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Development and functionalization of magnetic nanoparticles as powerful and green catalysts for organic synthesis

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ABSTRACT

Magnetic nanoparticles are a highly worthy reactant for the correlation of homogeneous inorganic and organic containing catalysts. This review deals with the very recent main advances in the development of various nano catalytic systems by the immobilization of homogeneous catalysts onto magnetic nanoparticles. Catalytic fields include the use of mainly cobalt, nickel, copper, and zinc ferrites, as well as their mixed-metal combinations with Cr, Cd, Mn and sometimes some lanthanides. The ferrite nanomaterials are obtained mainly by co-precipitation and hydrothermal methods, sometimes by the sonochemical technique, micro emulsion and flame spray synthesis route. Catalytic processes with application of ferrite nanoparticles include degradation (in particular photocatalytic), reactions of dehydrogenation, oxidation, alkylation, C–C coupling, among other processes. Ferrite nano catalysts can be easily recovered from reaction systems and reused up to several runs almost without loss of catalytic activity. Finally, we draw conclusions and present a futurity outlook for the further development of new catalytic systems which are immobilized onto magnetic nanoparticles.
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Contents

Abbreviations: MNPs, magnetic nano particles; UV-Vis, ultraviolet-visible; FT-IR, Fourier transform infrared spectroscopy; TGA, thermogravimetric analysis; XRF, X-ray fluorescence; XRD, X-ray diffraction; EDX, energy-dispersive X-ray; SEM, scanning electron microscopy; TEM, transmittance electron microscopy; TBHP, tert-butylhydroperoxide; VSM, vibration sample magnetometer; ASS, atomic absorption spectroscopy; BET, Brunauer-Emmett-Teller; MMSNs, magnetic mesoporous silica nanoparticles; ^{1}H NMR, proton nuclear magnetic resonance; ^{13}C NMR, carbon^{13} nuclear magnetic resonance; RSM, response surface methodology; HR-TEM, high resolution transmittance electron microscopy; IC, ion chromatography; ROP, ring opening polymerization.

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1. Introduction

Green Chemistry is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical product. This encouraged the scientific community to look for efficient ways to separate homogenous catalysts from the reaction media and their subsequent recycling. The use of magnetic nanoparticles (MNPs) as efficient supports for catalysts has become a subject of intense investigation. Magnetic nanoparticles are a class of nanoparticle that can be manipulated using magnetic fields. Such particles commonly contains two components, a magnetic material, often iron, nickel and cobalt, and a chemical component that has functionality. While nanoparticles are smaller than 1 μm in diameter (typically 5–500 nm), the larger micro beads are 0.5–500 μm in diameter. Magnetic nanoparticle groups that are composed of a number of single magnetic nanoparticles are known as magnetic nanobeads with a diameter of 50–200 nm. Magnetic nanoparticle clusters are a basis for their further magnetic assembly into magnetic nanochains (Tadic et al., 2014; Kralj and Makovec, 2015). The magnetic nanoparticles have been attention of much seek recently because they have attractive properties which could see potential use in catalysis including nanomaterial-based catalysts, biomedicine and tissue specific targeting, magnetically tunable colloidal photonic crystals, microfluidics, magnetic resonance imaging, magnetic particle imaging, data storage, environmental remediation, nanofluids, and optical filters, defect sensor and cation sensors (Abu-Dief and Hamdan, 2016; Abu-Dief et al., 2016a,b; Ibrahim et al., 2017).

This is because MNPs can be well dispersed in reaction mixtures without a magnetic field, providing a large surface area that is readily accessible to substrate molecules. Moreover, after completing the reactions, the MNP-supported catalysts can be isolated efficiently from the product solution through simple magnetic separation, eliminating the need for catalyst filtration and centrifugation. Moreover, they can be reused up to several runs almost without loss of catalytic activity (El-Remaily and Abu-Dief, 2015; Abu-Dief et al., 2016a; Marzouk et al., 2017). Catalysts play a very important role in modern science and technology as they improve reaction yields, reduce temperatures of chemical processes and promote specific enantio selectivity in asymmetric synthesis. There are two main kinds of catalysis, heterogeneous, where the catalyst is in the solid phase with the reaction occurring on the surface and homogeneous, where the catalyst is in the same phase as the reactants (Abdel-Rahman et al., 2016a; Abu-Dief and Mohamed, 2017). Both processes have their benefits. For example heterogeneous catalysts can be readily separated from the reaction mixture but the reaction rate is restricted due to their limited surface area. Meanwhile homogeneous catalysts can react very fast and give a good diversion rate per molecule of the catalyst, but since they are miscible in the reaction medium, it can be a painstaking process to remove them from the reaction medium (Lu et al., 2004; Gupta and Gupta, 2005; Ramaswamy et al., 2015; He et al., 2012; Kavre et al., 2014; Mornet et al., 2006; Gleich and Weizenecker, 2005). The difficulty in removing homogenous catalysts from the reaction medium leads to problems in retaining the catalyst for reuse. The separation and recycling of the catalyst is highly suitable since catalysts are often very expensive. The bridge between heterogeneous and homogeneous catalysts can be achieved through the use of nanoparticles. Nanoparticles of catalytic material provide the benefit of increased surface area which allows for an increased reaction rate. When well dispersed, the nano particulate catalyst forms a stable suspension in the reaction medium allowing an elevated rate of reaction. In addition, nanoparticles can allow additional catalytic missions due to their single properties, for example titania nanoparticles exhibit photo oxidation on their surfaces while other nanoparticles can utilize light energy as a result of their photo physical properties (Hyeon, 2003; Natalie and Shouheng, 2014; Elliott and Zhan, 2001; Philip et al., 2006; Philip et al., 2003; Mahendran., 2012; Philip and Felicia, 2013). The physical and chemical properties of magnetic nanoparticles largely depend on the synthesis method and chemical structure. In most cases, the particles range from 1 to 100 nm in size and may show superparamagnetism (Lu et al., 2007).

2. Types of magnetic nanoparticles

2.1. Oxides: Ferrites

Ferrite nanoparticles or iron oxide nanoparticles (iron oxides in crystal structure of maghemite or magnetite) are the most explored magnetic nanoparticles up to date. Once the ferrite particles become smaller than 128 nm they turned into superparamagnetic which prevents self agglomeration since they exhibit their magnetic behavior only when an external magnetic field is applied. The magnetic moment of ferrite nanoparticles can be greatly increased by controlled clustering of a number of individual superparamagnetic nanoparticles into superparamagnetic nanoparticle clusters, namely magnetic nanobeads. With the external magnetic field turned off, the remanence falls back to zero. Just like non-magnetic oxide nanoparticles, the face of ferrite nanoparticles is often modified by surfactants, silica, silicones or phosphoric acid derivatives to increase their stability in solution (Kim and Mikhaylova, 2003).

2.2. Ferrites with a shell

The surface of a maghemite or magnetite magnetic nanoparticle is relatively inert and does not usually allow strong covalent bonds with functionalization molecules. However, the reactivity of the magnetic nanoparticles can be improved by coating a layer of silica onto their surface. The silica shell can be easily modified with different surface functional groups via covalent bonds between organo-silane molecules and silica shell. In addition, some fluorescent dye molecules can be covalently bonded to the functionalized silica shell as shown in Fig. 1. Ferrite nanoparticle clusters with narrow size distribution consisting of superparamagnetic oxide nanoparticles (~80 maghemite superparamagnetic nanoparticles per bead) coated with a silica shell have several advantages over metallic nanoparticles (Kralj et al., 2010a, 2010b; Kralj et al., 2012):

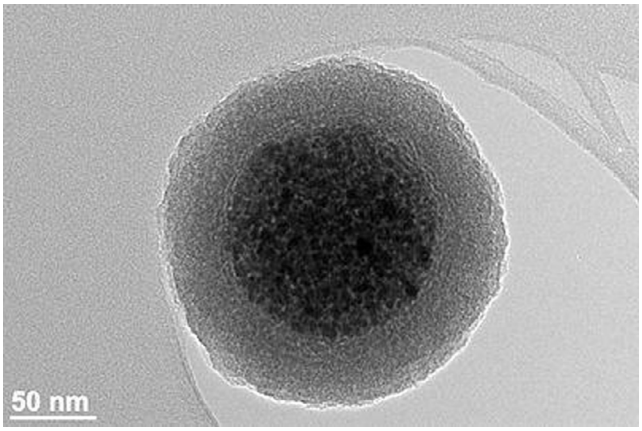


Fig. 1. TEM image of a maghemite magnetic nanoparticle cluster with silica shell.

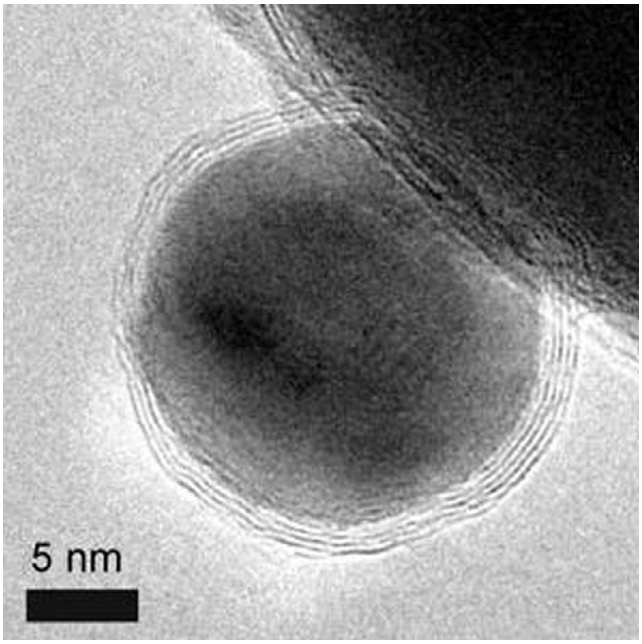


Fig. 2. Cobalt nanoparticle with graphene shell (note: The individual graphene layers are visible).

- Higher chemical stability (crucial for biomedical applications)
- Narrow size distribution (crucial for biomedical applications)
- Higher colloidal stability since they do not magnetically agglomerate
- Magnetic moment can be tuned with the nanoparticle cluster size
- Retained superparamagnetic properties (independent of the nanoparticle cluster size)
- Silica surface enables straightforward covalent functionalization

2.3. Metallic

Metallic nanoparticles may be useful for some technical applications due to their higher magnetic moment whereas oxides (maghemite, magnetite) would be beneficial for biomedical applications. This also implies that for the same moment, metallic nanoparticles can be made smaller than their oxide counterparts. On the other hand, metallic nanoparticles have the great abuse of being pyrophoric and reactive to oxidizing agents to various degrees. This makes their handling difficult and enables unwanted side reactions which makes them less appropriate for biomedical applications. Colloid formation for metallic particles is also much more challenging (Grass et al., 2007).

2.4. Metallic with a shell

The metallic core of magnetic nanoparticles may be passivated by gentle oxidation, surfactants, polymers and precious metals. In an oxygen environment, Co nanoparticles form an antiferromagnetic CoO layer on the surface of the Co nanoparticle. Recently, work has explored the synthesis and exchange bias effect in these Co core CoO shell nanoparticles with a gold outer shell as shown in Fig. 2. Nanoparticles with a magnetic core composed either of elementary Iron or Cobalt with a nonreactive shell made of graphene have been synthesized recently. The advantages compared to ferrite or elemental nanoparticles are (Johnson et al., 2010; Grass et al., 2006):

- Higher magnetization
- Higher stability in acidic and basic solution as well as organic solvents
- Chemistry on the graphene surface via methods already known for carbon nanotubes

3. Preparation of magnetic nanoparticles

3.1. Co-precipitation

Co-precipitation is an easy and convenient way to synthesize iron oxides (either Fe_3O_4 or γ-Fe_2O_3) from aqueous Fe^{2+}/Fe^{3+} salt solutions by the addition of a base under inert atmosphere at room temperature or at elevated temperature. The size, shape, and composition of the magnetic nanoparticles very much depends on the type of salts used (e.g. Chlorides, sulfates, nitrates), the Fe^{2+}/Fe^{3+}-ratio, the reaction temperature, the pH value and ionic strength of the media, and the mixing rate with the base solution used to provoke the precipitation (Fang et al., 2011; Gnanaprakash et al., 2006; Gnanaprakash et al., 2007; Ayyappan et al., 2009). The co-precipitation approach has been used extensively to produce ferrite nanoparticles of controlled sizes and magnetic properties. A variety of experimental arrangements have been reported to facilitate continuous and large–scale co–precipitation of magnetic particles by rapid mixing. Recently, the growth rate of the magnetic nanoparticles was evaluated in real-time during the precipitation of magnetite nanoparticles by an integrated AC magnetic susceptometer within the mixing zone of the reactants (Ayyappan et al., 2010; Chin et al., 2008; Ström et al., 2010).

3.2. Thermal decomposition

Magnetic nanocrystals with smaller size can essentially be synthesized through the thermal decomposition of alkaline organometallic compounds in high-boiling organic solvents containing stabilizing surfactants (Lu et al., 2007).

3.3. Microemulsion

Utilizing the microemulsion method, metallic cobalt, cobalt/-platinum alloys, and gold-coated cobalt/platinum nanoparticles have been synthesized in reverse micelles of cetyltrimethlyammonium bromide, using 1-butanol as the cosurfactant and octane as the oil phase (Rana et al., 2010).

3.4. Flame spray synthesis

Using flame spray pyrolysis and varying the reaction conditions, oxides, metal or carbon coated nanoparticles are produced at a rate of >30 g/h (Athanassiou et al., 2010) as shown in Fig. 3.

3.5. Hydrothermal synthesis

Another important chemical synthesis technique that involves the use of liquid–solid–solution (LSS) reaction and gives excellent control over the size and shape of the magnetic nano particles is the hydrothermal synthesis. This method involves the synthesis of magnetic nano particles from high boiling point aqueous solution at high vapor pressure (Abu-Dief and Hamdan, 2016; Abu-Dief et al., 2016a,b; Abu-Dief and Mohamed, 2017).

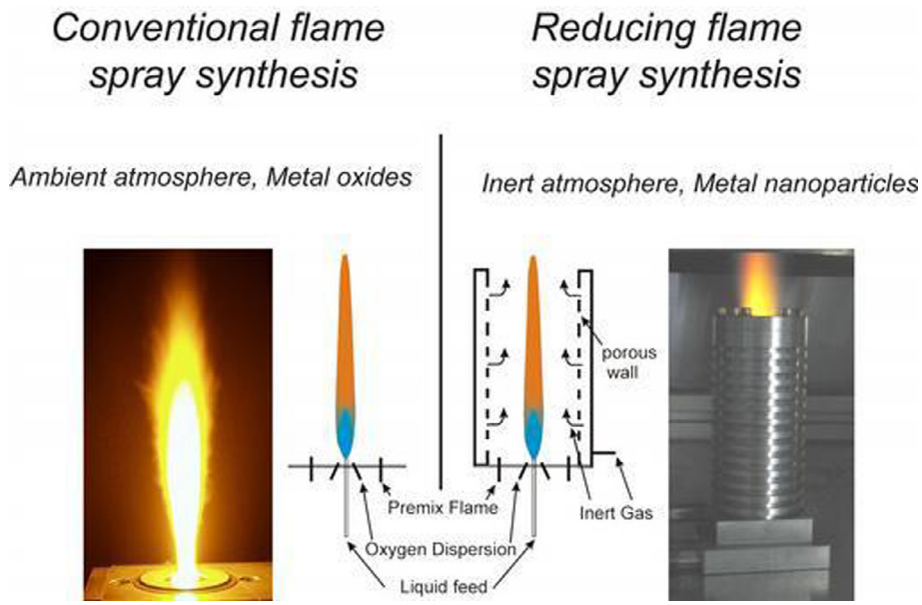


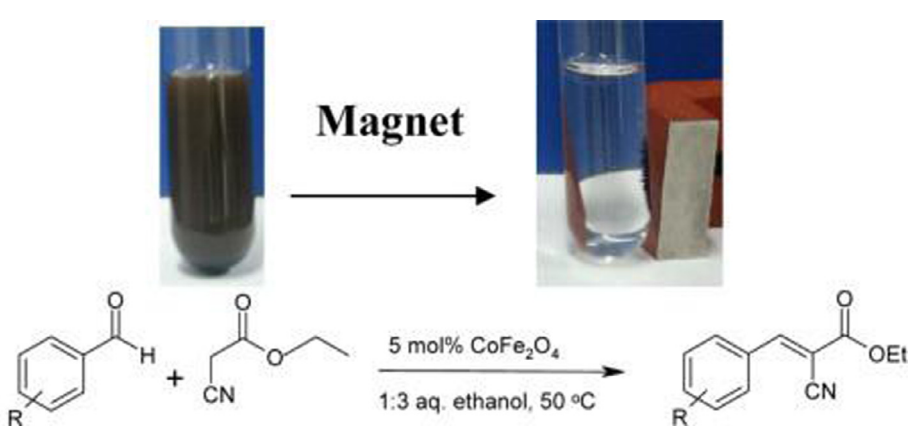
Fig. 3. Flame spray synthesis.

4. Importance of magnetic nanoparticles as catalyst in organic synthesis

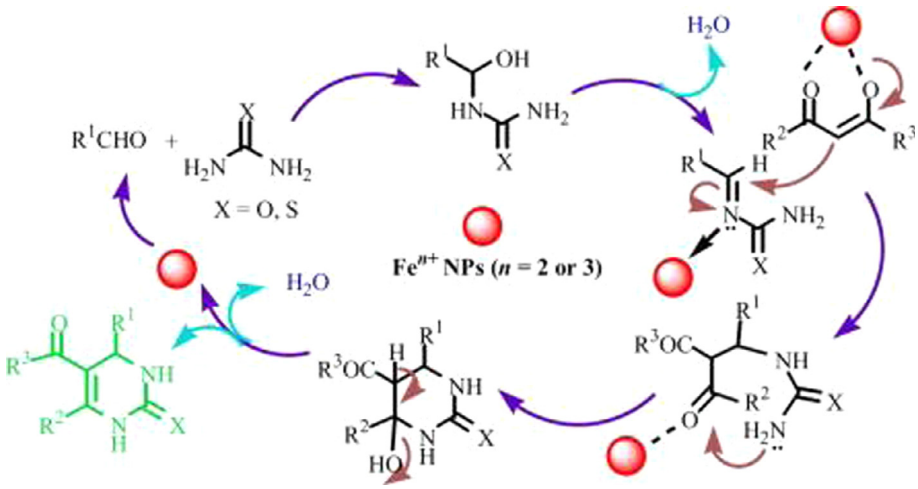
Magnetic nanoparticles are of potential use as a catalyst or catalyst supports (Schätz et al., 2010; Yoon et al., 2003; Rabias et al., 2010; Kumar and Mohammad, 2011; Kralj et al., 2013; Willhelm et al., 2016; Scarberry et al., 2008; Parera et al., 2010). In chemistry, a catalyst support is the material, usually a solid with a high surface area, to which a catalyst is affixed (Abdel-Rahman et al., 2015a,b; Abdel-Rahman et al., 2016b,c,d; Abu-Dief and Mohamed, 2017). The reactivity of heterogeneous catalysts takes place at the surface atoms. Consequently, great effort is made to maximize the surface area of a catalyst by distributing it over the support. The support may be inert or share in the catalytic reactions. Typical supports include various kinds of carbon, alumina, and silica. Immobilizing the catalytic pivot on top of nanoparticles with a large surface to volume ratio addresses this problem. In the case of magnetic nanoparticles it adds the property of facile a separation. An early example involved a rhodium catalysis attached to magnetic nanoparticles (Koehler et al., 2009; Yang et al., 2004; Norén and Kempe, 2009; Gupta and Gupta, 2005).

It is found *candida rugosa* lipase was immobilized on magnetic nanoparticles supported ionic liquids having different cation chain length (C_1, C_4 and C_8) and anions (Cl^-, BF_4^- and PF_6^-). Magnetic nanoparticles supported ionic liquids were obtained by covalent bonding of ionic liquids–silane on magnetic silica nanoparticles. The particles are superparamagnetic with diameter of about 55 nm. Large amount of lipase (63.89 mg/(100 mg carrier)) was loaded on the support through ionic adsorption. Activity of the immobilized lipase was examined by the catalysis of esterification between oleic acid and butanol. The activity of bound lipase was 118.3% compared to that of the native lipase. Immobilized lipase maintained 60% of its initial activity even when the temperature was up to 80 °C. In addition, immobilized lipase retained 60% of its initial activity after 8 repeated batches reaction, while no activity was detected after 6 cycles for the free enzyme nanoparticles (Jiang et al., 2009).

Spin coating colloidal solutions of mono disperse nanoparticles onto flat silica supports offers a facile and flexible way to produce model catalysts with well defined catalyst loading and particle size. By spincoating iron oxide (magnetite) nanoparticles with varying particle diameter we produce a model system for iron based Fischer–Tropsch catalysts. In this proof of principle study we employ a combination of surface spectroscopy (XPS) and transmission electron microscopy (TEM) to investigate the changes in surface chemistry and morphology of the model catalysts upon



Scheme 1. Cobalt ferrite magnetic nanoparticles as catalyst for Knoevenagel reaction.



Scheme 2. The catalytic activity of Fe_3O_4 nanoparticles in a one-pot three component condensation reaction.

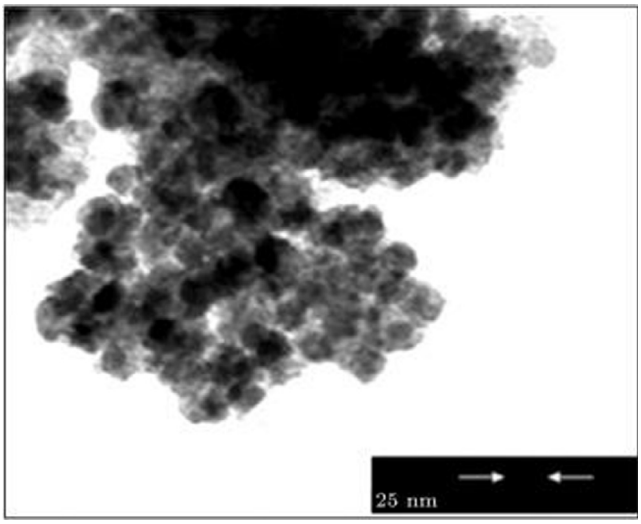


Fig. 4. TEM image of $CoFe_2O_4$ nanoparticles.

catalyst pretreatment and exposure to syngas (Moodley et al., 2010).

Preparation spinel cobalt ferrite magnetic nanoparticles (MNPs) with average sizes in the range 40–50 nm has been achieved using a combined sonochemical and co-precipitation technique in aqueous medium without any surfactant or organic capping agent. The nanoparticules form stable dispersions in aqueous or alcoholic medium. The uncapped nanoparticles were utilized directly as a reusable catalyst for Knoevenagel reaction in aqueous ethanol (1:3). Compartmentation and recovery of the catalyst from reaction medium was done with the aid of an external magnet as shown in Scheme 1. High yield of corresponding Knoevenagel products were obtained within a very short time in presence of just 5 mol% of the catalyst at 50 °C (Senapati et al., 2011).

The catalytic activity of Fe_3O_4 nanoparticles (NPs) in a one-pot three component condensation reaction consisting of an aromatic aldehyde, urea or thiourea, and a β-dicarbonyl under solvent-free conditions was investigated. This reaction affords the corresponding dihydropyrimidinones (thiones) in high to excellent yields as shown in Scheme 2. Compared with the classical Biginelli reactions this method consistently gives a high yield, easy magnetic separation, a short reaction time, and catalyst reusability (Esfahani et al., 2011).

Cobalt ferrite magnetic nanoparticles with mean sizes of 25 nm as a catalyst for the oxidation of various alkenes in the presence of *tert* – butylhydroperoxide (t-BuOOH) was prepared. This study has demonstrated that $CoFe_2O_4$ nanoparticles can act as an efficient catalyst for the conversion of alkenes to the related aldehydes or epoxides, with almost quantitative yields. The catalyst can be readily isolated by using an external magnet and no obvious loss of activity was observed when the catalyst was reused in five consecutive runs. The effects of some parameters, such as temperature, types of oxidant and solvents, on the oxidation reactions were also investigated as shown in Fig. 4. The results showed that when $CoFe_2O_4$ is used with t-BuOOH as oxidant for the oxidation of some alkenes, better results are obtained compared to most of the studied similar ferrites (Kooti and Afshari, 2012).

Pd nanoparticle supported on cobalt ferrite magnetic nanoparticles has been achieved by direct addition of Pd nanoparticles during synthesis of cobalt ferrite nanoparticles by ultrasound assisted co-precipitation in the absence of any surface stabilizers or capping agent. The catalytic performance of the Pd incorporated cobalt ferrite nanoparticles was examined in Suzuki coupling reaction in ethanol under ligand free condition as shown in Scheme 3. The reaction undergoes with low catalyst loading (1.6 mol%) and the catalyst could be recovered using an external magnet and reused for multiple cycles with sustained catalytic activity (Senapati et al., 2012).

A facile and rapid method for the one-pot synthesis of 5,5-disubstituted hydantoins in the presence of magnetic Fe_3O_4 nanoparticles has been developed. The multicomponent reactions of carbonyl compounds (aldehydes and ketones), potassium cyanide and ammonium carbonate were carried out under solvent-free conditions to obtain various hydantoin derivatives. The magnetic catalyst could be readily separated by an external magnet from the reaction mixture as shown in Fig. 5. This procedure has many advantages, such as the use of a reusable magnetic catalyst, high yields, short reaction times, simplicity and very easiness with implementing the methodology (Safari and Javadian, 2013).

Magnetic zinc ferrite ($ZnFe_2O_4$) nanoparticle and its photocatalytic dye degradation ability from colored wastewater was studied. Reactive Red 198 (RR198) and Reactive Red 120 (RR120) were used as model dyes. The characteristics of $ZnFe_2O_4$ were investigated using Fourier transform infrared (FT-IR), X-ray diffraction (XRD) and scanning electron microscope (SEM). Photocatalytic dye degradation by $ZnFe_2O_4$ was studied by UV–vis spectrophotometer and ion chromatography (IC). The effects of $ZnFe_2O_4$ -

Scheme 3. The catalytic performance of the Pd incorporated cobalt ferrite nanoparticles in Suzuki coupling reaction.

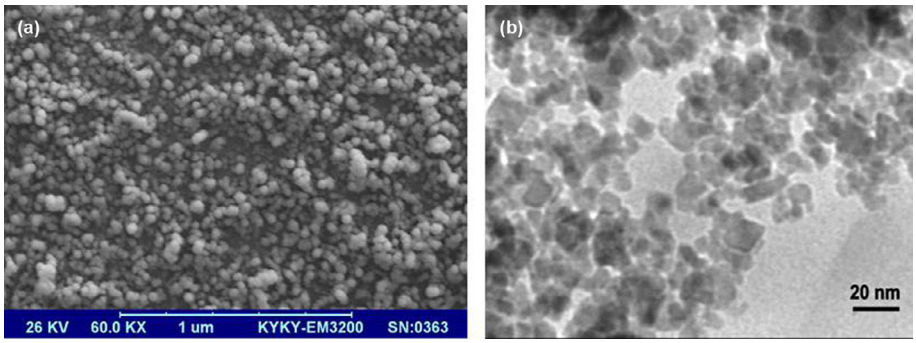
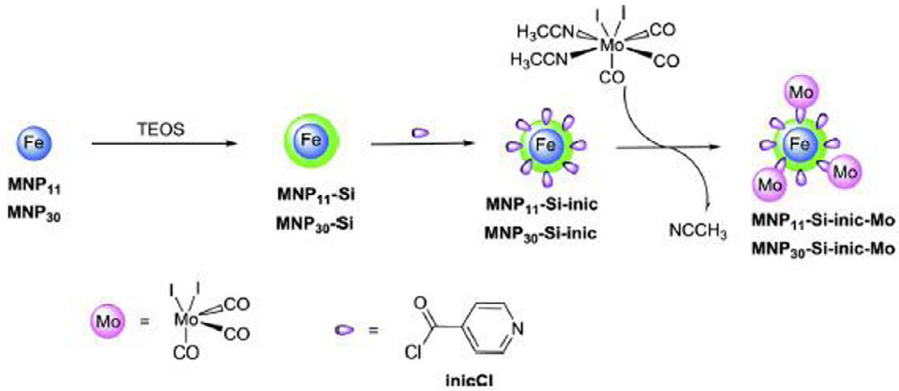


Fig. 5. SEM (a) and TEM (b) images of MNPs.



Scheme 4. Preparation of derivatized magnetic iron oxide nanoparticles with the Mo(II) precursor.

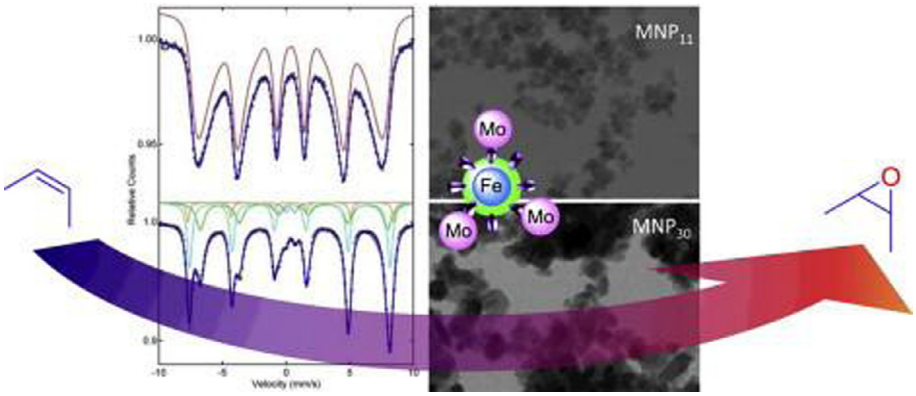
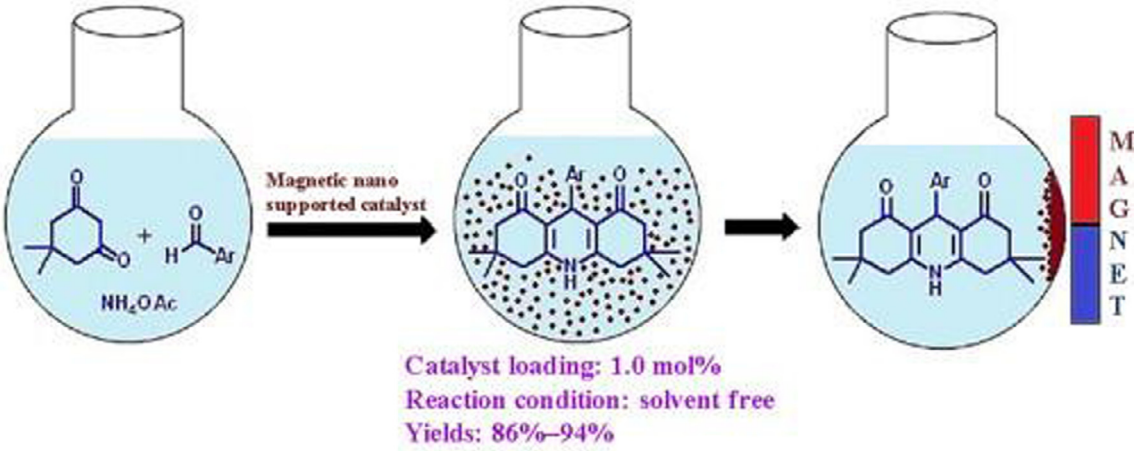


Fig. 6. The catalytic studies of the catalysts of olefin epoxidation.



Scheme 5. Synthesis of 1,8-dioxodecahydroacridines.

dosage, initial dye concentration and salt on dye degradation were evaluated. Formate, acetate and oxalate anions were detected as dominant aliphatic intermediate. Inorganic anions (nitrate and sulfate anions) were detected as dye mineralization products as shown in Scheme 4. The results indicated that $ZnFe_2O_4$ could be used as a magnetic photocatalyst to degrade dyes from colored wastewater (Mahmoodi, 2013).

The organometallic fragment $[MoI_2(CO)_3]$ was coordinated to magnetic iron oxide nanoparticles of different sizes (average size of 11 and 30 nm) which have been previously coated with a silica shell and grafted with a pyridine derivative ligand was studied. The Mo loading was found to be approximately 0.37 wt.% Mo and 0.57 wt.% Mo, corresponding to 0.150 mmol Mo g^{-1} and 0.230 mmol Mo g^{-1} for materials MNP30-Si-inic-Mo and MNP11-Si-inic-Mo, respectively. Preparation of these organometallic decorated magnetic nanoparticles was further confirmed by evidence obtained from extensive characterization by powder XRD, SEM/TEM analysis, as well as from data of ^{57}Fe Mössbauer and FT-IR spectroscopy. Olefin epoxidation of a variety of substrates promoted by these organometallic nano-hybrid materials using TBHP as oxidant, was performed with very good results. The catalytic studies show that the catalysts yield selectively the desired epoxides of a series of olefins as shown in Fig. 6. In addition, these catalysts are found to work under a wide temperature range and over several catalytic cycles without notorious performance loss in most cases (Fernandes et al., 2014).

A new magnetically separable catalyst consisting of ferric hydrogen sulfate supported on silica-coated nickel ferrite nanoparticles was prepared. The synthesized catalyst was characterized using vibrating sample magnetometry, X-ray diffraction, transmission electron microscopy, scanning electron microscopy, and Fourier transform infrared spectroscopy. This new magnetic catalyst was shown to be an efficient heterogeneous catalyst for the synthesis of 1,8-dioxodecahydroacridines under solvent-free conditions as shown in Scheme 5. The catalyst is readily recovered by simple magnetic decantation and can be recycled several times with no significant loss of catalytic activity (Khojastehnezhad et al., 2014).

Iron oxide nanoparticles, with size ranging from 50 to 100 nm, was synthesized by a solvothermal method. The amounts of iron (III) chloride precursor (from 2.5 to 10.0 mmol) and sodium hydroxide (between 10 and 30 mmol) were varied along with the synthesis temperature (180 or 200 °C). Depending on the synthesis conditions, samples with magnetic properties consisting of magnetite (Fe_3O_4), or by a mixture of magnetite and maghemite (γ-Fe_2O_3), and samples with no magnetism consisting of hematite (α-Fe_2O_3), were obtained. The catalytic activity of the materials was studied for the degradation of diphenhydramine using the photo-Fenton process. All materials performed well on the degradation of this emerging pollutant. The best compromise between catalytic activity and stability was obtained with pure magnetite nanoparticles prepared at 180 °C from a 4:1 M ratio between sodium hydroxide and iron(III) chloride. This catalyst was used in further studies at different pH (2.8–11.0), catalyst loads (up to 200 mg L^{-1}) and hydrogen peroxide concentrations (1–50 mM). Complete degradation of diphenhydramine with 78% of mineralization was achieved at relatively low leaching of iron species from the catalyst to the aqueous solution (1.9 mg L^{-1}). Acidic pH (2.8) is preferable to neutral or alkaline pH (i.e. 6.0, 7.0 and 11.0) resulting from the higher efficiency of H_2O_2 to promote the formation of hydroxyl radicals under those conditions. Complete degradation of the pollutant can be obtained at acidic pH even at very low catalyst load (20 mg L^{-1}). The use of stoichiometric H_2O_2 concentration allows for complete diphenhydramine conversion, maximum mineralization, and leaching of iron complying with European Directives as shown in Fig. 7. From recovery and reutilization experiments it was found that the selected magnetic catalyst might be easily recovered by magnetic separation, showing good stability and reusability properties (Martínez et al., 2015).

The non-toxic magnetic $CuFe_2O_4$ nanoparticles, was synthesized, characterized, and used as an efficient catalyst for synthesis of new derivatives for 1,2,4,5-tetrasubstituted imidazoles in excellent yields. The synthesized compounds work-up easy and purification of products are performed without chromatographic methods as shown in Scheme 6. The catalyst can be recovered for the subsequent reactions and reused without any appreciable loss (El-Remaily and Abu-Dief, 2015).

A robust synthesis for Magnetic $CoFe_2O_4$ nanoparticles via hydrothermal technique was investigated. The prepared magnetic nanoparticles were characterized by powder X-ray, SEM, TEM, HR-TEM, EDX, TGA, IR analysis and vibrating sample magnetometry. The prepared powder composed of ultrafine particles in nanometer size range with high homogeneous spherical shape and elemental composition. Moreover, the prepared magnetic $CoFe_2O_4$ nanoparticles has been used as an efficient catalyzed for synthesis of tetrahydropyridines and pyrrole derivatives in excellent yields, easy work-up and purification of products by non-chromatographic methods as shown in Scheme 7. The catalysts can be recovered for the subsequent reactions and reused without any appreciable loss (El-Remaily et al., 2016).

A new family of polyhedral oligomeric silsesquioxanes with eight triethoxysilane arms (APTPOSS) was anchored on the surface of Fe_3O_4 nanomagnetics and characterized by infrared

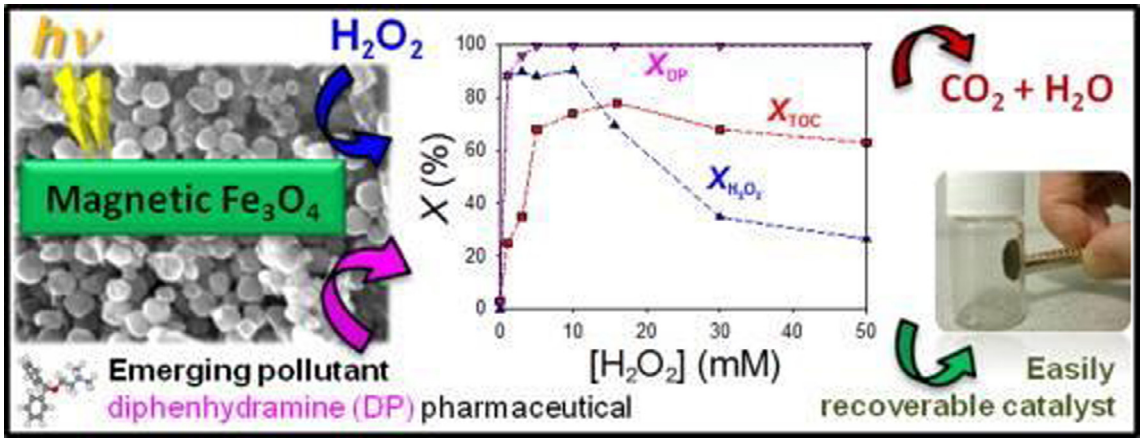
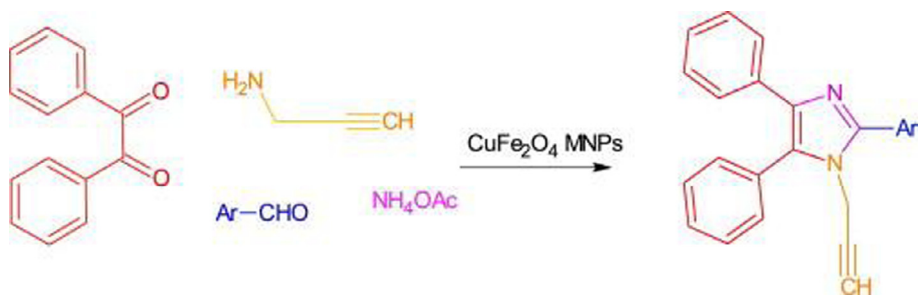
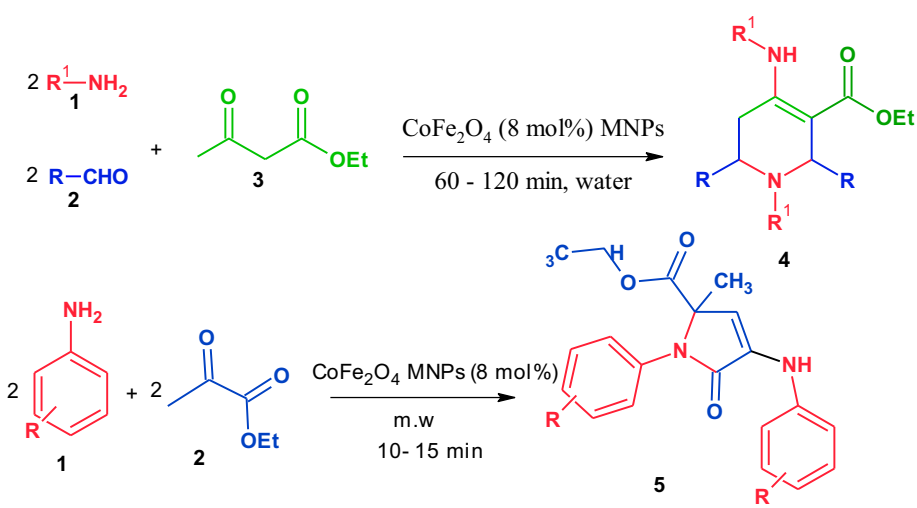


Fig. 7. The catalytic activity of the materials for the degradation of diphenhydramine.



Scheme 6. Synthesis of new derivatives for 1,2,4,5-tetrasubstituted imidazoles.



Scheme 7. Synthesis of tetrahydropyridines and pyrrole derivatives.

spectroscopy, X-ray diffraction spectroscopy, scanning electron microscope (cf. Fig. 8), Energy Dispersive Spectroscopy, thermogravimetric analysis, dynamic light scattering and vibrating sample magnetometer. Fe_3O_4@APTPOSS, as a magnetic nano catalyst for high-yield synthesis of pyrans has been employed (Ghomi et al., 2016).

Bacillus subtilis from slaughterhouse waste was isolated and screened for the production of protease enzyme. The purified protease was successfully immobilized on magnetic nanoparticles (MNPs) and used for the synthesis of series of glycinamides. The binding and thermal stability of protease on MNPs was confirmed by FT-IR spectroscopy and TGA analysis. The surface morphology of MNPs before and after protease immobilization was carried out using SEM analysis. XRD pattern revealed no phase change in MNPs after enzyme immobilization. The processing parameters for glycinamides synthesis viz. temperature, pH, and time were optimized using Response Surface Methodology (RSM) by using Design Expert (9.0.6.2). The maximum yield of various amides 2 butyramidoacetic acid (AMD-1,83.4%), 2-benzamidoacetic acid (AMD-2,80.5%) and 2,2′((carboxymethyl) amino)-2-oxoethyl)-2-hydroxysuccinyl)bis(azanediyl))diacetic acid (AMD-3,80.8%) formed was observed at pH-8, 50 °C and 30 min as shown in Fig. 9. The

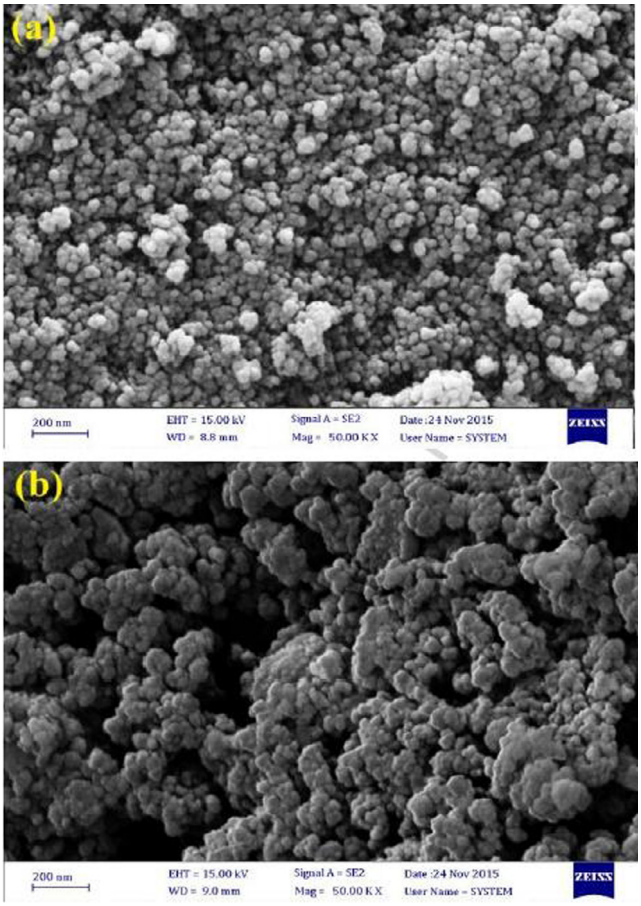


Fig. 8. SEM images of (a) Fe_3O_4, (b) Fe_3O_4@APTPOSS.

synthesized immobilized protease retained 70% of the initial activity even after 8 cycles of reuse (Sahu et al., 2016).

A novel and facile approach for one-pot synthesis of spinel cobalt ferrite ($CoFe_2O_4$) nanoparticles (NPs) was developed. The synthesis involves homogeneous chemical precipitation followed by hydrothermal heating, using tributylamine (TBA) as a hydroxylating agent. Polyethylene glycol (PEG) 4000 was used as surfactant. As-synthesized $CoFe_2O_4$ NPs were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM) (cf. Fig. 10), N_2 adsorption-desorption isotherm (BET) and vibrating sample magnetometry (VSM). TEM image showed formation of spherical particles of sizes 2–30 nm. These NPs were used as magnetically recoverable catalyst in oxidation of alcohols to their corresponding aldehydes by periodic acid. This oxidative procedure is found to be highly efficient affording products in very high yield and selectivity. The easy magnetic separation of the catalyst and efficient reusability are key features of this methodology (Paul et al., 2016).

A robust synthesis of magnetic $NiFe_2O_4$ nanoparticles was investigated via a hydrothermal technique. The prepared magnetic $NiFe_2O_4$ nanoparticles were characterized using powder X-ray diffraction (XRD), scanning electron microscopy, transmission electron microscopy (TEM), high-resolution TEM, energy-dispersive X-ray spectroscopy, thermogravimetric analysis, infrared spectroscopy and vibrating sample magnetometry. XRD and TEM analyses confirmed the formation of single-phase ultrafine nickel ferrite nanoparticles with highly homogeneous cubic shape and elemental composition. Moreover, the prepared magnetic $NiFe_2O_4$ nanoparticles were used as an efficient, cheap and eco-friendly catalyst for the Claisen–Schmidt condensation reaction between acetylferrocene and various aldehydes (aromatic and/or heterocyclic) yielding acetylferrocene chalcones in excellent yields, with easy work-up and reduced reaction time activity as shown in Scheme 8. The products were purified via crystallization. The structures of the produced compounds were elucidated using various spectroscopic analyses (1H NMR, 13C NMR, GC–MS). The catalyst is readily recovered by simple magnetic decantation and can be recycled several times with no discernible loss of catalytic. Furthermore, the prepared chalcone derivatives were evaluated for their anti-tumor activity against three human tumour cell lines, namely HCT116 (colon cancer), MCF7 (breast cancer) and HEPG2 (liver cancer), and showed a good activity against colon cancer (Abu-Dief et al., 2016).

The synthesis of mesoporous silica coated Fe_3O_4 core–shell nanoparticles or magnetic mesoporous silica nanoparticles

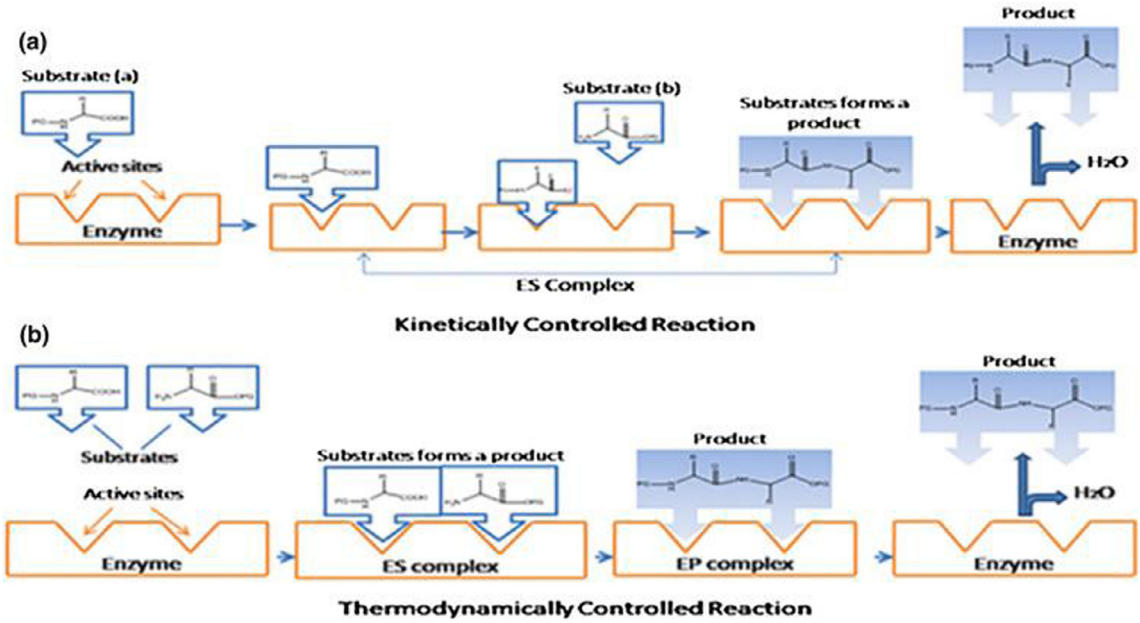


Fig. 9. Mechanism of enzymatic reaction (a) kinetically controlled (b) thermodynamically controlled.

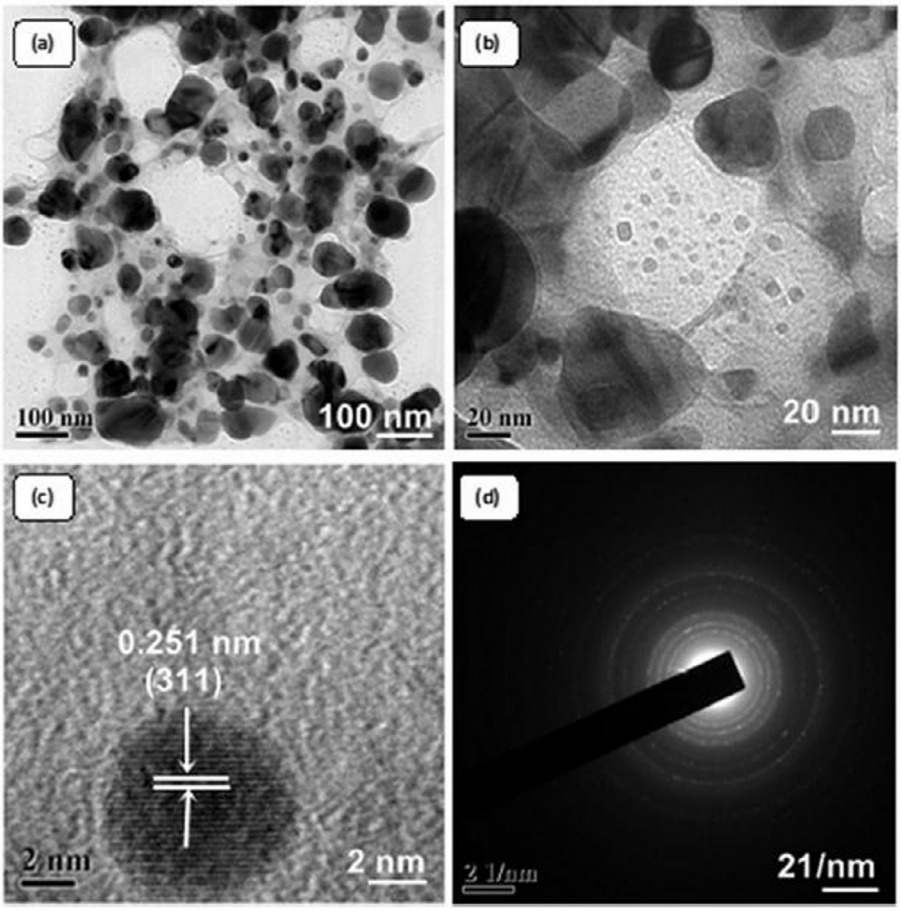
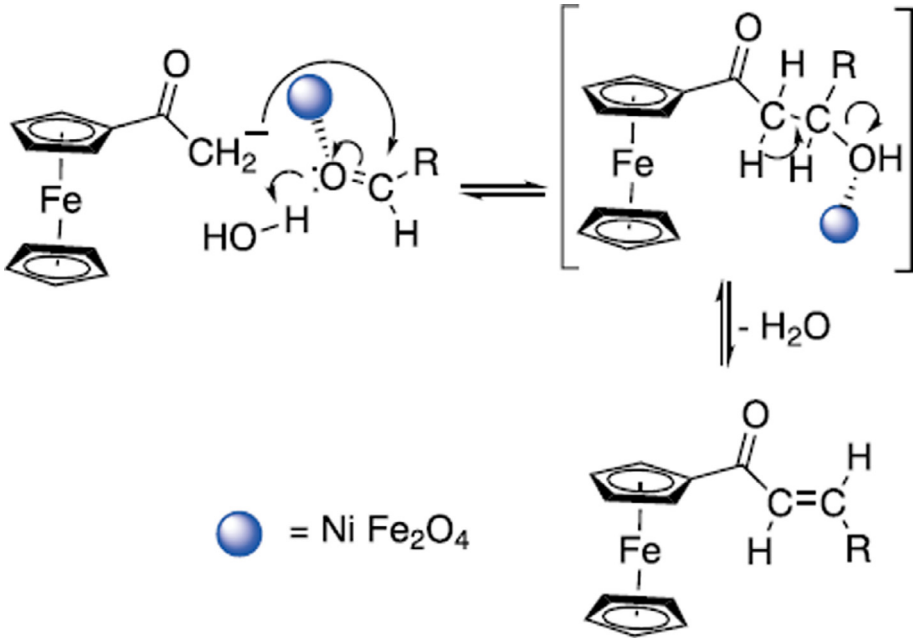
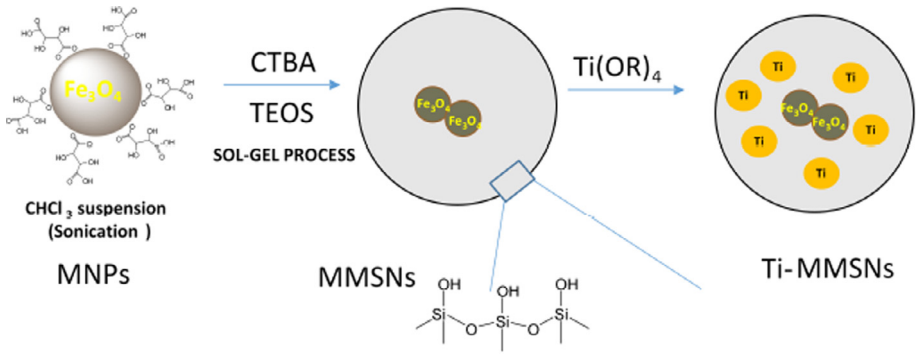


Fig. 10. (a,b) TEM image (c) HRTEM image (d) ED pattern of $CoFe_2O_4$ nanoparticles after five cycle.



Scheme 8. Proposed mechanism for the formation of the chalcone derivatives.

(MMSNs) via a surfactant templated sol–gel method using magnetite nanoparticles (MNPs) with tartrate as nucleation seeds was studied. The synthetic parameters have been carefully controlled in order to scale up the synthetic procedure to obtain more than 1 g of stable, high quality core–shell and biocompatible MMSNs per synthesis. MMSNs have been used as support to



Scheme 9. Heterogeneous titanium catalysts for ring opening polymerization (ROP) of ε-caprolactone.

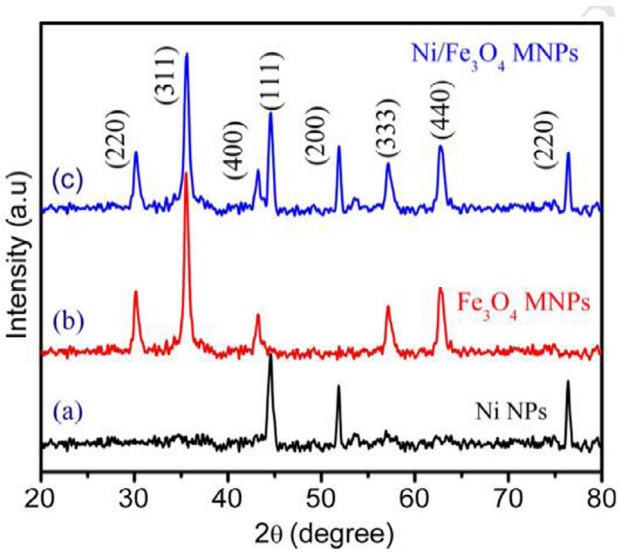


Fig. 11. Powder XRD pattern of (a) Ni NPs, (b) Fe_3O_4 NPs and (c) Ni/ Fe_3O_4 MNPs samples.

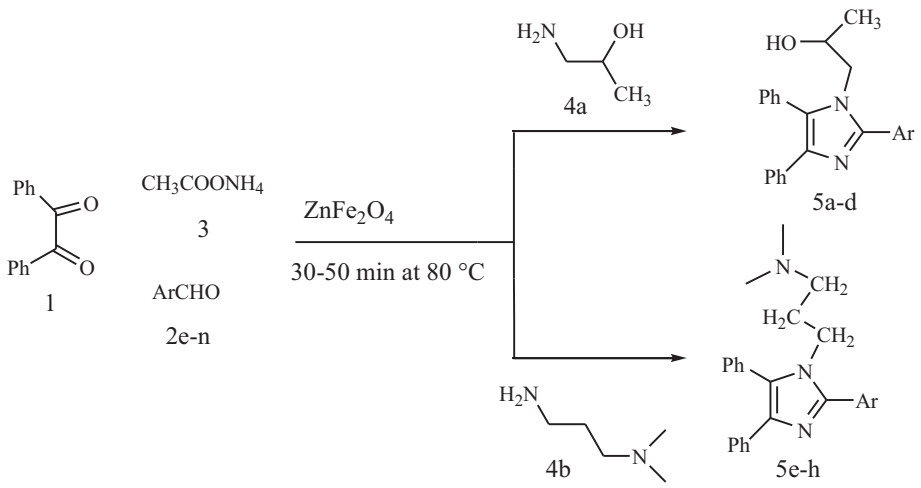
Scheme 10. Reduction of nitroarenes to arylamines.

prepare heterogeneous titanium catalysts for ring opening polymerization (ROP) of ε-caprolactone as shown in Scheme 9. The prepared materials have been fully characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF) N_2 adsorption-desorption, transmission electron microscopy (TEM), Fourier-transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TG-DTG), UV–vis and DRUV-vis techniques. In addition, extensive solid state electrochemical studies have been carried out in aqueous and organic medium demonstrating the coating of MNPs with a layer of mesoporous silica and the immobilization of titanium as electroactive species (Cruz et al., 2016).

A facile, low-cost and ecofriendly method for synthesis of nickel supported iron oxide magnetic nanoparticles (Ni/Fe_3O_4 MNPs) using *Moringa oleifera* (MO) leaves extract as reducing and capping agent was developed. The as-synthesized Ni/Fe_3O_4 nanocomposite was characterized by various physicochemical characterization techniques such as FT-IR, powder XRD, XPS, TEM and BET sorption methods. The results show that the Ni/Fe_3O_4 MNPs were exhibits spherical in shape with the size range of 16–20 nm. The room temperature magnetic measurements of composite clearly evince ferromagnetic natures with saturation magnetization (Ms) of 76.8 emu/g. The catalytic activity of Ni/Fe_3O_4 MNPs towards degradation of Malachite green (MG) dye was determined by UV–vis spectroscopy as shown in Fig. 11. The results show that as-synthesized Ni/Fe_3O_4 MNPs is an efficient catalyst for the degradation of Malachite green as compared to previous reports (Prasad et al., 2017).

A simple and efficient method to synthesize magnetically separable $NiFe_2O_4$@Cu nanocatalyst under co-precipitation condition was developed. X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), atomic absorption spectroscopy (AAS), Brunauer-Emmett-Teller (BET) and vibration sample magnetometer (VSM) analyses confirmed the construction of $NiFe_2O_4$@Cu nanoparticles. These nanoparticles showed satisfactory catalytic activity for the reduction of nitroarenes to arylamines with high yields as shown in Scheme 10. The catalyst can be easily separated by a magnet and reused seven consecutive runs with no obvious loss of activity (Zeynizadeh et al., 2017).

Marzouk et al. (2017), synthesized $ZnFe_2O_4$ magnetic nanoparticles hydrothermally and characterized them via SEM, TEM, HR-TEM, powder X-ray, EDAX, IR, TGA as well as magnetic measurements. Moreover, it was used as a robust catalyst for the synthesis of the biologically active series of multi-substituted imidazoles (MSI) by a multicomponent reaction by the reaction between of benzil with different aromatic aldehydes, ammonium acetate, and aliphatic amine (N,N-Dimethyl-1,3-propanediamine and 1-amino-2-propanol) under solvent-free conditions (Scheme 11). The key advantages of this method are shorter reaction times, very high yield, and ease of establishment. The thermally and chemically stable, benign and economical catalyst was easily recovered using an external magnet and reused in at least five successive runs without an appreciable loss of activity. All of these novel syn-



Scheme 11. Synthesis of 1,2,4,5-tetrasubstitutedimidazoles **5a-n.**

thesized compounds have been characterized from spectral data and their purity were checked by TLC and give one spot. Furthermore, the prepared compounds were tested for their anti-inflammatory activity.

5. Conclusion

Transition metal ferrite nanoparticles, utilized in catalytic reactions, possess different sizes, from ultrasmall 2 nm to 100 nm. They are obtained mainly by co-precipitation methods, sometimes combined with simple calcination at high temperatures, hydrothermal route are also frequently used. Sometimes, self-combustion techniques are applied. Due to magnetic properties, ferrite nano catalysts can be easily recovered from reaction systems and reused up to several runs almost without loss of catalytic activity. Standard transition metal salts (usually nitrates) are used as precursors, although some industrial wastes can also serve as a source of initial substances. Particle sizes of resulted spinel ferrites are dependent on the nature of transition metal and the synthesis method. A series of distinct shapes for ferrite nanoparticles have been observed, from spherical to nanorods and nanotubes. Forms/shapes of nanoparticles, ratios of doping atoms, impurities, specific surface area, etc., can considerably influence on the catalytic activity of ferrites. Catalytic processes with the application of ferrite nanoparticles are in a wide range. Notable attention is paid to synthesis of series of glycinamides. Other catalyzed organic reactions consist of oxidation of various alkenes, aldol, alkylation and dehydrogenation reactions, synthesis of various organic compounds such as, arylamines and acetylferrocene chalcones. We note that the total number of nano-ferrite applications for catalytic purposes is still relatively low, so it could be a perfect research niche for further applications of ferrite nanomaterials in a variety of organic processes.

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