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Magnetic Nanomaterial: A New Class of Heterogenous Catalysts In Organic Transformations

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ABSTRACT: Magnetic nanoparticles have received important place among other various nanoparticles as they exhibited various versatile applications in different disciplines like data storage, drug delivery, magnetic resonance imaging, biomedicine/biotechnology and electrochemical monitoring of metal and anion. Furthermore, magnetic nanoparticles also offer promising catalytic properties due to their high surface to volume ratio, high catalytic activity, biocompatibility and its paramagnetic nature that facilitates the separation of catalyst through external magnet makes the recovery of the catalyst easier and prevents loss of catalyst associated with conventional filtration or centrifugation methods.

KEYWORDS: Nano particles, magnetic nano particle, catalyst etc

I.INTRODUCTION

Catalyst is a substance that increases the rate of a reaction by lowering the activation energy that is required to convert reactants into products. By using a catalyst, the desired product can be obtained faster than without the presence of the catalyst. The new era of chemistry is shifting towards the path of innovative techniques for convert reactant into product which mainly concentrates on environmental aspects. Each and every component of the reaction is investigated on the basis of eco-friendly concepts such as use of nonhazardous solvent (water) and solvent free synthesis or inexpensive catalyst, without affecting the yield and quality of the reaction. Synthesis of heterocyclic core constitutes the important portion of organic synthesis because it has wide variety of pharmacological actions. Various methods have been adopted for the synthesis which includes the use of catalyst ultrasound irradiation and microwave irradiation. Although these methods have their own advantages, it also possesses certain disadvantages like expensive instruments, inaccessible materials, nonrecyclable and non-selectivity, and so forth. To overcome these, the role of nanocatalyst holds its application. Nanoscience is the cram of phenomenon on a nano meter range. Only a portion of catalysts used today can be termed as nanocatalysts. The small particle size leads to many unique properties of the nanoparticles. The term nanocatalyst is defined as a material that has catalytic properties on at least one nanoscale dimension. They possess immense surface-to-volume ratio because of their small size, which is why they act as attractive catalysts. Although the term nano was used until recent times, researchers traditionally focused on producing very small particles of active catalytic agents in order to maximize the reaction efficiency and to reduce the overall cost of the chemical process. A recent advance in synthetic methods for the production of nanomaterials has produced new nanocatalysts with novel properties and reactivity. Metal nanoparticles are attractive catalysts compared to the bulk materials due to high surface to volume ratio. Because of their small size, the nanoparticles will have more percentage of atoms on the surface, which leads to increased catalytic activity.

(a)Classification of nanomaterials / nanoparticles:

Nanomaterials have extremely small size which having at least one dimension 100 nm or less. Nanomaterials can be nanoscale in one dimension (eg. surface films), two dimensions (eg. strands or fibres), or three dimensions (eg. particles). They can exist in single, fused, aggregated or agglomerated forms with spherical, tubular, and irregular shapes. Common types of nanomaterials include nanotubes, dendrimers, quantum dots and fullerenes. Nanomaterials have applications in the field of nano technology, and displays different physical chemical characteristics from normal chemicals (i.e., silver nano, carbon nanotube, fullerene, photocatalyst, carbon nano, silica). According to Siegel,

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Nanostructured materials are classified as Zero dimensional, one dimensional, two dimensional, three dimensional nanostructures.

Nanomaterials are materials which are characterized by an ultra fine grain size (< 50 nm) or by a dimensionality limited to 50 nm. Nanomaterials can be created with various modulation dimensionalities as defined by Richard W. Siegel: zero (atomic clusters, filaments and cluster assemblies), one (multilayers), two (ultrafine-grained overlayers or buried layers), and three (nanophase materials consisting of equiaxed nanometer sized grains). (figure 1)

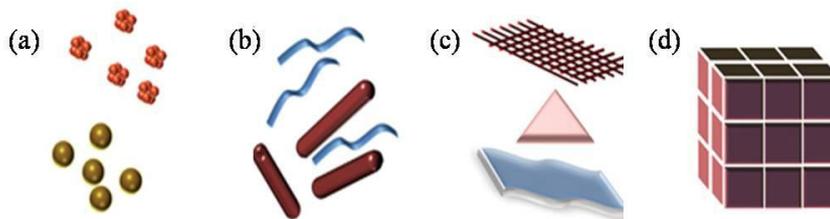


Figure: 2. (a) 0D spheres and clusters, (b) 1D nanofibers, wires, and rods, (c) 2D films, plates, and networks, (d) 3D nanomaterials.

(b) Synthesis of nanomaterials / nanoparticles: There is a tremendous research interest in the area of nanotechnology to develop reliable processes for the synthesis of nanomaterials over a range of sizes and chemical compositions. Although the conventional methods of synthesis of metal sols, known since the times of Michael Faraday, continue to be used for generating metal nanoparticles, there have been several improvements and modifications in the methods which provide a better control over the size, shape, and other characteristics of the nanoparticles. These developments have enabled studies of quantum confinement as well as other properties dependent on size, shape, and composition. Ligating nanoparticles with organic molecules and assembling these in one-, two-, or three-dimensional mesostructures have added another dimension to this field wherein collective properties of nanoparticles have been of special interest. The exciting potential of nanomaterials can be enroute to nanodevice applications, only with a combination of nanobuilding units and strategies for assembling them. Self-assembly of nanoparticles synthesized by the colloidal route on suitable supports is one of the interesting techniques currently being investigated for realizing such structures. Though the synthesis and organization of nanoparticles provide complementary tools for nanotechnology, processing of nanoparticles or nanopowders into bulk shapes, retaining nanosize is another challenging aspect, as far as structural and engineering applications are concerned. Synthesis and assembly strategies of nanoparticles mostly accommodate precursors from liquid, solid or gas phase; employ chemical or physical deposition approaches; and similarly rely on either chemical reactivity or physical compaction to integrate the nanostructure building blocks within the final material structure.

The varieties of techniques that can be used for nanomaterials synthesis is classified in top-down or bottom-up approaches. (Fig. 2) The bottom up approach of nanomaterials synthesis first forms the nanostructured building blocks (nanoparticles) and then assembles these into the final material an example of this approach is the formation of powder components through aerosol and sol-gel techniques (fig.3) and then the compaction of the components into the final material. Nanoparticles with diameters ranging from 2 nm to 10 nm with consistent crystal structure, surface derivatization, and a high degree of monodispersity can be processed by these techniques. Gas phase synthesis or aerosol processing of nanoparticles is based on evaporation and condensation (nucleation and growth) in a sub atmospheric inert gas environment; and the processing mainly is by combustion flame, laser ablation, chemical vapour condensation, spray pyrolysis, electro spray, and plasma spray. On the other hand, sol-gel processing is a wet chemical synthesis approach that can be used to generate nanoparticles by gelation, precipitation, and hydrothermal treatment. Besides, better size and stability control of nanoparticles can be achieved using inverted micelles, polymer-matrix architecture based on block copolymers or polymer blends, and *in situ* particle-capping techniques. Additional nanoparticle synthesis techniques include *in situ* chemical processing, hydrodynamic cavitation, and microemulsion processing. In sonochemistry, an acoustic cavitation process can generate a transient localized hot

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zonewith extremely high temperature gradient and pressure. Such sudden changes in temperature and pressure assist the destruction of the nonchemical precursor (e.g., organometallic solution) and the formation of nanoparticles. The technique can be used to produce a large volume of material for industrial applications. In hydrodynamic cavitation, nanoparticles are generated through creation and release of gas bubbles inside the sol-gel solution. By rapidly pressurizing in a supercritical drying chamber and exposing to cavitation disturbance and high temperature heating, the sol-gel solution is mixed. The erupted hydrodynamic bubbles are responsible for nucleation, growth, and quenching of the nanoparticles. Particle size can be controlled by adjusting the pressure and the solution retention time in the cavitation chamber. Microemulsions are another important processing technique—extensively used for synthesis of metallic, semiconductor and magnetic nanoparticles. By controlling the very low interfacial tension (~10.3 mN/m) by adding a cosurfactant (e.g., an alcohol of intermediate chain length), these microemulsions are produced spontaneously without the need for significant mechanical agitation. The technique is useful for large-scale production of nanoparticles using relatively simple and inexpensive hardware. The top-down approach begins with a suitable starting material and then sculpts the functionality from the material. This technique is similar to the approach used by the semiconductor industry in forming devices out of an electronic substrate (silicon), utilizing pattern formation (such as electron beam lithography) and pattern-transfer processes (such as reactive-ion etching) that have the requisite spatial resolution to achieve creation of structures at the nanoscale. This particular area of nanostructure formation has tremendous scope and is a driving issue for the electronics and chemical industry.

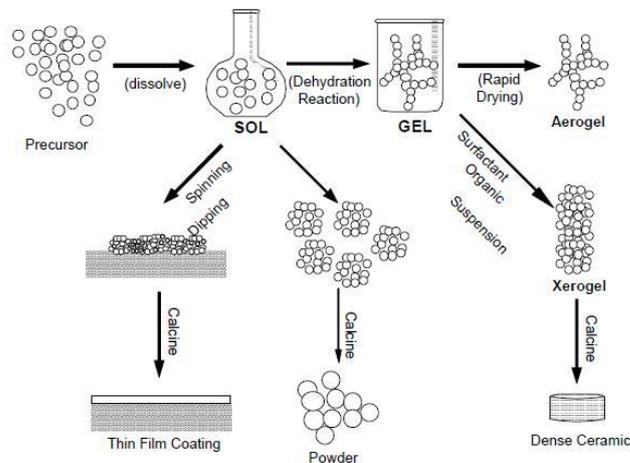
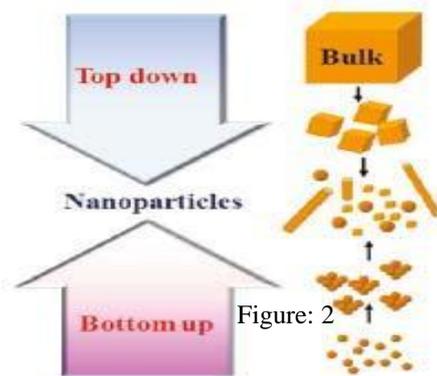


Figure 3. Sol-gel processes for synthesis of nanomaterials.

(c) **Surface modification of nanomaterial/ nanoparticle-** A range of surface modification methods have been developed

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in order to improve the surface characteristics of magnetic nanoparticles and to achieve specific applications. A variety of approaches have been developed for the surface modification of magnetic nanoparticles. They include covalent attachment and adsorption of either small molecules or polymers, resulting in core-shell structures based on polymerization of organic monomers or polycondensation of inorganic precursors through Stober and other sol-gel methods. As surface structure is one of the most important factors in choosing a coating approach, methods developed for magnetic nanoparticles of metals, alloys and oxides can often be applied to nonmagnetic counterparts that share similar surface chemistry, or vice versa. The strategy for modification or functionalization of nanoparticles depends on the specific atomic structures of the surfaces and their interactions with ligands. Nanoparticles with capped groups on their surfaces can be modified with organic or inorganic molecules, regardless of whether they are synthesized in aqueous or nonhydrolytic solutions. The hydroxyl group is one of the commonly used capping groups and it can react with carboxyl groups via its oxygen atom or with various silane groups through -O-Si bond. For nanoparticles synthesized using nonhydrolytic solutions, they have to be modified first to introduce functional groups such as hydroxyl and mercapto groups for further grafting or conjugation reactions. Amine and oxysilane are two other popular functional groups that are used for surface modification of nanoparticles. Nanoparticles of semiconducting quantum dots (QDs), Pt, Ag and Au can be modified with mercapto groups using well developed thiolate chemistry. The selected surface species can often prevent the nanoparticles from aggregating. To fulfill specific applications, primer molecules may be necessary to graft and activate the surface for further functionalization with other chemical or biological molecules. Usually, these primers have dual functional groups, one for surface binding and the other for initiating the designed chemical reactions. Silane coupling agents are such compounds which can change the surface of nanoparticles to be vitreophilic and make the further deposition of coating layers plausible. Electrostatic interactions and other types of Van der Waals interactions are the main driving forces in the preliminary surface modification of nanoparticles. Since these types of interactions, which are physical adsorption in nature, tend to be weak, chemical reactions are needed if strong binding is necessary. Au and Ag nanoparticles usually require sulfur as the bridging element due to the strong affinity between these metals and thiol groups. Other suitable reactions for the formation of surface coatings include silanization and polymerization. Emulsion and self assembly are other two commonly used strategies in the surface modification of nanoparticles. Besides direct ligand exchange and emulsion methods, microwave-assisted modification, dry mechanical coating techniques, and ozone deposition are other techniques that have been developed to facilitate the surface treatment. For surface modification with inorganic oxide layers, sol-gel methods are rather useful and the Stober method is among the most widely used strategy, which was originally developed for making silica layers.

(d) Characterization of nanomaterials / nanoparticles: It is done by Transmission Electron Microscopy/Scanning Electron Microscopy, (TEM/SEM), Atomic Force Microscopy (AFM), Dynamic Light Scattering (DLS), X-ray Photoelectron Spectroscopy (XPS), Powder X-ray Diffractometry (XRD), Fourier Transform Infrared spectroscopy (FTIR), Matrix Assisted Laser Desorption Time of Flight mass spectrometry (MALD –TOF) and Ultra – Violet Visible spectroscopy

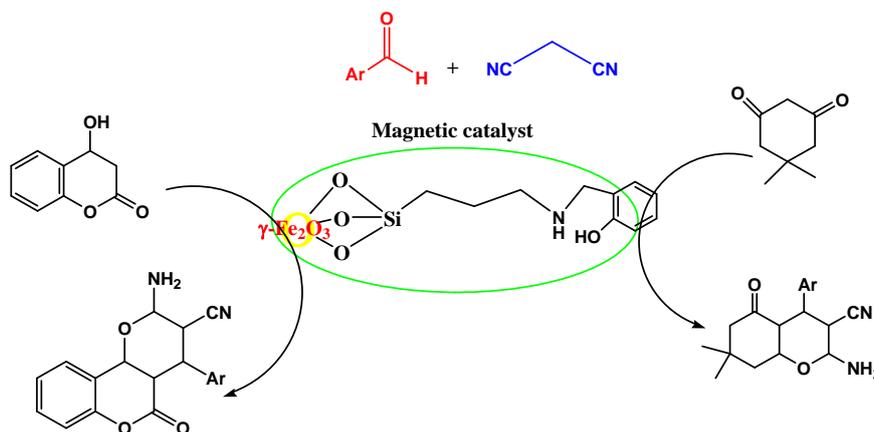
The use of NPs in catalysis appeared in the 19th century with photography (AgNPs) and the decomposition of hydrogen peroxide (PtNPs). Pioneering catalytic applications of NPs were reported in 1940 by Nord on nitrobenzene reduction in 1970 by Parravano on hydrogen-atom transfer between benzene and cyclohexane and oxygen-atom transfer between CO and CO₂ using AuNPs. The real breakthrough came with Haruta's seminal studies on oxide-supported AuNP-catalyzed CO oxidation by O₂ at low temperatures. In the 1970s, Bond and Sermon and Hirai et al. disclosed AuNP-catalyzed olefin hydrogenation. In 1986 Lewis demonstrated the colloidal mechanism for the catalysis of olefin hydrosilylation by silanes using organometallic complexes of Co, Ni, Pd, or Pt including the Speier catalyst (alcoholic H₂PtCl₆). These catalysts were formerly believed to follow the classic monometallic organometallic mechanism (oxidative addition of the Si-H bond of the silane onto the transition-metal center and subsequent alkene insertion and reductive elimination). That decade saw the beginning of extended NP catalytic studies especially in the fields of redox catalysis, photocatalysis (photocatalytic water splitting and photo-hydrogenation of alkenes, alkynes, and CO₂), hydrogenation of unsaturated substrates, and oxidation. In the mid 1990s, pioneering studies of PdNP catalysis were reported by Reetz for Heck C-C coupling, such as the reaction between butyl acrylate and iodobenzene or aryl bromides and styrene. The first years of the 21st century have seen an exponential growth in the number of

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publications in the NP field. A very important concept pioneered in the field of nanocatalysis is in 1970s that of catalysis using two different metals such as Au and Pd in the same NP. This idea has been beautifully developed by Toshima's group who used PVP to stabilize core-shell bimetallic Au-PdNPs, that is, NPs in which the core is Au and the shell is Pd. Enantioselective reactions have been carried out with metal NPs. The first example of an asymmetric reaction catalyzed by metal NPs was reported by the group of Lemaire, Besson, and Galez in 1994 for the RhNP-catalyzed hydrogenation of 2-methylanisole *o*-cresol trimethylsilyl ether induced by a RhNP with a chiral amine, *R*-dioctylcyclohexyl-1-ethylamine, as ligand. The literature covered in this report has been obtained from sci-direct using the keyword "nanocatalyst in organic synthesis" and other web sources. This report covers some contribution from recent literature. Recently M. Khoobi and co-workers reported a green and useful method (scheme 1) to obtain 4*H*-benzopyrans and 2-amino-5-oxo-4-aryl-4,5-dihydropyrano[3,2-*c*]chromene-3-carbonitriles in aqueous media by using magnetically inorganic-organic hybrid nanocatalyst supported on hydroxyapatite encapsulated γ -Fe₂O₃.



Scheme 1. Synthesis of 4*H*-benzopyrans and 2-amino-5-oxo-4-aryl-4,5-dihydropyrano[3,2-*c*]chromene-3-carbonitriles. An insight toward green nanocatalyst for the synthesis of pyrido[2,3-*d*]pyrimidine derivatives was provided by M. Mohsenimehr et al. They described a green, useful and rapid method (scheme 2) to synthesize pyrido[2,3-*d*]pyrimidine derivatives via one-pot synthesis in the presence of $[\gamma$ -Fe₂O₃@HAp-SO₃H] as a nanocatalyst at 60 °C under solvent-free conditions.



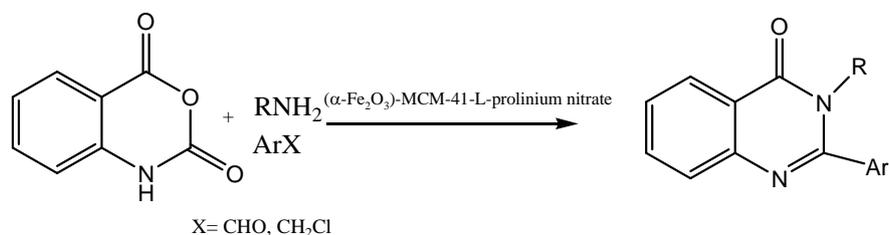
Scheme 2. synthesis of pyrido[2,3-*d*]pyrimidine derivatives

S. Rostamizadeh and co-workers reported first time that magnetic nanocatalyst (α -Fe₂O₃)-MCM-41-L-prolinium nitrate (scheme 3) are attributed both acidic and oxidative behavior for the synthesis of quinazolin-4(3*H*)-one.

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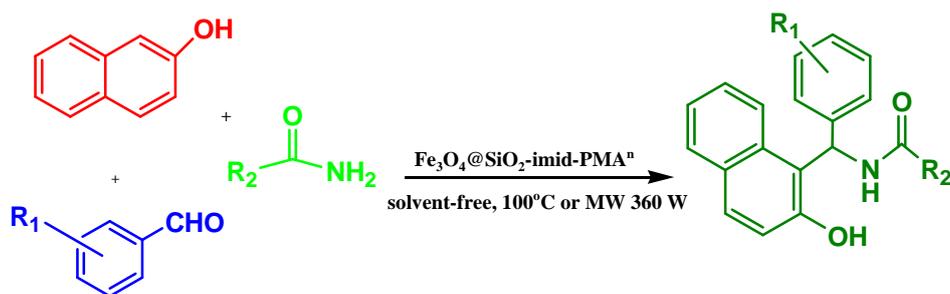
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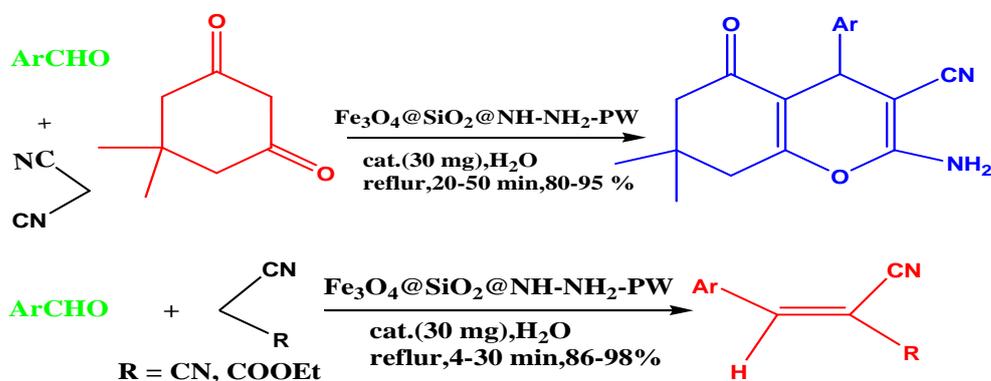
Scheme 3. Synthesis of quinazolin-4(3H)-one

Later M. Esmailpour group reported a recyclable nanocatalyst (scheme 4) for the synthesis 1-amidoalkyl-2-naphthols via one-pot condensation reaction of β -naphthol, aldehydes and acetamide, benzamide and urea in the presence of $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-imid-PMA}^n$ under solvent-free and microwave conditions.



Scheme: 4. Synthesis 1-amidoalkyl-2-naphthols via one-pot condensation reaction

Likewise FomeidaShahbazi and Kamal Amani have been reported Magnetite-polyoxometalate hybrid nanomaterials, for the synthesis of tetrahydrobenzo[b]pyrans. They were established a catalytic performance of $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{NH-NH}_2\text{-PW}$, in the synthesis of tetrahydrobenzo[b]pyrans (scheme 5) and Knoevenagel condensation in aqueous media.



Scheme 5. Synthesis of tetrahydrobenzo[b]pyrans using $\text{Fe}_3\text{O}_4@ \text{SiO}_2@ \text{NH-NH}_2\text{-PW}$ as a catalyst

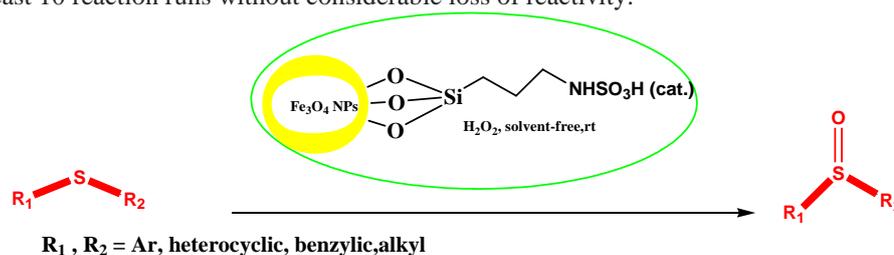
Carbon nanotubes are versatile nanomaterials in nanotechnology, M. Mirzaeian et al. were reported a mercaptan free gas stream, by using carbon nanotubes with a cobalt phthalocyanine (CoPc) complex. S. Rostamizadehand co-workers reported N-aryl-2-amino-1,6-naphthyridine derivatives by using $(\alpha\text{-Fe}_2\text{O}_3)\text{-MCM-41-SO}_3\text{H}$ magnetic nanocatalyst in synthesis as a catalyst. The catalyst recovered by simple magnetic filtration without any loss of activity. For the chemoselective oxidation of sulfides to sulfoxides A. Rostami et al. have been provide a

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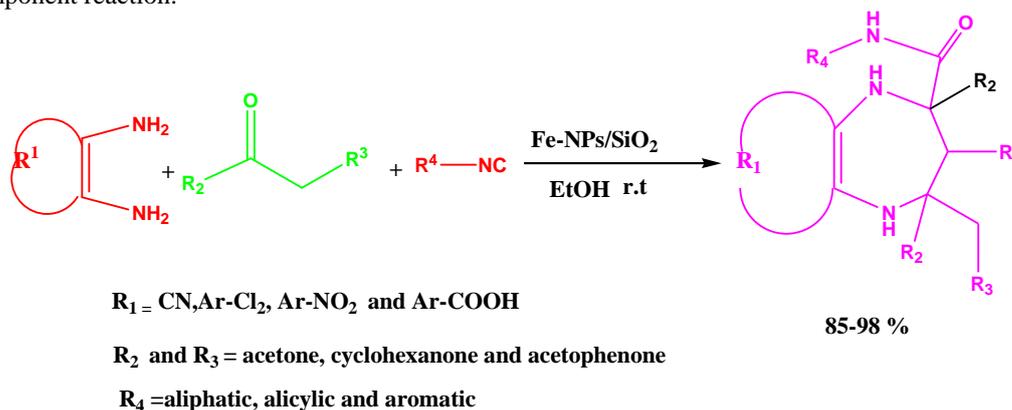
efficient and eco-friendly method, using 30% H_2O_2 in the presence of catalytic amounts of *N*-Propylsulfamic acid supported onto magnetic Fe_3O_4 nanoparticles (MNPs-PSA) under solvent-free conditions at rt (scheme 6). The used magnetic nanocatalyst was recyclable and readily recovered by applying an external magnet device and reused for at least 10 reaction runs without considerable loss of reactivity.



Scheme 6. Synthesis of *N*-aryl-2-amino-1,6-naphthyridine derivatives using $(\alpha\text{-Fe}_2\text{O}_3)\text{-MCM-41-SO}_3\text{H}$

magnetic nanocatalyst

In the studied of degradation of various azo dyes in the presence of nanocatalyst Afsaneh Safavi and Safieh Momeni have been provide palladium/hydroxyapatite/ Fe_3O_4 nanocatalyst and they were evaluated its catalytic activity towards the degradation of azo dyes (methyl red, methyl orange and methyl yellow) selected as test dye species. Many groups have been reported iron based nanomaterial as nanocatalyst for catalyse organic reaction due to efficient activity and easy separation after completion of chemical reaction. Ali Maleki was reported silica-supported iron oxide ($\text{Fe}_3\text{O}_4/\text{SiO}_2$) nanoparticles for the one-pot multicomponent synthesis of diazepine derivatives (scheme 7). He was carried out synthesis by using a 1, 2-diamine, a linear or cyclic ketone, and an isocyanide in the presence of iron oxide ($\text{Fe}_3\text{O}_4/\text{SiO}_2$) nanoparticles. Similarly Zohreh Mirjafary and his co-workers have been used ZnO nanoparticles for the synthesis of β -acetamido ketones/esters via a multicomponent reaction.



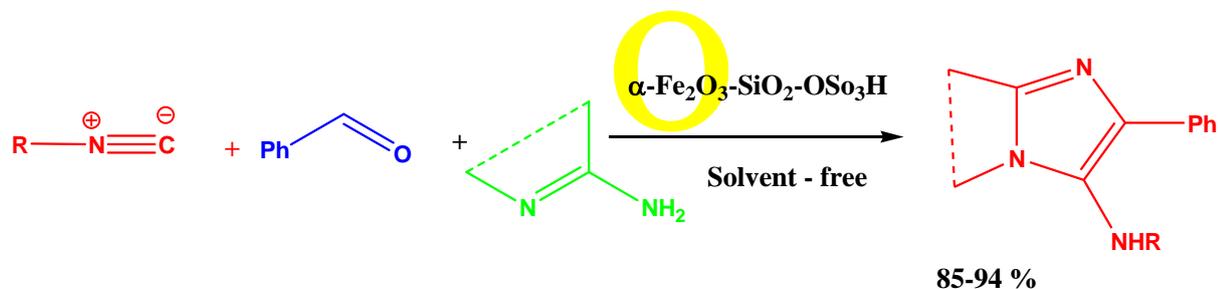
Scheme 7. One-pot multicomponent synthesis of diazepine derivatives silica-supported iron oxide ($\text{Fe}_3\text{O}_4/\text{SiO}_2$) nanoparticles

The Groebke-Blackburn-Bienaymé reaction is four-centre, three-component reaction which basically involves a reaction between aldehyde, 2-aminoazine and an isonitrile in the presence of suitable catalyst, to afford a substituted fused imidazole derivatives. Sadegh Rostannia et al. described Groebke-Blackburn-Bienaymé reaction (scheme 8) for the synthesis of aminoimidazopyridine, in the presence of nanomagnetically modified sulfuric acid ($\gamma\text{-Fe}_2\text{O}_3@/\text{SiO}_2\text{-OSO}_3\text{H}$), an efficient, fast, and reusable green nanocatalyst. The $\gamma\text{-Fe}_2\text{O}_3@/\text{SiO}_2\text{-OSO}_3\text{H}$ catalyst could be recovered and reused in five reaction cycles.

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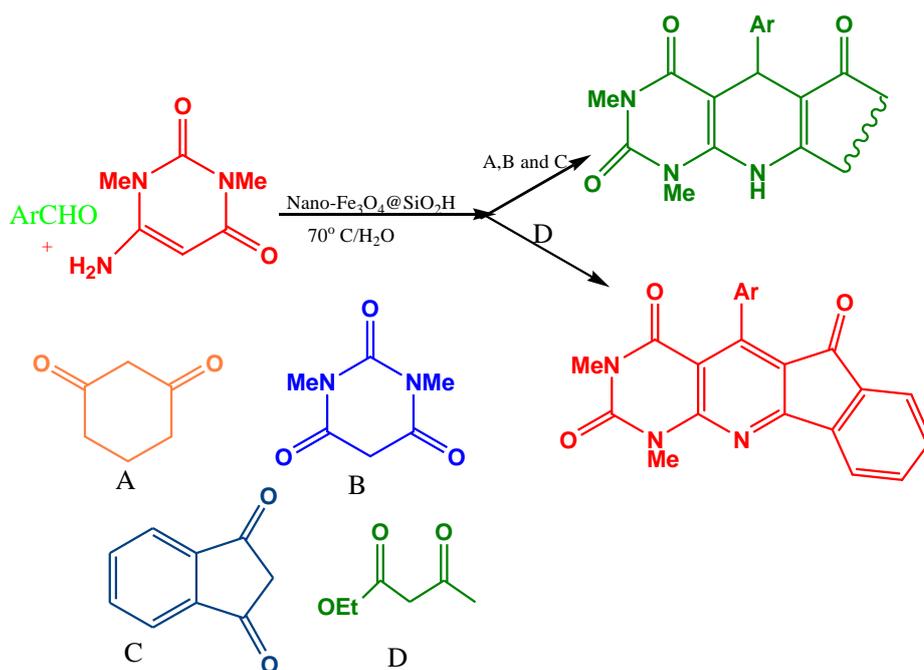
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Scheme 8. Synthesis of aminoimidazopyridine, in the presence of nanomagnetically modified sulfuric acid (γ - $\text{Fe}_2\text{O}_3@ \text{SiO}_2\text{-OSO}_3\text{H}$)

Firouzeh Nemati and Raheleh Saeedirad reported a series of pyrimido[4,5-*b*]quinolines and indeno fused pyrido[2,3-*d*]pyrimidines (scheme 9) via a acid catalyst multicomponent reaction in the presence of $\text{Fe}_3\text{O}_4@ \text{SiO}_2\text{-SO}_3\text{H}$ as a nano-magnetic in an aqueous medium and mild reaction condition.



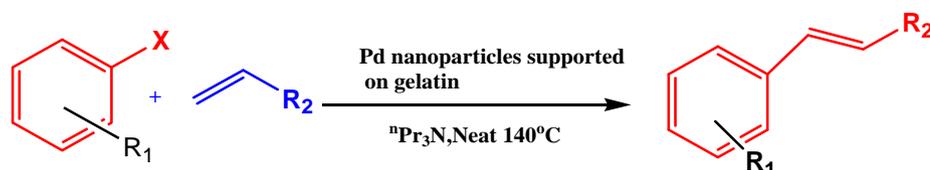
Scheme 9. Synthesis of pyrimido[4,5-*b*]quinolines

For Suzuki–Miyaura coupling Tatiana V. Magdesieva and his co-workers have been reported Polypyrrole–palladium nanoparticles. They are studied that this nanoparticle are efficient nanocatalyst for maximum yield. Similarly Ningzhao Shang group also reported a graphene oxide supported palladium nanoparticles for Suzuki–Miyaura reaction. They were reported a series of biphenyl compounds through the Suzuki–Miyaura reaction using $\text{GO-NH}_2\text{-Pd}^{2+}$ as catalyst. Later Habib Firouzabadi group reported palladium, based nanoparticle for Mizoroki–Heck reaction. (Scheme 10)

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Scheme 10. Synthesis of biphenyl compounds through the Suzuki–Miyaura reaction using GO-NH₂-Pd²⁺ as catalyst.

For a number of couplings reaction i.e. Suzuki, Heck and Sonogashira Pitchaimani Veerakumar and his co-workers have been reported heterogeneous catalysts (Pd/NH₂-SiO₂) in which an amine-functionalized silica (NH₂-SiO₂) as support for palladium nanoparticles (PdNPs). The synthesized Pd catalyst is well characterized by XRD, HRTEM, BET, SEM-EDX, FT-IR, and UV–vis spectral techniques. It exhibits efficient catalytic activity towards these coupling reactions.

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