CO₂ capture by metal organic frameworks

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Abstract

The Kyoto Protocol confirmed the existence of global warming and the anthropogenic CO₂ emission caused it. The increased CO₂ levels in the atmosphere have been creating number of problems; few of them are increase in average temperatures, temperature extremes, extreme weather events, ice melt, sea levels and ocean acidification. The CO₂ alone is not present in the atmosphere. The CO₂ capture is sensitive to the water vapour & another difficulty is the capture capacity. The current technologies for CO₂ capture are amine solvents solvents technology, technology, ionic carbonaceous adsorbents, and zeolite. The materials in the current use require the larger regeneration energies, less capturing capacity & selectivity. The cost is dependent of regeneration energy, capturing capacity & selectivity. The metal organic frameworks are very useful for gas capture. The MOF technology is promising for CO₂ capture. The MOF are reviewed in this paper on the basis of metals, ligands, pore dimension, functionalization of MOF, synthesis of MOF, thermal stability, CO2 capture on MOF, pre-synthetic modifications & post synthetic modifications.

Keywords: Metal organic framework, carbon dioxide, adsorption, CO₂ adsorption on MOF, Synthesis of MOF

1. Introduction:

United Nations Climate Change Conference 2015 Paris; set the goal of limiting global temperature increase well below 2°C. The Kyoto Protocol confirmed that the existence of global warming and the anthropogenic CO_2 emission caused it. There are number of sources of CO_2 emission^{1, 2}. The combustion of fossil fuel is related with the common man. While coal-fired power plants which are major sources of CO_2 emission is related with governmental level & no country is trying to stop the deforestation ^{3, 4}. The firepower used in the battlefield worldwide and the world wars have also increased the CO₂ emission.

Along with this the nature also is contributing by the means of volcanic emission so the emission of CO_2 is on the larger extent while the removal is on the photosynthesis & CO₂ dissolved in the sea water basis. The increased CO₂ levels in the atmosphere have been creating number of problems; few of them are increase in average temperatures, temperature extremes, extreme weather events, ice melt, sea levels and ocean acidification, social effects-loss of food security may, create havoc in international food markets and could spark food riots, political instability and civil unrest worldwide etc. In short the research topic has the interdisciplinary relevance with the number of domains like environment. climatology, biology, agriculture, oceanography, health science, economics, etc.

Challenges for CO₂ capture

There is need to treat CO₂ to reduce its level. perfect technology has not been The developed due to the number of difficulties. The first is the CO₂ alone is not present in the atmosphere. The atmosphere along with the CO₂ also contains different gases like N₂, CH₄, CO, SOx, NOx etc. The selectivity is very important in the capture⁵⁻⁸. The water vapours are present on the larger extent in the atmosphere. The CO₂ capture is sensitive to the water vapour. After selectivity another difficulty is the *capture capacity*. The different methods and materials have different capacities but the required capacity has not been satisfied yet. Another difficulty is the release of CO₂ from the captured material i.e. regeneration. The regeneration is possible by different ways e.g. temperature, pressure, vacuum etc. The materials in the current use require the larger regeneration energies. If the regeneration energies increases then the methods used for regeneration will cause the production of more CO₂. The cost is another difficulty in the CO₂ capture. The cost is dependent of regeneration energy, capturing capacity & selectivity. The cost also depends upon the method used.



Figure 1: Chemical Absorption

2. Chemical Absorption

2.1. Amine Solvents Technology

The amine solvents are in the use for the CO_2 capture ^{9, 10}. The primary, secondary and tertiary amines are useful. e. g. monoethanolamine (MEA), Nmethyldiethanolamine (MDEA), etc. The primary and secondary amines reacts with the CO_2 and forms the carbamate e.g. monoethanolamine (MEA) but tertiary amines have lower reactivity towards CO_2 and forms hydrogen carbonate e.g. Nmethyldiethanolamine(MDEA).

Alkanolamines have wide use for the CO₂ capture¹¹. Alkanolamines are the amines with one hydroxyl group. e.g. Monoethanolamine (MEA), Diethanolamine (DEA), N-methyldiethanolamine(MDEA).

The reactivity in the alkanolamines is primary > secondary > tertiary while the loading capacity is in the reverse order. The primary and secondary amine reacts with CO_2 and forms carbamate via zwitter ion while the ternary amines form bicarbonate.

The speciality amines i. e sterically hindered amines are also useful for the capture of CO₂. The CO₂ capture capacity of speciality amine depends on the steric hindrance and the basicity. e. g. AMP (2amino-2-methyl-1-propanol). AMP is the bulkier substituents which forms carbamate with lower stability hence it is a promising absorption solvent. Thus, the carbamate from sterically hindered amines can undergo hydrolysis to form bicarbonate and amine gets free to react with the CO_2 and increases the CO_2 loading capacity.

The limitations of the amine technology are ¹²

1. Solvent degradation by gases like O_{2} , SO_{2} , NO_{2} etc.

2. Higher regeneration energy

3. Heavy equipments

4. Less CO₂ loading capacity

2.2. Ionic Solvents Technology

Ionic liquids (ILs) are the pure salts that have a melting point less than 100 °C. Since an ionic liquid contains cations and anions hence by changing the nature of cations and anions large number of different ILs can be prepared.

The table shows how the different ILs can be prepared by mixing the cations and anions.

The important properties of ILs are very small vapour pressure, non-toxicity, and thermal stability and ability to dissolve gases which makes the ILs as a candidate for the CO₂ capture ¹³. The CO₂ can be captured with the help of the ILs because the ILs containing the amino functional group can react with the CO₂. But the capturing capacity of ILs is very low. The capturing capacity can be slightly increased by silica support method. By this method the CO₂ capture is up to 1.2 mol of CO₂ per mol of IL

Thus the limitations of the ILs are:

- 1. Low capturing capacity
- 2. High cost
- 3. High viscosity



2.3. Carbonaceous Adsorbents

the Carbonaceous Adsorbents Among charcoal, coal and activated carbon can be used for the CO2 capture 14, 15. The carbonaceous materials are advantageous because they inexpensive relative to the adsorbents like zeolite. other The carbonaceous material is also insensitive to moisture. The carbonaceous material has very low cost, plenty of availability. They are more eco-friendly. Along with these benefits the carbonaceous materials have some important limitations. The first is the capacity is very low in comparison with the other technology like MOF. Secondly the selectivity is reduced with the pressure increase. So due to low selectivity and capacity the carbonaceous materials are of less use.

2.4. Zeolite

The amine scrubber and the CCS (Carbon Capture & Storage) are the technology in the current use ¹⁶. The amine scrubber technology is useful in the petroleum sector. For example; the CO₂ from the natural gas is separated by the amine scrubbers. The main disadvantage of this technology is the larger regeneration energy. Due to larger regeneration energy the cost increases very drastically. Another technology CCS is useful for the power plants. thermal The CCS technology involves various processes like compression, transportation and storage. The CCS technology is not growing fast because capturing process takes 2/3rd of the total cost. To overcome, high regeneration energy of amine scrubber; the solid adsorbents like activated carbons, zeolites and MOF have been considered. Zeolites have high capacity for CO₂ capture at low pressure ¹⁷⁻¹⁹. The highly polar surface of zeolite also posses high affinity for H₂O, which severely diminishes CO₂ uptake ²⁰.

Thus zeolites have following limitations: 21-24

1. Zeolites have less selectivity in presence of moisture.

2. They have low capturing capacity.

3. They requires high regeneration temperature (generally >300 °C) and pressure.

4. This increases the cost for the use of zeolite.

To overcome these limitations a new class of materials called Metal Organic Framework or Coordination polymers has been developed.

2.5. Metal Organic Frameworks (MOF) / Coordination polymer

MOFs are a class of nanoporous materials containing periodic networks of metals held together by bridging organic linkers. They are also referred to as coordination polymers in the literature ²⁵.

e.g. M₃(BTC)₂.12H₂O

Where, M= Co, Ni, Zn and BTC = 1, 3, 5-Benzenetricarboxylic Acid ²⁶

Out of three coordination sites of BTC two are polymerised with metal centre and the remaining 3rd site is bonded to water. On heating, the water ligand is removed because it is bonded weakly as compared to metal BTC bonding. On liberation of water, there is creation of void and it yields an open framework in

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which the other molecule may be captured. E.g. The ammonia molecules successfully captured in this void. The molecules without the lone pair are not captured. The larger molecules are also not captured. Thus, the selective inclusion of guest molecule depends upon the size, shape and also on electronic structure.

e.g.	M ₂ (DOBDC)	also	known	as
M-M	OF-74			

IAThere	M =	$M\sigma$	Mп	Fρ	Co	Ni	C_{11}	and Zn
vvnere.	111 -	IVIY,	1V111,	ге,	$C_{U_{i}}$	INI,	Cu,	$unu \Delta n$

DOBDC4 – (2,5-dioxido-1,4benzenedicarboxylate or 2,5dioxidoterephthalate)



Figure 2: 3D topology containing divalent metal (M²⁺) sites

This MOF has a 3D topology containing divalent metal (M²⁺) sites and the organic DOBDC4-(2,5-dioxido-1,4-benzene dicarboxylate or 2,5dioxidoterephthalate) linker. Each M2+ site in the M-MOF-74 1,12 series is hexacoordinate; five coordination sites are occupied by oxygen atoms from DOBDC⁴⁻ ligands, and one site is occupied by the solvent. To activate the material for various purposes, the coordinating solvent can be removed, e.g., by heating in a vacuum, thus leaving the M²⁺ ions coordinated to five oxygen atoms in а square pyramidal The co-ordinatively arrangement. unsaturated metal centres can then, for example, interact with gas molecules using their open sites. There are many other MOFs with open metal sites.

Other examples of MOFs: 27, 28

[Zn₄O(btb)₂] (MOF-177) ,[Zn₄O(bdc)₃] (MOF-5), [Sc2(bdc)₃], [Cu₃(btc)₂], [Cr₃F(H₂O)₂O(btc)]₃ (MIL-100), [Ni₂(pbmp)], [Mg₂(dobdc)], [Al(OH)(bdc)] (MIL-53(Al)), [In(OH)(bdc)].

MOF are generally thermally steady, crystalline, and with high porosities (up to 90% free volume) and furthermore have high surface area.^{29, 30}. These properties make them great gas adsorbents.

By controlling the metal and linker the size and shape of the pores in the MOF can be altered.³¹

Current and Potential Uses of MOFs:

Gas Adsorption and Separation - MOFs are excellent candidates as gas adsorbents due to their high porosity and surface areas, Gas Storage and Delivery, Catalysis, Luminescent MOF, Magnetic MOF ³²⁻³⁸. The various factors in the metal organic frameworks can be described as follows:

2.6. Metals

The metal organic frameworks can be synthesized by using different metals like Al, In, Mg etc. but the transition metals are found very useful for the synthesis of metal organic framework. The number MOF has of been synthesized by using 1st row of transition metals. The different oxidation states of the transition metals are very useful. The d block and f block metals has been useful in the synthesis of MOF. Out of these the first row of transition series and second half of the second row metals are reported in MOF synthesis. The lanthanide series is also reported for the same. Following is the list of the metals reported ³⁹⁻⁵⁰. Sc, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pd, Ag, Cd Hg, La, Pr, Sm, Eu, Gd, Tb, Yb, K, Ca, Rb, Al, In. The variable and high oxidation states of the transition metals are the key factor for their usage in the MOF synthesis.

2.7. Ligands

The different organic molecules can be directly used as ligands or the ligands can be synthesized by using different organic molecules. From the reported MOF ,the ligands generally contains acidic functional group is-COO-.Along with this carboxylate functional group other functional groups like hydroxyl ,amine, ester, halogen, sulphuric acid, phosphoric acid etc has been use.47 In the MOF, ligands are connected to metals and they form the nets.

The guest molecule like e.g. CO_2 gets trapped in the cavity of the net. For the formation of the net it is necessary to select the ligand in such a way that it can connect minimum by two ends with the metals. In the earlier reported MOF, the ligands were containing two carboxylic acid functional groups pointed at the two ends to approach to the metal. For this type of ligands various carboxylic derivates had been used ⁵¹⁻⁵⁶.

e.g. Benzene dicarboxylic acid ,benzene tricarboxylic acid, etc.



In the second series of the ligands, derivatives of the aromatic compounds containing Nitrogen in the ring had been used as the ligands.

e.g. 4,4'-Bipyridine , Pyrazine,etc.



In the third series of the ligands, derivatives of the aromatic compounds containing 2 or 3

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Nitrogen in the ring had been used as the ligands.

e.g. Pyridine-3,5-dicarboxylate, 2,4,6-Tris(benzene-4-carboxyla to)-*s*-triazine

e. g. Derivatives of the imidazol , triazol etc



In the forth series of the ligands, derivatives of the above mixtures had been prepared.

Ligand	Structure
bdc=1,4-benzenedicarboxylate	in the second
btb=1,3,5-benzenetribenzoate	
NH ₂ bdc=2-amino-1,4-benzene dicarboxylate	
fma=fumarate	of to
bpdc=biphenyl-4,4'-dicarboxylate	но со
bpy=4,4'-bipyridine	
BPnDC=benzophenone- 4,4'-dicarboxylate	но
ndc=1,4-napthalenedi carboxylate	



btc=1,3,5-benezenetricarboxylate	e for e f f f f f f f f f f f f f f f f f f f
pbmp=N,N'-pipera zinebismethylenephosphonate	
H4dobdc=2,5-dihydroxyterephthalic acid	
p-cdc2_=deprotonated form of 1,12- dihydroxydicarbonyl-1,12-dicarba-closo-dodecaborane	СОСН
	● - (1) ● - C ● - SH
mtb=methanetetrabenzoate	орот Ссн _а
adc=4,4'-azobenzenedicarboxylate	но по
bptc=1,1'-biphenyl-3,3',5,5'-tetracarboxylate	но с с с с с с с с с с с с с с с с с с с
bttb=4,4',4'',4'''-benzene-1,2,4,5-tetrayltetrabenzoate	но страна
bbs= dianion of 4,4'-bibenzoic acid-2,2'-sulfone	

Pore dimension

The selective adsorption property of MOF is mainly due to

1 .Pore dimensions in which smaller molecules are allowed to pass while larger get blocked ⁵⁷.

2. Their interaction with the guest molecule.

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Figure 3: various sizes and shapes

The pore can be of various sizes and shapes 57-60 e.g. their shape might be square channel pore (MOF-2), hexagonally stuffed tube shaped channel (MOF-74), open metal center (MOF-505 Cu3(BTC)2), and amino-and alkvlfunctionalized pores (IRMOFs-3 and - 6), interpenetration (IRMOF-11), and the additional high porosity systems IRMOF-1 and MOF-61-63.

The kinetic diameters of CO₂, N₂, and CH₄ are 3.30, 3.64, and 3.80 Å, respectively. The (MOF-508b, BDC) 1, 4-benzene dicarboxylate, 4,4-Bipy) 4,4-bipyridine) with pore dimensions of 4×4 Å can separate CO₂ from CO₂/N₂ and CO₂/CH₄.

Aluminum naphthalene dicarboxylate $Al(OH)(1,4-NDC) \cdot 2H_2O$ forms two types of channels with square shape crosssection. The small channels are of 3.0 \times 3.0 Å² while the large channel is 7.7×7.7 Å² .The kinetic diameter of CO₂ is 3.3 Å, so the small channel don't allow the CO₂ to trap while large channels due to the favourable interactions of the hydroxyl group of the framework projecting outward to selectively capture CO₂ over N₂. The small channel can capture H₂. This suggests that the pore dimensions are not only the one but also the weak interactions between host and guest are also important in selective adsorption.



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Zn(ADC)(4,4'-Bpe)0.5 \hat{a} xG[ADC = 4,4'azobenzene dicarboxylate, and 4,4'-Bpe = trans-bis-(4-pyridyl) ethylene, G) guest molecules] have triply interpenetrative cubic structure with pore of 3.4 x 3.4 Å, which can adsorb CO₂ in CO₂/CH₄. 61 The pore size and steric factor are not the only factors that control the adsorption. The functional group can play important role in the adsorption. e. g. The CO₂ is more attracted towards the nitrogen by hydrogen bonding or by interaction with the lone pair of electron. Thus, it can be concluded that the pores in the metal organic frameworks are important in adsorption of CO₂. The pore size and shape can be varied by using different ligands. e. g. In the MOF-5, the pore size varied from 3.8 to 28.8 Å, by changing struts biphenyl, tetrahydropyrene, pyrene, and terphenyl.



Figure 4: Functionalization of MOF

organic frameworks The two metal M2(dobpdc) (M =Zn (1), Mg (2);dobpdc4-4,4'-dioxido-3,3'biphenyldicarboxylate) have the same structure in which the Mg MOF contains 18.4-Åthe channels of diameter. Although the direct capture of CO_2 is not possible because of larger size of channels which are unable to capture very smaller CO₂ having kinetic diameter of 3.3 Å 1. M₂(dobdc) (M = Mg, Mn, Fe, Co, Ni, Zn; (dobdc4- = 2,5-dioxido-1,4benzenedicarboxylate) contains high concent- ration of open metal sites; hence the fictionalization of this MOF will be easier. 1For the effective capture of CO₂, the Mg metal organic framework is functionalized with the N,N'-di methylethylenediamine (mmen) to give $Mg_2(dobpdc)$ -(mmen) $1.6(H_2O)0.4$ (mmen-Mg_2(dobpdc)).

In functionalize Mg MOF, one of the nitrogen of N,N'-dimethylethylenediamine is bonded to the Mg metal while the other nitrogen is free to capture the CO₂. At low pressure this MOF capture CO2 from air 2.0 mmol/g (8.1 wt %) at 0.39 mbar and 25 °C and 3.14 mmol/g (12.1 wt %) at 0.15 bar and 40 °C .On regeneration of the functionalized MOF, the purity of the CO2 is 98 %.

90



Figure 5: MOF's with and without amine fictionalization

The three MOF's with and without amine fictionalization are synthesized and studied for the CO₂ capture. USO-1-Al (Al(OH)(1.4-bdc) 0.8DEF) and USO-1-Al-A (amine functionalised)USO-2-Ni (Ni₂(1.4-bdc)2(dabco) 4DMF 0.5H2O) and USO-2-Ni-A (amine functionalised) USO-3-In (In(OH)(1.4-bdc) 1.25DEF) and USO-3-In-A (amine functionalised). Their surface area and pore volume is given in the following table.

USO-2-Ni has a three dimensional pore system while USO-1-Al and USO-3-In have one-dimensional pores. The effective pore sizes are 8 Å, 10 Å, 7 Å for USO-1-Al, USO-2-Ni, USO-3-In respectively. From the adsorption graphs it can be concluded that; in the USO-3-In, the adsorption is less because of the smaller pore size while it is high in USO-2-Ni because of larger pore size and absorption is in between in the USO-1-Al because its pore dimension is in between.

From the powder X-ray diffraction, all the amine functionalized MOFs are isostructural (not considering the amine substituents) to their non-functionalised analogues. The functionalized MOFs have lower specific surface area but higher absorption capacities than the nonfunctionalised MOFs. From, above examples it can be concluded that, the non-functionalised MOFs absorbs less CO₂ or can not absorb but after functionalisation with the suitable agents (e.g ethylene diamine) the absorption capacity increases ⁶⁵⁻⁷⁰. Hence the functionalization of MOF approach is very promising for the CO₂ capture.

Selectivity

The selectivity is very important in the CO_2 capture. The sample may contain different gases out of which along with the CO_2 , CH_4 , N_2 , CO etc. are very important. The sample also contains the water vapours. The selectivity concern is firstly related with the water and then with the other competing gases like CH_4 , N_2 , CO etc ⁷¹⁻⁷³.

The selectivity can be obtained on the basis of the polarity of the components. The polar adsorbents like zeoliltes can selectively adsorb polar molecules like H₂O and CO₂ while the other non-polar molecules like N2, O2, etc can be kept away. But again in the polar molecules to achieve further selectivity is a difficult; polar adsorbent like MOF's e.g. containing active metal centres can absorb polar molecules like H₂O and but out of these two the H2O CO_2 absorbs selectively because water has large permanent dipole 74.

То overcome this problem, the functionalization of MOF's or use of functional group approach is important ⁷⁵. e.g. The functionalization MOF's by ethylene diamine will selectively capture CO2. The functional group selectively captures the required gas molecules and increases the selectivity. The difference in the electronic properties (quadrupolar moment and polarization) can be useful to achieve the selectivity. To separate the CO_2/N_2 , the large quadrapole moment of CO₂ gives the desired selectivity. In another example of the separation of CH_4/N_{2} , the CH_4 adsorbs preferentially over N₂ due to higher polarizability of CO₂. Along with this, in MOF's the pore dimensions can be tuned in to obtain the desired selectivity.

e. g Zn(ADC)(4,4-Bpe)0.5âxG[1; ADC) 4,4-azobenzene dicarboxylate, 4,4-Bpe) trans-bis-(4-pyridyl)ethylene, G) guest molecules have triply interpenetrative cubic structure with pore of 3.4 3.4 Å, which can adsorb CO₂ in CO₂/CH₄. If MOF contains partial positive charges on the frameworks; the CO2 captures preferentially because of specific interactions positively charged of framework with the quadrapolar CO₂ molecule.

Synthesis of MOF

The metal organic frameworks can be synthesized by number of methods like hydrothermal, microwave, conventional heating etc. The same MOF can be synthesized by number of different routes ⁷⁶⁻⁷⁸.

e.g.: (Zn2(NDC)2(DPNI)), where (NDC) = 2,6-naphthalenedi carboxylate and DPNI =

N,*N*'-di-(4-pyridyl)-1,4,5,8-naphth alenetetracarboxydiimide.

The metal (2.0 mmol) and the ligands (4.0 mmol) had been taken in the dimethyl formamide (DMF) solvent. The mixture was then sonicated till get dissolved. After this the mixture is kept in oil bath at an 80°C for two days. The crystalline product (*C*) obtained was filtered with the DMF washings and air drying. In another synthesis method (*M*), the reagent after sonication were taken into the microwave heating at 120°C for 1 hour and set overnight. The same product was obtained.

The microwave yield was higher (27% vs 18%) There is no considerable difference in the adsorption properties of MFOF. But, 1-M'shows slightly lower capacity for CO₂ and CH₄ than 1-C', but it has much higher selectivity of CO2 over CH4, based upon the IAST analysis of the single-component isotherms. e.g. $[Cu_3(BTC)_2(H_2O)x]n$

MOF was prepared by hydrothermal approach. The ligand is dissolved in the ethanol. The metal and ligand (0.466 mol: 0.234 mol) are taken in autoclave after 30 The temperature of the min mixing. autoclave maintained at 383 K (or 423 K). After 18 hours cooled to ambient and crystals were filtered with water wash and allowed to dry 383K, overnight. From the various trials, it is observed that the crystallinity of the hydrothermal product is higher than the atmospheric conditions. This is also true for the yield. At higher temperature and pressure the formation of the 3D framework is promoted. The effect of agitation on the hydrothermal synthesis was studied. The HIGHER crystallinity and regular shape are obtained in the without agitation hydrothermal method. The higher

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temperature favours the reaction and temperature around 150 °C is suitable for the synthesis.

MIL-100 was synthesized by hydrothermal method, the temperature was 220° C for 4 days.MIL-101 was synthesized by hydrothermal method, the temperature was 220° C for 8 hours plus. CPO-27-Ni, was synthesized by hydrothermal method, the temperature was 110° C for 3 days. CPO-27-Mg was synthesized by hydrothermal method, the temperature was 120° C for 1 days.

Zn(ADC)(4,4'-Bpe)0.5axG[ADC = 4,4'azobenzenedicer boxylate, 4,4'-Bpe = trans-(4-pyridyl)ethylene, bis-G guest molecules]was synthesized by hydrothermal method, the temperature was 100 °C for 24 h. USO-1-Al (Al(OH)(1.4bdc) 0.8DEF) USO-1-Al-A and (amine functionalised)

USO-2-Ni (Ni2(1.4bdc)2(dabco) 4DMF 0.5H2O) and USO-2-Ni-A (amine functionalised). USO-3-In (In(OH)(1.4-bdc) 1.25DEF) and USO-3-In-A (amine functionalised) were synthesized by hydrothermal method, the temperature was 110 °C for 24 h. MOF-508a was synthesized by hydrothermal method, the temperature was 90 °C for 24 h. MIL-47 was synthesized by hydrothermal method; the temperature was 200 °C for 96 h.

Thermal stability

The metal organic framework nickel N,N'-piperazinebis

methylenephosphonate, Ni-STA-12 (Ni2L ³8H2O, L) O3PCH2 NC4H8NCH2PO3), is thermally stable up to 377 ^oC.This stability is due to the coordination of the ligand to metal via phosphonate oxygen atoms and а piperazine ring nitrogen atom. In the thermo gravimetric analysis of MOF; $Zn_2(NDC)2(DPNI)$ [NDC) {2,6naphthalenedicarboxylate, DPNI)N,N'di-(4-pyridyl)-1,4,5,8-naphthalene tetracarboxy diimide} shows the ~30% mass loss upto 200C which corresponds to the solvent loss. The MOF is stable ~400 \Box C, after this the decomposition starts. MOF [Cu₃(BTC)₂(H₂O)x]n is it is stable up to a temperature of about 300°C. CoII4(1-OH₂)4(MTB)₂(H₂O)₄]n_13nDMF_11nH2 O (SNU-15), in the TGA, shows weight losses of 11 % and 37.5% at 65 °C and 330 °C respectively. These weight losses are corresponds to the loss of 15H2O and 13DMF molecules. The MOF is stable up 400°C. Zn(ADC)(4,4 to the Bpe)0.5âxG[1;ADC) 4.4'azobenzenedicerboxylate, 4,4'-Bpe) transbis-(4-pyridyl)ethylene, G) guest molecules] in TGS studies shows the loss of solvent molecules to 180 °C and MOF

is stable upto 300 °C. From the above examples; it can be concluded that the MOFs can be thermally stable upto 400 °C.

Pore opening / breathing MOF

The solvent molecules in the MOFs can be removed by temperature or pressure method. In MIL-53, (M(OH)(O2C-C6H4-CO2)(M=Cr3+, Al3+, Fe3+); on application of the heat ,the solvent molecules get removed and the slightly deformed form of the framework is converted into the non deformed form. The change in shape is due to the loss of bonding between the hydrogen atoms of

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the water and the oxygen atoms of the carboxylate group^{79, 80.}



It is observed that the hydrated form is suitable for the capture of CO_2 from methane. Because CO_2 has a significant quadrupole moment that induces specific interactions with the metal organic framework.

Characterisation of MOF

For the characterization of the MOFs, various techniques are very useful. They include XRD, TGS, IR, NMR, etc.⁸¹⁻⁸⁸. The binding between the metal and the ligands is identified from the XRD .The XRD also gives the information about the structure of the MOF. The presence and numbers of solvent molecules are determined from the TGS analysis. The TGS also gives the thermal stability of the MOF. The UV and IR are also useful since they give the information about the functional groups in the MOF.

CO₂ adsorption on MOF

The MOF with different functionalities can be prepared by pre-synthetic synthetic modification or post modification⁸⁹⁻⁹⁶. Two functionalities can be added by pre-synthetic modification while four different functionalities can be added by post synthetic modification. Thus by controlling the ration of the ligands, MOF different with functionalities can be added. The post synthetic method is superior to pre synthetic method. In pre synthetic modification method have some drawbacks. The pore volume, pore environment, surface etc area get decreases which can lower the gas uptake. The lewis basic sites in the MOF decreases the uptake capacities of CO2 E.g. Uio-67, MOF-177, MIL 101 (Cr). The lewis basic sites have different role of surface chemistry in gas adsorption. The N containing compounds are very useful as lewis basic sites.

E.g. $-NH_2$ group or N-containing heterocyclic ligands. The lewis basic site with highly porous structures increases the high uptake capacity for gases like CO_2 . e.g UiO type MOF. The CO_2 adsorption capacity can be affected by textural properties. e.g. MIL-101 The surface area and pore volumes are not the only factors which determine the adsorption.

The sticking factor also plays the important role. E.g. IRMOF-8 Vs IRMOF-8-NO₂. The NO₂ functionalized MOF decreases the surface area and pore volume upto 50 % of IRMOF-8.But the decrease in uptake of gases CO₂,CH₄,H₂ is not great. So sticking factor is important. The factors are based on the molecular weights because of increased vander Waals forces of attraction. The

gas uptake study of the functionalized MOF can be performed by Density Functional Theory (DFT) and Grand Monte Carlo Canonical (GCMC) simulation techniques. The study provides comparative analysis of CO₂ uptake in and functionalized MOF. These technique points out that the polar functional groups can increase the CO₂ uptake. Thus, the ligand fictionalization of MOFs is a powerful route in increases CO₂ uptake have some other advantages such as verbi wide chemical flexibility, groups functional etc. The DFT calculations shows that the polar functional groups such as -NH₂, COOH,-OH have strong interactions with CO₂. The acid functionalization with -COOH increases the heat of adsorption of CO2 in comparison to NH2 and other groups. Then polar functional mainly work groups through the interaction polar lone pair and hydrogen bonding, CO₂ quadrapole interaction etc. The bifunctional orgaic linker e.g. carboxylate and triazolate can be useful to increase the selectivities for CO₂. E.g. 4-(1,2,3-triazol-4yl)-benzonate gives MTAF-1. So, the strategy of introducing a bifunctional linker is also a promising technology.

3. Conclusion

Pre functionalization with nitrogen based ligand is good system for MOF. Post functionalized with various alkyl amine will also increase CO_2 intake. Water stability problem can be overcome by doing post functionalization with amines for basic carboxylate mofs. Bv synthesising mofs in water as a solvent, this problem can be overcome. Many of the researchers have reported hybrid components zeolites, graphene, on polymers and other supports SiO₂, Al₂O₃ etc. but best combination to make better support for CO₂ capturing is amine functionalized with silica and this support is used for MOF. Similarly, other carbonaceous polymers with amine functionalization can be used as a support for MOF. Thus, MOF can be useful for the CO₂ gas capture. But, there is need

To increase the capturing capacity.

To increase the selectivity.

To decrease the regeneration energy.

To decrease the cost.

To develop the technology for different applications where pure gases are required e. g fuel cells.

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No

Ethical issue

No

Conflict of interest

no

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