Synthesis of binary mixture of nanocomposites and their application as a catalyst in the synthesis of heterocyclic compounds.

FOR

Master of Science(Hons) in chemistry
Lovely Professional University
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By

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DECLARATION

I namely **Madan Kumar,** hereby declare that the dissertation entitled "**Synthesis of binary mixture of nanocomposites and their application as a catalyst in the synthesis of heterocyclic compound**'' submitted in partial fulfillment of the requirement for the award of the degree of Master Of Science and submitted to the Department Of Physical Science (Chemistry) of Lovely Professional University is entirely an authentic record of my original work and all ideas and references have been duly acknowledged. It does not contain any work for the award of any other degree or diploma, other than described, at any University.

DATE: Madan Kumar

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CONTENTS

CHAPTER 1

INTRODUCTION

In modern era of science every pharmaceutical company, scientists, researchers are focusing on that particular class of compound which is easy to synthesize, having no or less side products, eco-friendly, cost effective and most importantly, vast applications in daily life. Heterocyclic compounds occupy an important place in this class. It is reported that approximately 80% of the commercially available drug contain heterocyclic ring[1]. Heterocyclic compounds are used as anti-HIV, antimalerial, antifungal, ant diabetic, antiviral, antifungal, antitumor, antidepressant, antibiotic, anti-inflammatory, herbicidal, insecticidal agents due to its presence in wide variety of drugs[2].

According to IUPAC GOLD BOOK cyclic compounds having as ring members atoms of at least two different elements, e.g. quinoline, 1,2-thiazole, bicyclo[3.3.1]tetrasiloxane[3].

Usually it may be defined as class of organic compound having one or more cyclic ring in which there should be a presence of at least one heteroatom other than carbon usually N(nitrogen), O(oxygen), S(sulfur)[4].

Heterocycles compound undergo various type of reaction like vilsmeier Haack reaction, bromination, friedel craft's alkyklation, tautomerism, Mannich reaction, Diel's alder reaction and hence shows various type of physiological and chemical properties.

The route of synthesis of such type of heterocycles are in very large number. They can be synthesized via cyclisation reaction like [1+4], [1+5], [2+3], [3+3][5]. Also they synthesized via amine (secondary or primary), aldehyde (or ketone) ,Carboxylic Acid ,Isocyanide via condensation. During the synthesis they undergo different type of name reaction like The Ugi reaction[6], Biginelli reaction [7], The Passerini Reaction[8]. Their synthetic examples are non-natural amino acids[9],benzodiazepines[10], carbacephems containing a beta lactum[11], Nummularine – F[12], Bicyclomycin[13], Hydrastine[14], Eurystatin A[15], rac-Monastrol[16], (–)-Ptilomycalin A[17], Saxitoxin[18].

In these type of reactions (given above) some organic solvent is used which is not eco-friendly i.e. it is toxic in nature and also hazardous for environment. If we use these type reactions and implies at industry level we will require a huge amount of organic solvent that again creates problem[19].

Now from there it is a consideration of use of different catalysts in the synthesis of heterocycles. As we know metal catalyst are available in industry in no. of forms and these catalyst can also prepared by hydrogenation reaction. The most common use catalyst are Platinum, Nickel, Palladium, Ruthenium and they undergo different industry level reaction like Heck reaction, Suzuki coupling reaction, Sonogoshira coupling reaction. In terms of inexpensive Copper is also used at industry level[1]. Use of solid phase catalyst like inorganic oxides, silica and modified silica, alumina, zeolites, clays, promotes various organic reactions in solution phase or in solvent-free conditions. This leads to greater attention of the chemists in the clean isolation of the products by simple filtration[20].

Also, according to Paul Anastas—one of the founders of the concepts of green chemistry, “Catalysis is a foundational stone of Green Chemistry” [21].

Till now various methods have been adopted for the synthesis of heterocycles which involve catalyst. Although these methods have their own advantages, However it also possesses certain disadvantages like ultrasound irradiation, microwave irradiation, expensive instruments, inaccessible materials, non-recyclable, non-selectivity, high temperature and multistep reaction[22].

This problem can be resolved by nanocatalysts, and from here we enter in the field of nanotechnology and nanosciences[23]. In nanoscience and nanotechnology we are dealing with extremely small things that it can across all the other science field like engineering, chemistry, physics, material science and biology. Physicist scientists **Richard feymann** is known as father of nanotechnology. The logic of nanotechnology and nanosciencies initiated from a talk that is “There’s a plenty of room at the bottom“, by Richard feymann in 1959 American Physical Society Meeting at The institute of California. He discussed a process that scientist can control every individual atom and molecule[24]. The word “Nanotechnology” was first given by a Japenese engineer, Norio Taniguchi in which we can control materials beyond micrometer[25]. Nanotechnology have vast no. of application like it is utilized in cancer treatment using Gold nano-particles, delivering of vitamins for skin care, sunscreen to protect from UV, powering plug in electric cars as lithium ion batteries, strength-ting of rod without increasing weight, film of titanium oxide kill bacteria by using the energy of light, cleaning products, Solar cells, sporting goods, chemical sensors, fabric, cleaner water, better air quality, fuel, space, fuel cells and many more[26].

One of the basic aspect of nanotechnology to create a material having one dimension is in nanoscale, called nanomaterials. In nanomaterials the nature of bulk is totally different from bulk material. Nanomaterials almost used in everyfield like in cosmetics, paint, sunscreens, textiles, coating, Organic light emitting diode, consumer products like metal oxide, carbon nanotube, nanosilver, nanoclays, nanocarbon, quantum dots, nanowire, fullerenes, dendrimer and many more[27].

As our topic focuses on nanocomposites as catalyst in the synthesis of heterocyclic compounds so we are focusing on nanocomposites portion.

Nanocomposites is related to composites having one of the dimension is in nanoscale. Nanocomposites can be act as monolithic as well as microcomposites due to outstanding properties. In nanocomposites some nanofillers are added to enhance the properties of resulting material also called doping. Generally nanocomposites contain two or more phase's shows variation in physical and chemical properties. Their novel properties are not shown by any other materials or constituents. The part of constituent(smaller) that is added/doped to enhance the properties of nanocompopsites are known as reinforcement or nanomaterials and the part that is present in more amount are called matrix. With doping of nanofiller, make the resultant product lighter than initial one. Due to great difference in single molecule and bulk material, nanomaterials attracted much of attention of researchers, especially in the field of catalysis[28].

Classification of nanocomposites :- Nanocomposites can be classify into major two categories that are polymer based and non polymer based. They can be further classify under different categories as given below in figure 1.

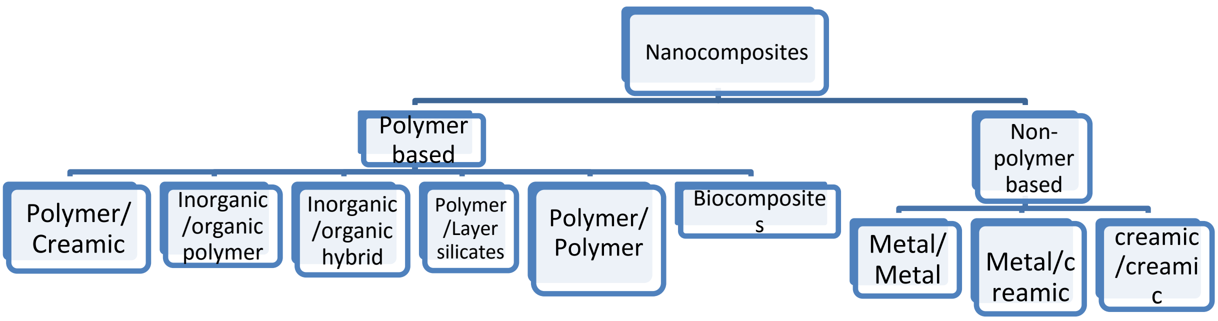


Figure 1

Examples of type of nanocomposites

- The polymer/ceramic based nanocomposites possess layered structure, good example of this is Barium titnates with polymers.
- The inorganic/organic polymer based nanocomposites possess clusters, good example of this is polymer nanofiber with zero valent nanoparticles.
- Inorganic/organic hybrid polymer based nanocomposites are nanocrystals, good example of this is Cds nanocrystals, poly-N-vinyl carbazole-PHOTOREFRACTIVITY.
- Good example of Polymer layer silicates is Nylon-6/montorillonite with silicate layer.
- Good example of this type are poly(p- phenylene oxide)-plastic scap recycling.
- Elastin and collagen are good example of biocomposites.
- The metal/metal nanocomposites are present either in the form of alloy or core shell structure.
- The metal/ceramics nanocomposites are present either in the form of nanotube or nanostructure.
- The ceramics/ceramics nanocomposites are alloy or ceramic per example Zirconia-toughened alumina.

Out of these two type, polymer and non polymer based nanocomposites polymer based nanocomposites are very important and unique as they possess High selectivity, reactivity, stability, surface area, re-generability, robustness improved hydraulic properties and most importantly low cost[29]. In terms of efficient synthesis for a catalyst these things are much required, so as from here it is a consideration of use the nanocomposites as catalyst.

Nanocatalyst are choosen for the synthesis of heterocyclic compound is due to its higher selectivity, reactivity, and stability. The catalytic reactivity and selectivity of nanocatalyst is strongly depend on crystallographic plane of nanoparticle by means we can also enhance the catalytic property of nanocatalyst by controlling the morphology. In many cases when the particle size is going to decrease the catalytic activity enhances, due to change in electronic property of surface, can also achieved by doping. Another advantage of nanocatalyst is that only negligible amount is required to give the significant result. Nanocatalyst has also numerous applications[30].

Synthetic Routes:

As we know the properties like magnetic, optical, electrical, biological is very much dependent on size and dimensions[31]. There are three important strategies vapor phase, solution phase, gas phase by which we can prepare nanocomposites. The other two strategies are top-down and bottom-up approach. In bottom up precursors are allow to construct and grow and they are prepared by chemical methods and top down are prepared by physical methods. The selection of the proper approach is totally dependent on what type of properties that we want to see in our final product in terms of size, morphology and lattice of crystal[32,33,34]. By physical method we can prepare huge quantity of nanocomposites, however in product there is no equality of size of particles, but the composites that are prepared from chemical or wet method there is equality in particle size and by doing variation in use of chemicals and condition we can also prepare nanorods, nanowire and nanotubes[35].

There are various wet or chemical method of preparation of nanocomposites however the most cost effective methods are co-precipitation, sol gel, and hydrothermal methods that are given below in brief.

Co-precipitation method: - These method are used for the preparation of mixed metal or metal ceramics, metal oxide nanoparticles in which generally inorganic metal salt is used as precursor and hydroxide, carbonates, oxalates, formates, and citrates are used as the precipitating agent[33]. For good and better result we have to use inorganic hydroxides for the preparation of metal oxide nanoparticles. In this process first inorganic metal salts are dissolved in water and then for better mixing of the salts these are stirred for 15-20 minutes. After this hydroxide are added to get powder after long stirring, then filter and dry, nanoparticles in the form of powder are obtained. These powders are calcinated at higher temperature that gives comparable small quantity and small size called as nanocomposites.[36]. The reason behind calcinations is that we cannot store nanopowders for long time as its size and dimensions can vary. However this route requires control in the concentration, pH, temperature and stirring speed of solution for desired product[37]. Doping is used for enhancing the respective properties. The variety of oxides and ceramics like ZnO-SnO, Zno-CuO, MgO-Al_2O_3, MgO-CuO, ZnO-Fe_3O_4, NiO.CeO_2.ZnO, Ag-talc, Ag-MMT, Ag-activated carbon, ZnO-activated carbon can prepared by this method[38].

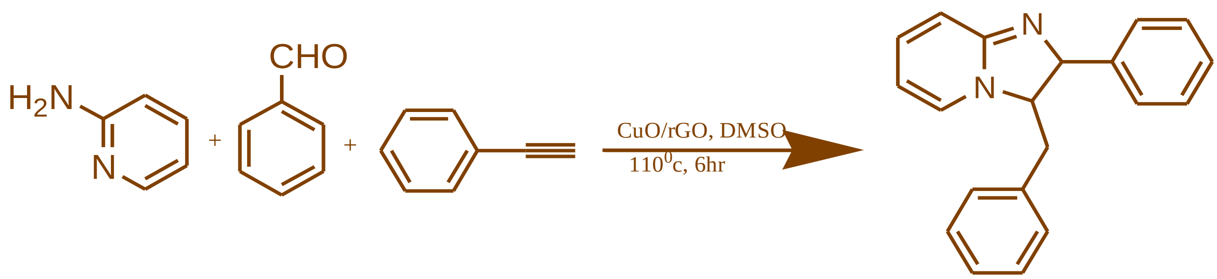
Sol- gel process: - This method requires mild condition with simple wet reaction based on hydrolysis and condensation of metal alkoxide that forms sol and by aging it results an integrated network as gel[39]. The final products are either colloidal powder [40] or films

[41]. More than one micro and nano-structures can also prepared by this method. The dimensions, size, shape are strongly influenced by the reaction condition. In this process Hydrolysis and poly-condensation reactions of an inorganic precursor dissolved in organic media that lead to the formation of three-dimensional polymers containing metal-oxygen bonds (sol or gel). On drying it gives a solid material and further on thermal treatment it gives nanocomposites. From this method we may prepare SiO_2/Ni, ZnO/Co, TiO_2/Fe_2O_3, La_2O_3/TiO_2, Al_2O_3/SiC, TiO_2/Al_2O_3, Al_2O_3/SiO_2, Al_2O_3/SiO_2/ ZrO_2, TiO_2/Fe_2/TiO_5, $NdAlO_3$/Al_2O_3[38].

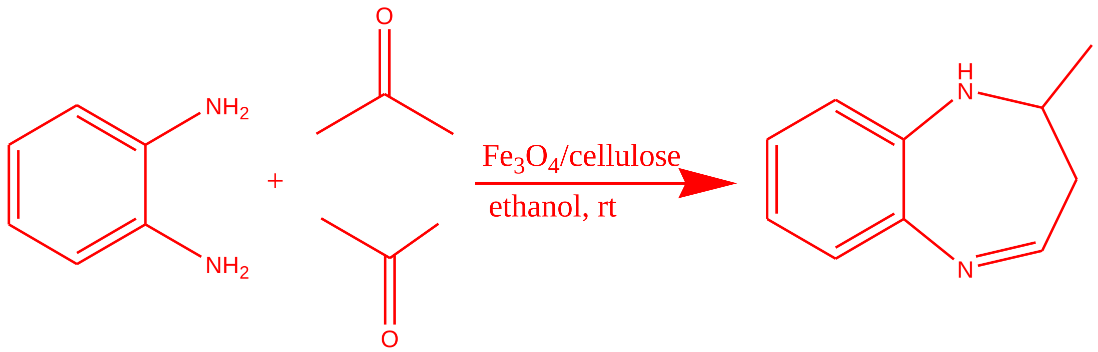
Hydrothermal process: - As we know due to hydrogen bonding water acts as good solvent for many ionic compounds. Under high pressure and high temperature water can also dissolve non-ionic covalent compounds .This strategies is implies in the preparation of fine powders of metal oxide via hydrothermal process. Hydrothermal processes lower down the activation energy and this process can speed up by increasing the temperature. The pressure rang for this method is 10-150 kilo bar which is strongly dependent on temperature setup. The forms of Powders are may be crystalline or amorphous depending on hydrothermal temperature chosen for the preparation[42, 43].

Nanocomposites as catalyst: - As we have discussed earlier due to high selectivity, reactivity, very less amount requirement, no waste or less, eco- friendly, cost effective, simple route of preparation of catalyst, mild conditions makes the synthesis of heterocyclic compounds as efficient process. Some of the examples of synthesis process are given below.

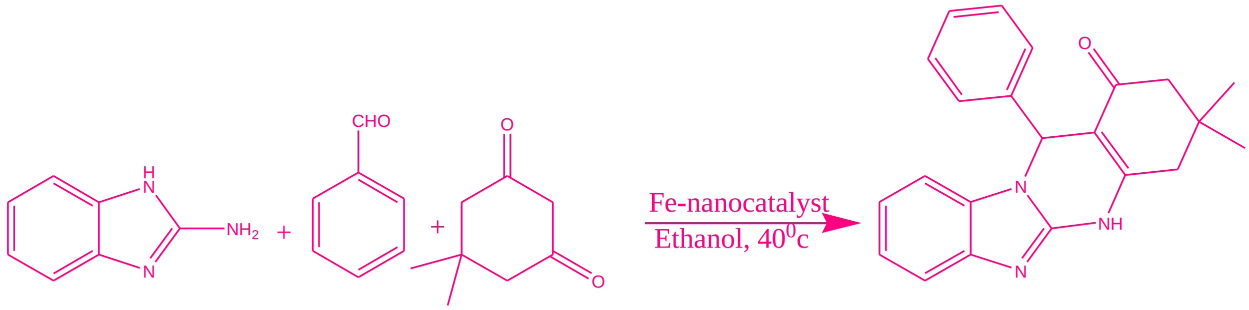
- Synthesis of imidazo[1,2-a] pyridines by using CuO/rGO nanocomposite catalyst in one pot three component coupling reaction. DMSO act as solvent and reaction occurred at 100^0c, 6hr[44].



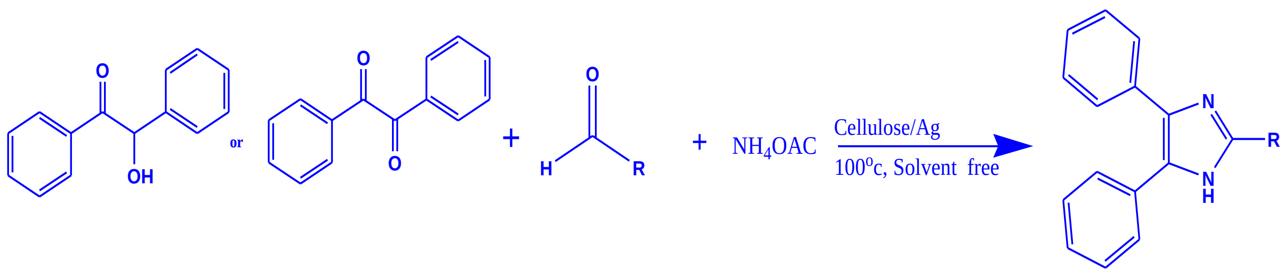
- Synthesis of benzodiazepines using Fe_3O_4-cellulose based nanocomposites. Ethanol is used as solvent. Reaction proceeds at room temperature[45].



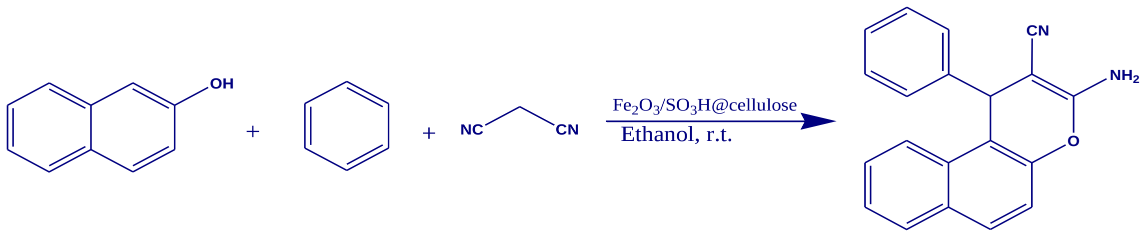
- Synthesis of benzimidazolo[2,3-*b*]quinazolinones by Fe-nanocatalyst, ethanol act as solvent, and at 100^0c temperature[46].

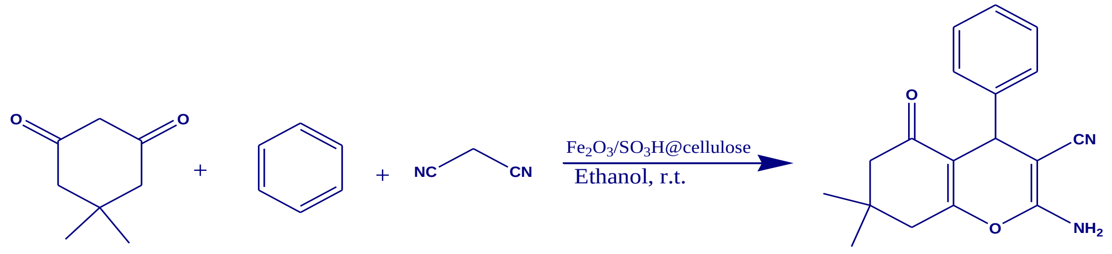


- Synthesis of 2,4,5-trisubstituted-1*H*-imidazoles using cellulose/Ag nanocatalyst under solvent free conditions and at 100^0c[47].



- Synthesis of Chromene Derivatives by using cellulose@Fe_2O_3/SO_3H nanocomposites using, ethanol at room temperature[48].


OH
NC
CN
Fe_2O_3/SO_3H@cellulose
Ethanol, r.t.
CN
NH_2
O


O
O
NC
CN
Fe_2O_3/SO_3H@cellulose
Ethanol, r.t.
O
CN
O
NH_2

CHAPTER 2

LITERATURE SURVEY

Heterocyclic compounds are present in 80% of the drug molecule having antifungal antidepressant, antimalerial, antibacterial, antiHIV, anticancer, antiviral and many more properties. These heterocyclic compounds are synthesized via several approaches like by using organic solvent, inorganic catalysts, nanoparticles and nanocomposites as catalyst. However the most significant approach is to use nanocatalyst as composites.

Nanotechnology is a field in which we deal with very small size particle having range in nanometer i.e. at the level of atomic and molecular level. Dealing with nanometer size enhances its optical, electrical, magnetic, mechanical and catalytical properties. Use of nanoparticles as catalyst is another approach; however the enhancement of properties due to nanocomposites makes it stable, reactive, eco-friendly cost-effective less or no waste and significant amount requirement catalyst.

Moreover these properties can also enhance by doping i.e. is a process of addition of some external impurities. Selection of material for doping and what thing to doped is also overviewed in this literature survey in the form of abstract of research papers.

Nano-composites are high performance material that exhibit unusual property combinations and give unique design possibilities. An estimated annual growth rate is about 25% and fastest demand in engineering plastics and elastomers due to their potential that is so striking hence they are useful in several areas. In this overview the three types of matrix nano-composites are presented are the need for these materials, their processing methods and recent results on structure, properties and potential applications including need for such type of materials in future space mission and other interesting applications in terms of market and safety aspects. Natural materials such as clay based chrysotile, lingo-cellulosic fibers and minerals are also highlighted. As environmentally friendly, applications of nano-composites offer new technology and business opportunities for several sectors like, aerospace, automotive, biotechnology industries and electronics[49].

Due to their abundance, biodegradability, high strength, stiffness and low weight nano-scale cellulose fiber materials serve as promising agents for production of bio-nanocomposite. These materials are the subject of research and commercially interesting terms for new products in pulp, paper industry and the agricultural sector. Cellulose nanofibers are extracted from various plant sources, although the mechanical separation of plant fibers into smaller elementary constituents has typically required high energy. Chemical or enzymatic fiber has been developed to overcome this problem. A challenge associated with using nanocellulose in composites and its methods have been explored. This review tells the progress in nanocellulose preparation (particular focus on microfibrillated cellulose) and also discusses bio-nanocomposite fabrication recent developments based on nanocellulose[50].

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This review gives the academic and industrial preparation, characterization, materials properties, crystallization behavior, and processing of polymer/layered silicate nanocomposites. These materials are attracting considerable interest in polymer science research. For the preparation of nanocomposites Hectorite and montmorillonite are the most commonly used smectite-type layered silicates. Due to their high adsorptive properties, cation exchange capacities, surface area, surface reactivity and in the case of hectorite, high viscosity and transparency in solution makes it as important part of industry. In their pristine due to hydrophilic nature, makes it very difficult to disperse into a polymer matrix. The most easy way to remove this difficulty is to replace interlayer cations with ammonium or phosphonium cations (preferably with long alkyl chains)[51].

The summary of the progress in polymer nanocomposites, presented in this paper are based on different methods uses of polymer-layered silicate (PLS) nanocomposites and at what extent properties are enhanced. The types of polymers used in PLS nanocomposites preparation morphologies that are most commonly achieved, i.e. structure, properties of layered silicates, and the most common techniques used for characteriziation[52].

Heterocyclic compounds are an important base line having both industrial and pharmaceutical applications. Their synthesis carry conditions such as the use of expensive catalyst, toxic solvent, harsh reaction condition like the use of base, high temperature, and multistep reaction. However the chemistry arena is now shifted towards the greener way eco-friendly route of synthesis. Nanocatalyst has an important place in the green synthesis. This is due to high reactivity, selectivity surface area and negligible amount requirement to give the significant. The current review enlists the various types of Nanocatalyst, involved in the heterocyclic ring formation and also some other important points[22].

This review reports recent developments in the field of polymer–layered silicate nanocomposites. Due to existence of dramatic improvement in properties at very low filler contents these materials have attracted attention both of academic and industrial. The structure, preparation, detailed examples and properties of polymer–layered silicate nanocomposites are discussed in general form[53].

For fabrication of polymer nanofibers "Electro spinning" has gained much attention as an efficient technique. In recent years mostly in solvent solution and some in melt form, various polymers have been successfully electrospun into ultrafine fibers. They use as reinforcement in nanocomposites in development have been known. A overview is presented on the researches and developments related to electrospun polymer nanofibers including processing conditions, structure and property characterization, applications, and modeling and simulations. Information of those polymers together with their processing for electrospinning of ultrafine fibers has been summarized in the paper. Other issues like technology limitations, research challenges, and future trends are also mentioned[54].

The imidazo[1,2-a]pyridines are an important class of nitrogen ring containing heterocyclic compounds, which has wide range of applications in medicinal chemistry and drug molecule production. The reported synthetic way provides a fast access to substituted imidazo[1,2-a]pyridines with excellent yields. CuO/rGO nanocomposite material was found to be highly active catalyst for this reaction. It takes shorter reaction times from previously reported having advantages of functional group tolerance, additives free and recyclable catalyst[44].

A method for immobilizing in a sol–gel silica matrix is developed for dendrimer encapsulated nanoparticles (DENs). DENs were added at two different times to analyze time effects for DEN addition in the sol–gel preparation, platinum: before the condensation reactions and 24 h after the condensation reactions (after the sol formation before gelled). The catalyst prepared after sols had formed, however this catalyst was substantially less active for toluene hydrogenation. Infrared spectroscopy of adsorbed CO indication conforms this information[55].

Polymeric nanocomposites have been deeply investigated due to the performance improvement achieved by a small amount addition of nanosized particles in a polymer matrix.

The remarkable changes are observed in terms of physical and mechanical, explained by the huge surface area, increases the interaction between the polymer and nanoparticles. Nanocomposites can also be produced using polymer processing techniques, which makes them particularly interesting in terms of production point. Therefore, this overview discusses about different routes for preparation of polymer-based nanocomposites[33].

In this review the synthesis of heterocyclic compounds, applications of heterogeneous catalysis, microwave irradiation are reviewed. A detailed summary of the different catalysts is given; the work not focuses on the preparation or characterization of the catalyst. The synthesis of these compound more profound due to large number of heterocycles having N, the preparation of other heteroatom compounds is also given in detail. The literature data summarized the classification of heterocyclic compounds. The green aspects of the individual synthetic approaches are also given[1].

Carbon nanotubes (CNTs) carries exceptional multifunctional characteristics and mechanical properties increases interest to apply CNTs in different fields, led to efforts that develop dispersion and functionalization techniques. CNTs promises as effective reinforcement in polymer nanocomposites supports the information of proper dispersion and appropriate interfacial adhesion between polymer matrix and CNTs. This paper mainly focuses on (i) the principles and techniques for functionalization and dispersion of CNT and (ii) their effects on the properties of CNT/polymer nanocomposites. The potential applications fabrication techniques of CNT/polymer nanocomposites are also discussed[56].

In this article, for the synthesis of benzodiazepines in a range of good to excellent yields under very normal conditions, nanocomposite of Fe3O4 /cellulose having high amount of nanoparticles is taken as catalyst. It is observed that there is a good relation between the amount of surface acid sites, catalytic activity and surface morphology of the catalysts. This process has been found as simple, efficient in terms of eco-friendly, and economical as they can reuse, recycle by any significant loss in its catalytic properties[45].

A simple and efficient approach via multi-component reaction, which involves the condensation of 2-aminobenzimidazole, dimedone and various aldehydes using chitosan-supported metal nanocomposite for the synthesis of tetraheterocyclic benzimidazolo[2,3-*b*]quinazolin-1-ones has been developed as a green, reusable and eco-friendly catalyst system. The major attributes of this one-pot procedure is environmental friendly, cost-effectiveness, easy workup, recyclability and excellent yields[46].

In this work, new method is used for the synthesis of heterocyclic compounds; cellulose-based silver nanocomposite is used as a catalyst. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were obtained characterization and morphology studies of the nanocomposite[47].

This works reports about nanocomposites in which by adding TiO2 nanoparticles refractive index is introduced. We discussed the comparison between *in situ*/*ex situ* preparation methods; properties of nanocomposites. Two-photon polymerizations (2PP) of synthesized nanocomposites are especially examined. All prepared samples shows suitable optical transparency at specific wavelengths of laser. By inducing a femto second laser 3-D structures glowed by two-photon polymerization effect[57].

Zinc sulfide nanoparticles and nanocomposites can prepared by chemical precipitation method using sulfur sources and zinc acetate. Its properties are characterized by scanning electron microscopy (SEM) X-ray diffraction(XRD), ultraviolet-visible(UV) and fourier transform infra-red(FTIR). The crystal structure is investigated by XRD.. Morphology is investigated by SEM. The Fuctionality is discussed by FTIR. The optical properties is discussed by ultraviolet-visible absorption spectrum[58].

The pyran annulated heterocycles are synthesiszed by one-pot three-component reaction by condensing aromatic aldehydes, and acidic compounds having (C-H active) in the presence of ethano and 4-(dimethylamino)pyridine (DMAP) as a catalyst under reflux conditions. This trends provide catalyst a simple, eco-friendly, high yields, non-aqueous, less work-up, and recyclability tool[59].

Metal or metal oxide surrounded by MWCNTs i.e. multi walled carbon nanotubes holds the application over huge catalysts as it possess properties like synergistic, hybrid, physical, and chemical properties. As a result it acts as a tool of highly active catalytic sites having high chemo-selectivity. In this work we discussed(1) process of metal or metal oxide covered with MWCNTs, (2) characterization tools for nanocomposites(Heterogeneous) and (3) role of nanocomposites as metal or metal oxide for the preparation of heterocyclic compounds. This review summarizes the important requirements for developing new nanocomposites and its use in the synthesis of important heterocycles used in industry[60].

This work mainly focuses on the composites of thermally conductive polymer that bears several applications in field of power electronics, motors and generators and heat exchangers.

The advantages of polymers composites like light weight, corrosion inhibitor and easy route of processing leads to interest to improve the thermal conductivity of polymers is focused on the selective addition of nanofillers with high thermal conductivity. Unusually high thermal conductivity makes carbon nanotube (CNT) the best promising candidate material for thermally conductive composites. However, the thermal conductivities of polymer/CNT nanocomposites are relatively low compared with expectations from the intrinsic thermal conductivity of CNTs. The 2 challenge primarily comes from the large interfacial thermal resistance between the CNT and the surrounding polymer matrix, which hinders the transfer of phonon dominating heat conduction in polymer and CNT. This article reviews the status of worldwide research in the thermal conductivity of CNTs and their polymer nanocomposites. The dependence of thermal conductivity of nanotubes on the atomic structure, the tube size, the morphology, the defect and the purification is reviewed. The roles of particle/polymer and particle/particle interfaces on the thermal conductivity of polymer/CNT nanocomposites are discussed in detail, as well as the relationship between the thermal conductivity and the micro- and nano-structure of the composites[61].

Nanocomposites of various classes have been prepared by sol-gel routes. For this reason, prefabricated nanoparticles of SiO_2 have been dispersed after modification of surface. A profound effect is observed on surface modification in all cases. It is found that properties like mechanical, optical sharply depend on the dispersion and modification of surface. By results, nanocomposites play major role in chip coupling, hard coatings (polycarbonate) and CR 39[62].

Nanoparticles gained much of attraction in many fields since last decade. The reason behind this fact is addition of inorganic/organic hybrid molecular network. The physical properties like electrical, optical, catalytically properties of nanoparticles also may be used for tailoring of material. For this literature survey is done as advanced. Moreover, based on studies, examples are given to recognize the effect of nanoparticles on two component i.e. (TEOS) type of hybrids composed of(1) ethyl ortho-silicate (2) (MTEOS/MTMOS) i.e. methylethoxy/methoxytriethoxy silane). It is shown that nanocomposite hybrid sols of SiO_2 can dried in form of thick films up to 14m after one step i.e. dip-coating process, led to increase in ability and flexibility of relaxation. nanocomposite based on TEOS, MTEOS and particularly SiO_2 has been developed for industrial process. A new type of environmentally friendly glass fiber mat is developed by increasing the temperature up to 600^0C[63].

In this work processing techniques, properties of surface, behavior of polymer nanocomposites are overviewed. Crystalline and amorphous nature of polymer nanocomposites are also overviewed[64].

CHAPTER 3

ORIGIN OF PROBLEM

However there are various approaches to synthesize heterocyclic compounds, but somehow these synthesis carries some type of demerits like harsh condition, multistep process, expensive catalyst, toxic solvent, microwave irradiation ultrasound irradiation, expensive instruments, inaccessible materials, non-recyclable, non-selectivity, excess waste, and not eco-friendly makes it problematic. This problem is going very big at industry level that focuses to look for field like nanotechnology and nanosciences.

On the contrary nanocomposites due to its efficient properties like higher surface area, higher selectivity, higher reactivity, high stability, recyclability, low cost, easy route of preparation, no waste or very less, requirement of very small quantity, solvent free condition or solvent like water, ethanol and mild condition makes it eco-friendly and hence gained much of attention of industries, researchers, academies towards itself.

CHAPTER 4

EXPERIMENTAL DETAILS

As we have discussed the importance of nanocompites as ZnO, doping effect, and its catalytic properties and its reason behind important part is also discussed in detail in introduction part.

In this project nanocomposites of binary mixture are prepared by maintaining the reference condition to all via two different approaches (1) powder method and (2) solid state reaction. These two ways are given below in detail. In which 1st step is methodology and 2nd step is collection of apparatus and chemicals.

Methodology

First we find out the area where majority of researchers, industries, academies are working on a particular class of compounds as they must possess various applications. We found such classes of compounds are heterocyclic compounds, then we find for a particular greener synthesis that makes everything effective and efficient. So from literature survey we find the efficient way is to prepare nanocomposites as catalyst and via doping we may also enhance its catalytic activity.

Next step is to what type of chemicals we will take for preparation of powder and then composites. We found for literature survey that ZnO bears a high potential application and having wide characteristics properties of its surface that focuses much of attention towards preparation of ZnO nanocomposites and from studies we found that properties can also enhanced by doping. But to know the doping effect on its catalytic activity we focuses on preparing binary mixtures of nanocomposites.

Then we do certain type of calculations and after that we follow two methods having easy routes of preparation in which 1st one is via powder method and 2nd is via solid state reaction according to chemical availability. For this we have taken Zincacetate dehydrate. According to literature survey studies for a powder formation we have to first make the homogeneous soln. of $ZnAc.2H_2O$ by water and then for powder we have to use some hydroxide. The reason behind use of NaOH is, as it acts as inorganic hydroxide which is good for precipitation of inorganic oxides and cheaper price. One thing we take care that pH must be in range b/w 8-8.5

so that we can control on particle size and by using long stirring of 4-4.5 hr at room temperature such that there would be a preparation of equal size particle. Same thing would be done for other mixture in different sets In which we use $SnCl_2.2H_2O$ as a inorganic metal salt. Next startegies is to stay for a day so powder can come up and other solvents settele down and after by doing filtaration, dry in oven at 50-60^{0}c for 4 hr so that there woulid be a complete evaporation of solvents. Next process is to be make the powder in stable form by annealing at high temp. by slow increment of temp and we will stop muffle furnace for 5mins at 100^{0}c 200^{0}c 300^{0}C, 400^{0}c, 500^{0}c and then 600^{0}c for 1hr such that its dimensions, size would not affect by time and having complete calcinations i.e. also studied from our studies.

The other things that are taken into considerations are carefully calculations for doping, proper amount of solvent is to be used, proper stirring time, proper reaction temperature i.e. room temperature, proper filtration, drying process and sample storing.

For 2nd approach first only ZnO powder are prepared by above technique then it is to be mixed with powders of V_2O_5 using some volatile solvents for 2-3 hr. This mixing process is to be done in motor pastal and we have to use acetone for mixing but in a few quantities so that it can mix well and easily. evaporate Same thing is to be done for other mixture. The next step is to make its pellets and then do the annealing as given above

Collection of apparatus and chemicals

Chemicals required for this process are Zinc acetate dehydrate (219.49g/mol) by RANKEM, Water (18g/mol), Sodium hydroxide (39.99g/mol) by Alpha Chemika, Tin chloride dehydrate (225.65g/mol) by Alpha Chemika, Vanadium pentaoxide(181.88g/mol) by MOLYCHEM and the apparatus are 250ml, 100ml beaker, crucible, oven, glass rod, motor pestle, whatmann filter paper, funnel, watch glass, spatula, tripod stand, petri dish.

Procedure

Procedure is categorized in two ways first is preparation of 1) Sn/ZnO nanocomposites and 2) V_2O_5/ZnO nanocomposites.

1) Sn/Zno

For the preparation of binary nanocomposites of Sn/Zno, Tin chloride dihydrate (225.65g/mol), Zinc acetate dehydrate (219.49g/mol) and Sodium hydroxide (39.99g/mol) are taken. For 0%, 5%, 10%, 15%, 20% doping the simple procedure in the form of flow chart is followed i.e. given below in fig. 2(reference), fig 3(doping with Sn). $ZnAc.2H_2O$ exactly 10g taken from analytical balance and fill with 100 ml distilled water a 250ml in cleaned beaker. For well mixing placed the beaker on stirring for 20-25 minutes. After well mixing we added NaOH slowly and we observed that there is formation of powder slowly. We stopped addition of NaOH when pH reaches at 8.As a result the soln. of powder becomes thicker and for making it homogeneous soln. we kept the beaker at constant stirring for 4:30 hrs.

By doing same thing in other sets, the difference is that we have added $SnCl_2.2H_2O$ with $ZnAC.2H_20$ at a very first stage. One thing that we kept constants are amount of NaOH and water as given above in table. We kept this soln. for constant stirring at room temperature.

After keeping every set at constant stirring and placing them for constant time i.e. 4:30 hrs, we kept them at a safety place for 24 hrs. So that water and other organic layer settle down and powder accumulate on the upper part. Then we filtered it by using whatman filter paper (normal quality) and also give washing with water three times so that we can get fresh powder. For removal of water and other organic layer we placed all the sets in oven at 50c for 4 hrs. The dried powder are kept safely in a petri dish and numbered them 1, 2, 3, 4, 5 respectively.

The last stage is annealing in which powder are placed in a crucible and kept them in digital muffle furnace and by increasing the temp. slowly and kept these samples for 10mins at 100, 200, 300, 400, 500 and at 600c kept these sample for 1hr for complete calcination. As a result there is formation of nanocomposites in the form of fine powder.

2) V_2O_5/ZnO

In this part first ZnO powder is prepared by following the above procedure i.e. up to dry in oven and for then 4 doping of V_2O_5 (0%, 5%, 10%, 15%) is made by following the simple flow chart given below fig 4, fig 5. For this amount, of ZnO is fixed i.e. 3g for each doping and weighed by analytical balanced, placed them in motor pestle, measured V_2O_5 by analytical balance for each doping, add them one by one in respective motor pestle and numbered them 1, 2, 3, 4. By using little amount of acetone (voltaile solvent) time to time mixed the both powder and grind them gently for 2 hrs (solid state reaction). In the next step mixed powders are converted into powder by using KBr press and then placed for annealing as same as mentioned in above procedure. Last step is our characterization step, given in next chapter.

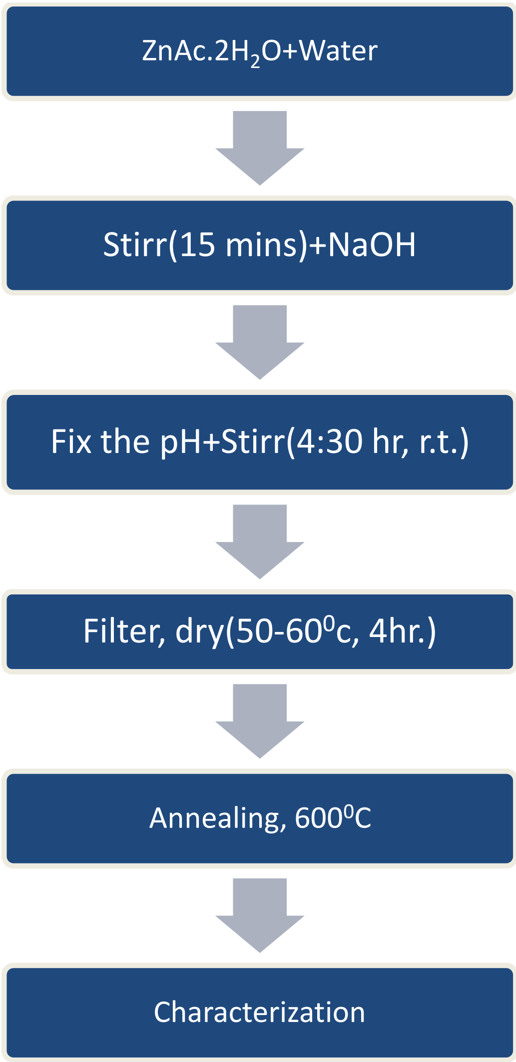

fig. 2-: Reference

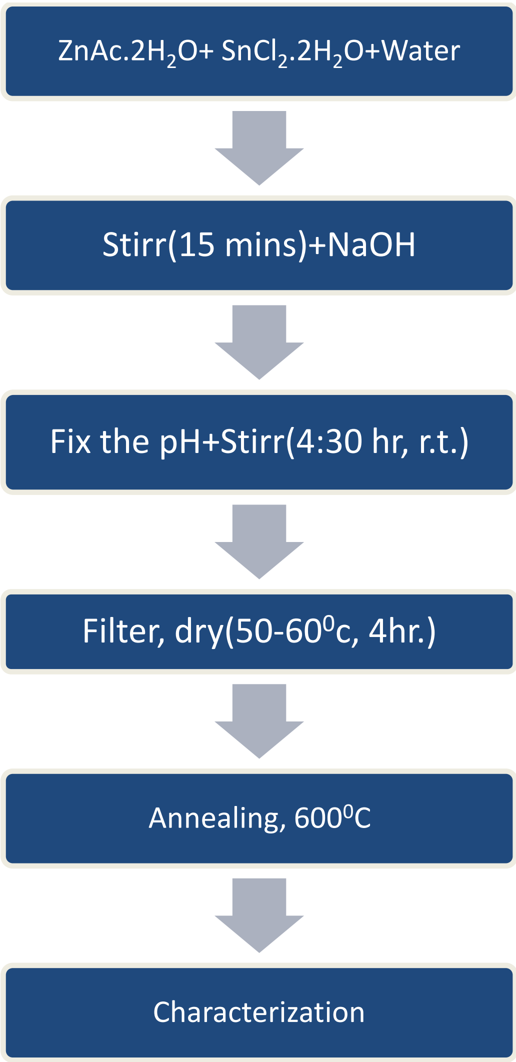

fig. 3-: Doping with Sn

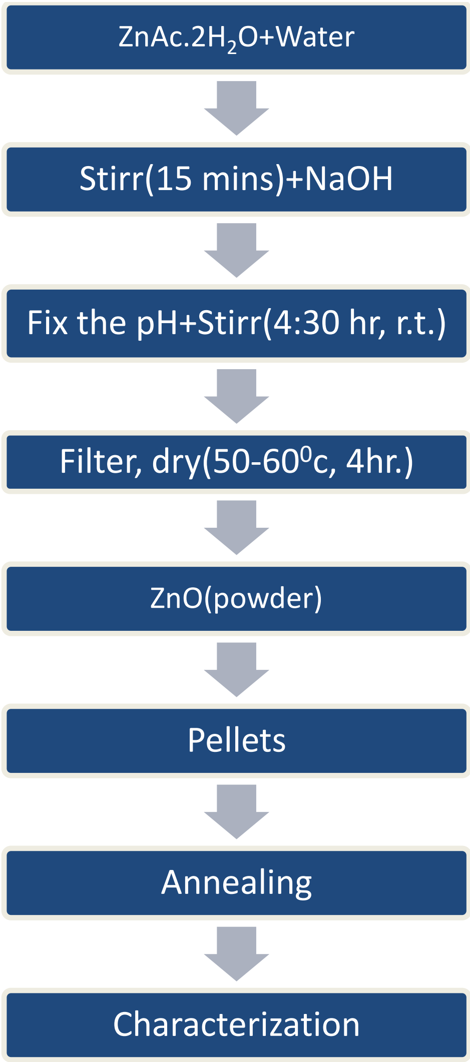

Fig. 4 Reference

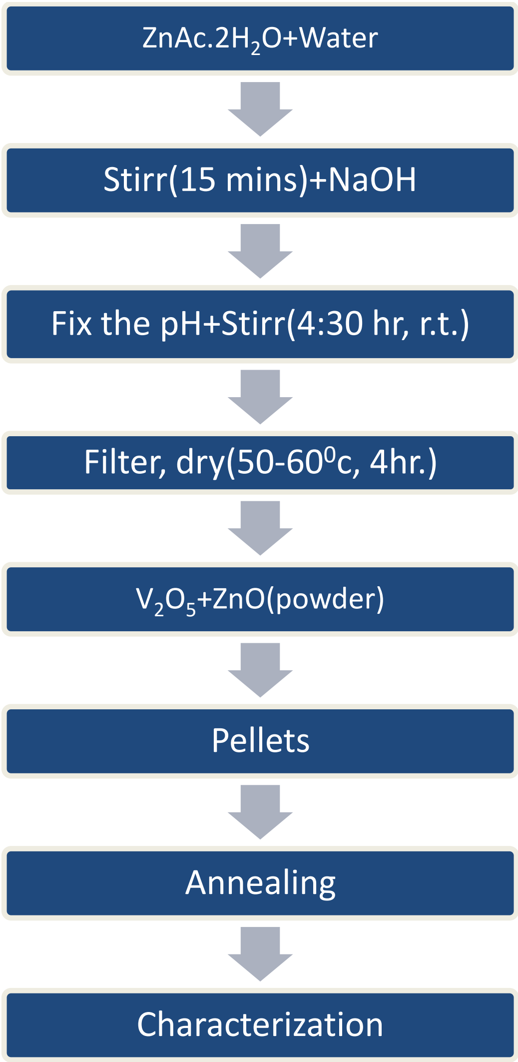

fig. 5 Doped withV_2O_5

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