“Green Synthesis of Nanocatalysts in Heterocyclic Compound Containing Nitrogen and Oxygen as a Heteroatom”

Prakash D. Kokare, Ashwini S. More, Santosh B. Kamble

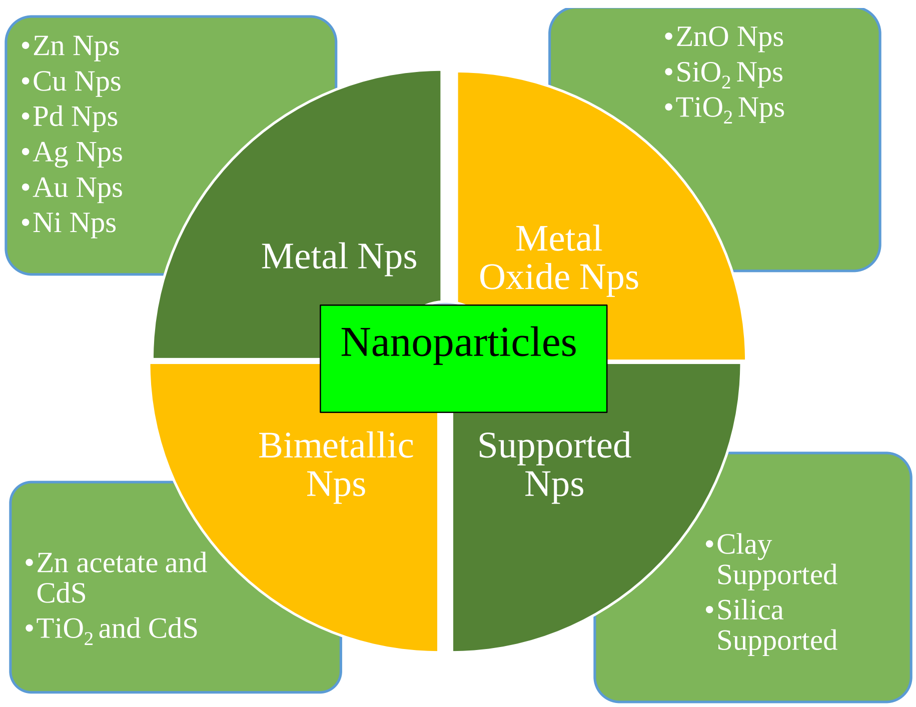
Department of Chemistry, Yashavantrao Chavan Institute of Science, Satara. Maharashtra India.

Abstract:

A past decade researchers were used a catalyst which are hazardous for human health and environment also. So, many environmental issues are created such as pollution. So, now a days researchers used a green catalyst such as nanoparticles. Nanoparticles are not hazardous for environment. Nanoparticles are small in size so provide large surface area for reaction so high product is formed in organic synthesis. Many nanoparticles are used in heterocyclic synthesis. Heterocyclic compound containing nitrogen and oxygen as a hetero atom then this heterocyclic compound has more useful in drug synthesis. So, use of nanoparticles in heterocyclic compound synthesis is often towards the green chemistry.

Key words: Heterocyclic compound, Nanoparticles

Contents:

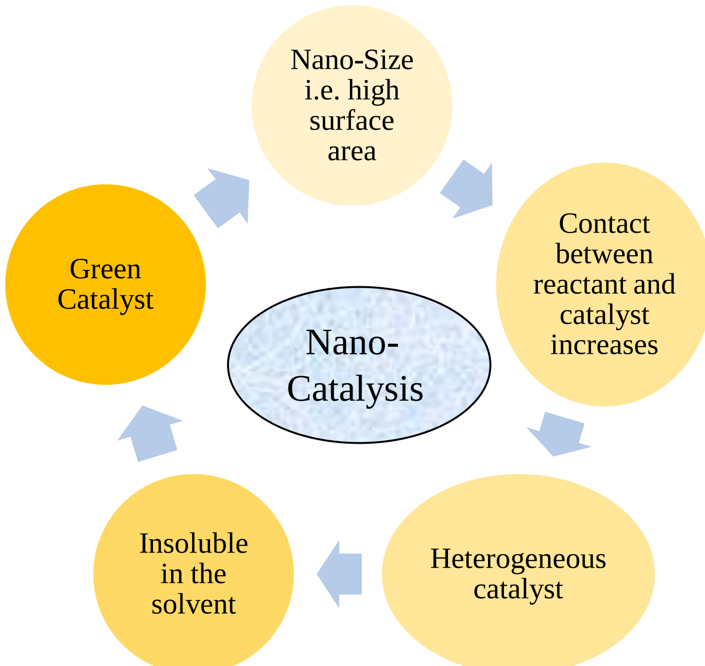


1. Introduction:

The history of heterocyclic chemistry began in the 1800s, in step with the development of organic compound.[1] Heterocyclic compound means the compound containing other than carbon atom such as oxygen, nitrogen and Sulphur. The heterocyclic compound first discovered by Brugnatelli in 1818 by isolates alloxan from uric acid. The heterocyclic compounds are classified as aromatic and nonaromatic heterocyclic compounds such as pyrroles, pyridine, indole and benzofuran, benzothiophene. The benzofused aromatic heterocyclic compounds are more useful in pharmaceutical as well as medicinal chemistry[2]. From a past decade many researchers were used a catalysts which are harmful environment. Due to this catalysts increases the pollution and their worse effect in human being. There is a need to minimize the pollution from environment. So, now, researchers used green catalyst for organic synthesis. Nanoparticles are green catalyst which minimize the toxic chemical from synthesis. The nitrogen containing heterocyclic compound is more important among the United States Food and Drug Administration (USFDA) approved drugs.[3] [4] [5] The heterocycles plays important rule when it is combine with other drug in therapeutic uses. [6] These synthesized drug used in the clinical uses according to the literature.

Heterocyclic compounds are present in a large variety of products, such as molecular materials, natural and also in regularly marketed drug. Heterocyclic compounds are of great importance due to their biological properties such as anticancer, anti-inflammatory, antioxidant, antiviral, antimicrobial, anticonvulsant, antibacterial, antipyretic, cardiovascular, antihypertensive, anti-hyperglycemic activity.[7] From an industrial point of view, the majority of the pharmaceuticals, bioactive agrochemicals, additives, and modifiers are heterocyclic in nature.

The huge use of heterocycles as pharmaceuticals is because of their high abundance in nature and they are used as a building block for bio macromolecules such as DNA or RNA.



The terminology of catalysis is introduced by Swedish chemist Jons Jacob Berzelius in 1836. Catalyst is used in organic synthesis for increase the rate of reaction. There are two types of catalysis, homogeneous and heterogeneous catalysis. [1] Homogeneous catalysis means catalyst and reactants are in similar phase. Heterogeneous catalysis means catalyst and reactants are in different phase. The concept of nanoparticles is firstly invented by Richard Feynman in 1959. Nanoparticles are green catalyst and it is hazardless catalyst. It is better catalyst than regular catalyst. Nanoparticles are classified as metal NPs, Non-metal NPs, Metal oxide Nps, supported nanoparticles[8].

Two different approaches majorly involves in synthesis of metal nanoparticles, one is top down approach or dispersion method and another method is bottom up approach or condensation method. In top down method, larged size particles are divided into small size particles are used in synthesis of nanoparticles .this nanoparticles synthesized by ultrasonic method.[9] In bottom up method, small particles are attach to each other and form nanoparticles.[10] The bottom up method is more superior to top down method because of their feasibility, less toxicity and cost effective. (d iagram

Nano- materials are important in many areas from basic research to various applications in electronics, catalysis and energy. Nanoparticles are more important in organic synthesis[11]. Because it is small in size so it provides large surface area for reaction.[12] Nanoparticles are the green catalyst.[13] It reduces the environmental pollution. Many researchers used hazardous solvent in organic synthesis, it increases the environmental pollution. But now green solvent like water is used in synthesis, because water is easily available, non- toxic and Inexpensive. In synthesis of heterocyclic compound many metal nanoparticles are used such as Fe_3O_4, Ag NPs, Pd NPs etc. These nanoparticles are synthesized by natural resources like plant extract so NPs are eco-friendly, non- hazardous and give high productivity.[14] The synthesized nanoparticles characterized by XRD, SEM, TEM.[13]

2. Metal Nanoparticles:

In organic transformation metal nanoparticles are play an important role which gives safest reaction and gives more yield than conventional catalyst without affecting the environment. The key feature of nanoparticles is show unique physicochemical properties as compared bulk metals There are many application of metal nanoparticles and metal oxide nanoparticles in C-H activation, asymmetric C-C activation, and asymmetric C-C bond formation and in biomedical application. The different fields use of nanoparticle like molecular biology, physics , Organic and inorganic chemistry ,medicine and material science is unexpected augmented nowadays .[15] Metal nanoparticles are used in synthesis of heterocyclic compound. There are many metals are used as a nanoparticles in organic transformation such as Ag NPs, Au NPs, Ti NPs, Cu NPs, Zn NPs etc. Metal nanoparticles provide more surface area, high durability and high reusability than other catalyst. Metal nanoparticles are more important because it replace existing homogeneous/ heterogeneous catalyst, because they provide quasi-homogeneous phase for reaction under mild condition. The metal nanoparticles are prepared by reduction of metal salts and on the thermal degradation of organometallic complexes. The stability of nanoparticles are depend upon the electrostatic interaction between ionic compounds, especially in water.

The synthesis of metal nanoparticles by green method, so the produced particles has provide more connectivity and also protect from toxic effect. Green synthesis of nanoparticles in three important condition, one is selection of environment friendly solvent, second is selection of good reducing agent and third is stabilizing agent. The aim of researchers is green synthesis of metal nanomaterial's because this synthesized metal nanomaterial's are nontoxic ,also high effective and ecofriendly .[16] Metal nanoparticles most important quantities in understanding thermodynamics of particles because its possess lagers surface energy. Metal nanoparticles important in drug delivery system because it's have large surface area and it's provide more possible reactive site and surface energy which make them ideal candidates in drug delivery.

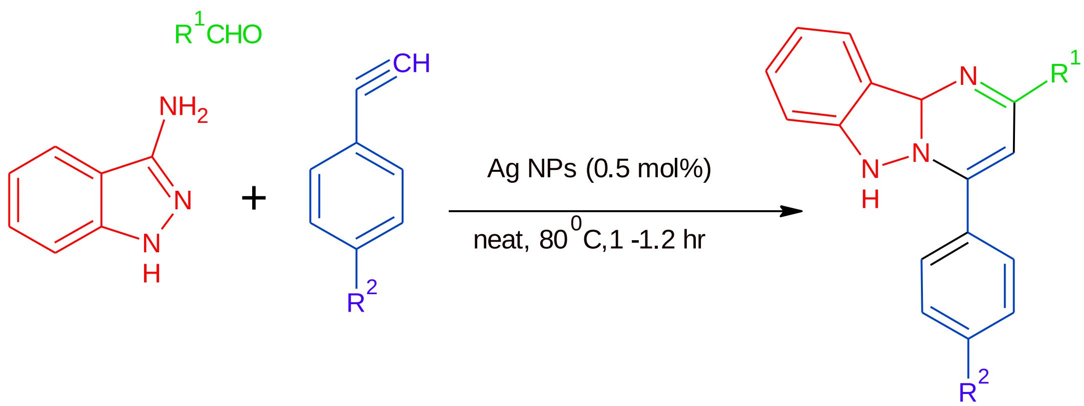
.

2.1 Silver Nanoparticles:

At Present researchers high attention on green synthesis of silver nanoparticles because it's have extraordinary biological activity and important uses like drug delivery ,sensing ,food preservation ,bio labeling ,wound healings ,water purification and cosmetic. Other application of silver nanoparticles are textiles, electronics, catalysts and paints. The branch of plant mediated green synthesis of silver nanoparticles is newly developing in nanotechnology field Recently most useful of this method because synthesized nanoparticles are eco environmental and effective cost with lesser toxicity as compared to chemical method . The green synthesis of silver nanoparticles have sever advantages like as less toxicity, hazardous materials and it show less consume of energy ,5 Green synthesis of silver nanoparticles by plant mediated method use in different parts of the plant like as leaf ,bark ,stem ,root ,fruit, latex, and this method preference to microbe-mediated synthesis[17]. The plant extract and microbes acts as reducing agent for reduction of Ag^+ to Ag and capping agent in synthesis of nanoparticles [18].In below table compare the synthesis of silver nanoparticles for use in different plant extract , its biological activity, parameters and its characterization. In pytochem initial step is reduction of silver ion and stabilization, directing the shape and size of nanoparticles. In synthesis of silver nanoparticles many affect able factors are Concentration of substrate, temperature, reaction time and pH. The silver nanoparticles characterized by SEM, TEM, FTIR, UV visible spectroscopy and etc. The green synthesis of silver nanoparticles synthesized by using different pant extract to its show different biological activity such as Calatora procera plant extract show Antimicrobial activity[19], Piper nigrum plant extract showed anti-cancer activity [20] and Anti-oxidant activity showed by officinate plant extract.[21]

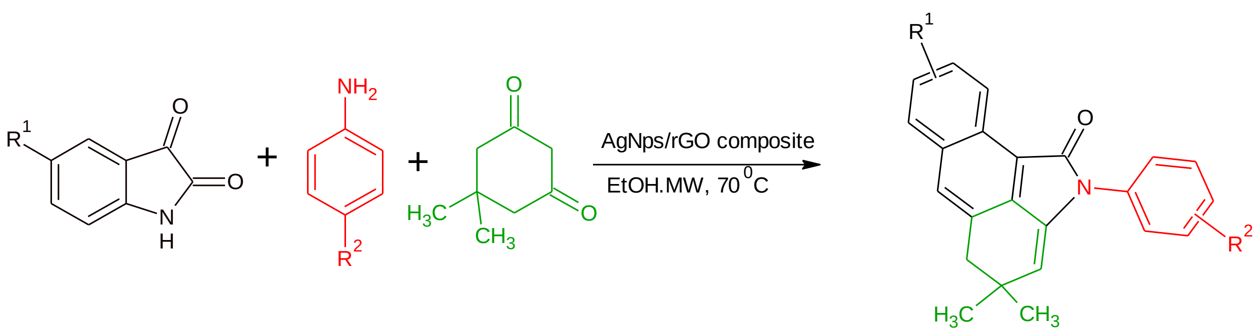
Silver nanoparticles are used in synthesis of heterocyclic compounds. Silver nanoparticles are obtained from plant extract of Radix puerariae. The extract is treated with the AgNO3 and monitored by using UV- Vis spectroscopy. The synthesized Ag Nps are characterized by SEM, TEM, and XRD.

Balwea et.al. Synthesized pyrido (1,2-b) indazole derivatives using silver NPs. This Ag NPs are obtained from the plant extract of Raddix purariae. This plant extract is treated with silver nitrate in presence of base and Ag NPs was monitored by using UV-Vis spectroscopy, TEM, EDX. In UV-visible spectroscopy the absorption peak observed at 400-430 nm, it indicated the formation of silver nanoparticles. [22] Also, Rokade et al. reported synthesis of Ag NPs by using starch i.e. by green method. The synthesized NPs were characterized by SEM, TEM method. The size of NPs is 50 nm. Nanoparticles showed antibacterial activity.[23]



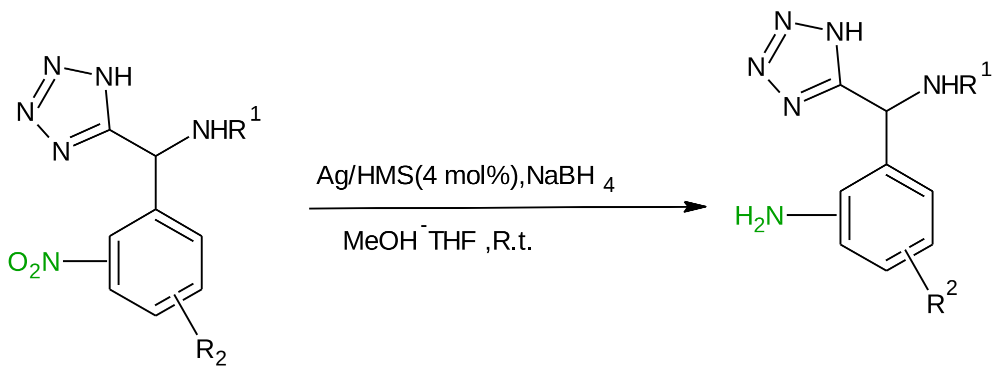
Scheme 1: Synthesis of pyrimido[1,2-b] indazole using Ag NPs under solvent free condition

Endevour Dandia et al. reported a synthesis of pyrrolo(2,3,4-kl) acriding-1-ibes by using Ag NP-decorated reduced grapheme oxide. The synthesis of Bps by green method via the reduction of graphene oxidse and preparation of Ag NPs on it. The NPs are characterized by XPS, SEM, TEM, EDX. [24]



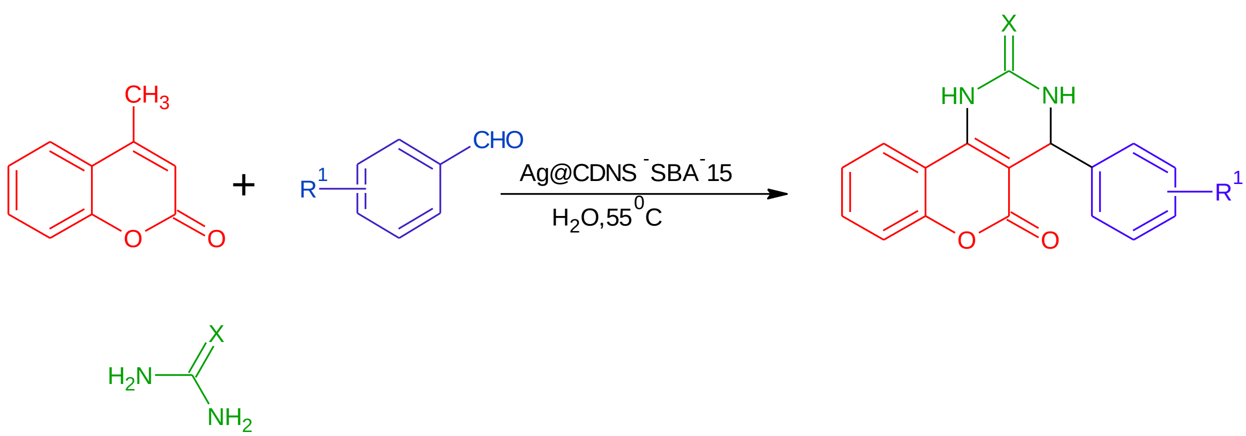
Scheme 2: Ag NP- catalyzed synthesis of pyrrolo[2,3,4-kl] acridin-1-ones.

Dandia et. al. reported the synthesis of pyrano(2,3-c,6,5,-c) dipyrazol-2-ones by using green Ag NP-decorated GO composite as a catalyst on water. The NPs act as a lewis acid and used in knoevenagel condensation –michael addition and cyclization. By using SEM and TEM images the recovered catalysts revealed the integrity of catalyst form this know the there is no loss of catalytic activity of catalyst.[24] [25]



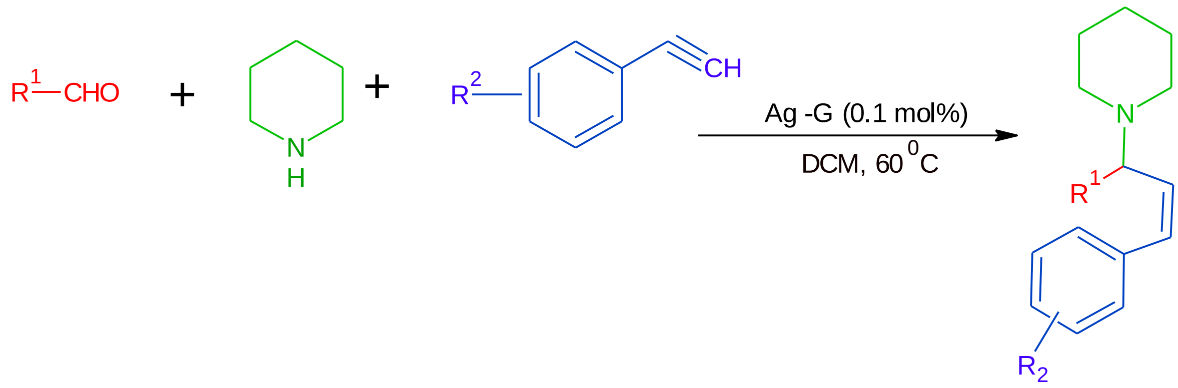
Scheme 3: Ag NP-catalyzed chemoselective reduction nitroarenes and synthesis.

Porco et. Al. reported the use of Ag NP-catalyzed Diels-Alder cycloaddition for synthesis of cycloadduct from chalcone and diene . The Ag Nps are synthesized from via the reduction of $AgBF_4$by using tetrabutyl ammonium borohydride with silica gel in DCM .[26]



Scheme 4: Synthesis of benzopyranopyrimidines by using Ag NPs.

Lykakis et. al. reported a reduction of tetrazoles containing nitroarenes by using Ag NPs supported mesoporous silica catalyst[27].

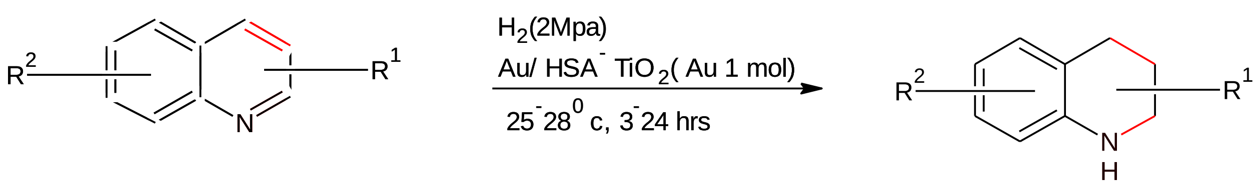


Scheme 5: Silver-graphene nanocomposite-catalyzed synthesis of propargyl amines.

2.2 Gold Nanoparticles :

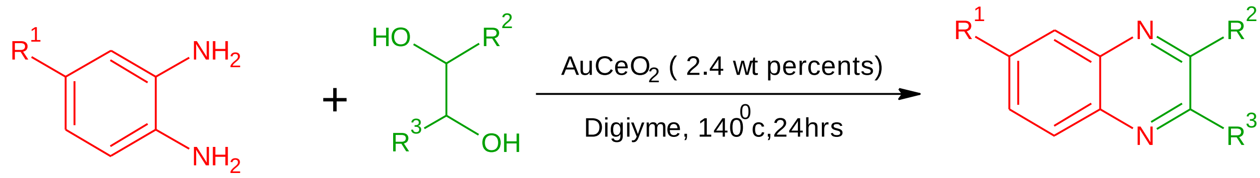
Gold nanoparticles are used in biomedical science because it has unique and tunable surface plasma resonance. The gold nanoparticles are mainly used in tissue imaging, photochemical therapy and immune chromatographic identification of pathogens in clinical specimens. Many researchers are interested in synthesis of gold nanoparticles by green method. Moharpuria wrote a review on synthesis of nanoparticles by using microorganism and plant extract. Narayanam and sakanines used coriander leaf for the synthesis of gold nanoparticles. The Daizy Philip used honey for the synthesis of gold nanoparticles Honey is composed by fructose and glucose and it contains amino acid which are helpful for buildup calcium in the body[28]. Daizy Philip green synthesized gold NPs are biologically important because it is synthesized from honey and which show antioxidant property. Gold NPs are characterized by UV-visible spectroscopy. Daizy Philip reported a crystalline nature of gold NPs was confirmed from X-ray diffraction. Gold NPs are also characterized by FTIR[29]. FTIR gives information about biomolecules which are responsible for capping and efficient stabilization of gold NPs. The biomolecules such as glucose, fructose, and protein are photoluminescent. The PL spectra of gold NPs is at 300 nm.[30]

Naeimi et al. reported a synthesis of tetrahydro-4H-chromones by using gold nanoparticles supported on thiol- functionalized reduced grapheme oxide The synthesis of tetrahydro-4H-chromones from substituted benzaldehyde and malononitrile in aqueous medium under reflux.(scheme 1)[31]



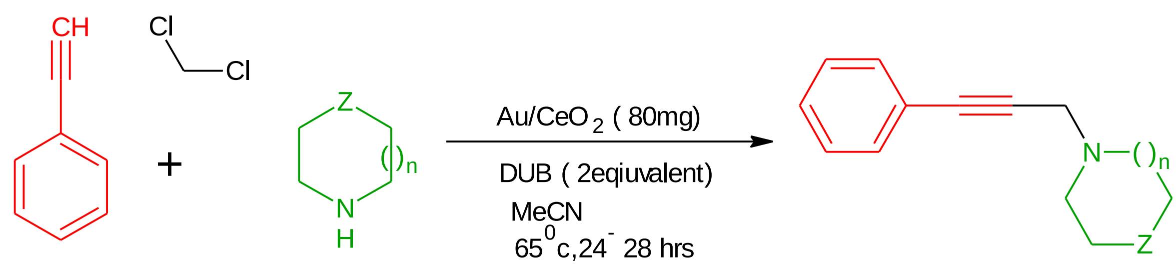
Scheme 6: 3 Chemoselective hydrogenation of quinolines (35a) catalyzed by Au NPs

Che et al. reported a synthesis of polysubstituted quinolones by using substituted anilines with alkyl aldehyde using Sio2 supported gold Nps under oxygenated environment.(scheme 2)[32]



Scheme 7: Synthesis of polysubstituted quinolones.

Iboroca et al. reported synthesis of quinoxalines synthesis of quinoxalines using Au NPs supported on CeO_2 from two component such as O-phenyllens diamine and biomass derived substituted alycols or nicinal diols. The synthesis of quinoxalines using Au NPs supported on CeO_2 as the catalyst and diglyne as the solvent free at 140°C under base free condition. The synthesized NPs characterized by high-angle annular dark field scanning transmission electron microscopy. The author percentage conversion to final compound studied by four catalytic cycles. (Scheme 8)[33]



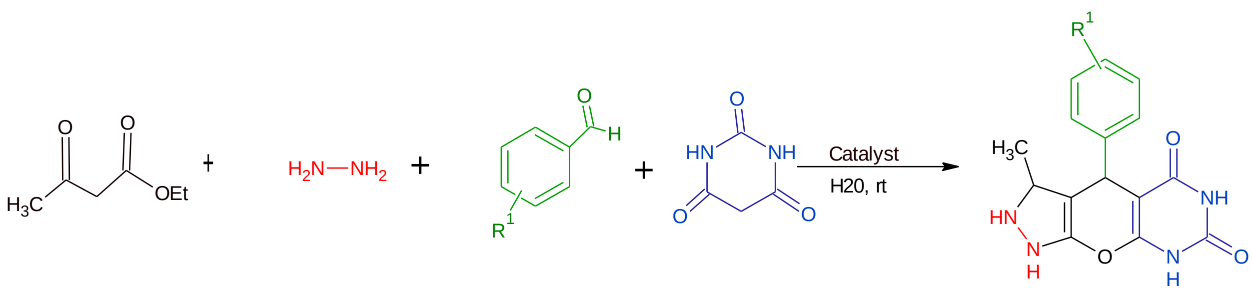
Scheme 8: synthesis of heterocyclic compound by Au NPs

2.3 Copper nanoparticles:

Recently, researchers aimed to explore the green synthesis of copper nanoparticales by using plant extract. The synthesized copper nanoparticles by chemical methods are toxic ,cariogenic and non-degradable, but green synthesized copper nanoparticles are ecofriendly, less toxic and its show biological activity[34] .The important application of nanoparticles in various industry such as textile ,leather, tanning, paper cosmetic, pharmaceutical and plastic[35]. The chemically method synthesis of copper nanoparticles are highly toxic, carcinogenic and non-degradable and this effect created dangerous diseases such as skin diseases, cancer, allergic reaction and mutation for people. Therefore need to green synthesis of nanoparticles because its ecofriendly, cost effective and I show photo catalytic application in the degradation of organic dyes. The green synthesis of nanoparticles by various method such as plant extract, microbial, antivirals, bacterial and yeast.

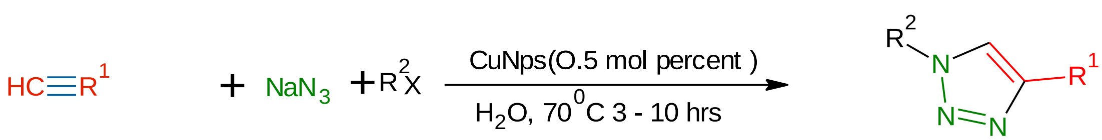
The agriculture sector plant diseases a remain issue and we are this problem controlled by using different kind of pesticides, herbicides and antimicrobial substances. But three substances created various side effect such as soil pollution and bio magnification in living organism. The researchers are more attention towards green synthesis of copper nanoparticles because it's less toxic and antimicrobial efficiency to control plant disease and copper nanoparticles shows antifungal activity[36]. The main properties of copper nanoparticles are its show electrical conductivity and it's optical, antifungal and antibacterial[37]. The green synthesized copper nanoparticles characterized peak are present to 269 nm and this peak analysis by UV spectroscopy. Spherical shape of particle and size of nanoparticles characterized by SEM and TEM. The synthesized of copper nanoparticles are presence in –OH, -C=C-, and –C-H function groups are confirmed by FT-IR.

Green synthesis of pyrazolopyranopyrimidine-5-7diones using copper immobilized mesoporous silica nanoparticles in aq. Medium. The synthesis of pyrazolopyranopyrimidine from one pot multicomponent such as barbituric acid, substituted aromatic aldehydes, ethyl acetoacetate and hydrazine hydrate. The synthesized nanoparticles are characterized by XRD, SEM, TEM, dispersive X-ray ,thermal analysis (TGA-DTA) and FT-IR studies.[38] [39]



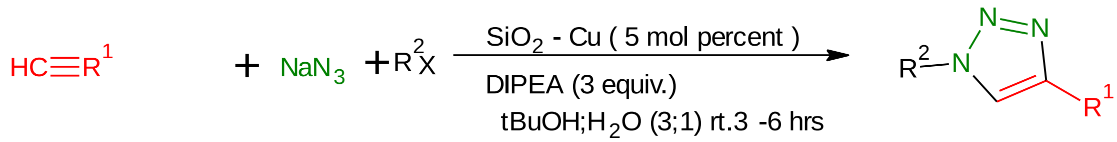
Scheme13: Cu2 +@MSNs (CO2)2-catalyzed synthesis of pyrazolopyranopyrimidine-5,7-diones.

One pot multicomponent synthesis of 1,2,3-triazoles from alkyl halide ,sodium azide and substituded alkynens / acetylenens with using copper nanoparticles (Cu Nps) on activated charcols The synthesized nanoparticles characterized by ICP-MS,TEM,EDX,XPS and selected one electron diffraction pattern (SAED).[40]



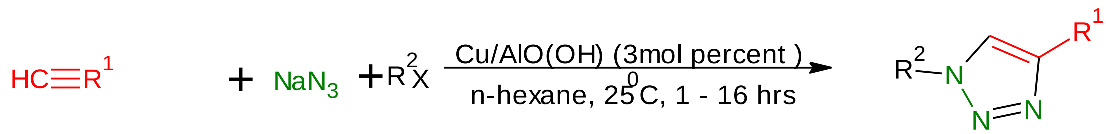
Scheme 14 : Synthesis of substituted triazoles using Cu NPs

Coelho et al. repoeted synthesis of triazole by using sol gel entrapped copper in a silica matric . The synthesis of triazole from alkyl halide, sodium azide and substituded alkynens acetylenes. The synthesis of nanoparticles characterized by SEM, TEM, EDS, and EPR. [41]



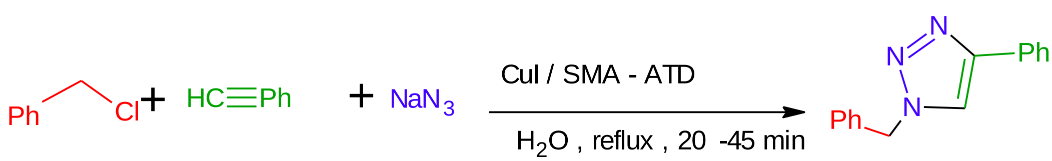
Scheme 15: Synthesis of N-substituted triazoles catalyzed by CuNPs entrapped in a silica matrix.

Park et al. reported synthesis of triazole withaout additives catalyzed by copper nanoparticles in aluminium oxihydroxide nanofiber using n hexane as a solvent at room temperature. The synthesis of trizole from alkyl halide, sodium azide and substituted alkynes. The synthesized nanoparticles are characterized by SEM, TEM, XPS , ICP and nitrogen isotherms.[42]



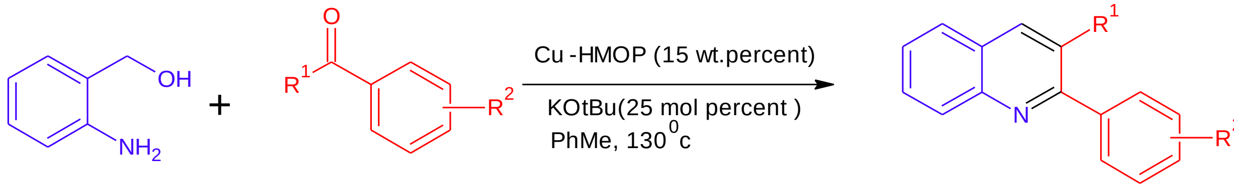
Scheme16: Synthesis of 1,4-disubstituted triazoles from alkyne and azide catalyzed by Cu NP.

The two component synthesis of triazole from terminal alkynes and substituted azide by using Cu (I) NPs immobilized on modified polystyrene , co-maleic anhydride . the Cu NPs are characterized by H^1NMR , SEM, TEM, FT-IR, EDAX and ICP- AES.[43]



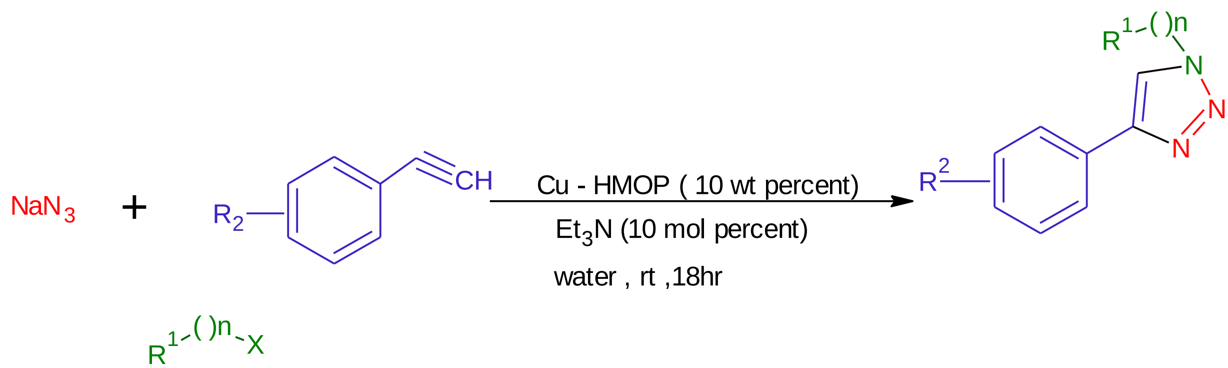
Scheme 17: Click reaction for the synthesis of triazoles catalyzed by Cu NPs.

Frieldiander synthesis of quinolone by using copper loaded hirochiral mesopores organic polymer NC- catalyzed. The synthesis of quinoline form 2-amino benzyl alcohol and aryl ketones. [44]



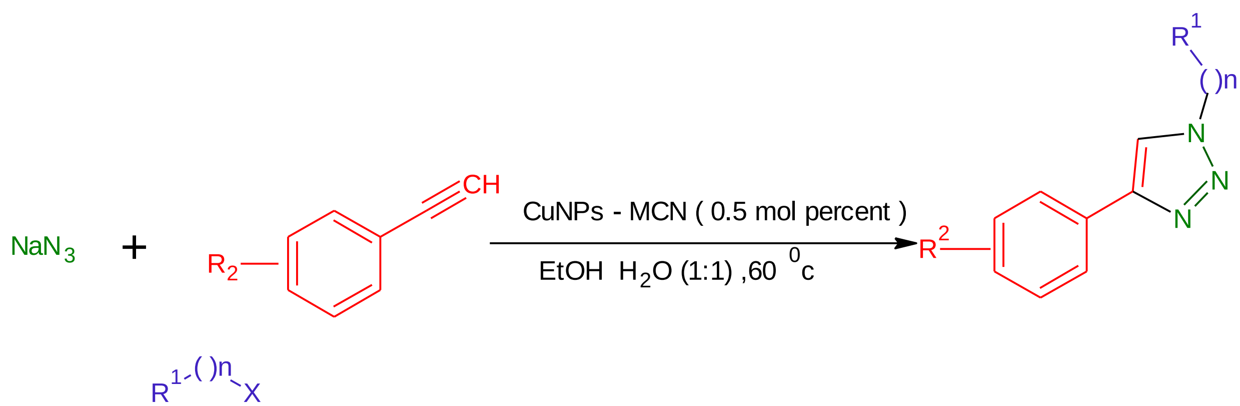
Scheme 18: Frieldlander synthesis of quinolines catalyzed by Cu HOMP .correction

The synthesis of 3- substituted 4-phrenyl-1-H-1,2,3-triazole by using Cu Nps of copper loaded hierarchical mesoporous organic polymer(HMOP) NC- Catalyzed. The synthesis of 3- substituted 4-[jemu;-1,2,3-triazole from sodium azide, substituted phenyl acetylene with alkyl halides.[44]



Scheme 19: Click reaction for the synthesis of triazoles catalyzed by Cu-HMOP.

Dabiri et.al reported synthesis of 1,2,3-triazole by using Cu NPs supported on mesoporous carbon nitride(Cu NPs-MCN). The synthesis of 1,2,3-triazoles from sodium azide, alkyl halide and alkyne in 78-88%.[45]



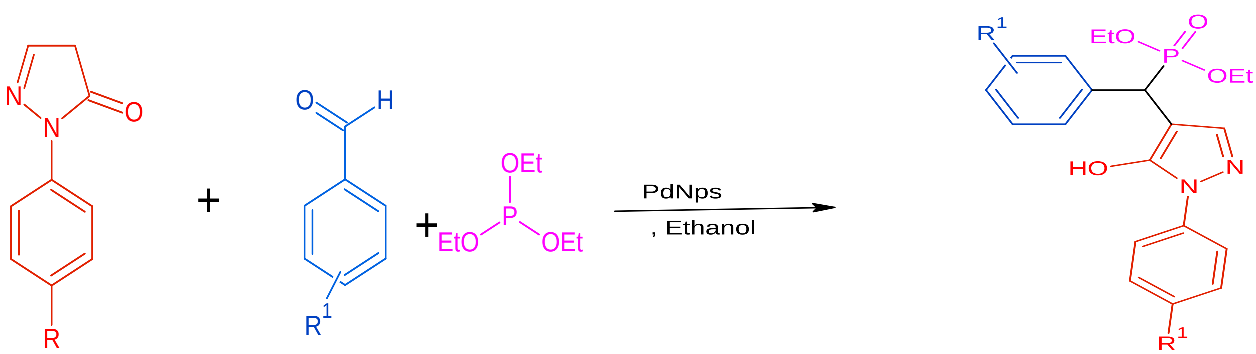
Scheme 20: Cu NP-catalyzed 1,3-dipolar cycloaddition for the synthesis of triazoles

2.3 Palladium Nanoparticles :

Among many transition metal nanoparticles, palladium nanoparticles shows high catalytic activity in organic transformation. Preparation of palladium NPs by using many green method and it is expensive so it is palladium nanoparticles are ecofriendly[46].

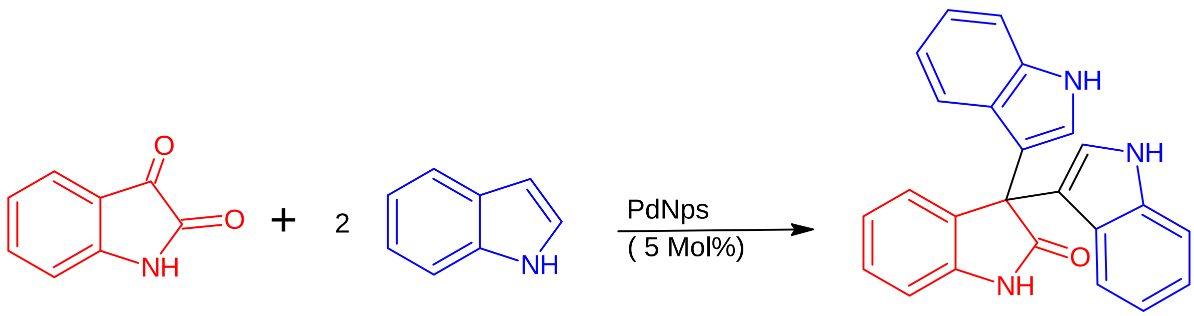
Palladium nanoparticles were synthesized by plant extract of Euphorbia thymifolia and this nanoparticles were used in synthesis of heterocyclic compound[47]. Palladium nanoparticles were also synthesized by $PdCl_2$ by green method. The sour cherry tree gum is grind in grinder then this powder mixed in distilled water and centrifuge this solution. This solution is mixed with aqueous solution of $PdCl_2$ at 80^0C. This prepared nanoparticles are characterized by the UV–vis, XRD and TEM methods. And this prepared nanoparticles are used in sonogashira coupling reaction i.e. in synthesis of heterocyclic compound. Palladium Nps also synthesized by aqueous extract of Perilla frutescens leaf. This leaf act as a bioreductant for conversion of Pd^{+2} to Pd^0 without using any capping agent. This prepared nanoparticles are characterized by UV-visible spectroscopy[48]. Transmission electron microscopy showed spherical nanoparticles, ranging in size between 10 and 17 nm confirming the crystallinity of the nanoparticles with a face centered cubic (fcc) structure. Energy dispersive X-ray spectroscopy confirmed the presence of palladium.

Nagaraj Basavegowda et al. Green synthesis of Polyphosphosponates by using Pd NPs (palladium nanoparticles). Green synthesis of Pd NPs by using Frutescens leaf extract. One spot multicomponent synthesized poly phosphosponates from 3- methyl -1-phenyl -5- pyrazoe , arylaldehyde and triethylphosphite with using Pd NPs and ethanol solvent . The green synthesized Pd NPs characterized by UV Spectroscopy, TEM, FTIR Spectroscopy and TGA Spectroscopy. Green synthesized Pd NPs show distinct peak near to 425 nm and author this distinct peak analyzed by UV spectroscopy.Size and Morphology of green synthesized Palladium NPs confirmed by TEM.[49] [50] [51]



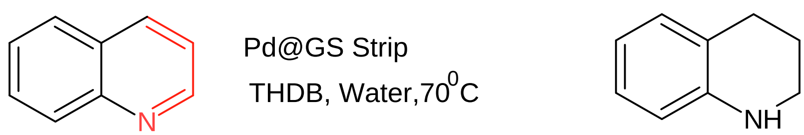
Scheme 20: Synthesis of polyphosphosponates by using PdNps Catalyst

Naushad Edayaduiia et al. green synthesis of di(indolyl) indolin-2-ones by using Pd Nps . The green of PdNps by using Aannua extract. One pot green synthesis of di(indolyl) indolin-2-ones from isatin and indole with Pd Nps in presence of water solvent . The green synthesized Pd Nps characterized by UV spectroscopy, TEM, TGA, XRD, and FTIR spectroscopy. Author bio reduction of Pd NPs confirmed by UV spectroscopy and crystalline structure confirmed by TEM spectroscopy. Green synthesized Pd NPs size range 20 to 30 confirmed by XRD spectroscopy and bioactivity confirmed by TGA spectroscopy.[52] [53] [54]



Scheme 21: Synthesis of di(indolyl) indolin-2-ones from isatin and indole with Pd NPs in presence of water solvent

M. Nasiruzzaman Shaikh et al. synthesis of tetrahydroquinoline by using green synthesis nanoparticles on green support as dip catalyst in water solvent. The region and chemoselective hydrogenation of quinolone from tetrahydroquinolene by using Pd@GS. The green synthesized palladium nanoparticles by using jute plant. Green synthesized nanoparticles characterized by SEM, TEM, XPS, and FTIR spectroscopy. The author element mapping by SEM spectroscopy and average Pd nanoparticle have diameter 15-20nm confirmed by TEM spectroscopy. Author oxidation state of palladium analysis by XPS spectroscopy .[55] [56]



Scheme 23: Regio and chemicoselectivity hydrogenation of tetrahydroquimoline from quinoline by using Pd@GS .

3. Metal oxide Nanoparticles:

There were many methods were employed during the synthesis of metal oxide nanoparticles can change the characteristics and control the properties of synthesized nano-oxides. The functionality of nanostructured metal oxide depend on their composition, geometry morphology etc. The novel chemical and physical properties of metal oxide nanoparticles are high density and limited size of corners and edges on their surface.[57]

Metal oxide nanoparticles play is an important role in the fields of material chemistry, catalysis, medicine and environment[58]. As the size of nanoparticles is decreases then the surfaces area is increases. The size of nanoparticles can change the magnetic, conducting and chemical properties. The magnetic and chemical properties of metal oxide nanoparticles is depend on the size and shape of the nanoparticles[59].

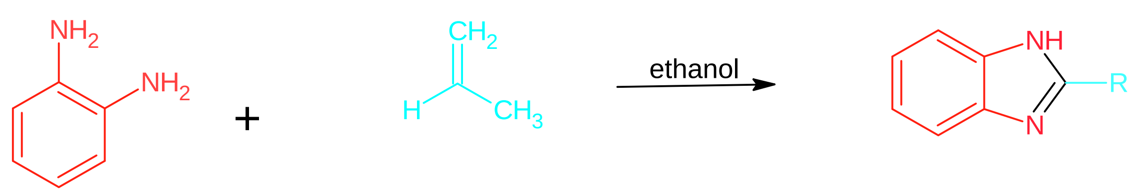
3.1 ZnO NPs:

Zinc is an active element and it is strong reducing agent, according to its reduction potential it can easily oxidize and for zinc oxide. Zinc plays an important role in human being as it is the most essential microelements[60]. It is present in all body tissues. ZnO as unique chemical sensing, optical and semiconducting properties. It has high band gap (3.3 eV) in UV-spectrum and high binding energy (60 meV) at room temperature. ZnO is present in two main forms – hexagonal wurtzite and cubic zinc blende.

The wurtzite structure is more stable at ambient conditions. ZnO nanostructures formed by using different chemical, physical and biological methods such as thermal evaporation technique, chemical reduction and synthesized by using plant extracts. The ZnO NPs are synthesized by physical, chemical and biological methods[61]. Out of this synthesis of ZnO NPs by biological method is ecofriendly.[62] Synthesis of ZnO NPs by using bacteria , yeast fungi and plant extracts.[63]

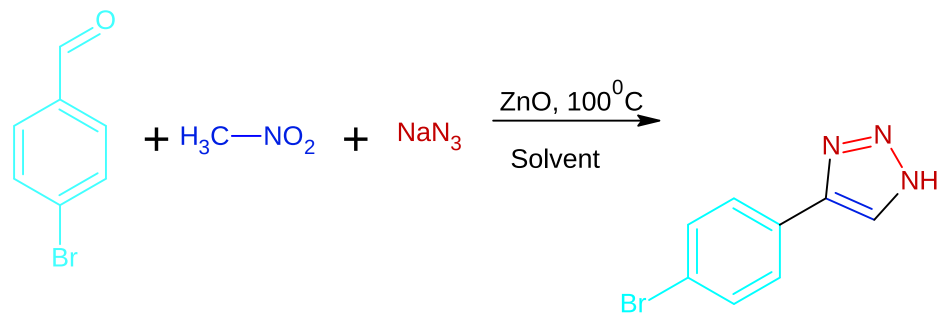
The synthesis of ZnO NPs with plants carried out using physical alkekengi, Trifolium pretense flowers, Cassia Auriculata. The synthesized ZnO NPs is characterized by XRD, TEM and SEM[64]. ZnO NPs has an antimicrobial activity and antifungal activity[65].

Bappi paul et al. green synthesis of benzimadazole by using green synthesized ZnO nanoparticles. The green synthesized ZnO nanoparticles by using parkoaronburghii seeds. One pot synthesis of benzimadazole from aldehyde, o-phenylenediamine and ZnO NPs in presence of ethanol solvent. Green synthesized ZnO NPs characterized by FTIR , XRD , SEM , TEM spectroscopy.[66] [67]



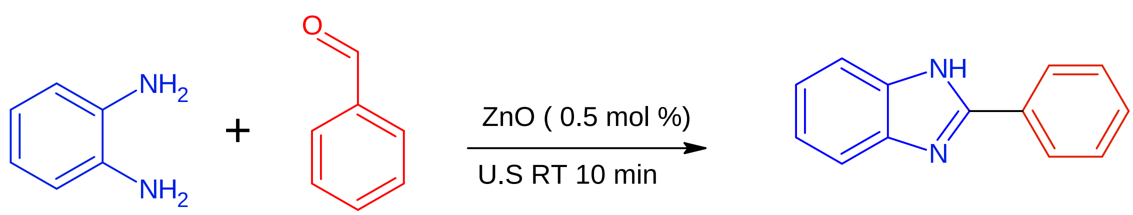
Scheme 24 : Green synthesis of benzimadazole by using ZnO nanoparticle.

Pramita Phukan et.al one pot three component synthesis of 4-aryl-NH-1,2,3-triazole by using green synthetic zinc oxide nanoparticle. The synthesis of 4-aryl-Nh-1,2,3-triazole from bromobenzaldehyde , nitromethane and sodium azide in presence of green synthetic zinc oxide nanoparticle. The green synthesis zinc oxide nanoparticle by using PEG 400 in presence of water solvent. The green synthesized ZnO nanoparticles characterize by FTIR,XRD,SEM,TEM spectroscopy.[68] [69]



Scheme 25: one pot three component synthesis of 4-aryl-NH-1,2,3-triazole by using green synthetic zinc oxide nanoparticle.

Bappi poul et.al one pot two component synthesis of 2-benzimidazole by using green synthetic zinc oxide nanoparticle. The synthesis of 2-benzimadazole from ortho phenylenediamine and benzaldehyde in presence of zinc oxide nanoparticle.green synthesis of zinc oxide nanoparticle by using the seed of Parkiaroxburghi. The green synthesized ZnO nanoparticles characterize by FTIR, XRD, SEM, TEM spectroscopy.[68]

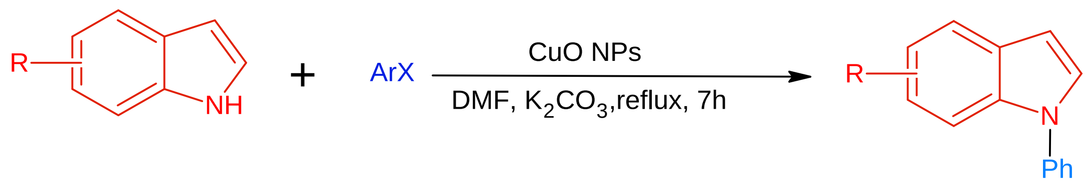


Scheme 26: One pot two component synthesis of 2-benzimidazol by using green synthetic ZnO NP.

3.2 CuO NPs:

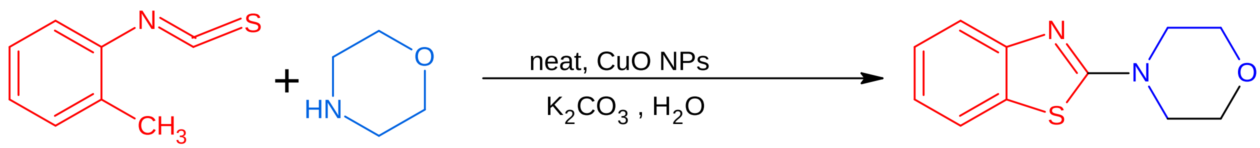
CuO NPs plays an important role due to their applications as antimicrobials and in gas sensors, batteries.[70] Human beings used copper and copper complexes from many centuries such as in water purifier, fungicides, algaecides and as an antibacterial. For synthesis of Cu NPs.[71] Magnolia leaf extract and other plant extracts have been used. The NPs also used for administration of cancer therapy. CuO NPs were act as an antimicrobial against E. Coil, Baccillus subtilis. There were many methods used for synthesis of CuO NPs such as sol-gel, sonochemical, precipitation method by using organic solvents and harsh reducing agents. But now-a-days NPs are synthesized by plants and it is more stable and the production rate of NP is more. The CuO nanoparticles were synthesized from gum karaya. The synthesized nanoparticles were characterized by SEM, TEM and XRD. SEM showed the CuO NPs distributed on the surface of gum matrix XRD gave information about the structure of CuO NPs. According to XRD the CuO NPs are monoclinic in structure.[72]

Mahmoud Nasrollahzadeh et al. reported the N-arylation of indoles with aryl halide in presence CuO NPs. The reaction is carried out at reflux in presence of base. The reaction required 7 hr. [73]



Scheme 28: N-arylation of indoles with aryl halide.

Saroj Rout et al. reported the synthesis of 2-substituted benzothiazole by using CuO NPs. The carried out at room temperature in presence of base and water as a solvent.[74] [72]



Scheme 29: Synthesis of 2-substituted benzothiazole.

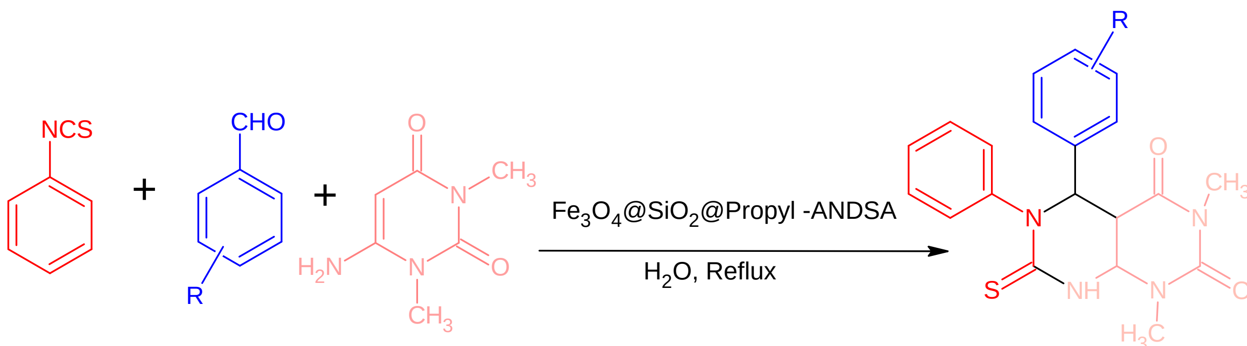
3.3 SiO_2 NPs:

Many scientists used SiO_2 NPs as a support materials because it is more stable, high thermal stability and do not react with magnet and light. The SiO_2 NPs were synthesized from plant extract such as bamboo leaves. There were many application of SiO_2 NPs such as it is used in biomedical, agriculture and other environmental application. The bamboo leaves used for synthesis of SiO_2 NPs because it contain large of SiO_2, it present in more abundant in nature and it grow more easily. The SiO_2 NPs were synthesized by sol-gel method. SiO_2 NPs used to remove Cu^{2+} and nitrate ions from water. The synthesized nanoparticles were characterized by FT-IR. It gives band at 340 cm^{-1} and 1635 cm^{-1} due to OH group and silanol group present on SiO_2 NPs. Also SiO_2 synthesized from lemon peel extract.

Sachin Otari et al. reported a synthesis of dihydroquinoline from benzaldehyde and 1-(2-aminophenyl) ethan-1-one by using Ag-BSiO_2 nanohybrid. The reaction carried out at 60°C in acetonitrile. Firstly synthesized SiO_2 NPs then synthesized BSiO_2 and then it was used for synthesis of Ag-BSiO_2 NPS. These synthesized nanoparticles characterized by SEM, TEM and XRD. These nanoparticle showed highly catalytic activity. Dihydroquinoline is used in pharmaceutical it is used as an antitumor drug .[75] [76]

Scheme 30: Synthesis of dihydroquinoline.

Ramin Ghorbani-Vaghei et al. reported a synthesis of pyrimido[4,5-d]pyrimidine by using Fe_3O_4@SiO_2Propyl-ANDSA NPs. The reaction carried out in aqueous medium and reflux it. The nanoparticles synthesized by Massart's method. The synthesized nanoparticles were characterized by FT-IR, TEM, TGA, XRD and X-ray spectroscopy (EDX) .[77] [78]

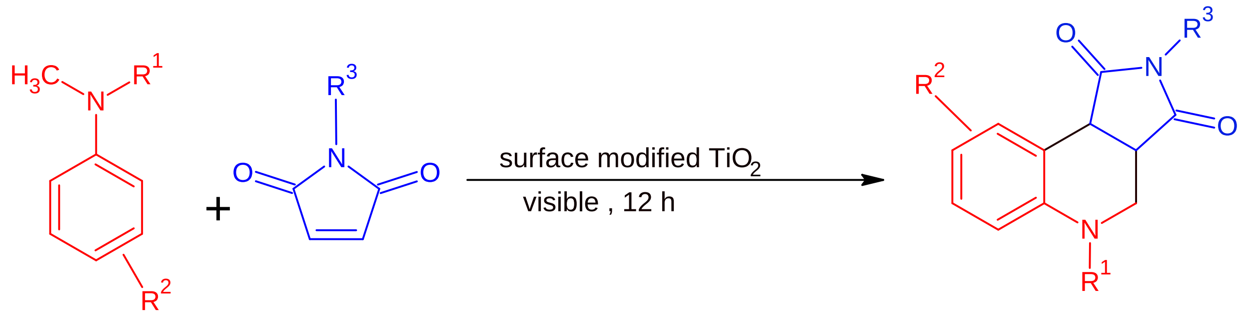


Scheme 31: Synthesis of pyrimido[4,5-d]pyrimidine.

3.4 TiO_2 NPs:

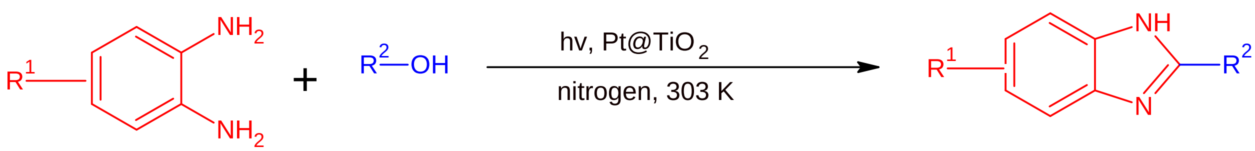
TiO_2 is an inorganic compound. It is white color solid. It is present in three phases at different temperature. It has remarkable physical and chemical properties so it is used in various field such as in industrial, antibacterial product and dye also. TiO_2 NPs are synthesized by various method including sol-gel method, co-precipitation, CVD and green synthesis method. Out of this green synthesis method is ecofriendly method because in this method nanoparticles are synthesized from plant extract, fungi, bacteria and enzymes. The TiO_2 NPs were synthesized from aloe vera plant extract. It is a medicinal plant. It contain vitamin and folic acid.

Satish Patil et al. Reported a visible light cyclization reaction by using NiO surface modified TiO_2 nanoparticles. The reaction carried out under the visible light and it required 12 hrs for completion of the reaction. The NiO_2 introduced on the surface of TiO_2 by using chemisorption-calcination-cycle (CCC) technique.[79]



Scheme 32: Visible light cyclization reaction.

Yasuhiro Shiraishi et al. reported a synthesis of benzimidazole by using Pt@TiO2 nanoparticles. This reaction was carried out under light. It was synthesized from alcohol and ortho-arylenediamines under presence of light. The wavelength of light is above 300nm. The Pt@TiO2 nanoparticle is a heterogeneous catalyst. The conversion of alcohol into aldehyde was carried out on the titanium surface and condensation of aldehyde and ortho-arylenediamines was carried out on the platinium surface.[80]



Scheme 33: Synthesis of benzimidazole.

4. Bimetallic nanoparticles :

Bimetallic nanoparticle is a combination of two different type of metals. This metals exhibit a novel properties. Bimetallic nanoparticles can be present in the different form such as alloys, core shell. When it is used as a catalyst in a chemical reaction then it show more activity than monometallic nanoparticles. Bimetallic nanoparticle has more activity, selectivity and inexpensive. The size of bimetallic nanoparticles determine the properties of itself as a catalyst. The synthesis of bimetallic nanoparticles are flexible. There are various method of synthesis of bimetallic nanoparticles and for their characterization. The electronic properties arises due to the bi-metallization is a novel property of bimetallic nanoparticles. The synthesis of bimetallic nanoparticles by using co-reduction, successive reduction and reduction of complexes containing both metal. Bimetallic nanoparticles are present in different structure such as crown jevel structure, hollow structure, core-shell and alloyed structure. Bimetallic nanoparticles show antimicrobial and antibacterial properties. There are clay supported bimetallic nanoparticles, zeolite supported bimetallic nanoparticles, fiber supported bimetallic nanoparticles, polymer supported bimetallic nanoparticle, graphene supported bimetallic nanoparticles and non-supported bimetallic nanoparticles.

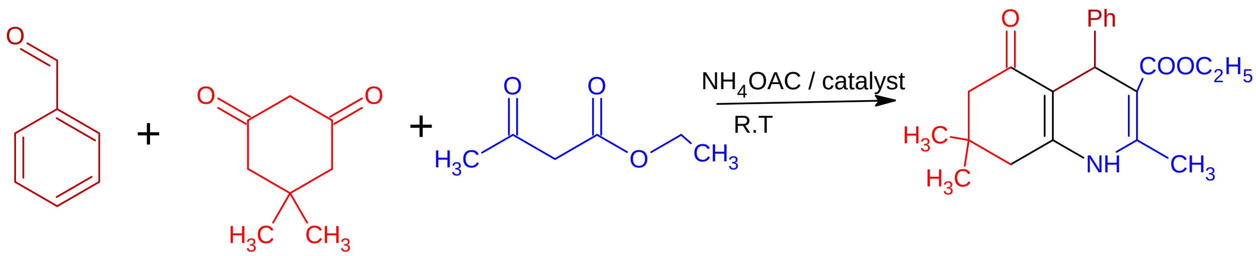
5. Supported Nanoparticles :

There are many applications of supported nanoparticles in chemical synthesis. Supported metal nanoparticles are used as a catalyst in oxidation and hydrogenation reaction. It has easily recover and reuses in many another chemical reaction. Metal nanoparticles are difficult to separate out from reaction mixture for further use because of their small size and solubility in reaction media. So to overcome this problem we used supported metal nanoparticles as a catalyst in a chemical reaction. The metal nanoparticles anchored onto the solid support. The support used in the form of oxides such as silica, zeolites and alumina. For synthesis of supported metal nanoparticles firstly, we have to synthesized solid support is important. The cold plasma method and laser electro dispersion methods are used for the preparation of supported metal nanoparticles. The supported nanoparticles is very useful than the metal nanoparticles because it is easily separate out from reaction mixture i.e. it is heterogeneous catalyst. In heterogeneous catalysis, the catalyst mostly used is solid. For the preparation of solid catalysts commonly used alumina, silica and titania as a support. [81]

5.1 Clay supported NPs:

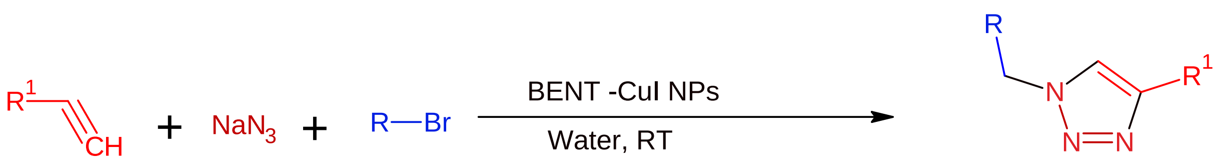
Clay or supported clay have widely used in organic reactions due to their inexpensive, eco-friendly, easily available and it has ability to act as acidic or basic catalyst. Clay is a part of soil, non-toxic and non-corrosive material. It has many application in organic synthesis. There are many types of clays and they are widely used in organic transformation. Because it has a large surface, good cation exchange capacity and having different physicochemical properties. Among different type of clay montmorillonite type of clay is more used in organic transformation. This clay is able to host different type of modifiers such as metal, metal salts and organic molecules. The montmorillonite clay consists of one octahedral sheet which is compressed between two tetrahedral sheets. It consist of divalent or trivalent metal cations which are surrounded by oxygen or hydroxyl anions in octahedral structure. There are four methods of clay modification such as acid activated clays, cation exchanged clays, pillared clays and porous clay. Acid activated clay is prepared by treating the clay with acid with continuous stirring at desired temperature. Hydrochloric acid, sulphuric acid are commonly used acid for synthesis of clay acid. The montmorillonite K10 and KSF. K10 are formed by treating clay with HCL and H_2SO_4 respectively. The pillared clays are prepared by inorganic species compressed between clay layers. Porous clay is a type of pillar clays. It is composed of silica pillars present between the clay interlamellar spaces. [82]

Lakshi saikia et.al reported multicomponent one pot synthesis of Hantzsch polyhydroquinoline by using clay supported Ni nanoparticle without using any organic solvent. The one pot polyhydroquinoline synthesis from aldehyde, dimedone, ethylacetoacetate and ammonium acetate at room temperature. The clay supported Ni nanoparticle characterized by using PXRD ,XRD and TEM spectroscopy.[83]



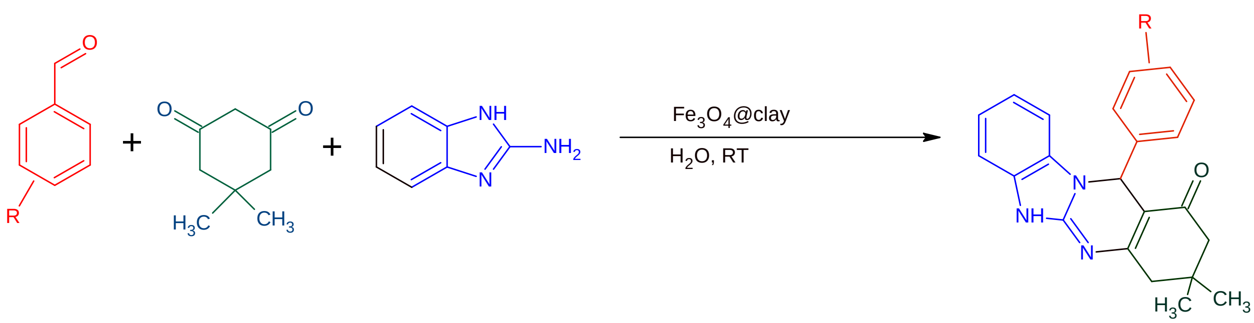
Scheme 34 : Green synthesis polyhydroquinoline by using clay supported Ni nanoparticle.

Pramod Chavan et al. reported a synthesis of 1,2,3-triazoles by using three components in presence of BENT- Cu nanoparticles. BENT- Cu nanoparticles means Bentonite clay supported CuI nanoparticles. It is heterogeneous catalyst. This reaction was carried out in aqueous medium at room temperature. [84]



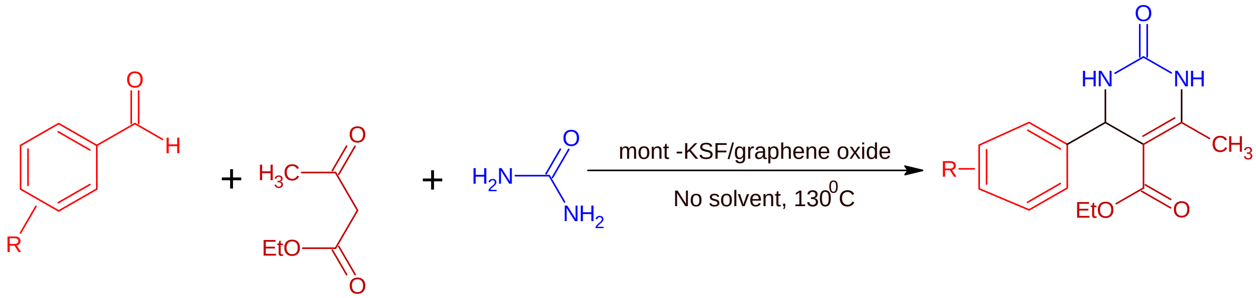
Scheme 35: BENT-CuI NPs catalyzed diversity oriented synthesis of 1,2,3- triazoles.

Ali Maleki et al. reported a synthesis of imidazo(thiazolo)pyrimidines by using Fe_3O_4@clay nanocatalyst. The reaction is carried out in aqueous medium under sonicator at room temperature. The nanocatalyst is a heterogeneous catalyst and it was easily removed from reaction by using magnet. The reaction carried out under sonicator so it is a green reaction. (Scheme 36)[85]



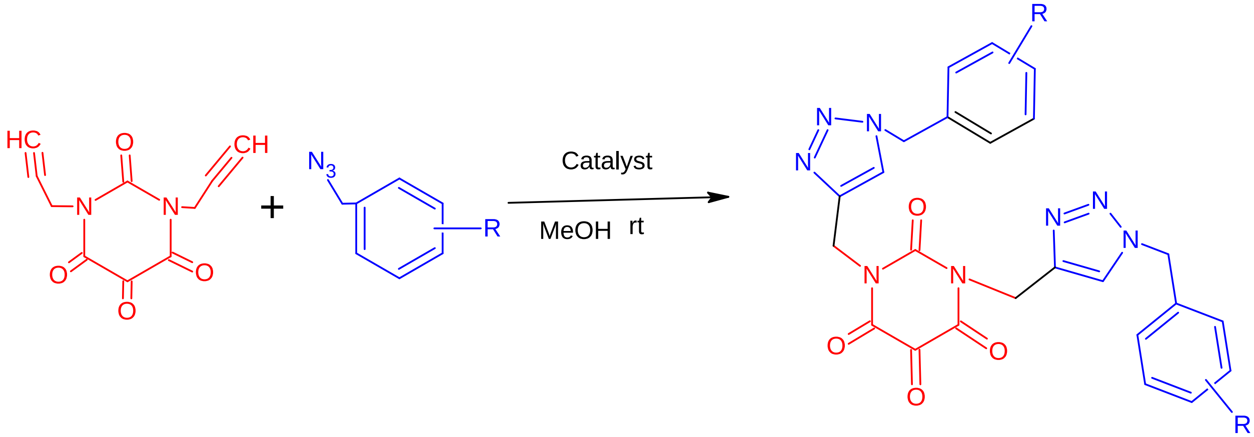
Scheme 36: Ultrasonic-assisted synthesis of imidazo(thiazolo)pyrimidines by using Fe_3O_4@clay nanocatalyst

Gopalpur Nagendrappa et al. reported a Biginelli reaction by using mont-KSF/grapheme oxide. The reaction carried out at 130°C without using solvent. The catalyst was reused and recyclable after 8th cycles. The desired product i.e. dihydropyrimidinone was obtained from benzaldehyde, ethylacetoacetate and urea. [82]



Scheme 37: Biginelli reaction benzaldehyde mont.-KSF/graphene oxide

Nitin Dubey et.al reported synthesis of 1,4-disustituted 1,2,3-triazole by using clay supported Cu(II) catalyst. The synthesis of 1,4-disubstituted 1,2,3-triazole from terminal alkyne and substituted azide. The synthesized clay supported Cu(II) catalyst characterized by SEM,XRD and TEM spectroscopy. [86] [87]

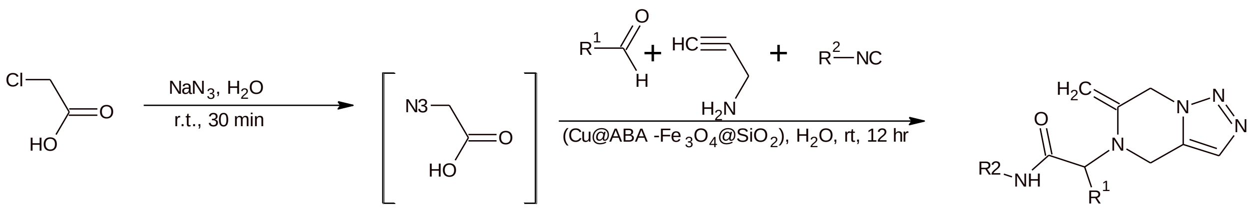


Scheme 38: Synthesis of 1,4 disustituted 1,2,3-triazole by using clay supported Cu(II)catalyst.

5.2 Silica supported NPs:

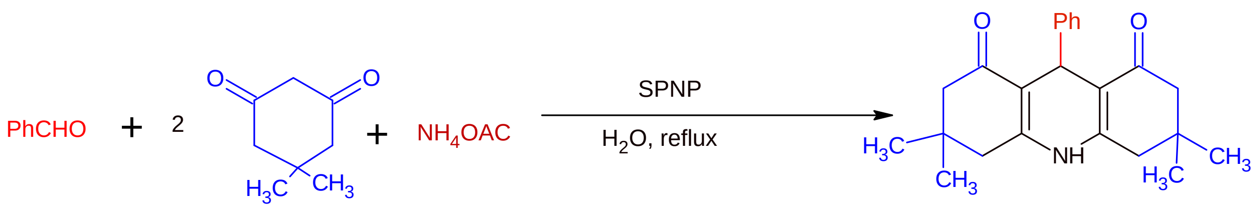
Silica has unique properties such as it provide large surface area, high chemical and thermal stability, tunable pore size and high adsorption capacity. Silica having different types depending upon its pore sizes such as micro porous, mesoporous and macro porous. The micro porous having pore size upto 2nm, mesoporous having pore size 2-50 nm and macro porous having pore size more than 50 nm. In heterogeneous catalysis, the macro porous size of silica is mainly used because it has large surface area. Different methods are used for immobilize metal nanoparticles over the surface of silica. Wet impregnation, deposition-precipitation, colloidal immobilization methods, solid-state grinding and post synthetic grafting method used for deposition of metal nanoparticle over silica. Silica-supported nanoparticles are used as a catalyst in chemical reaction which gives good yields, stability. It is used in coupling reaction, oxidation and hydrogenation.[88] [89]

Mohammad Sadegh Asgari et al. reported a synthesis of N-alkyl-2-aryl-2-(6-oxo-6,7-dihydro-4H-[1,2,3]triazolo[1,5-a]pyrazin-5-yl)acetamides by using [Cu@ABA-Fe3O4@SiO2] catalyst. Firstly 2-chloroacetic acid was reacted with sodium azide to give azide. The reaction was carried out in aqueous medium at room temperature. Then in second step aromatic aldehyde, prop-2-yn-1-amine, alkyl isocyanide added to azide to form desired product. (Scheme 39)[90] [91]



Scheme 39: Synthesis of N-alkyl-2-aryl-2-(6-oxo-6,7-dihydro-4H- [1,2,3]triazolo[1,5-a]pyrazin-5-yl)acetamides.

Ali Javid et al. reported a synthesis of 1,8-dioxodecahydroacridines by using silica-supported preyssler nanoparticles (SPNP). The reaction was carried out in aqueous medium under reflux. The SPNP is an acidic catalyst. (Scheme 40)[92]



Scheme 40: Synthesis of 1,8-dioxodecahydroacridine

References:

[1] T. M. Dhameliya *et al.*, “A decennary update on applications of metal nanoparticles (MNPs) in the synthesis of nitrogen- and oxygen-containing heterocyclic scaffolds,” *RSC Adv.*, vol. 10, no. 54, pp. 32740–32820, 2020, doi: 10.1039/D0RA02272A.

[2] A. Rusu, I.-A. Lungu, O.-L. Moldovan, C. Tanase, and G. Hancu, “Structural Characterization of the Millennial Antibacterial (Fluoro)Quinolones—Shaping the Fifth Generation,” *Pharmaceutics*, vol. 13, no. 8, p. 1289, Aug. 2021, doi: 10.3390/pharmaceutics13081289.

[3] E. Vitaku, D. T. Smith, and J. T. Njardarson, “Analysis of the Structural Diversity, Substitution Patterns, and Frequency of Nitrogen Heterocycles among U.S. FDA Approved Pharmaceuticals: Miniperspective,” *J. Med. Chem.*, vol. 57, no. 24, pp. 10257–10274, Dec. 2014, doi: 10.1021/jm501100b.

[4] M. D. Delost, D. T. Smith, B. J. Anderson, and J. T. Njardarson, “From Oxiranes to Oligomers: Architectures of U.S. FDA Approved Pharmaceuticals Containing Oxygen Heterocycles,” *J. Med. Chem.*, vol. 61, no. 24, pp. 10996–11020, Dec. 2018, doi: 10.1021/acs.jmedchem.8b00876.

[5] A. P. Taylor, R. P. Robinson, Y. M. Fobian, D. C. Blakemore, L. H. Jones, and O. Fadeyi, “Modern advances in heterocyclic chemistry in drug discovery,” *Org. Biomol. Chem.*, vol. 14, no. 28, pp. 6611–6637, 2016, doi: 10.1039/C6OB00936K.

[6] P. Das, M. D. Delost, M. H. Qureshi, D. T. Smith, and J. T. Njardarson, “A Survey of the Structures of US FDA Approved Combination Drugs,” *J. Med. Chem.*, vol. 62, no. 9, pp. 4265–4311, May 2019, doi: 10.1021/acs.jmedchem.8b01610.

[7] D. C. Blakemore *et al.*, “Organic synthesis provides opportunities to transform drug discovery,” *Nature Chem*, vol. 10, no. 4, pp. 383–394, Apr. 2018, doi: 10.1038/s41557-018-0021-z.

[8] H. Duan, D. Wang, and Y. Li, “Green chemistry for nanoparticle synthesis,” *Chem. Soc. Rev.*, vol. 44, no. 16, pp. 5778–5792, 2015, doi: 10.1039/C4CS00363B.

[9] M. Sengani, A. M. Grumezescu, and V. D. Rajeswari, “Recent trends and methodologies in gold nanoparticle synthesis – A prospective review on drug delivery aspect,” *OpenNano*, vol. 2, pp. 37–46, 2017, doi: 10.1016/j.onano.2017.07.001.

[10] K. R. Brown, D. G. Walter, and M. J. Natan, “Seeding of Colloidal Au Nanoparticle Solutions. 2. Improved Control of Particle Size and Shape,” *Chem. Mater.*, vol. 12, no. 2, pp. 306–313, Feb. 2000, doi: 10.1021/cm980065p.

[11] A. Gellé, T. Jin, L. De La Garza, G. D. Price, L. V. Besteiro, and A. Moores, “Applications of Plasmon-Enhanced Nanocatalysis to Organic Transformations,” *Chem. Rev.*, vol. 120, no. 2, pp. 986–1041, Jan. 2020, doi: 10.1021/acs.chemrev.9b00187.

[12] V. Polshettiwar and R. S. Varma, “Green chemistry by nano-catalysis,” *Green Chem.*, vol. 12, no. 5, p. 743, 2010, doi: 10.1039/b921171c.

[13] I. Khan, K. Saeed, and I. Khan, “Nanoparticles: Properties, applications and toxicities,” *Arabian Journal of Chemistry*, vol. 12, no. 7, pp. 908–931, Nov. 2019, doi: 10.1016/j.arabjc.2017.05.011.

[14] S. Mourdikoudis, R. M. Pallares, and N. T. K. Thanh, “Characterization techniques for nanoparticles: comparison and complementarity upon studying nanoparticle properties,” *Nanoscale*, vol. 10, no. 27, pp. 12871–12934, 2018, doi: 10.1039/C8NR02278J.

[15] V. J. Garole, B. C. Choudhary, S. R. Tetgure, D. J. Garole, and A. U. Borse, “Palladium nanocatalyst: green synthesis, characterization, and catalytic application,” *Int. J. Environ. Sci. Technol.*, vol. 16, no. 12, pp. 7885–7892, Dec. 2019, doi: 10.1007/s13762-018-2173-1.

[16] D. Nath and P. Banerjee, “Green nanotechnology – A new hope for medical biology,” *Environmental Toxicology and Pharmacology*, vol. 36, no. 3, pp. 997–1014, Nov. 2013, doi: 10.1016/j.etap.2013.09.002.

[17] K. Seth, S. R. Roy, D. N. Kommi, B. V. Pipaliya, and A. K. Chakraborti, “Silver nanoparticle-catalysed phenolysis of epoxides under neutral conditions: Scope and limitations of metal nanoparticles and applications towards drug synthesis,” *Journal of Molecular Catalysis A: Chemical*, vol. 392, pp. 164–172, Oct. 2014, doi: 10.1016/j.molcata.2014.05.011.

[18] V. K. Gupta, N. Atar, M. L. Yola, Z. Üstündağ, and L. Uzun, “A novel magnetic Fe@Au core–shell nanoparticles anchored graphene oxide recyclable nanocatalyst for the reduction of nitrophenol compounds,” *Water Research*, vol. 48, pp. 210–217, Jan. 2014, doi: 10.1016/j.watres.2013.09.027.

[19] M. Qasim, N. Udomluck, J. Chang, H. Park, and K. Kim, “Antimicrobial activity of silver nanoparticles encapsulated in poly-N-isopropylacrylamide-based polymeric nanoparticles,” *IJN*, vol. Volume 13, pp. 235–249, Jan. 2018, doi: 10.2147/IJN.S153485.

[20] K. S. B. Naidu, P. Govender, and J. K. Adam, “Nano Silver Particles in Biomedical and Clinical Applications : Review”.

[21] R. Kaur, J. Bariwal, L. G. Voskressensky, and E. V. Van Der Eycken, “Gold and silver nanoparticle-catalyzed synthesis of heterocyclic compounds,” *Chem Heterocycl Comp*, vol. 54, no. 3, pp. 241–248, Mar. 2018, doi: 10.1007/s10593-018-2259-1.

[22] S. G. Balwe, V. V. Shinde, A. A. Rokade, S. S. Park, and Y. T. Jeong, “Green synthesis and characterization of silver nanoparticles (Ag NPs) from extract of plant Radix Puerariae: An efficient and recyclable catalyst for the construction of pyrimido[1,2-b]indazole derivatives under solvent-free conditions,” *Catalysis Communications*, vol. 99, pp. 121–126, Aug. 2017, doi: 10.1016/j.catcom.2017.06.006.
[23] A. A. Rokade, M. P. Patil, S. I. Yoo, W. K. Lee, and S. S. Park, “Pure green chemical approach for synthesis of Ag_2O nanoparticles,” *Green Chemistry Letters and Reviews*, vol. 9, no. 4, pp. 216–222, Oct. 2016, doi: 10.1080/17518253.2016.1234005.
[24] A. Dandia, A. Sharma, V. Parewa, B. Kumawat, K. S. Rathore, and A. Sharma, “Amidic C–N bond cleavage of isatin: chemoselective synthesis of pyrrolo[2,3,4- *kl*]acridin-1-ones using Ag NPs decorated rGO composite as an efficient and recoverable catalyst under microwave irradiation,” *RSC Adv.*, vol. 5, no. 111, pp. 91888–91902, 2015, doi: 10.1039/C5RA11747J.
[25] Y. Deng *et al.*, “When can ionic liquids be considered readily biodegradable? Biodegradation pathways of pyridinium, pyrrolidinium and ammonium-based ionic liquids,” *Green Chem.*, vol. 17, no. 3, pp. 1479–1491, 2015, doi: 10.1039/C4GC01904K.
[26] H. Cong and J. A. Porco, “Total Synthesis of (±)-Sorocenol B Employing Nanoparticle Catalysis,” *Org. Lett.*, vol. 14, no. 10, pp. 2516–2519, May 2012, doi: 10.1021/ol300800r.
[27] D. Iordanidou, T. Zarganes-Tzitzikas, C. G. Neochoritis, and I. N. Lykakis, “Application of Silver Nanoparticles in the Multicomponent Reaction Domain: A Combined Catalytic Reduction Methodology to Efficiently Access Potential Hypertension or Inflammation Inhibitors,” p. 78.
[28] D. Philip, “Honey mediated green synthesis of gold nanoparticles,” *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 73, no. 4, pp. 650–653, Aug. 2009, doi: 10.1016/j.saa.2009.03.007.
[29] S. Aswathy Aromal and D. Philip, “Green synthesis of gold nanoparticles using Trigonella foenum-graecum and its size-dependent catalytic activity,” *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, vol. 97, pp. 1–5, Nov. 2012, doi: 10.1016/j.saa.2012.05.083.
[30] G. A. Monti, N. M. Correa, R. D. Falcone, G. F. Silbestri, and F. Moyano, “Gold Nanoparticles Stabilized by Sulfonated-Imidazolium Salts as Promising Catalyst in Water,” *ChemistrySelect*, vol. 4, no. 46, pp. 13496–13502, Dec. 2019, doi: 10.1002/slct.201903396.
[31] D. Ren *et al.*, “An Unusual Chemoselective Hydrogenation of Quinoline Compounds Using Supported Gold Catalysts,” *J. Am. Chem. Soc.*, vol. 134, no. 42, pp. 17592–17598, Oct. 2012, doi: 10.1021/ja3066978.
[32] M. J. Climent, A. Corma, J. C. Hernández, A. B. Hungría, S. Iborra, and S. Martínez-Silvestre, “Biomass into chemicals: One-pot two- and three-step synthesis of quinoxalines from biomass-derived glycols and 1,2-dinitrobenzene derivatives using supported gold nanoparticles as catalysts,” *Journal of Catalysis*, vol. 292, pp. 118–129, Aug. 2012, doi: 10.1016/j.jcat.2012.05.002.
[33] A. Berrichi, R. Bachir, M. Benabdallah, and N. Choukchou-Braham, “Supported nano gold catalyzed three-component coupling reactions of amines, dichloromethane and terminal alkynes (AHA),” *Tetrahedron Letters*, vol. 56, no. 11, pp. 1302–1306, Mar. 2015, doi: 10.1016/j.tetlet.2015.01.132.
[34] N. K. Ojha, G. V. Zyryanov, A. Majee, V. N. Charushin, O. N. Chupakhin, and S. Santra, “Copper nanoparticles as inexpensive and efficient catalyst: A valuable contribution in organic synthesis,” *Coordination Chemistry Reviews*, vol. 353, pp. 1–57, Dec. 2017, doi: 10.1016/j.ccr.2017.10.004.
[35] K. Cheirmadurai, S. Biswas, R. Murali, and P. Thanikaivelan, “Green synthesis of copper nanoparticles and conducting nanobiocomposites using plant and animal sources,” *RSC Adv.*, vol. 4, no. 37, p. 19507, 2014, doi: 10.1039/c4ra01414f.
[36] S. Shende, A. P. Ingle, A. Gade, and M. Rai, “Green synthesis of copper nanoparticles by Citrus medica Linn. (Idilimbu) juice and its antimicrobial activity,” *World J Microbiol Biotechnol*, vol. 31, no. 6, pp. 865–873, Jun. 2015, doi: 10.1007/s11274-015-1840-3.

[37] C. Chemistry International, “Green synthesis of copper nanoparticles by Citrus limon fruits extract, characterization and antibacterial activity,” Open Science Framework, preprint, Jun. 2021. doi: 10.31219/osf.io/76k8r.

[38] D. Vargas-Hernández *et al.*, “Furfuryl alcohol from furfural hydrogenation over copper supported on SBA-15 silica catalysts,” *Journal of Molecular Catalysis A: Chemical*, vol. 383–384, pp. 106–113, Mar. 2014, doi: 10.1016/j.molcata.2013.11.034.

[39] Z. Nasresfahani and M. Z. Kassaee, “Cu-Immobilized Mesoporous Silica Nanoparticles [Cu $^{2+}$ @MSNs-(CO $_2$ $^-$) $_2$] as an Efficient Nanocatalyst for One-Pot Synthesis of Pyrazolopyranopyrimidines in Water,” *ChemistrySelect*, vol. 2, no. 30, pp. 9642–9646, Oct. 2017, doi: 10.1002/slct.201701452.

[40] F. Alonso, Y. Moglie, G. Radivoy, and M. Yus, “Multicomponent Synthesis of 1,2,3-Triazoles in Water Catalyzed by Copper Nanoparticles on Activated Carbon,” *Adv. Synth. Catal.*, vol. 352, no. 18, pp. 3208–3214, Dec. 2010, doi: 10.1002/adsc.201000637.

[41] P. Diz *et al.*, “Sol–gel entrapped Cu in a silica matrix: An efficient heterogeneous nanocatalyst for Huisgen and Ullmann intramolecular coupling reactions,” *Applied Catalysis A: General*, vol. 502, pp. 86–95, Aug. 2015, doi: 10.1016/j.apcata.2015.05.025.

[42] I. S. Park, M. S. Kwon, Y. Kim, J. S. Lee, and J. Park, “Heterogeneous Copper Catalyst for the Cycloaddition of Azides and Alkynes without Additives under Ambient Conditions,” *Org. Lett.*, vol. 10, no. 3, pp. 497–500, Feb. 2008, doi: 10.1021/ol702790w.

[43] F. Ebrahimpour-Malamir, T. Hosseinnejad, R. Mirsafaei, and M. M. Heravi, “Synthesis, characterization and computational study of CuI nanoparticles immobilized on modified poly (styrene-co-maleic anhydride) as a green, efficient and recyclable heterogeneous catalyst in the synthesis of 1,4-disubstituted 1,2,3-triazoles via click,” *Appl Organometal Chem*, vol. 32, no. 1, p. e3913, Jan. 2018, doi: 10.1002/aoc.3913.

[44] S. Elavarasan, A. Bhaumik, and M. Sasidharan, “An Efficient Mesoporous Cu-Organic Nanorod for Friedländer Synthesis of Quinoline and Click Reactions,” *ChemCatChem*, vol. 11, no. 17, pp. 4340–4350, Sep. 2019, doi: 10.1002/cctc.201900860.

[45] S. Kazemi Movahed, P. Salari, M. Kasmaei, M. Armaghan, M. Dabiri, and M. M. Amini, “Copper nanoparticles incorporated on a mesoporous carbon nitride, an excellent catalyst in the Huisgen 1,3-dipolar cycloaddition and *N* -arylation of *N* -heterocycles,” *Appl Organometal Chem*, vol. 32, no. 1, p. e3914, Jan. 2018, doi: 10.1002/aoc.3914.

[46] O. Piermatti, “Green Synthesis of Pd Nanoparticles for Sustainable and Environmentally Benign Processes,” *Catalysts*, vol. 11, no. 11, p. 1258, Oct. 2021, doi: 10.3390/catal11111258.

[47] M. Nasrollahzadeh, S. M. Sajadi, E. Honarmand, and M. Maham, “Preparation of palladium nanoparticles using Euphorbia thymifolia L. leaf extract and evaluation of catalytic activity in the ligand-free Stille and Hiyama cross-coupling reactions in water,” *New J. Chem.*, vol. 39, no. 6, pp. 4745–4752, 2015, doi: 10.1039/C5NJ00244C.

[48] K. B. Narayanan, N. Sakthivel, and S. S. Han, “From Chemistry to Biology: Applications and Advantages of Green, Biosynthesized/Biofabricated Metal- and Carbon-based Nanoparticles,” *Fibers Polym*, vol. 22, no. 4, pp. 877–897, Apr. 2021, doi: 10.1007/s12221-021-0595-8.

[49] N. Basavegowda, K. Mishra, and Y. R. Lee, “Ultrasonic-assisted green synthesis of palladium nanoparticles and their nanocatalytic application in multicomponent reaction,” *New J. Chem.*, vol. 39, no. 2, pp. 972–977, 2015, doi: 10.1039/C4NJ01543F.

[50] T. T. Dang, Y. Zhu, J. S. Y. Ngiam, S. C. Ghosh, A. Chen, and A. M. Seayad, “Palladium Nanoparticles Supported on ZIF-8 As an Efficient Heterogeneous Catalyst for Aminocarbonylation,” *ACS Catal.*, vol. 3, no. 6, pp. 1406–1410, Jun. 2013, doi: 10.1021/cs400232b.

[51] M. Skowyra, V. Falguera, N. Azman, F. Segovia, and M. Almajano, “The Effect of Perilla frutescens Extract on the Oxidative Stability of Model Food Emulsions,” *Antioxidants*, vol. 3, no. 1, pp. 38–54, Jan. 2014, doi: 10.3390/antiox3010038.

[52] N. Edayadulla, N. Basavegowda, and Y. R. Lee, “Green synthesis and characterization of palladium nanoparticles and their catalytic performance for the efficient synthesis of biologically interesting di(indolyl)indolin-2-ones,” *Journal of Industrial and Engineering Chemistry*, vol. 21, pp. 1365–1372, Jan. 2015, doi: 10.1016/j.jiec.2014.06.007.
[53] J. Lei and H. Ju, “Signal amplification using functional nanomaterials for biosensing,” *Chem. Soc. Rev.*, vol. 41, no. 6, p. 2122, 2012, doi: 10.1039/c1cs15274b.
[54] T. Tachikawa and T. Majima, “Single-Molecule, Single-Particle Approaches for Exploring the Structure and Kinetics of Nanocatalysts,” *Langmuir*, vol. 28, no. 24, pp. 8933–8943, Jun. 2012, doi: 10.1021/la300177h.
[55] M. N. Shaikh, “Pd nanoparticles on green support as dip-catalyst: a facile transfer hydrogenation of olefins and *N* -heteroarenes in water,” *RSC Adv.*, vol. 9, no. 48, pp. 28199–28206, 2019, doi: 10.1039/C9RA06285H.
[56] Z. Zhang, N. A. Butt, and W. Zhang, “Asymmetric Hydrogenation of Nonaromatic Cyclic Substrates,” *Chem. Rev.*, vol. 116, no. 23, pp. 14769–14827, Dec. 2016, doi: 10.1021/acs.chemrev.6b00564.
[57] J. Jeevanandam, Y. S. Chan, and M. K. Danquah, “Biosynthesis of Metal and Metal Oxide Nanoparticles,” *ChemBioEng Reviews*, vol. 3, no. 2, pp. 55–67, Apr. 2016, doi: 10.1002/cben.201500018.
[58] J. Singh, T. Dutta, K.-H. Kim, M. Rawat, P. Samddar, and P. Kumar, “‘Green’ synthesis of metals and their oxide nanoparticles: applications for environmental remediation,” *J Nanobiotechnol*, vol. 16, no. 1, p. 84, Dec. 2018, doi: 10.1186/s12951-018-0408-4.
[59] S. Kanagasubbulakshmi and K. Kadirvelu, “Green synthesis of Iron oxide nanoparticles using Lagenaria siceraria and evaluation of its Antimicrobial activity,” *Def. Life. Sc. Jl.*, vol. 2, no. 4, p. 422, Nov. 2017, doi: 10.14429/dlsj.2.12277.
[60] M. Saha and A. R. Das, “Nanocrystalline ZnO: A Competent and Reusable Catalyst for the Preparation of Pharmacology Relevant Heterocycles in the Aqueous Medium,” *CGC*, vol. 7, no. 1, pp. 53–104, May 2020, doi: 10.2174/2213346107666200218122718.
[61] S. R. Attar, B. Shinde, and S. B. Kamble, “Enhanced catalytic activity of bio-fabricated ZnO NPs prepared by ultrasound-assisted route for the synthesis of tetraketone and benzylidenemalonitrile in hydrotropic aqueous medium,” *Res Chem Intermed*, vol. 46, no. 10, pp. 4723–4748, Oct. 2020, doi: 10.1007/s11164-020-04233-5.
[62] A. Kumar, D. Saxena, and M. K. Gupta, “Nanoparticle catalyzed reaction (NPCR): ZnO-NP catalyzed Ugi-reaction in aqueous medium,” *Green Chem.*, vol. 15, no. 10, p. 2699, 2013, doi: 10.1039/c3gc41101j.
[63] F. T. Thema, E. Manikandan, M. S. Dhlamini, and M. Maaza, “Green synthesis of ZnO nanoparticles via Agathosma betulina natural extract,” *Materials Letters*, vol. 161, pp. 124–127, Dec. 2015, doi: 10.1016/j.matlet.2015.08.052.
[64] B. Shinde *et al.*, “pH-Transformed ZnO-NPs /NaPTS: The First Room-Temperature Brisk Synthesis of Flavanones in Aqueous Medium,” *ChemistrySelect*, vol. 3, no. 46, pp. 13197–13206, Dec. 2018, doi: 10.1002/slct.201802189.
[65] A. Dandia, V. Parewa, S. L. Gupta, and K. S. Rathore, “Cobalt doped ZnS nanoparticles as a recyclable catalyst for solvent-free synthesis of heterocyclic privileged medicinal scaffolds under infrared irradiation,” *Journal of Molecular Catalysis A: Chemical*, vol. 373, pp. 61–71, Jul. 2013, doi: 10.1016/j.molcata.2013.02.010.
[66] B. Paul, S. Vadivel, S. S. Dhar, S. Debbarma, and M. Kumaravel, “One-pot green synthesis of zinc oxide nano rice and its application as sonocatalyst for degradation of organic dye and synthesis of 2-benzimidazole derivatives,” *Journal of Physics and Chemistry of Solids*, vol. 104, pp. 152–159, May 2017, doi: 10.1016/j.jpcs.2017.01.007.

[67] E. Selvarajan and V. Mohanasrinivasan, “Biosynthesis and characterization of ZnO nanoparticles using Lactobacillus plantarum VITES07,” *Materials Letters*, vol. 112, pp. 180–182, Dec. 2013, doi: 10.1016/j.matlet.2013.09.020.

[68] P. Phukan, S. Agarwal, K. Deori, and D. Sarma, “Zinc Oxide Nanoparticles Catalysed One-Pot Three-Component Reaction: A Facile Synthesis of 4-Aryl-NH-1,2,3-Triazoles,” *Catal Lett*, vol. 150, no. 8, pp. 2208–2219, Aug. 2020, doi: 10.1007/s10562-020-03143-w.

[69] W. Zhao *et al.*, “Self-Assembled ZnO Nanoparticle Capsules for Carrying and Delivering Isotretinoin to Cancer Cells,” *ACS Appl. Mater. Interfaces*, vol. 9, no. 22, pp. 18474–18481, Jun. 2017, doi: 10.1021/acsami.7b02542.

[70] S. Payra, A. Saha, S. Guchhait, and S. Banerjee, “Direct CuO nanoparticle-catalyzed synthesis of poly-substituted furans via oxidative C–H/C–H functionalization in aqueous medium,” *RSC Adv.*, vol. 6, no. 40, pp. 33462–33467, 2016, doi: 10.1039/C6RA04181G.

[71] B. Shinde *et al.*, “‘In water’ exploration of Alpinia zerumbet-fabricated CuO NPs in the presence of NaPTS at room temperature: green synthesis of 1,8-dioxooctahydroxanthene derivatives,” *Res Chem Intermed*, vol. 47, no. 3, pp. 1221–1237, Mar. 2021, doi: 10.1007/s11164-020-04351-0.

[72] A. Bhattacharjee and M. Ahmaruzzaman, “CuO nanostructures: facile synthesis and applications for enhanced photodegradation of organic compounds and reduction of p-nitrophenol from aqueous phase,” *RSC Adv.*, vol. 6, no. 47, pp. 41348–41363, 2016, doi: 10.1039/C6RA03624D.

[73] M. Laxman and M. M. Sharma, “Reduction of Isophorone With Sodium Borohydride: Change in Regioselectivity with Hydrotropes,” *Synthetic Communications*, vol. 20, no. 1, pp. 111–117, Jan. 1990, doi: 10.1080/00397919008054621.

[74] S. K. Rout, S. Guin, J. Nath, and B. K. Patel, “An ‘on-water’ exploration of CuO nanoparticle catalysed synthesis of 2-aminobenzothiazoles,” *Green Chem.*, vol. 14, no. 9, p. 2491, 2012, doi: 10.1039/c2gc35575b.

[75] S. V. Otari *et al.*, “Biomolecule-entrapped SiO2 nanoparticles for ultrafast green synthesis of silver nanoparticle–decorated hybrid nanostructures as effective catalysts,” *Ceramics International*, vol. 45, no. 5, pp. 5876–5882, Apr. 2019, doi: 10.1016/j.ceramint.2018.12.054.

[76] R. Behling, S. Valange, and G. Chatel, “Heterogeneous catalytic oxidation for lignin valorization into valuable chemicals: what results? What limitations? What trends?,” *Green Chem.*, vol. 18, no. 7, pp. 1839–1854, 2016, doi: 10.1039/C5GC03061G.

[77] R. Ghorbani-Vaghei and N. Sarmast, “Green synthesis of new pyrimido[4,5-d]pyrimidine derivatives using 7-aminonaphthalene-1,3-disulfonic acid-functionalized magnetic Fe_3O_4@SiO_2 nanoparticles as catalyst,” *Appl Organometal Chem*, vol. 32, no. 2, Feb. 2018, doi: 10.1002/aoc.4003.

[78] S. Badvel, R. R. Gopireddy, T. B. Shaik, S. Hasti, V. R. Tummaluru, and N. R. Chamarthi, “An efficient one-pot three-component synthesis of pyrimido[4,5-d]pyrimidine derivatives in aqueous medium,” *Chem Heterocycl Comp*, vol. 51, no. 8, pp. 749–753, Aug. 2015, doi: 10.1007/s10593-015-1769-3.

[79] S. A. Dake *et al.*, “Phosphonium Ionic Liquid: A Novel Catalyst for Benzyl Halide Oxidation,” *Synthetic Communications*, vol. 39, no. 21, pp. 3898–3904, Oct. 2009, doi: 10.1080/00397910902840835.

[80] Y. Shiraishi, Y. Sugano, S. Tanaka, and T. Hirai, “One-Pot Synthesis of Benzimidazoles by Simultaneous Photocatalytic and Catalytic Reactions on Pt@TiO2 Nanoparticles,” *Angewandte Chemie International Edition*, vol. 49, no. 9, pp. 1656–1660, Feb. 2010, doi: 10.1002/anie.200906573.

[81] M. J. Ndolomingo, N. Bingwa, and R. Meijboom, “Review of supported metal nanoparticles: synthesis methodologies, advantages and application as catalysts,” *J Mater Sci*, vol. 55, no. 15, pp. 6195–6241, May 2020, doi: 10.1007/s10853-020-04415-x.

[82] G. Nagendrappa and R. R. Chowreddy, “Organic Reactions Using Clay and Clay-Supported Catalysts: A Survey of Recent Literature,” *Catal Surv Asia*, vol. 25, no. 3, pp. 231–278, Sep. 2021, doi: 10.1007/s10563-021-09333-9.

[83] L. Saikia, D. Dutta, and D. K. Dutta, “Efficient clay supported Ni0 nanoparticles as heterogeneous catalyst for solvent-free synthesis of Hantzsch polyhydroquinoline,” *Catalysis Communications*, vol. 19, pp. 1–4, Mar. 2012, doi: 10.1016/j.catcom.2011.12.013.

[84] P. V. Chavan, S. P. Charate, U. V. Desai, C. V. Rode, and P. P. Wadgaonkar, “Bentonite - Clay - Supported Cuprous Iodide Nanoparticles (BENT- CuI NPs): A New Heterogeneous Catalyst in Diversity - Oriented Synthesis of 1, 2, 3- Triazoles in Aqueous Medium,” *ChemistrySelect*, vol. 4, no. 24, pp. 7144–7150, Jun. 2019, doi: 10.1002/slct.201900421.

[85] A. Maleki and M. Aghaei, “Ultrasonic assisted synergetic green synthesis of polycyclic imidazo(thiazolo)pyrimidines by using Fe3O4@clay core-shell,” *Ultrasonics Sonochemistry*, vol. 38, pp. 585–589, Sep. 2017, doi: 10.1016/j.ultsonch.2016.08.024.

[86] N. Dubey, P. Sharma, and A. Kumar, “Clay-Supported Cu(II) Catalyst: An Efficient, Heterogeneous, and Recyclable Catalyst for Synthesis of 1,4-Disubstituted 1,2,3-Triazoles from Alloxan-Derived Terminal Alkyne and Substituted Azides Using Click Chemistry,” *Synthetic Communications*, vol. 45, no. 22, pp. 2608–2626, Nov. 2015, doi: 10.1080/00397911.2015.1099675.

[87] P. Zoumpoulakis *et al.*, “Synthesis of novel sulfonamide-1,2,4-triazoles, 1,3,4-thiadiazoles and 1,3,4-oxadiazoles, as potential antibacterial and antifungal agents. Biological evaluation and conformational analysis studies,” *Bioorganic & Medicinal Chemistry*, vol. 20, no. 4, pp. 1569–1583, Feb. 2012, doi: 10.1016/j.bmc.2011.12.031.

[88] A. Javid, A. Khojastehnezhad, M. Heravi, and F. F. Bamoharram, “Silica-Supported Preyssler Nanoparticles Catalyzed Simple and Efficient One-Pot Synthesis of 1,8-Dioxodecahydroacridines in Aqueous Media,” *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*, vol. 42, no. 1, pp. 14–17, Jan. 2012, doi: 10.1080/15533174.2011.609221.

[89] M. S. Asgari *et al.*, “Magnetic silica nanoparticle-supported copper complex as an efficient catalyst for the synthesis of novel triazolopyrazinylacetamides with improved antibacterial activity,” *Chem Heterocycl Comp*, vol. 56, no. 4, pp. 488–494, Apr. 2020, doi: 10.1007/s10593-020-02685-6.

[90] M. S. Asgari *et al.*, “Magnetic silica nanoparticle-supported copper complex as an efficient catalyst for the synthesis of novel triazolopyrazinylacetamides with improved antibacterial activity,” *Chem Heterocycl Comp*, vol. 56, no. 4, pp. 488–494, Apr. 2020, doi: 10.1007/s10593-020-02685-6.

[91] M. H. Shaikh *et al.*, “1,2,3-Triazole derivatives as antitubercular agents: synthesis, biological evaluation and molecular docking study,” *Med. Chem. Commun.*, vol. 6, no. 6, pp. 1104–1116, 2015, doi: 10.1039/C5MD00057B.

[92] A. Javid, A. Khojastehnezhad, M. Heravi, and F. F. Bamoharram, “Silica-Supported Preyssler Nanoparticles Catalyzed Simple and Efficient One-Pot Synthesis of 1,8-Dioxodecahydroacridines in Aqueous Media,” *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*, vol. 42, no. 1, pp. 14–17, Jan. 2012, doi: 10.1080/15533174.2011.609221.