



SYNTHESIS OF $Zn_4O(BDC)_3$ - (MOF-5) AND ITS APPLICATION AS PHOTOCATALYST

S. M. Ramteke ^a, S. R. Thakare ^a

^a Department of chemistry, Govt. Institute of Science, R.T. Road, Civil
Lines, Nagpur – 440001 (MS) India.
Email : sanjaythakare@yahoo.co.uk

Abstract :

A metal-organic framework (MOF) is composed of two major components: a metal ion or cluster of metal ions and an organic molecule called a linker. MOFs are easily prepared and we used the room temperature synthetic method of MOF to prepare MOF-5. The observations of properties of MOFs are seen in the areas of catalysis, sorption, separation, luminescence, bioactivity, magnetism, etc. Motivated by the recent discovery of $Zn_4O(BDC)_3$ i.e. MOF-5 as a semiconducting material, the application of MOFs in photocatalysis is emerging as an interesting topic since its cavity dimension sits exactly between molecular bio-enzymes and porous solid catalysts. The $Zn_4O(BDC)_3$ MOF, has an absorption spectrum that extends to 400 nm and can undergo photochemical processes upon photo excitation of the organic linker. Synthesis of MOF-5 is cheap and convenient and we used it for application on photocatalytic study with methylene blue dye. MOF-5 used as photocatalyst and reacted with methylene blue dye by using Philips light as a source of light for the reaction. Degradation on graph after photocatalytic reaction of MOF-5 and methylene blue shows positive result.

Introduction:-

Metal-organic frameworks (MOFs) are a new member in the vast field of porous materials. MOFs are the fastest growing class of novel inorganic-organic materials. They are also known as coordination polymers and regarded to have first been developed around 20 years before. MOFs are crystalline compounds consisting of metal ions or clusters coordinated to often rigid organic molecules to form one-, two-, or three-dimensional structures that can be porous. The void spaces in MOFs span from a few Angstroms to tens of nanometers. A metal-organic framework (MOF) is composed of two major components: a metal ion or cluster of metal ions and an organic molecule called a



linker. The organic units are typically mono-, di-, tri-, or tetravalent ligands. The choice of metal and linker has significant effects on the structure and properties of the MOF. The metal's coordination preference influences the size and shape of pores by dictating how many ligands can bind to the metal and in which orientation. The metal organic frameworks (MOFs) have evolved to be an important family and a corner stone for research in the area of inorganic chemistry. The progress made since 2000 has attracted researchers from other disciplines to actively engage themselves in this area. This cooperative synergy of different scientific believes have provided important edge and spread to the chemistry of metal-organic frameworks. The ease of synthesis coupled with the observation of properties in the areas of catalysis, sorption, separation, luminescence, bioactivity, magnetism, etc., are a proof of this synergism. The continuing interests in MOFs are driven by the fact that they are easily prepared and have structures comparable to the aluminosilicate zeolites. In addition, the organic moiety can have (i) chiral centers and (ii) impart chirality to the MOF structures and (iii) provide functionalities to the framework. The structural advantages are important in realizing many properties in MOFs, some of which are potential. The MOF possess excellent sorption capabilities, which are due to the open nature of the structures. The presence of coordinatively unsaturated metal centers in MOF structures can also provide ideal reaction sites (catalyst) for many important reactions. Interesting optical behavior can be observed in MOFs as the organic moiety can be easily excited through optical means, which would transfer the energy to the metal centers. This is especially true for compounds prepared using the lanthanide ions. Thus, MOFs not only have interesting structures, but also exhibit properties that can be modified to suit the requirements. Having established the behavior of MOF-5 as a semiconductor, a logic step forward has been to test its photoactivity towards the degradation of phenol. Very few MOFs have



been realized for such important functions. This is mainly because the MOFs need to have the capacity to absorb solar energy to initiate the catalysis, which has been rarely fulfilled. Motivated by the recent discovery of $Zn_4O(BDC)_3$ (MOF-5) as a semiconducting material, the application of MOFs in photocatalysis is emerging as an interesting topic since its cavity dimension sits exactly between molecular bioenzymes and porous solid catalysts. MOF was first used as photocatalyst to degrade organic pollutants by Mahata et al. in 2006, and other types of MOFs including MOF-5, isoreticular MOFs (IRMOF-1, IRMOF-2, IRMOF-7, IRMOF-8, IRMOF-9), MIL-53 (M = Al, Cr, Fe), UiO-66, and UiO-673 are subsequently reported. However, all of the above photocatalysts need either the assistance of a sacrificial agent, a co-photocatalyst such as Ir, Re, and Ru complexes, or UV-light as the energy source. Thus the application of MOFs in photocatalysis is still underdeveloped compared to inorganic oxide photocatalysts. In this context metal-organic frameworks (MOFs) may offer certain advantages for applications that need semiconducting properties. There is strong evidence showing that MOFs can be semiconductors and this property opens a new area in nanoscience. One of the most common applications of semiconductors is in photocatalysis where a solid converts light into chemical energy. The most common application of photocatalysis is the oxidative degradation of organic compounds in the gas or aqueous phase. Having established the behavior of MOF-5 as a semiconductor, a logic step forward has been to test its photoactivity towards the degradation of phenol. The temporal evolution of the phenol degradation was observed when this pollutant is submitted to irradiation through pyrex in aerated suspensions containing MOF-5, P25 TiO_2 or ZnO. The reason to compare these three materials is that zinc oxide should be the closest semiconductor in the case that the structure of MOF-5 collapses during the experiment in aqueous medium, while P25 TiO_2 is the benchmark photocatalyst to which the other photocatalysts should be compared. One pre-requisite



for the use of a solid in photochemical applications is its photostability upon prolonged exposures to light. Light stability is certainly an important issue that has been mostly ignored when pursuing the use of MOFs as semiconductors. Taking into account that one of the major applications of ZnO, TiO₂ and other semiconductors is the photocatalytic degradation of organic compounds and that MOFs contain an organic linker, the photostability of MOFs should be submitted to a survey. The Zn₄O(BDC)₃ MOF, commonly referred to as MOF-5, has an absorption spectrum that extends to 400 nm and can undergo photochemical processes upon photo excitation of the organic linker. Here, we treated MOF-5 as a photocatalyst using methylene blue as a dye solution in presence of light (Philips light).

Synthesis of MOF-5:-

We used the Room temperature synthetic method to prepare MOF-5 as it is suitable and convenient to our laboratory condition. Terephthalic acid (5.065 g, 30.5 mmol) and triethylamine (8.5 mL) were dissolved in 400 mL of DMF. Zn(OAc)₂.2H₂O (16.99 g, 77.4 mmol) was dissolved in 500 mL of DMF. The zinc salt solution was added to the organic solution with stirring over 15 min, forming a white precipitate, and the mixture was stirred for 2.5 h. The precipitate was filtered and immersed in DMF (250 mL) overnight. It was then filtered again and immersed in CHCl₃ (350 mL, HPLC grade). The solvent was exchanged 3 times over 7 days: after 2 days, 3 days, and 7 days. The bulk of the solvent was decanted and the product was evacuated overnight to a pressure of 10 mTorr. It was activated at 120°C and 10 mTorr for 6 h, at which point it was transferred to a glovebox and weighed (4.92 g, 63%)

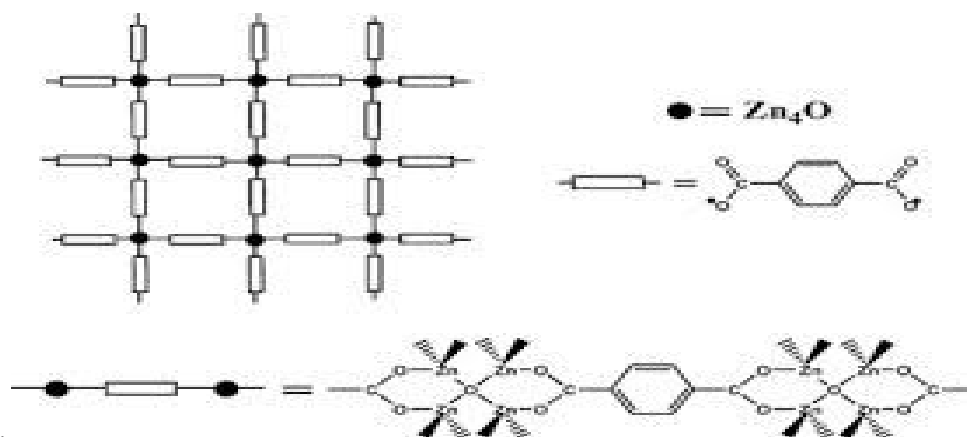
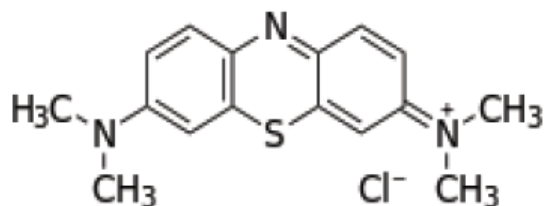


Fig1; Schematic presentation of the formation of MOF-5

Methylene Blue: The basic dye used in this study is Methylene blue, it is a heterocyclic aromatic compound. A.R.grade supplied by S.D. Fine Chemicals Mumbai. MB in commercial purity was used without further purification. The accurate weighted quantity of the dye was dissolved in double distilled water to prepare the stock solution (1 ppm) experimentally dilution. Dye concentration was determined by using absorbance value measured before and after the treatment with UV-Visible Spectrophotometer.



Experimental method:-

Stock solution of 1 ppm MB solution was prepared and 100 ml Methylene blue solution was treated with 0.1 g of MOF-5 solution and provide light source using Philips bulb 40V from downward side of round bottom flask. Oxygen is provided using aerator from one side of three neck R.B. The solution is centrifuged after completion of reaction. Absorbance of pure MB solution and the solution when decolorized by photocatalytic reaction with MOF-5 was taken using UV-Visible spectrophotometer.

Results and discussion:-

Photocatalytic destruction of organic compounds is based on semiconductor photochemistry. The most effective photocatalyst for this purpose is titanium dioxide. This is a non-toxic, material that is a constituent of toothpastes and many cosmetics. In order to fully appreciate the characteristics of photocatalysis with this semiconductor it is necessary to understand the basic physics of semiconductor materials. However, here a simple description is given. The titania catalyst is illuminated by UV radiation with a wavelength sufficient to displace electrons from the valence band of the catalyst; for titanium dioxide this is below 387.5 nm. An electron/hole pair is produced on the semiconductor surface. The photocatalytic oxidation of an organic species often proceeds via adsorption of the pollutant on the surface of the catalyst, followed by direct subtraction of the pollutant's electrons by positively charged holes. Another possible way is oxidation with OH radicals, generated from water of the aqueous environment, which takes place at the catalyst surface or in its vicinity. Both reactions may proceed simultaneously and which mechanism dominates depends on the chemical and adsorption properties of the pollutant. Figure 1 illustrates direct oxidation of an adsorbed species on the catalyst surface while the simple general reactions (R1) and (R2) give an idea of what occurs for the case of hydroxyl radical generation.

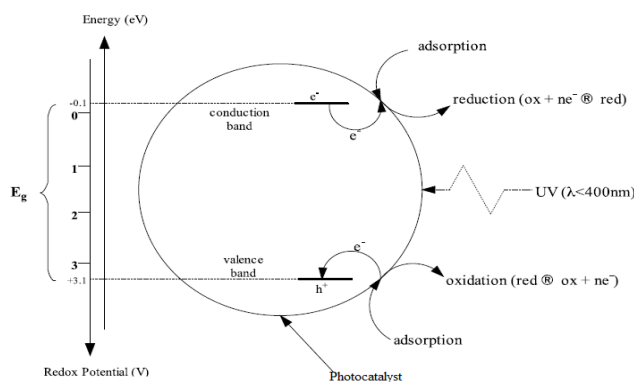
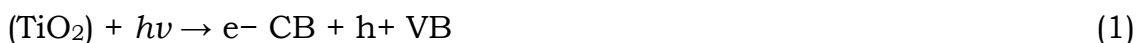


Figure 1.

Among the new oxidation methods or advanced oxidation processes (AOP), heterogeneous photocatalysis appears as an emerging destructive technology leading to the total mineralization of most of the organic pollutants, following the usually proposed mechanism.

1. Absorption of efficient photons ($h\nu \geq EG = 3.2$ eV) by titania

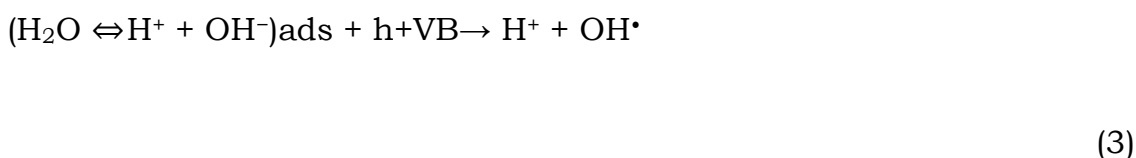


2. Oxygen ionosorption (first step of oxygen reduction; oxygen's oxidation degree passes from

0 to $-1/2$)



3. Neutralization of OH^- groups by photoholes which produces OH^\bullet radicals



4. Neutralization of $\text{O}_2^{\bullet -}$ by protons $\text{O}_2^{\bullet -} + \text{H}^+ \rightarrow \text{HO}_2^\bullet$

(4)

5. Transient hydrogen peroxide formation and dismutation of oxygen



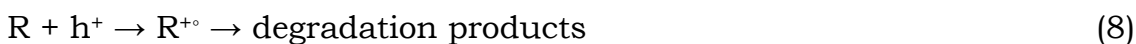
6. Decomposition of H_2O_2 and second reduction of oxygen



7. Oxidation of the organic reactant via successive attacks by OH^\bullet radicals



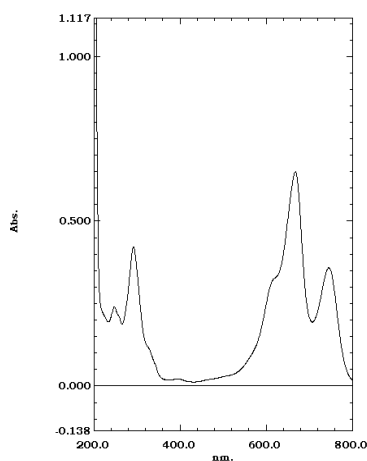
8. Direct oxidation by reaction with holes



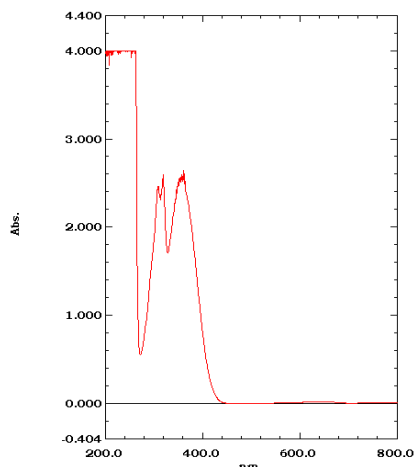
As an example of the last process, holes can react directly with carboxylic acids generating CO_2



From the above reaction it seems that, the two peaks of pure MB solution was disappeared due to photocatalytic reaction. The blue color of MB becomes colorless within one hour.



Pure MB



Degradation of MB after one hour

Conclusion:-

Porous MOFs are emerging as powerful platforms for many incredible functional applications. This article has demonstrated that porous MOFs open the door to the following relatively new topics in the last five years: chromatographic separation, (gas-phase) heterogeneous catalysis, as supports/host matrices for small metal NPs, and as templates/nanoreactors for other new material syntheses. Photocatalytic degradation of MB was studied using a prepared MOF-5. MB was successfully decolorized but also degraded and mineralized. So beside all this applications we can say that MOF-5 is also applicable as photocatalyst for degradation of various dyes.



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photocatalysis is one of important application of MOF as it can be used as photocatalyst.