Metal Organic Frameworks: Giant Rescuers

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Abstract

MOFs are gigantic molecules consisting of a unique combination of organic as well as inorganic moieties. These complex molecules show the potential for selective gas adsorption, storage and recovery. MOFs can be regarded as an advanced version of zeolites. Here we describe their structure, right from the basics, their synthesis and applications.

Keywords: Metal organic frameworks, gas adsorption, gas storage, Zeolitic imidazolate frameworks.

1. Introduction

Materials which can separate molecular species on the basis of their size are considered as molecular sieves. Zeolites are one such type of molecular sieves which have been used for several years. Zeolites are basically crystalline silicates or alumino silicate frameworks with channels or pores of diameter less than 1.2nm. They consist of only inorganic moieties (tetrahedral species like SiO_4, PO_4, AsO_4, SO_4 with metallic cations having 4, 5 or 6 co ordination states). MOFs can be regarded as an advanced version of zeolites. MOFs are frameworks consisting of both organic and inorganic moieties. They can be considered as extended arrays consisting of isolated metal atoms or clusters. These clusters may be linked by polyfunctional organic ligands (L). MOFs are based on M-L-M connectivity.[1]

Basically, the skeletal structures of both zeolites and MOFs consist of basic units which repeat in a regular manner called secondary building units (SBUs).[2]

It is important to note that the following are not included in metal organic frameworks:
1. supramolecules
2. situations having organic guest within inorganic host
3. organic – inorganic as separate phases[1]

2. Classification of Metal Organic materials:[3]

The figure 1 clearly explains the link between MOFs and other metal organic materials (MOMs).

Many a times, co ordination polymers are mistaken to be the same as MOFs. However, a distinction exists between the two which is clearly explained below.

SBUs of MOFs are polyatomic while those of co ordination polymers are monoatomic. The framework in MOFs is neutral while that in co ordianation polymers may be charged. The pores in MOFs can be empty while those in co ordination polymers must contain counter ions. The free bond valency of MOFs is ½ while that of co ordination polymers is zero.[3]

MOFs can further be classified into[4]-

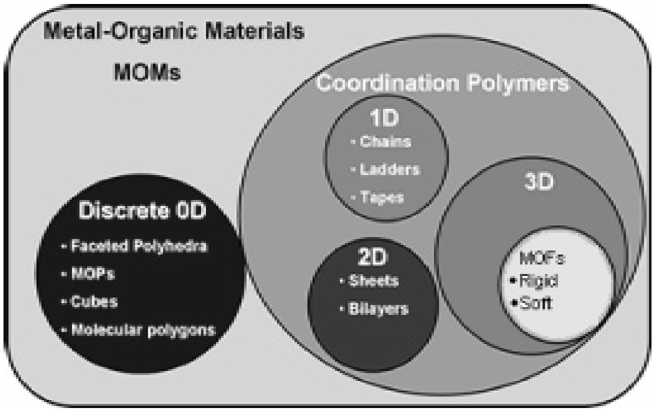

Figure 1. Classification of Metal Organic Materials
Reference : Jian-Rong Li, Ryan J. Kuppler, Hong-Cai Zhou, Selective Gas adsorption and Separation In Metal Organic Frameworks, Chemical Society Reviews, 38, 2009, 1477-1504.

i) IRMOFs (Isoreticular metal organic frameworks)
ii) MMOFs (Micro porous metal organic frameworks)
iii) PCPMOFs (porous co ordination polymers)
iv) PCNs (porous coordination networks)

Even around 1970's, some 1D co ordination polymers and zeolitic materials were known. Zeolitic materials were classified by Pauling around 70 years ago depending on their dimensionality.

A number of 0D, 1D, 2D as well as 3D inorganic framework structures were known. However structures based on solely organic moieties were less diverse. They were mainly 0D. A few polymers and proteins of 1D class were known. 2D and 3D frameworks were not well known except in case of few cross linked polymers and covalent organic frameworks containing borates.

In 1990's people thought of combining organic and inorganic moieties. It was felt that some rigid, polyfunctional organic molecules could serve as bridges between metal cations or clusters to form extended arrays. 1D MOFs are basically chain based. They have low surface area and reduced microporous volumes.[1,5]

There are some exceptions to this classification. Cobalt Diphosphonate is 1D with respect to M-L-M connectivity and 2D with respect to inorganic connectivity. Therefore it is 3D overall. Various possible dimensionalities of metal organic materials are shown in the table below. Materials with higher dimensionality are rare. Attempts are being made to effectively synthesize the MOMs of higher dimensionality. Table 1.

3. Structure of MOFs, Building up from the Basics

A new emerging class of MOFs is that of ZIFs. These molecules show great potential structural features and possible diversification and for use in a variety of applications.

	0	1	2	3
0	Molecular Complexes I^0O^0	Hybrid Inorg. Chains I^1O^0	Hybrid Inorg. Layers I^2O^0	3-Inorg Hybrids I^3O^0
1	Chain Coordination Polymers I^0O^1	Mixed inorg-org Layers I^1O^1	Mixed inorg-org 3-D framework I^2O^1	-
2	Layered Coordination Polymers I^0O^2	Mixed inorg-org 3-D framework I^1O^2	-	-
3	3-D Coordination Polymers I^0O^3	-	-	-

Table 1 : Dimensionality of MOMs

Reference : Anthony K. Cheetham, C. N. R. Rao, Russell K. Feller, Structural Duversity and Chemical Trends in Hybrid inorganic-organic framework materials, Chemical Communication, 45, 2006, 4780-4795.

Structurally ZIFs are extremely similar to zeolites and hence the name.

An analogy between ZIFs and zeolites shows that tetrahedral linkers like Si, Al, P in zeolites are replaced by transition metal atoms such as Zn, Co, in ZIFs. Also the bridging oxides in zeolites are replaced by Imidazolates (IM). Thus, zeolites show M-O-M type linkage while ZIFs show M-IM-M linkages. Thus bond angle M-X-M (X=IM, O) is 145 degrees.[6]

3.1. Formation of ZIFs[6]

The organic moieties in ZIFs are basically IM structures. There are nine such structures (IM, bIM, eIM, nIM)

The inorganic moieties consists of tetrahedrally arranged Zn and Co complexes. e.g. ZnN_4, CoN_4
IM and these inorganic complexes when arranged in a certain form give rise to a number of basic structures called 'poz' structures. Figure 2.

These poz structures are the building blocks for the general structure of ZIFs. Slight variation in these structures with regards to some atoms and linkages give ZIF structure.

Eg: IM + metal - → poz structures (a,b,c,d) -→ general structures (sod)-→ZIFs

3.2 Details about the Organic Linkers used in MOFs[1,4]

The linkers used to bridge two metal ions or clusters are mainly organic moieties. These linkers contain Oxygen or Nitrogen donors.

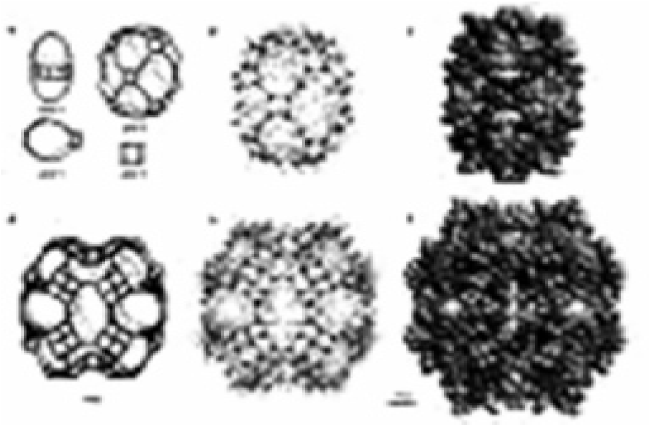

Figure 2 Poz Structures and General Structures of MOFs

Reference : Rahul Banerjee, Anh Phan, Bo Wang, Carolyn Knobler, Hiroyasu Furukawa, Michael O'Keeffe, Omar M. Yaghi, High Throughput Synthesis of Zeolitic Imidazolate Frameworks and Applications of CO2 Capture, Science, 319, 15 February 2008, 939.

Some of the donors containing Oxygen are mono or polycarboxylates, mono or polyphosphonates, rarely sulphates are also used. These can be used in combination also.

Some of the linkages through nitrogen include polyazahetero aromatic compounds such as cyanides, pyridines, imidazolates, pyrazoles, triazoles and tetrazoles in their anionic forms. These are attractive ligands for the design of MOFs because of their ability to bridge multiple metal sites, a superexchange capacity reflected in their magnetic properties and the ease with which they can be derivatized to provide bridging ligands with additional functionality.

4. Nomenclature[4]

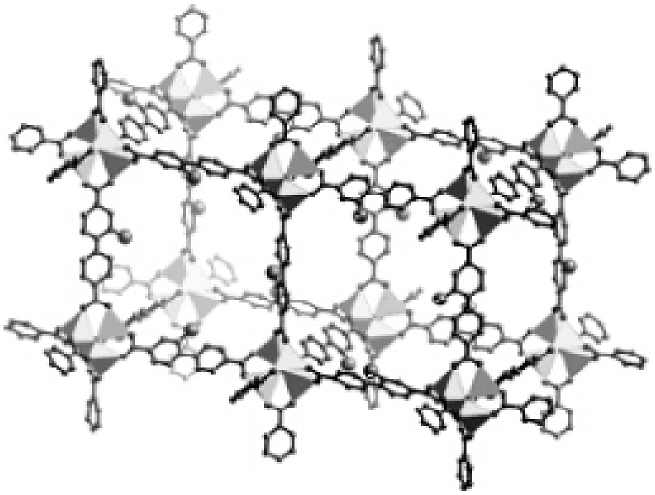

Figure 3 : MOF: SBUs and Organic Linkers

Different poz structures are named using single small letters of the English alphabet (a,b,c,d) The general structures of ZIFs which are formed by a combination of different poz structures are represented by small letters, each name consists of 3 alphabets. (Letters are always in BOLD). Similarly the general structure of zeolites are represented by capital letters, each name consisting of 3 alphabets. The three letters generally indicate the geographical origin of the product[3]

5. Synthesis of MOFs[4]

MOFs are usually synthesized at low temperatures (<250°C). When the synthesis is to be done below 100°C, certain classical methods are used whereas if it is to be carried out above 100°C then solvothermal methods need to be used. Primarily, water is used as the solvent. Other solvents such as alcohol, dialkyl formamide, pyridine and so on may also be used as per the requirements. At times, the addition of various amines favours the reaction.

A few methods of synthesis are as follows-

1) Classical and Solvothermal methods[7] - Solution of metal salts are reacted with organic ingredients which are primarily different acids, in polar organic solvents. The metal organic frameworks are formed within few hours by self assembly, on proper agitation. These may be formed right from room temperatures upto temperatures of about 200°C.
2) Hydrothermal synthesis[4] - Hydrothermal process is a method of synthesis of single crystals which depends on solubility of minerals in hot water under high pressure. This process is carried out in an autoclave into which nutrient is supplied along with water. A temperature gradient is maintained at the ends of the chamber so that the hotter end dissolves the nutrient and the cooler causes seeds to grow additionally. A mixture of non miscible solvents is used in this method. The product is formed at the interphase of the biphasic mixture.
3) Electrochemical Route[7] - In this method, the metal which needs to be incorporated in the MOF is used as an electrode. The linker is dissolved in the electrolyte. Electrolyisis occurs and the product precipitates out. Further, filtration is done to separate the product from the electrolyte and the solid product thus obtained is dried. Finally processing and shaping is done.
4) Microwave Synthesis - This method is used to obtain dense solids and inorganic porous compounds. The main advantages of this method are that it requires less time, narrow particle distribution and pure, crystalline products are obtained. It is easy to control the product morphology and an efficient evaluation of the process can be undertaken.
5) High Throughput synthesis - After synthesis, complete removal of the template solvent from the voids and pores is essential for obtaining a solid with pores that are accessible for further adsorption. Thus proper activation is essential as the surface area, accessibility of pores and pore volume depends on it and these influence adsorption and catalytic properties.

For example, activation conditions influence adsorption of CO_2 on MIL-101 (a MOF). This happens as the content of terephthalic impurities, strength of interactions at loading and the CO_2 capacity vary depending on the activation conditions.[8,9]

Large scale production of MOFs may turn out to be more efficient than zeolite synthesis.[7,10]

5.1. Parameters which Influence the Final Structure of the Product

1) Effect of pH
2) Effect of Solvent
3) Effect of Reaction Temperature
4) Concentration of metal salts in the solvent
5) Nature of the starting metallic salt.
6) Counter ion of the metal salts.

5.2 Difficulties arising during synthesis of MOFs [11]

1) As nature dislikes vacuum, occupation of counter anions in the channels.
2) Need to readily form an interpenetrating network
3) Channel network may be disrupted upon removal of guest molecules.

6. Activation of MOFs

After the synthesis, complete removal of template or solvent molecules from voids and channels should be done to obtain a solid with activated pores. Proper activation is essential as surface area, accessibility of pores and the pore volume, which will influence adsorption and catalytic properties, are dependent upon it. Hydrogen bonded frameworks of molecules remain intact even after the loss of guest molecules.[12] High temperature is required in order to evacuate metal bound solvent molecules. This can cause loss of crystallanity and long range ordering. If such change in crystallanity occurs, it becomes difficult to study the metal- hydrogen bond. Cyano bridged frameworks are more stable, show better crystallanity and can be studied more easily.[5]

7. Salient feature of MOFs: Breathing[13]

The phenomenon in which MOFs are able to respond to external stimuli such as changes in temperature, pressure, guest molecules and so on is called breathing. Usually the inorganic moieties help to give rigidity while the organic parts are associated with flexibility. The amounts of each of these components will influence the amount of breathing.[14] This phenomenon is associated with a structural transition between two states, separated by energy barriers higher than thermal vibrational energy. The transformation is reversible. Contraction or expansion of about 25 to 230% in cell volume is possible.

E.g. MOF 5 can undergo contraction or expansion of about 0.7-1.5% in cell volume depending upon the guests such as hexane or ethanol.

These structural transitions are fast and typically require less than 100 picoseconds.

In 1 D class of MOFs, voids between the chains are occupied by small molecules and can exhibit ion exchange. In 2 D class, stacking of layers is influenced by guests. In 3D structures, interlayer elongation and shortening is realized. The expanding and shrinking frameworks act as sponges.

Reasons for the phenomenon of Breathing in MOFs[4]

1) Host guest interaction (H- bonding, Van der Waal's forces, π-π interaction)
2) Intrinsic flexibility of the framework itself. This is induced by existence of weak points (e.g. Non rigid ligands) within the

skeleton which allows the deformation of the network by certain stimuli.

The extent of the deformation depends on the strength of interaction.

8. Mechanism

8.1 Adsorption Mechanism

Depending upon the channel size, structural similarity and electric charge on ligands, metals and guest molecules, specific molecules occupy voids within the structure and get adsorbed by Van der Waal or H-bonding forces.[15, 16]. With regards to the aperture size, if the aperture is small relative to the molecular size, repulsive forces dominate and hence more energy is required to adsorb the guest molecules.[17]

8.1.1 Adsorption of Hydrogen.[5] H_2 adsorption may be chemisorption or physisorption. Mostly Van der Waal's interactions are found between H_2 and frameworks. But as it has only two electrons, bonds formed are very weak. Very less adsorption is observed at room temperature. Maximum H_2 adsorption is achieved at 77K. Affinity of the interacting materials can be enhanced by minimizing the pore size so as to increase the contact surfaces and hence the van der waal forces with H_2 molecules. Thus, it is advantageous to have large volumes with small voids. Catenation or interpenetration would help to create large number of small voids. However, due to interpenetration the surface area of the material would reduce because of the framework-framework interactions. Since the bonds between H_2 and MOFs are only weak Van der Waal type, the high thermal energy of molecules at high temperatures is sufficient to break these weak bonds.[18] Unsaturated metal centers can also be introduced within MOFs which can take part in binding of H_2 by forming a stronger bond due to dipole-dipole interaction. The variety of metal atoms which can be incorporated is limited by the weight. This is so since greater weight is inappropriate for hydrogen fuel tanks. Hence so far, magnesium and aluminium have been chosen as suitable for introduction into the framework. Active metal sites (unsaturation) are created by removing metal bound volatile species or by incorporation of metal species within the organic linkers or impregnation of MOFs with metal ions. Different metal ions show variable change in adsorption enthalpy. Transition metals have much higher affinity for H_2 than other metals. From the Langmuir Adsorption Isotherms, we can find the optimal adsorption enthalpy for a given temperature.[13, 19.] A certain research showed that in case of imidazolate, adsorption of H_2 occurs in 2 steps. H_2 gets adsorbed at both sides of imidazolate ring and is close to the imidazolate carbon carbon double bond. In next step, H_2 molecules get further adsorbed in the pore channels which are secondary adsorption sites. The following MOFs have been identified as the best for hydrogen storage at 77K [4]

1) MOF-5- 5.1 wt% at saturation,
   SSA (sp surface area)$_{BET}$- 2296m^2/g
   SSA Langmuir- 3840m^2/g
2) MIL-53- 3.8 % and 4.5 % at 15bar and at saturation respectively.
   SSA$_{BET}$-1100m^2/g
   SSA$_{Langmuir}$-1540m^2/g

These MOFs have a good adsorption and storage capacity but the only problem is that they are usable only at low temperatures due to thermal instability.

8.1.2. Adsorption of Carbon dioxide

In 2005, global consumption of petroleum exceeded 83 million barrels resulting in the release of around 11 billion metric tonnes of CO_2 into the atmosphere. Climate change due to rising CO_2 levels is a major problem that mankind is facing today. Thus various methods are being employed in order to sequester the CO_2 from the atmosphere. Attempts to capture and store CO_2 in minerals, oceans, solvents and so on are on. However most of these methods have certain limitations. Separating CO_2 from high volumes of flue gases having low concentration is difficult. High capital is involved in installing such separating systems. A great amount of energy is required to release CO_2 from solvents after the adsorption is done.[20]

MOFs have been found to be advantageous for CO_2 sequestration and storage. CO_2 molecules get coordinated to metal centres of dehydrated solids. The storage is possible due to adsorption of CO_2 molecules onto metal oxides with basic sites, forming carbonate species.[9] Capacity of MIL-100 was found to be 40mmol/g at 5MPa pressure and 303K temperature whereas MIL-100 can store up to 18mmole/g under same conditions as above. MOF-177 which is best up till now for CO_2 storage has capacity of 33.5mmol/g at 4.2 MPa and 298K. Also ZIFs like ZIF-100 and ZIF-69 can store around 30L/L and 82.6L/L of CO_2 at 273K. The CO_2 adsorption is good and it has been said that no CO_2 escapes until you want it to.[21]

8.2. Selectivity in Gas Adsorption

Selective adsorption occurs when different affinities for different substances on the surface of an adsorbent emerge at given conditions.[3] Selective adsorption is possible in MOFs due to following reasons (domains).[16]

1. Pore Apertures make them size and shape selective. Materials with bigger pores provide larger surface area. However selectivity deceases.
2. Internal (Langmuir) Surface area provides a platform for interaction between MOFs and guest molecules.
3. Active Domain (these are the recognition sites which are highly specific for incoming guest molecules with respect to stereo electronic arrangements) give MOFs the ability to differentiate species with similar size and shape on the basis of their charge or electronic arrangement.

MOFs without active domains (e.g. MOF-5, MOF-100) provide passive platform for adsorption. MOFs with active domain (e.g. recent MOFs like MOF-1001, MOF-1002) have open structure which allows substrate to diffuse freely from solution, through pores and finally dock in domains.[16]

Selection of adsorbent is important in purification processes as strong adsorption interactions are necessary in order to obtain a highly pure product.

In order to estimate the pore volume and apparent surface area of the framework, the gas and vapour sorption isotherms for the desolvated sample can be studied using an electromicrogravimetric balance set up.[22] The pore volume can be calculated using the Dubinin-Raduskhvich equation.[15]

8.3. Regeneration of MOFs after adsorption [23]

Regeneration is quite simple. It can be done by reducing pressure so that the guest molecules vaporize and can be removed from structure. Or suitable solvent can also be used to dissolve the guest molecule.

In case of CO_2 adsorption, if CO_2 has formed carbonate species, a small vacuum is unable to remove CO_2 completely. Temperature of 303 K is required for complete extraction.

Experiments were conducted and it was observed that no further changes in adsorption occurred beyond 473 K. it is thus concluded that such kind of regeneration can be done under fairly mild conditions.

Hydrogen may be desorbed from the MOF by increasing temperature.

It has been shown that evacuation of guest molecules, did not affect the framework.[15, 24, 25, 26]

9. Advantages of MOFs over traditional molecular sieves.[4, 9]

1) In MOFs, the solvent itself plays a role of the template during synthesis whereas in case of zeolites, organic and inorganic substances like amines, quaternary ammonium salts need to be added.
2) MOFs have a neutral skeleton, while zeolites have a cationic skeleton which often collapses during the removal of the template due to host-guest interactions.
3) In MOFs, interaction between solvent and MOF is weak and hence the structure can be formed at low temperature. Also the resulting frameworks are intact and have easily accessible porosities.
4) Adsorption properties can be influenced by the existence of hydrophobic and hydrophilic parts both of which exist in the pores due to the presence of both organic and inorganic moieties in the structure.
5) High density of active centres, which are spatially separated from each other and fully exposed, make the MOFs a very good catalyst.
6) A large variety of ions can be incorporated into the structure of MOFs resulting in wide variety of species. On the other hand, zeolites have a select few cations such as Si or Al.
7) Great variation can also be obtained by modification in the organic ligand.
8) Have higher adsorption area, greater adsorption space, show easily reversible adsorption and greater selectivity as compared to zeolites and BPL carbon.
9) Cost of regeneration is not as high as zeolites and activated carbon.
10) MOFs have a higher mechanical strength as compared to zeolites. The low strength of zeolites restricts their usage in certain applications such as drying. The zeolites may be subjected to high pressure as the vapour pressure of water increases as the temperature increases and thus under these conditions, in the presence of water, zeolites reduce to a powder form.[17]

10. Applications of MOFs

1) Catalytic applications[1, 4]

This is an important application of MOFs which has great scope and is in its developmental stages. For use in catalysis, five types of catalyst systems or active sites have been utilized. They are as follows-

i) Homochiral MOFs One of the limitations in the use of zeolites for catalysis is that they fail to impart effective shape selectivity based on molecular handedness as it is extremely difficult to obtain enantiomerically pure zeolites. It is comparatively much easier to make suitable chiral hybrid materials such as MOFs. The mechanism of this kind of catalysis is similar to heterogenous enzymatic catalysis.

E.g. i) Lin and his co workers have synthesized a homochiral porous MOF containing Cd. Its molecular formula is $[Cd_3Cl_6L_3]$ X.Titanium isopropoxide is chemisorbed onto its hydroxyl units, then it catalyses $ZnEt_2$ additions to aromatic aldehydes. This enantiomeric asymmetric heterogeneous catalysis is extremely effective and may even surpass its homogenous counterparts.

ii) Zn based MOF with bdc and lactate ligands shows good size and enantioselective properties when considering capturing of guest molecules. Also good catalytic activity with respect to size and chemoselectivity is seen and good conversion is observed in oxidation of thioethers to sulphoxides.It has been a point of concern however that chiral organics may be affected in hydrothermal reaction conditions. Study is still on to estimate the gravity of this problem.

ii) Metal ions or ligands in metal organic frameworks

This is a popular method of catalysis. Some of the reactions that can be catalyzed by this method are cyanosilation, Diels Alder reaction, hydrogenation, esterification, CO oxidation

E.g. Some phosphonate frameworks are used in this technique.

iii) Coordinately unsaturated metal (CUM) centres in the metal organic porous materials. There is a regular arrangement of metal centres in pore channels which helps in giving shape and size selectivity.

iv) Metal complexes in supramolecular porous frameworks

This can facilitate in heterogeneous catalysis if metal complexes are entrapped in MOFs by supramolecular frameworks through $\pi-\pi$ interactions and H bonding. The entrapment may be done using self assembly. These showed size and shape selective catalytic activity.

E.g. used in the oxidation of phenols with hydrogen peroxide to form dihydroxybenzenes.

v) Highly dispersed metal or metal oxides in the pores. - This is comparatively rare.

E.g. Pd and Pt phosphonates were active catalysts for use in photochemical production of hydrogen. Also used in the production of hydrogen peroxide from hydrogen and oxygen.

3) PCPs can be used to carry out precision polymerization reactions.[27]
   The polymers produced by these reactions possess certain special properties which they acquire as a result of confinement. They have a regular structure, controllable channel sizes and shapes, a designable surface functionality and a flexible framework. Polymerisation can be made to occur within the nanochannels of PCPs. Some of the properties of these such as molecular weight, stereoregularity, reactive sites, composition can be controlled. Recent studies also indicate that even inorganic polymers or metal nanoparticles can be formed within PCPs.[27]

4) Gas purification.[10, 28]
   MOFs with open metal sites are used for gas purification as they can remove electron rich, odour creating molecules like phosphines, amines, alcohol, water, sulphur containing molecules by chemisorption. MOFs with open metal sites chemisorb (>30 KJ/mol) odour generating, electron rich molecules.[14]

5) Gas separation[4,10]
   Gas mixtures having components with concentrations in the same order of magnitude are used for separation. Distillation or pressure or thermal swing adsorption-desorption is used to separate the components of mixture.
   E.g. Separation of Xe-Kr by pressure swings adsorption.
   CO_2 separation is one of the important processes in industry. It is mostly achieved by reversible stoichiometric reaction (chemisorption) with an aqueous amine solution at room temperature. Whereas in MOFs, CO_2 is physisorbed. But in this case energy of adsorption is low therefore high pressure is required for sufficient adsorption.

6) Gas Storage[4,10]
   Guest molecules trapped in MOFs can be retained in the structure for a long time under suitable conditions. Volumetric specific gas storage capacity can be enhanced above known levels due to the absence of dead volume in MOFs. Maximum benefit of increased volume can be obtained when the gas is in its true gaseous phase and not in liquid phase. i.e. MOFs cannot compress a gas to a higher density than its liquid state density. Hydrogen gas is stored as metal hydrides in MOFs. Hydrogen is adsorbed by physisorption and not by redox reaction. Metal-oxygen clusters act as adsorption sites. Hydrogen- MOF interactions being weak, temperature of storage should be very low to prevent the escape of the gas. A MOF –filled gas cylinder can hold up to 35% more natural gas than hollow cylinders used at present.

7) Porous Magnets[4]
   Inorganic porous solids do not seem of much interest for use as magnets as they have very low magnetic ordering temperatures. MOFs however, may find use as magnets. The magnetic ordering temperature of these frameworks may be modified by guest molecules.[1] Different ligands used determine the magnetic properties. For example, ligands with phenyl rings may be used as they have delocalized π electrons which render them the necessary magnetic properties. This kind of a delocalization helps to establish long range interactions even for 0D co ordination polymers. Transition metal containing MOFs usually possess these magnetic properties. In 2 D solids dipolar magnetic interactions also take place. The strength of magnetic interactions depends on the nature of the magnetic carriers i.e. the metal ions and also on the geometry ie. the M-X-M bond angles. (The strength is high if the M-X-M bond angle is about 180° and is low if the angle is around 90°).The critical magnetic temperatures of MOF based magnets do not exceed 10K because the structures are only linked by edges and faces and this is not suitable for high critical temperatures. The critical temperature does not exceed even if the dimensionality is increased[2]. Thus MOFs can show magnetic transition temperatures above that of liquid nitrogen and good magnetic hardness, exceeding all know oxide magnets.[29]

8) Optics[1, 4, 30]

MOFs can be used as luminescent materials. Hence they can be used as phosphores or fluorescent probes. There may be five different ways in which MOFs generate luminescence.

1. Linkers may have luminescent groups such as conjugated organic compounds.
2. Transition metal ions in the framework may be quenchers. However some like lanthanoid ions show weak luminescence. An antenna effect resulting in increased luminiscence may occur if these ions are close to some organic flourophores
3. Adsorbed lumophores - molecules which occupy the voids may be luminescent.
4. Exciplex formation – π-π interaction between two linkers or between a linker and a guest molecule results in the formation of an excited complex which is luminescent.
5. Lumophores bound to MOF surface.
   Both metals and linkers can be used to create luminescence and also they can interact via antenna effects thereby leading to an increase in quantum efficiency of otherwise weakly emitting lanthanide ions.[31]

9) Formation of monodisperse nanomaterials

Nanodispersed species fill the available space in the pores depending upon their dimensions and the pore size. Large species naturally occupy the larger pores, leaving the smaller species with different properties to occupy these smaller pores. Such selective placement of guest molecules may lead to the formation of monodisperse nanomaterials which are multifunctional. They are made by placing a powdered sample of the MOF in an aqueous solution of the salt whose ions are to be incorporated for a certain amount of time. Thus besides simply gas adsorption for the removal or storage of gases, incorporation in a monodisperse mode may lead to useful materials with varied physical properties. Such cages may also find applications in drug delivery systems.

10) Conduction[4]

Conductivity is associated with mobility of species or delocalization of electrons. Conductivity in MOFs has not been considerable due to the following two reasons. 1) for electronic delocalization, mixed valence species are required which are not usually found in MOFs.

2) Most MOFs are co ordination polymers which are 0D in the inorganic part, but atleast 1 D is essential for conduction. MOFs can be made to conduct by introducing lithium in the frameworks electrochemically.

If the size of channels and cavities increases, porous structures which can hold the medium to large molecules can be obtained. Thus some organic and also biomolecules may be incorporated into the structure. Hence, these MOFs may see important applications in the areas of green chemistry such as use as nano-reactors for catalysis or certain reactions. In the field of materials science also these MOFs find applications as biocomposite materials for sensors and polar inclusion compounds.[31]

11. Drawbacks of MOFs

1) They have a low thermal stability upto 350-400°C, rarely more than 500°C.
2) Some MOFs such as MOF 171 decompose very easily upon moisture adsorption.

Prediction of crystal structures is a big challenge but it is not a prerequisite for developing new structures.[31]

12. Infinite Co ordination Polymers(ICPs) : Improvement over MOFs[32]

Infinite coordination polymers- These are made up of repeating ligands interconnected by metallic nodes. They have better structural talorability with respect to size and morphology dependent properties. These substances can be depolymerised under milder conditions and at a much faster rate than MOFs. ICPs at times are catagorised under MOFs. However, not all ICPs are crystalline unlike MOFs. They may be amorphous or semi-crystalline as well. Hence they are lately separated into a new class of materials as ICPs.

These are used in certain applications where MOFs are not suitable such as probes in imaging applications, drug delivery materials and other bio- medical applications.

The MOFs such as the ZIFs are relatively easy to make from cheap starting materials, so they should not be too expensive to use for industrial carbon capture. They may even be used to purify gas.[23] MIL-100 is already being used commercially for gas adsorption.[18] MOFs have several far fetching applications, few of which have already been discussed in detail. They may soon find applications in fuelling of automobiles using natural gas. These versatile molecules feature in a wide variety of applications right from catalysis to gas storage, imaging to drug delivery. These may soon be useful in complex functions such as modification of the carbon dioxide that they adsorb. This can be done by modifying the existing MOFs to produce low co ordinate metals which will be able to activate the CO_2 and convert it into a valuable fuel.[33]

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