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MgO nanoparticles: Synthesis, characterization, and applications as a catalyst for organic transformations

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ABSTRACT

Currently, the size and shape selective synthesis of nanoparticles (NPs) and their varied catalytic applications are gaining significant enthusiasm in the field of nanochemistry. Homogeneous catalysis is crucial due to its inherent benefits like high selectivity and mild reaction conditions. Nevertheless, it endures with serious disadvantages of catalysts and/or product separation/recycles compared to their heterogeneous counterparts restricting their catalytic applications. The utilization of catalysts in the form of nano-size is an elective methodology for the combination of merits of homogeneous and heterogeneous catalysis. Magnesium oxide (MgO) NPs are important as they find applications for catalysis, organic transformation, and synthesis of fine chemicals and organic intermediates. The applications of MgO NPs in diverse organic transformations including oxidation, reduction, epoxidation, condensation, and C-C, C-N, C-O, C-S bond formation in a variety of notable heterocyclic reactions are also discussed. The use of MgO NPs in organic transformation is advantageous as it mitigates the use of ligands; the procurable separation of catalyst for recyclability makes the protocol heterogeneous and monetary. MgO NPs gave efficacious catalytic performance towards the desired products due to high surface area. By considering these efficient merits, scientists have focused their attentions towards stupendous applications of MgO NPs in selective organic transformation. In the current review article, we summarized the synthesis of MgO NPs and numerous characterization techniques, whereas the application section illustrates their utility as a catalyst in several organic transformations. We believe this decisive appraisal will provide imperative details to further advance the application of MgO NPs in selective catalysis.

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1. Introduction

In recent years, metal oxide NPs are notable for their magnificent and eclectic applications in the disciplines of bio-technology, catalysis, medicine, bio-engineering, agriculture, textile engineering and water treatment [1-6]. The NPs addition-nally have huge significant applications in other areas such as photocatalysis, biosensors, cancer therapeutics, labeling for cells, cosmetics, magnetics, solar cells, optoelect-ronics and space industry [7-12]. The synthesis of metal oxide NPs and their multifarious applications in these areas are of great and imperative interest for further study. The preparation of size and shape selective nanosize NPs has generated an innumerable enthusiasm due to their distinctive structures, size, and their peculiar chemical, physical, as well as biological features/properties compared with their bulk compounds [1]. Magnesium and its compounds are important materials through-hout the history, finding multifarious remarkable applications (Figure 1). MgO NPs are used for the production of industrially valuable compounds in pharmaceuticals, agro-chemicals and their profitable intermediates [13,14]. Several researchers have developed novel protocols for the rapid synthesis of MgO NPs along with their applications in various fields such as photocatalyst, sensors, electronic devices, drug

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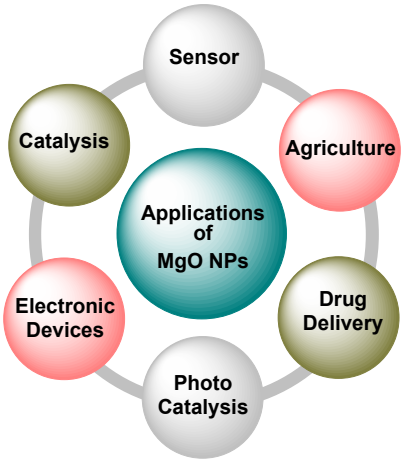


Figure 1. Various applications of MgO NPs.

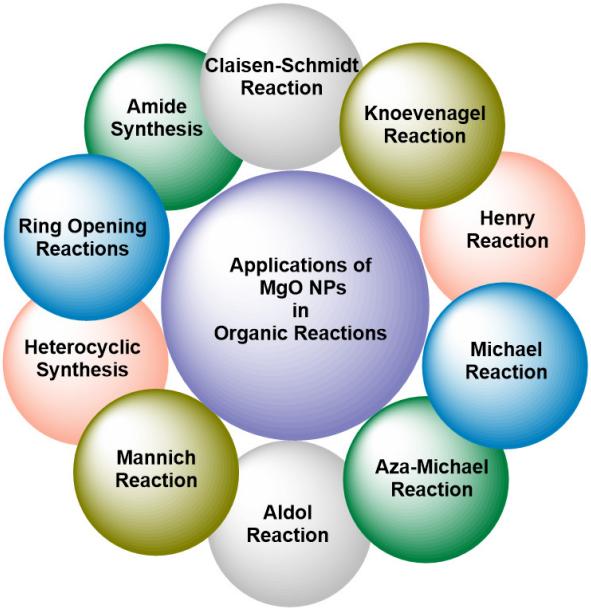


Figure 2. Applications of MgO NPs in organic reactions.

delivery, agriculture and catalysis [15-20]. Moreover, MgO NPs also showed the biological properties such as antibacterial [21], antifungal, cytotoxic [22], antioxidant [15] and anticancer activity [23].

Present review article covers the procurable synthesis of MgO NPs by chemical, physical and biological approaches along with their recent diverse characterization techniques followed by a discussion on MgO nano catalysis. MgO NPs play an overriding role as a sustainable catalyst due to their distinctive features/properties for several organic transformations which are extensively discussed here.

2. Scope of the review

Despite a few sporadic reports, there is no any comprehensive overview covering the current catalytic uses of MgO NPs for organic transformations. This review discusses the applications of MgO NPs as catalysts for diverse reactions, including oxidation, reduction, epoxidation, condensation, and notable heterocyclic reactions (Figure 2). The synthetic strategies and relevant examples of MgO NPs are discussed with brief descriptions of relevant characterization techniques such as UV-visible spectroscopy, X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Energy Dispersive Spectroscopy (EDS), Fourier Transform Infrared (FTIR) Spectroscopy, Atomic Absorption Spectroscopy (AAS), Dynamic Light Scattering (DLS), Electrophoretic Light Scattering (ELS), Atomic Force Microscopy (AFM), Scanning Tunneling Microscopy (STM) and X-ray Photoelectron Spectroscopy (XPS). We believe that a detailed overview of the current protocols for preparing MgO NPs and their multifarious applications would be encouraging to a broad community of scientists working in the disciplines of chemical engineering, inorganic chemistry, material chemistry, nanotechnology and organic chemistry. Moreover, most of the chemistries detailed in this review, namely, various reactions in benign media, such as water, ethanol, and recyclability of nanocatalyst, will address the current outstanding developments in the field of nanochemistry.

3. Synthesis of MgO nanoparticles

3.1. Chemical approach

In chemical approaches, the chemical reduction method is commonly used for the fabrication of NPs.

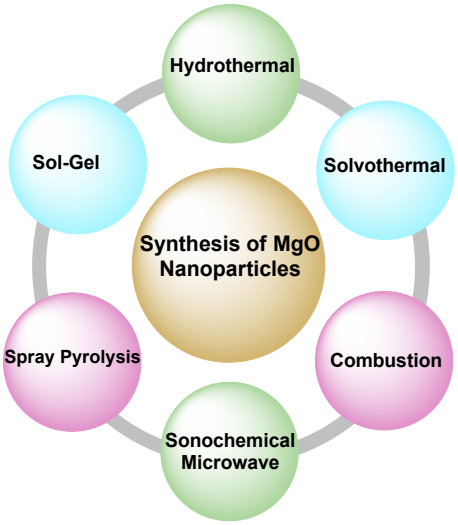


Figure 3. Synthesis of MgO NPs by different chemical methods.

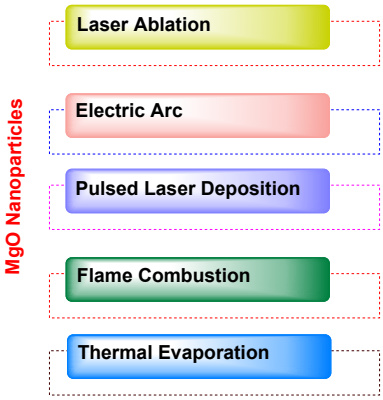


Figure 4. Synthesis of MgO NPs by different physical methods.

Along with this approach, chemical syntheses include chemical vapor deposition (CVD) [24], sol-gel [25], thermal decomposition [26], co-precipitation [27], micro-emulsion [28], wet chemical method [29], chemical precipitation [30], sono-chemical [31], microwave assisted [32], solvothermal [33], hydrothermal [34], spray pyrolysis [35], chemical bath [36], combustion [37], ionic liquid assisted [38], polyol-mediated [39], and template assisted method [40] and reverse micellar method [41] (Figure 3) etc. for the synthesis of MgO NPs. In the case of chemical reduction, magnesium metal salts are reduced by a reducing agent forming a magnesium nucleus and the growth of the nucleus of a particle is controlled by a capping agent who also resists aggregation by electrostatic repulsion.

Various sources of magnesium salt were used for the synthesis of MgO NPs like MgCl, $Mg(NO_3)_2$, $Mg(OAc)_2$, along with $NaBH_4$, phytochemicals present in plants, algae, bacteria, fungus and yeast which play different roles such as reducing, stabilizing and capping agents [21-30].

At the time of fabrication of MgO NPs, the magnesium salt precursor mixed with suitable solvent and capping agents are used to control the morphology of MgO NPs, which minimizes agglomeration and an apt reducing agent reduces the starting magnesium salt precursor in favorable conditions for the subsequent formation of MgO NPs.

3.2. Physical approach

Chemical routes for the synthesis of NPs usually include noxious chemicals, which can be pernicious to the environment and human beings. Although this approach creates shape and size selective MgO NPs, they need a capping agent, stabilizer as well as special additives to mitigate the agglomeration of MgO NPs whereas, physical approaches do not involve perilous chemicals and are usually rapid. Physical synthesis mostly includes the laser ablation [42], electric arc [43], thermal evaporation [44], flame combustion [45], and pulsed laser deposition [46] for synthesis of MgO NPs (Figure 4). One of the important benefits of exploring physical method over chemical for the synthesis of NPs is there is no probability of solvent contamination.

3.3. Green approach

Nowadays, research in biosynthesis is a completely greener domain for the fabrication of NPs. The magnesium metal salt, reducing and capping agents are efficient compounds in chemical methods of the production of MgO NPs. Nevertheless, in the biological approach, the reducing, capping and/or stabilizing agents can be used as natural sources from various plant extracts for the facile synthesis of MgO NPs of selective size and shape. Many researchers have focused on facile and greener approaches for the biogenic synthesis of NPs (Figure 5). Essien *et al.* applied greener approaches to the eco-benign synthesis of MgO NPs using the leaf extract of *Manihot esculenta* as capping agents with hexagonal shaped MgO NPs, having average size 36.7 nm [47].

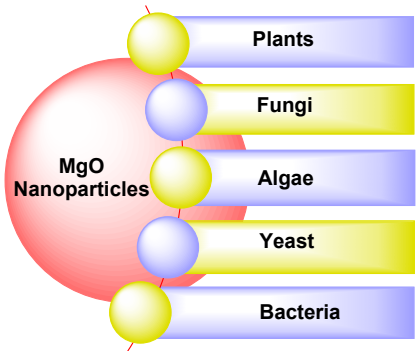


Figure 5. Synthesis of MgO NPs by different biological methods.

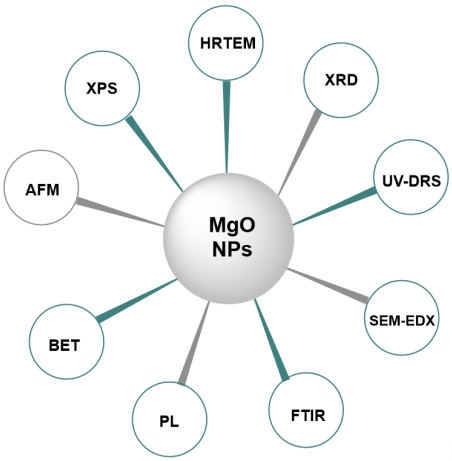


Figure 6. Various characterization techniques for MgO NPs.

Ogunyemi *et al.* reported the green synthesis of MgO NPs of diameter 18.2 nm using *Matricaria chamomilla* flower extracts as a stabilizing/capping agent at room temperature [48]. Joghee *et al.* demonstrated green synthesis of ball-like shaped MgO NPs of average size 50.95 nm from the leaf of *Pisonia grandis* [49].

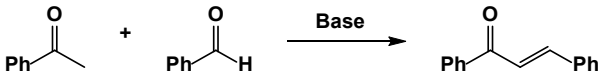
Recently, researchers developed novel protocols for the procurable synthesis of MgO NPs using diverse plant extracts as herbal capping agents to get various sizes and shapes of MgO NPs [50]. For instance, the MgO NPs synthesis was achieved using Banyan latex [51], *Bauhinia purpurea* leaf extract [52], *Calotropis gigantea* floral extract [53], *Carica papaya* leaf extract [54], *Chromolaena odorata* leaf extract [55], *Clitoria ternatea* extract [56], *Costus pictus* leaves extract [57] *etc.* Jain *et al.* demonstrated the biogenic synthesis of MgO NPs by using *Syzygium aromaticum* extracts and their application for the sensing of Fe^{3+} in real water samples [58].

The use of microorganisms [59,60] and fungi [61,62] plays an extensive role in the synthesis of MgO NPs. The reducing and stabilizing constituents can be found in bacteria, fungi, yeasts, algae, or plants which reduce the magnesium salt and control the size and shape of MgO NPs. In biosynthesis, magnesium ions are precipitated and stabilized by various functional groups of the cell wall of fungi or bacteria. Mohanasrinivasan *et al.* demonstrated MgO NPs from *Lactobacillus sp.* [59], Sayyad *et al.* used the *Penicillium chrysogenum* fungi for the synthesis of MgO NPs [63]. Mohanasrinivasan *et al.* reported the biosynthesis of spherical MgO NPs using microorganism and examined their anticancer activity against human leukemia cell line HL-60 [59]. In another study, Ibrahem *et al.* evinced the fungus-mediated biosynthesis of spherical-shaped MgO NPs using *Aspergillus niger* with average size 43-91 nm [62].

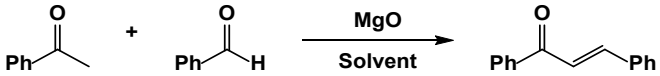
4. Characterization of MgO NPs

The characterization of MgO NPs is an important and imperative step in the production of MgO NPs. The stability, size, topography, and surface area of NPs are the important features/properties used to characterize the synthesis of MgO NPs. There are ample number of techniques (Figure 6) which are used for the characterization of NPs viz. UV-visible spectroscopy, X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Photo Luminescence (PL), Energy Dispersive Spectroscopy (EDS), Fourier Transform Infrared (FTIR) Spectroscopy, Atomic Absorption Spectroscopy (AAS), temperature-programmed desorption of carbon dioxide (CO_2-TPD), Dynamic Light Scattering (DLS), Electrophoretic Light Scattering (ELS), Atomic Force Microscopy (AFM), Scanning Tunneling Microscopy (STM) and X-ray Photoelectron Spectroscopy (XPS) [1-6, 64].

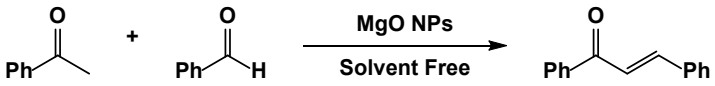
UV-visible spectroscopy is the most generally used technique for the characterization of noble NPs, which affirms the formation of NPs and their stability. The wavelength in the range of 200-800 nm is generally used for the characterization of NPs. The broad surface plasma absorption band in the range of 500-550 nm is used in characterization of MgO NPs. The functional groups attached to the surface of NPs and surface chemistry of NPs were characterized by FTIR Spectroscopy. The microscopic characterization techniques such as SEM, TEM, AFM, and STM are employed to reveal the exact surface topography and size of MgO NPs. The techniques additionally utilized for the characterization of size and surface charge of NPs are BET, XPS, Zeta Sizer Nano (ZS), utilizing DLS and ELS, respectively [1-6]. CO_2-TPD is used to determine basicity of the material.



Scheme 1. Claisen-Schmidt reaction.



Scheme 2. Claisen- Schmidt reaction using MgO NPs.



Scheme 3. Solvent-free Claisen- Schmidt reaction using MgO NPs.

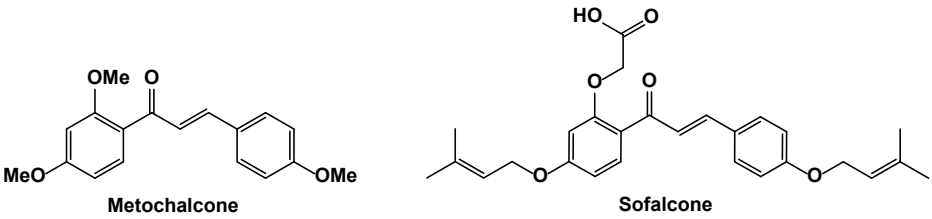


Figure 7. Structures of clinically approved chalcone based drugs.

From XRD, the average particle size of the synthesized MgO NPs can also be achieved by using Scherrer's Equation (1) as:

$$B(2\theta) = \frac{K\lambda}{D\ Cos\ \theta} \quad (1)$$

where, D: the average dimension of crystallites in nm, λ: the wavelength of the X-ray radiation, K: the Scherrer's constant (usually taken as 0.94), B: the line width at half-maximum height (FWHM) in radians and θ: the Bragg's angle.

The phase determination and crystal planes of the synthesized NPs are also characterized by XRD technique [65]. EDS is used to determine the purity and elemental composition of NPs.

5. Applications of MgO NPs in organic transformation

The investigation into NPs catalyzed reactions is projected in modern research because NPs play an important role in several organic transformations *via* heterogeneous catalysis. Nanomaterials showed good catalytic performance and selectivity due to their topography, size, and high surface area to volume ratio [1]. The NPs have diverse merits in catalysis, such as NPs are insoluble in the reaction medium, mild reaction conditions, easy workup, excellent yield, easy separation and recyclability of catalyst. Strikingly, the organic transformations using NPs do not need any ligand source, they accelerate the reaction using usually low catalyst loading with low temperature, which makes the protocol simple, one pot, affordable, and cost effective.

MgO NPs have been used as catalysts for a wide variety of organic transformations. They are especially appealing to this goal because they often enable organic reactions to be conducted under durable or green reaction conditions that would mitigate the performance of conventional catalysts. This section describes the MgO NPs as a catalyst for various organic transformations like oxidation, reduction, epoxidation, condensation, and C-C, C-N, C-O, C-S bond formation in a variety of notable heterocyclic reactions.

5.1. Claisen-Schmidt reaction

Claisen-Schmidt's reaction is one of the old yet essential reactions utilizing carbonyl groups containing starting materials and yields chalcone as a product. Specifically, the reaction between an aldehyde and ketone having α-hydrogen with an aromatic carbonyl compound without α-hydrogen results in the formation of chalcone shown in (Scheme 1). The chalcones are having several applications such as antioxidative, antibacterial, antihelmintic, amoebicidal, antiulcer, antiviral, insecticidal, antiprotozoal, anticancer, cytotoxic and immune-suppressive [66]. The activities exhibited by chalcones are dependent upon the substituents present over it.

Chalcone is the precursor of compounds for flavonoids biosynthesis in plants and drug discovery [67]. These natural products and synthetic compounds have shown numerous interesting biological activities with clinical potential against several diseases. Some of the active chalcone based molecules are represented in Figure 7.

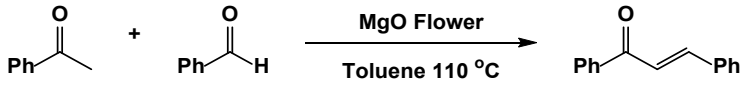
The Claisen- Schmidt reaction is reported by various bases such as NaOH, LiOH, KOH, Mg $(OH)_2$ and Ba$(OH)_2$ [68]. The MgO NPs prepared by different methods are extensively used in chalcone synthesis due to their basic properties. There are several merits of MgO NPs over other inorganic bases such as easy to prepare, eco-friendly, fast reaction, and ease in separation.

Ganguly *et al.* synthesized MgO NPs by reverse micellar method, which gave MgO NPs with particle size 8-10 nm [41]. The characterization of MgO NPs was done with the help of HR-TEM, SEM, XRD, and FTIR to conclude the formation of MgO NPs. The synthesized MgO NPs were used in Claisen-Schmidt reaction (Scheme 2).

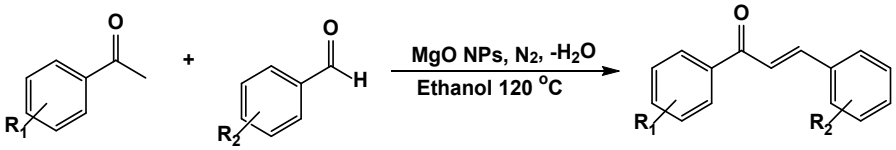
MgO nanocrystal was synthesized by novel and green methods by Patil et al. MgO NPs were prepared from a mixture of magnesium acetate and 1,4-butanediol keeping in sunlight. The synthesized MgO NPs was confirmed by spectroscopic and microscopic techniques.

Table 1. Textural and catalytic properties of the synthesized MgO with various morphologies.

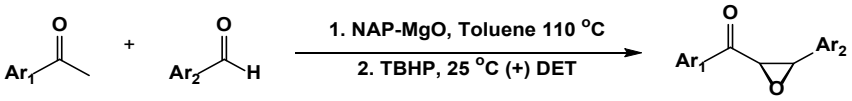
Sample (Morphology)	Surface area (m^2/g)	Crystallite size (nm)	Yield (%)
Rod	115	6	99
Big flowers	82	7	99
House of cards	91	6	97
Small flowers	87	6	94
Random flakes	97	6	96
Spheres	62	8	83
Cubes	33	9	57
Plates	75	7	89
Bulk	28	27	23



Scheme 4. Claisen-Schmidt reaction in toluene using MgO flower.



Scheme 5. Claisen-Schmidt reaction in ethanol using MgO NPs in the N_2 atmosphere.



Scheme 6. Claisen-Schmidt condensation asymmetric epoxidation catalysed by MgO NPs.

Therefore, the synthesized MgO NPs were used for chalcone synthesis, where different derivatives acetophenone and benzaldehyde reacted in the presence of 10 mol % MgO NPs at 140 °C for 4 hrs. under solvent-free conditions (Scheme 3) [69].

Sutradhar *et al.* synthesized MgO nanomaterials with different morphologies, such as random nanoflakes, arranged nanoflakes toward flowers and house of card structure spheres, cubes, and hexagonal plates, through the calcination of magnesium carbonate hydrate (MCH) intermediate via hydrothermal, solvothermal methods. The particle size and surface properties of materials are identified with the aid of techniques like TEM, SEM-EDX, XRD, *etc*., which confirms different morphologies with particle size ranging from size 6-27 nm. Basicity of the synthesized MgO nanomaterial was determined with the help of CO_2-TPD technique [64]. The MgO nanomaterials were subjected to Claisen-Schmidt reaction. In the general reaction, the mixture of (5 mmol) acetophenone and (5.2 mmol) benzaldehyde with 10 % (weight) of MgO nanomaterials catalyst was stirred at 150 °C for 5 hrs. in nitrogen atmosphere and the yield was reported as shown in Table 1. The synthesized materials were found to provide excellent yields of the desired product.

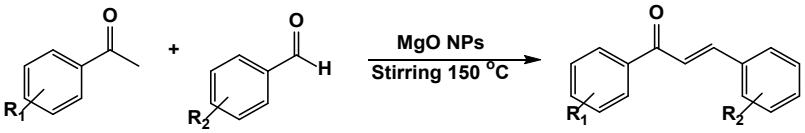
Micrometer size nanostructured flower-like MgO was synthesized by Bain *et al.* using magnesium acetate and ethylene-glycol mediated self-assembly process. The morphology of the synthesized MgO flowers was confirmed by electronic scanning techniques. The comparative study of synthesized MgO flowers and commercially available MgO was done using Claisen-Schmidt reaction (Scheme 4). In the present research paper, they studied the catalytic activity of synthesized MgO flowers and commercial MgO flowers at different temperatures, and the synthesized MgO flowers were found to show high catalytic activity at 80 and 50 °C [70].

Jadhav *et al.* synthesized MgO NPs in different ionic liquids (ILs) by microwave (MW) irradiation [71]. They found a profound effect of ionic liquids on the growth and shape of the MgO nanostructures under microwave irradiation. Due to the synergetic effect of ionic liquid, it produces various basic sites on the surface of the MgO nanocrystals. The morphology and basicity of the synthesized MgO NPs were analyzed by XRD and CO_2-TPD techniques and the materials were tested with Claisen-Schmidt reaction (Scheme 5). The reaction was tried in various solvents at different temperatures. The optimized conditions were the use of ethanol as a solvent at 140 °C under N_2 atmosphere utilizing 10 mol% of catalyst. The catalyst shows excellent activity producing desired products in very high yields (69-95%). Recyclability of MgO NPs was also tested for six successive runs, revealing consistent catalytic activity. Even after six consecutive runs, the textural properties are found to be same which is confirmed by electronic microscopic technique [71].

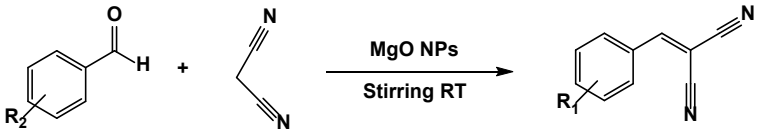
Choudhary *et al.* worked out Claisen-Schmidt reaction (Scheme 6) between aromatic aldehydes and ketones followed by epoxidation with the help of commercial, conventionally prepared MgO NPs and MgO prepared through aerogel method (NAP-MgO) to get chiral epoxy ketone [72]. The same reaction was also studied by Roy *et al.* under the heading of C-C bond formation [73].

Similarly, Roy *et al.* synthesized MgO NPs by rapidly mixing the solutions of magnesium acetate and ammonium carbonate at room temperature, after calcination, the formation of MgO NPs was confirmed by electronic microscopic techniques such as SEM-EDS, TEM and XRD [73]. The catalytic activity of prepared MgO NPs was investigated against Claisen-Schmidt (Scheme 7) and Knoevenagel reactions [20]. The catalyst was found to produce expected product with great yields.

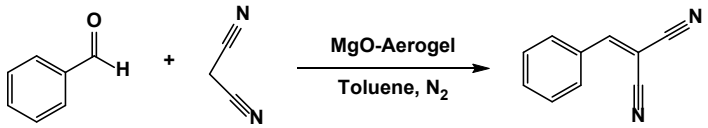
The reaction of acetophenone and benzaldehyde was taken as a model, and various reaction parameter like the effect of solvent, catalyst loading, and temperature was optimized. After optimization of conditions, the protocol was used for the synthesis of various derivatives. The recyclability of MgO NPs catalyst was studied for five successive reactions and were found to provide excellent recyclability.



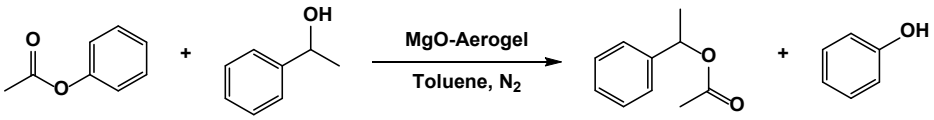
Scheme 7. Claisen-Schmidt condensation catalysed by MgO NPs.



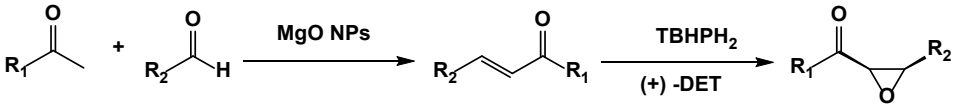
Scheme 8. Knoevenagel condensation catalysed by MgO NPs at room temperature.



Scheme 9. Knoevenagel condensation reaction was carried out in the toluene and N_2 atmosphere.



Scheme 10. Trans-esterification of phenyl acetate with 1-phenyl ethanol carried out in toluene and N_2 atmosphere.



Scheme 11. Claisen-Schmidt reaction catalysed by MgO NPs.

5.2. Knoevenagel reaction

The reaction of the compound having an active methylene group with substituted aromatic aldehydes generally referred to as Knoevenagel reaction, the resultant product can be used for the synthesis of novel heterocyclic molecules. This reaction is reported to be catalyzed by using several bases ranging from strongly basic to bases having weak basicity. The MgO NPs have strong basic properties, as a result it was also explored for Knoevenagel reaction as a catalyst. In this context, Roy *et al.* explored this reaction by condensing malononitrile with an aromatic aldehyde in 50% ethanol and MgO NPs as a heterogeneous recyclable catalyst at RT (Scheme 8).

The reaction was carried out at room temperature, the time reported for different aldehydes ranging from 25 to 90 min, providing more than 85 % yield of the desired products. The solvent effect was also studied and it was found that in ethanol it gives 99 % yield. The study of the effect of the amount of catalyst was also explored and the protocol was used to synthesize library of products [20]. Vidruk *et al.* synthesized MgO-aerogel by sol-gel method using $Mg(OEt)_2$, MeOH, and toluene. Characterization was done with electronic microscopic techniques such as SEM-EDS, TEM, XRD, XPS, and the basicity was obtained by titration method and CO_2-TPD technique as well [74]. The synthesize MgO-aerogel was subjected to following reactions as depicted in Schemes 9 and 10.

The effect of densification of magnesia aerogel precursor on the surface basicity of nanostructured MgO material was tested by the authors. The densified nanostructured MgO material showed higher basic sites compared to un-densified magnesium aerogels. The synthesized material was used for the organic transformations as mentioned above.

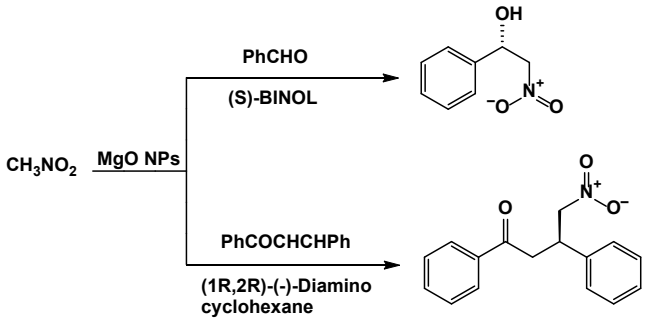
The rate of reaction was found to be multiple fold greater when the densified nanostructured MgO material was used as the base catalyst.

Nanocrystalline MgO was also reported in the asymmetric synthesis by Roy *et al.* They discussed the applications of MgO NPs in C-C bond formation reactions such as Claisen-Schmidt reaction followed by asymmetric epoxidation (Scheme 11), Henry (Scheme 12) and Michael Reactions (Scheme 13) [73]. The catalyst was found to provide good to excellent yields of the desired products in all reported transformations.

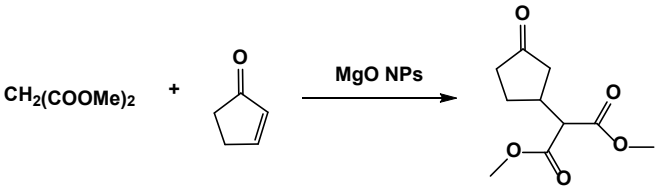
Choudary *et al.* reported the asymmetric Aldol reaction using NAP-MgO as a catalyst (Aerogel prepared MgO nanoparticles) (Scheme 14) [75]. The reactions were carried out in different solvents, where THF was found to provide better yield and ee (75 % & 17% ee). Different aldehydes were allowed to react with acetone to produce different products. The products were obtained in moderate to good yield (50-75 %). The NAP-MgO catalyst was reused for four consecutive times [75].

Similarly, Chuodary *et al.* reported the asymmetric Henry and Michael reaction using MgO NPs (Schemes 15 and 16) [75]. They reported MgO as a heterogeneous and recyclable catalyst for said transformations.

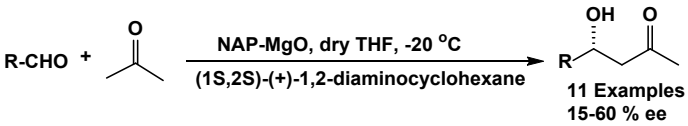
They tried various commercially available and synthetically prepared MgO materials, where the highest yield of the product was reported with MgO NPs. Different chiral ligands were used to study the impact on the enantiomeric excess of products and effect of different solvents on the outcome of reaction was checked. The best results were recorded with toluene and THF, it gives more than 90 % yield of desired products in both cases [76].



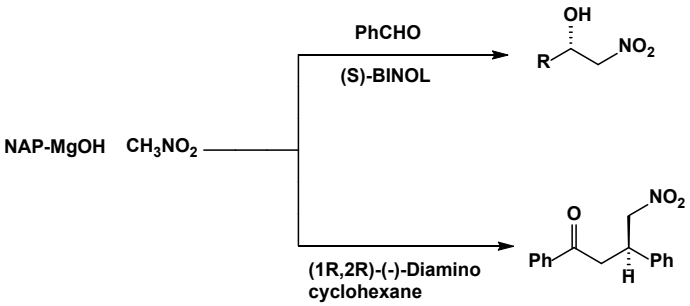
Scheme 12. Henry reaction catalysed by MgO NPs.



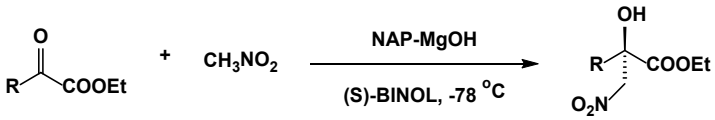
Scheme 13. Michael reaction catalysed by MgO NPs.



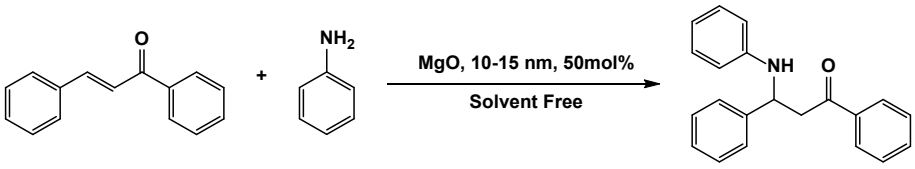
Scheme 14. NAP-MgO catalysed asymmetric Aldol reaction.



Scheme 15. Asymmetric Henry and Michael Reactions catalysed by Nanocrystalline MgO NPs.



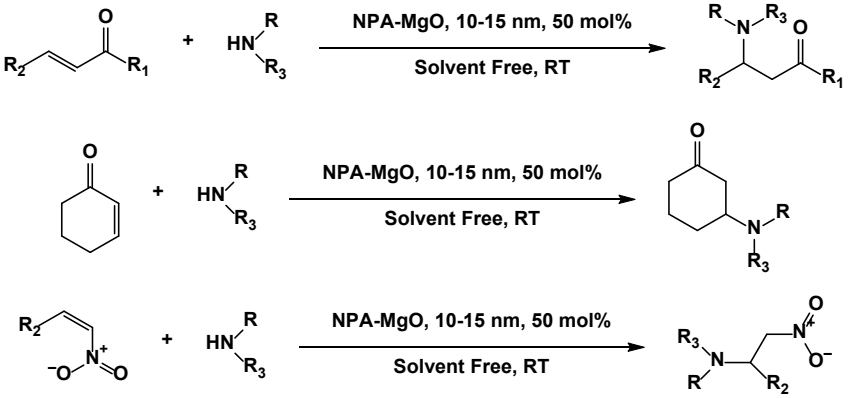
Scheme 16. Asymmetric Henry reaction of keto-esters with nitromethane catalysed by NAP-MgO.



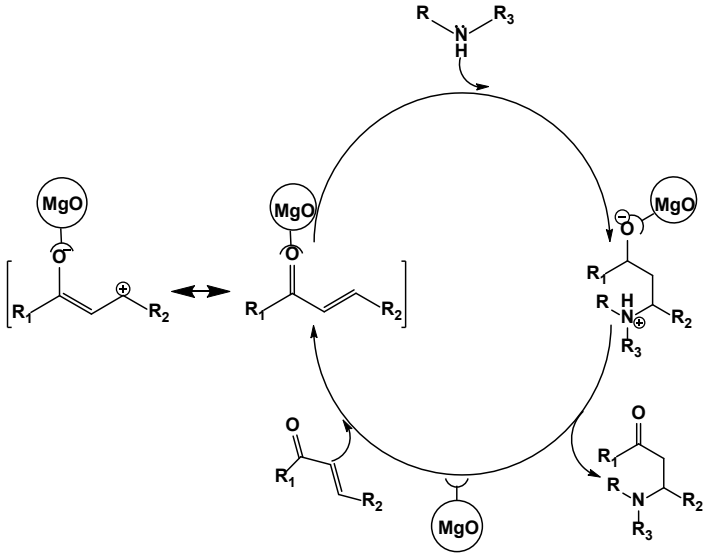
Scheme 17. The reaction of chalcone with aniline as a model reaction.

Aza-Michael reaction catalyzed in the presence of MgO NPs was reported by Tajbakhsh *et al.* [77], where unsaturated carbonyl compounds were reacted with aniline in the presence of MgO NPs as a catalyst under solvent-free conditions as shown in reaction Scheme 17.

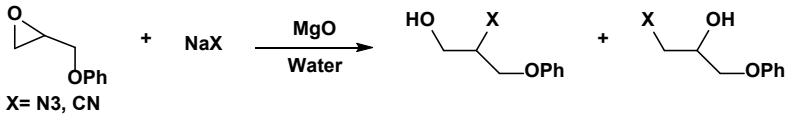
They studied the effect of various catalysts on the outcome of the reaction, where the highest yield of the product was obtained with MgO NPs. The protocol was used to prepare a variety of products with the aid of different unsaturated compounds and amines at room temperature (Scheme 18).



Scheme 18. Aza-Michael reaction of various aromatic amines with α, β-unsaturated compounds catalysed by MgO (nano) at room temperature.



Scheme 19. The proposed mechanism of Aza-Michael addition catalysed by MgO NPs.



Scheme 20. Regioselective ring opening of epoxide in water with MgO NPs.

The possible mechanism of Aza-Michael reaction with MgO NPs was reported by the authors as shown in Scheme 19.

Epoxide serves as a precursor in the synthesis of many target molecules, due to their high reactivity and selectivity. Therefore, many regioselective ring opening reactions of epoxide with the verity of nucleophilic reagents were reported. Hosseini-Sarvari *et al.* reported the synthesis of 2-substituted alcohols by regioselective ring-opening of epoxides in water using MgO NPs (Scheme 20) [78].

The effect of solvent and temperature was studied, where the reaction of NaN_3 at 80 °C in water gives a 95 % yield in 4.5 hrs and that of NaCN at 50 °C in water gives a 95 % yield in 4 hrs [76].

Mashayekh-Salehi *et al.* reported the ozonation of acetaminophen as pharmaceutical contaminants by using MgO NPs as catalyst. The MgO NPs were prepared by thermal/ sol-gel method [79]. Similarly, Mohammadi *et al.* did ozonation of 2,4-dichlorophenol in an aqueous environment with the help of synthesized MgO NPs [80]. The ozonation of 2,4-dichlorophenol in aqueous environment was done in the ozonation reactor as shown in Figure 8.

5.3. Synthesis of heterocyclic compounds

Heterocyclic compounds play a key role in many fields of chemistry like organic synthesis, pharmaceuticals, agriculture, dyes, pigments, etc. Everywhere heterocyclic compounds are present and the synthesis of such biologically active heterocyclic compounds containing different hetero atom is a challenge towards researchers. The synthesis of various active heterocyclic compounds such as pyrazole, imidazole, thiazole, pyridine, chromene, coumarin and many more were reported by using MgO NPs as a catalyst, in this section light is thrown on such organic transformations.

5.3.1. Synthesis of chromenes

Benzopyran is a polycyclic organic compound that results from the fusion of a benzene ring with a heterocyclic pyran ring

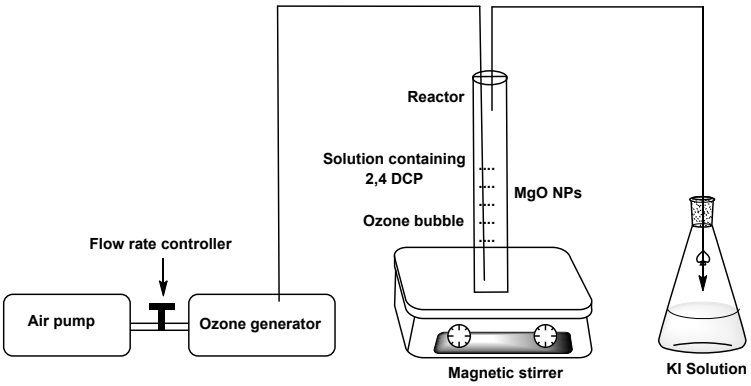
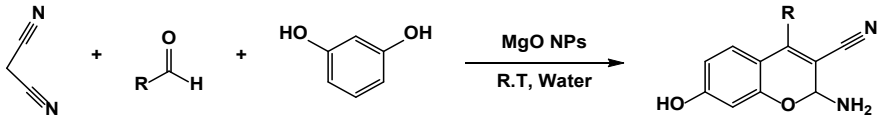
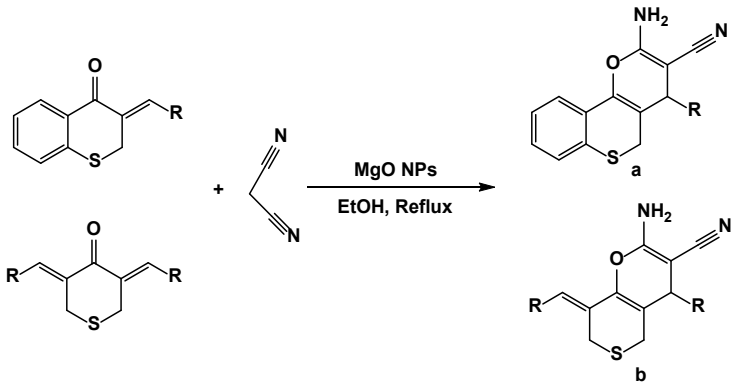


Figure 8. Schematic of the used catalytic ozonation reactor (Reproduced from ref. [80]).



Scheme 21. Nanocrystalline MgO catalysed MCRs leading to 2-amino-4*H*-chromenes.



Scheme 22. Synthesis of 2-amino-4,5-dihydro-4- aryl thiochromeno[4,3-b]pyran-3-carbonitrile and (8*Z*)-2-amino-8-arylidene-4,5,7,8-tetrahydro-4-arylthiopyrano[4,3-b]pyran-3-carbonitrile derivatives over MgO nano-powders.

referred to as chromene, and they are recognized as antimicrobial, antiviral, mutagenic, antiproliferative, antitumor agents, and useful in cosmetic formulations and pigments. Safari *et al.* reported a simple, convenient, and eco-friendly multicomponent reaction (MCR) for the synthesis of chromenes using MgO NPs as a catalyst (Scheme 21) [81]. The reaction was exploited in aqueous medium and found to give excellent yields of the product at room temperature [81].

Green synthesis of MgO NPs using plant extract of *Rosmarinus officinalis* leaves and its use as a catalyst in the synthesis of thiochromeno[4,3-b]pyran and thiopyrano[4,3-b]pyran derivatives (Scheme 22) was reported by Ghashang *et al.* [82].

The MgO nanopowder was synthesized by using *Rosmarinus officinalis* leaves extract, carboxylic acid as chelating group and ammonia solution. The MgO nano powder was characterized by FE-SEM and XRD techniques and later utilized as a catalyst for the synthesis of a variety of products. The possible mechanism for the synthesis of MgO nanopowder and thiochromeno[4,3-b]pyran and thiopyrano[4,3-b]pyran derivatives is as shown in Schemes 23 and 24, respectively.

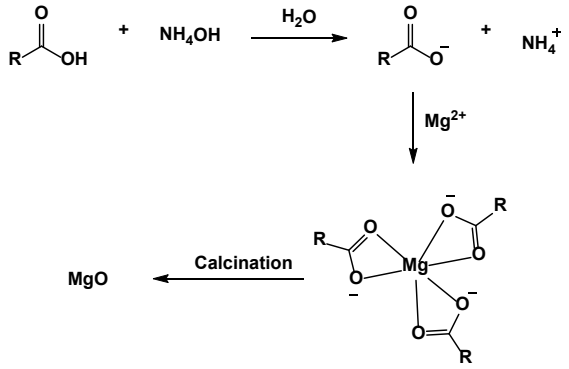
Brahmachari *et al.* reported the synthesis of nano-MgO-catalyzed one-pot synthesis of phosphonate ester functionnalized 2-amino-3-cyano-4*H*-chromene scaffolds at room temperature [83].

In the reaction, substituted salicylaldehyde, active methylene group-containing compounds and phosphonate esters were reacted in the presence of the catalytic amount of MgO NPs in 50% ethanol at room temperature to yield 2-amino-4*H*-chromene as the product. The reaction was tried in various solvents, and the best result were obtained in 50% ethanol (Scheme 25). The study of the catalyst was done by SEM-EDS and XRD techniques.

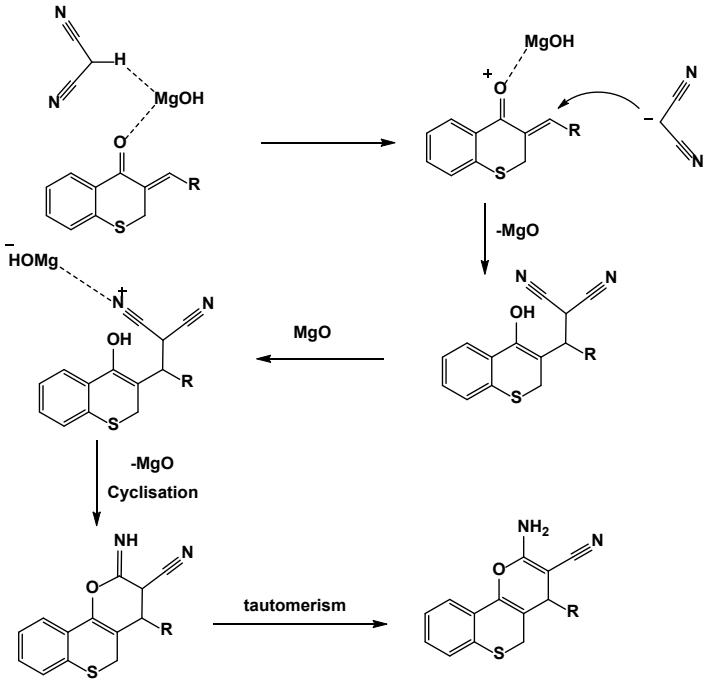
Kumar *et al.* reported the rapid and green synthesis of substituted 2-amino-2-chromenes (Scheme 26) by using MgO NPs under ambient conditions [84]. The group explored a similar catalytic system for the Knoevenagel condensation reaction and for the synthesis of 2-amino-4*H*-pyran and 2-amino-5-oxo-5,6,7,8-tetrahydro-4*H*-chromenes (Schemes 27-29) [85].

The synthesized compounds were screened for their antibacterial activity against three bacterial strains, namely, *Escherichia coli* (MTCC 41), *Staphylococcus aureus* (MTCC 1144) and *Pseudomonas putida* (MTCC 1072) and are found to provide satisfactory comparable results.

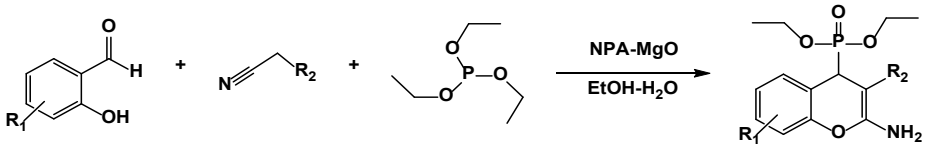
The synthesis of spirooxindole was reported in aqueous media using MgO NPS as a catalyst by Karmakar *et al.* [86]. In general reaction isatin, malononitrile, and cyclohexane-1,3-dione were reacted with MgO NPS in aqueous medium which yields spirooxindole as a product as show in Scheme 30.



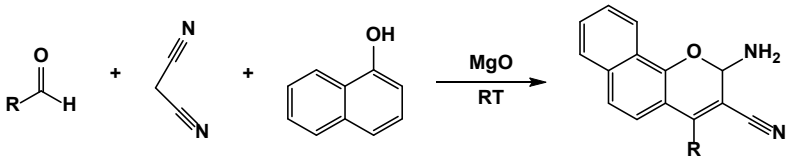
Scheme 23. Proposed mechanism for the preparation of MgO nano-powders.



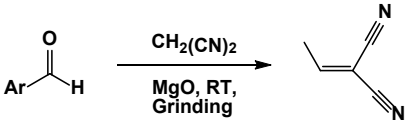
Scheme 24. Proposed mechanism for the preparation of thiochromeno[4,3-b]pyran derivatives.



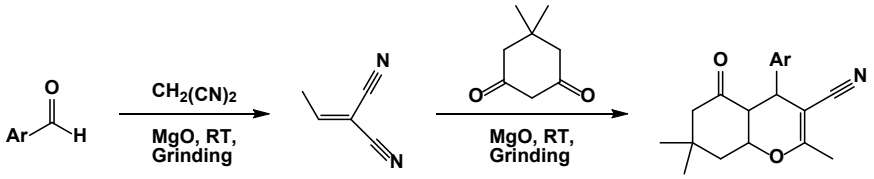
Scheme 25. Synthesis of (2-amino-3-cyano-4*H*-chromene-4-yl) phosphonic acid diethyl esters using MgO.



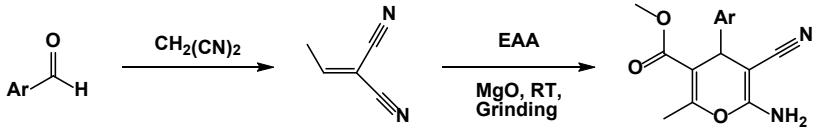
Scheme 26. Synthesis of substituted 2-amino-2-chromenes catalysed by MgO NPs.



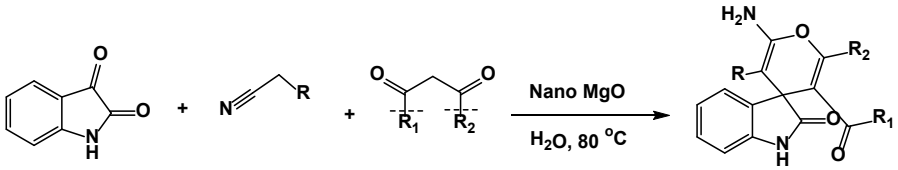
Scheme 27. Knoevenagel reaction catalysed by MgO NPs.



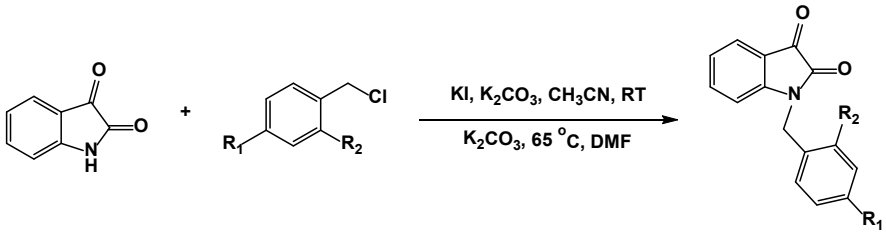
Scheme 28. Synthesis of 2-amino-4*H*-pyran using MgO NPs.



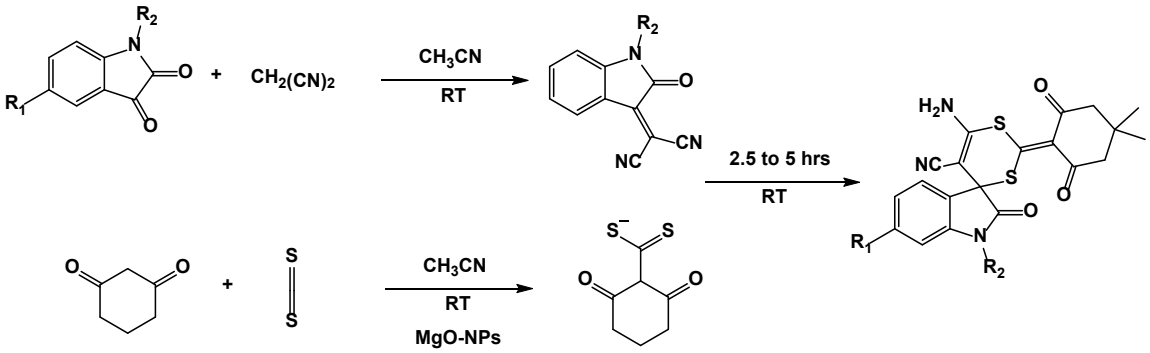
Scheme 29. Synthesis of tetrahydro-4*H*-chromenes using MgO NPs.



Scheme 30. Multicomponent synthesis of spirooxindoles using MgO NPs.



Scheme 31. Synthesis of 1-(aryl)indoline-2,3-dione.

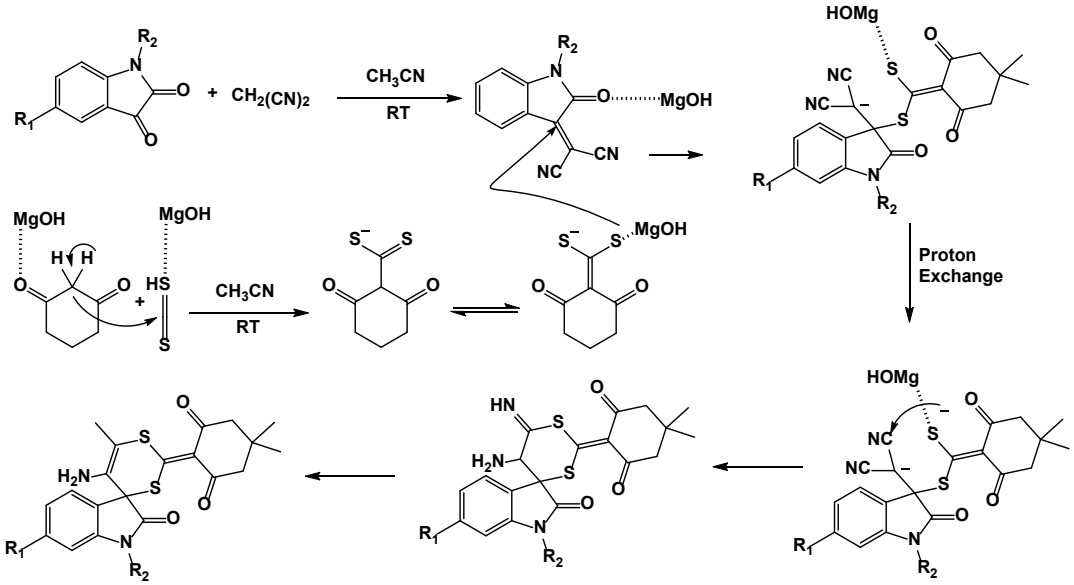


Scheme 32. Multicomponent synthesis of derivatives 6'-amino-2'-(4,4-dimethyl-2,6-dioxocyclohexylidene)-2-oxospiro[indoline-3,4'-[1,3]dithiine]-5'-carbonitrile using MgO NPs.

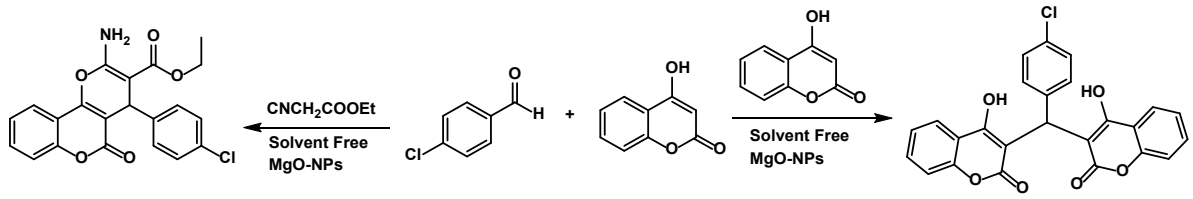
The reaction was carried out by changing the various bases, and the maximum yield was recorded with MgO NPS. The effect of temperature on reaction outcome was checked, which reveals that the reaction can proceed smoothly at 80 °C. The protocol employs green and ecofriendly water as a medium for the reaction and the catalyst recyclability was tested up to four runs, which provides good to excellent yields (83-93%). After successive cycles, the morphology of the catalyst was examined by analytical techniques such as SEM and XRD, which shows no appreciable change in morphology and claims the robust nature of catalyst.

Synthesis of derivatives of 1-(aryl)indoline-2,3-dione and various spiro compounds using MgO NPs as a catalyst was reported by Moghaddam-Manesh and group [87]. The model reaction schemes are as depicted in Schemes 31 and 32. Characterization of synthesized MgO NPs was done by electronic spectroscopy such as SEM and XRD techniques. The group also the proposed plausible mechanism for the synthesis of spiro compounds with MgO NPs as in Scheme 33. and further used for the synthesis of spiro compounds [87].

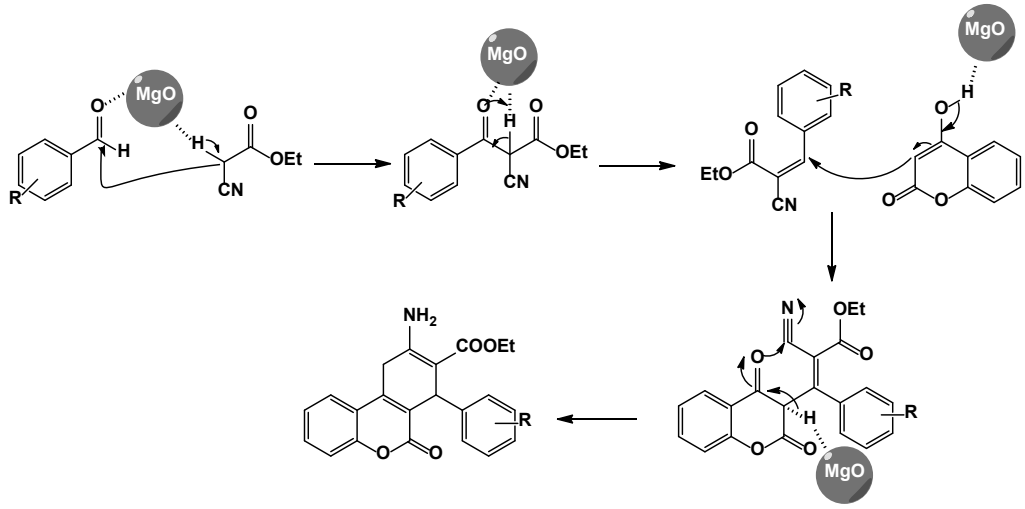
The structures of the synthesized organic compounds were confirmed by spectroscopic techniques such as ^{1}H NMR, ^{13}C NMR, FTIR, and elemental analysis. Antimicrobial evaluation of the synthesized compounds was tested such as antibacterial and antifungal activity against eight Gram-positive and Gram-negative bacteria, along with that antioxidant activity was also studied which shows average results when compared with standards.



Scheme 33. Plausible mechanism using MgO NPs.



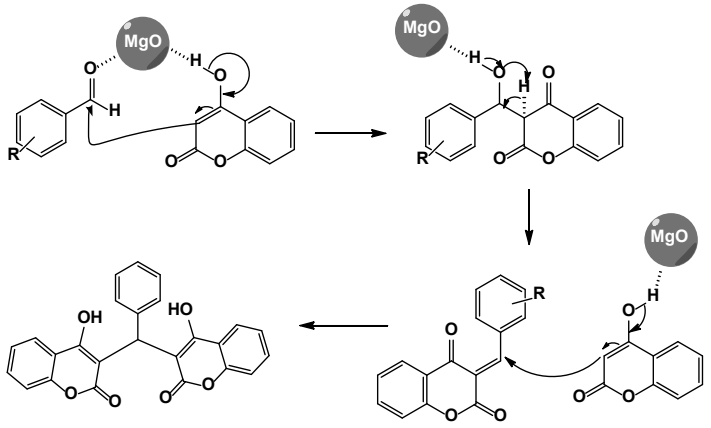
Scheme 34. Synthesis of dihydropyran[3, 2-c]chromene and biscoumarin derivatives using MgO NPs.



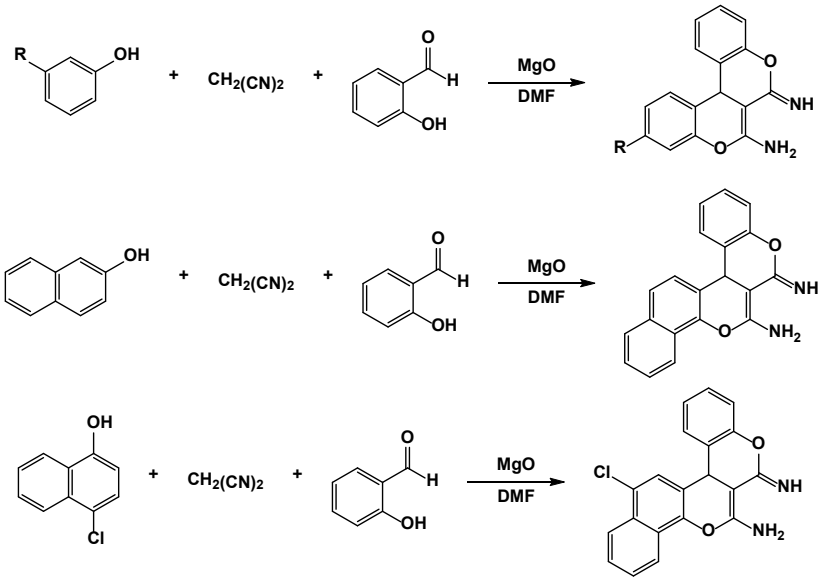
Scheme 35. The proposed mechanism for the synthesis of dihydropyrano[3,2-c]chromenes catalyzed by MgO NPs (Reproduced from ref. [88]).

Solvent-free Synthesis of dihydropyrano[3,2-c]chromene and biscoumarin derivatives using MgO NPs as a recyclable catalyst was reported by Safaei-Ghomi *et al.* (Scheme 34) [88]. The MgO NPs were synthesized using magnesium nitrate and PVP as surfactant exploring ultrasound technique and were characterized by SEM and XRD techniques. The possible mechanism is suggested for both reactions are shown in Schemes 35 and 36.

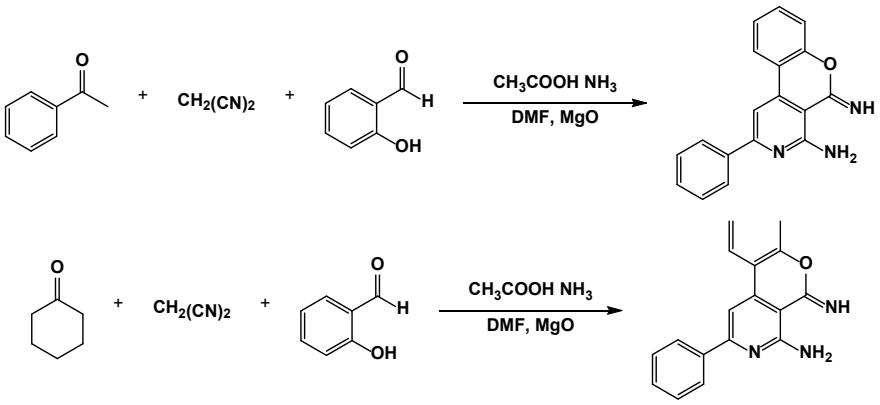
A convenient one-pot synthesis of new chromeno[3,4-c]chromene and chromeno[3,4-c]pyridine derivatives utilizing magnesium oxide was reported by Mohammadzadeh *et al.* (Schemes 37 and 38) [89]. The high surface MgO material were obtained by the rehydration of $Mg(OH)_2$. The calcination was carried out at different temperatures, MgO produced by calcination at 450 °C for 2 hrs shows good surface area. Further increase in calcination temperature was found to show a decline in surface area and activity. The reaction was carried out using commercial as well as synthesized MgO in DMF as the solvent. The effects of reaction parameters on reaction outcome were tested. It has been reported that the synthesized MgO having high surface area shows high yields (80-90%) compared to commercially available MgO (50-78%) [89].



Scheme 36. The proposed mechanism for the synthesis of biscoumarins catalyzed by MgO NPs (Reproduced from ref. [88]).



Scheme 37. Synthesis of chromeno[3,4-c]chromene using MgO NPs.

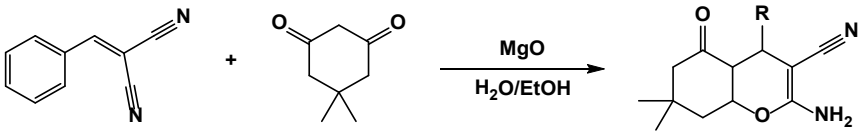


Scheme 38. Synthesis of chromeno[3,4-c]pyridine derivatives using MgO NPs.

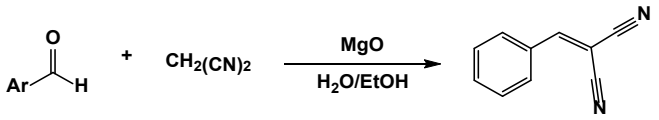
Synthesis of tetrahydrobenzopyran and 3,4-dihydropyrano [c]chromene derivatives in aqueous media was reported by Seifi *et al.* (Scheme 39) [90]. The MgO NPs prepared by the same procedure reported in [89]. The catalyst was also tested for Knoevenagel condensation reaction and found to provide excellent results (Scheme 40). All reactions were carried out in aqueous ethanol as a medium, and MgO NPs was found to provide good to excellent yields of the desired products at ambient conditions.

5.3.2. Synthesis of coumarins

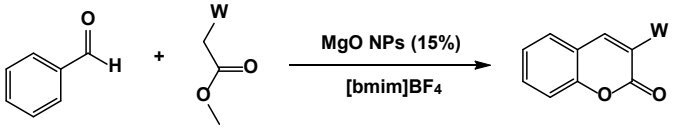
Coumarin and its derivatives are widespread and are essential organic compounds.



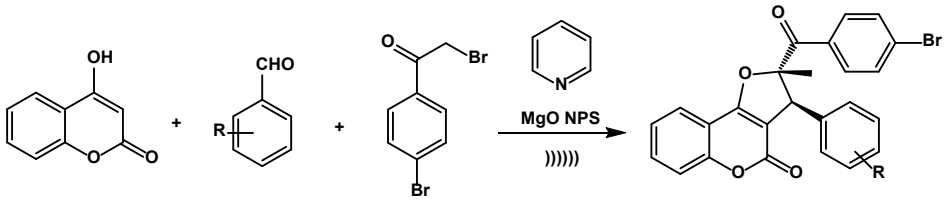
Scheme 39. Michael addition of (I) to dimedone catalysed by MgO NPs.



Scheme 40. MgO NPs catalysed Knoevenagel reaction.



Scheme 41. MgO nanoparticles catalysed solvent-free synthesis of coumarins. (W = CO_2Et, CO_2Me, CN).



Scheme 42. One-pot syntheses of furo[3,2-c] coumarins in the presence of MgO nanoparticles under sonication conditions.

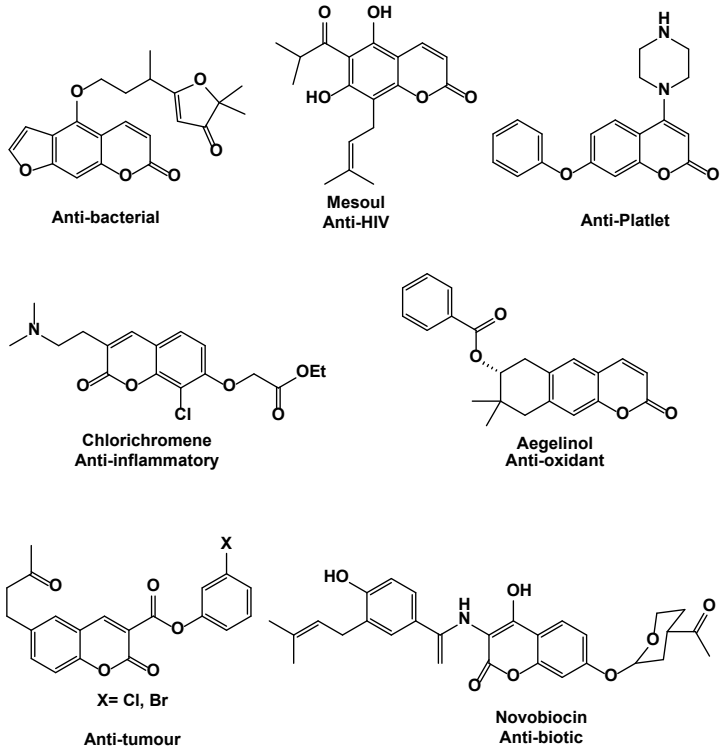
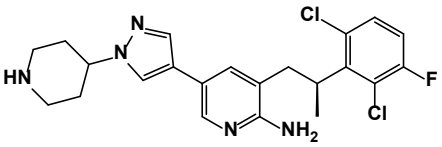
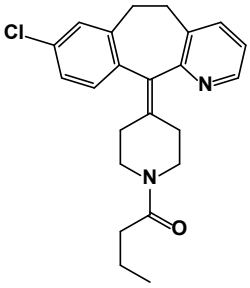


Figure 9. Biologically active coumarin containing drug molecules.

These compounds have attracted much attention due to their wide range of biological and pharmacological activities. Some biological properties such as molluscacidal, anthelmintic, and hypnotic activities and anticoagulant agents were reported for them (Figure 9). Coumarin derivatives also find applications in fragrance, agrochemical industries, food, cosmetics, optical brighteners, dispersed fluorescent, and laser dyes. Therefore, the synthesis of coumarins and their derivatives is of increasing interest.

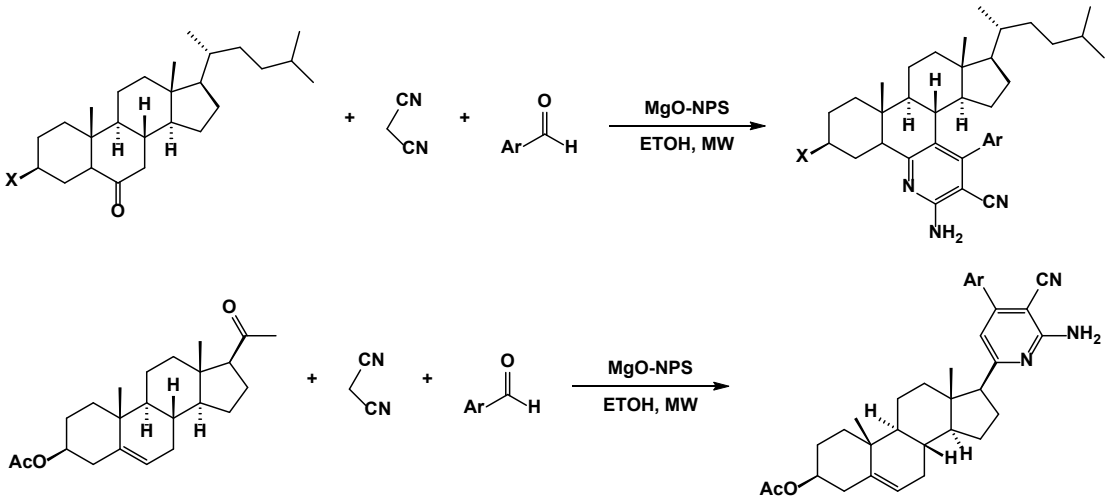


Crizotinib: treatment of lung cancer



Claritin: treatment of allergies

Figure 10. Biologically active molecules containing pyridine ring (Reproduced from ref. [93])



Scheme 43. Synthesis of steroidal pyridine derivatives using MgO NPs.

Several routes have been reported for the synthesis of coumarins such as Pechmann, Perkin, Knoevenagel, Reformatsky, and Wittig reactions.

Recently, coumarins are synthesized using NPs as the catalyst, the best-known basic NPs is MgO. Many authors reported the synthesis of coumarin derivatives using MgO NPs which were in turn are synthesized by different methods.

Dinparast and Valizadeh reported MgO nanoparticles as an efficient and eco-friendly catalyst for the rapid synthesis of coumarin derivatives in [bmim]BF_4 without use of solvent (Scheme 41). The salicylaldehyde was reacted with active methylene compound in the presence of MgO NPs as a catalyst in [bmim]BF_4 at solvent-free conditions to yield coumarin derivatives as a product. The MgO NPs were recovered, wash, dried, and further used for the second cycle, it was found that the yield of the product comparatively decreased from the first cycle [91].

Safaei-Ghomi *et al.* reported the diastereoselective synthesis of trans-2,3-dihydrofuro[3,2-c]coumarins by using MgO nanoparticles under ultrasonic irradiation (Scheme 42) [92]. The MgO NPs was synthesized by reported methods [88], elucidation of the structure was done by SEM and XRD techniques and later were used as a catalyst for aforesaid transformation. The analysis of the synthesized compounds was done by spectroscopic techniques.

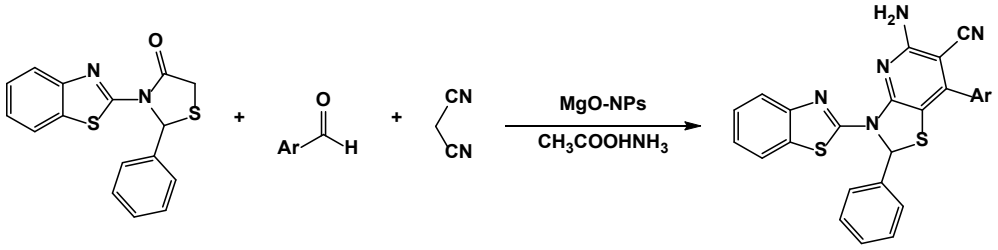
5.3.3. Synthesis of pyridines

Pyridines represent an important class of bioactive molecules and are particularly useful synthetic intermediates in the preparation of complex nitrogenous natural products and pharmaceutical targets (Figure 10) [93]. Pyridines have a widespread natural occurrence and are used to treat a broad spectrum of medical conditions, such as asthma, epilepsy, cancer and kidney diseases, etc. [93-95].

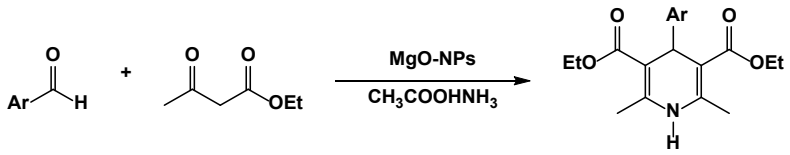
Ansari *et al.* synthesized the MgO nanoparticles using precipitation method and characterized with the help of analytical tools like XRD, SEM, FTIR, TGA/DTA, etc. The well-characterized MgO nanoparticles were later explored for the synthesis of a series of poly-substituted steroidal pyridines [94]. During the synthesis, steroidal carbonyl compounds were reacted with a substituted aromatic aldehyde, malononitrile, ammonium acetate (Scheme 43), and catalytic amount of MgO NPs. The authors tested the effect of various parameters on the reaction outcome, viz., effect of base, solvent, time, temp, etc., and the optimized conditions were used for the synthesis of a library of poly-substituted steroidal pyridines. The analysis of the product was done with the help of FTIR, NMR, and Mass techniques.

Similarly, Agarwal *et al.* reported the synthesis of poly-substituted pyridine using MgO NPs as catalyst [93]. The MgO NPs were synthesized using magnesium nitrate and characterization was done by FTIR, XRD, and TGA/ DTA methods. In the current article, the authors tried reaction in various organic solvents and the best results were obtained in DMSO, where 80% yield of the desired product was noted. The developed conditions were used for the synthesis of derivatives of poly-substituted pyridines. The recyclability and reusability of magnesium oxide NPs was studied, which shows a continuous decrease in yield of the product after successive runs, and it suggests that the efficiency of MgO NPs decreases with successive reactions (Scheme 44).

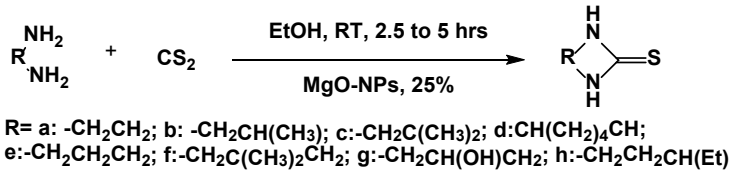
Hanztsch synthesis is one of the famous methods to obtain pyridine derivatives. Mirzaei *et al.* reported the Hanztsch synthesis of pyridine using MgO NPs [95].



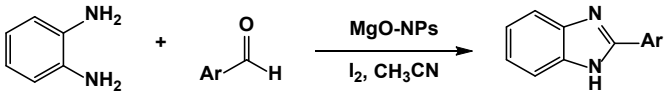
Scheme 44. Synthesis of 5-amino-3-benzothiazol-2-yl-7-(phenyl)-2-phenyl-2,3-dihydro-thiazolo[4,5-b]pyridine-6-carbonitrile derivatives using MgO NPs.



Scheme 45. Synthesis of Hantzsch 1,4-dihydropyridines catalysed by MgO NPs.



Scheme 46. Total synthesis of thiourea derivatives using MgO NPs.



Scheme 47. Synthesis of 2-substituted benzimidazoles from o-phenylenediamine and aryl aldehydes in the presence of nanocrystalline MgO/I_2 using MgO NPs.

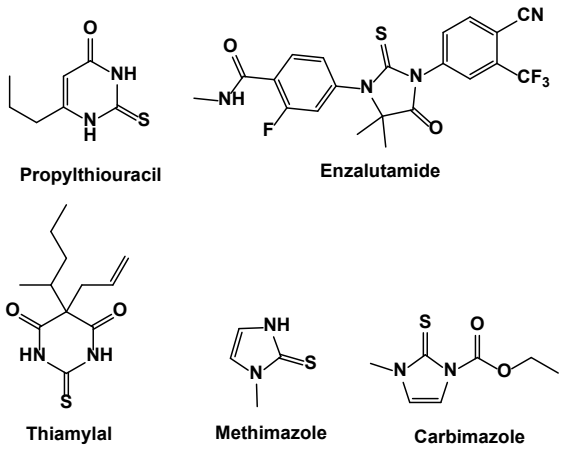


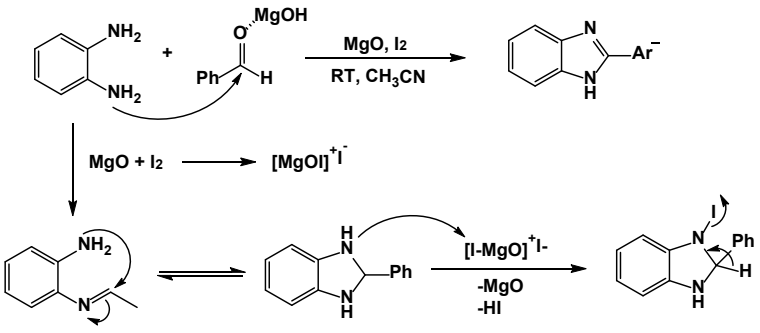
Figure 11. Some biologically active drugs with imidazolidine and tetrahydropyrimidine-2-thione skeletons.

The MgO NPs were synthesized by microwave assistance sol-gel method in which magnesium nitrate was used as the precursor and deionized water as solvent and calcination was done at 500 °C. The analysis of MgO NPs was done using BET surface area analyzer, XRD, SEM, TEM, and it was found that the synthesized MgO had a high specific surface area of 243.2 m^2/g and particle size ranges from 9.5 to 10.5 nm. The catalytic property of MgO NPs was studied against Hantzsch reaction in which aromatic aldehydes, active methylene group-containing compound, and ammonium acetate were reacted in the presence of catalytic amount of MgO NPs to yield 1,4-dihydropyridines as a product as shown in Scheme 45.

5.3.4. Synthesis of imidazoles

The imidazolidine- and tetrahydropyrimidine-2-thione derivatives show excellent medicinal properties such as antiviral, antitumor, anti-inflammatory, and analgesic activities, and some of the active molecules are shown in Figure 11. Application of NPs for the synthesis of such compounds is also noted in literature.

Beyzaei *et al.* reported the synthesis of cyclic thiourea using MgO NPs (Scheme 46), which can be used in the synthesis of imidazolidine and tetrahydropyrimidine-2-thione derivatives [96].



Scheme 48. Proposed mechanism for synthesis of 2-substituted benzimidazole derivatives using a nanocrystalline MgO system (Reproduced from ref. [97]).

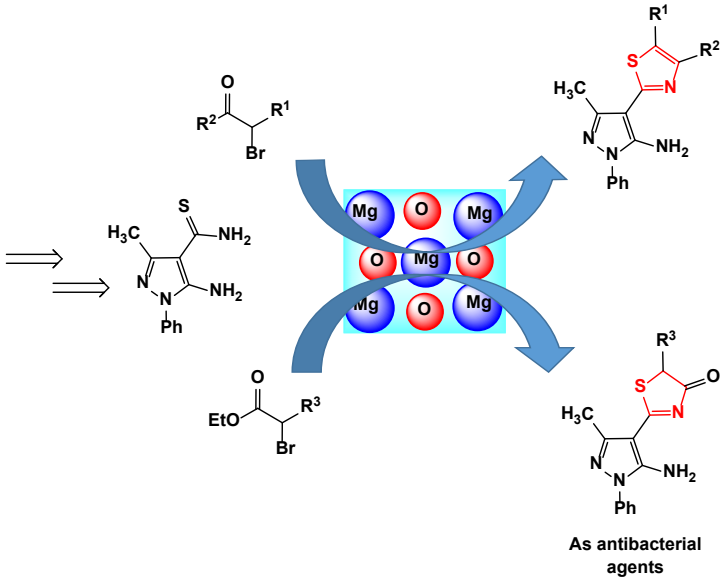


Figure 12. Hanztsch thiazole synthesis (Reproduced from ref. [98]).

The reaction was optimized at different amounts of catalyst and it was found that the higher % of yield was obtained at the maximum concentration of MgO NPs. Antibacterial activity of newly synthesized compounds was studied against 14 pathogenic bacteria including Gram-positive and Gram-negative strains.

An efficient single-step synthesis of 2-substituted benzimidazole derivatives by nanocrystalline MgO as a solid base catalyst and supported by iodine under acetonitrile solvent at room temperature has been reported by Naeimi *et al.* (Scheme 47) [97].

The MgO nanocrystals were synthesized using PVA (Polyvinyl alcohol), the characterization was done by XRD, SEM, TEM and used as a catalyst in the above said reaction. The reaction was tried in different solvents and different available MgO materials. The reaction was found to give the best result in acetonitrile (95% yield), also the catalytic activity of nanocrystalline MgO was found to be superior compared with commercial MgO [97]. The proposed mechanism for the reaction is as shown in Scheme 48.

5.3.5. Synthesis of thiazoles

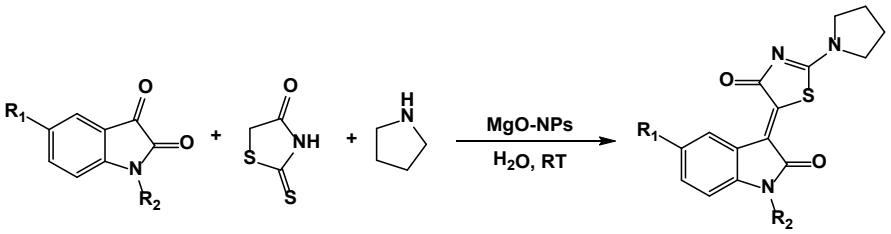
Thiazole moiety plays an important role in the construction of many drugs molecules such as antimicrobial acinitrazole, sulfathiazole, antibiotic penicillin, antidepressant pramipexole, antineoplastic agents bleomycin, tiazofurin, anti-HIV drug ritonavir, antiasthmatic drug cinalukast, antiulcer agent nizatidine contain thiazole ring. The synthesis of thiazole was reported by many researchers using different methods, nanoparticles are also studied for the synthesis of this type of materials, and here some such reports are discussed.

Beyzaeil *et al.* synthesized MgO NPs by wet chemical method in which starch and magnesium nitrate were used along with NaOH. The synthesized MgO nanoparticles were explored for the synthesis of novel 4-thiazolylpyrazoles by the modified Hantzsch method, under solvent-free conditions (Figure 12) [98].

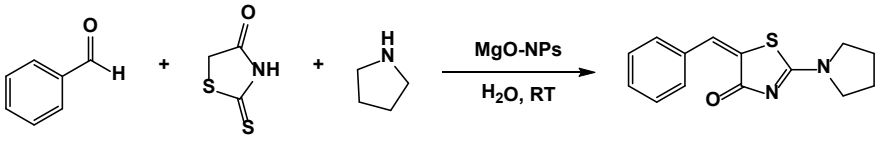
The authors reported good to excellent yields of the desired product under optimized conditions. The synthesized organic compounds were tested against 21 Gram-positive and -negative bacterial strains and the results were compared with standard antibiotic drugs like ceftriaxone and penicillin. Some of the synthesized compounds shows excellent activity against the pathogen tested.

Baharfar *et al.* reported an efficient one-pot synthesis of novel isatin-based 2-amino thiazol-4-one conjugates using MgO NPs as catalyst in aqueous media [99]. Thiazolidinone derivatives have been shown to exhibit a wide range of interesting biological activities such as antitumor, anticonvulsant, antibacterial, antiviral, cardiotonic, and antidiabetic properties (Scheme 49).

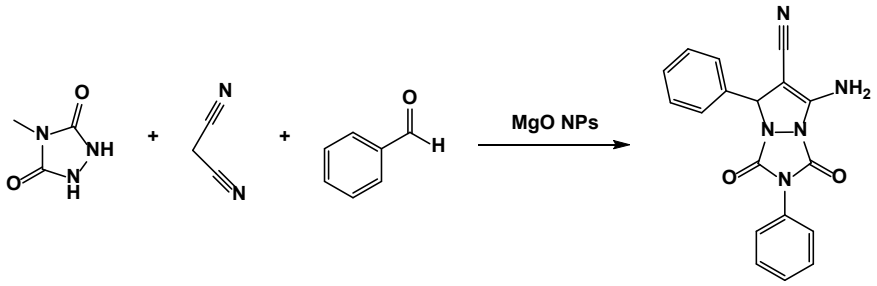
In the current investigation, the reaction was studied using various inorganic bases along with MgO NPs in different proportions and various amines are tried in aqueous medium at room temperature. The best results were obtained by using 0.3 (eq.) MgO NPs in water at room temperature.



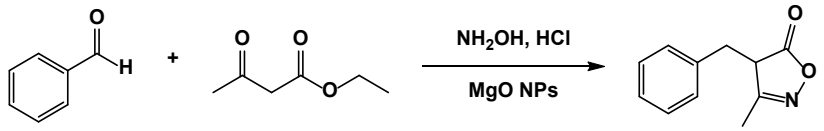
Scheme 49. Preparation of isatin-based 2-amino thiazol-4-one conjugates using MgO NPs.



Scheme 50. Preparation of 2-amino-5-arylidenethiazol- 4-ones using MgO NPs.



Scheme 51. Synthesis of pyrazolotriazoles.



Scheme 52. The reaction of the green synthesis of 3,4-disubstituted Isoxazole-5(4*H*)-ones using MgO NPs.

The characterization of the synthesized compounds was done with the help of analytical techniques such as IR and NMR, and also physical properties such as bond length of the synthesized compounds were calculated using ORTEP software. A similar reaction was reported and studied by the same author with aromatic aldehyde as one of the reactants [100], as shown in reaction Scheme 50.

5.3.6. Synthesis of pyrazoles

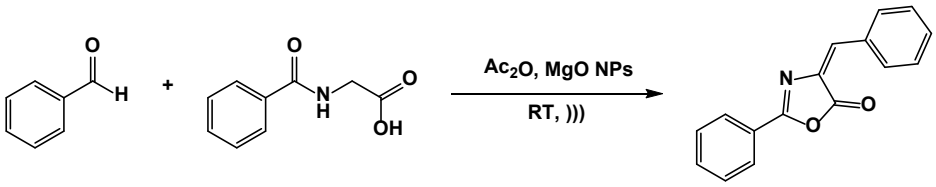
Pyrazole and its derivatives represent one of the most active class of compounds, which show a variety of biological activities like antibacterial, anti-convulsant, analgesic, anti-microbial, anti-inflammatory, anti-diabetic, sedative anti-rheumatic, anticancer, and anti-tubercular activities. Synthesis of pyrazoles was reported by various methods in which the use of metal NPs are among the best methods.

Naeimi *et al.* reported the one-pot synthesis of pyrazolotriazoles in the green medium using MgO NPs as a catalyst [101]. MgO NPs were prepared using a reported procedure and characterized by XRD and TEM techniques. In general, the aromatic aldehydes, 4-phenyl-1,2,4-triazolidine-3,5-dione, and malononitrile or alkyl cyanoacetates were reacted in one pot in presence of catalytic amount of nanocrystaline MgO material to produce the desired product. The reported protocol has some advantages like excellent yields of desired products, easy workup process, use of greener medium, and reusability of the catalyst (Scheme 51).

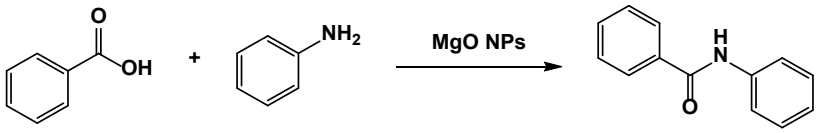
5.3.7. Synthesis of isoxazole

Isoxazole is a member of heterocyclic compounds, contains several biological activities such as antidiabetic, anti-fungal, and was used for different purposes, by understanding the utility of isoxazole many researchers interested in the green synthesis of it. Kiyani and Ghorbani reported the green synthesis of 3,4-disubstituted isoxazole-5(4*H*)-ones catalyzed by nano-MgO [102]. The MgO NPs were synthesized using precipitation and hydrothermal methods and characterizations were done by XRD and SEM techniques. The synthesis was attempted with various inorganic and organic bases and the best results were obtained with MgO NPs as catalyst (Scheme 52).

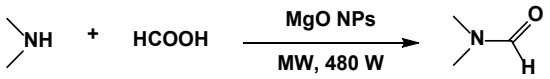
Similarly, Sadeq *et al.* reported one-pot synthesis of 4-arylmethylidene-2-phenyl-4*H*-oxazole-5-ones using nano-MgO as an efficient catalyst exploring ultrasonic waves (Scheme 53). Nano-MgO was prepared by the solution combustion technique, magnesium nitrate and amino acid were taken in petri dish and heated to get semisolid material which on calcination at 400 °C gave MgO NPs. The characterization was done with the help of XRD, SEM, and TEM. The well-characterized material was then used for the aforesaid reaction, which provided good to excellent yields of the desired product at room temperature under ultrasonic conditions [103].



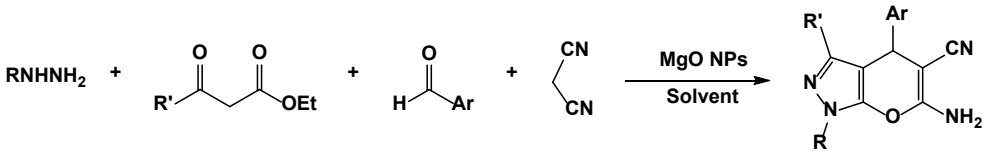
Scheme 53. Synthesis of 4-arylmethylidene-2-phenyl-4*H*-oxazole-5-ones using nano-MgO as catalyst under ultrasonic conditions.



Scheme 54. Synthesis of amides using MgO NPs.



Scheme 55. Formylation of amine using MgO NPs.



Scheme 56. Synthesis of pyranopyrazoles via a tandem four-component reaction using MgO NPs.

5.3.8. Synthesis of amides

Synthesis of amide was reported by Das *et al.* using MgO NPs under solvent-free conditions [104]. MgO NPs were prepared and analyzed by electronic microscopic techniques such as SEM and TEM, FTIR, EDX, and XRD were used for further analysis. The catalytic activity of MgO NPs was tested for amide synthesis as shown in Scheme 54.

The reaction of acid with amine was carried out with different solvents and under solvent-free conditions as well. The reaction was found to provide excellent yield under solvent-free conditions in just 10 minutes using MgO NPs as catalyst.

The formylation of amine was reported with the help of MgO-NPs by Bhanage *et al.* [105]. MgO NPs were prepared by microwave irradiation method and the characterization of MgO-NPs was done by FT-IR, XRD, SEM, TEM, and CO_2-TPD. In the present paper, the comparative catalytic study was done by taking commercial and synthesized MgO-NPs (Scheme 55). The developed conditions were used for the synthesis of a library of N-formylated products. The products were well characterized by analytical tools like FTIR, mass, and NMR.

5.4. Other reactions

Babaie and Sheibani reported a four-component reaction of involving hydrazine hydrate or phenyl hydrazine, ethyl 3-alkyl-3-oxo propanoate, aldehydes and malononitrile using MgO NPs as highly efficient catalyst to produced 6-amino-3-alkyl-4-aryl-5-cyano-1,4-dihydropyrano[2,3-c]pyrazole derivatives in good to excellent yields and in a short period of time (Scheme 56). The reaction was carried out in various solvents among which water and acetonitrile gave excellent yields of desired heterocycles within 10-20 minutes. The developed protocol was explored for the synthesis of number of derivatives [106].

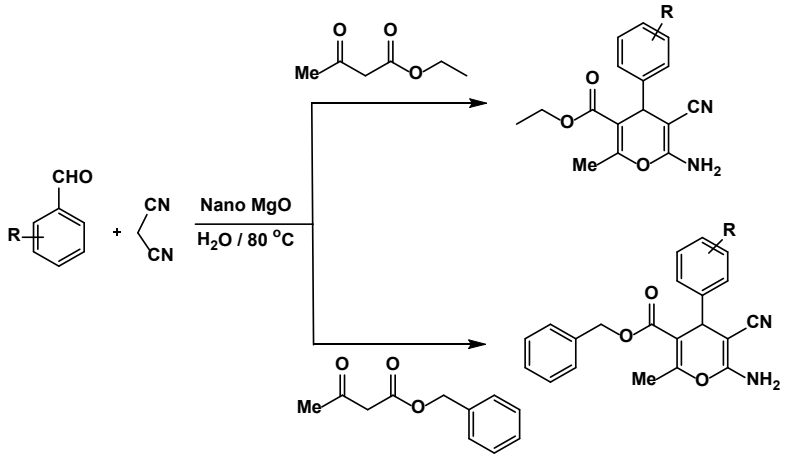
Sojoudi and Mokhtary one-pot synthesis of 6-amino-4-aryl-5-cyano-2-methyl-4*H*-pyran-3-carboxylates using MgO NPs as a catalyst in water as a solvent [107]. The MgO NPs are prepared by reported methods and are confirmed by analytical tool like XRD, TEM and BET analysis. The so prepared MgO NPs were utilized to carry out multicomponent reaction wherein aldehyde, malononitrile and ethyl acetoacetate or benzyl acetoacetate are allowed to react in water at 80 °C (Scheme 57). The protocol found to produce well to excellent yields of 6-amino-4-aryl-5-cyano-2-methyl-4*H*-pyran-3-carboxylates derivatives. The catalyst was found to be reusable up to 5 consecutive cycles without much loss in its activity.

Safaei-Ghomi *et al.* reported the one-pot synthesis of synthesis of 2,6-dicyanoanilines and 1,3-diarylpropyl malononitrile under different conditions using MgO nanoparticles as an efficient, green and reusable catalyst [108].

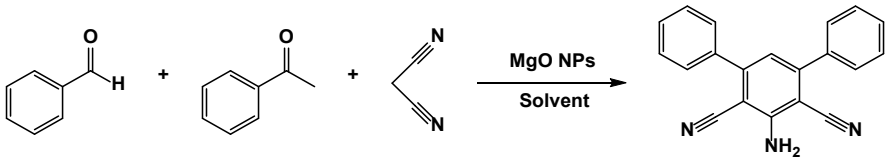
The MgO NPs material was obtained by using magnesium nitrate, the synthesized MgO NPs was characterized using electronic microscopy such SEM, and the nature of MgO NPs was found with help of XRD techniques. The catalytic activity was tested against organic transformation and found to be an active catalyst as shown in Scheme 58.

Benzylation of Aromatic Compounds with Different Crystallites of MgO NPs was reported by Choudary *et al.* (Scheme 59) [109]. The article reports the use of various MgO crystallites for the benzylation reaction. The commercial MgO (CM-MgO), MgO prepared using conventional method (CP-MgO (30)), aerogel prepared MgO having different surface area [AP-MgO (390) and AP-MgO (590)], silylated conventionally prepared and aerogel prepared MgO (Sil-CP-MgO and Sil-AP-MgO) particles are tested for the said reaction. Among the various tested materials CP-MgO (30) was found to be the most active.

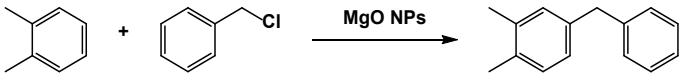
Another important application of MgO NPs was reported by Wang *et al.* The article reports the preparation of MgO nanosheets, nanodisks, and nanofibers using suitable surfactants. The synthesized materials were characterized using techniques like XRD, HRTEM, CO_2-TPD, FT-IR and XPS.



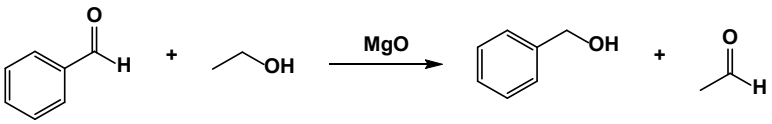
Scheme 57. Synthesis of 6-amino-4-aryl-5-cyano-2-methyl-4H-pyran-3-carboxylates catalyzed by nano MgO in water



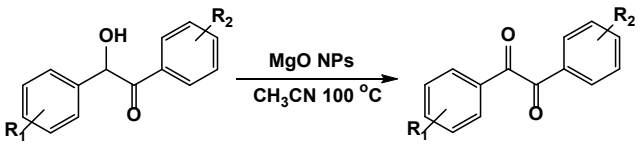
Scheme 58. The three-component reaction of aldehydes, acetophenone, and malononitrile catalysed by MgO NPs.



Scheme 59. Benzylation of aromatic compounds using MgO NPs.



Scheme 60. Meerwein-Ponndorf-Verley reaction.



Scheme 61. Oxidation of benzoin derivatives to benzil derivatives using nanocrystalline MgO.

The MgO nanosheets, nanodisks, and nanofibers are then used for the Meerwein-Ponndorf-Verley reaction (Scheme 60) [110]. The MgO nanosheets and nanodisks shows higher activity over MgO nanofibres.

Zarnegar *et al.* reported the green synthesis of benzil using MgO NPs as shown in Scheme 61 [111]. The MgO NPs are synthesized using a previously reported method using magnesium nitrate as a precursor in polyvinyl alcohol (PVA) and water. The synthesized MgO NPs were then used for the oxidation of benzoins to benzils. The reactions were carried out at 100 °C using just 2 mol% of catalyst which provided the desired products. The catalyst was reused for five runs which shows the drop-in yield of the product from 98 to 85 %.

6. Conclusion

Over the past decades, researchers have concentrated on the synthesis and development of shape and size-selective nanocrystals. Several scientists have made attempts towards the fabrication of MgO NPs, but few of them accomplished size and shape-controlled NPs. In this review, we firstly summarized the current advances in protocols for the synthesis of MgO NPs, including chemical, physical and biological synthesis routes and their diverse properties/features. Then we discussed the characterization of MgO NPs by different known techniques. Finally, we have discussed several MgO NPs catalyzed organic transformations such as epoxidation, condensation, and C-C, C-N, C-O, C-S bond formation in a variety of notable heterocyclic reactions.

Notably, the catalysis using MgO NPs does not necessitate any ligand precursor, but the low catalyst loading at low temperature, mild reaction conditions, and easy separation of the catalyst with recyclability makes it attractive.

Although there have been important developments in the preparation of MgO NPs in terms of the diversity of structures that can be obtained, the reactions they can undergo, and the selectivity they can achieve, many challenges remain to be explored. In particular, a systematic investigation on the

recyclability of MgO NPs needs to be study. As the reactions are carried out at moderate to high temperatures, a study on leaching of metals must also be considered. Investigation on the doping of MgO with some other metals and its consequences on catalytic action must also be explored. Catalytic application of MgO NPs for organic transformations on a bulk scale must also need to be done.

Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest.
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