GREENER SYNTHESIS & CATALYTIC APPLICATIONS OF METAL OXIDE NANOMATERIALS

Abstract

There has been increasing attention on the development of green synthetic methodologies for synthesizing a wide range of nanomaterials including metal/metal oxides nanomaterial as it is observed sustainable, effective and ecological method for the application as an effective nanocatalyst. It has been well demonstrated that nanomaterials are significant class of materials that involves of an extensive range of examples with dimensions in the range of 1 to 100 nm size. There has been an incredible improvement in recent years, for the synthesis of nano and microparticles with selective shape and size because of their exceptional physical-chemical properties. There has been a need to develop techniques to reduce the destructive effects associated with the traditional methods of synthesis for nanoparticles commonly utilized in laboratories and industry. To develop greener approaches for the synthesis of nanomaterials it has been observed that transition-metal nanoparticles possess a wide scope of applications as they carry multiple oxidation states and improved surface area which proves a better reactivity when compared to their bulk counterpart and rendering them an interesting research topic. This chapter aims to explore greener synthesis of transition-metal oxide-based nanomaterials mainly involving Cu_2O, NiO, & MgO nanomaterials with their characterization by different spectral techniques. Moreover, the application of Copper Oxide, Nickel Oxide & Magnesium oxide nanomaterials in organic transformations suggests a greener pathway for the synthesis of varied organic compounds with effective results.

Keywords: Nanomaterials, Transition Metal Oxide, Crystal structure, Catalytic properties

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I. INTRODUCTION

A few years before in chemical research the study of nanoparticle & its application is a considered as challenging area as very less knowledge about them is available, since the study of nanoparticles were an untouched area by researchers, as it has been understood that nanomaterials primarily in the form of dust and smoke. They were utilized in materials used in construction, stained glass, and in pigments, well before their nature and properties were revealed and understood **[1]**. The better catalytic activity of nanoparticles (NPs) is a rich source both in industry and in academia to perform various chemical processes **[2,3]**. NPs have diverse applications in effective energy transformation & its restoration, bulk chemical manufacturing, environmental technology, and in biological applications **[4,5].** It has been observed in last few years that there has been extensive applications of transition metal nanoparticles as heterogeneous catalysts and it has generated outstanding revenues for petrochemical companies. It is seen that NPs often exhibit distinctive quantum properties which is well diverse from its parent bulk materials because of their unique differences in sizes and shapes. The great interest in nanocatalysts has encouraged their synthesis by different methods and investigation of highly different functionalized NPs as nanocarbon catalysts, nano graphene-based compounds, and also several metal nanostructures **[6-11].** This advanced methods are well studied & assisted by improved developments in synthetic methodology which shows varied compositions, shapes, sizes and structures of NPs.

NPs are functional materials comprised of material with at least dimensions below 100 nm and show some distinctive properties at the nano level. Metals obtained from earth has been utilized for the preparation of nanomaterials which has gain considerable attention because of their catalytic property & proved to be practicable alternatives as rare and inexpensive noble metal catalysts & hence applied to numerous conventional commercial chemical methods **[12]**. In the past few decades researcher has observed that catalysis has undergone great improvisation concerning its size, shape and composition concerning catalytic material properties is a concern. A lot of researchers have made efforts in the modification of surface characteristics of catalysts at the nanoscale level, which has led to the beginning of nanocatalysis **[13, 14]**. The catalytic properties of nanoparticles is directly associated with the increase of the surface-to-volume ratio at the nanoscale level, which increases available surface area and active site density required for catalytic reaction. In particular, nanocrystalline oxides have been observed to be advantageous to researchers in the laboratory and industry due to their good activation properties and improved reaction rate, greater selectivity, easy work-up procedures, recyclability of the supports, and ecofriendly reaction conditions **[15].**

The great diversity of oxide compounds can be achieved by using metal elements, which can help to adopt structural geometry possessing metallic, semiconductor or insulator characteristics **[16]**. For industrial applicability, effective catalysts should involve an oxide as an active phase, promoter or support for better reaction conversions. At the nanoscales, these catalytic materials are effective enough to show diverse physical and chemical properties due to their nano size and high density such as edges, corners, and point defects **[17]**. Oxide materials can present ionic or mixed ionic conductivity and it is experimentally well established that both can have influence the nanostructure of the solid **[18]**. The advanced structural and electronic properties of this materials certainly drive the physical and chemical properties of the solid due to their effective naosize with wide range of band gaps and a low reactivity. A decrease in the average size of an oxide particle imparts a change in band gap

with change in the overall conductivity and chemical reactivity. Overall study suggests that the nanoparticles to be more reactive because of their higher surface area and low coordinating sites. The improved surface area of the catalyst increases enormously when size decreases upto nano levels which implies higher catalytic activity with improved efficiency, selectivity and yield of catalytic processes **[19-20]**. Thus, metal oxide nanoparticles are found to be effective heterogeneous catalysts to convert many organic transformations as a part of their improvised morphological structure & properties.

II. SYNTHESIS OF NANOMATERIALS

Nanomaterials can be mainly be synthesized by two approaches one is Top-Down approach and Bottom-up approach depending upon the starting materials used for its synthesis.

1. **Top Down Approach:** In this approach the bulk /bigger size materials are processed to produce nanostructured/smaller materials. For this different methods employed for the synthesis of nanoparticles by using bottom up approaches are-

- **Mechanical Milling:** It is considered as economical method for producing materials at nano-level from bulk materials. Mechanical milling is used to produce oxide and carbide supported aluminum alloys, wear resistant coatings, metal-based nano alloys and for preparation of nanocomposite materials **[21].**

- **Lithography:** It is a useful tool for preparation of nano-structure materials of size range of 1 to 100 nm by irradiating beam of light or electrons. Lithography has two main types: masked lithography and maskless lithography.

- **Sputtering:** By this method nanomaterials are produced by irradiating high energy particles on solid surfaces with plasma or gas. It is cost effective method in which thin films of nanomaterials is produced by bombarding high energetic gaseous ions on the solid surfaces **[22].**

- **Arc Discharge Method:** In this method, a direct current arc voltage is applied across two graphite electrodes which is immersed in an inert gas such as helium. This method is suitable in the preparation of fullerene based nanomaterials.

- **Laser Ablation:** It is most common method for nanoparticle generation by irradiation of laser beam on target material which vaporizes source material due to the high energy of the laser irradiation resulting into nanoparticle preparation. The use of laser ablation technique for the generation of metal nanoparticles is considered as a grenner technique as in this no need of using stabilizing agents or chemicals **[23]**. The range of nanomaterials can be effevtively produced through this reliable method like metal nanoparticles **[24]**, carbon based nanomaterials **[25-26]**, oxide based composites **[27]** & ceramics **[28]**.

2. Bottom-up Approaches

- **Chemical Vapor Deposition (CVD):** Chemical vapor deposition is the deposition of a thin film of gaseous reactants onto a substrate via the chemical reaction. The deposition is carried out in a reaction chamber at ambient temperature by combining gas molecules. A chemical reaction occurs when a heated substrate comes in contact with the combined gas. This reaction produces a thin film of product on the substrate surface that is recovered and used. Due to high temperature the decomposition of the gas releases carbon atoms, which recombine to form carbon nanotubes on the substrate **[29]**.

- **Solvothermal and Hydrothermal Method:** In the hydrothermal method heterogeneous reaction is carried out in an aqueous medium at high pressure and temperature around the critical point in a sealed vessel to produce nanostructured materials **[30]**. The main difference between solvothermal method & Hydrothermal Method is that the solvothermal method is carried out in a non-aqueous medium & hydrothermal method in an aqueous medium at high pressure & temperature **[31]**. The use of microwave technique for hydrothermal method has recently received importance for preparation engineering nanomaterials **[32]**.

- **Sol-Gel Method:** This method is commonly used for the development of various classes of high-quality metal-oxide-based nanomaterials & it is considered as a wet chemical technique. In this technique, the liquid precursor is converted to a sol and the sol is then converted into a network structures that is entitled a gel, for the synthesis of the metal-oxide nanoparticles. The nanoparticles synthesis by the sol-gel method can be completed in several steps. In the first step, the hydrolysis of the metal oxide takes place in water or using alcohol to form a sol & in next step, the condensation carried out to increase in the solvent viscosity for preparation of porous structures which is allowed to keep long time. In the condensation process, hydroxo (M-OH-M) or oxo (M-O-M) bridges are formed which results in the formation metal-hydroxo or metal-oxo-polymer in solution **[33]**. The polycondensation continues in aging process with results in the change in the structure, properties, and porosity. The aging process results for decreases in porosity and the distance between the colloidal particles increases. In drying process the efforts are done to remove water and organic solvents from the gel followed by calcination to achieve nanoparticles.

- **Microemulsion method or Reverse Micelles:** Thermodynamically stable phase of water and oil which is formed with coordination of surfactants are called as microemulsion. This is categorized as normal microemulsion i.e. oil-in-water or reverse water-in-oil **[34]**. Reverse micelle process involved two immiscible liquids which are mixed and stirred to form emulsion. In this method surfactants were terminated by hydrophilic and hydrophobic groups on opposite ends then tiny drops called as micelles are formed. These micelles are found to be thermodynamically stable which can be acts as nonreactors.

3. **Green or Biological Synthesis:** Biological materials like plant extract and microorganisms including bacteria, fungi, algae, yeast and actinomycetes were used in the synthesis of nanoparticles. It is considered as ecofriendly, simple and cost effective

method for synthesis of nanoparticles. The progress of efficient green synthesis utilizing natural reducing, capping and stabilizing agents without the use of toxic, expensive chemicals and high energy consumption have attracted researchers towards biological methods **[35]**.

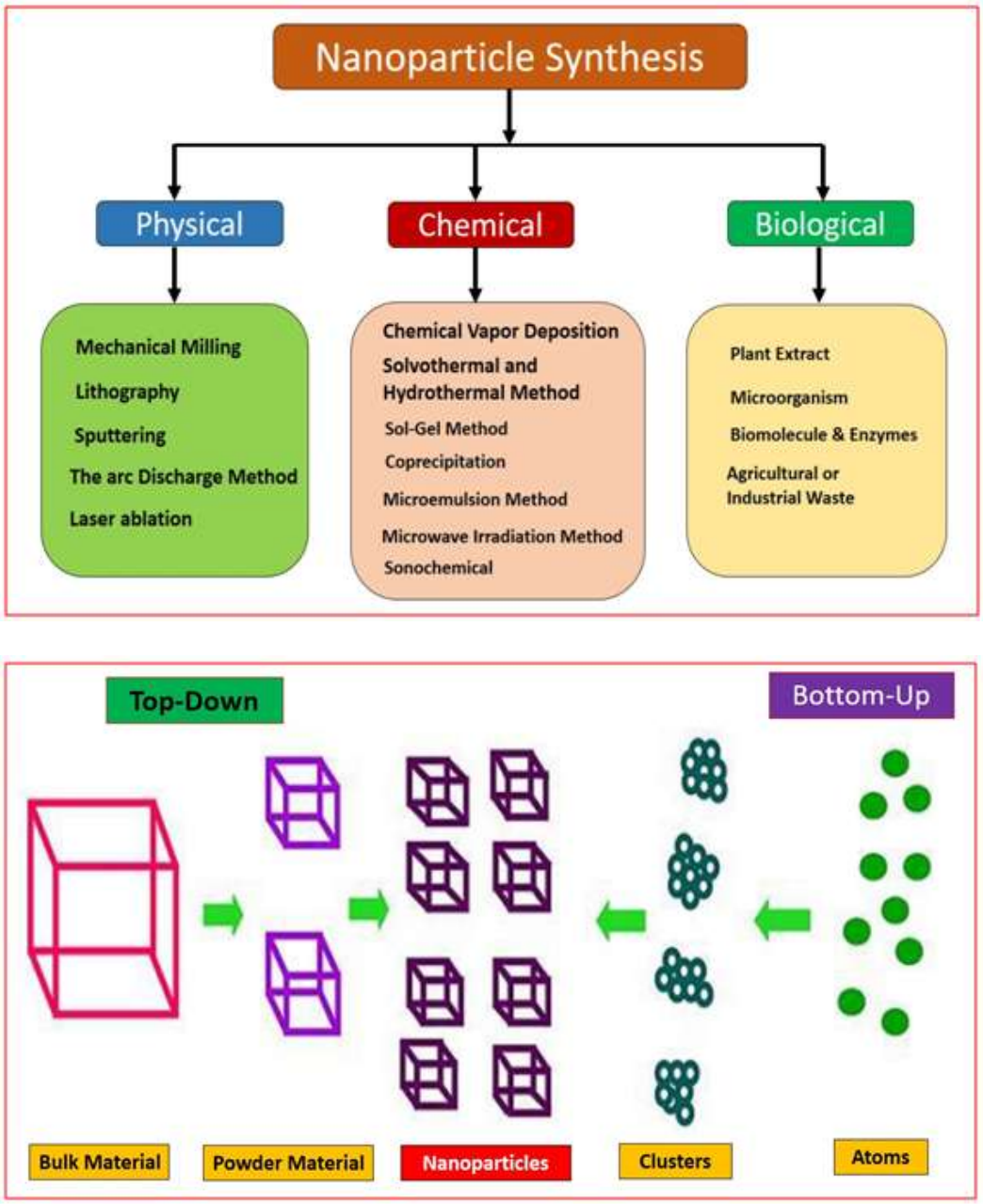


Figure 1: The Top-Down and Bottom-up Approaches for the Synthesis of Nanomaterials

Most of the methods discussed for the synthesis of nanomaterials were selective & are in the nano range but they have certain drawbacks such as use of excess and toxic reagents, use of high temperature and pressure for the reaction, multistep synthesis, requirement of extra capping agents, use of reducing agents, utilization of expensive reagents, long reaction time. Most of the method required high energy consumption, use of specialized instrument set-up and addition of external additives during the reaction.

Hence there is increasing demand for development of simple procedures, greener route, robust conditions, economic and convenient method for synthesis of metal oxide nanoparticles which are superior & eliminates drawbacks & exhibit better catalytic activity.

III. METHODOLOGY

1. **Copper Oxide Based Nanoparticles:** Copper metal is from transition metal and possessing some interesting physio-chemical properties **[36]**. The various reports explain that Copper-based materials can promote ranges of reactions due to its varied oxidation states (Cu^0, Cu^I, Cu^{II}, and Cu^{III}), which enable reactivity. Copper-based nanocatalysts have shown numerous applications in nanotechnology, including their catalytic activity to transform organic reactions due to its distinctive characteristics and properties.

   - **Greener Synthesis of Copper Oxide Nanoparticles:** The simple and efficient synthesis is reported for the preparation of Copper oxide (Cu_2O & CuO) nanoparticles in aqueous medium by using copper precursors, bases and capping agents. The results show formation of uniform cubic, wire, rod and belt shaped Copper oxide NPs (**Table 1**). This method explores the formation of Cu_2O nanoparticles by using ascorbic acid & formation of CuO nanoparticles by using cinnamic acid, oxalic acid, adipic acid, fumaric acid & succinic acid with the same reaction conditions. It is seen that, each earlier mentioned capping agent has different binding sites to bind the nanoparticles & it results in the formation of different morphology of nanoparticles. The diffrent bases such as NaOH, KOH and Na_2CO_3 are used & it shows impact on the surface morphology of synthesized Copper Oxide Nanoparticles. The reaction is carried out at room temperature having less reaction time & synthesized nanoparticle shows excellent catalytic activity [**37**].

Table 1: The use of different Copper Precursors, bases and Capping Agents to Achieve Morphology of Selective Nanostructures

Copper Precursors	Capping Agents	Bases	Morphology of Nanostructures
Copper Acetate	Ascorbic Acid	NaOH	Cu_2O Nanocubes with particle size in the range 200 nm to 500 nm. CuO Nanorods, Nanowires, Nanobelts with particle size 40–120 nm
Copper Chloride	Cinnamic acid	KOH	
Copper Nitrate	Oxalic Acid	Na_2CO_3	
Copper Sulphate	Adipic Acid		
	Fumaric acid		
	Succinic Acid		

   - **Ultrasound Assisted Synthesis of Cu_2O:** The sonochemical reduction method were employed for the synthesis of Cu_2O nanocubes by taking Copper Sulfate pentahydrate (0.01 M) ($CuSO_4.5H_2O$) in a sonication vessel under nitrogen atomosphere to provide inert conditions. The Ascorbic acid (0.01 M) were dissolved in of ethylene glycol (15 ml) & added slowly to the $CuSO_4.5H_2O$ solution under vigorous stirring at room temperature during 20 min. Ascorbic acid acted both as an antioxidant and reducing agent as it act as protective agent to prevent the oxidation of Cu_2O to CuO. Then PVP (0.04 g) used as stabilizing agent & added to the above mixture with continuous

stirring and followed by slow addition of NaOH (1 M) to maintain the pH around 11. The color of the mixture has changed to green at this pH range. The green colour solution changed to yellow and to a deep orange color indicating the formation of Cu_2O nanocubes **[38-39]**.

- **Greener Synthesis of CuO Nanoparticles using Plant Extract:** The plant materials *Lantana camara* were isolated which is clean & dried. The 2.5 wt% plant extract solution in water is prepared for the synthesis CuO. The Copper (II) Acetate solution (0.375 M), plant extract (2.5 wt%) and water were mixed together in vessel under continuous stirring at 65 ^oC. Then NaOH solution (1.125 M) was added dropwise to raise the pH-12 of the reaction mixture. The reaction mixture was further heated under stirring for around 2 h. The reaction mixture was then cool to room temperature & the product was isolated by centrifugation, dried in an oven & subjected to calcination at 400 ^0C for 2 h. Flower extract of *Lantana camara* plant used as capping cum shape directing agent to control the spherical shape of CuO NPs with size 15-40 nm with excellent catalytic activity **[40]**.

- **Microwave assisted synthesis of Copper Oxide NPs:** Copper (II) nitrate hemipentahydrate $Cu(NO_3)_2$. 2.5 H_2O was added to deionized water then sonicated for 1 hr. Then hydrazine hydrate were added to the entire mixture & heated using a microwave oven, filtered, washed with deionized water. Then dried in an oven till constant weight of catalyst is obtained. The synthesized CuO nanoparticles noticed of size around 20 nm & possessing high catalytic activity **[41]**.

- **Microwave Assisted Synthesis of Cuprous Oxide:** The $Cu(CH_3COO)_2$ [0.4 g] is dissolved in benzyl alcohol [20 mL] & transferred to teflon liner tube which is kept inside a microwave oven for 3 min at 600 W. Afterwards colourless reaction mixture observed to be changes to dark red indicating formation of cuprous oxide. The reaction mixture was then added a small quantity of above mother liquor quantity and it was subjected to centrifugation to separate the product. The isolated product was washed with absolute ethanol and at 60 °C for 4 h to obtain powdered Cu_2O. The results showed that the size of Cu_2O particles was in the nano region & possessing good catalytic activity **[42].**

- **Microwave Assisted Synthesis of Cuprous Oxide:** The $Cu(CH_3COO)_2 \cdot H_2O$ [0.5 g] was mixed to 1,3-propanediol [10 mL] in a 100 mL glass beaker and placed inside a domestic microwave oven for 3 min at power 600 W for 30 s. The reaction progress was observed with change in colour of the reaction mixture from blue to brick-red, justifying the formation of Cu_2O. The product was separated & washed with distilled water and absolute ethanol and dried 70 °C for 1 h. The morphology of the Cu/Cu_2O NPs seems to be slightly irregular and it was observed that the particles are in the nano region, with particle size ranging from 70 nm to 110 nm, which has high surface area for catalytic activity **[43]**.

2. Nickel Oxide Based Nanoparticles

- **Microwave Assisted Synthesis of NiO:** The NiO nanorods were synthesiszed by taking Nickel Acetate (0.5 gm) & dissolving in 1,4-butanediol (5 ml) in glass beaker

and kept inside the domestic microwave oven for 2 min at 360 W. After microwave heating, the reaction progress was monitored by change in the colour from a blue to green indicating the formation of $Ni(OH)_2$ powder. The synthesized $Ni(OH)_2$ was collected by centrifugation & residue was washed with absolute ethanol with drying under vacuum at 80 ^oC. The gray black coloured NiO nanomaterials were obtained by calcinations of $Ni(OH)_2$ powder at 400 ^0C in a furnace. The morphology of NPs shows that the formation of NiO nanorods with spherical as well as cubic shapes & has applicability to use as as a catalyst **[44]**.

- **Microwave Assisted Synthesis of Nickel Oxide Nanomaterial:** The mixture of of $Ni(CH_3COO)_2$ [1.0 g] was added to benzylamine [10 mL] & transferred to Teflon liner tube which is kept inside the microwave oven for 2 min at 360 W. After microwave heating, reaction mixture changes to green colored turbid solution indicating formation of $Ni(OH)_2$ which is then washed with distilled water and ethanol. The $Ni(OH)_2$ was separated by centrifugation dried in an oven, which on calcination at 400 ^0C for 5 h to get NiO NPs. In this Benzylamine plays various role such as solvent, promoter and base under microwave irradiation. The particles of NiO are in nano range of 4-12 nm with well dispersed & exhibits remarkable catalytic activity with recyclability **[45].**

- **Ultrasound Assisted Synthesis of NiO:** The $Ni(OAc)_2$ (1.0 g) & α-cyclodextrins (200 mg) mixture were dissolved in distilled water (20 mL). Then drop wise addition of benzylamine (10 mL) gave formation of a light green coloured precipitate. The solution was irradiated under ultrasound for 90 pulses at 30 amplitude. Green coloured $Ni(OH)_2$ was formed and thereafter it was separated by centrifugation & washed with distilled water followed by ethanol washing. The product was dried at 80 ^0C in an oven. The cyclodextrin act as capping agent leads to formation of aerated nano-structure in the nano range **[46]**.

- **Synthesis of NiO Nanoparticles:** The Nickel Acetate (0.5 g) and of water 2.5 mL were added in to flask containing of methanol (50 mL). The solution was heated to 60 ^0C. To this solution, potassium hydroxide (KOH, 0.5 g) was added followed by methanol was slowly dropped in above reaction mass. After heating for 2 hrs at 60 ^0C, a small amount of water was added to increase the NiO nanocrystal growth. Dried this under vacuum, the precursors were calcined in an oven, then NiO nanoparticles were obtained with promising catalytic activity **[47]**.

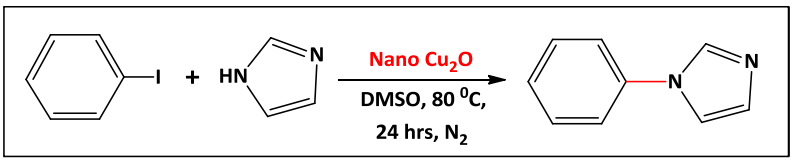
3. Magnesium Oxide Based Nanoparticles

- **Synthesis of MgO Nanoparticles under Microwave Irradiation:** The mixture of $Mg(CH_3COO)_2 .4H_2O$ (1.0 g) and Benzylamine (10 mL) was transferred to Teflon tube and kept in a microwave oven for 2 min at 360 W. After microwave heating, the white turbid precipitate was formed which indicates the formation of $Mg(OH)_2$ NPs. These particles were separated by centrifugation and then washed twice with distilled water followed by ethanol. The calcination of $Mg(OH)_2$ NPs was carried in an oven at 550 ^0C for 5 h. It shows higher surface area, stronger basic sites & observed good catalytic activity towards organic transformation **[48]**.

- **Synthesis of Magnesium oxide by Greener Approach:** A Magnesium Acetate (1.0 g) and 1,4-Butanediol (5 mL) were mixed in a round bottom flask having air condenser. Then this mixture were irradiated under solar radiations for 6 h of stirring for one minute interval of 30 min irradiation. As this solar effect is spatial and progressive to protect the repeatability, so each experiment was carried out in noon time during summer days. Methanol (5 mL) was then added to the reaction mass and subjected for high speed centrifugation for 20 min to separate white mass. The calcination at 400 °C for 5 h was then carried out to get nanocrystalline MgO in the range of 5-20 nm which was found to be excellent and reusable catalyst **[49]**.

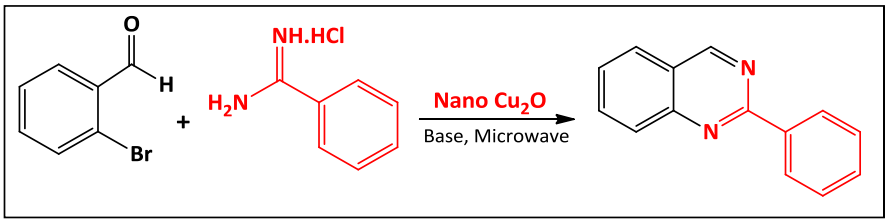
IV. CATALYTIC APPLICATION METAL OXIDE NANOPARTICLES

1. **Catalytic Applications of Copper oxide Based NPs:** Copper Oxide NPs were prepared by using precursor Copper Sulphate & ascorbic acid as a capping agent for the Carbon-Nitrogen bond formation of Buchwald-Hartwig amination reaction, this synthesized NPs are having cubic shape and size. For this reaction was performed by taking Iodobenzene, Imidazole, Nanocatalyst Cu_2O (10 mol%), KOH (2 mmol) & DMSO for about 24 hrs at temperature 80 ^oC. The reaction gives excellent yield (94%) for the formation of 1-phenyl-1H-imidazole [37] [Scheme 1].



Scheme 1: Catalytic Application of Copper Oxide NPs for coupling reaction of Iodobenzene with Imidazole

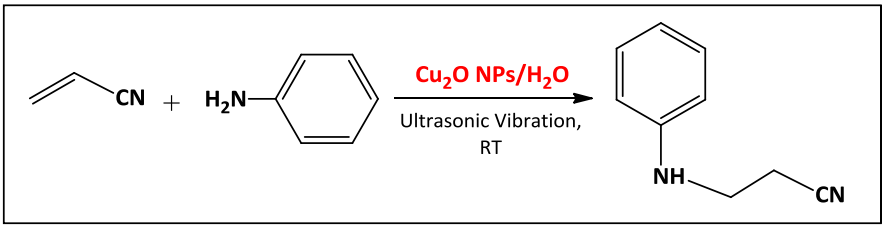
The reaction was held by reacting 2-Bromobenzaldehyde & Benzamidine hydrochloride in the presence of Cu_2O nanocatalyst, which is prepared by ultrasound assisted synthesis **[38-39]**, base & solvent under domestic microwave for 4 minutes. The reaction was optimized by reacting 2-Bromobenzaldehyde with Benzamidine hydrochloride in the presence of Cu_2O nanocatalyst (5 mol%), Cs_2CO_3 (2.0 equivalent) in ethylene glycol at 160W microwave for 4 minutes gives 2-phenylquinazoline in 51% to 90% yield **[Scheme 2]**.



Scheme 2: Catalytic Application of Copper Oxide for the synthesis of 2-Phenylquinazoline

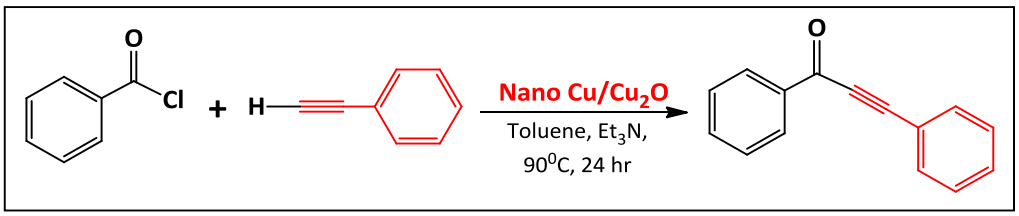
The flower plant *Lantana Camara* was identified for extraction of phytochemicals its water extract (2.5 wt%) solution was prepared for the synthesis of Cu_2O nanoparticles as per mentioned in section **3.3**. The aza-Michael addition reaction has optimized to prove

good catalytic activity of the prepared CuO NPs under room temperature & ultrasonic vibrations. For this substrate Acrylonitrile (65 ml, 1 mmol) and aniline (91 ml, 1 mmol) was reacted by using CuO (1 mg, 0.012 mmol) as a nanocatalyst at room temperature & under solvent-free conditions. The substrates were taken in a round bottom flask which is with a reflux condenser and stir till progress of the reaction. After reaction completion the reaction the products are extracted from ethyl acetate & water **[40]**. The CuO nanocatalyst exhibits good catalytic activity towards the Aza-Michael reaction by taking substrate Acrylonitrile with primary/secondary aliphatic and aromatic amines under ultrasonic vibration. This protocol gives a greener pathway to prepare ranges of substituted Aza-Michael products with better results & conditions **[Scheme 4].**



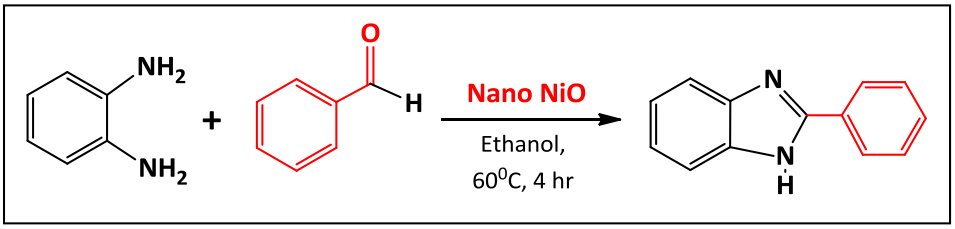
Scheme 4: Aza-Michael addition reaction catalyzed by CuO NPs

The microwave assisted synthetic method was developed for the preparation of Cu/Cu_2O nanoparticle as per mentioned in earlier section **3.5**. The greener path demonstrated for the preparation of nanocrystalline Cu/Cu_2O showed better good results for the Sonogashira coupling reaction of Alkynes with Acyl chlorides **[43]**. To set reaction conditions Phenylacetylene (1 mmol) was reacted with Benzoyl Chloride (1.2 mmol) by taking nanocatalyst Cu_2O (10 mol%), Triethyl amine (2 mmol) in toluene (2 mL) at temperature upto 90 °C for 24 h under inert atmosphere to give good yields of the corresponding products **[Scheme 5]**.



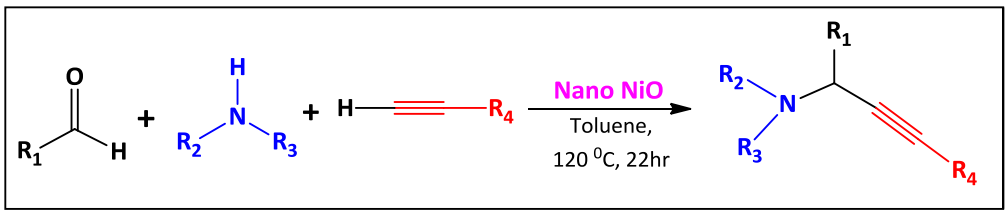
Scheme 5: Cu_2O catalysed Sonogashira coupling reaction of Phenylacetylene with Benzoyl Chloride

2. **Catalytic Applications of Nickel Oxide Based Nanoparticles:** The synthesis of NiO has been carried out under microwave assisted method for this Nickel (II) Acetate was taken as a precursor in solvent 1,4-butanediol as per mentioned earlier in section **3.5**. The NiO nanorods obtained by this method shows good catalytic activity for greener synthetic route for the preparation of substituted benzimidazole, benzothiazole and benzoxazole. For this reaction, o-Phenylene Diamine (1 mmol) was mixed with Benzaldehyde (1 mmol) and nanocatalyst NiO (10 mol%) under ethanol as a solvent **[44]**. Then the reaction mass was stirred at 60 ^{0}C for about 4 h & the product was obtained after extraction from ethyl acetate to give good yield of products **[Scheme 6].**



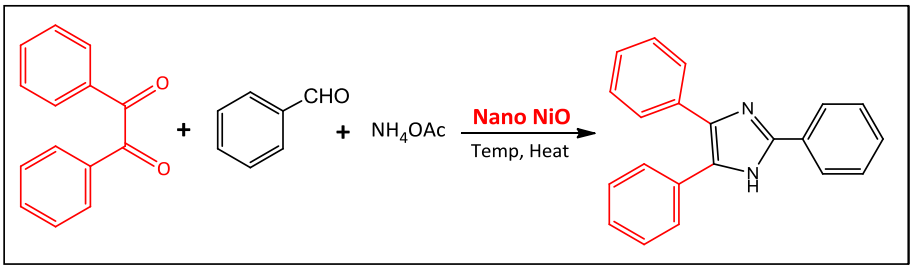
Scheme 6: Synthesis of 2-substituted benzimidazole by using Nano NiO

Microwave assisted efficient protocol for the preparation of Nickel oxide NPs was developed by taking Nickel Acetate and Benzylamine as mentioned in earlier section **3.6**. For this reaction, aldehyde, amine & terminal alkynes is taken as a three component coupling system with heterogeneous catalyst NiO to show good yield of respective products. To optimized reaction parameters, the aldehyde (1.0 mmol), amine (1.2 mmol), phenylacetylene (1.5 mmol) were coupled bu using NiO nanocatalyst (15 mol%) and toluene as a solvent at 120 °C for 22 h under inert atmosphere **[45] [Scheme 7]**.



Scheme 7: The coupling of Aldehyde, Amine & Terminal alkyne in presence of Nano NiO

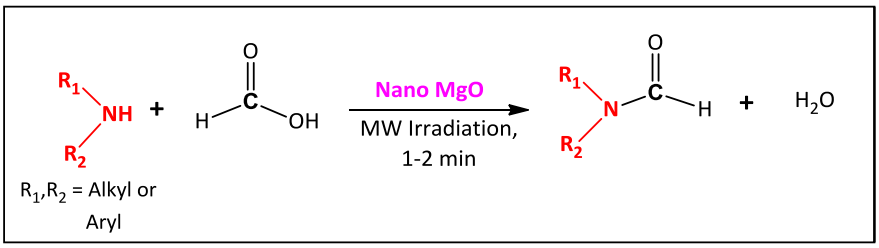
The NiO nanoparticles were prepared under ultrasound assisted system by taking Benzylamine as a base and cyclodextrins as capping agents as mentioned in earlier section 3.7. The NiO NPs were effectively catalyzed preparation of 2,4,5-Trisubstituted Imidazole. For this reaction, the 1,2-Diketone (1 mmol) is mixed with Aldehyde (1 mmol), Ammonium Acetate (2.5 mmol) in a reaction vial and of NiO NPs (10 mg) as a catalyst. The reaction was carried out at 120 ^{0}C. After the reaction completion the solid product was extracted from ethyl acetate (20 mL) and the catalyst was separated & washing with water and ethanol. The product obtained was recrystallized from ethanol to give corresponding 2,4,5-Trisubstituted Imidazoles **[46] [Scheme 8]**.



Scheme 8: The nano NiO catalyzed synthesis of 2, 4, 5-Trisubstited Imidazole

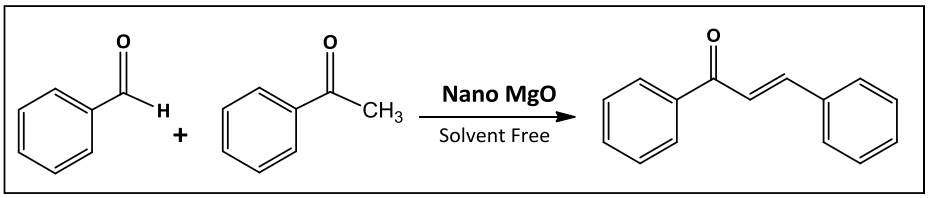
3. **Catalytic Applications of Magnesium Oxide Based Nanoparticles:** The Magnesium Acetate was mixed with Benzylamine under microwave irradiation for the preparation of

MgO nanoparticles as mentioned in earlier section 3.9. For the formylation of amines, the reactions was performed by taking an Amine (1 mmol) with formic acid (3 mmol) and MgO NPs (20 mg) under microwave irradiation at 480 W for about 2 min to produce N-formylation products with good results of products **[48] [Scheme 9]**.



Scheme 9: The nano MgO catalyzed N-formylation of Amines

The Magnesium Acetate and 1,4-butanediol was mixed under solar radiations for the preparation of nanocrystalline MgO through greener approach as mentioned in earlier section 3.10 & effectively catalyzed Claisen-Schmidt condensation reaction. For this protocol the Benzaldehyde (1.2 mmol), Acetophenone (1 mmol) was reacted by taking MgO NPs (0.1 mmol, 10 mol %) under solvent free condition. The reaction was stirred for around 4 h at 140 °C. After the reaction is over ethyl acetate was added to the reaction mass and the catalyst was separated to isolate product **[49]**. Thus MgO NPs were applied as a catalyst in Claisen-Schmidt condensation reaction for the chalcone synthesis under solvent free reaction conditions **[Scheme 10]**.



Scheme 10: MgO NPs catalysed Claisen-Schmidt condensation reaction

Thus, the nanoparticle was observed to be more reactive due to its higher surface area and low coordinating sites. It has been shown that the surface area of the catalyst increases immensely when size of material decreases to nano levels which are having good catalytic activity and have the potential for improving the efficiency, selectivity and yield of catalytic processes. In the present part, few green synthetic methodologies for the synthesis of Cu_2O, NiO, & MgO nanocrystalline catalyst has been discussed with their catalytic potential to convert organic transformation with more effective way to provide good result as compared to conventional catalyst.

V. CONCLUSION

It has been observed that from last few years greener approach for the synthesis of metal & metal oxide nanoparticles has been a highly attractive research area as it is a sustainable way to perform many chemical conversions in an environmentally benign way. To summarize it can be concluded that, the metal oxide nanoparticles proved to be a greener

approach with reaction conditions are competitively milder and catalyst satisfactorily catalyzed the synthesis of most of the organic compounds with more simple experimental procedures. So there is a lot of scope and good potential in future to improve the functioning of such metal oxide nanocatalysts on large scale to achieve sustainable outputs in greener way.

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