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ADSORPTION PROPERTIES OF Mg-MOF-74: A REVIEW OF LITERATURE DATA AND APPLICATION PROSPECTS

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Abstract. This review examines published data on gas adsorption in Mg-MOF-74 and the relationship between its structural features and adsorption performance. The roles of open magnesium sites, equilibrium CO_2 uptake, gas mixture separation, and the effects of water vapor on active site accessibility are analyzed. Application prospects are shown to depend on the combined effects of selectivity, working capacity, regenerability, and framework stability over repeated adsorption-desorption cycles. Directions for developing effective adsorbents and mixed-matrix membranes for selective carbon dioxide capture are discussed.

Keywords: Mg-MOF-74, carbon dioxide, adsorption, open metal sites, selectivity, regeneration.

Introduction. Mg-MOF-74, also known as CPO-27-Mg or Mg_2(dobdc), is a microporous metal–organic framework. The $dobdc^{4-}$ ligand is 2,5-dioxido-1,4-

benzenedicarboxylate. Removal of coordinated solvent exposes magnesium sites within the channels, providing a high affinity for CO_2 [1, 2]. This review aims to compare the reported adsorption characteristics of the material and identify conditions favorable for its potential applications.

The combination of pore geometry and the chemical affinity of the internal surface is fundamental to gas separation. In frameworks containing open metal sites, selectivity can arise even when the channels are sufficiently large to accommodate both components. For Mg-MOF-74, this distinction is particularly relevant to CO_2/CH_4 and CO_2/N_2 mixtures: molecular access to the pore space and preferential retention represent different aspects of the process [1-4].

Approach to the literature analysis. This review compares studies of single-component adsorption equilibria, dynamic separation, adsorbate-framework interactions, and membrane composites. Numerical results are interpreted with reference to temperature, pressure, sample condition, and measurement method. This comparison identifies established advantages of the material and issues requiring further investigation. The findings presented here constitute a literature analysis rather than original experimental results.

Structure and adsorption mechanism. The one-dimensional channels of Mg-MOF-74 combine accessible pore space with a regular arrangement of open Mg^{2+} sites. Caskey et al. demonstrated that metal substitution in an isostructural framework substantially alters CO_2 uptake [1]. Consequently, specific surface area alone cannot explain differences among the analogues; the chemical nature of the metal nodes and the accessibility of coordination sites must also be considered.

Queen et al. related differences in the adsorption properties of the M_2(dobdc) series to specific interactions between CO_2 molecules and metal sites [4]. Primary binding occurs through an oxygen atom of the adsorbate. As loading increases, weaker adsorption sites and interactions between guest molecules become more significant. Synthesis and activation procedures also affect pore accessibility [5, 6].

Dynamic studies support the feasibility of gas separation [2]. These characteristics make Mg-MOF-74 a model system for investigating energetic heterogeneity in microporous adsorbents.

Activation and site availability. The accessibility of Mg^{2+} nodes depends on the removal of coordinated guest molecules. Activation is therefore an integral part of preparing a functional adsorbent rather than simply a drying procedure. Incomplete desolvation reduces the number of accessible sites, whereas excessively harsh treatment may impair the material. The heating protocol should be selected in conjunction with monitoring residual solvent and the preservation of the porous structure [5, 6, 8].

Equilibrium capacity and temperature dependence. Bao et al. investigated CO_2 and CH_4 adsorption at 278, 298, and 318 K and pressures up to 1 bar. At 298 K and 1 bar, their sample exhibited capacities of 8.61 mmol/g for CO_2 and 1.05 mmol/g for CH_4, with a BET specific surface area of 1174 m^2/g [3]. These values describe a particular sample under specified experimental conditions and should not be treated as universal characteristics of all Mg-MOF-74 materials.

When comparing published isotherms, the pressure of a pure gas must be distinguished from the partial pressure of a component in a mixture. A capacity measured at 1 bar of pure CO_2 cannot be directly applied to a stream containing a low carbon dioxide fraction at the same total pressure without accounting for the different partial pressure. The basis of the reported capacity must also be specified, including whether it refers to the mass of activated powder or a formulated pellet. Binders, residual solvent, and differences in activation can affect the result without changing the nominal framework composition.

Thermodynamic characterization. Isotherms measured at several temperatures can be used to estimate the isosteric heat of adsorption. Its positive magnitude can be expressed as $q_{st}=-R[\partial \ln p/\partial(1/T)]_a$, where p is the equilibrium pressure, T is the temperature, R is the gas constant, and a denotes a fixed adsorption

loading. Under this sign convention, the enthalpy of exothermic adsorption is negative. Distinguishing between the heat and enthalpy of adsorption avoids ambiguity when comparing studies [3, 4].

The loading dependence of the adsorption heat provides information on the sequence of site occupation. At low loading, the most energetically favorable sites are occupied preferentially; the contribution of other regions of the pore space subsequently increases. However, the shape of this dependence cannot be attributed solely to surface heterogeneity. Adsorbate-adsorbate interactions, changes in the local environment, and the accuracy of isotherm interpolation must also be considered. Direct microcalorimetry could complement equilibrium measurements and test the proposed interpretation.

The pronounced difference in the uptake of the two gases supports the preferential affinity of the framework for CO_2. Nevertheless, the ratio of single-component capacities cannot directly be equated with mixture separation selectivity. Process evaluation requires data at matched partial pressures, calculations of the adsorbed-phase composition, and validation under dynamic conditions. Mason et al. evaluated frameworks in the context of cyclic carbon dioxide capture [7].

Selectivity and mixture models. Equilibrium selectivity between two components is defined as $S_{ij}=(x_i/x_j)/(y_i/y_j)$, where x denotes the mole fraction in the adsorbed phase and y the mole fraction in the gas phase. Selectivity depends on composition, temperature, and pressure. Models based on single-component isotherms, including ideal adsorbed solution theory, can be used for preliminary calculations. Their predictions should be validated experimentally, particularly when gas molecules and water compete for metal sites.

Kinetics and dynamic testing. Equilibrium capacity determines the attainable loading, while the rate at which it is reached affects adsorbent bed utilization during operation. For one-dimensional channels, the diffusion path length, particle size, and potential blockage of channel entrances must be considered.

Smaller crystals may shorten transport distances, but this effect should be distinguished from changes in accessible porosity and the extent of activation [3, 6].

Breakthrough experiments establish the duration of CO_2 retention in the presence of a second gas. The shape of the outlet concentration profile reflects not only adsorbate affinity but also mass transfer, flow distribution, and thermal effects. Reproducibility requires documentation of the mixture composition, flow rate, bed dimensions, adsorbent mass, and temperature. Comparing breakthrough times without accounting for these parameters can lead to misleading conclusions about the superiority of a particular sample [2].

Regeneration and working capacity. Mason et al. evaluated frameworks for CO_2 capture using temperature swing regeneration [7]. In a cyclic process, the difference between adsorption and desorption loadings is crucial. A high maximum capacity does not necessarily imply a high working capacity if a substantial fraction of the gas remains adsorbed after regeneration. Selection of an operating protocol should account for thermal energy requirements, cycle duration, and the retention of material properties.

Working capacity can be expressed as $\Delta a = a_{ads} - a_{des}$, representing the difference between the loadings under the conditions of the two cycle stages. For regeneration by pressure reduction, residual gas retention following depressurization is important. Temperature swing regeneration additionally requires consideration of adsorbent heating and cooling before the next cycle. Strong interactions with CO_2 therefore enhance uptake at low pressure but may also increase the energy required for its subsequent release [7].

Cyclic evaluation should include working capacity retention, desorption duration, and the extent to which the initial state is restored. A single regeneration step demonstrates that the adsorbate can be removed but does not establish sorbent durability. Practical evaluation requires determining whether water or impurities

accumulate and whether the breakthrough profile changes over repeated cycles. This approach distinguishes reversible loading from a progressive loss of accessible sites.

Effects of moisture. Open magnesium sites interact with water, making humidity a significant factor in Mg-MOF-74 performance. DeCoste et al. investigated the effects of water adsorption on the structure and porosity of Mg-MOF-74 and other frameworks [8]. The review by Burtch et al. emphasizes the need to distinguish water uptake from material stability upon exposure to water [9]. Consequently, a high capacity measured in dry gas requires separate validation for humid streams.

Both competitive occupation of adsorption sites and possible irreversible framework changes should be evaluated. Following humidification and reactivation, residual CO_{301} capacity, accessible porosity, and phase composition should be measured. Retention of diffraction peaks does not replace verification of adsorption performance. For actual gas mixtures, exposure duration, temperature, and the history of preceding cycles are also important [8, 9].

Application prospects. The most substantiated applications include CO_2 removal from dry gas mixtures and methane enrichment through the purification of CO_2-containing gases. The strong affinity for carbon dioxide makes Mg-MOF-74 attractive for processes operating at low CO_2 partial pressure. However, the choice between pressure swing and temperature swing operation should be based on working capacity and regeneration requirements [3, 7]. Translating laboratory results into industrial processes requires assessing the effects of humidity and impurities.

A further application involves incorporating Mg_2(dobdc) nanocrystals into polymer membranes. Bae and Long showed that performance depends on the polymer matrix: CO_2 permeability and CO_2/N_2 selectivity improved in a glassy polyimide, whereas permeability decreased in the rubbery polymers investigated

[10]. Composite design must therefore preserve pore accessibility and ensure effective interfacial contact.

Adsorption and transport are closely coupled in membrane composites. Preferential CO_2 sorption in the filler may facilitate separation, but overall permeability also depends on diffusion through the polymer and the condition of the interface. Interfacial voids may create nonselective transport pathways, while penetration of polymer chains into the pores may reduce the contribution of the framework. Increasing filler content therefore does not guarantee a proportional improvement in performance [10].

Shaping and scale-up. Adsorbent beds require particles with sufficient mechanical strength and an acceptable pressure drop. A binder should provide pellet integrity while maintaining access to the micropores. During development, capacity should be measured per unit mass of the formulated material, and attrition should be monitored. Comparisons restricted to powders do not capture the performance losses that may arise after shaping and operation in a flowing gas stream.

Conclusions. Mg-MOF-74 combines a high affinity for CO_2 with accessible open Mg^{2+} sites. Published studies support its potential for gas separation and membrane composites. The principal requirements for application are reproducible activation, capacity retention under humid conditions, and effective regeneration. Process selection should be based on complete cycle performance rather than maximum uptake alone.

Further evaluation should therefore combine structural characterization, isotherms at several temperatures, adsorption heat measurements, breakthrough experiments, and extended cycling tests. A priority is to establish the relationship between Mg^{2+} site accessibility and working capacity in multicomponent environments. Addressing moisture resistance, shaping, and regeneration energy requirements will determine the conditions under which the advantages of the framework can be realized in practice.

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