

Gas Storage and Separation in Metal Organic Frameworks

Hind A. Satar¹, Dina S. Ahmed^{2*}, Ahmed A. Ahmed¹, Omar Al-Khazrajy³, EmadYousif¹

¹Department of Chemistry, College of Science, Al-Nahrain University, Baghdad, Iraq

²Department of Medical Instrumentation Engineering, Al-Mansour University College, Baghdad, Iraq

³Department of Chemistry, College of Education for Pure Science (Ibn Al-Haitham), University of Baghdad, Baghdad, Iraq

*Corresponding Author: Dina S. Ahmed, Department of Medical Instrumentation Engineering, Al-Mansour University College, Baghdad, Iraq, E-mail: dinasaadi86@gmail.com

ABSTRACT

Highly porous materials as storage media, and porous metal–organic frameworks (MOFs) which have exceptionally high surface areas as well as chemically-tunable structures are playing an unusual role in this respect. In this article we provide an overview of the current status of clean energy applications of porous MOFs, including hydrogen storage, methane storage and carbon dioxide capture.

Keywords: Organophosphate esters; Carbon dioxide Storage; Metal Organic Frameworks; Gas Storage; Adsorption

INTRODUCTION

In the last few decades, the demand for energy has dramatically increased as the population expands worldwide and the need for efficient energy storages is imperative to face the forthcoming energy crisis [1]. The terms of gas storage and separation are closely related to clean energy and environmental protection in the modern society [1]. Therefore, the development of renewable, safe, clean, and sustainable energy storage and conversion technologies has thus become a research topic of interest. Even though porous materials (e.g. zeolites, activated charcoals and porous glass) are being widely used in many applications, the field of porous materials showed more attraction to energy researchers.

One of the well study materials in the fields of energy storage is metal-organic frameworks (MOFs) [1]. The structure of MOFs, also known as porous coordination polymers, is consists of metal ions and organic ligand (e.g. carboxylates, tetrazolates, sulfonates) connected via coordination bonds into a three-dimensional structure [2]. This bonding offers both organic and inorganic readily active sites in their core [3]. MOFs showed high porosity and thermal stability [4] and have been used in a wide range of applications including catalysis [5] magnetism [6] luminescence [7], and particularly in gas storage [8] and separation [9].

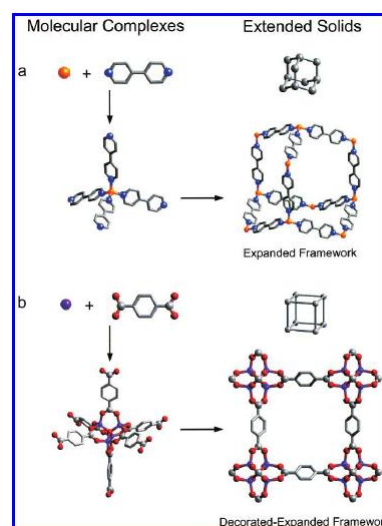


Figure 1. Assembly of metal-organic frameworks (MOFs) by the copolymerization of metal ions with organic linkers

POROSITY OF MOFS

Porosity of MOFs comes from coordinating linkers and space-inefficient packing of the polymer chains [10]. For example, spirocyclic and tetrahedral compounds have been successful used in the preparation of soluble and insoluble microporous polymers [11, 12], which can be used to introduce a wide range of chemical functionalities into the pores [13]. Furthermore, the embedding of transition metal sites into MOPs could open up second-generation porous materials with useful combined chemical and physical properties [13] and offers potential as

heterogeneous catalysts for various organic reactions such as general hydrogenations [14], oxidation of thiols [15], Suzuki Miyaura couplings [16] and so forth [17]. The introduction of metal catalytic moieties into functional MOPs has at least two advantages: i) the homogeneous distribution of active metal nanoparticles (NPs) is enabled by the strong interaction with the functional porous supports, which has been believed to give effective catalytic activity and selectivity [18]; ii) the metal leaching could be greatly suppressed in the process of catalyst separation for recycling [19]. Therefore it is highly desirable to investigate methods to incorporate a variety of functionalities into MOPs.

MOFs AS GAS STORAGE AND SEPARATION

In this energy and environmental scenario, the selective capture of CO₂ from flue gases or during the purification of natural gas, for example CO₂/N₂ (post combustion), CO₂/H₂ (pre-combustion), CO₂/O₂ (air separation), and CO₂/CH₄ (natural gas purification), poses an exigent challenge. Literature reports indicate that the principle of linker pre-functionalization can be well-exploited to develop multifunctional MOFs [20]. In recent times, quite a few coherent design-principle-based strategies have been developed in this regime [21]. An amine (-NH₂) decorated/tethered MOF could display easy-on/easy-off reversible CO₂ uptake phenomenon ideally amalgamated with selectivity adsorption attribute.[22] Amine-rich nano-space has been proficiently harnessed in quite a few MOFs culminating in the CO₂-selective interplay of the framework voids, and consequently letting them emerge as one of the cornerstone materials' class aimed at environmental standpoint of manoeuvring energy-efficient separations [23]. A large number of MOF materials with tremendous structures and specific applications have been constructed through the judicious combination of metal centers and organic linkers. Moreover, various functional groups can be readily incorporated into MOFs via either ligand design or post-synthetic modifications [24], which afford a unique advantage over other traditional porous materials.

MOFs AS HYDROGEN STORAGE

From 2003, when the MOFs reported as hydrogen adsorbent, over 200 MOFs have been studied for their potential ability as hydrogen gas storages [25]. The physicochemical properties of those MOFs have been found to

enhance hydrogen storage capacity in comparison to other porous materials [26]. The main aim of most of those studies is to explore MOFs that have high hydrogen uptake at low temperature and atmospheric pressure (77 K and 1 atm), and these studies can be very useful and instructive at this early stage of exploration for hydrogen storage materials [27].

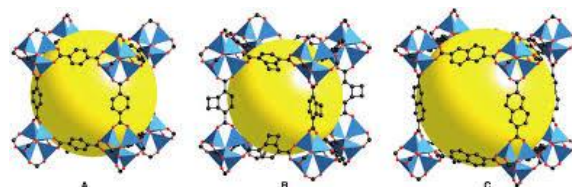


Figure 2. Single-crystal x-ray structures of MOF

MOFs AS CARBON DIOXIDE STORAGE

The concern of worldwide warming has drawn unexampled public attention to the problem of dioxide emission. Greenhouse gas, generated principally through combustion of fuel, accumulates at an alarming rate thanks to the speedy enlargement of the energy consumption worldwide. To stabilize dioxide levels within the atmosphere, it's imperative to develop viable greenhouse gas capture and sequestration technologies. Current technologies square measure dominated by amine-based scrubbing systems, that square measure pricey and inefficient [28]. Surface assimilation of dioxide victimisation extremely porous solids has been of accelerating interest for greenhouse gas capture applications,[29] and porous MOFs are positioned at the forefront thanks to their high surface areas along side functionalizable pore walls [30]. to boost dioxide uptake in porous MOFs, the incorporation of pendant alkyl group alkane functionalities inside the pores has recently been pursued either by the direct use of Associate in Nursing alkane primarily based bridging matter,[31] or via post artificial approaches [32].

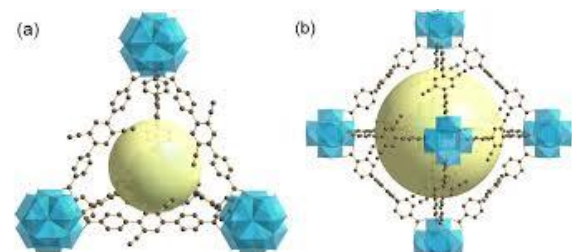


Figure 3. Crystalline structure, the cavities are highlighted with yellow spheres

MOFs AS METHANE STORAGE

Similarly as with hydrogen, methane is likewise viewed as a perfect vitality gas. Contrasted with

oil, it can give considerably more vitality in view of its higher hydrogen-to-carbon proportion, and has much lower carbon emanation. What's more, stores of methane-containing gaseous petrol are more boundless internationally than those of oil, and its refinement (filtration) to a vitality fuel is a lot more straightforward than that of rough oil to gas or diesel powers. Methane is additionally created by decay of natural waste and by microscopic organisms in the guts of ruminants and termites. As far as close term down to earth use and advancements vital for commercialization, methane seems, by all accounts, to be an all the more encouraging option for portable applications [33]. The primary detailed estimation of methane take-up by a permeable MOF could go back to as ahead of schedule as 1997 revealed by Kitagawa and collaborators however with extremely restricted methane Uptake [34]. Be that as it may, the field of methane stockpiling on MOFs has not created as fast as the hydrogen-stockpiling field, and concentrates on methane stockpiling in permeable MOFs are far less various than hydrogen [33].

CONCLUSION

Porous MOFs will continue to draw interest and inquiry by both academia and industry. They have shown great promise for the adsorptive storage of hydrogen, methane, and carbon dioxide in clean energy applications.

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