Green Synthesis of Metal and Metal

Oxide Based Nanomaterials & Their

Catalytic Applications

**Dr. Vikrant S. Palekar**

Assistant Professor, Department of Chemistry,

Gokhale Education Society’s, Arts, Commerce & Science College, Jawhar,

Palghar-401 603, Maharashtra, India

E-Mail: vspalekar82@gmail.com

ABSTRACT

Green synthesis has gained extensive attention as a sustainable, effective and ecological methodology for synthesizing a wide range of nanomaterials including metal/metal oxides nanomaterials, advanced materials and materials in the form of nanocatalyst. Nanomaterials are found important class of materials that consists of a extensive spectrum of examples with at least one dimension in the range of 1 to 100 nm. There has been a incredible improvement in the recent years in the shape and size selective synthesis of nano and microparticles because of their excellent and unique physical-chemical properties. Green synthesis is regarded as an important technique to reduce the destructive effects associated with the traditional methods of synthesis for nanoparticles commonly utilized in laboratory and industry. Transition-metal nanoparticles possess a wide scope of applications due to their multiple oxidation states and large surface areas, thereby allowing for 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 nanomaterial mainly involve Cu2O, NiO, & MgO nanomaterials with their characterization by different spectral techniques. Moreover the application of synthesized transition-metal oxide based nanomaterials for their catalytic application in organic transformations suggesting greener pathway.

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

# 1. INTRODUCTION

 In Chemical research the study of nanoparticle application is a considered as younger branch. Few years ago, these words would have sounded surprising to many researcher despite the fact that nanoparticles, primarily in the form of dust and smoke. They were utilized in construction materials, pigments, and stained glass well before their nature and properties were uncovered and understood **[1]**. The catalytic activity of nanoparticles (NPs) represents a rich resource for chemical processes, employed both in industry and in academia **[2,3]**. NPs have applications in diverse fields, including energy conversion and storage, chemical manufacturing, biological applications, and environmental technology **[4,5]**.It has been observed from last few years, transition metal nanoparticles were extensively promoted as heterogeneous catalysts and generated notable revenues for petrochemical companies. NPs often exhibit activity different from that of the corresponding bulk materials because of their different sizes, shapes, which give rise to distinctive quantum properties. The great interest in nanocatalyst has encouraged its synthesis by diverse methods and exploration of highly diverse functionalized NPs including nanocarbon catalysts, graphene-based catalysts, and magnetite supported nanocatalysts and also various metal nanostructures **[6-11]**. The study of these diverse methods has been assisted by speedy developments in synthetic methodology that have supported the preparation of NPs with variable compositions, shapes, sizes, and structures, which are on their own or supported on other materials.

Nanomaterials are functional materials comprised of material with at least one dimension below 100 nm and show some distinctive properties at the nano level. A considerable attention has been attracted by nanomaterials prepared from earth abundant and inexpensive metals because of their potential as practicable alternatives to the rare and expensive noble metal catalysts used in many conventional commercial chemical processes **[12].** Researcher has observed from the past few decades, catalysis has undergone path breaking improvisation with respect to size, shape and composition of the catalytic material is concern. A lot of researchers have made efforts in tuning and modification of surface characteristics with fundamental understanding of catalysts at nanoscale which has led to the emergence of Nanocatalysis **[13,14**]. The catalytic properties of nanoparticles can be directly associated with the increase of the surface to volume ratio at the nanoscale level, which increases both available surface area and active site density for catalytic reaction. In particular, nanocrystalline oxides have proved to be useful to chemists in the laboratory and industry due to the good activation of adsorbed compounds and reaction rate enhancement, selectivity, easier work-up, recyclability of the supports and the eco-friendly reaction conditions **[15].**

The metal elements can form a great diversity of oxide compounds, which can adopt structural geometry with an electronic structure which has metallic, semiconductor, or insulator character **[16]**.Forindustrial applications of catalysts involve an oxide as active phase, promoter or support for better conversions. At the nanoscales, these compounds can show unique physical and chemical properties due to their limited size and a high density of defect sites 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 structural and electronic properties obviously drive the physical and chemical properties of the solid, and this properties is influenced by size. In the bulk state many oxides, have wide band gaps and a low reactivity. A decrease in the average size of an oxide particle does in fact change the magnitude of the band gap with changes in the conductivity and chemical reactivity. In general, the nanoparticle is considered to be more reactive because it offers higher surface area and low coordinating sites. The surface area of the catalyst increases tremendously when size decreases to nano levels which are responsible for the higher catalytic activity and have the potential for improving the efficiency, selectivity and yield of catalytic processes **[19-20]**. Metal oxide nanoparticles are found to be promising heterogeneous catalysts in a variety of organic transformations due to its improvised morphological structure & properties.

# Synthesis of Nanomaterials

Two main approaches are used for the synthesis of nanomaterials top-down approaches and bottom-up approaches.

1. **Top-Down approaches :** In top-down approaches, bulk materials are divided to produce nanostructured materials. Different methods for the synthesis of nanoparticles via bottom up approach are-
2. **Mechanical Milling**: Mechanical milling is an effective method for producing blends of different phases and in the production of nanocomposites. It is used to produce oxide and carbide strengthened aluminum alloys, wear resistant spray coatings, aluminum/nickel/magnesium/copper-based nano alloys, and many other nanocomposite materials **[21].**
3. **Lithography** : Lithography is a useful tool for developing nano architectures using a focused beam of light or electrons. Lithography has two main types: masked lithography and maskless lithography.
4. **Sputtering**: Sputtering is a process used to produce nanomaterials by bombarding solid surfaces with high energy particles such as plasma or gas. Sputtering is considered to be an effective method for producing thin films of nanomaterials **[22].**
5. **The Arc Discharge Method**: In this method a vapor is created by an arc discharge between two carbon electrodes in the presence of a catalyst. The two graphite rods are adjusted in a chamber in which a certain helium pressure is maintained. Filling the chamber with pure helium is important as the presence of moisture or oxygen inhibits fullerene formation. This method has great significance in the generation of fullerene nanomaterials Carbon rod vaporization is driven by arc discharge between the ends of the graphite rods.
6. **Laser ablation** : It involved synthesis of nanoparticle generation using a powerful laser beam that hits the target material. During this the source material or precursor vaporizes due to the high energy of the laser irradiation, resulting in nanoparticle formation. The use of laser ablation technique for the generation of noble metal nanoparticles can be considered as a green technique, as there is no need for stabilizing agents or other chemicals **[23]**. A wide range of nanomaterials can be produced through this technique such as metal nanoparticles **[24]**, carbon nanomaterials **[25-26]**, oxide composites **[27]**, and ceramics **[28]**.
7. **Bottom-up Approaches :**
8. **Chemical Vapor Deposition (CVD) :** In this method a thin film of gaseous reactant is deposited on the substrate surface via the chemical reaction of vapor-phase precursors. The deposited thin film when takes place in reaction chamber then a chemical reaction takes place as combining gas in contact with the heated substrate, due to which on the surface of substrate a thin film of product produced. During the generation of carbon nanotubes by CVD method a substrate is placed in an oven and heated to high temperatures. Afterwards a gas containing carbon/hydrocarbon is slowly introduced to the system as a precursor. Due to high temperature the decomposition of the gas releases carbon atoms, which recombine to form carbon nanotubes on the substrate **[29]**.
9. **Solvothermal and Hydrothermal Method:** In the hydrothermal method, nanostructured materials are attained through a heterogeneous reaction carried out in an aqueous medium at high pressure and temperature around the critical point in a sealed vessel **[30]**. The main difference between solvothermal method & Hydrothermal Method is that the solvothermal method is carried out in a non-aqueous medium. Hydrothermal and solvothermal methods are generally carried out in closed systems **[31]**. The microwave assisted hydrothermal method has recently received significant consideration for engineering nanomaterials, combining the merits of both hydrothermal and microwave methods **[32]**.
10. **The Sol-Gel Method :** This method is a wet-chemical technique that is extensively used for the development of various classes of high-quality metal-oxide-based nanomaterials. As this technique is called a sol-gel method, as during the synthesis of the metal-oxide nanoparticles, the liquid precursor is transformed to a sol and the sol is finally converted into a network structure that is called a gel. The synthesis process of nanoparticles by the sol-gel method can be completed in several steps. During the first step, the hydrolysis of the metal oxide takes place in water or with the assistance of alcohol to form a sol. In the next step, condensation takes place to increase in the solvent viscosity to form porous structures that are left to age. In the condensation or polycondensation process, hydroxo (M-OH-M) or oxo (M-O-M) bridges form results the formation metal-hydroxo or metal-oxo-polymer in solution **[33]**. Next in the aging process, polycondensation continues with changes to the structure, properties, and porosity. During aging, the porosity decreases and the distance between the colloidal particles increases. Afterwards drying takes place, in which water and organic solvents are removed from the gel. Lastly, calcination is performed to achieve nanoparticles.
11. **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 two immiscible liquids 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 in the continuous oil medium. These micelles are found to be thermodynamically stable which can be acts as nonreactors.
12. **Green or Biological Synthesis:** Biological synthesis involves the synthesis of nanoparticles by using biological materials like plant extract and microorganisms including bacteria, fungi, algae, yeast and actinomycetes. It is ecofriendly, simple and cost effective method for synthesis of nanoparticles. Since the 19th century scientists have been well aware of the ability of biological entities to reduce metal precursors. 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]**.

 

**Fig. 1 The synthesis of nanomaterials via Top-Down and Bottom-up approaches**

However, most of these methods synthesized selective nanomaterials in nano regime, but they have certain disadvantages like the use of excess and toxic reagents, high temperature and pressure, multistep synthesis, need of extra capping agents and reducing agents, utilization of expensive reagents, long reaction time which increases more energy consumption, need of specialized instrument and requirements of external additives during the reaction. Hence there is a need for development of simple, greener, robust, economic and convenient method for synthesis of metal oxide nanoparticles which overcomes the above drawbacks & exhibit excellent catalytic activity.

# Methodology

1. **Copper Oxide Based Nanoparticles:**

Copper is a 3d transition metal and has some interesting physical and chemical properties **[36]**. Cu-based materials can promote and undergo a variety of reactions due to varied oxidation states of copper(Cu0, CuI, CuII, and CuIII), which enable reactivity via both one and two-electron pathways. Cu-based nanocatalysts have found many applications in nanotechnology, including catalytic organic transformations due to its unique characteristics and properties.

**3.1 Greener Synthesis of Copper Oxide Nanoparticles:**

The simple and efficient synthesis of copper oxide (Cu2O and CuO) nanoparticles in aqueous medium is reported with use of copper precursors, bases and capping agents results show formation of uniform cubic, rod, wire and belt shaped copper oxide nanostructures (**Table 1**). The formation of Cu2O nanoparticles with ascorbic acid and CuO nanoparticles with cinnamic acid, oxalic acid, adipic acid, fumaric acid and succinic acid on same reaction conditions. It is observed that, every capping agent has different binding sites to bind the nanoparticles, result into the formation of different morphology of nanoparticles & also different bases such as NaOH, KOH and Na2CO3 has impact on the surface morphology. All the reactions were carried out at room temperature with shorter 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 | Cu2O 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 | Na2CO3 |
| Copper Sulphate | Adipic acid |  |
|  | Fumaric acid |  |
|  | Succinic acid |  |

* 1. **Ultrasound assisted synthesis of Cu2O nanocubes**

Cu2O nanocubes were synthesized via sonochemical reduction method. The copper sulfate pentahydrate (0.01 M) (CuSO4.5H2O) was taken in a sonication vessel and nitrogen gas was purged for 30 min to remove dissolved oxygen. Subsequently, ascorbic acid (0.01 M) dissolved in of ethylene glycol (15 ml) was added slowly to the CuSO4.5H2O solution under vigorous stirring at room temperature for about 20 min. Ascorbic acid acted both as an antioxidant and reducing agent as it act as protective agent to prevent the oxidation of Cu2O to CuO. Then PVP (0.036 g) used as stabilizing agent & directly added to the above mixture with continuous stirring and then NaOH (1 M) was added drop wise to maintain the pH around 11. The color of the mixture changed to green at this pH range. The green solution changed first to yellow and to a deep orange color indicating the formation of Cu2O nanocubes **[38-39]**.

**3.3 Green synthesis of CuO nanoparticles using flower extract**

The phytochemicals were isolated from *Lantana camara* plant materials, clean, dried & was used to prepare a solution of 2.5 wt% extract in water. For the synthesis CuO, copper(II) acetate solution (10 mL; 0.375 M), plant extract (30 mL, 2.5 wt%) and appropriate volume of water were mixed together in a stopper glass vessel under continuous stirring at 65 oC. After 10 minutes of stirring NaOH solution (13 mL, 1.125 M) was added dropwise to raise the pH of the reaction mixture to 12. The reaction mixture was further heated under stirring for 2 h, then the reaction mixture was allowed to cool to room temperature naturally. The product was isolated by centrifuged, dried & subjected to calcination in a muffle furnace at 400 0C for 2 h. Flower extract of *Lantana camara* plant played the role of capping cum shape directing agent to control the size 15-40 nm and spherical CuO NPs shape with excellent catalytic activity **[40]**.

* 1. **Microwave Assisted Synthesis of Copper Oxide Nanoparticles**

Copper (II) nitrate hemipentahydrate Cu(NO3)2. 2.5 H2O was added to deionized water (50 mL), then sonicated for 1 hr. Then hydrazine hydrate were added to the entire mixture & heated using a microwave oven, filtered, washed with deionized water and then ethanol, finally, dried in oven till constant weight of catalyst. The synthesized CuO nanoparticles noticed of size around 20 nm & possesing high catalytic activity **[41]**.

* 1. **Microwave assisted synthesis of nanosize cuprous oxide**

The mixture of of Cu(CH3COO)2 [0.2 g] in benzyl alcohol [10 mL] was transferred to teflon liner tube and kept inside a microwave oven for 3 min at 600 W with on off mode having time interval of 30 s. Afterwards colourless reaction mixture changes to dark red indicating formation of cuprous oxide. A small quantity of mother liquor was added to the reaction mixture and it was subjected to centrifugation to separate the product. The isolated product was then washed with absolute ethanol and dried under vacuum at 60 °C for 4 h to obtain powdered Cu2O. The results showed that the size of Cu2O particles was in the nano region **[42].**

* 1. **Microwave assisted synthesis of cuprous oxide**

Cu(CH3COO)2·H2O [0.4 g] was added to 1,3-propanediol [10 mL] in a 100 mL glass beaker and placed this inside a domestic microwave oven for 3 min at electric power 600 W for 30 s. The reaction progress was observed by the change in colour of the reaction mixture, and finally it converted from blue to brick-red, signifying the formation of Cu/Cu2O. The product was separated & washed with distilled water and absolute ethanol and dried in an oven at 70 °C for 1 h. The morphology of the Cu/Cu2O 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 leads to the availability of a high surface area for catalytic activity **[43]**.

1. **Nickel Oxide Based Nanoparticles:**

**3.5 Microwave assisted synthesis of NiO nanorods**

The synthesis of NiO nanorods is carried out by taking Nickel Acetate (1 gm) & dissolved in 1,4-butanediol (10 ml) in a 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 of reaction mixture which was converted from a blue to green indicating the formation of Ni(OH)2 powder. The synthesized Ni(OH)2 was collected by centrifugation. The separated Ni(OH)2 residue was washed with absolute ethanol for several times and dried under vacuum at 80 oC for 2 h. The gray black coloured NiO nanomaterials were obtained by calcinations of Ni(OH)2 powder at 400 0C in a furnace **[44]**. The morphology shows that the tips of the obtained NiO nanorods are spherical as well as cubic in shape & has applicability to use as as a catalyst.

**3.6 Microwave assisted synthesis of Nickel oxide Nanomaterial**

The mixture of of Ni(CH3COO)2 [1.0 g] in benzylamine [10 mL] was transferred to Teflon liner tube and kept in inside a 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 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. Benzylamine plays various role in this reaction 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].**

**3.7** **Ultrasound-assisted synthesis of NiO nanoparticles**

The mixture of Ni(OAc)2 (500 mg) & α-cyclodextrins (100 mg) were dissolved in of distilled water (10 mL). Then drop wise addition of benzylamine (10 mL) gave formation of a light green coloured precipitate. Then 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. The product was dried at 80 0C h. The cyclodextrin act as capping agent leads to formation of aerated nano-structure in the nano range **[46]**.

**3.8 Synthesis of NiO Nanoparticles**

Firstly nickel acetate (0.646 g, 2.6 mmol) and of water 2.5 mL were added in to flask containing of methanol (42 mL). The solution was heated to 60∘C & dissolved solution of potassium hydroxide (KOH, 0.485 g) was into of methanol was dropped slowly in above reaction mass. After heating for 2 hrs at 60∘C, a small amount of water was added to increase the NiO nanocrystal growth. Dried under vacuum, the precursors were calcined in oven, then NiO nanoparticles were obtained with promising catalytic activity **[47]**.

1. **Magnesium Oxide Based Nanoparticles :**

**3.9** **Formation of MgO nanoparticles under microwave irradiation**

In a typical procedure, the mixture of 1.0 g of Mg(CH3COO)2 .4H2O and 10 mL benzylamine was transferred to a 30 mL Teflon lined tube and kept in a microwave oven for 2 min at 360 watts (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 Mg(OH)2 NPs was calcinationed in oven at 550 0C for 5 h which gave MgO NPs. They shows the higher BET surface area, stronger basic sites observed catalytic activity towards organic transformation **[48]**.

**3.10** **Green Approach for the Nanocrystalline Magnesium oxide Synthesis**

A mixture of magnesium acetate (1.0 g) and 1,4-butanediol (5 mL) were taken in a round bottom flask fitted with air condenser. This mixture was irradiated under solar radiations for 6 h with manual stirring for one minute after an interval of 30 min irradiation. As the solar effect is spatial and temporal to protect the repeatability each experiment was carried out in noon time in summer days. After irradiation, methanol (5 mL) was added to the reaction mass and then 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. Nanoparticles in the range of 5-20 nm was prepared & found to be excellent and reusable catalyst **[49]**.

1. **Catalytic Application Metal oxide Nanoparticles**

**4.1 Catalytic Applications of Copper Oxide Based Nanoparticles**

##### The Cu2O nanoparticles having uniform cubic shape and uniform size synthesized using copper sulphate as a precursor and ascorbic acid as a capping agent was tested for the C–N bond formation Buchwald-Hartwig amination reaction reaction. The reaction was carried out by reacting iodobenzene with imidazole with Cu2O nanoparticles 10 mol% [37], KOH (2 mmol) & DMSO for 24 hrs at 80 oC shows excellent yield (94%) 1-phenyl-1H-imidazole product [Scheme 1].

#####

**Scheme 1:** Catalytic Application of Copper Oxide NPs for coupling reaction of iodobenzene with imidazole

The reaction was done with 2-bromobenzaldehyde and benzamidine hydrochloride as substrates in the presence of Cu2O nanocatalyst prepared by ultrasound assisted synthesis **[38-39]**, base, solvent under domestic microwave for 4 minutes. The cyclization of 2-bromobenzaldehyde with benzamidine hydrochloride in the presence of Cu2O nanocatalyst (5 mol%), of Cs2CO3 (2.0 equivalent) in ethylene glycol at 160W microwave for 4 minutes furnished 2-phenylquinazoline in 51% to 90% yield **[Scheme 2]**.



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

The phytochemicals were isolated flower extract of *Lantana camara* plant & 2.5 wt% water extract solution was prepared to synthesis CuO nanoparticles as per mentioned in section **3.3**. The catalytic activity of the synthesized CuO NPs was tested for aza-Michael addition reaction under ambient condition & ultrasonic vibrations. The acrylonitrile (131 ml, 2 mmol) and aniline (183 ml, 2 mmol) as a substrates, and CuO (2 mg; 0.024 mmol) nanocatalyst under the solvent-free condition at room temperature. All substrates were mixed in a round bottom fask fitted with a reflux condenser and allowed to progress the reaction. After completion of the reaction, the reaction mixture was extracted with ethyl acetate and water respectively **[40]**. The synthesized CuO NPs exhibits excellent catalytic activity towards the aza-Michael reaction of acrylonitrile with primary and secondary aliphatic and aromatic amines under ultrasonic vibration condition & provides a greener pathway to produce a variety of substituted aza-Michael products **[Scheme 4].**



**Scheme 4 :** CuO catalyzed aza-Michael addition reaction

One-step synthetic strategy for the preparation of Cu/Cu2O NPs via a microwave method was developed as per mentioned in earlier section **3.5**. The nanocrystalline Cu/Cu2O showed excellent catalytic activity in the Sonogashira coupling reaction of alkynes with acyl chlorides **[43]**. The reaction conditions were phenylacetylene (1 mmol), benzoyl chloride (1.2 mmol), nano-Cu/Cu2O (10 mol%), Et3N (2 mmol) in toluene (2 mL) at 90 °C for 24 h under an N2 atmosphere to give good yields of the corresponding products **[Scheme 5]**.



**Scheme 5 :** Cu2O catalysed Sonogashira coupling reaction of acyl chlorides with alkynes

* 1. **Catalytic Applications of Nickel Oxide Based Nanoparticles:**

The synthesis of nickel oxide nanorods has been achieved via microwave assisted method by using nickel (II) acetate as a precursor in 1,4-butanediol as a solvent as per mentioned earlier in section 3.5. The synthesis of NiO nanorods which serve as effective catalysts offering a green synthetic route for substituted benzimidazole, benzoxazole, and benzothiazole. In a typical experimental procedure taken o-Phenylene diamine (1 mmol) and benzaldehyde (1 mmol), nano NiO (10 mol%) as catalyst and ethanol (5 mL) as solvent **[44]**. The reaction mixture was stirred at 60 0C for 4 h & the product was extracted with ethyl acetate to give excellent yield of products **[Scheme 6].**



**Scheme 6 :** Nano NiO catalyzed synthesis of 2-substituted benzimidazole

Microwave assisted efficient protocol for the synthesis of NiO NPs by using Nickel Acetate and benzylamine was developed as mentioned in earlier section **3.6**. The three component coupling reaction of aldehyde, amine with terminal alkynes is carried out by use of heterogeneous catalyst NiO to give good yield of respective products. The coupling of aldehyde (1.0 mmol), amine (1.2 mmol), phenylacetylene (1.5 mmol), NiO NPs (15 mol%), solvent toluene (2 mL) at 120 °C for 22 h under N2 atmosphere **[45] [Scheme 7]**.



**Scheme 7:** NiO NPs catalyzed coupling reaction of aldehyde, amine with terminal alkyne

##### The ultrasound assisted synthesis of NiO nanoparticles using benzylamine as a base and different types of cyclodextrins as capping agents as mentioned in earlier section 3.7 was developed mentioned in earlier section 3.7 to catalyze synthesis of 2,4,5-trisubstituted imidazoles. The mixture of 1,2-diketone (1 mmol), aldehyde (1 mmol), ammonium acetate (2.5 mmol) was taken in a reaction vial and of NiO NPs (10 mg) was added as a catalyst. The reaction vial was placed in an oil bath and heated at 120 0C. After completion of the reaction the solid product was dissolved in ethyl acetate (20 mL) and the catalyst was separated by centrifugation followed by washing with water (10 ml) and ethanol (10 mL). The product was recrystallised from ethanol, which gives the corresponding of 2,4,5-trisubstituted imidazoles [46] [Scheme 8].



**Scheme 8**: Synthesis of 2,4,5-trisubstited imidazoles catalysed by NiO NPs.

* 1. **Catalytic Applications of Magnesium Oxide Based Nanoparticles**

A preparation of MgO nanoparticles using magnesium acetate in benzylamine under microwave irradiation as mentioned in earlier section **3.9** for the formylation of amines. This reactions was performed using an amine (1 mmol), formic acid (3 mmol) and MgO NPs (20 mg) out under microwave irradiation at 480 W for 2 min to give N-formylation products with good results **[48] [Scheme 9]**.



##### Scheme 9 : N-formylation of amines catalysed by MgO NPs

##### A green approach for the nanocrystalline magnesium oxide synthesis using reaction of mixture of Magnesium Acetate and 1,4-butanediol under solar radiations was carried out as mentioned in earlier section 3.10 for the Claisen-Schmidt condensation. For this reaction benzaldehyde (0.127 g, 1.2 mmol), acetophenone (0.120 g, 1 mmol) with (0.004 g, 0.1 mmol, 10 mol %) of MgONPs were added under solvent free condition. The reaction mixture was stirred for 4 h at 140 °C. After completion of the reaction, ethyl acetate (10 mL) was added to the reaction mixture and the mixture was centrifuged to separate the catalyst [49]. MgO NPs were applied as a catalyst in Claisen-Schmidt condensation reaction for the synthesis of chalcones and its derivatives under solvent free condition [Scheme 10].



**Scheme 10:** MgO NPs catalysed Claisen-Schmidt condensation reaction

In general, the nanoparticle is considered to be more reactive because it offers higher surface area and low coordinating sites. The surface area of the catalyst increases tremendously when size decreases to nano levels which are responsible for the higher 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 Cu2O, 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.

**Conclusion**

Green synthesis of metal and metal oxide nanoparticles has been a highly attractive research area over the last few years, as it provide sustainable way to carry out many important chemical transformations in an environmentally benign manner. In conclusion, the use of metal oxide nanoparticles as a green, mild and effective catalyst satisfactorily catalyzed the synthesis of most organic compounds with more simple procedures. A lot of scope and enormous potential in future to enhance the functioning of such nanocatalysts on large scale to achieve sustainable outputs.

##### REFERENCES

1. Heiligtag, F. J.; Niederberger, M. The fascinating world of nanoparticle research. Mater. Today 2013, 16 (7−8), 262−271
2. Senanayake, S. D.; Stacchiola, D.; Rodriguez, J. A. Unique Properties of Ceria Nanoparticles Supported on Metals: Novel Inverse Ceria/Copper Catalysts for CO Oxidation and the Water-Gas Shift Reaction. Acc. Chem. Res. 2013, 46, 1702−1711.
3. Bordiga, S.; Groppo, E.; Agostini, G.; van Bokhoven, J. A.; Lamberti, C. Reactivity of Surface Species in Heterogeneous Catalysts Probed by In Situ X-Ray Absorption Techniques. Chem. Rev. 2013, 113, 1736−1850.
4. Laurent, S.; Forge, D.; Port, M.; Roch, A.; Robic, C.; Vander Elst, L.; Muller, R. N. Magnetic Iron Oxide Nanoparticles: Synthesis, Stabilization, Vectorization, Physicochemical Characterizations, and Biological Applications. Chem. Rev. 2008, 108, 2064−2110.
5. Gawande, M. B.; Branco, P. S.; Parghi, K.; Shrikhande, J. J.; Pandey, R. K.; Ghumman, C. A. A.; Bundaleski, N.; Teodoro, O.; Jayaram, R. V. Synthesis and Characterization of Versatile MgO-ZrO2 Mixed Metal Oxide Nanoparticles and Their Applications. Catal. Sci. Technol. 2011, 1, 1653−1664.
6. Bell, A. T. The Impact of Nanoscience on Heterogeneous Catalysis. Science 2003, 299, 1688−1691.
7. Wang, D.; Astruc, D. Fast-Growing Field of Magnetically Recyclable Nanocatalysts. Chem. Rev. 2014, 114, 6949−6985.
8. Zeng, H. C. Integrated Nanocatalysts. Acc. Chem. Res. 2013, 46, 226−235.
9. Georgakilas, V.; Otyepka, M.; Bourlinos, A. B.; Chandra, V.; Kim, N.; Kemp, K. C.; Hobza, P.; Zboril, R.; Kim, K. S. Functionalization of Graphene: Covalent and Non-Covalent Approaches, Derivatives and Applications. Chem. Rev. 2012, 112, 6156−6214.
10. Gawande, M. B.; Shelke, S. N.; Zboril, R.; Varma, R. S. Microwave-Assisted Chemistry: Synthetic Applications for Rapid Assembly of Nanomaterials and Organics. Acc. Chem. Res. 2014, 47, 1338−1348.
11. Andres, R. P.; Bielefeld, J. D.; Henderson, J. I.; Janes, D. B.; Kolagunta, V. R.; Kubiak, C. P.; Mahoney, W. J.; Osifchin, R. G. Sel assembly of a Two-Dimensional Superlattice of Molecularly Linked Metal Clusters. Science 1996, 273, 1690−1693.
12. Zaera, F. Nanostructured Materials for Applications in Heterogeneous Catalysis. Chem. Soc. Rev. 2013, 42, 2746−2762.
13. K. Hemalatha, G. Madhumitha, A. Kajbafvala, N. Anupama, R. Sompalle, S. Mohana 17 Roopan, Function of nanocatalyst in chemistry of organic compounds revolution: An 18 overview, J. Nanomater. 2013 (2013).
14. V. Polshettiwar, R.S. Varma, Green chemistry by nano-catalysis, Green Chem. 12 (2010) 743.
15. Jalal Albadi, Abdolhossein Razeghi, Hossein Abbaszadeh, and Azam Mansournezhad. Journal of Nanoparticles (2013), 1-5 .
16. Rodriguez, J.A. and Fernandez-Garcia,M. (2007). Synthesis, Properties and Applications of Oxides Nanomaterials, John Wiley & Sons, Inc., Hoboken, USA.
17. Fern\_andez-García, M., Martínez-Arias, A., Hanson, J.C., and Rodriguez, J.A. (2004) Nanostructured oxides in chemistry: characterization and properties. Chem. Rev., 104, 4063-4104.
18. Chiang, Y.-M., Lavik, E.B., Kosacki, I.,Tuller, H.L., and Ying, J.H. (1997) Nonstoichiometry and electrical conductivity of nanocrystalline CeO2\_x. J. Electroceram (1), 7–14.
19. Mohanraj V.J and Chen.Y,). (2006) .Nanoparticles: a review,” Tropical Journal of harmaceutical Research. ( 1)561–573.
20. Astruc. D. (2007). Palladium nanoparticles as efficient green homogeneous and heterogeneous carbon-carbon coupling precatalysts: a unifying view,” Inorganic Chemistry, (6) 1884–1894.
21. Moreno-Manas. M and Pleixats.R. (2003). Formation of carboncarbon bonds under catalysis by transition-metal nanoparticles,”Accounts of Chemical Research, (8) 638–43.
22. P. Ayyub, R. Chandra, P. Taneja, A. K. Sharma and R. Pinto, Appl. Phys. A: Mater. Sci. Process., 2001, 73, 67–73.
23. V. Amendola and M. Meneghetti, Phys. Chem. Chem. Phys., 2009, 11, 3805.
24. J. Zhang, M. Chaker and D. Ma, J. Colloid Interface Sci., 2017, 489, 138–149.
25. R. A. Ismail, M. H. Mohsin, A. K. Ali, K. I. Hassoon and S. Erten-Ela, Phys. E, 2020, 119, 113997.
26. J. Chrzanowska, J. Hoffman, A. Małolepszy, M. Mazurkiewicz, T. A. Kowalewski, Z. Szymanski and L. Stobinski, Phys. Status Solidi, 2015, 252, 1860–1867.
27. J. Duque, B. Madrigal, H. Riascos and Y. Avila, Colloids Interfaces, 2019, 3, 25.
28. S. S. Su and I. Chang, Commercialization of Nanotechnologies– A Case Study Approach, Springer International Publishing, Cham, 2018, pp. 15–29.
29. K. A. Shah and B. A. Tali, Mater. Sci. Semicond. Process., 2016, 41, 67–82.
30. J. Li, Q. Wu and J. Wu, Handbook of Nanoparticles, Springer International Publishing, Cham, 2015, pp. 1–28.
31. A. Chen and P. Holt-Hindle, Chem. Rev., 2010, 110, 3767–3804.
32. T. K. Tseng, Y. S. Lin, Y. J. Chen and H. Chu, Int. J. Mol. Sci., 2010, 11, 2336–2361.
33. M. Parashar, V. K. Shukla and R. Singh, J. Mater. Sci.: Mater. Electron., 2020, 31, 3729–3749.
34. Hussain I, Singh NB, Singh A, Singh H, Singh SC. Green synthesis of nanoparticles and its potential application. Biotechnology letters. 2016; 38(4):545-60.
35. Bera D, Qian L, Tseng T, Holloway PH. Materials. 2010; 3:2260-2345.
36. Zhang, J.; Liu, J.; Peng, Q.; Wang, X.; Li, Y. Nearly Monodisperse Cu2O and CuO Nanospheres: Preparation and Applications for Sensitive Gas Sensors. Chem. Mater. 2006, 18, 867− 871.
37. M. A. Bhosale, S. C. Karekar and B. M. Bhanage, Chemistry Select 2016, 1, 6297-6307.
38. K. Kaviyarasan, S. Anandan, R. V. Mangalaraja, T. Sivasanka, M. Ashokkumar, Ultrasonics Sonochemistry, 2016, 29, 388–393.
39. Debao Wang, Dabin Yu, Maosong Mo, Xianming Liu, [Yitai Qian](https://www.sciencedirect.com/author/36040759400/yitai-qian), Ultrasonics Sonochemistry, Volume 261, Issue 2, 2003, Pages 565-568.
40. Rakesh Chowdhury, Aslam Khan and Md. Harunar Rashid, RSC Adv., 2020, 10, 14374-14385.
41. Waad Mohsen, M. A. Sadek and Hany A. Elazab, International Journal of Applied Engineering Research, Volume 12, Number 24 (2017), 14927-14930.
42. M. A. Bhosale, K. D. Bhatte, B. M. Bhanage, Powder Technology, [Volume 235](https://www.sciencedirect.com/journal/powder-technology/vol/235/suppl/C),  2013, 516-519.
43. M.A. Bhosale, T. Sasaki and B.M. Bhanage, Catal. Sci. Technol. 2014, 4, 4274-4280.
44. M. A. Bhosale, B. M. Bhanage. Advanced Powder Technology, 26(2), 2015, 422-427.
45. AL Gajengi, T Sasaki, B M Bhanage. Catalysis Communications 72, 2015, 174-179.
46. A L Gajengi, S Chaurasia, Eric Monflier, A Ponchel, J Ternel, B M. Bhanage, Catalysis Communications, 161, 2021, 106366.
47. H Sachdeva, D Dwivedi, R. R. Bhattacharjee, S Khaturia, and R Saroj. Journal of Chemistry, 2013 (5), 1-10.
48. A.L. Gajengi, T. Sasaki, B. M. Bhanage. Advanced Powder Technology, 2017, 28, 1185-1192.
49. A B. Patil, B M. Bhanage. Catalysis Communications, 2013, (36), 79-83.