



## Review

## Effect of the structural constituents of metal organic frameworks on carbon dioxide capture



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## ABSTRACT

Currently one of the heightened global concerns is increasing CO<sub>2</sub> atmospheric concentration which is argued to be one of the main contributing factors in rising global temperature and climate change. Carbon capture and storage technologies show promise in this field with most of the research currently focused on large CO<sub>2</sub> emission sources such as coal fired power plants. Competitive CO<sub>2</sub> capture capacities were obtained with metal organic frameworks (MOFs), an emerging class of crystalline materials, as adsorbents at the CO<sub>2</sub> partial pressures expected in flue gas or lower, owing to their unique properties including high surface area, well-defined porosity, and ease of chemical tunability of the framework structure for introduction of additional physical and/or chemical properties. This review paper summarizes the recent and notable works in the area of CO<sub>2</sub> capture using MOFs as adsorbents with an emphasis on their structure–property-relationship, i.e., structural variations of MOF frameworks and their consequences to CO<sub>2</sub> capture performance. Structures of the MOFs reported are discussed and compared based on the effects of the choice for the main constituting parts such as metal centers and organic ligands. Effect of addition of functional groups have been found to be significant over the years and also discussed here. Various synthesis routes to achieve MOF crystals, and the role of MOFs particles within mixed matrix membranes for CO<sub>2</sub> separation are also examined. Lastly, an economic analysis of MOF synthesis techniques and implementation are discussed.

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## 1. Introduction

At the present time the world faces the large and complex problem of environmental pollution. While some of the pollution comes from naturally occurring processes, the most easily mitigated portion is composed of anthropogenic components that are the results of human activity. Gases like NO<sub>x</sub>, SO<sub>x</sub>, CO<sub>x</sub>, H<sub>2</sub>S, and volatile organic compounds all largely contribute to air pollution [1]. Among the greenhouse gases, carbon dioxide has been recognized as a significant contributor to the rise in average global earth temperature. The United Nations Intergovernmental Panel of Climate Change (IPCC) claims that a significant reduction by 50% of current carbon dioxide emissions is required to avoid a global average temperature rise of 2–2.5 °C by the year 2050. In the United States alone in 2012 CO<sub>2</sub> emissions were estimated to be about 5.4 billion metric tons, and the contribution to this from fossil fuel combustion was around 94% [2]. In order to try and limit this

source of carbon emissions, decarbonization of post-combustion waste gas and the ambient air is currently being studied.

In 2010, the International Energy Agency (IEA) pronounced carbon capture and sequestration (CCS) technologies as vital tools for the reduction of carbon dioxide emissions and current levels in the atmosphere [3]. This technology encompasses CO<sub>2</sub> capture and CO<sub>2</sub> separation from other gases present in the ambient air or postcombustion flue gas, transportation of captured CO<sub>2</sub>, and its proper storage [4,5]. As of 2012, there were eight examples of implementation of CCS on a large scale [6,7], and this technology has primarily been applied to the capture of CO<sub>2</sub> emissions from sources such as coal fired power plants, refineries, and other industrial carbon dioxide sources [8]. There are various routes available to capture CO<sub>2</sub> at the industrial scale, which either can be retrofitted onto existing plants or require alterations of the current combustion process. Pre-combustion capture and oxy-fuel combustion for instance both involve redesign of the combustion process. The most commonly implemented and studied process is postcombustion capture, which can be applied to already established plants without significant changes [9,10]. In this review, we will mostly focus on the capture from ambient air and from

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post-combustion waste gas, as well as on the separation from other post-combustion products using physical adsorbent materials, specifically metal organic frameworks (MOFs). While current aqueous amine based chemical absorption is highly effective and commercially available, the process is also highly energy intensive and can result in equipment corrosion and adsorbent material degradation due to the presence of other flue gas components, such as SO<sub>2</sub> and NO<sub>2</sub> [4,9].

Physical adsorption onto solid porous materials is one of the methods used in CCS for CO<sub>2</sub> capture from flue gas, and MOFs are considered strong candidates for potential adsorbent materials [11]. Adsorbents operating mainly on physisorption processes are known to be the most economical for capture and separation of greenhouse gases such as CO<sub>2</sub> and CH<sub>4</sub>. Other porous solids such as zeolites, activated carbons, and mesoporous silica have also been considered, but these materials face the challenges of low CO<sub>2</sub> uptake capacities, instability in the presence of water, and demanding conditions for material regeneration [4,12].

There are currently a number of review papers available describing the performance of metal organic frameworks specifically tested for carbon dioxide capture [1,13–20]. Metal organic frameworks (MOFs) are a new class of hybrid materials where inorganic and organic counterparts form single phase crystalline materials. These frameworks are also called porous coordination polymers or coordination networks. The frameworks are composed of metal nodes, which can be represented by metal ions, metal centers, or metal clusters; and organic ligands, which play the role of linkers between those metal nodes. Interest in these materials was sparked in the 1990s, with hundreds of these frameworks now known. This interest in MOFs is related to their unique properties, including crystallinity, high porosity and large specific surface areas. Due to their unique construction from metal and organic ligand counterparts, it is also believed that the choice of these components can be used to create a large variety of final crystals with alterable properties for the application of interest. However, since MOFs are synthesized through self-assembly carefully controlled synthetic procedures are required to obtain high quality crystals and the permanent porosity of the frameworks is not always guaranteed. Various synthetic routes such as hydrothermal, solvothermal, and microwave synthesis have been studied to reduce the cost of synthesis and to obtain high quality crystals. In this review, the various synthetic methods and the choice of both metal and organic components in the MOF crystal will be discussed, with specific focus on how these various changes alter carbon capture performance. Specifically, these materials will be compared according to the following factors which have been identified as important for the practical implementation of any solid adsorbent for carbon dioxide capture, including: i) operational conditions of the adsorbate gas at which the adsorbent material should be effective, e.g. atmospheric pressure of ambient air, high temperature of post-combustion flue gas, the presence of humidity, etc.; ii) selectivity of the adsorbent material for CO<sub>2</sub> over other components of the adsorbate gas; iii) energy requirements for regeneration of the adsorbent material; iv) cost of production of the adsorbent material at a large scale [21]. Further alterations through post synthesis functionalization, such as the recently reported use of MOFs in mixed matrix membranes will also be briefly discussed. And finally, a review of the current economic outlook and research on MOFs for carbon capture at the industrial scale will be presented.

## 2. Synthetic routes

The past two decades have witnessed immense interest in metal-organic framework technology, with particular focus

centered on the industrial viability of using MOFs for CO<sub>2</sub> capture. The synthesis of these MOFs has normally proceeded either via hydrothermal or solvothermal techniques. However, these methods present some challenges which must be resolved before industrial application is feasible, for instance long synthesis times, the high cost of solvents, and potential issues with scale up [22]. In the following sections, we will discuss new synthesis techniques for the creation of MOFs which address these challenges.

### 2.1. Microwave synthesis

Microwaves, discovered in 1946, are high frequency, alternating current electromagnetic waves with wavelengths ranging from 1 mm to 1 m from crest to crest. It has been shown that microwave-assisted synthesis can greatly reduce the reaction time for MOF synthesis [23]. This reduction in reaction time is believed to be due to the solvent-superheating effect. This is characterized by a change in the boiling point and heating rates of the solvent, caused by a decrease in the formation of a boiling nuclei [24]. The large heat generation caused by the microwave interaction with the solvent then provides energy to speed up the synthesis reaction at sites where the formation of boiling nuclei has been reduced. Because of this reduction in reaction time, microwave assisted synthesis has become an attractive alternative for the synthesis of MOFs.

There are two main mechanisms by which heat is generated due to the microwave interaction, dipole polarization and ionic conduction [25]. The dipole moments within the solvent molecule tend to align with the microwaves as they enter, and as the waves propagate the molecules must rotate in order for the dipoles moments to stay aligned. This causes friction and dielectric losses, quickly generating heat that then provides energy to speed up the synthesis reaction. Ionic conduction makes this energy transfer process more efficient, as even a small amount of ion within the solvent used for microwave synthesis will increase the rate of heat transfer. This is due to the ion moving along the path of the applied microwave, increasing the rate of collision within the solvent. This excess heat generated leads to an increase in the rate of reaction, speeding up the synthesis.

When microwave synthesis is applied to generate MOFs, it could potentially provide control over the resulting crystal size and pore distribution along with high yield in short times. In 2006, Ni and Masel formed IRMOF 1 (also known as MOF-5), IRMOF 2, and IRMOF 3 using microwave-assisted synthesis, originally synthesized by Eddaoudi et al. via conventional synthesis methods [26]. The microwave assisted method provided greatly decreased reaction times, and led to the formation of smaller particles with little size variation throughout the sample [27].

According to experiments conducted by Choi et al., a higher quality MOF-5 can be synthesized in a much shorter time via microwave assisted synthesis. The synthesis was performed by mixing 2.93 g of zinc nitrate hexahydrate (Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, SIGMA), 0.55 g of terephthalic acid (H<sub>2</sub>BDC, SIGMA) and 50 mL of 1-methyl-2-pyrrolidinone (NMP, SIGMA) in a Teflon pressure vessel, then heating in a commercial microwave system (Milestone Microwave Labstation, ETHOS SEL) for 30 min [28]. The produced MOF-5 showed similar capacities for CO<sub>2</sub> capture with those produced using the standard reflux technique in a much shorter time, with both achieving CO<sub>2</sub> capacities above 800 mg/g, with standard synthesis providing slightly higher adsorption capacity and surface area. Lu et al. performed this synthesis as well, and showed that microwave assisted M-MOF-5 had a higher adsorption capacity than MOF-5 produced using standard techniques, although they were not able to achieve the very high Langmuir surface areas and adsorption capacities of Choi et al. [28,29]. Currently one of the best MOF adsorbents, M/DOBDC series with Ni and Mg metal sites, have

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