Review Article: Progressive Types of Fe₃O₄ Nanoparticles and Their Hybrids as Catalysts

Heshmatollah Alinezhad¹ 🧔 , Parvin Hajiabbas Tabar Amiri^{2,*} 🧔 , Sahar Mohseni Tavakkoli,¹

Raed Muslim Muhiebes³ 🙆 , Yasser Fakri Mustafa ⁴ 🧕

¹Department of Organic Chemistry, Faculty of Chemistry, University of Mazandaran, Babolsar, Iran

²Department of Chemistry, Damghan University, Damghan, Semnan, Iran

³ Department of Biochemistry, College of Medicine, Misan University, Iraq

⁴ Department of Pharmaceutical Chemistry, College of Pharmacy, University of Mosul, Mosul, Iraq



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<u>A B S T R A C T</u>

Here, we discuss about several important procedures of preparing Fe_3O_4 nanoparticles and their hybrids as magnetically and recoverable catalysts. Magnetic nanoparticles could be simply separated by applying the magnetic interaction using a magnetic field. As classified in this study, several groups were used to develope a sequence of magnetic nanoparticles as heterogeneous catalysts in organic transformations and other usages. The progressive preparation of supporting materials is emphasized in this article to develop the quality of magnetic nanoparticles.

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*Corresponding Author: Parvin Hajiabbasi (parvinhajiabbasi@yahoo.com)

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1. Introduction

t the present time, magnetic catalysts attract enormous interest [1-5] and have an extensive variety of potential uses due to their high surface area, biocompatibility, and unique magnetic properties [6–10]. Furthermore, magnetic nanoparticles separated simply by applying the magnetic interaction using a magnetic field [11-14].

In the family of nanomagnetic materials, magnetite Fe_3O_4 exhibits excellent application such as magnetic bio-separations [15], drug delivery [16, 17], magnetic resonance imaging (MRI) [18], hyperthermia treatment of cancer cells [19, 20], and catalysts [21, 22]. Thus, we

investigate the existence and prepration of some types of Fe_3O_4 nanoparticles and their hybrids as catalysts in this study.

2. Various types of Fe₃O₄ nanohybrid catalysts

Most Schemes for iron-based nanoparticles recovery is the result of the magnetic particle (Fe, Fe₃O₄, Fe₂O₃, etc.) as a support which is announcer to a different catalytically active metal [23]. Catalyst training is performed when the second metal [24-26] or organo catalyst [27, 28] is anchored via a linker to the nanoparticle directly or instead of a protective polymer [29, 30] or silica coating [31, 32]. As depicted in **Figure 1**, some clusters have devolved a series of magnetic nanoparticles as beneficial catalysts in organic transformations.

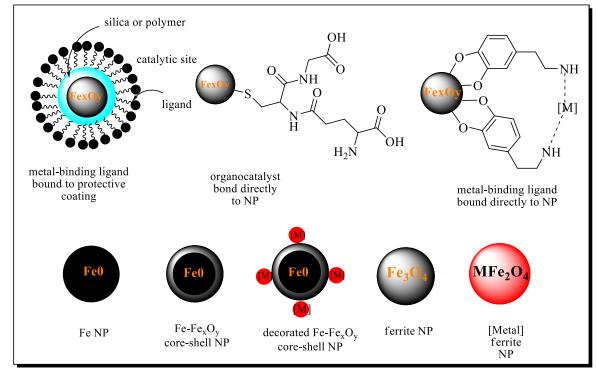


Figure 1. Various types of magnetically nanoparticles

3. Nanohybrid Fe₃O₄ catalysts having silica as protective coating

Some types of nanohybrid Fe_3O_4 catalysts having silica as protective coating (1-7) are displayed in the **Figure 2**.

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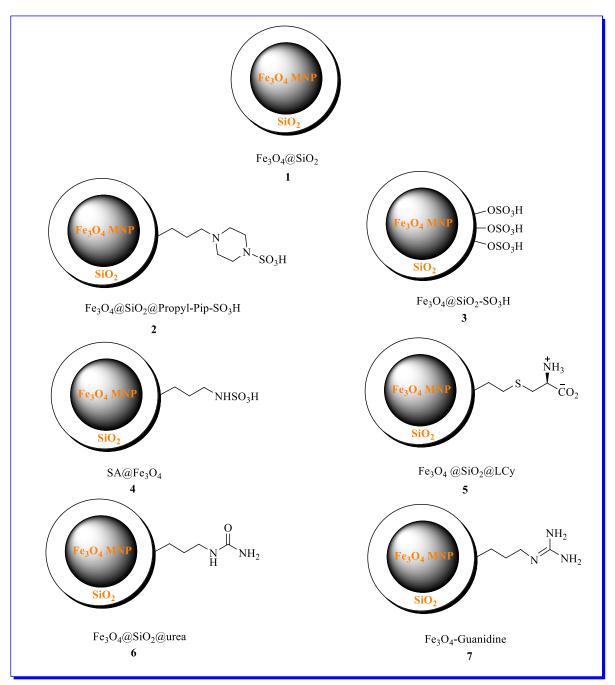
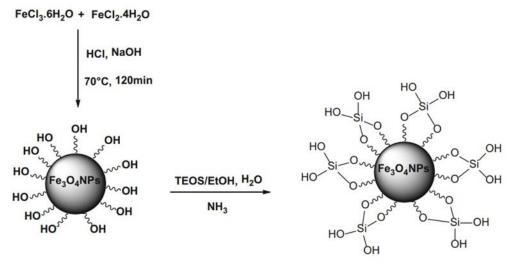


Figure 2. Typical nanohybrid Fe₃O₄ catalysts having silica coating

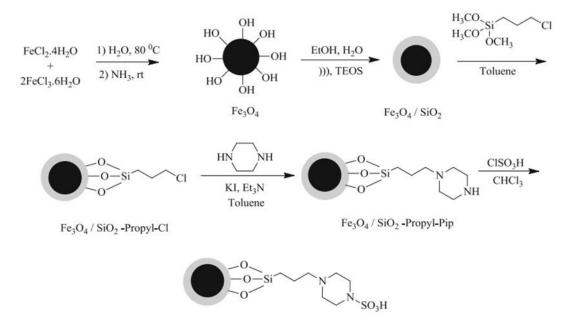
Fe₃O₄@SiO₂ nanoparticles (**1**) were prepared according to **Scheme 1** procedure by Hu *et al.* [33] using the chemical co-precipitation method. In this procedure, FeCl₃·6H₂O and FeCl₂·4H₂O were dissolved in aqueous HCl. Then, aqueous NaOH was added under vigorous stirring to produce black precipitate instantly [34].



Scheme 1. Synthetic steps of preparing Fe₃O₄@SiO₂ nanoparticles (1) [34]

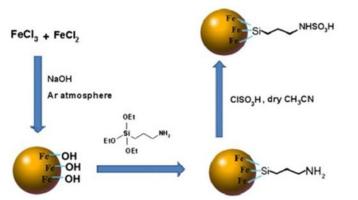
The synthetic method for preparing the Fe_3O_4/SiO_2 -PropylPip-SO₃H magnetic nanoparticles (MNPs) is shown in **Scheme 2** [35]. In the procedure, silica was coated on Fe_3O_4 MNPs, then condensation of hydroxyl groups of MSNPs with (3-chloropropyl) trimethoxysilane (CPTMS) yielded Fe_3O_4/SiO_2 -Propyl-Cl MNPs. Subsequently, the reaction of the chloro groups

of Fe₃O₄/SiO₂-Propyl-Cl with the amine group of piperazine gained Fe₃O₄/SiO₂-supported piperazine (Fe₃O₄/SiO₂-Propyl-Pip). At the last step, Fe₃O₄/SiO₂-Propyl-Pip was condensed with chlorosulfonic acid which produced *N*-propylpiperazine sulfonic acid-functionalized Fe₃O₄ magnetic nanoparticles (Fe₃O₄/SiO₂-Propyl-Pip-SO₃H).



Scheme 2. Preparation of Fe₃O₄/SiO₂-Propyl-Pip-SO₃H magnetic nanoparticles (2) [35]

In this protocol, for surface modification, magnetic nanoparticles were covered with APTES to achieve aminofunctionalized magnetic nanoparticles. Finally, reaction of amino groups and chlorosulphuric acid yielded SA–MNPs (sulphamic acid-functionalized magnetic Fe₃O₄ nanoparticles) (**Scheme 3**) [36].



Scheme 3. Preparation of SA-MNPs (sulphamic acid functionalized magnetic Fe₃O₄ nanoparticles) [36]

In addition, the prepration of some other magnetic nanoparticles was found to have silica as protective coating in the reported articles such as $Fe_3O_4@SiO_2-SO_3H$ [37], Fe_3O_4 @SiO_2@LCy [38], Fe_3O_4/SiO_2 -urea [39], MNPs-Guanidine [40], and etc. 3.1 Nanohybrid Fe₃O₄ catalysts supported heteropolyacids

Some types of nanohybrid Fe_3O_4 catalysts having silica supported heteropolyacids (8-10) are indicated in the **Figure 3**.

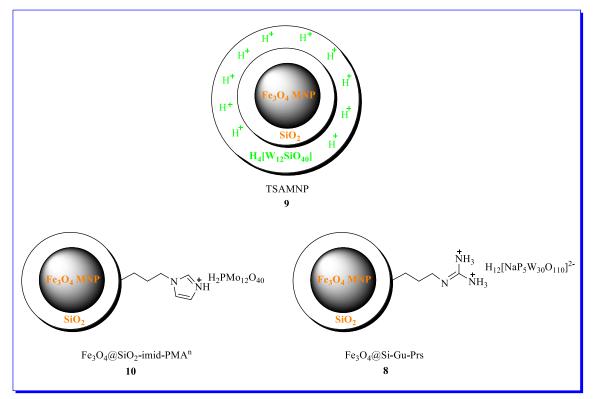
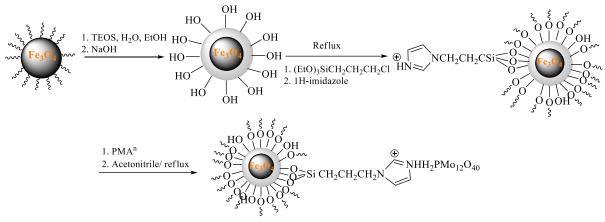


Figure 3. Typical nanohybrid Fe₃O₄ catalysts having silica supported heteropolyacids

 $Fe_3O_4@SiO_2$ -imid- $H_3PMo_{12}O_{40}$ nanoparticles (**10**) were produced from immobilization of phosphomolybdic acid nanoparticles on imidazole functionalized $Fe_3O_4@SiO_2$ [41]. In this procedure, $Fe_3O_4@SiO_2$ was added to the solution of 3-chlorotriethoxypropylsilane and

imidazole in *p*-xylene to prepare $Fe_3O_4@SiO_2$ imid. Then, $Fe_3O_4@SiO_2$ -imid was added to an acetonitrile solution of PMAⁿ. Likewise, the similar process was used for the synthesis of $Fe_3O_4@SiO_2$ -imid-PMA^b (PMAⁿ = nano $H_3PMo_{12}O_{40}$, PMA^b= $H_3PMo_{12}O_{40}$) (Scheme 4).



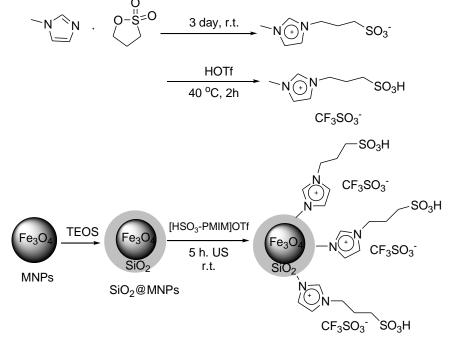


Scheme 4. Synthetic steps of Fe₃O₄@SiO₂-imid-PMAⁿ

Furthermore, the prepration of some other magnetic nanoparticles was found to have silica supported heteropolyacids reported in articles such as $Fe_3O_4@Si$ -Gu-Prs (8) [42], TSAMNP catalyst (9) [43], and etc.

3. 2 Nanohybrid Fe₃O₄ catalysts supported ionic liquids

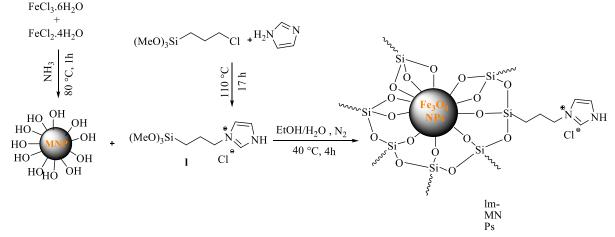
The synthetic procedure of acidic IL supported on magnetic nanoparticles ([HSO₃PMIM]OTfSiO₂@MNPs) is demonstrated in **Scheme 5**. The coresponding ionic liquid [HSO₃PMIM]OTf was produced by treatment of 1-methyl-3*H*-imidazole with 1,3-propanesultone, followed by treatment with HOTf. Finally, the silica coated magnetite nanoparticles was treated with [HSO₃PMIM]OTf in dichloromethane by sonication to produce [HSO₃PMIM]OTf-SiO₂@MNPs [44].



[HSO₃-PMIM]OTf-SiO₂@MNPs Scheme 5. Preparation of [HSO₃PMIM]OTf-SiO₂@MNPs [44]

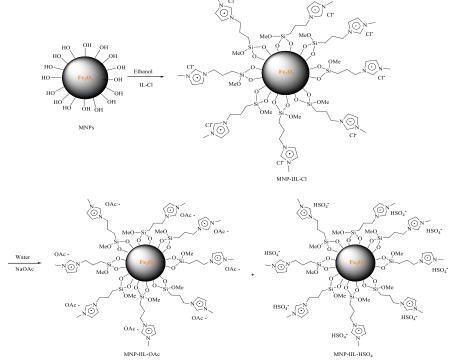
Imidazole functionalized magnetic Fe_3O_4 nanoparticles are reported by Nazari et al. [45]. In the present study, the reaction of (3-chloropropyl)-trimethoxysilane with imidazole

led to product 1 (Si-Im). Finally, MNPs were coated with Si-Im to reach the desired nanoparticles (**Scheme 6**).



Scheme 6. Preparation of imidazole functionalized magnetic nanoparticles [45]

After preparing Fe_3O_4 -MNPs, 1-methyl-3-(3trimethoxysilylpropyl) imidazolium chloride (IIL-Cl) was attained from the reaction of *N*methyl imidazole with (3-chloropropyl) trimethoxysilane. Then, the immobilized chloride IL on MNPs (MNP–IIL–Cl) and an excess amount of NaOAc (or KHSO₄) were added into the deionized water. As depicted in the **Scheme 7**, MNPs-IIL-OAc and MNPs-IIL-HSO4 were obtained as a powder. In this procedure, 1methyl-3-(3-trimethoxysilylpropyl) imidazolium hydrogen sulfate (MNPs-IIL-HSO₄), 1-methyl-3-(3-trimethoxysilylpropyl) imidazolium acetate (MNPs-IIL-OAc), and 1methyl-3-(3-trimethoxysilylpropyl) imidazolium chloride (MNPs-IIL-Cl) were prepared [46].

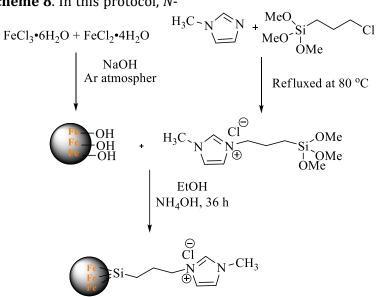


Scheme 7. Preparation steps of producing MNPs-IILs [46]

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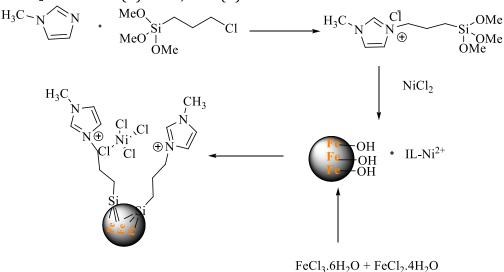
The ionic liquid 1-methyl-3-(3-trimethoxysilylpropyl) imidazolium chloride immobilized functionalized on Fe_3O_4 nanoparticles (IL-MNPs) was further reported by Safari and Zarnegar. The synthetic steps are shown in the the **Scheme 8**. In this protocol, *N*-

methyl imidazole reacted with (3-chloropropyl) trimethoxysilane to prepare 1-methyl-3-(3trimethoxysilylpropyl) imidazolium chloride (IL). Then, IL was added to the external surface of MNPs to attain IL-MNPs [47].



Scheme 8. Preparation steps of IL-Fe₃O₄ nanoparticles [47]

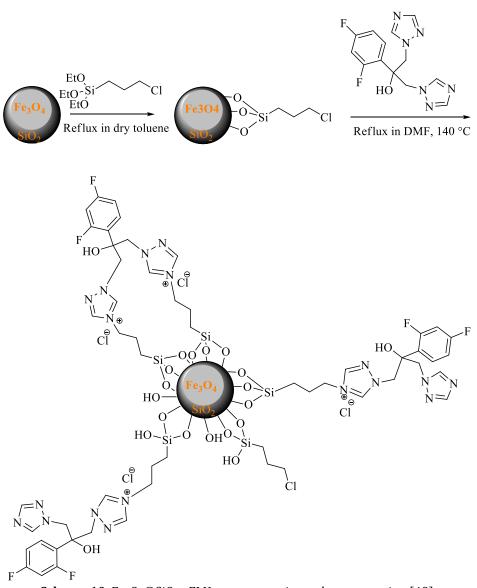
As illustrated in the **Scheme 9**, IL-Ni(II)functionalized magnetic Fe_3O_4 nanoparticles are prepared. The IL addition to an acetonitrile solution of NiCl₂ led to IL-Ni(II). Then, IL-Ni(II) immobilized on the external surface of Fe_3O_4 nanoparticles to achieve IL-Ni(II)-MNPs as the desired product [48].



Scheme 9. IL-Ni(II)-MNPs preparation steps [48]

The $Fe_3O_4@SiO_2 \sim FLU$ nanomagnetic catalyst was organized as depicted in the **Scheme 10**. Edvidently, iron oxide is coated by a silica layer to immobilize organic catalyst on the surface of

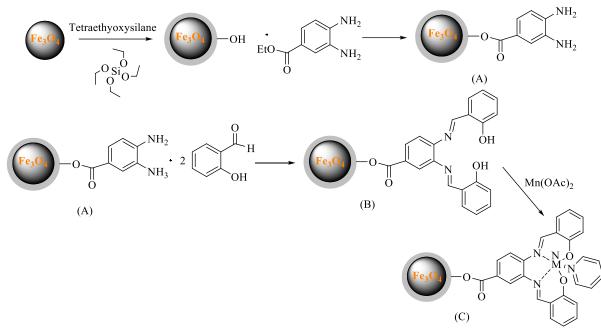
inorganic support because of that organosilanes can act as a linker between the organic catalyst and the support. As reported, chloride in the linker was replaced by nitrogen of the triazole via an SN_2 reaction [49].



Scheme 10. Fe₃O₄@SiO₂~FLU nanomagnetic catalyst prepration [49]

3. 3 Nanohybrid Fe₃O₄ catalysts supported metal bounds

Herein, synthesis steps of manganese (III) salen complex immobilized on Fe_3O_4 nanoparticles reported by S.M. Sadeghzadeh *et al.* is demonstrated in **Scheme 11**. For the synthesis of compound (A) MNP, $Fe_3O_4 \setminus SiO_2$ MNPs were added to ethyl 3,4-diaminobenzoate. Then, for synthesis of $Fe_3O_4 \setminus SiO_2 \setminus Salen \setminus Mn$ nanoparticles (C), compound (A) was reacted with the solution of salicylaldehyde and subsequently with $Mn(OAc)_2$ [50].

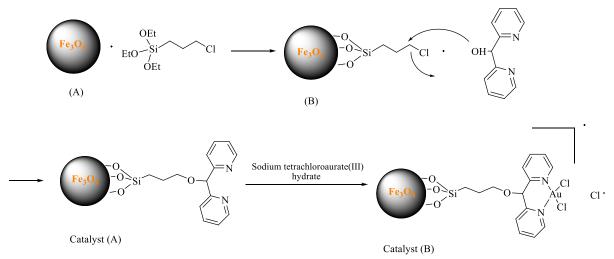


Scheme 11. Synthesis steps of Fe₃O₄\SiO₂\Salen\Mn nanoparticles [50]

Another Fe₃O₄ supported gold dipyridine complex nanoparticles was formed via sodium

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tetrachloroaurate(III) hydrate attaching to a dipyridine ligand (**Scheme 12**) [51].

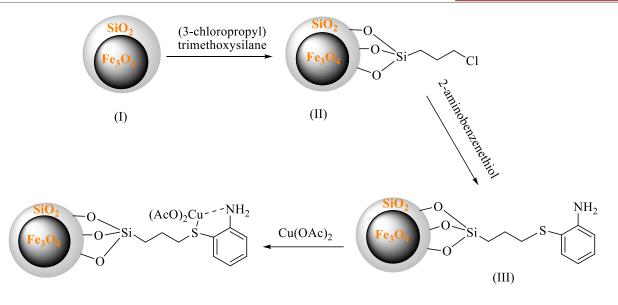


Scheme 12. Fe₃O₄ supported gold dipyridine complex nanoparticles synthesis [51]

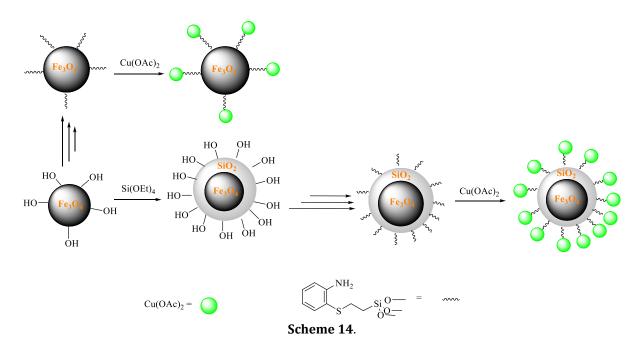
Cu(II)/2-Aminobenzenthiol complex immobilized on Fe_3O_4/SiO_2 NPs is reported to catalyze synthesis of 1,2,3-triazoles. As depicted in **Scheme 13** and **Scheme 14**, $Fe_3O_4@SiO_2$ -(3-chloropropyl) trimethoxysilane was prepared to

react with 2-aminobenzenethiol and subsequently, copper acetate was added to the mixture in order to prepare $Fe_3O_4@SiO_2-ABT/Cu(OAc)_2$ [52].

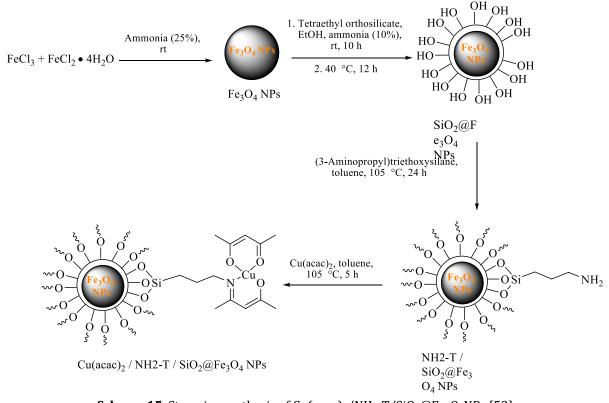
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(IV) **Scheme 13.** Cu(OAc)₂/2-aminobenzenthiol complex coated on Fe₃O₄/SiO₂NPs formation [52]

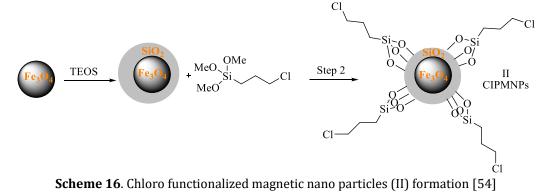


 $Cu(acac)_2/NH_2$ -T/SiO₂@Fe₃O₄NPs was prepared through immobilization of copper(II) acetylacetonate on the external surface of amine-terminated Fe₃O₄/SiO₂ NPs (**Scheme 15**). In this protocol, the synthesized NH_2 -T/SiO₂@Fe₃O₄NPs was added to a solution of [Cu(acac)₂] [53].

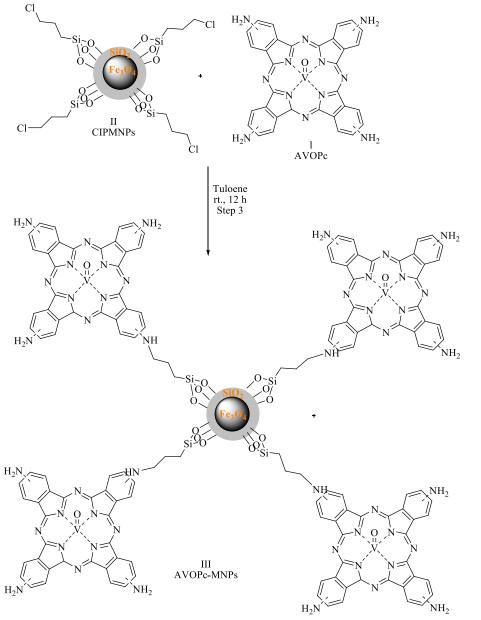


Scheme 15. Stepwise synthesis of Cu(acac)₂/NH₂-T/SiO₂@Fe₃O₄NPs [53]

 $Fe_3O_4@SiO_2@SiO_2(CH_2)_3@AVOPc$ was formed by covalent binding of an amino vanadium oxo phthalocyanine, on the surface of Fe_3O_4/SiO_2 NPs [54]. $Fe_3O_4@SiO_2@SiO_2(CH_2)_3Cl$ (ClPMNPs) were prepared as depicted in **Scheme 16**. In the next step for covalently linking the ClPMNPs to AVOPc, CIPMNPs was sonicated and subsequently, they were added to the AVOPc in order to produce Fe₃O₄@SiO₂@SiO₂(CH₂)₃@AVOPc (AVOPc-MNPs) (**Scheme 17**) [54].



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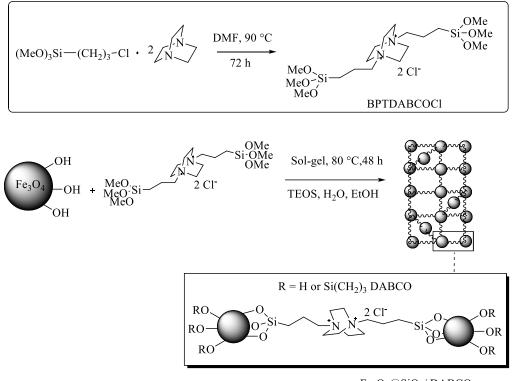
Scheme 17. Synthesis of AVOPc-MNPs [54]

Another type of magnetic nano particles based on a biimidazole Cu(I) complex was produced by covalent binding of biimidazole on chloridefunctionalized Fe_3O_4/SiO_2 NPs, followed by reacting with CuI [55].

3.4. Nanohybrid Fe_3O_4 catalysts supported an additional bound

An organic-inorganic type of silica with ionic liquid basis was produced as indicated in **Scheme 18**. In this protocol, diazoniabicyclo [2.2.2] octane dichloride groups, [(MeO)₃Si(CH₂)₃N⁺(CH₂CH₂)₃N⁺(CH₂)₃

 $Si(OME)_3]Cl_2$, were produced as a precursor reagent to achieve the desired nano particles [56].

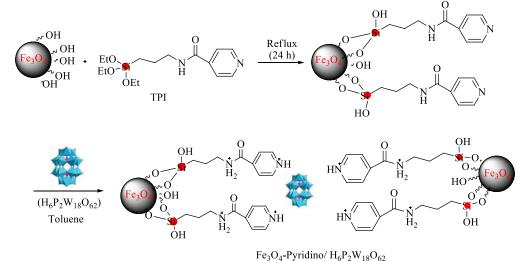


Fe₃O₄@SiO₂/DABCO

Scheme 18. Prepration steps of Fe₃O₄@SiO₂/DABCO [56]

An inorganic-organic type of MNPs $H_6P_2W_{18}O_{62}/pyridino-$ Fe₃O₄ (HPA/TPI-Fe₃O₄) produced by Tayebee *et al.* (Scheme 19). The Wells-Dawson heteropolyacid $H_6P_2W_{18}O_{62}$

immoblized on the external surface of Fe₃O₄ nanoparticles with *N*-[3-(triethoxysilyl)propyl] isonicotinamide (TPI) linker [57].



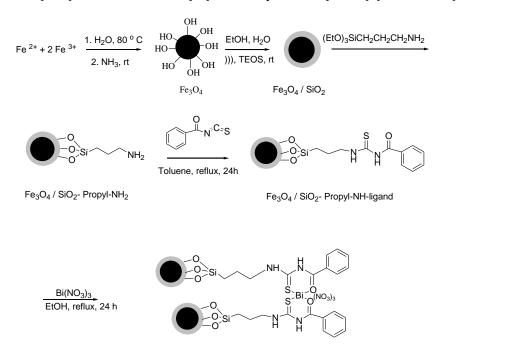
Scheme 19. HPA/TPI-Fe₃O₄ nano particles as catalyst [57]

The *N*-propylcarbamothioyl benzamide complex of Bi(III) fixed on Fe_3O_4/SiO_2 NPs has been reported by Mobinikhaledi et al. [58]. In this report, Fe_3O_4/SiO_2 reacted with (3aminopropyl) triethoxysilane (APTES) to yield Fe_3O_4/SiO_2 -NH₂ MNPs. Then, the condensation reaction of amino groups of Fe_3O_4/SiO_2 -NH₂ with benzoyl isothiocyanate led to Fe_3O_4/SiO_2 supported carbamothioyl benzamide (Fe_3O_4/SiO_2 -NH-ligand) formation. Lastly, the

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reaction of Fe_3O_4/SiO_2 -supported carbamothioyl benzamide with $Bi(NO_3)_3$ · $5H_2O$ led to Bi(III)

complex of Fe₃O₄/SiO₂-NH-ligand magnetic nanoparticles (MNPs) (**Scheme 20**).



Fe₃O₄ / SiO₂- Propyl-NH-ligand-Bi(III) Scheme 20. Preparation of Fe₃O₄ / SiO₂- propyl-NH-ligand-Bi(III) MNPs [58]

4. Nanohybrid Fe₃O₄ catalysts directly bounded in the absence of silica

Multi-walled carbon nanotubes supported Fe_3O_4 nano particles is prepared according to the synthetic procedure which was depicted in

Scheme 21. In this study, carboxylic acid functionalized MWCNTs used as starting materials. Finally, the solution of NH₃ was added to produce black magnetic Fe₃O₄NPs/MWCNTs [59].



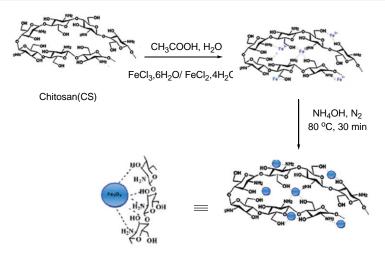
Fe₃O₄ NPs -

Scheme 21. Simplified schematic exhibition of the synthesis of Fe₃O₄ NPs/MWCNTs [59]

As the synthetic steps are illustrated in the **Scheme 22**, chitosan-coated Fe_3O_4 (Fe₃O₄@CS) synthesized via in situ co-precipitation of Fe²⁺

and Fe^{3+} ions with an aqueous solution of chitosan [60].



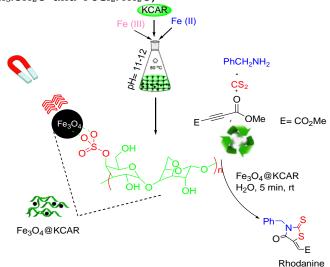


Fe₃O₄@CS

Scheme 22. Preparation steps for fabricating heterogeneous Fe₃O₄@CS nanoparticles [60]

Herein, Fe₃O₄@KCAR was synthesized in the presence of natural κ -carrageenan (KCAR) biopolymer (**Scheme 23**). KCAR dissolved in water is added to FeCl₃.6H₂O and FeCl₂.4H₂O,

and then aqueous ammonia was added to the solution in order to produce the desired product [61].



Scheme 23. A schematic pathway for synthesis of Fe₃O₄@KCAR and rhodanine [61]

A dehydroascorbic acid covered Fe_3O_4 NPs (DHAA-Fe₃O₄) is also synthesis as the structure of the catalyst is illustrated in the **Figure 4**. For preparing DHAA-capped magnetite nanoparticles (DHAA-Fe₃O₄) Fe(OH)₃ solution

was prepared by addition of $FeCl_3.6H_2O$ aqueous solution to NaHCO₃ solution. Subsequently, a solution of vitamin C was reacted gradually to Fe^{3+} [62].

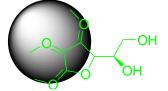


Figure 4. DHAA-capped magnetite nanoparticles [62]

In addition, Fe_3O_4 -proline MNPs was produced with no additional linkers as shown in the **Figure 5**. In this process $FeCl_3$ · $6H_2O$ and $FeCl_2$ · $4H_2O$ salts were dissolved in deionized water and subsequently, proline and NH_4OH solution was added to produce the desired Fe_3O_4 -proline nanoparticles [63].

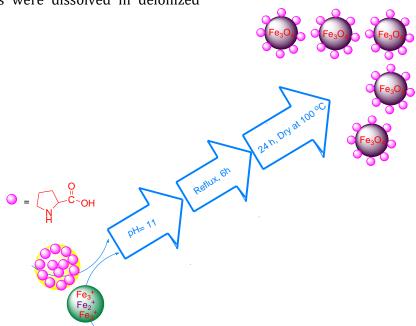
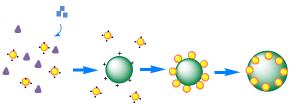


Figure 5. Preparation of Fe₃O₄-proline MNPs [63]

Moreover, $Pd@agarose-Fe_3O_4$ nanoparticles were synthesized. In this protocol, palladium nanoparticles supported on an agarose hydrogel which is attached to magnetic Fe_3O_4 nanoparticles [64]. The Fe₃O₄/ZIF-8 nanoparticles were prepared via the reaction between 2-methylimidazolate (MeIM) and zinc nitrate in the presence of Fe₃O₄ NPs as displayed in the **Figure 6** [65, 66].



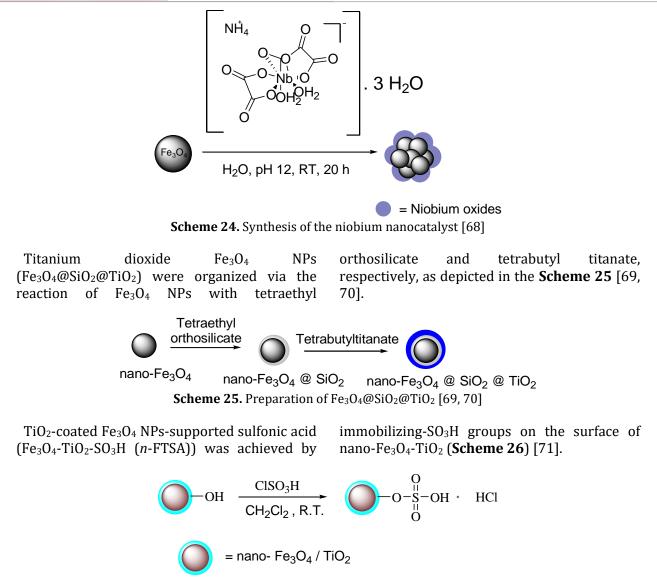
 \bigcirc Fe₃O₄-PAA \blacktriangle MelM \blacksquare Zn ²⁺ \bigcirc ZIF-8 Figure 6. Fe₃O₄/ZIF-8 particles prepration. PAA=polyacrylic acid [65, 66]

A magnetic organic-inorganic Fe_3O_4 NP was prepared and called (Fe_3O_4 /PAA-SO_3H) sulfonated-phenylacetic acid immoblized on Fe_3O_4 NPs. Phenylacetic acid immoblized initially on manufactured Fe_3O_4 NPs. Then, the Fe_3O_4 /PAA was sulfonated by numerous amounts of chlorosulfonic acid to give Fe_3O_4 /PAA-SO_3H [67].

The $Fe_3O_4@Nb_2O_5$ nanocatalyst was prepared by coating magnetite nanoparticles with

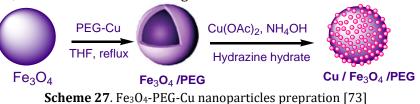
niobium oxide by using a simple wet impregnation method (**Scheme 24**). The $Fe_3O_4@Nb_2O_5$ nanocatalyst was formed using ammonium niobate oxalate hydrate ($C_4H_4NNbO_9$ · $3H_2O$) as the niobium source. The hydrolysis of the niobium precursor in alkaline medium led to aggregation of niobium hydroxides over the surface of Fe_3O_4 nanoparticles [68].





Scheme 26. Fe₃O₄/TiO₂-supported sulfonic acid nanoparticles formation [71]

Polyethylene glycol-Cu nanocomposite (Fe₃O₄-PEG-Cu) synthetic steps is depicted in **Scheme 27**. First, cyanuric chloride reacted with PEG-(OH)₂ to prepare PEG-Cl₄ [72]. Second, PEG-Cl₄ was linked with Fe₃O₄ NPs via covalent bindings (Fe₃O₄-PEG). Finally, the Fe₃O₄-PEG-Cu catalyst was produced by reducing copper ammonia complexes using hydrazine hydrate on the surface of Fe₃O₄-PEG nanocomposite [73].



 $Fe_3O_4/HAp/Au$ was prepared by magnetic metal oxides (Fe_3O_4), noble metals Au, and hydroxyapatite (HAp, hydroxyapatite). This catalyst is an efficient one for many responses

such as photocatalysis, molecular imaging, and drug delivery. Synthesis of Fe₃O₄/HAp/Au composite NPs was performed in three steps as demonstrated in **Figure 7** including syntheses of

 Fe_3O_4 NPs (A), magnetic hydroxyapatite (Fe_3O_4 /HAp) NPs (B), and Fe_3O_4 /HAp/Au (C).

Finally, the prepared catalyst was utilized for efficient photocatalytic application [74].

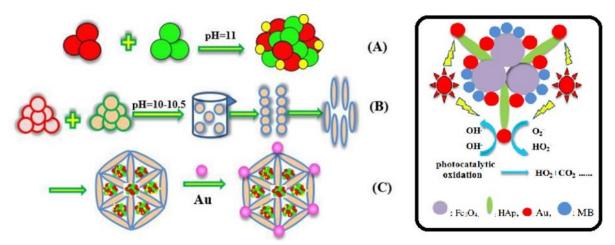


Figure 7. Synthetic procedure (A-C) and photocatalytic reaction of Fe₃O₄/HAp/Au [74]

4.1 Hybrid Pd- Fe₃O₄ nanoparticles for various C-C coupling reactions

The Suzuki-Miyaura coupling, Mizoroki-Heck, and Sonogashira reactions are important reactions using Pd catalysts to produce C-C coupling reactions. Recently Pd-Fe₃O₄ NPs were applied in C-C coupling reactions [75-77].

FePd-Fe₃O₄ composites were synthesized in various Fe/Pd ratios as the synthetic procedure is illustrated in the **Figure 8**. Additionally, TEM image of the urchin-like FePd–Fe₃O₄ composite nanoparticles is depicted in the **Figure 8** [78].

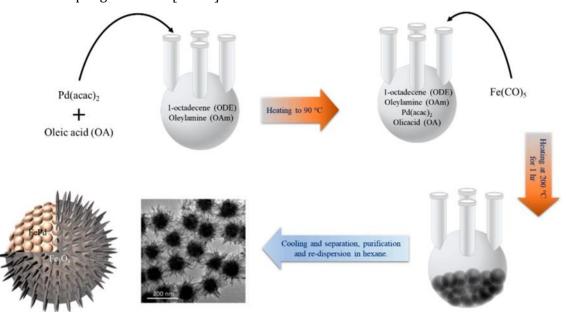


Figure 8. Synthetic procedure of urchin-like FePd-Fe₃O₄ [78]

A simple route based on time-dependent growth was performed to synthesize nanospheres Pd/Fe_3O_4 (**Figure 9**) using $FeCl_3 \cdot 6H_2O$ as the single iron resource, polyvinylpyrrolidone (PVP) as the capping

agent, and sodium acetate as the precipitation agent. To investigate the catalytic activity of the catalyst Heck reaction of iodobenzene and styrene was selected which is illustrated in **Scheme 28** [79, 80].

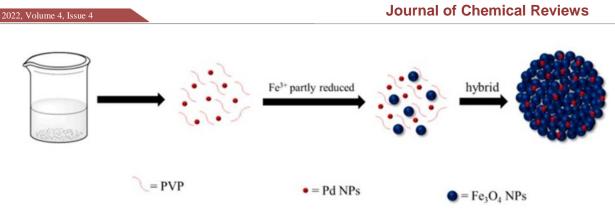
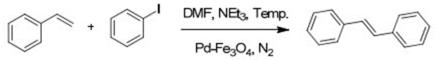
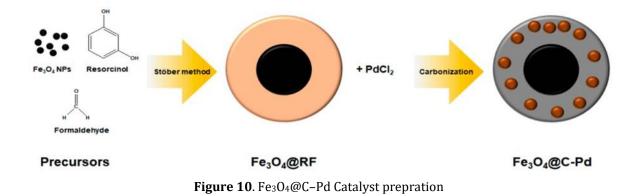


Figure 9. Synthetic procedure of Pd/Fe₃O₄ nanospheres [79, 80]



Scheme 28. Heck reaction using Pd/Fe₃O₄ nanospheres [79, 80]

 $Fe_3O_4@C-Pd$ catalyst synthesis was proceed via Stöber method in the synthesis of resin spheres composed of resorcinol-formaldehyde (RF) which were transformed to carbon spheres (**Figure 10**). The catalytic efficiency of the synthetic nanocomposite was studied in the Suzuki coupling reactions of diverse aryl halides and aryl boronic acids [81-84].

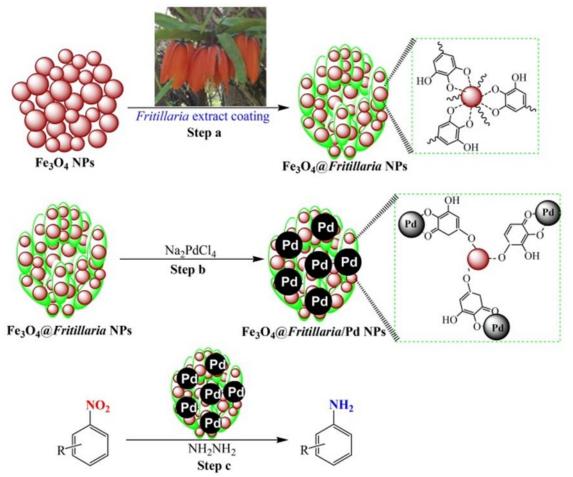


4.2 Flower-Like organic capping agent of hybrid Fe₃O₄ NPs

Palladium nanoparticles fabricated magnetic Fe_3O_4 nanocomposite over Fritillaria imperialis flower extract synthesized to many uses such as as using as an efficient recyclable catalyst for the

reduction of nitroarenes. In this catalyst, hybrid magnetic nanocomposite Fe_3O_4 NPs are at core and Pd NPs are at outer shell. For the goal synthasis, Fe_3O_4 nanocomposite, Fe_3O_4 @Fritillaria using the plant extract, and Fe_3O_4 @Fritillaria/Pd NPs was prepared, respectively (**Scheme 29**) [85].

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Scheme 29. Synthetic steps of Fe₃O₄@Fritillaria/Pd to reduce nitroarenes [85]

5. Conclusion

Fe₃O₄ magnetic nanoparticles and their hybrids display capable applications in heterogeneous catalysis because of their ease of separation and good reusability. Preparation techniques of these nanocomposites are undergoing rapid development. In this report, we highlight the preparation of support materials to develop the quality of magnetically recoverable catalysts. Typical advancement on preparation of surfacemodified MNPs was illustrated to obtain different type of Fe₃O₄ magnetic nanomaterials. Progressive types of Fe₃O₄ nanoparticles and their Hybrids as catalysts will be prepared in the future which will impress other type of known and unknown organic reactions.

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Conflict of Interest

The author declares that there is no conflict of interest.

Orcid:

Heshmatollah Alinezhad <u>https://www.orcid.org/0000-0002-7189-2961</u> Parvin Hajiabbas Tabar Amiri <u>https://www.orcid.org/0000-0001-9065-1779</u> Raad Muslim Muhiebes <u>https://www.orcid.org/0000-0002-4835-0873</u> Yasser Fakri Mustafa <u>https://www.orcid.org/0000-0002-0926-7428</u>

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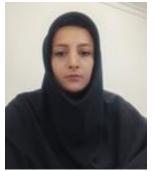
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Parvin Hajiabbas Tabar Amiri: She was born in1984 in Babol, Mazandaran, Iran. She received her B.Sc. degree in chemistry from Tehran University, Tehran, Iran in 2006, her M.Sc. degree in organic chemistry from Tehran University, Tehran, Iran, in 2010 and her Ph.D degree in organic chemistry at Alzahra University, Tehran, Iran in 2015. She has various teaching experiences, such as Organic Chemistry, General chemistry, Spectrometric analysis and etc. She has many published work in reputable international publishing houses and reviewer in many international journals. She is presently enduring her researches in the synthesis of organic compounds, heterocycles, natural products and medicinal compounds.



Sahar Mohseni Tavakkoli: She was born in1983 in Ghaemshahr, Mazandaran, Iran. She received her B.Sc. degree in chemistry from University of Mazandaran, Babolsar, Iran in 2007, her M.Sc. degree in organic chemistry from University of Mazandaran, Babolsar, Iran, in 2010 and her Ph.D degree in organic chemistry from University of Mazandaran, Babolsar, Iran in 2014. She is presently working in fertilizer production company.





of Pharmacy and Chemistry.

Raed Muslim Muhibes: He was born in Baghdad, Iraq, in 1978. He received his B.Sc. in Chemistry from the College of Science at the University of Baghdad in 2007. Also, he acquired the M.Sc. and Ph.D. degrees in Organic Chemistry from the College of Chemistry/College of Sciense / Southern Fdrution University of Russian, Baghdad, Iraq, in 2014 and 2021, respectively. He had various teaching experiences, such as Organic Chemistry, Analytical Chemistry, Biochemistry. Also, he is an editorial member of several documented journals, such as, Journal of Medicinal and Chemical Sciences, Eurasian Chemical Communications, Chemical Methodology and Asian Journal of Green Chemistry.

Yasser Fakri Mustafa: He was born in Mosul, Iraq, in 1976. He received his B.Sc. in Pharmacy from the College of Pharmacy at the University of Mosul in 1999. Also, he acquired the M.Sc. and Ph.D. degrees in Pharmacy/Pharmaceutical Chemistry from the College of Pharmacy/University of Mosul, Mosul, Iraq, in 2005 and 2017, respectively. He had various teaching experiences, such as organic pharmaceutical chemistry, inorganic pharmaceutical chemistry, chemistry of natural products, chemotaxonomy, and heterocyclic compounds. Also, he is an editorial member of several documented journals, such as the Iraqi Journal of Pharmacy, Mosul Journal of Nursing, Journal of Medicinal and Chemical Sciences, Eurasian Chemical Communications, and the International Journal

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