Chapter 2

Literature Review
The emergence of coordination polymers (CPs) or metal–organic frameworks (MOFs) as functional materials with ultrahigh surface area is one of the most exciting recent growths in solid–state, inorganic and material chemistry. These materials are a class of hybrid materials that exist as infinite crystalline lattice with inorganic vertices and molecular–scale organic connectors. A very useful property such as large surface area and their shape, ultra–low density and the availability of uniformly structured cavities with portals of molecular dimensions characterize these functional coordination polymers. Porous coordination polymer have been classified in three generations [80]. The 1st generation compounds have microporous framework, which substan only with guest molecules and show irreversible framework collapse on removal of guest molecules. The 2nd generation compounds have stable and robust porous framework, which show permanent porosity without any guest molecules in the pores. The 3rd generation compounds have flexible and dynamic frameworks, which respond to external stimuli in the form of guests, temperature, etc. These materials have caught the imagination of chemists for the creation of nanometer–sized spaces with useful practical application such as separation [81, 82] storage [83, 84], proton conduction [85, 86] and so on.
Chapter 2

2.1 Gas Adsorption Studies

Depletion of fossil fuel deposits and the escalating threat of global warming have put clean energy research as a prime research area, which includes the search for clean energy carriers such as hydrogen and methane as well as the reduction of carbon dioxide emissions, on the urgent agenda. Porous metal–organic frameworks (MOFs) which have exceptionally high surface areas as well as chemically–tunable structures are playing an important role for adsorption of gases like H₂, CH₄ and CO₂ and so on.

The first report of gas adsorption in a coordination polymer was in the year 2000 and described the adsorption of CH₄ in [Cu(4,4'–bpy)SiF₆]ₙ, which shows an adsorption capacity comparable to that of zeolites and active carbons [87]. In 2003, Yaghi and his coworkers [88] reported the first example of H₂ storage in a metal–organic framework. They have synthesized MOF–5 of composition Zn₄O(BDC)₃ (BDC = 1,4–benzenedicarboxylate) with a cubic three–dimensional extended porous structure adsorbed hydrogen up to 4.5 wt % (17.2 hydrogen molecules per formula unit) at 78 K (Figure 2.1).
Kaskel and coworkers reported [89] a porous metal–organic framework (DUT–9), which is formed by btb linkers (btb = benzene–1, 3, 5–tribenzoate) and $[\text{Ni}_5(\mu_3-O)_2(O_2C)_6]$ clusters. X–ray crystallographic study reveals that five octahedrally coordinated Ni(II) ions are bridged by two ($\mu_3$–O) atoms and six carboxylate groups (Figure 2.2). These five Ni(II) ions are coplanar. The central metal ion is coordinated by four carboxylate oxygen atoms and the two ($\mu_3$–O) atoms to form a three–dimensional metal–organic framework. According to thermal analysis, DUT–9 is stable at least up to 200 °C. Partial de–solvated framework shows a nitrogen uptake (1406 cm$^3$ g$^{-1}$ in saturation) and a pore volume of up to 2.18 cm$^3$ g$^{-1}$. DUT–9 (super critically dried) shows a maximum hydrogen excess uptake of 4.99 wt% (52 mg g$^{-1}$) at 45 bar. A remarkable increase of the gas uptake up to 5.85 wt% at 40 bar and 77 K could be achieved by additional thermal activation in vacuum after supercritical drying.
A tripodal linker, incorporating a tetrazole moiety at each terminal (BTT) has been used by Long and coworkers [90] to synthesize a Mn(II) containing MOF (Figure 2.3). The structure shows a 8-connected [Mn₄Cl]⁷⁺ node linked by 3-connected BTT³⁻ ligands. The fundamental building unit in the structure is a truncated octahedron sharing square faces to generate a cubic framework structure as in sodalite. In the solvated material, the encapsulated Mn(II) cations are coordinated by DMF and methanol. To generate a porous material, the DMF was exchanged with methanol followed by de-solvation under vacuum to afford a material with partially de-solvated Mn(II) cations and exposed coordination sites. The material has a BET surface area of 2,100 m²g⁻¹ and can absorb 6.9 wt% by of H₂ at 90 bar and at 77 K. Significantly, the excess volumetric adsorption reaches 60 g L⁻¹ of H₂.

Figure 2.2 (a) [Ni₅(µ₃–O)₂(O₂C)₆(OH)₈] clusters in DUT-9, (b) view along [001] and (c) adsorption isotherms.
Figure 2.3 Views of (a), (b) BTT$^{3-}$ linker and its connection to metal ions and (c) the crystal structure of sodalite structure.

Interesting, borderline microporous–ultramicroporous neutral sodalitic frameworks (Figure 2.4) have been synthesized by Navarro and coworkers [91] from Pd(II) and 2-hydroxypyrimidine or 4-hydroxypyrimidine ligands that can readily adsorb H$_2$, N$_2$, CO, and CO$_2$ molecules in their cavities. Isomorphic incorporation of fluorine in the framework causes pore functionalization and influences the gas adsorption properties.

Figure 2.4 Structural motives found in the crystal structures of $\{[\text{Pd}(2\text{-pymo})_2]\cdot2\text{H}_2\text{O}\}_n$ (left) and isotherms at 77 K for the adsorption of H$_2$ and N$_2$. 

47
Férey and coworkers [92] reported breathing phenomenon in an MOF (MIL-53). In its hydrated form, the pores are slightly deformed due to hydrogen-bonding interactions between H₂O molecules and the O atoms of the carboxylate and the hydroxo groups. It is interesting to note that dehydrated MIL-53 showed different adsorption behaviors for CH₄ and CO₂. The adsorption isotherm of CH₄ was typical for a microporous material, whereas the CO₂ isotherm exhibited two steps; above the first step at low pressure the CO₂ adsorption capacity greatly exceeded that of CH₄ (Figure 2.5).

![Figure 2.5](image)

**Figure 2.5** (a) Framework structure of MIL-53 and (b) gas adsorption isotherms of MIL-53 at 304 K

The 3D coordination polymer \{[Cd (bpydb)] · 6H₂O\}ₙ built using a novel rigid ligand 4,4'-(4,4'-bipyridine-2,6-diyl)dibenzoicacid (H₂bpydb) and Cd(NO₃)₂·6H₂O shows hexagonal channels [93] filled with water molecules (Figure 2.6). Integrity of the framework is maintained upon removal of the water
molecules by heating to afford a highly porous framework. Low pressure N$_2$ adsorption and high pressure H$_2$ and CH$_4$ adsorption have been studied.

![Figure 2.6](image)

**Figure 2.6** (a) High pressure H$_2$ adsorption isotherm and (b) excess methane physisorption isotherm

### 2.2. Magnetic Studies

Magnetic materials are extremely important with an ever growing number of uses. In recent years, considerable efforts have been made for the synthesis of new types of magnetic materials and high dimensional metal–organic hybrid materials containing paramagnetic metal ions [94]. Organic ligands bearing carboxylate as bridging ligands have been used several times to synthesize magnetic materials because of their diverse binding capabilities that can efficiently transmit magnetic coupling. Other bridging ligands like imidazole, triazole or tetrazole having strong ability to form polynuclear compounds [95] are also studied. Combination of these donor moieties in a ligand can potentially tune the magnetic exchange and lead to
interesting magnetic properties such as ferromagnetic, antiferromagnetic, spin canting, metamagnetism, single chain magnets and so on [96, 97].

Kepert et al. reported [98] a nanoporous spin crossover coordination polymer based on \textit{trans}-4, 4'-azopyridine (azpy) as a ditopic ligand. The crystal structure of the resulting complex \{[Fe\textsubscript{2}(azpy\textsubscript{4})(NCS\textsubscript{4})\cdot EtOH\textsubscript{n}\} consists of a double interpenetrated 2D grid layers built up by the linkage of Fe(II) ions by azpy ligands with EtOH molecules in the channels (Figure 2.7). After evacuation there are several structural changes which can

![Diagram](image)

**Figure 2.7** Structure of as--synthesized and evacuated complex and the temperature dependent magnetic moment of (○) as--synthesized, (□) evacuated, and (Δ) evacuated structure exposed to 1–propanol

also be macroscopically detected. The as--synthesized sample exhibits a constant effective magnetic moment of 5.3\(\mu_B\) between 300 and 150 K. Below this temperature, the magnetic moment decreases reaching a constant value of 3.65\(\mu_B\) due to a spin–crossover interconversion coming from a fraction of the Fe(II) ions. In contrast, the evacuated sample does not show spin–crossover behavior exhibiting a constant magnetic moment around 5.1\(\mu_B\), corresponding to two
crystallographic high-spin Fe(II) ions. Surprisingly, spin-crossover is recovered after re-admission of guest solvent molecules. Indeed, when an evacuated crystalline sample is immersed in methanol, ethanol or propanol as solvent, the magnetic properties are similar to those observed for the as-synthesized sample.

A Cu(II) coordination polymer \([\text{Cu}_2(\text{cpa})_2]_n\) built with a semi-rigid ditopic ligand, 4-carboxyphenoxacetonic acid (cpaH) exhibits [99] spin-canting behavior imposed by the relative orientation in the space of the magnetic orbitals of neighbouring Cu atoms (Figure 2.8). This spin-canting is very weak and thus no hysteresis or a clear step in the \(M \text{ versus } H\) data is observed down to 2 K.

![Figure 2.8](image-url)

**Figure 2.8** (a) A view of the coordination polymer showing 2D sheet with layer structure and (b) \(\chi T\) vs. \(T\) plot inset: susceptibility plot. In both plots, \(\circ\): susceptibility data at an applied field of 1.0 T, \(\Delta\): susceptibility data at an applied field of 50 G

Dunbar and coworkers reported [100] the 3D coordination polymer \{[\text{Co}_2(\text{H}_{0.67}\text{bdt})_3]\cdot20\text{H}_2\text{O}\}_n\) that shows 1.5 wt% H\(_2\) uptake by weight at 120 kPa
and exhibits single–chain magnetic behavior and reversible changes in magnetic properties upon solvation and de–solvation (Figure 2.9).

Figure 2.9 (a) View of the single chain and 3D polymer linked by Hbdτ ligand, (b) N₂ gas adsorption and (c) slow relaxation of magnetization

A honeycomb–layered Co(II) coordination polymer, [Co(N₂H₄)(N₃)₂]ₙ constructed with [101] hydrazine and azide as mixed ligands, exhibits spin–canted weak ferromagnetism with $T_N$ of 13.5 K (Figure 2.10).

Figure 2.10 View of the 2D honeycomb layer of \{Co(N₂H₄)(N₃)₂\}_n and $\chi_M$ vs $T$ plot
Chapter 2

2.3. Heterogeneous Catalytic Studies

Zeolites are crystalline aluminosilicates constructed from interconnected SiO$_4$ and AlO$_4$ tetrahedra with charge-balancing organic and inorganic cations or protons. The resulting 3D frameworks are microporous with channels/cavities of up to 1.0 nm. These well-defined pore environments provide size- and shape-selectivity during the catalytic processes, and as such, zeolites have been widely used as selective catalysts in the petrochemical industry. Such heterogeneous catalytic reactions improve gasoline quality, and significantly reduce the pollution from combustion engines. It is difficult to obtain zeolites with pore sizes larger than 1 nm, which limits the catalytic applications of zeolites to relatively small organic molecules.

MOFs can be constructed by linking a large variety of organic bridging ligands with many metal centers of diverse oxidation states and coordination geometries. Effectively, MOFs can be synthesized from an infinite number of metal/ligand combinations and thus have far greater diversity in structures, functional groups, and pore sizes and shapes. Greater tunability of porous MOFs should then allow for their use in catalytic reactions that may not be realized with zeolites.

Active catalytic sites in MOFs can be generated in several ways. Firstly, the metal or metal cluster connecting points can be used to catalyze organic
transformations. A metal connecting point with a free coordination site can be used as a Lewis acid catalyst after removal of coordinated solvent molecules from the metal center [102]. Metal cluster connecting points have also been used as active catalytic sites [103]. Secondly, active catalytic sites can also be generated from the functional groups within a MOF scaffold [104, 105]. However, unlike traditional immobilized catalysts, the active catalytic sites generated in this fashion are arranged in a predictable and tunable manner due to the periodically ordered nature of the porous MOFs.

Kim and coworkers reported [106] a homochiral metal–organic framework POST–1, (Figure 2.11) that allows enantioselective inclusion of metal complexes in its pores and catalyses transesterification reaction in an enantioselective manner. The pyridyl groups are exposed towards the center of the channel and facilitate guest binding properties.

![Figure 2.11](image.png)

**Figure 2.11** (a) Hexagonal framework with chiral channels in POST–1 and (b) catalytic activity of POST–1 in transesterification reaction
Tanaka and coworkers used 5,50–dicarboxy–substituted BINOL as a bridging ligand to react with copper nitrate under solvothermal conditions [107]. The resulting 2D infinite framework \{[\text{Cu}_2(L)(\text{H}_2\text{O})_2]·\text{MeOH}·\text{H}_2\text{O}\}_n \text{ contains copper paddle–wheels as SBU}s and are stacked along the b axis with an interlayer Cu–Cu distance of 15.6 Å (Figure 2.12a).

![Figure 2.12(a)](image)

**Figure 2.12(a)** Schematic representation of the synthesis of MOF and (b) asymmetric ring–opening reaction of epoxide with amine catalyzed by the MOFs

The water molecules terminating the copper paddle–wheels were removed upon heating, allowing the exposed copper centers to function as Lewis acid catalytic reaction centers. To test the catalytic activity of framework, the
asymmetric ring-opening of epoxides with amines was examined (Figure 2.12b). Following 48h of reacting at 25°C in toluene, a maximum of 54% yield with 45% enantiomeric excess was obtained. The catalyst was recovered by filtration and recycled without detrimental effect to the reactivity and enantioselectivity. Interestingly, enantioselectivity and reactivity both improved under solvent-free conditions.

Kitagawa and coworkers reported a 3D MOF constructed by tridentate amide linkers and Cd(II) ion [108]. The pyridine groups on the ligand 4-btapa act as binding sites to the octahedral cadmium centers, while the amide groups can provide the functionality for interaction with the incoming substrates (Figure 2.13). Specifically, the –NH moiety of the amide group can act as electron acceptor whereas the –C=O group can act as electron donor to activate organic substrates for subsequent reactions. The amide groups were used as weak bases to catalyze Knoevenagel condensation reactions of benzaldehyde with cyano group–based active methylene compounds. Three cyano compounds with different sizes, malononitrile, ethyl cyanoacetate and cyanoacetic acid tert-butyl ester, showed very different results. The smallest substrate, malononitrile, gave 98% conversion of the addition product, while the largest one, cyano–acetic acid tert–butyl ester, gave no conversion at all (Figure 2.13c). Such a guest selective reaction indicated that the reaction was catalyzed inside the crystal channel instead of the surface.
Chapter 2

Figure 2.13 (a) Representation of ligand, (b) two-fold interpenetrated structure showing 3D channels and (c) Knoevenagel condensation reactions catalyzed by the MOF

A new flexible porous coordination polymer (PCP), \{[Gd_2(L)_3(DMF)_4]·4DMF·3H_2O\}_n, was synthesized under solvothermal condition. The complex \{[Gd_2(L)_3(DMF)_4]·(4DMF)·(3H_2O)\}_n underwent cyanosilylation and Knoevenagel condensation reactions upon exposure to vapors of trimethylsilyl cyanide and malononitrile, respectively (Figure 2.14) [109].
Figure 2.14 Single-crystal to single-crystal observation of the cyanosilylation (a) and Knoevenagel condensation reactions (b)

Same group has also synthesized a coordination polymer, [Cd(L)₂(DMF)₂] at room temperature. This compound catalyzes cyanosilylation reactions of aromatic aldehydes in dichloromethane under mild conditions in heterogeneous fashion (Figure 2.15) [110].

Figure 2.15 (a) A view of [Cd(L)₂(DMF)₂] showing —ABAB— stacking mode of grid layers 2D rhombus grid networks with cell edges and (b) Time conversion plot for the cyanosilylation reactions of different aromatic aldehydes catalyzed by {[Cd(L)₂(DMF)₂]}. 
Chapter 2

A family of isoreticular chiral metal–organic frameworks (CMOFs) of the primitive cubic network topology was constructed from \([\text{Zn}_4(\mu_4-O)(\text{O}_2\text{CR})_6]\) secondary building units and systematically elongated dicarboxylate struts that are derived from chiral Mn–Salen catalytic subunits. These CMOFs 1–5 were synthesized by directly incorporating three different chiral Mn–Salen struts into the frameworks under solvothermal conditions [111]. The open channels and pore size of the CMOFs series vary systematically, owing to the tunable dicarboxylate struts and controllable interpenetration patterns. These frameworks were shown to be highly effective catalysts for asymmetric epoxidation of a variety of unfunctionalized olefins with up to 92% ee (Figure 2.16). The CMOFs catalysts are recyclable and reusable and retain their framework structures after epoxidation reactions. This work highlights the potential of generating highly effective heterogeneous asymmetric catalysts via direct incorporation of well–defined homogeneous catalysts into framework structures of MOFs.

Figure 2.16 View of structure of MOFs that catalyze asymmetric epoxidation reactions of olefins
Recently, Telfer et al. [112] presented a general strategy for incorporating organocatalytic moieties into a metal–organic framework (Figure 2.17). The organocatalytic units are protected by a thermolabile protecting group during MOF synthesis and then unveiled by a simple postsynthetic heating step. The strategy is exemplified using a thermolabile tert–butoxycarbonyl (Boc) protecting group for a proline moiety, the removal of which endows the resulting cubic Zn(II) based MOFs with catalytic activity for asymmetric aldol reactions. The bulky Boc groups also prevent framework interpenetration, producing open MOFs that can admit relatively large substrates.

Figure 2.17 (a) A schematic representation of thermolytic expulsion of the BOC moiety to generate MOFs and (b) Aldol condensation catalyzed by the MOFs
The discussions on the synthesis of CPs and their utility in certain contemporary areas of research are by no means complete. However, from the above discussions, it is obvious that these materials will find innumerable applications in the near future and their studies constitute an important area of research in inorganic chemistry.

2.4. Proton conduction

Crystalline coordination polymers (CPs) can be readily and conveniently synthesized in good yields from metal ions and suitable ligands by employing the modular approach and under hydro(solvo)thermal conditions. Proton conduction in solid-state materials is important due to potential applications in transport dynamics, electrochemical devices, and fuel cells, and most importantly to understand the complex biological ion channels. The design and synthesis of new proton conductors are enormously important for clean energy applications, where the efficiency of proton exchange membrane–based fuel cells could be greatly improved in terms of both cost and performance. It is well known that Nafion has been extensively used as a proton conductor in fuel cells under anhydrous conditions. However, Nafion suffers a limitation of operating at temperatures above 80°C. Owing to this importance, some attempts have been made to design inorganic or organic–based materials for proton conductors. Also, the activation energy should be comparable to that of Nafion (0.22eV). In this context, porous
MOFs, show high thermal stability offer excellent opportunities as proton conducting separator materials. In MOFs, designability of the channels in terms of size, shape and its environment allows control over loading of guests into the channels. Organic conductive polymers are promising candidates, but because of their amorphous nature, it is difficult to optimize the ion-hopping path and to characterize the conduction behavior. Recently, a few works on the proton conductivity of CPs have also been reported. CPs also has several advantages for the construction of proton conductors. It is the inner surface characteristics of CPs, such as hydrophilicity and acidity, that are expected to affect the concentration and mobility of proton carriers; hence, proton conductivity can be widely controlled by substituting functional groups. As a key structural basis, these materials need proton carriers such as $\text{H}_3\text{O}^+$ or $\text{H}^+$, given by acid or hydroxy groups, and proton-conducting pathways composed of hydrogen-bond networks for proton conduction. Recently, Kitagawa and co-workers reported the first example where the proton conductivity has been widely controlled by substitution of ligand functional groups in an isostructural series of porous frameworks of MIL-53. Their group investigated proton conductivities of the porous coordination polymers $\text{M(OH)(bdc-R)} \ [\text{H}_2\text{bdc} = 1,4\text{-benzenedicarboxylic acid}; \text{M} = \text{Al, Fe}; \text{R} = \text{H, NH}_2, \text{OH, (COOH)}_2]$ under humid conditions [113]. Good correlations among pKa, proton conductivity, and activation energy were observed. MIL-53(Fe)-(COOH)$_2$
Recently, Bharadwaj and coworkers reported [114] high proton conductivity by a metal–organic framework, \([\{\text{Zn}_{0.25}\text{(O)}\}\text{Zn}_6\text{(L)}_{12}\text{(H}_2\text{O})_{29}\text{(DMF)}_{69}\text{(NO}_3\text{)}_2\}_n\), where \(\{\text{L}=\text{1,3–bis(4–carboxyphenyl)imidazolium}\}\), incorporating \(\text{Zn}_8\text{O}\) clusters with aligned imidazolium groups decorating the channels.

![Space-filling diagram showing methylene groups of the imidazolium moieties are aligned inside the channels and proton conductivity dependence on water uptake.](image)

**Figure 2.20** Space–filling diagram along a axis showing methylene groups of the imidazolium moieties are aligned inside the channels and proton conductivity dependence on water uptake.