable adsorption sites.

Molecular Dynamics (MD): Studies the movement of molecules over time to understand diffusion within MOFs.

8. Combined Experimental and Computational Approaches:.....

9. Advanced Techniques and Developments:.....

10. Practical Considerations:.....

Conclusion:.....

References and Further Reading: (No this reference)

Books:

"Metal-Organic Frameworks: Applications from Catalysis to Gas Storage" by David Farrusseng.

Review Articles:

"Gas Adsorption in Metal-Organic Frameworks: Fundamentals and Applications" (Chemical Reviews).

Research Papers:

Studies demonstrating the identification of adsorption sites in specific MOFs using the above methods.

Online Resources:

The Cambridge Structural Database (CSD) for crystal structures of MOFs.

Figure S101. The answer provided by the o1-preview model to the question "How to determine the adsorption sites in MOFs adsorbents?"

Determining adsorption sites in Metal-Organic Frameworks (MOFs) is crucial for understanding their adsorption behavior and optimizing their performance in various applications, such as gas storage, separation, catalysis, and sensing. Adsorption sites are specific locations within the MOF structure where guest molecules (e.g., gases like CO₂, CH₄, H₂O, etc.) interact with the framework. These interactions can be physical (van der Waals forces) or chemical (covalent bonding). Below is a step-by-step guide to determining adsorption sites in MOFs:

```
### 1. **Understand the Structure of the MOF**.....  
### 2. **Simulate Gas Adsorption Using Computational Methods**.....  
### 3. **Visualize Adsorption Sites**.....  
### 4. **Experimental Techniques to Confirm Adsorption Sites**  
- **In-situ Spectroscopy**:  
  - **Infrared (IR) Spectroscopy**: Monitor changes in vibrational modes of functional groups upon adsorption. This can indicate interactions between the adsorbate and specific sites on the MOF.  
  - **Nuclear Magnetic Resonance (NMR)**: .....  - **X-ray Absorption Spectroscopy (XAS)**: .....  - **Neutron Diffraction**: .....  - **Temperature-Programmed Desorption (TPD)**: .....### 5. **Analyze Interaction Mechanisms** .....### 6. **Validate Results Against Experimental Data** .....
```

Summary of Key Steps:.....

By combining computational modeling with experimental validation, you can accurately determine the adsorption sites in MOFs and gain a deeper understanding of their adsorption properties.

Figure S102. The answer provided by the Qwen-Max model to the question "How to determine the adsorption sites in MOFs adsorbents?"

Determining adsorption sites in Metal-Organic Frameworks (MOFs) is a critical step in understanding their gas storage, separation, and catalytic properties. Adsorption sites are the specific locations within the MOF where guest molecules interact with the framework. Here are several methods used to identify and characterize these sites:

1. **Computational Methods**

- **Density Functional Theory (DFT):** DFT calculations can be used to model the interaction between the MOF and the adsorbate molecule.....

- **Grand Canonical Monte Carlo (GCMC) Simulations:** GCMC simulations can provide insights into the adsorption behavior of gases in MOFs by simulating the distribution of adsorbates over time.....

2. **Experimental Techniques**

- **In-situ X-ray Diffraction (XRD):** In-situ XRD can reveal structural changes in the MOF upon adsorption, indicating where the adsorbate interacts with the framework.....

- **Infrared Spectroscopy (IR):** IR spectroscopy can identify functional groups involved in adsorption by observing changes in vibrational modes when the adsorbate interacts with the MOF.....

- **Nuclear Magnetic Resonance (NMR):** Solid-state NMR can provide detailed information about the local environment around nuclei, helping to pinpoint adsorption sites.....

- **Scanning Probe Microscopy (SPM):**

3. **Gas Adsorption Isotherms and Kinetics**.....

4. **Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)**.....

5. **Quasi-Elastic Neutron Scattering (QENS)**.....

Conclusion:

To comprehensively determine adsorption sites in MOFs, a combination of computational and experimental methods is often employed. Computational methods like DFT and GCMC provide theoretical insights, while experimental techniques such as XRD, IR, NMR, and SPM offer direct evidence of adsorption interactions. Combining these approaches allows for a more complete understanding of the adsorption mechanism in MOFs.

Figure S103. The answer provided by the Qwen-Plus model to the question "How to determine the adsorption sites in MOFs adsorbents?"

Determining adsorption sites in metal-organic frameworks (MOFs) is crucial for understanding their adsorption behavior and optimizing their performance in various applications, such as gas storage, separation, and catalysis. MOFs are porous materials composed of metal ions or clusters connected by organic linkers, forming well-defined pores and cavities that can selectively adsorb specific molecules.....

Step 1: Obtain the MOF Structure.....

Step 2: Prepare the MOF Model.....

Step 3: Identify Potential Adsorption Sites.....

Step 4: Calculate Adsorption Energies

Once potential adsorption sites are identified, the interaction energies between the adsorbate molecule and each site need to be calculated. This can be done using computational methods such as DFT or molecular mechanics simulations.

- **DFT Calculations:** Provide accurate but computationally expensive results. They are suitable for small systems or when high precision is required.

- **Molecular Mechanics Simulations:** Are less accurate but much faster, making them suitable for larger systems or when screening multiple adsorption sites.

Step 5: Analyze Adsorption Behavior.....

Step 6: Validate with Experimental Data.....

To confirm the accuracy of the computational predictions, it is essential to compare the results with experimental data. Techniques such as gas adsorption isotherms, infrared spectroscopy, or **nuclear magnetic resonance (NMR)** can provide insights into the adsorption behavior and help validate the identified adsorption sites.....

Step 7: Optimize MOF Design.....

Conclusion

Determining adsorption sites in MOFs is a multi-step process that combines structural analysis, computational modeling, and experimental validation. By understanding where and how adsorbate molecules interact with the MOF framework, researchers can gain valuable insights into the material's properties and optimize its performance for various applications.

Figure S104. The answer provided by the QwQ-32B model to the question "How to determine the adsorption sites in MOFs adsorbents?"

The primary challenge is ensuring reliable regeneration under industrial conditions. Materials with intrinsic stability and acceptable long-term durability would be ideal.

Figure S105. The answer generated by the trained Qwen2.5-7B-Math model to the question: “What are the current bottlenecks for HKUST-1 in industrial gas separation applications?”

Metal-Organic Frameworks (MOFs) offer several key advantages over zeolite materials in vacuum swing adsorption (VSA):

High Specific Surface Area: MOFs can achieve significantly higher surface areas than zeolites (up to 3000 m²/g), providing increased interactions with adsorbates and improved selectivity.

Tailorable Porosity: By modifying organic linkers, functional groups, and metal cations/cluster nodes, MOFs allow for precise control over pore size, shape, and chemistry, leading to improved molecular size/molecular weight separation capabilities.

Defect Engineering: Introducing defects in MOFs increases accessibility to pore interiors, improving mass transport rates and facilitating breakthrough of intermediates like N₂ in CO₂/N₂ equilibria.

Flexibility in Mixed-Metal Frameworks: Different coordination numbers among metal cluster nodes enable unique host-guest interactions relevant to specific separation applications.

Exogenous Selectivity Without Phase Separation: Certain MOFs (e.g., IRMOF-3, CuBTC, HKUST-1) show selectivity directly from aqueous solutions without the need for separate solvents/monolithic solid supports, simplifying the VSA cycle.

Lower Regeneration Temperatures and Costs: Many MOFs resist crystallization during desorption cycles, allowing for regeneration at lower temperatures and lower pressure, reducing energy demand.

Improved Stability Under Extreme Conditions: Chemically robust MOFs constructed with materials like Mg(OH)₂ demonstrate favorable performance in humid air environments.

Despite these advantages, MOFs face challenges such as working pressure limits (<1 bar) and slow mass-transfer kinetics, indicating opportunities for further research into efficient coupling methods with supporting matrices.

Figure S106. The answer generated by the trained Qwen2.5-7B-Math model to the question: “Compared with zeolite materials, what are the advantages of MOFs (Metal-Organic Frameworks) materials in vacuum swing adsorption?”

To enhance the water stability of MOFs and ensure their effectiveness under operational conditions, several strategies have been proposed:

Choosing water-soluble linker-based MOFs: Functional groups capable of stabilizing metal-metal connections play a key role. For instance, certain tritopic pyridinic carboxylic acid linker-based MOFs retain their porosity even under acidic conditions.

Hydrophobic post-synthetic modification of carboxylate linkers: Replacing carboxylate linkers with hydrophobic alternatives before activation improves water resistance.

Creating defect sites via high-energy activation: Increasing the coordination number of metal sites enhances stability and porosity simultaneously.

Defect engineering through mixed ligand substitution: Incorporating hydrophobic ligands into defective frameworks increases framework thickness and strength.

Hybrid post-synthetic treatments combining solvothermal and non-volatile steps: Techniques like supercritical CO_2 activation coupled with supercritical ethylene oxide activation offer enhanced crystal quality and water retention capacity.

Tuning pore space using porous organic polyhedra: Designing MOFs with programmable pore sizes and surfaces allows selective functionalization and improved durability in humid environments.

The choice of strategy depends on factors such as the desired target application (e.g., gas adsorption), the specific properties required from the final material (e.g., porosity, selectivity), and cost considerations.

Figure S107. The answer generated by the trained Qwen2.5-7B-Math model to the question: "How can the water stability of MOFs be enhanced to ensure their effectiveness under operational conditions?"

regeneration of MOFs involves removing an adsorbed substance, such as pollution particles, from MOF materials to maximize storage efficiency and optimize cyclical use in industrial processes. Effective regeneration requires addressing several key factors:

1. Adsorbate-Aggregate Interaction Strength: Strong non-specific interactions (e.g., van der Waals forces) limit regeneration efficacy since they cannot typically compensate for thermodynamic shifts required to restore original adsorption capabilities. Thus, optimizing this force becomes crucial.

2. Material Stability Over Operating Conditions: Many MOFs degrade under extreme conditions, necessitating careful selection of component metals (e.g., Cr, Fe) that resist corrosion and swelling while maintaining integrity under fluctuations in temperature, humidity, and exposure to oxidants or acids.

3. Regeneration Efficiency Strategies:

- **Thermal Methods (TSA):** Relies on elevated temperatures to liberate pre-adsorbed ligands, enabling their resynthesis. However, high-energy costs pose sustainability risks.

- **Pressure/Vacuum Methods (PSA/VSA):** Alternates adsorption/desorption phases according to ambient pressure/vacuum levels, promoting selective recovery of target species. This technique avoids residual contamination but demands precise controls.

- **Hybrid Techniques:** Combines microwaves or UV radiation with traditional vapor transport mechanisms (VTT), offering rapid reactions devoid of pressure dependencies but introducing radiological risks.

4. Cost and Scalability Concerns: Despite advancements, current methods face challenges related to expensive regeneration media, energy-intensive utilities, and insufficiently durable MOF structures. Innovations in fabrication ("breathy" MOFs synthesized via self-assembled monolayers) aim to address these gaps via lightweight, scalable designs reminiscent of polymeric composites.

In essence, MOF regeneration hinges on engineering favorable chemical bonding geometries, tailoring operating parameters smartly, and synthesizing materials capable of enduring diverse industrial environments while sustaining their physicochemical properties over countless cycles.

Figure S108. The answer generated by the trained Qwen2.5-7B-Math model to the question: "What is the regeneration performance of MOFs adsorbent?"

MOFs serve as highly effective adsorbents for removing heavy metal ions from water due to their unique structural and functional properties. Here's a structured analysis of their role:

Key Mechanisms of Adsorption

Hydrogen Bonding: Functional groups (e.g., $-\text{OH}$, $-\text{NH}_2$) on MOFs coordinate with metal ions, forming strong bonds. Example: Zr-MOFs show high uptake of Pb^{2+} ($\sim 30 \text{ mg/g}$).

π - π Interactions: Aromatic linkers enable selective adsorption of metals exploiting conjugated π -electron systems. Example: UiO-66 variants using aromatic ligands enhance PCDD/F removal.

van der Waals Forces: Size-selective uptake occurs based on MOF pore diameter and accessibility. Larger pores accommodate more ions per site. Example: NTU-38 enhanced CAFB absorption through amide functionalization.

Electrostatic Interactions: Positively charged MOFs attract negative charges (e.g., Cl^- , PO_4^{3-}). Example: Fe^{3+} -HKUST-1 selectively chelates Cd^{2+} ($\sim 1 \log$ improvement).

Ion Exchange/Binding: Pre-formed ligands engage in irreversible coordination bonds. Example: NU-1000 Fe^{3+} -Ni coordination yields Fe^{2+} oxides.

Redox Catalysis: Pre-designed redox-active sites accelerate oxidation/reduction reactions involving MnO_2 . Example: ZIF-8 supports MnO_2 for CO reduction.

Structural Tunability & Performance Metrics

- High Surface Area & Porosity: Enable massive ion capture pathways.
- Selectivity: Controlled through pore chemistry/topology; e.g., UiO-66-Cu shows dual functionality for both Pb^{2+} and Au^+ .
- Stability: MOFs degrade less efficiently than traditional adsorbents, making them suitable for water purification.

Applications & Challenges

- Applications: Laboratory-scale breakthrough experiments to field testing demonstrate robustness across pH (5–12) and diverse metals (e.g., Cr(VI)/As(III)).
- Challenges: High production cost, long-term stability in salty/water-dominated conditions, and environmental impacts of non-toxic ligands.
- Future Directions: Combining MOFs with bioactive components (e.g., hydroxy terminated polypyrrole add-ons) improves selectivity further.

Overall, MOFs' synergy of designability, efficiency, and adaptability makes them a promising technology for remedying heavy metal contamination in aqueous systems, balancing cost-effectiveness with real-world constraints.

Figure S109. The answer generated by the trained Qwen2.5-7B-Math model to the question: "What is the effect of MOFs adsorbent on removing heavy metal ions in water treatment?"

Introducing functional groups in the design of MOFs enhances their specific interactions with contaminants, improving their adsorption capacity and selectivity. Functional groups such as carboxyl (-COOH), hydroxyl (-OH), and amine (-NH₂) promote π - π electron resonance effects and create additional active sites for binding with target molecules. Studies show that these modifications not only increase surface density but also improve mass transfer within the framework, enabling more efficient contaminant removal. For instance, graphene-based MOFs stabilized with -COOH, -OH, and -NH₂ exhibit enhanced adsorption capacities due to increased surface area and defect stabilization. Additionally, these groups ensure structural stability during heat treatment, preventing frameworks from collapsing. Overall, functionalization allows precise tuning of MOF properties for specific adsorbents and environmental conditions, making them highly effective for removing various pollutants.

Figure S110. The answer generated by the trained Qwen2.5-7B-Math model to the question: “Why is the introduction of functional groups important in the design of Metal-Organic Framework for contaminant removal?”

Dynamic evaluations involve predicting transient response characteristics based on theoretical calculations and advanced materials design principles, whereas static analyses focus on comparing key adsorption indicators like selectivity and capacity across different frameworks.

Figure S111. The answer generated by the trained Qwen2.5-7B-Math model to the question: “How are the dynamic and static adsorption performances of MOFs usually evaluated?”

Adsorption sites in MOFs can be determined using experimental techniques that capture the exact shape, size, polarity, and coordination environment of the pores.

Figure S112. The answer generated by the trained Qwen2.5-7B-Math model to the question: “How to determine the adsorption sites in MOFs adsorbents?”

Bottlenecks include ensuring the stability of the material under harsh conditions, improving accessibility and transferability, addressing challenges with moisture-induced structural degradation, and enhancing selectivity in competing gases.

Figure S113. The answer generated by the fine-tuned DeepSeek-R1-Distill-Qwen-7B model (without reasoning process) to the question: “What are the current bottlenecks for HKUST-1 in industrial gas separation applications?”

MOFs offer **larger pores** and **higher surface areas** compared to zeolites, which increases their CO₂ capture capacity. Additionally, their **programmable pore structures** enable better control over the separation process.

Figure S114. The answer generated by the fine-tuned DeepSeek-R1-Distill-Qwen-7B model (without reasoning process) to the question: “Compared with zeolite materials, what are the advantages of MOFs (Metal-Organic Frameworks) materials in vacuum swing adsorption?”

Water stability can be improved by using **water-resistant linkers** and frameworks that are resistant to hydrolysis or through methods like **templating**, **encapsulation**, and **immobilization**.

Figure S115. The answer generated by the fine-tuned DeepSeek-R1-Distill-Qwen-7B model (without reasoning process) to the question: “How can the water stability of MOFs be enhanced to ensure their effectiveness under operational conditions?”

MOFs can be regenerated **through various methods**, but their regenerability remains a challenge due to the need for energy-intensive steps and the influence of pore fillers on regeneration efficiency.

Figure S116. The answer generated by the fine-tuned DeepSeek-R1-Distill-Qwen-7B model (without reasoning process) to the question: “What is the regeneration performance of MOFs adsorbent?”

MOFs have shown potential for efficient removal of heavy metals from water through physisorption, offering **high affinity** and **selectivity**.

Figure S117. The answer generated by the fine-tuned DeepSeek-R1-Distill-Qwen-7B model (without reasoning process) to the question: “What is the effect of MOFs adsorbent on removing heavy metal ions in water treatment?”

Functional groups can increase the interaction strength between water molecules and metal sites, improving the **stability** and **selectivity** of MOFs for specific contaminants.

Figure S118. The answer generated by the fine-tuned DeepSeek-R1-Distill-Qwen-7B model (without reasoning process) to the question: “Why is the introduction of functional groups important in the design of Metal-Organic Framework for contaminant removal?”

Dynamic performance is assessed by studying adsorption capacity, **breakthrough curves**, and cyclic stability. Static performance metrics include adsorbent saturation **capacity** (e.g., g cm⁻³) and regenerative capacity for specific molecules.

Figure S119. The answer generated by the fine-tuned DeepSeek-R1-Distill-Qwen-7B model (without reasoning process) to the question: “How are the dynamic and static adsorption performances of MOFs usually evaluated?”

Determine the adsorption sites using techniques like **X-ray diffraction** (XRD), **IR spectroscopy**, **NMR**, and solid-state ¹H/NMR or ²³Na ¹H-NMR.

Figure S120. The answer generated by the fine-tuned DeepSeek-R1-Distill-Qwen-7B model (without reasoning process) to the question: “How to determine the adsorption sites in MOFs adsorbents?”

Table S8. The evaluation results of the MOFReasoner, fine-tuned Qwen-7B-Math and fine-tuned DeepSeek-R1-Distill-Qwen-7B (without reasoning process) models.

Model	Correct	Inaccurate	Wrong or controversial	Serious error	Missing	Total score
MOFReasoner	25	2	1	0	10	25.5
fine-tuned Qwen-7B-Math	17	5	3	4	18	14
fine-tuned DeepSeek-R1-Distill-Qwen-7B (without reasoning process)	12	7	0	1	23	14.5

Section S4. Details of adsorption of benzothiophene by metal SBUs

Computational Details. DFT calculations were carried out using the CP2K code.¹ All calculations employed a mixed Gaussian and planewave basis sets. Core electrons were represented with norm-conserving Goedecker-Teter-Hutter pseudopotentials,²⁻⁴ and the valence electron wavefunction was expanded in a triple-zeta basis set with polarization functions⁵ along with an auxiliary plane wave basis set with an energy cutoff of 360 Ry. The generalized gradient approximation exchange-correlation functional of Perdew, Burke, and Enzerhof (PBE)⁶ was used. Each configuration was optimized with the OT algorithm with SCF convergence criteria of 1.0×10^{-8} au. To compensate the long-range van der Waals dispersion interaction between the adsorbate and the MOFs, the DFT-D3 scheme⁷ with an empirical damped potential term was added into the energies obtained from exchange-correlation functional in all calculations.

The adsorption energy between the adsorbate and the SBUs can be calculated using the following equation:

$$\Delta E_{ads} = E_{adsorbate@MOF} - E_{MOF} - E_{adsorbate} \quad (1)$$

In Eq. (1), $E_{adsorbate@MOF}$ and E_{MOF} represent the total energies of substrate with and without adsorbate, respectively. $E_{adsorbate}$ is the energy of the adsorbate. According to this equation, a negative adsorption energy corresponds a stable adsorption structure.

MOFReasoner reasoning process and answers

<|begin_of_thought|>

Okay, so I need to figure out how to rank these paddle-wheel SBUs (Cu^{2+} , Zn^{2+} , Co^{2+}) based on their adsorption strength for benzothiophene. Let me start by recalling what I know about metal SBUs and their adsorption properties.

First, paddle-wheel SBUs are metal clusters where two metal ions are connected by carboxylate ligands in a square-planar arrangement. The strength of adsorption for a molecule like benzothiophene probably depends on the metal's size, charge, and the nature of the ligands involved.

I remember that the adsorption strength can be influenced by the Lewis acidity of the metal center. More acidic metals might have stronger interactions with electron-rich molecules like benzothiophene. So, the metal's Lewis acidity would be a key factor here.

Let me think about the common paddle-wheel SBUs. For example, Zn^{2+} is known for its Lewis acidity, which is often used in catalysis and adsorption. Co^{2+} is also a Lewis acid but maybe less so than Zn^{2+} ? Cu^{2+} is a transition metal, but how does its Lewis acidity compare?

Wait, I think the order of Lewis acidity for transition metals in this context might be something like $Zn^{2+} > Co^{2+} > Cu^{2+}$. Because Zn^{2+} is in the first transition series and has a +2 charge, while Co^{2+} is in the third, and Cu^{2+} is in the fourth. But maybe the actual acidity values are different. I should check some data or examples.

Alternatively, maybe the size of the metal ion affects the adsorption. Larger ions might create a more open structure, allowing better interaction. But paddle-wheel SBUs are usually pretty compact. However, the charge density might matter. Higher charge density (like Zn^{2+} compared to Co^{2+}) could lead to stronger electrostatic interactions.

Another angle: the coordination number. Paddle-wheel SBUs typically have a coordination number of 4, but if the metal is part of a larger cluster, maybe the number of ligands around it changes. But the question specifies paddle-wheel SBUs, so maybe each SBU is a 4-coordinate cluster. In that case, the charge and size of the metal would still be the main factors.

I recall that in some studies, the adsorption of benzothiophene on metal SBUs was compared. For example, in a paper by Smith et al., they found that $Co(II)$ SBUs showed higher adsorption of benzothiophene compared to $Zn(II)$ SBUs. Wait, but that might be because $Co(II)$ has a higher Lewis acidity? Or maybe the size of the metal ion affects the pore space.

Wait, another thought: the size of the metal ion might influence the accessibility of the adsorption site. If the metal ion is too large, the pore might be too big, making it harder for benzothiophene to fit. But paddle-wheel SBUs are usually small enough to allow certain molecules to enter. Alternatively, if the metal is smaller, the coordination environment might be more open, leading to stronger interactions.

Alternatively, the d-orbital participation. For transition metals, the d-orbitals' ability to participate in bonding might affect adsorption. For example, Co^{2+} has d^7 configuration, which might engage in more covalent bonding with benzothiophene compared to Zn^{2+} (d^{10}), which has a closed d-shell. But I'm not sure if that's the case here.

Wait, benzothiophene is a planar molecule with a conjugated system. The adsorption might involve the aromatic ring interacting with the metal cluster. The Lewis acidity of the metal would determine how strongly the molecule is held. So a more acidic metal would form stronger bonds.

So, ranking the metals by their Lewis acidity. Zn^{2+} is more acidic than Co^{2+} , which is more acidic than Cu^{2+} . Therefore, Zn paddle-wheel SBU would have the strongest adsorption, followed by Co , then Cu .

But I should verify this. Let me think of specific examples. For instance, in some metal-organic frameworks (MOFs), Zn paddle-wheel SBUs are known to have good adsorption of certain molecules due to their Lewis acidity. Co paddle-wheel SBUs might be used in applications where moderate acidity is needed, and Cu might be less effective unless in specific conditions.

Another consideration: the size of the metal ion. Zn^{2+} is smaller than Co^{2+} , which is smaller than Cu^{2+} . Smaller ions might create a more open structure, allowing better interaction. But if the metal is too small, maybe the coordination environment is too tight. Alternatively, a balance between size and charge.

Alternatively, the charge-to-size ratio. Zn^{2+} has a higher charge density compared to Co^{2+} and Cu^{2+} . Higher charge density could lead to stronger electrostatic interactions, which might be beneficial for adsorption. So Zn would be better than Co, which is better than Cu.

But I'm not entirely sure. Maybe I should look for some data or references. For example, in a study by Zhang et al., they compared the adsorption of benzothiophene on various metal SBUs. They found that Co(II) SBUs showed higher adsorption capacity than Zn(II) and Cu(II) SBUs. Wait, that contradicts my earlier thought. If that's the case, then maybe Co is better than Zn, which is better than Cu.

But why would that be? Maybe the coordination environment in Co(II) is more suitable for benzothiophene's structure. Alternatively, the d-orbital participation is different. Co^{2+} has a d^7 configuration, which might engage in more bonding with the benzothiophene's aromatic ring compared to Zn^{2+} (d^{10}) or Cu^{2+} (d^9).

Alternatively, maybe the number of coordination sites available. If the Co(II) SBU has more open sites or a different geometry that allows better interaction with the benzothiophene's electron-rich regions.

Wait, another angle: the isosteric heat of adsorption. If Co(II) has a higher isosteric heat, that would indicate stronger adsorption. But I don't have exact values here.

Alternatively, considering the size of the pore. If the Co(II) SBU has a larger pore, it can accommodate benzothiophene more easily, leading to higher adsorption. But paddle-wheel SBUs are usually small, so maybe the accessibility is limited.

Alternatively, the steric hindrance around the metal site. If the metal is smaller, the molecule might fit better, but the adsorption strength might be lower. So there's a balance between size and Lewis acidity.

Hmm, this is a bit confusing. Let me try to summarize:

Lewis acidity: $Zn^{2+} > Co^{2+} > Cu^{2+}$ (if Zn is more acidic)

Size: Zn^{2+} is smaller than Co^{2+} , which is smaller than Cu^{2+}

Charge density: Zn^{2+} has higher charge density

Possible d-orbital involvement: Co^{2+} has d^7 , which might interact differently

If Lewis acidity is the main factor, then Zn paddle-wheel SBU would be the most suitable, followed by Co, then Cu. But if steric factors or d-orbital interactions are more important, the order might be different.

Alternatively, maybe the stability of the SBU is a factor. More stable SBUs might be more likely to adsorb. But the question is about adsorption strength, not stability.

Another thought: the adsorption is also influenced by the polarity of the metal-ligand bonds. Zn^{2+} has a higher electronegativity compared to Co^{2+} and Cu^{2+} , so the bonds might be more polar, leading to stronger interactions with the aromatic ring of benzothiophene.

Alternatively, the electronic structure of the benzothiophene molecule. If the metal can stabilize the molecule through charge transfer or π - π interactions, then the adsorption strength would be higher. For example, if the metal has a vacant d-orbital that can interact with the π -system of benzothiophene, that would enhance adsorption.

Co^{2+} has a d^7 configuration, which might have a vacant d-orbital that can interact with the π -electrons of benzothiophene. Zn^{2+} is d^{10} , so no d-orbital available for such interaction, but it has a strong Lewis acidity. Cu^{2+} is d^9 , which might also have some d-orbital participation.

Wait, but d^{10} ions like Zn^{2+} don't have available d-orbitals for bonding, so they rely more on Lewis acidity. Co^{2+} , with d^7 , might have some d-orbital involvement, which could be beneficial. Cu^{2+} , with d^9 , also has some d-orbital participation.

So maybe the order is determined by both Lewis acidity and d-orbital involvement. If Co^{2+} has a better combination of these factors, it might be better than Zn^{2+} , even if Zn is more acidic.

But I'm not sure. Let me think of specific examples. For instance, in some MOFs, Co(II) paddle-wheel SBUs have been used for adsorbing benzothiophene. If that's the case, then Co might be more suitable than Zn, which might be less effective.

Alternatively, maybe the size of the metal ion affects the accessibility. If Zn^{2+} is too small, the pore might

be too tight, preventing benzothiophene from entering. Co^{2+} is larger, providing more space for the molecule, while Cu^{2+} is even larger, but maybe the interaction is weaker due to lower Lewis acidity.

So, perhaps the ranking is Co paddle-wheel SBU > Zn paddle-wheel SBU > Cu paddle-wheel SBU, based on a balance of size and Lewis acidity. Co offers a moderate size with decent Lewis acidity, providing both a suitable pore size and strong interaction through Lewis acid-base chemistry.

But I'm still a bit unsure. Another approach: look up some data or studies that compare these SBUs for benzothiophene adsorption. For example, in a paper by Johnson et al., they might have measured the adsorption capacities. If Co(II) shows higher capacity than Zn(II) and Cu(II) , then that would support the $\text{Co} > \text{Zn} > \text{Cu}$ order.

Alternatively, in another study by Lee et al., they found that Co(II) SBUs have higher adsorption of benzothiophene compared to Zn(II) and Cu(II) SBUs. If that's the case, then the ranking would be $\text{Co} > \text{Zn} > \text{Cu}$.

But I need to be careful here. Since I don't have specific data, I have to rely on general trends. Let me try to think of the common understanding.

From what I remember, transition metals with higher Lewis acidity tend to have stronger adsorption. So Zn^{2+} is more acidic than Co^{2+} , which is more acidic than Cu^{2+} . Therefore, the order would be $\text{Zn} > \text{Co} > \text{Cu}$. However, steric effects and d-orbital interactions might change this.

Alternatively, the size of the metal ion. If the metal is too small, the pore might be too narrow, reducing adsorption. So Co^{2+} , being larger than Zn^{2+} , might provide a better balance between size and Lewis acidity.

But I think the primary factor is Lewis acidity. So Zn paddle-wheel SBU would have the strongest adsorption, followed by Co, then Cu. However, in practice, maybe Co is better because of its moderate size and some d-orbital interactions.

Alternatively, maybe the number of available sites. Co(II) might have more open sites or a different coordination geometry that allows better interaction with benzothiophene.

Wait, another thought: the d-electron count. Co^{2+} has a d^7 configuration, which might have a different electron configuration compared to Zn^{2+} (d^{10}) and Cu^{2+} (d^9). The d^7 configuration might allow for more effective bonding with the aromatic ring.

Alternatively, the redox potential of the metal. If the metal is more redox-active, it might facilitate electron transfer, enhancing adsorption. But I'm not sure how that applies here.

In summary, considering the primary factors of Lewis acidity and d-orbital interactions, the ranking would likely be $Zn^{2+} > Co^{2+} > Cu^{2+}$. However, if steric effects and pore size are significant, Co might be better than Zn. Since the question is about adsorption strength, which is primarily a chemical interaction, the Lewis acidity is the main driver. Therefore, Zn^{2+} paddle-wheel SBU would be the most suitable, followed by Co, then Cu. <|end_of_thought|>

<|begin_of_solution|>

Based on the adsorption strength of benzothiophene on metal paddle-wheel SBUs, the ranking is determined primarily by the Lewis acidity and the d-orbital interactions of the metal centers. Here's the step-by-step reasoning:

Lewis Acidity:

Zn^{2+} exhibits higher Lewis acidity compared to Co^{2+} and Cu^{2+} due to its higher charge density and smaller ionic radius, creating stronger electrostatic interactions with the electron-rich benzothiophene molecule.

d-Orbital Interactions:

Co^{2+} (d^7 configuration) may engage in more covalent bonding with the benzothiophene's aromatic ring due to its partially filled d-orbitals, enhancing adsorption strength.

Steric Effects:

While Zn^{2+} is smaller than Co^{2+} , the latter provides a balance between size and Lewis acidity, which might be advantageous for accommodating benzothiophene while maintaining strong interaction.

Final Ranking by Adsorption Strength:

Zn^{2+} (Paddle-Wheel SBU)

Highest Lewis acidity and favorable d-orbital interactions.

Co^{2+} (Paddle-Wheel SBU)

Moderate size and effective bonding with the aromatic ring.

Cu^{2+} (Paddle-Wheel SBU)

Least effective due to lower Lewis acidity and larger size, limiting interaction with benzothiophene.

Conclusion: The suitability for adsorbing benzothiophene decreases in the order $Zn^{2+} > Co^{2+} > Cu^{2+}$. <|end_of_solution|>

Step 1. Frame the adsorption problem (must)

Define the task as a reasoning problem requiring interpretation of adsorption behavior rather than recall of fixed facts.

**Step 2. Review relevant conceptual frameworks (must)**

Recall general theories and principles commonly used to interpret adsorption and metal–guest interactions.

**Step 3. Analyze plausible interaction mechanisms (must)**

Examine candidate mechanisms that could govern adsorption, without prematurely selecting a single dominant pathway.

**Step 4. Integrate multiple perspectives (maybe)**

Synthesize insights from different mechanisms into a coherent reasoning chain while acknowledging uncertainty.

**Step 5. Draw a cautious conclusion (maybe)**

Provide a reasoned but non-absolute assessment that reflects the complexity of the problem.

Figure S121. Expected reasoning path for the reasoning-type question “Considering adsorption strength, which metal SBUs are most suitable for benzothiophene adsorption?”, highlighting alternative reasoning modes based on integrative analysis and mechanism-focused inference.

DeepSeek R1's Reasoning: Okay, the user is asking about choosing metal SBUs for adsorbing benzothiophene. They've listed three paddle-wheel options: Cu^{2+} , Zn^{2+} , and Co^{2+} . I need to figure out which two are most suitable based on adsorption strength.

First, I recall that benzothiophene is a sulfur-containing aromatic compound, common in fuels. The goal is to remove it via adsorption. The key factors here would be the metal's affinity for sulfur and the strength of interaction.

Soft acid-base theory comes to mind. Benzothiophene has sulfur atoms which are soft bases. Metals that are soft acids should bind more strongly. Among the options, Cu^{2+} and Co^{2+} are softer than Zn^{2+} . Zn^{2+} is borderline, so it might not form as strong bonds with sulfur.

Copper is often used in desulfurization studies. It's known for strong interactions with sulfur compounds. Cobalt also has a good affinity, though maybe a bit less than copper. Zinc tends to have weaker interactions.

I should check the d-electron configurations. Cu^{2+} is d9, which is good for π -backbonding. Benzothiophene's aromatic ring can interact through π -electrons. Co^{2+} is d7, which also supports such bonding. Zn^{2+} is d10, so no d-orbitals available for backbonding, leading to weaker interactions.

Experimental data supports this. Studies show Cu-based MOFs like HKUST-1 are effective for benzothiophene adsorption. Co-based ones also perform well, while Zn-based are less effective.

The user might be designing an adsorbent for fuel desulfurization. They need efficient removal, so prioritizing metals with strong sulfur affinity makes sense. They might not have mentioned, but cost or availability could be factors. Copper is common and cost-effective, cobalt might be pricier. Zinc is cheaper but less effective here.

So, the top two should be Cu^{2+} and Co^{2+} . Zinc would be the less effective one. The user might also appreciate knowing why Zn isn't as good, so explaining the d-orbital part would help.

Figure S122. Reasoning trace generated by DeepSeek R1 for the benzothiophene adsorption task, illustrating a mechanism-driven reasoning process based on sulfur–metal interactions and electronic structure considerations to rank different paddle-wheel metal SBUs.

Table S9. Calculated adsorption energies (ΔE_{ads}) of benzothiophene on paddle-wheel metal sites (Zn, Cu, and Co).

Metal Site	Zn	Cu	Co
Paddle-Wheel (hartree)	-333.7417015	-308.8449858	-503.58878
Benzothiophene (hartree)	-274.4719485	-249.5797098	-444.31362
benzothiophene and Paddle-Wheel (hartree)	-59.25116851	-59.25116851	-59.251169
ΔE_{ads} (hartree)	0.018584507	0.01410747	0.023994
ΔE_{ads} (kJ/mol)	48.79362443	37.03916193	62.99703

Atomic coordinates of benzothiophene

C 13.0489357340 19.2552538534 0.0693099690

C	13.7834323311	18.0515196461	0.0602694936
C	15.1707706455	18.0634828637	19.9544099114
C	15.8535121093	19.2945667130	19.8546493900
C	15.0913586529	0.4972849917	19.8653458789
C	13.6940316189	0.4875690671	19.9722087983
S	16.1381032521	1.9071926893	19.7305906886
C	17.5598110340	0.8825070982	19.6628605199
C	17.2640575646	19.5511157968	19.7375239583
H	11.9611939238	19.2243833284	0.1534510636
H	13.2544924839	17.0999405742	0.1374745550
H	15.7351723161	17.1284445503	19.9480236890
H	13.1238768876	1.4178909343	19.9793904199
H	18.5375848374	1.3493962837	19.5701572546
H	18.0208971033	18.7672513992	19.7108318480

Atomic coordinates of Co Paddle-Wheel

O	8.1605104993	10.2197726978	12.0327273738
O	8.0772046593	7.5562201918	9.3667898518
O	8.0761838113	7.5560818506	12.0313262079
O	8.1603617872	10.2222710044	9.3677473313
O	10.4444478771	10.1976947844	9.3847568681
O	10.3576991585	7.4714531494	12.0260263964
O	10.3593061808	7.4845738332	9.3653944880
O	10.4429441485	10.1248448174	12.0908391870
Co	8.1520852849	8.8889572402	10.6993882017
Co	10.3713126773	8.8120615407	10.7020062927
C	9.3086957173	10.5735466675	12.4762166174
C	9.2044797834	7.1101779524	8.9577805565
C	9.2022595721	7.1030935626	12.4363806892
C	9.3105093481	10.6245739401	8.9749001360
H	9.3232979737	11.4176705983	8.2090754087
H	9.1805648071	6.3282103597	8.1813800888
H	9.1755629699	6.3220428896	13.2136081112

H	9.3178838495	11.3396095165	13.2690021363
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Atomic coordinates of Cu Paddle-Wheel

O	8.2309608523	10.7017113618	12.1830511296
O	8.2311132398	7.8992659603	9.3804793359
O	8.2310231624	7.8989484605	12.1830234253
O	8.2314504264	10.7018191742	9.3802093075
O	10.5345930736	10.7013431143	9.3806400565
O	10.5344147590	7.8986143868	12.1830048740
O	10.5344197286	7.8991396603	9.3803244062
O	10.5340834607	10.7015324612	12.1835774312
Cu	8.1240420221	9.3009827105	10.7815718069
Cu	10.6413221230	9.3003609570	10.7822967320
C	9.3824696759	11.0827617604	12.5660465705
C	9.3827600689	7.5169609495	8.9988789924
C	9.3825938600	7.5170006624	12.5649035120
C	9.3831531996	11.0828204141	8.9977667993
H	9.3839142991	11.8637509491	8.2139912363
H	9.3826661885	6.7344449289	8.2165281352
H	9.3824420217	6.7335680364	13.3463272426
H	9.3818893147	11.8635623333	13.3500771617

Atomic coordinates of Zn Paddle-Wheel

O	8.1562628854	11.0352783450	12.5174418200
O	8.0731476280	8.1478019007	9.7052841102
O	8.0709718937	8.1502190763	12.5152438359
O	8.0710345808	11.0275690333	9.6319995130
O	10.3644624703	10.9513035593	9.6304188460
O	10.3643355266	8.1491649252	12.5905107513
O	10.3658731440	8.1336869750	9.7056085544
O	10.4496078103	11.0282141612	12.5097490235
Zn	7.9580341969	9.6217368350	11.1036411818
Zn	10.5421860379	9.5517987169	11.1152227942
C	9.3066030977	11.4311888237	12.9035314963

C	9.2151214775	7.7406664465	9.3152524527
C	9.2037417996	7.7526295007	12.9435273846
C	9.2309978039	11.3713520292	9.2256052967
H	9.2545662487	12.1290650193	8.4185235172
H	9.2133632132	6.9474441818	8.5429891155
H	9.1785141974	6.9620788700	13.7185599769
H	9.3101564959	12.2233243433	13.6766026507

Atomic coordinates of benzothiophene and Co Paddle-Wheel

O	8.1548102864	1.2316375305	11.0225019306
O	8.0009575441	18.5975886778	8.2950256344
O	8.0718852644	18.5266431206	10.9458211756
O	8.0878990648	1.3028741634	8.3204219017
O	10.3675107597	1.1556527512	8.2290603039
O	10.3573389549	18.5206374639	11.0275599154
O	10.2807451836	18.4344365843	8.3104107930
O	10.4405974201	1.2348044189	10.9468770843
Co	8.1256265971	19.9181663992	9.6353186200
Co	10.3822290668	19.8354962140	9.6283426308
C	9.3083928975	1.6363806187	11.3888313031
C	9.1124038355	18.1057608065	7.9033238469
C	9.1987859059	18.1206473814	11.3909442714
C	9.2366548042	1.6323981434	7.8696419426
H	9.3359362664	2.4143227635	12.1714320844
H	9.0625778266	17.3145963616	7.1357358185
H	9.1718144141	17.3399788318	12.1706856031
H	9.2594264379	2.4100272089	7.0866688344
C	13.6036832511	15.7862598227	10.0534867334
C	14.3146987324	15.8821950298	11.2632543150
C	14.5275549655	17.1186380299	11.8723515748
C	14.0214613446	18.2828220599	11.2674608860
C	13.3183488613	18.1597893989	10.0426548561
C	13.0994826171	16.9283667770	9.4253813156

S	12.7876766610	19.7486370823	9.4603895564
C	13.4749836280	0.5316999146	10.8866020017
C	14.0923948801	-0.3461874934	11.7196151761
H	13.4402340171	14.8080027262	9.5985292211
H	14.7015180539	14.9760217901	11.7321258461
H	15.0777164856	17.1884809386	12.8127709947
H	12.5328182374	16.8630106826	8.4968546804
H	13.3502054758	1.6051206194	10.9939485849
H	14.5870166488	-0.0451377389	12.6431798892

Atomic coordinates of benzothiophene and Cu Paddle-Wheel

O	8.1562000000	1.2646000000	11.0040000000
O	8.1096000000	18.5218000000	8.2594000000
O	8.1064000000	18.5210000000	11.0032000000
O	8.1594000000	1.2654000000	8.2600000000
O	10.3828000000	1.2250000000	8.2626000000
O	10.3298000000	18.4808000000	11.0058000000
O	10.3330000000	18.4814000000	8.2620000000
O	10.3796000000	1.2242000000	11.0066000000
Cu	7.9300000000	19.8968000000	9.6314000000
Cu	10.5592000000	19.8492000000	9.6346000000
C	9.2748000000	1.6488000000	11.4100000000
C	9.2144000000	18.0972000000	7.8560000000
C	9.2102000000	18.0964000000	11.4090000000
C	9.2790000000	1.6496000000	7.8570000000
H	9.3436000000	2.4526000000	12.2156000000
H	9.2558000000	17.2914000000	7.0508000000
H	9.2498000000	17.2902000000	12.2142000000
H	9.3498000000	2.4538000000	7.0522000000
C	13.5752058032	15.6813662437	9.8716257446
C	14.0719446599	15.6161372757	11.1882150941
C	14.2680748204	16.7737776211	11.9365295096
C	13.9679738154	18.0270790675	11.3678852674

C	13.4777755492	18.0658826803	10.0355463830
C	13.2728277883	16.9083989000	9.2801167917
S	13.1729256641	19.7313997157	9.5286019767
C	13.6717596220	0.3354029749	11.1062195351
C	14.0659303207	-0.6583911628	11.9495907595
H	13.4212244057	14.7609068002	9.3060133011
H	14.3022295064	14.6438442728	11.6268013160
H	14.6478911157	16.7180567748	12.9586902122
H	12.8700713940	16.9649697956	8.2688282298
H	13.6202178929	1.4048580624	11.2908380181
H	14.4106629788	-0.4750357342	12.9669806873

Atomic coordinates of benzothiophene and Zn Paddle-Wheel

O	8.1562000000	1.2646000000	11.0040000000
O	8.1096000000	18.5218000000	8.2594000000
O	8.1064000000	18.5210000000	11.0032000000
O	8.1594000000	1.2654000000	8.2600000000
O	10.3828000000	1.2250000000	8.2626000000
O	10.3298000000	18.4808000000	11.0058000000
O	10.3330000000	18.4814000000	8.2620000000
O	10.3796000000	1.2242000000	11.0066000000
Zn	7.9300000000	19.8968000000	9.6314000000
Zn	10.5592000000	19.8492000000	9.6346000000
C	9.2748000000	1.6488000000	11.4100000000
C	9.2144000000	18.0972000000	7.8560000000
C	9.2102000000	18.0964000000	11.4090000000
C	9.2790000000	1.6496000000	7.8570000000
H	9.3436000000	2.4526000000	12.2156000000
H	9.2558000000	17.2914000000	7.0508000000
H	9.2498000000	17.2902000000	12.2142000000
H	9.3498000000	2.4538000000	7.0522000000
C	13.5702423135	15.7191071980	9.7854885143
C	14.0183387193	15.6199417504	11.1159038450

C	14.1652966794	16.7559017089	11.9088025496
C	13.8625141953	18.0200992872	11.3690642181
C	13.4224037552	18.0913261017	10.0230893027
C	13.2671359609	16.9598440489	9.2213633620
S	13.1123685393	19.7743376440	9.5572706242
C	13.5280266935	0.3338400011	11.1826073885
C	13.9099877281	-0.6824657031	11.9992893405
H	13.4523813654	14.8153879065	9.1856436297
H	14.2488899997	14.6378978065	11.5318696594
H	14.5061862053	16.6733966417	12.9425571956
H	12.8979827675	17.0427768243	8.1993571416
H	13.4378415060	1.3938681840	11.4013665791
H	14.2087774312	-0.5302484723	13.0362120263

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