HETEROCYCLES, Vol. 85, No. 3, 2012, pp. 545 - 586. © 2012 The Japan Institute of Heterocyclic Chemistry
Received, 7th December, 2011, Accepted, 2nd February, 2012, Published online, 13th February, 2012
DOI: 10.3987/REV-11-725

APPLICATION OF NANOMATERIALS IN HETEROCYCLIC CHEMISTRY

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Abstract – This review focused on the application of nano-materials in heterocyclic chemistry. The main part of review is constituted by sections in which the reactions catalyzed by nanomaterials. In the last part of this review, emphasis is given to the heterocyclic supported nanomaterials and their importance in the catalysis.

CONTENTS

1. INTRODUCTION

Major advances have been made in the field of nanoscale chemistry have important effect on industry, environment and society. Nano-materials can made synthesis more economic, greener and more sustainable.

These materials, notable for their extremely small size, have the potential for wide-ranging industrial, biomedical, and electronic applications. As a result of recent improvement in technologies to see and manipulate these materials, the nanomaterials field has seen a huge increase in funding from private enterprises and government, and academic researchers within the field have formed many partnerships.

Nanomaterials can be metals, ceramics, polymeric materials, or composite materials. Their defining characteristic is a very small feature size in the range of 1-100 nanometers (nm).

A heterocyclic compound is defined as any organic compounds where their molecules are characterized by rings containing at least one atom other than carbon. It is this rich diversity of physical and biological properties that has lead to intense study of heterocyclic compounds.

2. APPLICATION OF NANOMATERIALS IN PREPARING HETEROCYCLIC COMPOUNDS

2.1 THREE- MEMBERED HETEROCYCLIC COMPOUNDS

Epoxides

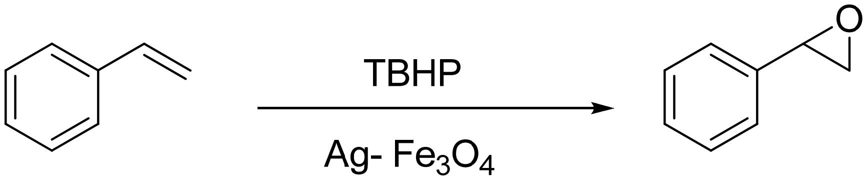
The alkenes epoxidation has attracted considerable interest of the scientific community due to the epoxides versatility as organic synthesis intermediates and widely used in production of paints, epoxy resins and surfactants.

Oxygenated molecules, such as epoxides, alcohols and ketones, are key-intermediates of the fine chemical industry. They are indeed involved in the massive production of commodity chemicals, such as polymers, paints, plastics, *etc.*

When formed as particles of less than ~ 10 nm in dimension and supported on metal oxides, Au is an active catalyst with unusual, size-dependent activity and selectivity which has been demonstrated for Olefine epoxidation.[1-6]

Silver nanoparticles catalyzed reaction between ethylene with oxygen afforded epoxide.[7]

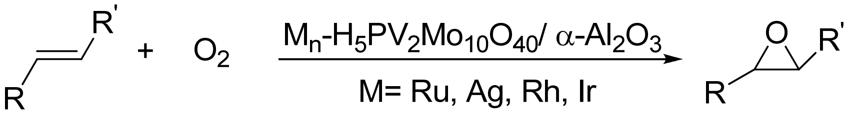
Olefin epoxidation can be done with magnetically recyclable catalyst (**Scheme 1**).[8,9]



Scheme 1

By a sequence of redox reactions and supported on α-alumina, Ag and Ru nanoparticles was prepared. These particles stabilized with $H_5PV_2Mo_{10}O_{40}$. They were used as efficient catalysts for the direct aerobic epoxidation of alkenes in the liquid phase.

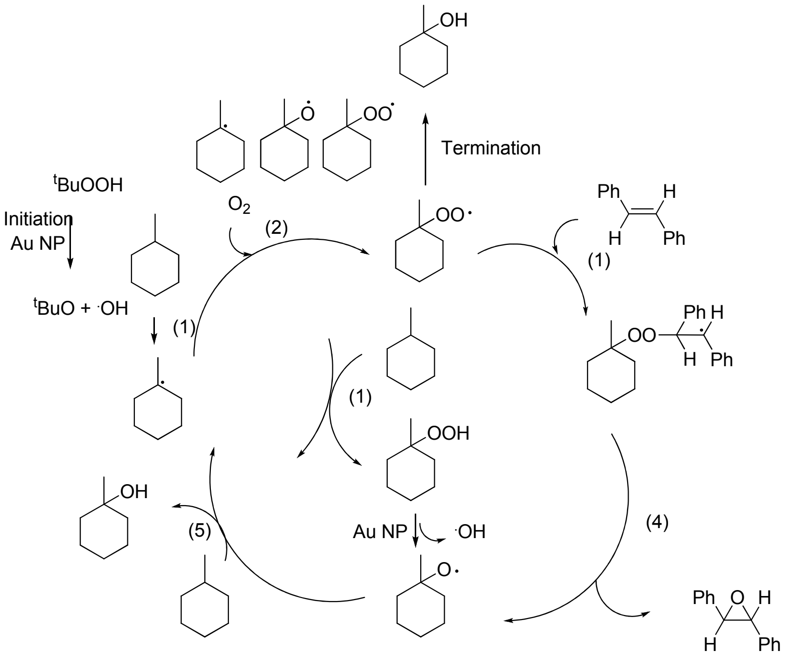
Polyoxometalates, such as $H_5PV_2Mo_{10}O_{40}$ have special characters. They inhibit auto oxidation reactions of free radicals so C-H homolytic bond cleavage of hydrocarbons may be inhibited by them. They stabilized nanoparticles because they have electrostatic repulsion because of their high anionic charge. They prevent particle aggregation and improved selectivity and efficiency of catalyst (**Scheme 2**).[10]



Scheme 2

Mendez *et al.* showed that supported gold nanoparticles can catalyze methylcyclohexane/stilbene co-oxidation reaction. They used gadolinium-doped titania nanocrystallites as support for gold nanoparticles. It has little influence on gold catalytic activity although reaction rated can be affected.

Support of catalyst can be obtained from mild hydrolysis of a new $Gd_4TiO\ (OPr^i)_{14}$ bimetallic oxoalkoxide. In epoxidation of stilbene, catalyst, $Au/TiO_2:Gd^{3+}$, was the powerful catalyst and it has the same potency as hydrophobic Au/SiO_2 catalyst (**Scheme 3**).[11]



Scheme 3

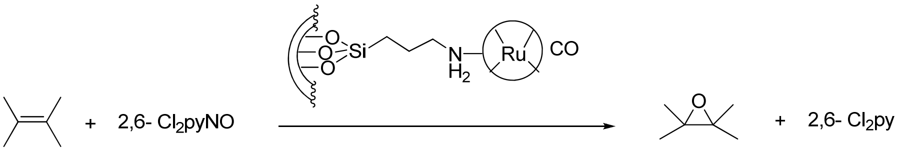
Recently mesoporous crystalline silicas, especially MCM-41, have been widely applied as a catalyst.

In epoxidation of olefins with *tert*-BuOOH in 1,2-dichloroethane as solvent, MCM-based catalyst was successfully used. Immobilization of $MO_2(acac)_2$ on Mobil Catalytic Material, MCM-41, afforded heterogeneous catalyst (**Scheme 4**).[12]

Scheme 4

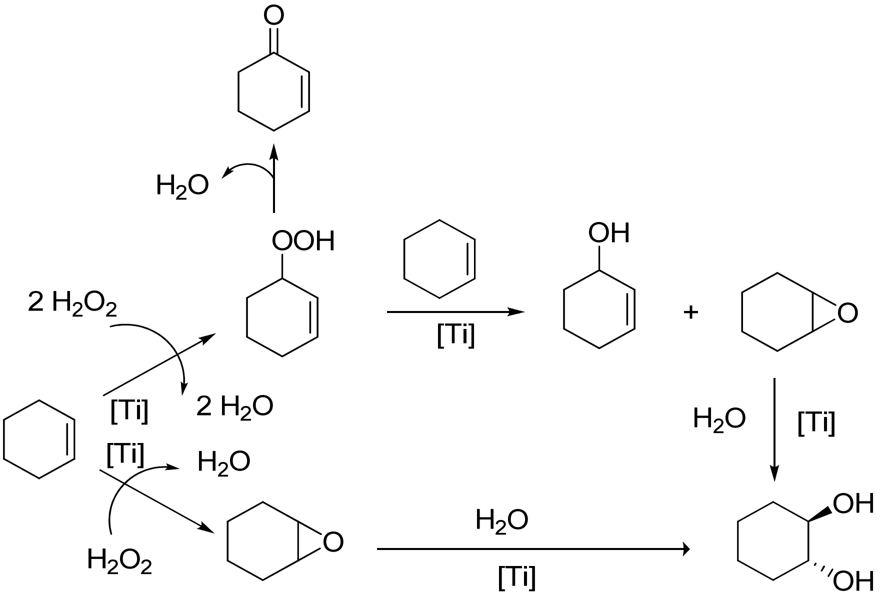
Active catalysts can be obtained by encapsulation of chiral ruthenium porphyrin [RuII(D4-Por*)CO] in modified mesoporous silica supports. This catalyst was applied for asymmetric epoxidation of alkenes by 2,6-dichloropyridine *N*-oxide.[13]

MCM-48 contains a three dimensional network, and MCM-41 has one dimensional straight channel system, so MCM-48 provides a large surface area for high accessibility of reactant(s) to active sites within the porous network structure. This catalyst was used in the asymmetric epoxidation of styrene with 2,6-Cl_2pyNO catalyzed (**Scheme 5**).



Scheme 5

MCM-41 supported titanium catalysts was prepared and used in epoxidation reaction. Epoxidation of cyclohexene with 30% hydrogen peroxide in *tert*-butyl alcohol at 354 K proceed with this catalyst (**Scheme 6**). This catalyst led to epoxidise active hydroperoxotitanium species directly to cyclohexene.



Scheme 6

This different behaviour can be described with different titanium species that form two or three bonds with the surface or the higher titanium dispersion. Proposed idea can be assigned to larger surface of MCM-41.[14]

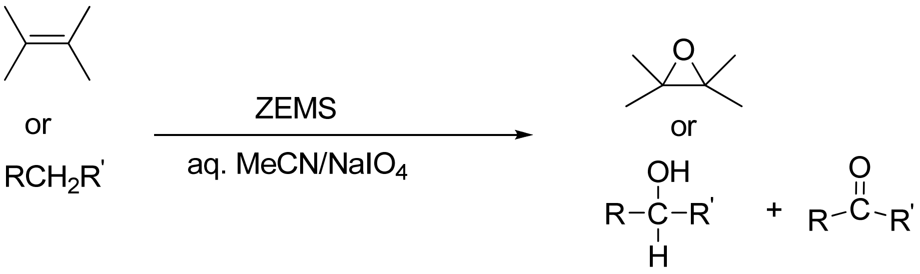
Improving hydrophobicity of catalyst with silylation of the surface of Ti-MCM-41 and removing water from the reaction media, increase catalytic activity of Ti-MCM-41 materials in the epoxidation of olefins. First approach influence catalyst directly but second one inhibit catalyst deactivation because removing water, reduce formation of diol produced by ring opening of epoxide.[15]

Self-assembled materials can be made by adsorption of titanium (IV) silsesquioxane complex in an all-silica MCM-41 molecular sieve. This heterogeneous catalyst used in alkene epoxidation in liquid phase applications.[16]

In oxidation of cyclohexene using aqueous H_2O_2, selectivity for epoxide formation (>98%) was acquired by using trialkylsiloxy-modified Ta (V) centers on mesoporous silica.[17]

By grafting titanium on a structured mesoporous SBA15 by means of titanium tetrachloride in the gas phase, new catalyst, TiO_2-SiO_2 has been synthesized. They used in the selective epoxidation of cyclooctene, cyclohexene, (*R*)-limonene and α-pinene. In presence of hydrogen peroxide (H_2O_2), *tert*-butyl hydroperoxide (TBHP) or cumyl hydroperoxide (CHP), as an oxidant, the selectivity is 100%. In reaction with H_2O_2, the catalyst is partially leached out but in the case of TBHP and CHP, no leaching of titanium is observed after four successive reaction cycles.[18]

Zeolite-encapsulated Mn (III) - salophen (ZEMS) was used as catalyst for biomimetic alkenes epoxidation and hydroxylation with sodium periodate catalyzed by Mirkhani *et al.* (**Scheme 7**).[19]



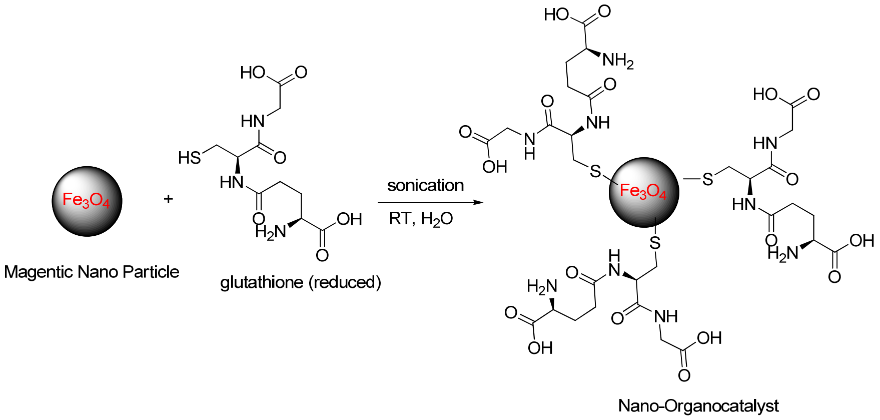
Scheme 7

2.2 FIVE- MEMBERED HETEROCYCLIC COMPOUNDS

Pyrrole

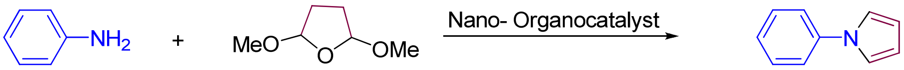
Cysteine and glutathione have highly reactive thiol group, which can be used for anchoring to the nano-ferrite surfaces, keeping active sites free for catalysis. They are aminoacids and glutathione found as an essential component of plant or human systems.

Polshettiwar *et al.* used both of them as a catalyst for Paal-Knorr reaction under same condation. They found that glutathione was more active than cysteine so glutathione was selected for preparing nano-organocatalyst (**Scheme 8**).



Scheme 8

Resulting catalyst was used in Paal-Knorr reaction (**Scheme 9**). It can be recovered by using external magnet.[20]



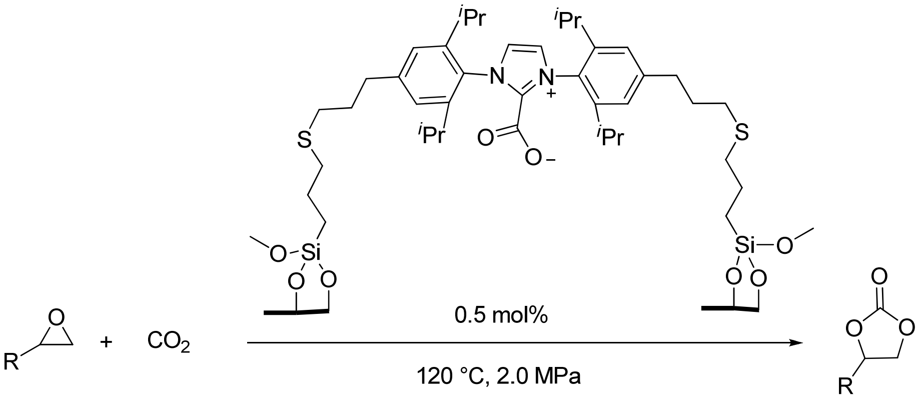
Scheme 9

Carbamates

Energy and getting warm of earth are serious challenge, attracted much attention. Fixation of carbon dioxide is proposed solution for solving the problem.

Polymer-supported gold NPs have been used in reaction between epoxides and CO_2 that generate carbamates.[21]

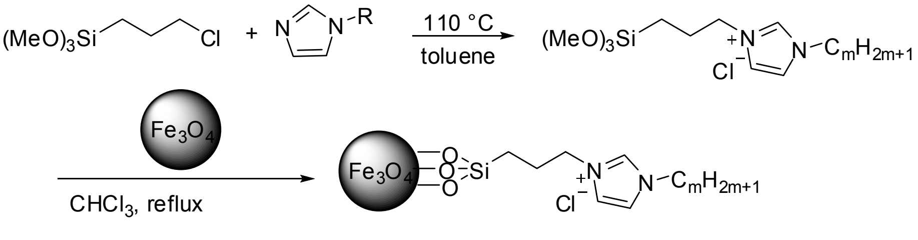
Another heterogeneous catalyst is MCM-41-IPr-CO_2 adduct, it can be act as regioselective catalyst under mild conditions (**Scheme 10**). CO_2 act as protective group for effectively stabilizing the NHC anchored on MCM-41 though catalyst can reused multiple times without loss in activity.[22]



Scheme 10

MNP-supported ionic liquid catalysts were synthesized and used in CO_2 cycloaddition reactions.[23] Magnetic nanoparticles have several advantages such as; good stability, easy synthesis and functionalization, high surface area and facile separation by magnetic forces, low toxicity and price so they can be used as catalyst support. Resulting catalyst can be recovered and reused.

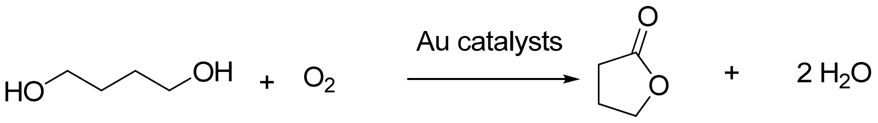
The procedure for preparing magnetic nanoparticle supported IL catalyst MNP was shown in **Scheme 11**.



Scheme 11

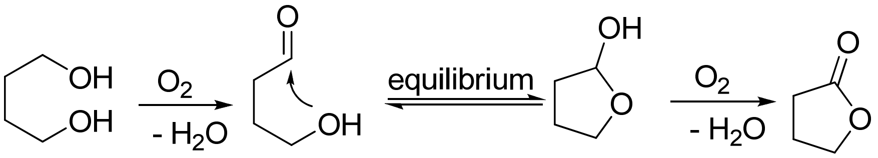
Lactones

Mitsudome used hydrotalcite-supported Au nanoparticles (Au/HT) as efficient catalysts for oxidative lactonization of various diols using molecular oxygen. Lactonization of 1,4-butanediol gave γ-butyrolactone is a fantastic reaction with high yields (**Scheme 12**).[24] The catalyst can be easily recovered by simple filtration and reused in another reaction.



Scheme 12

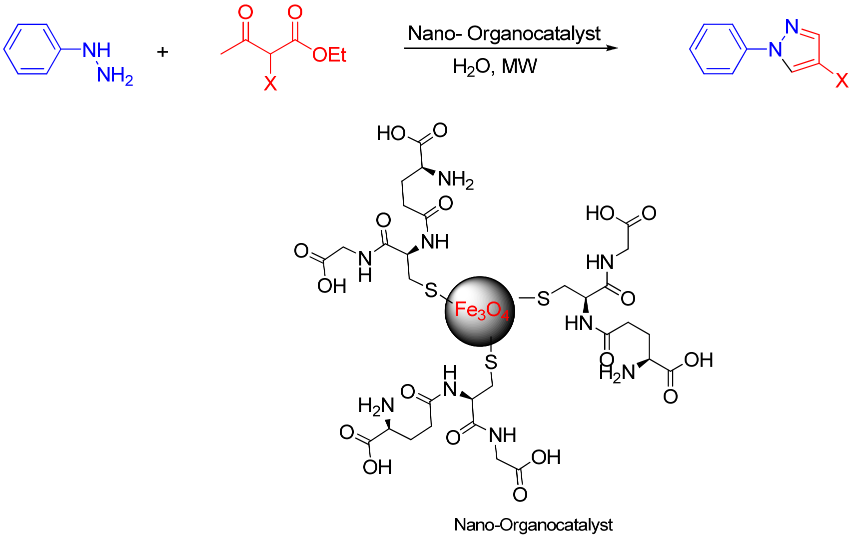
Formation of an Au–alcoholate species was promoted by basic site on the HT. These species led to generate hydroxyaldehyde, by smooth oxidation of one of the hydroxyl groups of the diol. Equilibrium exists between hydroxyaldehyde and a lactol. Further oxidation of the lactol converted it to corresponding lactone (**Scheme 13**).



Scheme 13

Pyrazoles

Pyrazoles can be prepared by different methods but these processes have long reaction times and most of them were done in organic solvents. She *et al.* decided to use nano-organocatalyst for the synthesis of pyrazole derivatives (**Scheme 14**).[20]



Scheme 14

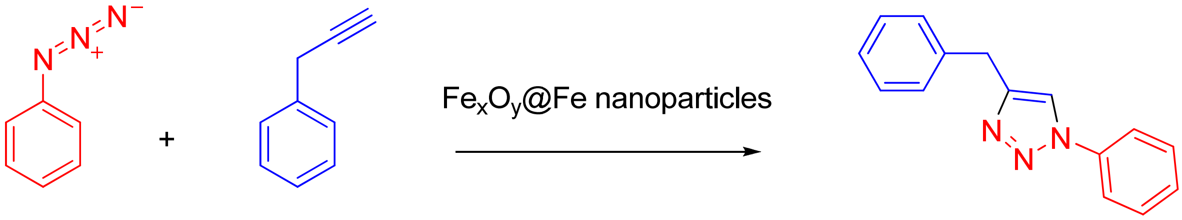
Reaction between hydrazines or hydrazides with 1,3-diketones or β-keto esters proceeded in aqueous medium in short time was catalysed with nano-organocatalyst. Pyrazoles, products, were simply extracted by ethyl acetate.

Tetrazoles

Tetrazoles were synthesized by [2+3]-cycloaddition of sodium azide with nitriles. Nanocrystalline ZnO catalyzed this process.[25]

1,2,3-Triazole

1,2,3-Triazole was prepared by a "Click" cycloaddition (**Scheme 15**). Reaction was catalyzed by nanoparticles but residual metal concentration must be controlled in products. With Fe*x*O*y*@Fe nanoparticles, a host of transition metal ions (Co^{2+}, Cu^{2+}, Ni^{2+}, Ru^{X+}, Rh^{X+}, Pd^{2+}, Ag^{+}, and Pt^{4+}) were sequestered from aqueous media. This method can help to reduce residual metal to pharmaceutical standards.[26]

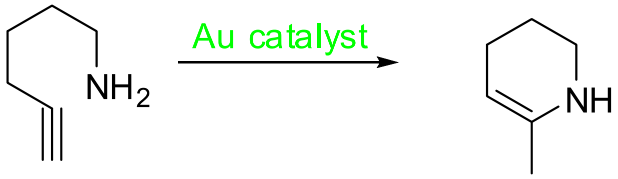


Scheme 15

2.3 SIX-MEMBERED HETEROCYCLIC COMPOUNDS

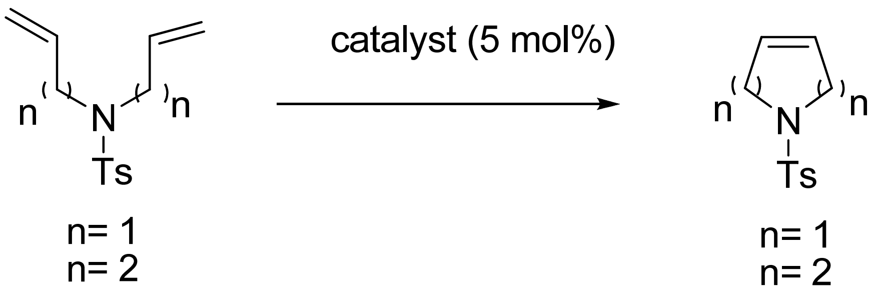
Pyridine

Fukuda and co-workers reported intramolecular cyclization of 5-alkynylamines to form tetrahydropyridine derivatives catalyzed by gold complexes (**Scheme 16**).[27,28]



Scheme 16

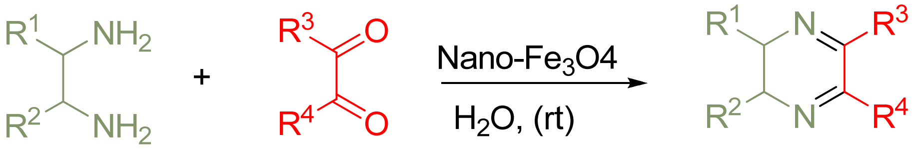
Ring-closing olefin metathesis was preceded by gold catalyst, prepared by monolayer-protected gold clusters with a Ru-carbene complex (**Scheme 17**). It showed same catalytic activity as simple Grubbs type or thioacetate-functionalized Ru-complexes and can be recovered and reused multiple.[29]



Scheme 17

Qinoxaline

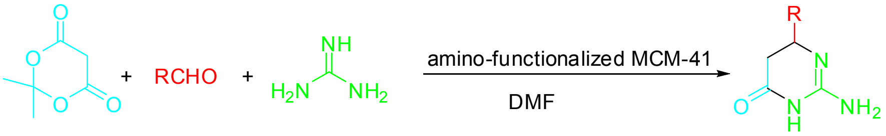
Reaction between 1,2-diamines and 1,2-dicarbonyl compounds in water was catalyzed by magnetic Fe_3O_4 nanoparticles to afforded quinoxaline derivatives (**Scheme 18**).[30] By using external magnet, the catalyst can be recovered and reused without loss of activity in five cycled.



Scheme 18

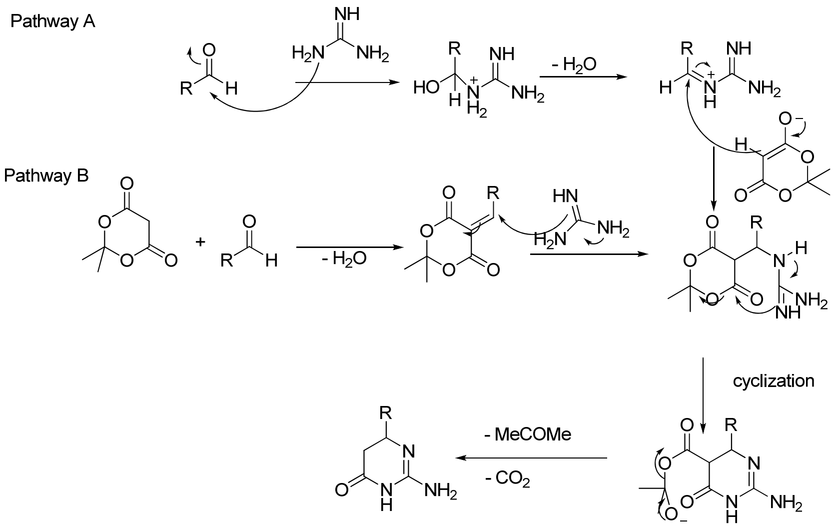
Pyrimidine

Biginelli reaction is an acid catalyzed three component reaction between an aldehyde, β-ketoester or β-diketone and urea or thiourea which produced 4-dihydropyrimidin-2(1*H*)-ones and 3, 4-dihydropyrimidin-2(1*H*)-thiones. Cyclocondensation of Meldrum's acid, aldehydes and guanidinium carbonate was catalyzed with a catalytic amount of amino-functionalized MCM-41 produce 2-amino-5, 6-dihydropyrimidin-4(3*H*)-one (**Scheme 19**). It is worth noting that mentioned method had some advantages such as; high yields, short reactions times and ease of product isolation.[31]



Scheme 19

They proposed a mechanism for this reaction, as shown in **Scheme 20**.



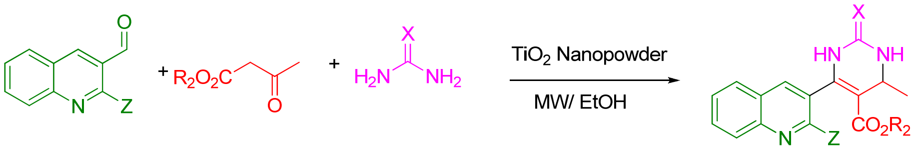
Scheme 20

Mirjalili *et al.* used nano-silica supported boron trifluoride (nano-$BF_3.SiO_2$) as an efficient catalyst for preparing 3,4-dihydropyrimidin-2(1*H*)-ones and 3,4-dihydropyrimidin-2(1*H*)-thione under solvent free reaction. Good to excellent yield, mild reaction condition, ease of operation and workup, short reaction time and high product purity can be mentioned as advantages of this method.[32]

4-amino-5-pyrimidinecarbonitriles was synthesized by three-component reaction of malononitrile, aldehydes, and *N*-unsubstituted amidines, under aqueous conditions. ZnO nanoparticles used as catalyst that has remarkable activity and it can be recycled.[33]

Uhm *et al.* carried out stereoselective Biginelli reaction in the presence of l-proline and Ni encapsulated nanoparticles to get more *S*-enantiomer for 3,4-dihydropyrimidine (DHPM) with an excess of about 18%.[34] Ni and Cu nanoparticles were coated by Methane (CH_4) gas. Core diameters were 10 and 30 nm for Ni and Cu nanoparticles, respectively and thickness of thin carbon layer was 2-3 nm for both of them.

Another modification to Biginelli reaction was reported by Naik *et al.*[35] They used titanium dioxide (TiO_2) nanopowder as an efficient catalyst and microwave induced, led to reducing time reaction (**Scheme 21**).

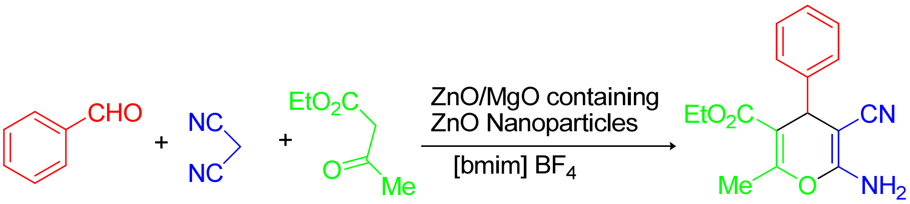


Scheme 21

Pyranes

Valizadeh *et al.* used inexpensive and available catalyst, ZnO/MgO solid sample containing ZnO nanoparticles, in one pot reaction for synthesizing 4*H*-pyrans and coumarins in ionic liquid, [bmim]BF_4

(**Scheme 22**). High yields, short reaction times, and mild solvent-free reaction conditions were advantages of this method.[36]



Scheme 22

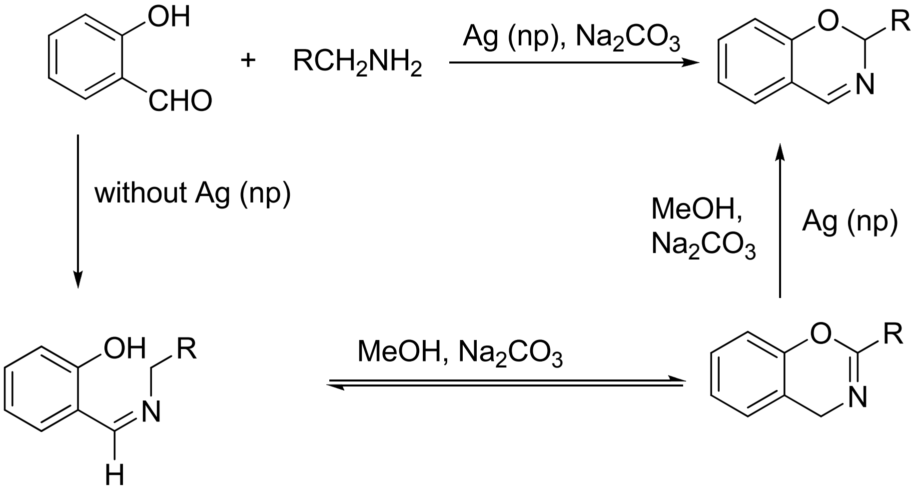
Tetracyanoethylene and various activated CH-acid compounds reacted to afford the corresponding pyran annulated heterocyclic ring systems, Shaabani *et al.* used pyridine-functionalized MCM-41 as a catalyst in reaction. They mentioned this catalyst can be recycled and reused without loss of efficiency.[37]

2.4 BENZO-FUSED HETEROCYCLIC COMPOUNDS

4H-Benzo[e][1,3]oxazine.

Treatment of $AgNO_3$ with a macrocyclic Schiff base ligand benzildiethylenetriamine as a reductant and low molecular weight organic compound, thiosalicylic acid (TSA) as a protective agent, produces highly concentrated and stable suspension of Ag-nanoparticles (**Scheme 23**).

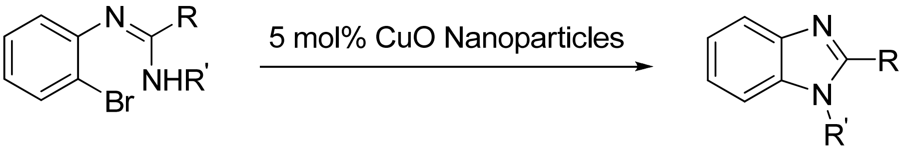
Ag-nanoparticles, used as efficient catalyts for synthesizing heterocyclic compounds. By using 10 mol% of Ag-nanoparticles in the presence of Na_2CO_3 in MeOH, salicyldehyde coupled with aliphatic amines through the oxidative cyclization of Schiff base. Prevention from using metal oxides or organic oxidizing agents is the most remarkable character of this method.[38]



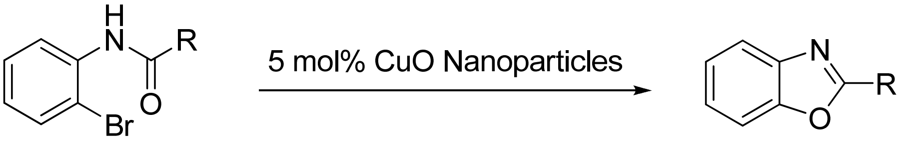
Scheme 23

Benzimidazole, Benzthiazole, Benzoxazole

Intramolecular cyclization of *o*-bromoaryl derivatives produced substituted benzimidazoles, 2-aminobenzimidazoles, 2-aminobenzothiazoles, and benzoxazoles (**Schemes 24 and 25**). Copper (II) oxide nanoparticles as a heterogeneous catalyst, catalyzed reaction. It can be recovered and recycled.[39]



Scheme 24

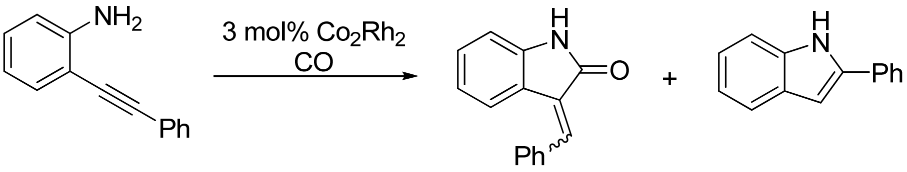


Scheme 25

2-Substituted benzimidazoles were synthesized by reaction of aldehydes with *o*-phenylenediamine. This reaction was efficiently catalyzed with $FeCl_3$-doped polyaniline nanoparticles.[40]

Oxindole

Park *et al.* found that carbonylative cycloaddition of 2-alkynylanilines was catalyzed by Co_2Rh_2 (**Scheme 26**). Resulted oxindoles are synthetic intermediates for biologically active natural products.

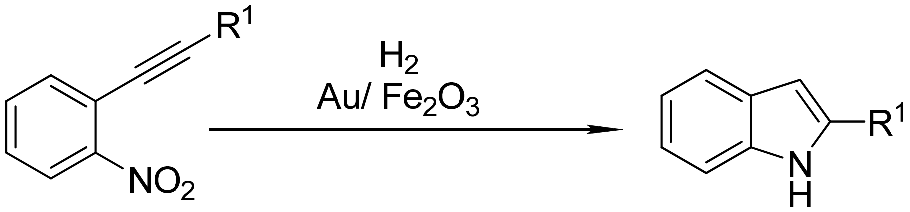


Scheme 26

Reaction temperature, the pressure of CO, and the reaction solvent determined the yield of reaction. The optimized reaction conditions were established as follows: 20 atm of CO, 90 °C, and 5 h.[41]

Indole

Au nanoparticles supported on Fe_2O_3 catalyzed conversion of (2-nitroaryl) alkynes to indoles by hydrogenation/hydroamination.[42]



Scheme 27

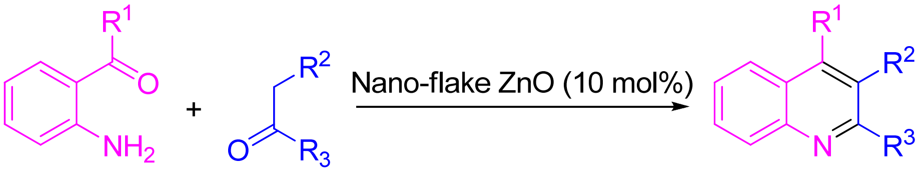
Isoindole

Morphology of Pd (0) nanoparticles is dependent on nature of the precursors. Among precursors can be named, non-phosphine-containing cyclopalladated *N*-heterocycles possessing either sp^2 C–Pd (II) or sp^3 C–Pd (II) bonds and simple Pd (II) salts. Life time of catalyst increased by addition of polyvinylpyrrolidone (pvp). By the water–gas shift reaction at ambient temperature in the presence of carbon monoxide, nanoparticles produced. Temperature required for preparing nanoparticles reduced by addition of allen.

A variety of 5- and 6-membered *N*-heterocycles including isoindolones, *N*-aminoisoindolones, phthalazones, dihydroisoquinolines, and isoquinolones can be prepared by catalyzed reaction.[43]

Quinoline

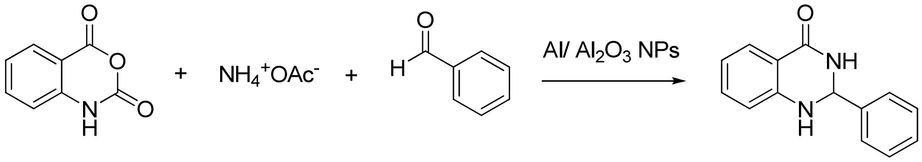
By heating of a solution of ZnOAc.2H_2O and urea, nano-flake ZnO has been prepared and used as an efficient catalyst reaction for synthesizing of quinoline derivatives and their related polyheterocycles (**Scheme 28**). Catalyst was recoverable and it can be reused multiple times.[44]



Scheme 28

2-Phenyl-2,3-dihydroquinazoline-4(1H)-one

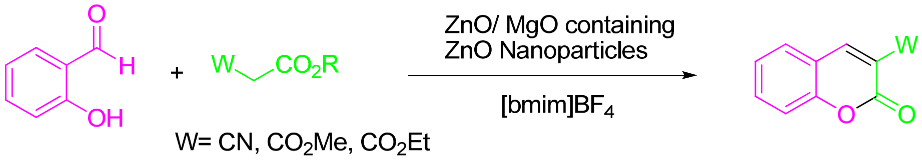
One-pot reactions for the synthesis of 2-phenyl-2,3-dihydroquinazoline-4(1*H*)-one as well as its *o*-Cl, *o*-OMe, *m*-Br, *m*-NO_2, *p*-OH, *p*-NO_2, *p*-CN, *p*-$PhCH_2O$, *p*-Cl, *p*-F, *p*-Br, *p*-Me, and *o,m*-dichloro derivatives promoted by using arc discharge fabricated Al/Al_2O_3 nanoparticles as a catalyst. The catalyst increased product yield in short time and it can be recovered and reused without loss of significant activity.[45]



Scheme 29

Coumarin

Coumarin derivatives synthesized *via* Pechmann, Perkin, Knoevenagel, Reformatsky and Wittig reactions. Knoevenagel reaction due to simple and inexpensive starting materials has been widely used. Treatment of 2-hydroxybenzaldehyde derivatives with some active methylene compounds in aqueous media and also in ionic liquids to form coumarin derivatives was catalyzed by ZnO/MgO containing ZnO nanoparticles (**Scheme 30**). This heterogeneous solid base catalyst is more efficient than homogeneous organic basic catalysts.[36]

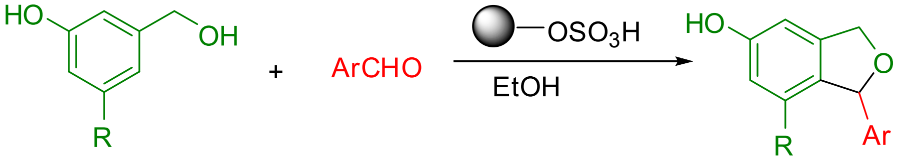


Scheme 30

Phthalans (1,3-dihydroisobenzofurans)

Lewis acid assisted intramolecular cyclization, which is also known as the oxa-Pictet–Spengler reaction produce phthans.

The rapid synthesis of 3-hydroxyphthalans *via* condensation of aromatic aldehydes and 3-hydroxybenzyl alcohols under conventional heating and microwave irradiation in presence of nanosilica sulfuric acid as a powerful and reusable heterogeneous catalyst was reported (**Scheme 31**). The procedure can be mentioned as a green method for preparing these heterocycles because the reaction does not require the use of toxic or organic solvents or reagents.[46]

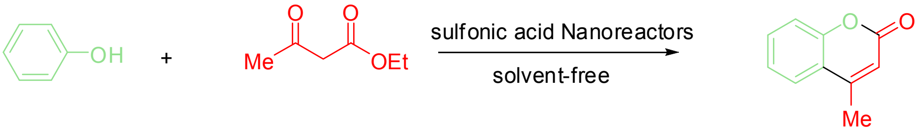


Scheme 31

4-Methyl-2H-chromen-2-one

von Pechmann reaction was efficiently catalyzed by different sulfonic acid nanoreactors especially nanoreactor having both acidic sites and phenyl groups located inside the mesochannels of SBA-15. A synergistic means of an efficient approach of the reactants to acidic sites, enough space for the subsequent cyclization, and suitable hydrophobicity to drive out the water byproduct, provided by the mesochannels, and covalently anchored organic groups.

Coupling reaction of resorcinol (1,3-dihydroxyphenol) with ethyl acetoacetate under solvent-free condition were catalyzed by Brønsted acid nanoreactors (**Scheme 32**).[47]



Scheme 32

3-Methyl-4-[(chromon-3-yl) methylene]-1-phenylpyrazolin-5-(4H)-ones

MCM-41-SO_3H catalyzed the condensation of 4-oxo-4*H*-1-benzopyran-3-carbaldehydes with 3-methyl-1-phenylpyrazolin-5-(4*H*)-ones to form 3-methyl-4-[(chromon-3-yl)methylene]-1-phenylpyrazolin-5-(4*H*)-ones (**Scheme 33**).[48]

Scheme 33

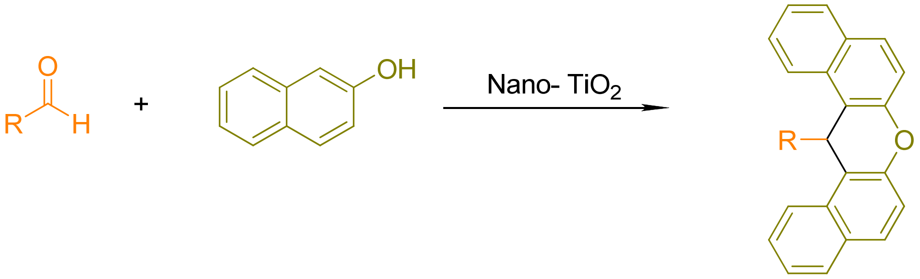
Other benzocyclic compound

Benzoheterocycles include quinoxaline, benzoxazine, and benzothiazine, can be synthesized from wide range of substrate, in high yields without organic solvents by recyclable CuO nanoparticles.[49]

2.5 OTHER HETEROCYCLIC COMPOUNDS

Xanthenes

Nano-TiO_2 can used as an active catalyst in preparing 14-aryl or alkyl-14*H*-dibenzo [*a,j*] xanthenes (**Scheme 34**). Advantages of this method mentioned such as; short reaction times, high yields, a clean process, simple methodology, easy work-up and green conditions. Nano-TiO_2 in synthesis of dibenzoxanthenes is more efficient than bulky TiO_2.[50]

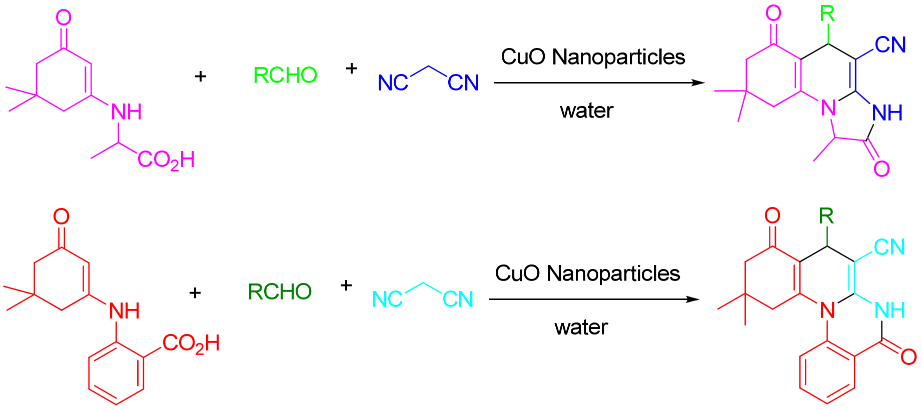


Scheme 34

Heravi *et al.* reported one pot synthesis 1,8-dioxo-octahydroxanthenes was catalysed with silica-supported Preyssler nano particles.[51] They also used silica-supported Preyssler nano particles in synthesis of 4(3*H*)-quinazolinones,[52] carbamoalkyl naphthols,[53] bis (indolyl) alkanes.[54] Catalytic activity of silica-supported Preyssler nano particles for photodegradation of methyl orange was characterized.[55] Employing Nano-SiO_2-supported Preyssler heteropolyacid as an efficient catalyst in esterification of salicylic acid with aliphatic and benzylic alcohols was demonstrated.[56]

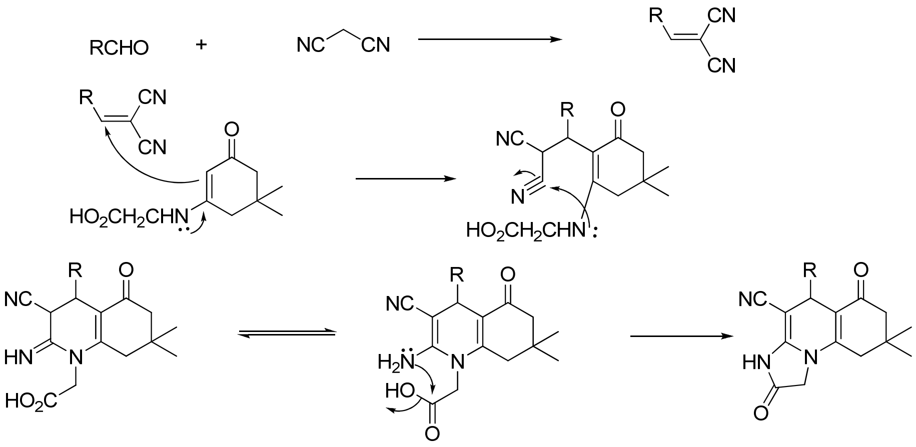
Quinolines

One-pot, three-component condensation for synthesizing of imidazo [1,2-*a*] quinoline and quinolino [1,2-*a*] quinazoline derivatives catalyzed by nanocrystalline copper (II) oxide.[57]



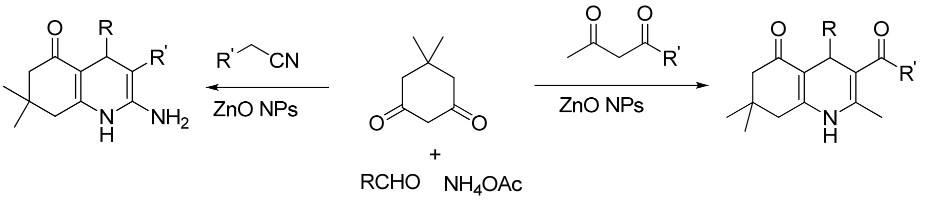
Scheme 35

Aldehydes condensed with malononitrile to form 2-arylidenemalononitrile. Product was added to enaminones. Adduct converted to intermediate that can undergo intermolecular cyclization and dehydration to afford target molecule.



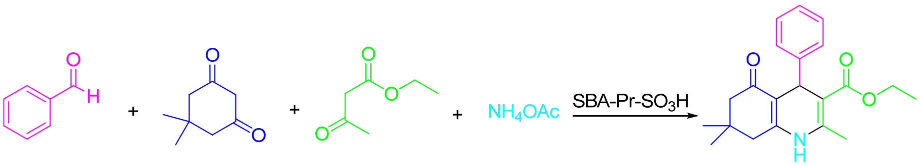
Scheme 36

Zinc oxide nanoparticles catalyst promoted one-pot, four-component couplings of aldehydes, dimedone, active methylene compounds, and ammonium acetate to form polyhydroquinoline derivatives under solvent-free conditions at room temperature (**Scheme 37**). High yields, short reaction times, simplicity in the experimental procedure, using recyclable and reusable catalyst were the advantages mentioned for this method.[58]



Scheme 37

Hantzsch four component condensation reaction of aldehydes, β-ketoesters, dimedone and ammonium acetate under solvent free conditions used for preparing polyhydroquinolines derivatives. Sulfonic acid functionalized SBA-15 (SBA-Pr-SO_3H) is a heterogeneous nanoporous solid acid catalyst that promoted reaction efficiently in short time (**Scheme 38**) and it can be easily recovered by simple filtration and reused without significant decrease in activity.[59]

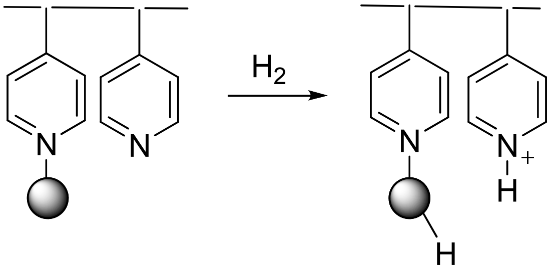


Scheme 38

3. NANOMATERIALS AS A CATALYST FOR REACTION OF HETEROCYCLIC COMPOUNDS

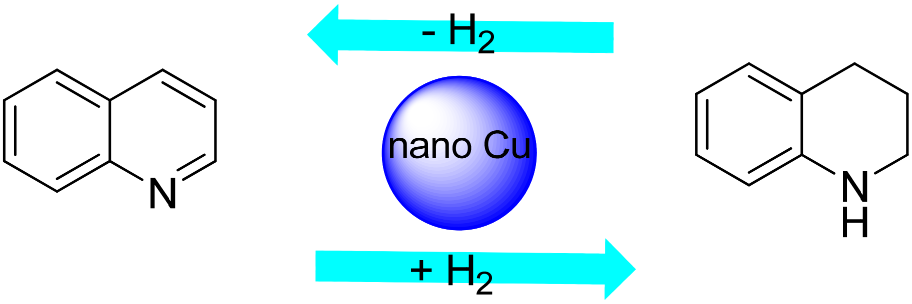
3.1 HYDROGENATION

Several research teams have reported hydrogenation of quinoline catalyzed by nanoparticle catalyst.[60-63] Ruthenium nanoparticles immobilized on poly (4-vinylpyridine) catalyzed hydrogenation of quinoline.[63] Reduction of $RuCl_3.3H_2O$ by $NaBH_4$ in methanol in the presence of the polymer resulted in series of catalysts composed of ruthenium nanoparticles immobilized on poly (4-vinylpyridine). Formation of nano-sized particles was proved by TEM measurements. Selective hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline at 100–120 ºC and 30–40 bar H_2 was catalyzed by these catalysts (**Scheme 39**). Increasing hydrogen pressure up to 40 bar, increase activity but quinoline concentration had no effect on activity. Ionic mechanism suggested based on heterolytic hydrogen activation by polar solvents that enhanced catalytic efficiency.



Scheme 39

Reversible dehydrogenation and hydrogenation of tetrahydroquinoline-quinoline under an atmospheric pressure of H_2 can be catalyzed by an active heterogeneous catalyst, copper nanoparticle on a titania surface (Cu/TiO_2) (**Scheme 40**).[61]

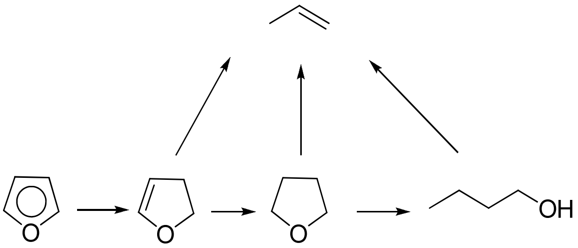


Scheme 40

Temperature had a dramatic effect on size of Pd^0 nanoparticles on hydroxyapatite (HAP). Control on size of particles achieved by manipulation of temperature. Nano-sized Pd^{II} species (with diameters between 1 and 1.5 nm) on the HAP surface (Pd^{II}HAP) reduced by molecular htdrogen.

Regioselective hydrogenation of quinolines to the corresponding 1,2,3,4-tetrahydroquinolines under mild reaction conditions can be efficiently catalyzed by HAP-supported Pd^0 nanoparticles (with average diameters of 1.5 nm). Catalyst can be recovered and reused without noticeable loss of efficiently and selectivity.[60]

Furan and hydrogen in argon atmosphere reacted to produce corresponding products. Pt can be used as a powerful catalyst for promoting reaction (**Scheme 41**).[64]

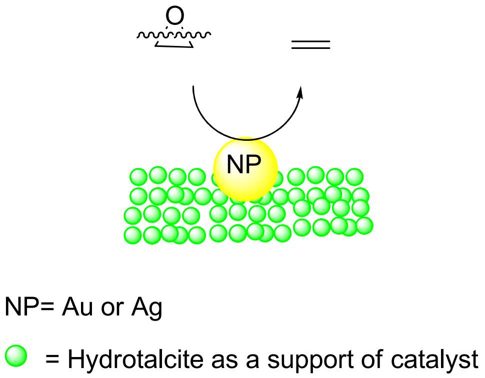


Scheme 41

3.2 DEOXYGENATION

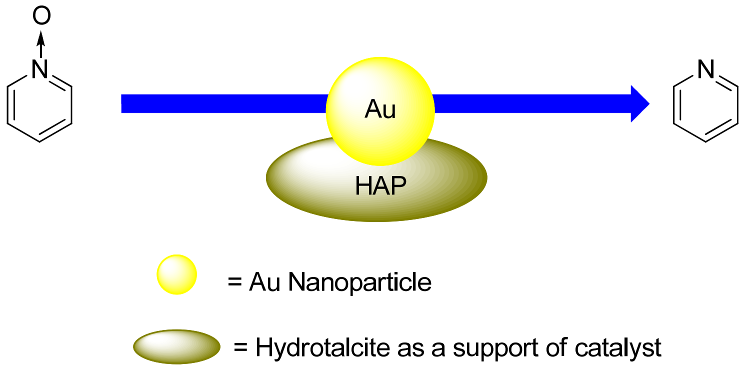
Mitsudome *et al.* demonstrated highly efficient gold & silver nanoparticle catalyzed deoxygenation of epoxide[65-67] and pyridine *N*-oxides.[68]

Deoxygenation of epoxides to alkenes in water at room temperature under CO at atmospheric pressure and in the absence of organic solvents using CO/H_2O as a reductant catalyzed by hydrotalcite-supported gold and silver nanoparticles (Au/HT & Ag/HT) (**Scheme 42**). The catalyst was an efficient and selective one which can be reused without loss of activity and selectivity.



Scheme 42

Amides, sulfoxides, and pyridine *N*-oxides deoxygenated with silanes as reductants to form the corresponding products were efficiently catalyzed by hydroxyapatite-supported gold nanoparticles with excellent turnover numbers (**Scheme 43**).

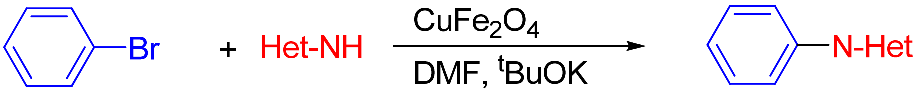


Scheme 43

3.3 *N*-ARYLATION

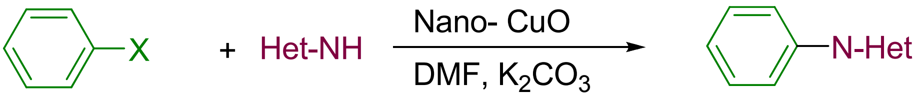
N-Arylation of heterocycles using nanocatalyst was reported by several authors.[69-73]

Copper ferrite nanoparticles used as a catalyst in the *N*-arylation of heterocycles with aryl halides (**Scheme 44**). This catalyst has dual characters of iron and copper. Copper catalyzed *N*-arylation reactions and magnetic nature of ferrite make catalyst recoverable and the catalyst can be reused because of negligible leaching of Cu and Fe in consecutive cycles.[69]



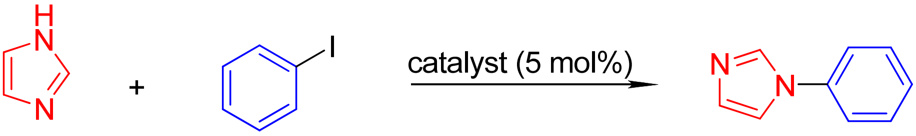
Scheme 44

N-Arylation of heterocycles with activated chloro- and fluoroarenes using potassium carbonate as base was catalyzed by nanocrystalline copper oxide (**Scheme 45**). High yields of product and reuseability of catalyst were be mentioned.[70]



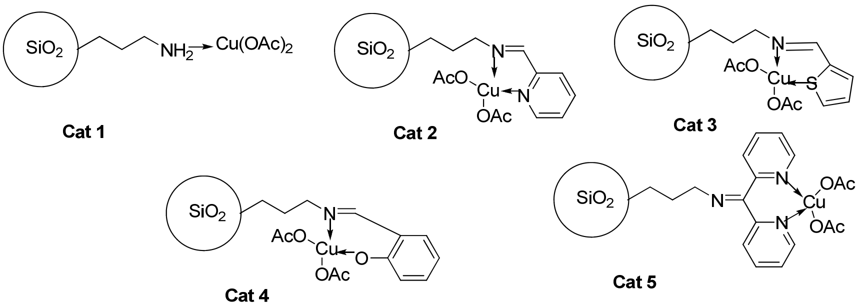
Scheme 45

N-Arylation of N (*H*)-heterocycles and benzyl amines with aryl halides and arylboronic acids were catalyzed by an active catalyst, silica tethered copper complexes (**Scheme 46**).[71]



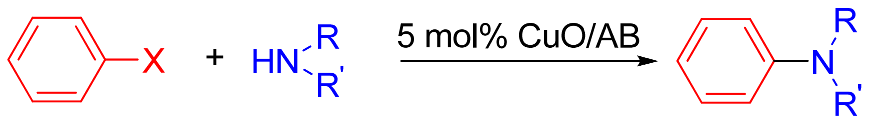
Scheme 46

Different catalysts used for promoting the reaction. They used reaction between iodobenzene with imidazole in toluene using Cs_2CO_3 at 100 °C under nitrogen atmosphere, as a model reaction. Among them the catalyst derived from pyridine-2-carboxaldehyde (**Cat2**) was the best one because it was powerful catalyst and it can be easily recovered and reused multiple times without loss of significant activity. Efficiency of another catalyst, the catalyst derived from 2-bipyridyl ketone (**Cat5**) was equal but potency of reusability was low. **Cat3** had moderate activity and efficiency of **Cat1** and **Cat4** were very low (**Scheme 47**).



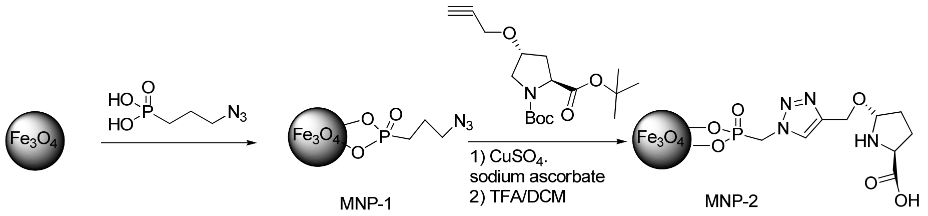
Scheme 47

N-Arylation of a variety of nitrogen-containing heterocycles to form corresponding products in high yields was done in presence of CuO/AB as an efficient catalyst (**Scheme 48**). The catalyst was prepared by sonication method at room temperature *via* immobilization of CuO hollow particles on acetylene carbon black (AB).[72]



Scheme 48

Coupling reactions of aryl/heteroaryl bromides with various nitrogen heterocycles to produce the corresponding *N*-aryl products was catalyzed with magnetic nanoparticle-supported proline ligand (**Scheme 50**). The catalyst was prepared in same processes shown in **Scheme 49**. This catalyst has special character; it can be separated easily with using an external magnet and reused multiple times without significant loss of activity.[73]



Scheme 49

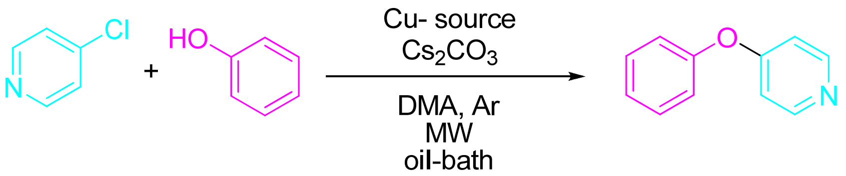
$$\text{Ar-Br} \quad + \quad \text{Het-NH} \xrightarrow[\text{CuI (10 mol\%)}]{\text{MNP-2 (20 mol\%)}} \text{Ar-N-Het}$$

Scheme 50

3.4 ULLMANN REACTION

Base-free Ullmann heterocyle-aryl ether syntheses were catalyzed by nanoparticulate copper by Engels *et al.*[74,75]

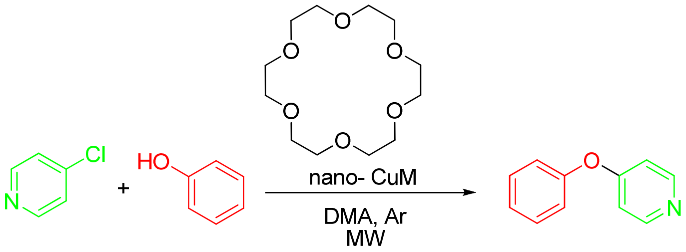
Nanoparticulate copper catalysts used in reaction between stable chloropyridine salts and unactivated phenol (**Scheme 51**). Stability and reusability of copper nanoparticles were higher than other copper forms.[74]



Scheme 51

Reaction between PVP/ethylene glycol mixture containing Cu $(OAc)_2$ and sodium hypophosphite coreductant resulted in poly (*N*-vinylpyrrolidone) (PVP)-capped Cu nanoparticles. Crude suspension with acetone purified to form particles with a mean diameter of 9.6 ± 1.0 nm.

Liquid − liquid Ullmann etherification process promoted by CuZn and CuSn nanoparticle catalysts in conjunction with microwave heating. There is no need to use solid and expensive bases. Catalyst can be reused several times, yield of product was excellent and addition of 18-crown-6 as a kinetic promoter improve the condition (**Scheme 52**).[75]



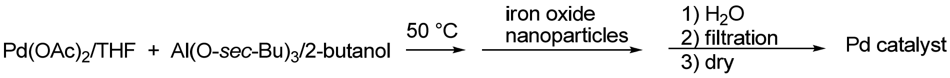
Scheme 52

3.5 RING OPENING

By sol-gel process of palladium nanoparticles and superparamagnetic iron oxide nanoparticles in aluminum oxyhydroxide matrix, magnetically separable palladium catalyst was synthesized. Resulted catalyst used in selective epoxide hydrogenolysis at room temperature under 1 atm H_2. Catalyst can be separated by using magnetic and reused multiple times.[76]

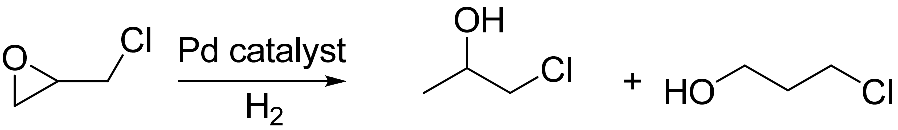
Recyclable palladium catalysts can be produced by Pd $(PPh_3)_4$ under aerobic conditions that converted to palladium nanoparticles. Solubility of Pd $(PPh_3)_4$ in the reaction mixture was a challenge that reduced palladium content of resulting catalyst to about 3wt%. With substituting palladium acetate for Pd $(PPh_3)_4$, without losing activity per mol of Pd, the palladium content could be increased up to 10 wt%.

Before gelation, superparamagnetic iron oxide nanoparticles mixed with the suspension of palladium nanoparticles. Treatment of palladium acetate, Al (O-*sec*-Bu$)_3$, 2-butanol, and THF produce black suspension that included palladium nanoparticles. Addition of iron oxide nanoparticles dispersed in ethanol and then water, convert black suspension to black gel. By filtration of gel, washing it with acetone, and drying it at 120 °C for 5 h, catalyst as dark brown powder was prepared (**Scheme 53**).



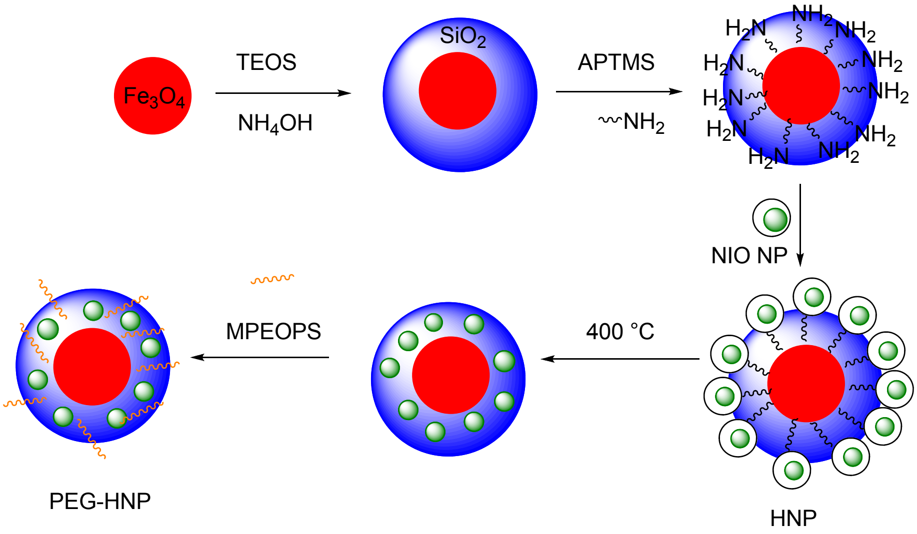
Scheme 53

Resulted catalyst used in reaction between epoxide and hydrogen to produce alcohols. Regioselectivity and catalytic activity were evaluated (**Scheme 54**).



Scheme 54

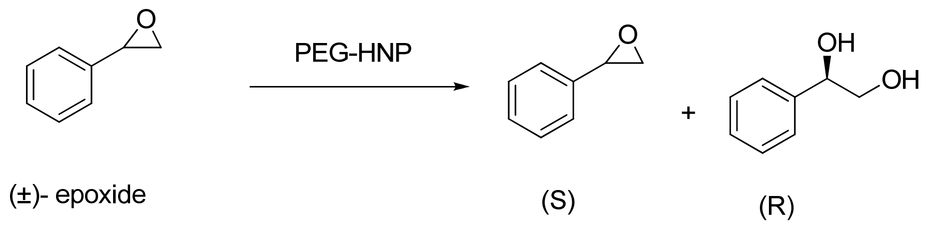
By assembly of NiO nanoparticles at the surface of magnetic silica, a hybrid superstructure can be prepared (**Scheme 55**) this hybrid superstructure used as a carrier for a magnetically separable biocatalyst system.[77]



Scheme 55

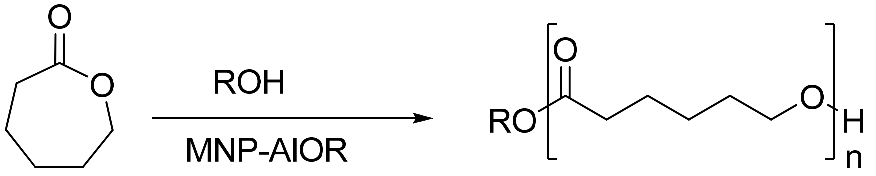
The assembly of NiO nanoparticles at the Fe_3O_4–silica sphere produced hybrid Fe_3O_4–silica–NiO superstructures. By immobilization, anchoring His-tagged enzymes was done. Activity of enzyme preserved.

Enantioselective resolution of racemic styrene oxide carried out by immobilized enzymes as a selective catalyst. The catalyst can be recovered by magnetic separation and reused (**Scheme 56**).



Scheme 56

The ring-opening polymerization of ε-caprolactone was catalyzed by magnetic nanoparticle supported aluminium isopropoxide (**Scheme 57**).[78]

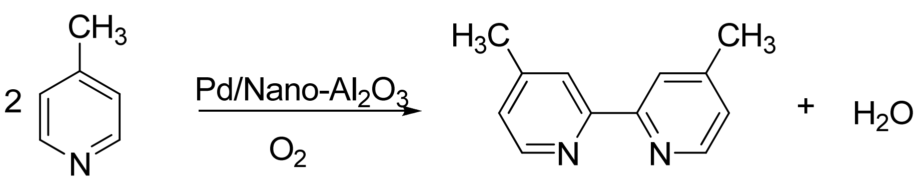


Scheme 57

3.6 COUPLING

4-Methylpyridine reacted with 4,4-dimethyl-2,2-bipyridine *via* oxidation coupling afforded bipyridines over palladium oxide. Large-scale production of bipyridine products required to improve catalyst because the reaction is slow and the palladium catalyst deactivates during reaction. Catalysts supported on several nanoparticle oxides were tested in the oxidative coupling of 4-methylpyridine (**Scheme 58**).

Neal *et al.* prepared two types of active catalyst with varying properties, first group are very high surface area materials supported palladium, Pd/Al_2O_3 and Pd/MgO and second group was metal oxide supported palladium, e.g. Pd/ZrO_2, Pd/(ZrO_2 + CeO_2) and Pd/ZnO.[79]

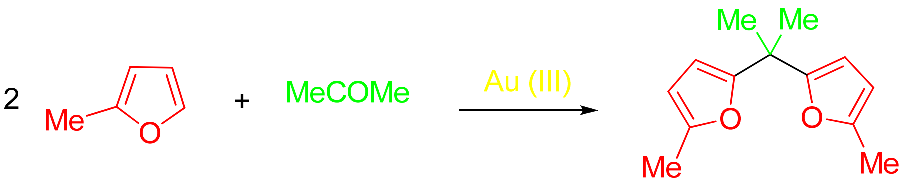


Scheme 58

Cross-coupling reactions of various N/O nucleophilic reagents with aryl chlorides in absence of ligands and strong base to form variety of products including *N*-arylimidazoles and aryl ethers in good yields were catalyzed with CuI nanoparticles under mild conditions.[80]

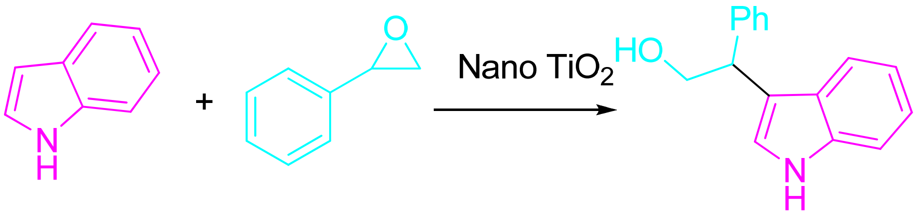
3.7 ALKYLATION OF HETEROCYCLES

Condensation of furans with carbonylic compounds in low temperature was done in presence of gold (III) chloride as an efficient catalyst (**Scheme 59**).[81]



Scheme 59

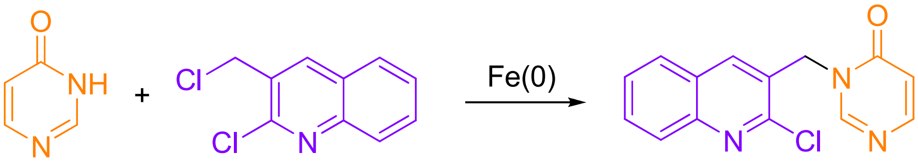
Friedel–Crafts alkylation of indoles using epoxides was catalyzed regioselectively by nanocrystalline titanium (IV) oxide to form 3-alkylindole derivatives. Ring opening of epoxide with indoles as a nucleophile, in presence of nano TiO_2 as a catalyst produce corresponding product in good yield and high regioselectivity (**Scheme 60**).[82]



Scheme 60

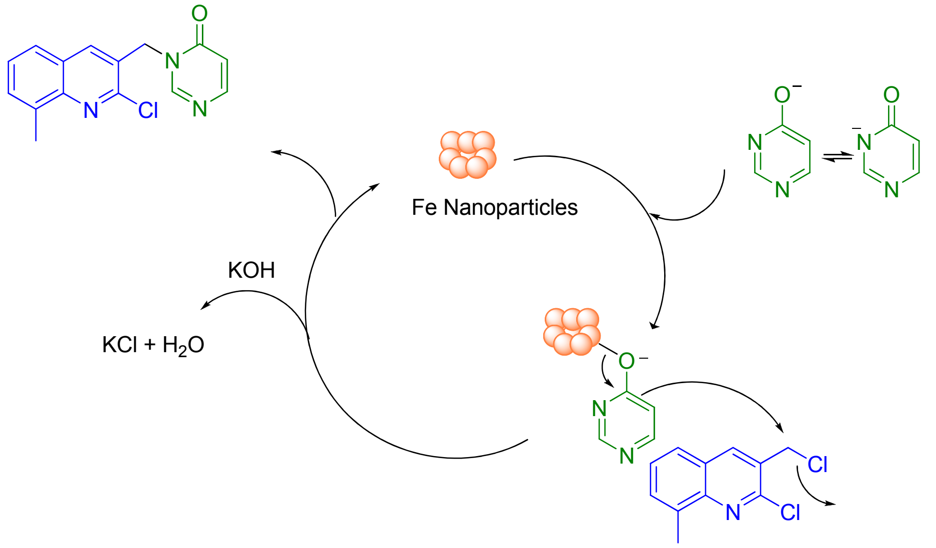
3.8 THE C–N BOND FORMATION

N-Alkylation of 4(3*H*)-pyrimidone with various electrophiles was catalyzed by Fe nanoparticles regioselectivity (**Scheme 61**). 3-[(2-Chloroquinolin-3-yl]methyl)pyrimidin-4(3*H*)ones were prepared from reaction between equimolar 4(3*H*)-pyrimidone and 2-chloro-3-(chloromethyl) quinolines in the presence of KOH and Fe nanoparticle as an efficient catalyst (5 mol %) in DMSO solution under reflux condition.[83]



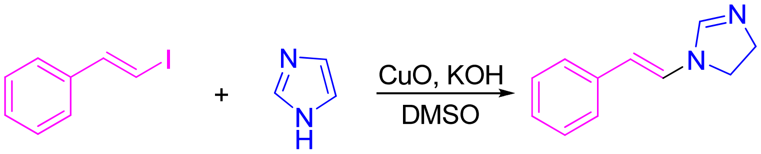
Scheme 61

The catalyst was initiator of *N*-alkylation of amide by alkyl chloride. It binds to enolate and activated nitrogen that is located in α-position to carbonyl so *N*-alkylation was done. The proposed mechanism was shown in **Scheme 62**.



Scheme 62

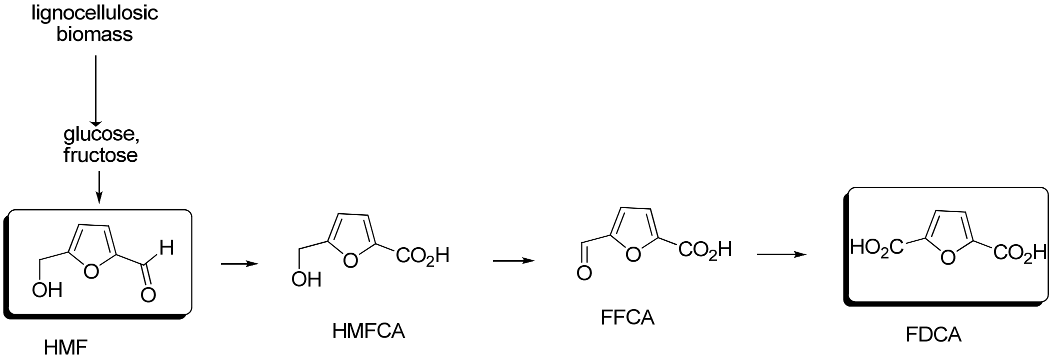
Treatment of imidazoles with vinyl halides under ligand-free conditions to form corresponding product with retention configuration, was catalyzed by recyclable copper oxide nanoparticles (**Scheme 63**). Vinylation of various imidazoles with different substituted vinyl halides was carried out in excellent yields in presence of copper oxide nanoparticles.[84]



Scheme 63

3.9 OXIDATION

Lignocellolusic biomass is a precursor for preparing 2,5-furandicarboxylic acid. Hydrotalcite-supported gold nanoparticle used as a catalyst in oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid (**Scheme 64**). Reaction carried out without addition of homogenous base in water at 368 k under atmospheric oxygen pressure.[85]

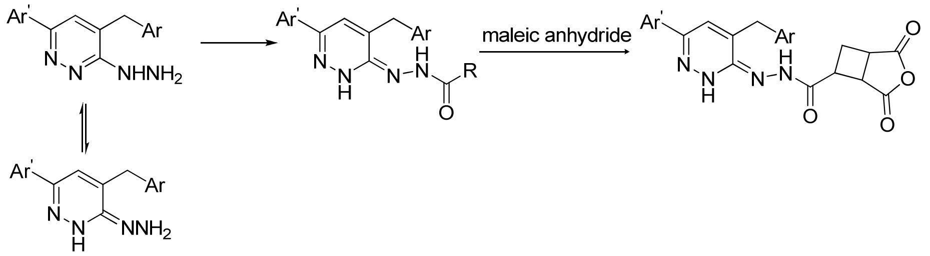


Scheme 64

3.10 PREPARING NEW HETEROCYCLES

New heterocyclic systems such as thiazolidine, phthalazine, pyrazolo, tetrazolo, hydrazide and new pyridazine derivatives prepared from 1-[4-(2-methoxybenzyl)-6-aryl-pyridazin-3(2*H*)-ylidene]hydrazines catalyzed by silver nanoparticles (**Scheme 65**).

They synthesized silver nanoparticles and used transmission electron microscopy (TEM) and UV studies to approve formation of nano-sized particles.[86]

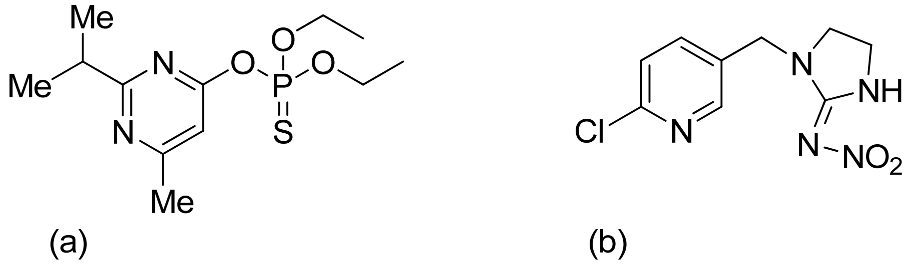


Scheme 65

3.11 DEGRADATION

Two agricultural organic pollutants (Diazinon and Imidacloprid as *N*-heterocyclic aromatics) were subjected to degradation and mineralization in aqueous solution by nanophotocatalysis using immobilized titania nanoparticles. Insecticides, Diazinon (**a**) and Imidacloprid (**b**) (**Scheme 66**), are stable pollutants in agricultural soil and watercourses. Their degradation is very slow.

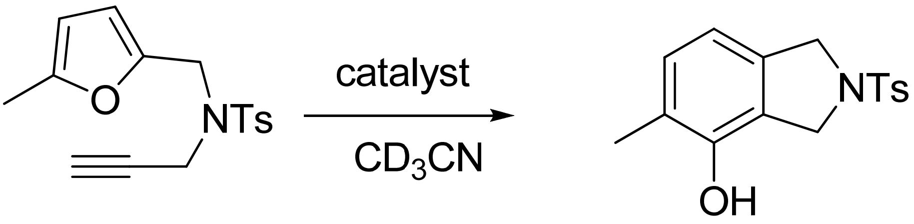
First they used immobilized titania nanoparticles as an efficient nanophotocatalysis for degradation of two mentioned pollutants then they found that amount of H_2O_2 and inorganic anions (NO_3^-, Cl^- and SO_4^{2-}) affected on the rate of photodegradation.[87]



Scheme 66

3.12 REARRANGMENT

2-Substituted furans having terminal C≡C triple bonds converted into phenol derivatives in presence of gold nanoparticles as a catalyst (**Scheme 67**).



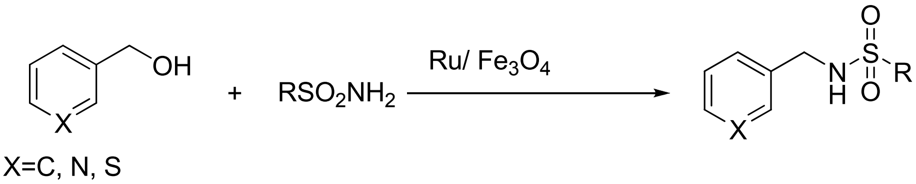
Scheme 67

Gold nanoparticles supported on nanocrystalline CeO_2 used as a catalyst in the rearrangement of ω-alkynylfurans to phenols.[88]

Support of nanoparticles play an important role in the activity of supported gold catalyst. Presence of Au (III) ions on the gold clusters were essentially because they act as carbonophilic Lewis acid sites. The presence of a larger population of positive gold species can be maintained by nanoparticulate ceria as support because ceria nanoparticles have a large deviation from the CeO_2 stoichiometry with a large number of lattice oxygen vacancies and a considerable ‘confusion’ between the IV and III cerium oxidation states.

3.13 OTHER REACTION

The direct coupling of sulfonamides and alcohols was catalyzed by Nano-Ru/Fe_3O_4 (**Scheme 68**). Catalyst efficiently promoted reactions of benzylic alcohols and sulfonamides including various heterocycles.[89]



Scheme 68

Doussineau and coworker introduced new host–guest systems.[90] 3-Hydroxyflavone (3-OHF) was incorporated in zeolite micropores led to constructing the molecule by reaction of small precursors within the cavity.

In 3-OHF molecules exhibit excited-state intramolecular proton transfer (ESIPT) happened and a tautomeric equilibrium existed between the 3-OHF-excited structures N* and T* exists. The protic nature and polarity of the surrounding medium affected this equilibrium.

4. HETEROCYCLIC SUPPORTED NANOMATERIALS: SYNTHESIS AND APPLICATION

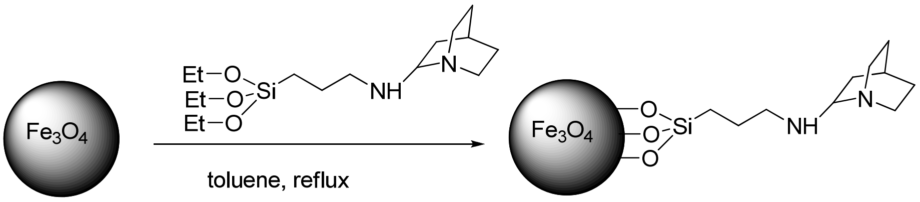
4.1 MAGNETIC NANOPARTICLE-SUPPORTED HETEROCYCLIC COMPOUND

Recently, Fe_3O_4 nanoparticles (magnetite nanoparticle) have attracted worldwide attention.[91]

Magnetical separation from the reaction mixture in comparison with filtration and centrifugation is simpler and efficient that prevents the loss of the catalyst.[92]

Morita–Baylis–Hillman reaction was catalyzed by a magnetic nanoparticle-supported quinuclidine.[93]

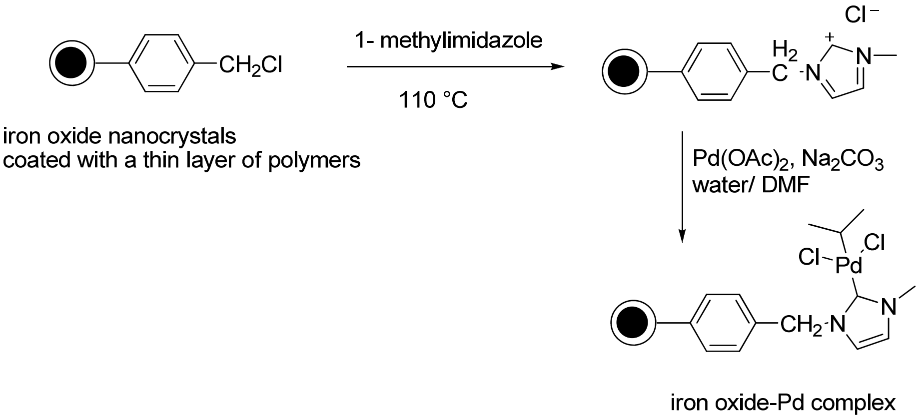
MNP-Supported quinuclidine was synthesized according to the procedure shown in **Scheme 69**. By co-precipitation procedure, polyvinylpyrrolidone (PVP)-protected magnetic nanoparticles were prepared.



Scheme 69

Strong complexes with Pd catalysts were introduced by Steven *et al.*[94] With loading 1-methylimidazole onto the surface of core/shell nanoparticles when nanoparticles with 1-methylimidazole mixed in a refluxing toluene solution resulted in immobilizing Pd catalyst (**Scheme 70**).

Deporotonation of the imidazolium group with Na_2CO_3 as a base generated *N*-heterocyclic carbenes (NHCs). NHCs can form robust complexes with Pd catalysts.

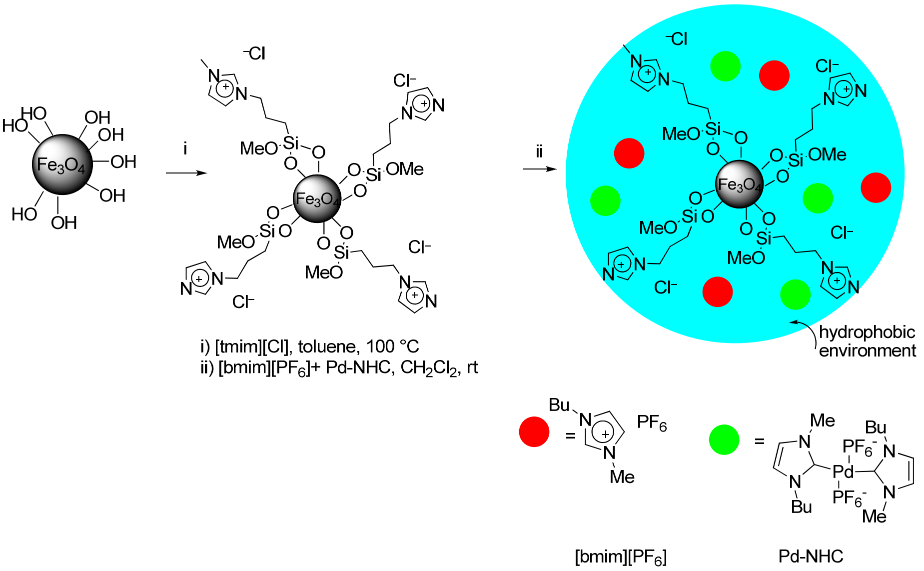


Scheme 70

Taher *et al.*[95] immobilized Pd-NHC–ionic liquid matrix into ionic liquid layers coated on the surface of Fe_3O_4 and as a catalyst for Suzuki coupling reaction.

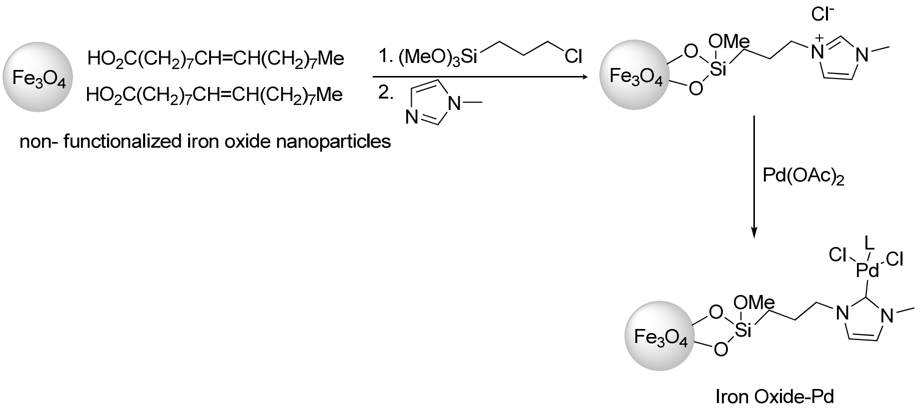
Coupling between aryl bromide and aryl boronic acid in water catalysed with efficient Pd-NHC-ionic liquids catalyst. Catalyst can be recovered by using external magnet and reused without loss of activity.

1-butyl-3-methylimidazolium hexafluorophosphate {[bmim][PF_6]} and $Pd(OAc)_2$ was immobilized into thin layers of [bmim][PF_6] coated on the surface of Fe_3O_4 resulted in Pd-NHC (**Scheme 71**).



Scheme 71

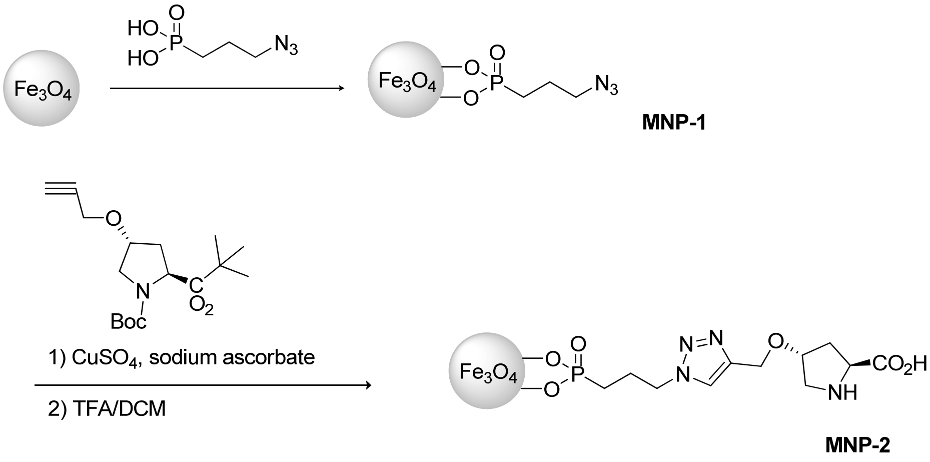
Zheng *et al*. synthesized maghemite nanoparticle-supported Pd catalyst Iron Oxide-Pd from nonfunctionalized iron oxide nanocrystals (**Scheme 72**).[96] They used the catalyst in solid-phase Suzuki reactions.



Scheme 72

Arylation of nitrogen nucleophiles was catalysed with CuI. Recyclable and recoverable ligand for this reaction was magnetic nanoparticle-supported proline that synthesised was outlined as fellow.[73]

Initial step was reaction between nanoparticles and the phosphonic acid ligand to produce azide functionalized magnetite (**MNP-1**) then the Cu (I)-catalyzed alkyne–azide [2 + 3] cycloaddition reaction of $CuSO_4$, sodium ascorbate and triethyl amine in a 1:1 mixture of *tert*-butyl alcohol and water at room temperature immobilized proline ligand to form the proline functionalized magnetic nanoparticles **MNP-2 (Scheme 73)**.

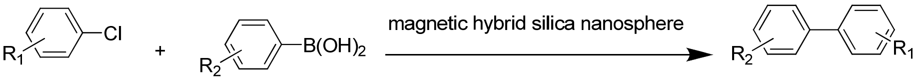


Scheme 73

Magnetic silica nanoparticles functionalized based on a reverse micelle strategy with a bulky *N*-heterocyclic carbene (*N*,*N*’-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), (denoted as IPr). Co-condensation of IPr-bridged organosilane and tetraalkoxysilane in a one-pot reaction resulted in it. Incorporation of IPr ligand onto magnetic silica nanoparticles was showed by FT-IR and XPS characterizations.[97]

These functionalized magnetic nanoparticles showed a good capability to coordinate with Pd (acac)$_2$ (acac = acetylacetonate). This Pd-loaded material is a robust catalyst for Suzuki–Miyaura couplings of aryl chlorides under relatively mild conditions that face to problems in other conditions (**Scheme 74**).

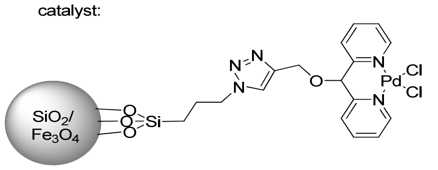
The activity of mesoporous silica-based catalysts is as same as a commercial Pd/C catalyst, but the functionalized nanoparticles is much activer than them.



Scheme 74

Click chemistry prepared a magnetic nanoparticle-supported di(2-pyridyl)methanol palladium dichloride complex (**Scheme 75**).[98]

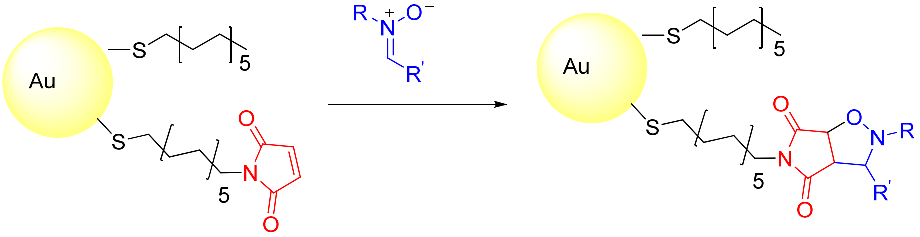
Suzuki coupling reaction of aryl bromides can be catalyzed by this complex as an active supported catalyst. By an external magnet can recover the catalyst and reuse it.



Scheme 75

4.2 GOLD NANOPARTICLE- SUPPORTED HETEROCYCLIC COMPOUNDS

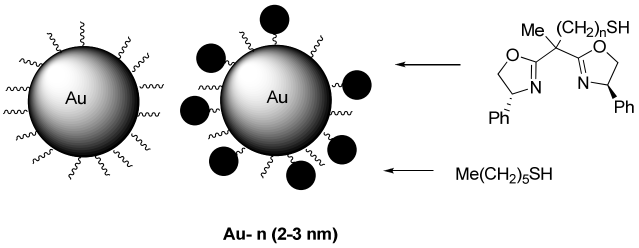
1,3-Dipolar cycloadditions under high-pressure conditions can be used in efficient synthesis of isoxazolidine-tethered monolayer-protected gold nanoparticles (MPGNs) (**Scheme 76**).[99]



Scheme 76

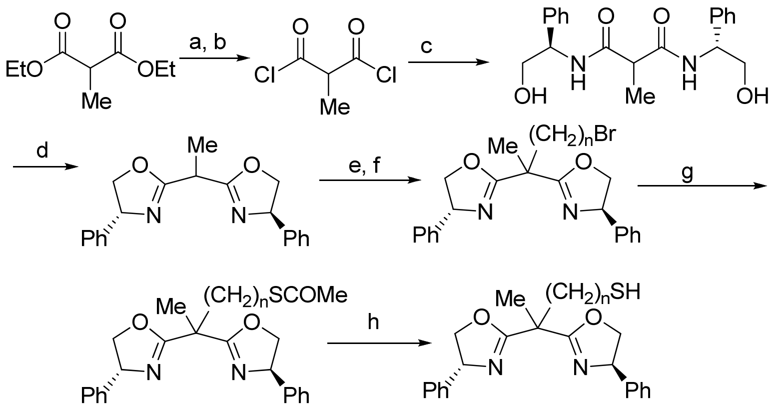
Interfacial 1,3-dipolar cycloaddition between a maleimide-modified mixed monolayer protected gold nanoparticle and a series of nitrones produce the corresponding isoxazolidine-modified nanoparticles. High pressure conditions were required for synthetic modification of the nanoparticles because this reaction proceeds slowly at atmospheric pressures. High pressure improved the rate of reaction but does not affect on size of gold nanoparticles, it was approved by TEM.

Ono *et al.* synthesized new types of nano-sized gold particle catalysts.[100] The catalysts were modified with two alkyl chains, one with simple alkyl sulfides and the other with alkyl sulfides having copper (II) complexes of chiral bisoxazoline ligands at the terminal (**Scheme 77**).



Scheme 77

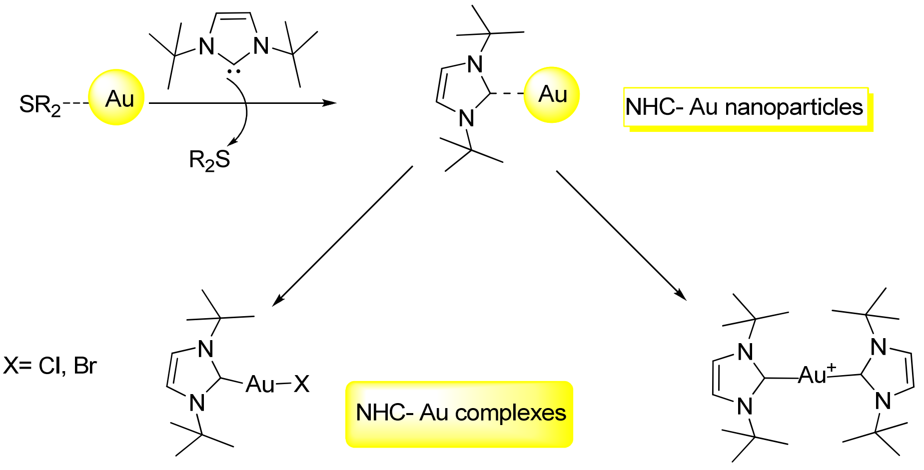
Diethyl methylmalonate can be used as a precursor for synthesizing bisoxazoline ligands. One method was described in (**Scheme 78**). Aqueous potassium hydroxide hydrolyzed methylmalonate ester then product was chlorinated with thionyl chloride. Resulted methylmalonyl chloride then reacted with (R)-phenylglycinol to produce bisamide. It was mesylated and cyclized into bisoxazoline. ω-Bromodecanyl bisoxazoline was prepared from deprotonation of bisoxazoline with butyllithium at -78 °C, and then by the alkylation with 1,10-dibromodecane.



(a) KOH, H_2O-EtOH = 1:3 v/v, reflux, 4 h;
(b) $SOCl_2$ (2.2 equiv), reflux, 3 h;
(c) (R)-2-phenylglycinol (2 equiv), Et_3N (2 equiv), CH_2Cl_2, rt, 12 h;
(d) MsCl (2 equiv), Et_3N (2 equiv), CH_2Cl_2, rt, 16 h;
(e) n-BuLi (1.1 equiv), -78 °C, THF;
(f) $Br(CH_2)10Br$ (4 equiv), rt, 6 h;
(g) MeCOSK (1.1 equiv), DMF, rt, 15 min;
(h) NaOH, MeOH, rt, 15 min

Scheme 78

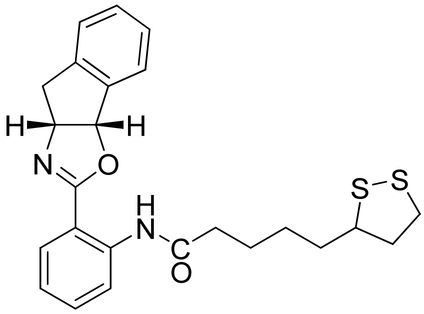
By a ligand exchange reaction, *N*-heterocyclic carbene coated Au and Pd nanoparticles were prepared. Thioether and phosphine ligands were displaced by carbenes from the nanoparticle surface. In solution, nanoparticles leached metal complexes and aggregated (**Scheme 79**).[101]



Scheme 79

Banks *et al.* prepared new modified 2-aryloxazoline ligands (**Scheme 80**). They attached aromatic portion of the oxazoline with an amid linked thioctic acid derived group, then whole system attached to gold nanoparticles.

This procedure modified ligands were subgroup of monodentate oxazolines so they had new characters for doing specific function.[102]



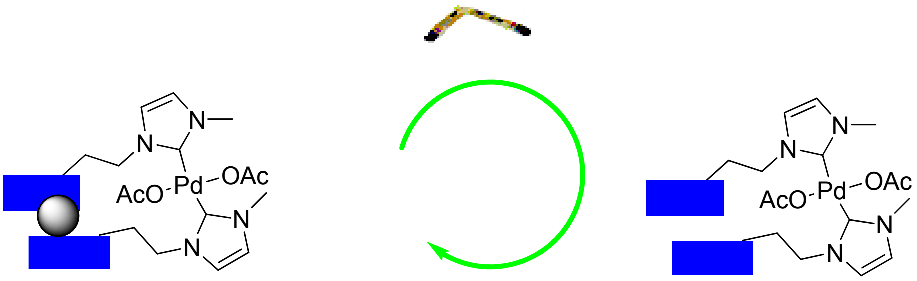
Scheme 80

Dash demonstrated addition of minute 1-methylimidazole additives, increased stability of gold and bimetallic nanoparticles in ionic liquids (ILs).[103]

4.3 PALLADIUM NANOPARTICLE- SUPPORTED HETEROCYCLIC COMPOUND

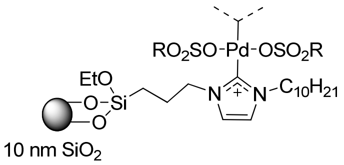
Noncovalent attachment of a Pd *N*-heterocyclic carbene complex to graphene-coated magnetic Co nanoparticles generates a catalyst catch–release system **(boomerang catalysis)**.

Pyrene tags were reversibly immobilized (**Scheme 81**; blue), can be released the homogeneous catalyst at elevated temperatures. Aryl halides, hydroxycarbonylated with this efficient catalyst.[104]



Scheme 81

Tandakar immobilized *N*-heterocyclic carbene–palladium (NHC–Pd) complexes on 10 nm silica nanoparticles (**Scheme 82**). Suspending of these nanoparticles in a variety of solvents and activity of catalytic site are remarkable. It used in Suzuki and Heck coupling reactions with high efficiency multiple times because it can be recovered and reused.[105]

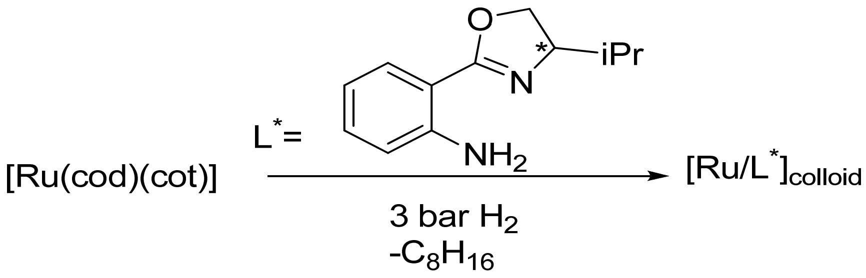


Recyclable Suzuki and Heck Coupling Catalyst

Scheme 82

4.4 OTHER NANOMATERIAL SUPPORTED HETEROCYCLIC COMPOUND

Jansat *et al.* synthesized stable ruthenium nanoparticles by decomposition of the organometallic precursor [Ru(cod)(cot)] (cod = 1,5-cyclooctadiene; cot = 1,3,5-cyclooctatriene) in the presence of optically pure ligands, **L***, namely (*R*)-2-aminobutanol 1, amino(oxazolines), hydroxy(oxazoline) and bis(oxazolines) (**Scheme 83**).[106]



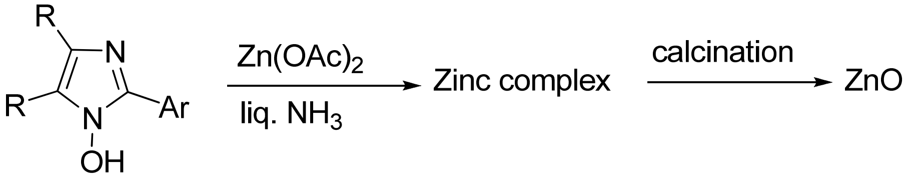
Scheme 83

Organic oxidations by TBHP can be catalyzed by *cis*-[RuII-(6,6'-Cl (6,6'-dichloro-2bpy)$_2$(OH$_2$)$_2$) (CF$_3$SO$_3$)$_2$ Cl$_2$bpy:6,6'dicholoro-2,2'-bipyridine). Recyclability and catalytic activity of this catalyst can be improved by immobilisation of it into MCM-41 channels that combine advantages of both homogeneous and heterogeneous catalytic systems.[107]

4.5 HETEROCYCLIC DERIVATIVES AS THE ORGANIC PRECURSOR OF NANO PARTICLES

Behaviour of the imidazole nucleus shows that charge within is delocalized. Self–assembly was as a result as forming three hydrogen bonds between the protonated amine, the oxime O-atom and the nitro group O-atom and the solvate water molecule.

Hydroxy imidazole derivative had structural feature that allows the metal ions to bind in. Zinc complex prepared from imidazole derivatives that subjected to calcinations and converted to zinc oxide nano particles (**Scheme 84**).[108]



Scheme 84

5. CONCLUSION

Today importance of heterocyclic compounds is relieved to everyone. They play important role in pharmacy, cosmetic, polymer and paint industry. Chemists look up to find a good way for preparing them more efficient.

Nanomaterial showed excellent potential for catalysis of reaction that heterocyclic compound involved in. They increased contact area due to smaller size in comparison with other catalysts. Another advantage of them is that they are heterogeneous catalysts so they can be recovered easily.

Mentioned advantages make nanomaterial as a powerful tool for applying in heterocyclic chemistry.

Magnetic nanomaterials have magic properties that help to recover them by simple magnet therefore catalyst based on magnetic were more efficient, greener (discarded use of organic solvent).

This review covered synthetic application of nanomaterials in heterocyclic chemistry. Reactions that mentioned in review show high potency of nanomaterial as a catalyst in preparing and using heterocyclic compounds.

6. ACKNOWLEDGEMENTS

The authors are thankful to Alzahra University Research Council for partial financial support.

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