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Ionic Liquids Immobilized on Magnetic Nanoparticles

Masoud Mokhtary

Additional information is available at the end of the chapter

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Abstract

Ionic liquids (ILs) immobilized on supports are among the most important derivatives of ILs. The immobilization process of ILs can transfer their desired properties to substrates. The combination of the advantages of ILs with those of support materials will derive new performances while retaining the properties of both moieties. As green media in organic catalytic reactions, based on utilizing the ability of ILs to stabilize the catalysts, they have many advantages over free ILs, including avoiding the leaching of ILs, reducing their amount, and improving the recoverability and reusability of both themselves and catalysts. This has critical significance from both environmental and economical points of view. Recently, ionic liquids immobilized on magnetic nanoparticles (MNPs) have drawn increasing attention in catalytic reactions and separation technologies and achieved substantial progress. The combination of MNPs and ILs gives magnetic-supported ionic liquids, which exhibit the unique properties of ILs as well as facile separation by an external magnetic field. The excellent efficiency of this kind of immobilized ionic liquids offers a great advantage compared with other sorts of magnetic supports. In this chapter, the green catalytic processes and recent advances in organic synthesis catalyzed by ionic liquids immobilized on magnetic nanoparticles are highlighted.

Keywords: ionic liquids, magnetic nanoparticles, green synthesis, retrievable catalysts

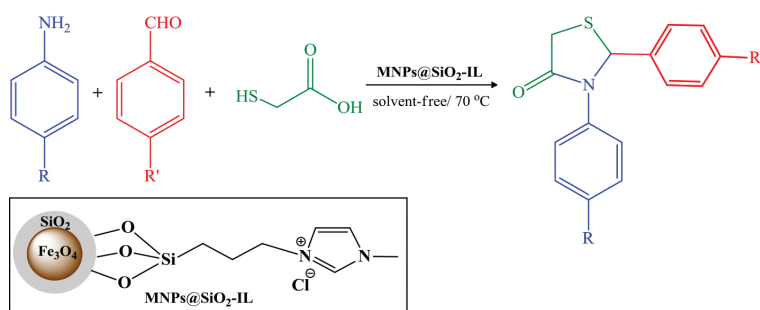
1. Introduction

Ionic liquids (ILs) are progressively being studied for targeted chemical tasks due to their unique chemical and physical properties such as nonvolatility, nonflammability, thermal stability and controlled miscibility [1]. In spite of the fact that ILs contained several advantages, but their extensive practical application was still prevented by some drawbacks like high viscosity, difficult recyclability and high cost of ILs in large-scale utilization [2]. Therefore, in

order to decrease these difficulties, immobilized IL had been prepared as a new heterogeneous catalyst with the useful features of ILs and inorganic acids for catalyzed reactions [3]. Among several usages of ILs in organic chemistry, imidazolium ionic liquid-type catalysts indicate one of the most successful developments [4]. This chapter focuses on the recent progress in organic synthesis catalyzed by ionic liquids immobilized on magnetic nanoparticles.

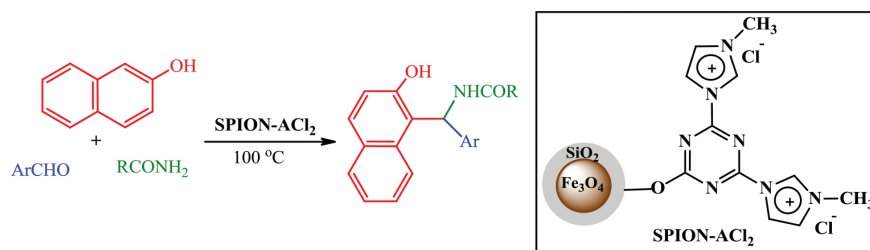
2. Ionic liquids immobilized on MNPs in multicomponent reactions

Recent studies represent that magnetic nanoparticles (MNPs) are excellent supports for ILs owing to their good stability, easily preparation and functionalization, high surface area, low toxicity and simple separation by external magnetic attractions [5]. These special features have made MNPs a convenient alternative to catalyst supports. As an example, a magnetically $\text{Fe}_3\text{O}_4@/\text{SiO}_2$ nanoparticle-immobilized ionic liquid (MNP@ SiO_2 -IL) was prepared by Azgomi and Mokhtary [6]. The MNP@ SiO_2 -IL was assessed as a recyclable catalyst for the one-pot synthesis of 1,3-thiazolidin-4-ones with good to great efficiency under solvent-less conditions. The catalyst could be simply recycled using a magnetic field and reused for 10 times with no considerable loss in its activity (**Scheme 1**).



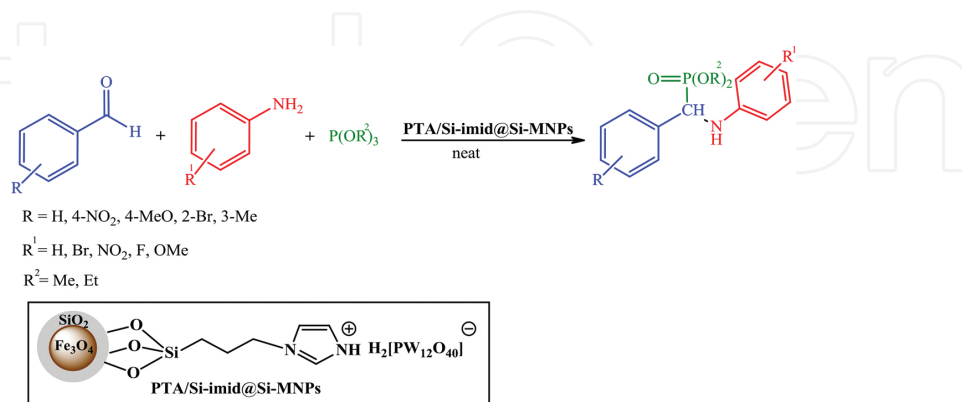
Scheme 1. One-pot synthesis of 1,3-thiazolidin-4-ones catalyzed using MNP@ SiO_2 -IL.

A dicationic ionic liquid immobilized on superparamagnetic iron oxide nanoparticles (SPION- AlCl_2) has been used as a green and powerful catalyst to effectively synthesis derivatives of β -amidoalkylnaphthol with high to excellent yields [7]. This catalyst could be recovered and reused for at least six times with no loss in catalytic activity (**Scheme 2**).



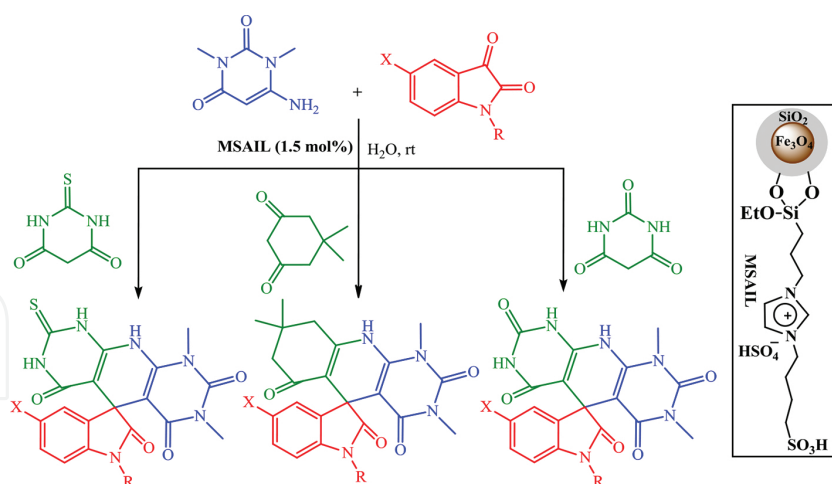
Scheme 2. Synthesis of β -amidoalkylnaphthols catalyzed by SPION- AlCl_2 .

The synthesis of a magnetic nanoparticle-supported polyoxometalate has been reported, and this nanoparticle has been used as an efficient heterogeneous catalyst to prepare α -amino phosphonates under solvent-less conditions at room temperature [8]. The catalyst is easily recovered by simple magnetic separation and can be recycled several times with no considerable loss in its catalytic activity (**Scheme 3**).



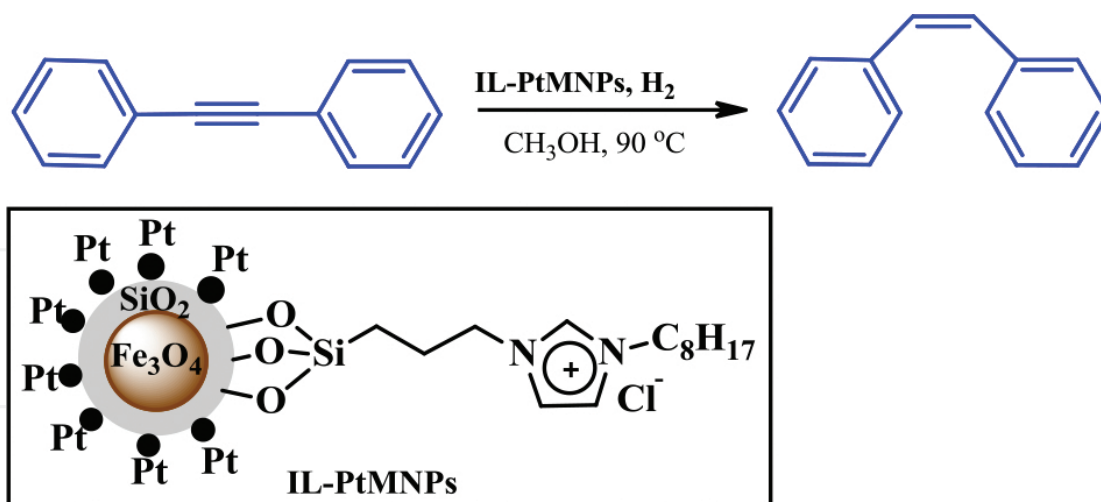
Scheme 3. PTA/Si-imid@Si-MNPs catalyzed synthesis of α -aminophosphonates.

In another research, a magnetic-supported acidic ionic liquid has been prepared and evaluated in one-pot synthesis of spirooxindoles [9]. Main properties of this approach are simplicity, low price, high efficiency, wide application scope, reusability and easy retrieval of the catalyst by an external magnet (**Scheme 4**).



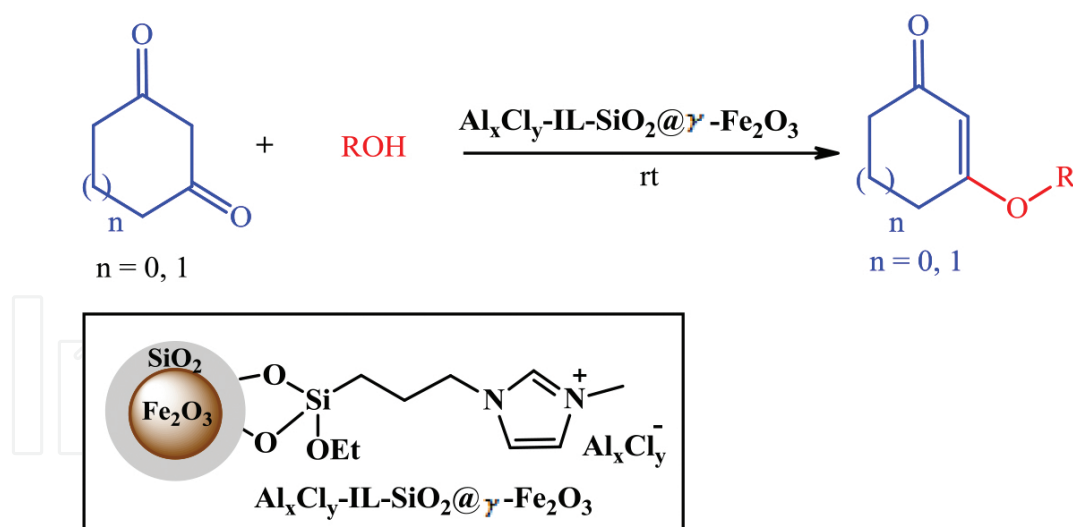
Scheme 4. Different synthesized spirooxindoles catalyzed by MSAIL.

A chemoselective hydrogenation of α,β -unsaturated aldehydes and alkynes was successfully demonstrated by Abu-Reziq et al. [10]. The Pt nanoparticles were adsorbed on the IL-functionalized MNPs via ion exchange with K₂PtCl₄ following by reduction with hydrazine. The diphenylacetylene was hydrogenated in methanol using this catalyst at 90°C under hydrogen pressure with the selective preparation of *cis*-alkenes (**Scheme 5**).



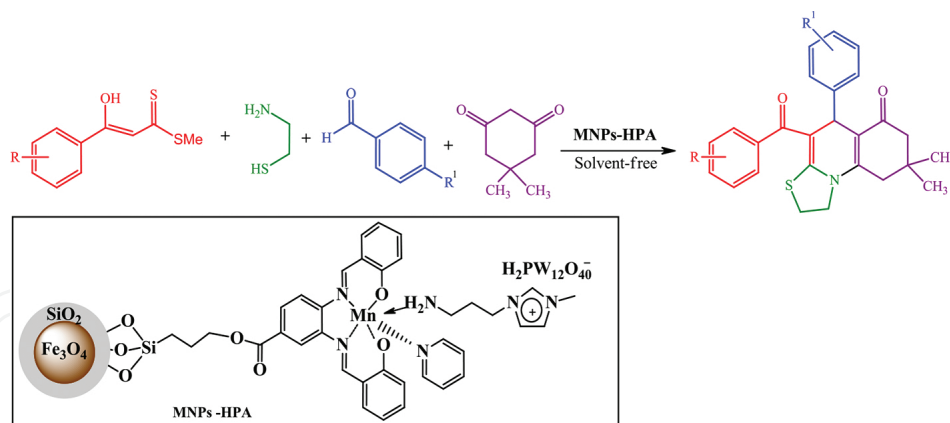
Scheme 5. Hydrogenation of diphenylacetylene in the presence of IL-PtMNPs.

Anchoring $\text{Al}_x\text{Cl}_y\text{-IL}$ onto the silica-coated $\gamma\text{-Fe}_2\text{O}_3$ particles afforded $\text{Al}_x\text{Cl}_y\text{-IL-SiO}_2@\gamma\text{-Fe}_2\text{O}_3$ [11]. The catalyst assessment was performed to synthesis of β -ketoenol ethers (**Scheme 6**). The effectiveness of immobilized catalyst was confirmed, and the products were produced in high with excellent efficiency at ambient temperature. Furthermore, the catalyst could be simply retrieved using an external magnet and reused for six times with no considerable loss in its catalytic activity.



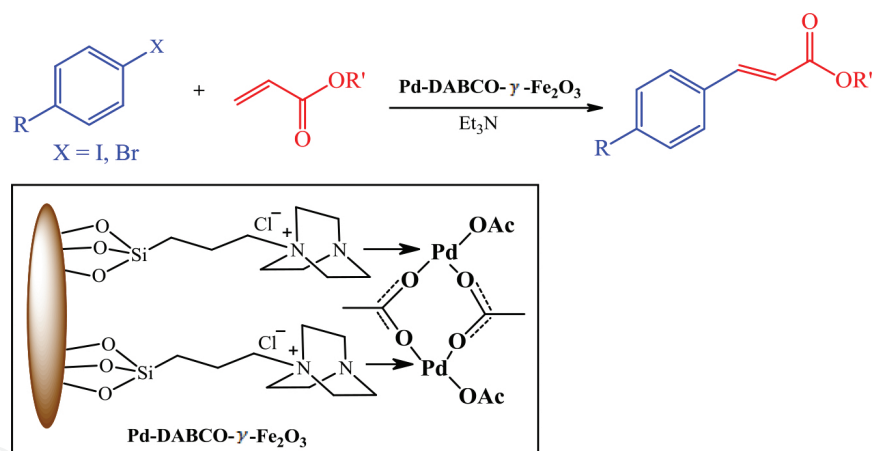
Scheme 6. Synthesis of β -keto enol ethers by $\text{Al}_x\text{Cl}_y\text{-IL-SiO}_2@\gamma\text{-Fe}_2\text{O}_3$.

The synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2/\text{salen}/\text{Mn}/\text{IL}/\text{HPW}$ has been performed through attaching $\text{H}_3\text{PW}_{12}\text{O}_{40}$ on magnetite nanoparticles modified with ionic liquid [12]. The catalyst was used for one-pot synthesis of thiazoloquinolines, in good to great efficiency under solvent-less conditions (**Scheme 7**). The catalyst could be simply recovered using a magnetic field and reused ten times with no significant loss in its activity.



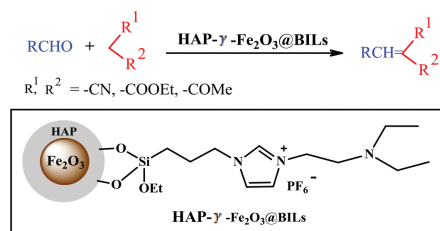
Scheme 7. Synthesis of thiazoloquinolines in the existence of MNPs-HPW.

Sobhani and Pakdin-Parizi have improved an efficient heterogeneous catalyst for the Mizoroki–Heck cross-coupling [13]. In this technique, γ - Fe_2O_3 magnetic nanoparticles immobilized with palladium-DABCO complex ($\text{Pd-DABCO-}\gamma\text{-Fe}_2\text{O}_3$) were prepared as a recyclable catalyst for Mizoroki–Heck cross-coupling reaction of aryl halides with olefins whose activity is not changed even after five times under solvent-less conditions (**Scheme 8**).



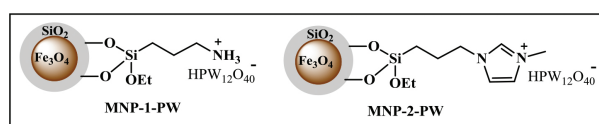
Scheme 8. Mizoroki–Heck cross-coupling reaction using $\text{Pd-DABCO-}\gamma\text{-Fe}_2\text{O}_3$.

The synthesis of hydroxyapatite-encapsulated magnetic nanoparticles immobilized with diethyl aliphatic amine basic ionic liquids ($\text{HAP-}\gamma\text{-Fe}_2\text{O}_3\text{@BILs}$) was reported, and it was applied as effective magnetic catalysts for Knoevenagel condensation reactions in aqueous medium (**Scheme 9**). The reactants were quantitatively converted under moderate conditions; the catalyst activity showed no significant loss after recovering via suitable magnetic field. The magnetic catalyst showed an excellent efficiency compared with homogeneous basic ionic liquid catalyst and the basic ionic liquid-modified polystyrene resin catalyst that was attributed to the cooperation between the base sites produced through framework HAP and the supported basic ionic liquids [14].



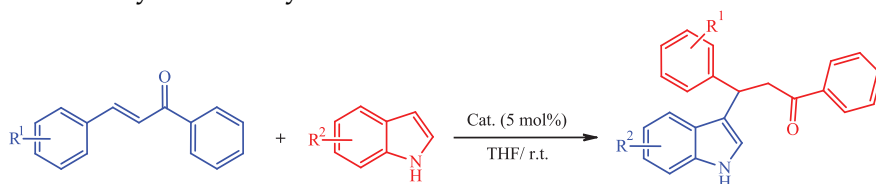
Scheme 9. A Knoevenagel condensation reaction catalyzed by HAP- γ -Fe₂O₃@BILs.

Magnetic nanoparticles supported with polyoxometalates (POMs) via ionic interaction were acquired through an easy sonication between modified magnetic nanoparticles and polyoxometalates. This material can be used as a highly active acid catalyst and as a catalyst support for chiral amines [15]. The immobilization of POM on MNPs was obtained by sonication of a mixture of MNPs (MNP-1 or MNP-2) and POM (H₃PW₁₂O₄₀) in dry THF (**Scheme 10**).



Scheme 10. Structure of MNP-1-PW and MNP-2-PW catalysts.

The Friedel-Crafts reaction of indole and chalcone was selected to examine the acidic catalytic activity and reusability of the prepared MNP-1-PW and MNP-2-PW catalysts. As observed in **Table 1**, the reactions between diverse chalcones and indoles continued efficiently to result the desired products with a high efficiency. Both magnetic POMs showed excellent activity and reusability for 12 recycles.



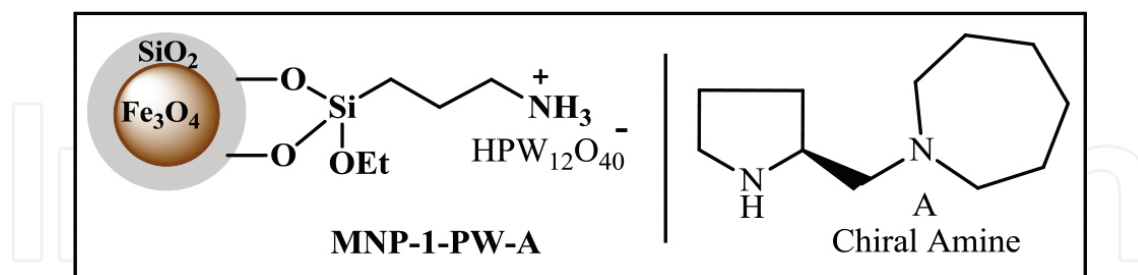
Entry	R ¹ R ²		MNP-1-PW		MNP-2-PW	
	t/h	Yield ^b (%)	t/h	Yield ^b (%)	t/h	Yield ^b (%)
1	H	5-MeO	20	93	20	94
2	H	5-Me	20	96	20	96
3	H	5-Br	7	98	6	97
4	H	5-Cl	7	97	6	97
5	H	5-I	7	99	6	98
6	H	6-Cl	7	98	6	98
7	4-Cl	H	12	90	12	92
8	4-Me	H	12	88	12	90

^aReaction conditions: catalyst (5 mol%), indole derivative (0.25 mmol), chalcone derivative (0.20 mmol) and THF (0.2 ml).

^bIsolated yield.

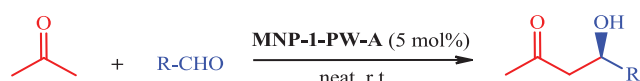
Table 1. Friedel-Crafts reactions of indoles and chalcones^a.

Also, chiral amine hybrids with magnetic POMs were easily prepared by mixing MNP-PW and chiral amine via sonication in dry THF (**Scheme 11**).



Scheme 11. Magnetic POM supported chiral amine catalyst MNP-1-PW-A.

The MNP-PW-immobilized chiral amine catalysts were next applied in typical enamine-based asymmetric direct aldol condensations. Acetone reacted with different aromatic aldehydes in the presence of 5 mol% of MNP-1-PW-A, to give the desired products with high efficiency and enantioselectivities (**Table 2**).



Entry	R	t/h	Yield ^b (%)	ee (%) ^c
1	2-NO ₂ C ₆ H ₄	12	83	89
2	3-NO ₂ C ₆ H ₄	12	87	89
3	4-CF ₃ C ₆ H ₄	30	81	90
4	2-CNC ₆ H ₄	30	80	87
5	2-ClC ₆ H ₄	48	72	87
6	2-BrC ₆ H ₄	48	77	88

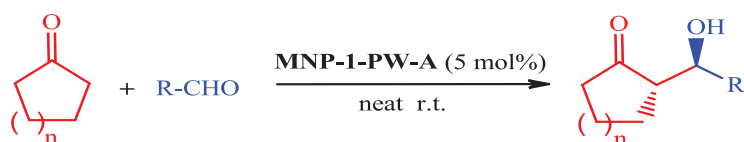
^aReaction conditions: catalyst (5 mol%), acetone (0.20 mL) and aldehyde (0.25 mmol).

^bIsolated yield.

^cDetermined by chiral HPLC.

Table 2. MNP-1-PW-A catalyzed aldol reaction of acetone^a.

Also, aldol donors such as cyclohexanone and cyclopentanone worked very well in this catalytic system (**Table 3**). Moreover, the outcomes achieved from the similar reactions with POM-chiral amine hybrid PW-A given in **Table 3** (entries 1 vs. 2). The magnetic POM-immobilized catalyst MNP-1-PW-A showed slightly higher stereoselectivity and enantioselectivity albeit with a little loss of activity. The resulted noncovalently immobilized catalyst could be reused up to 11 times with essentially no loss of activity and enantioselectivity.



Entry	N	R	t/h	Yield ^b (%)	Syn/anti ^c	ee ^d (%)
1	1	4-NO ₂ C ₆ H ₄	5	97	6:94	97
2 ^e	1	4-NO ₂ C ₆ H ₄	6	86	23:77	95
3	1	2-NO ₂ C ₆ H ₄	5	97	24:76	98
4	1	3-NO ₂ C ₆ H ₄	5	96	16:84	98
5	1	4-CF ₃ C ₆ H ₄	12	88	17:73	97
6	1	4-ClC ₆ H ₄	48	86	20:80	96
7	2	2-NO ₂ C ₆ H ₄	8	98	13:87	99
8	2	3-NO ₂ C ₆ H ₄	8	97	14:86	98
9	2	4-NO ₂ C ₆ H ₄	6	97	14:86	97
10	2	4-CF ₃ C ₆ H ₄	11	93	13:87	98
11	2	4-ClC ₆ H ₄	48	92	17:83	98

^aReaction conditions: catalyst (5 mol%), ketone (0.20 mL) and aldehyde (0.25 mmol).

^bIsolated yield.

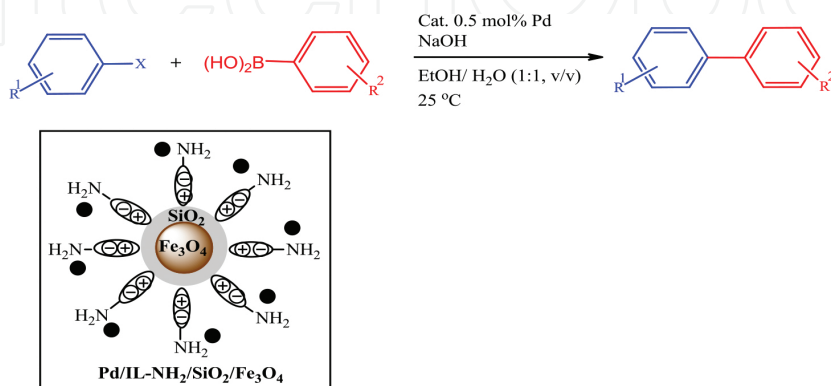
^cDetermined by chiral HPLC.

^dDetermined by chiral HPLC.

^ePW-A (1 mol%) was employed.

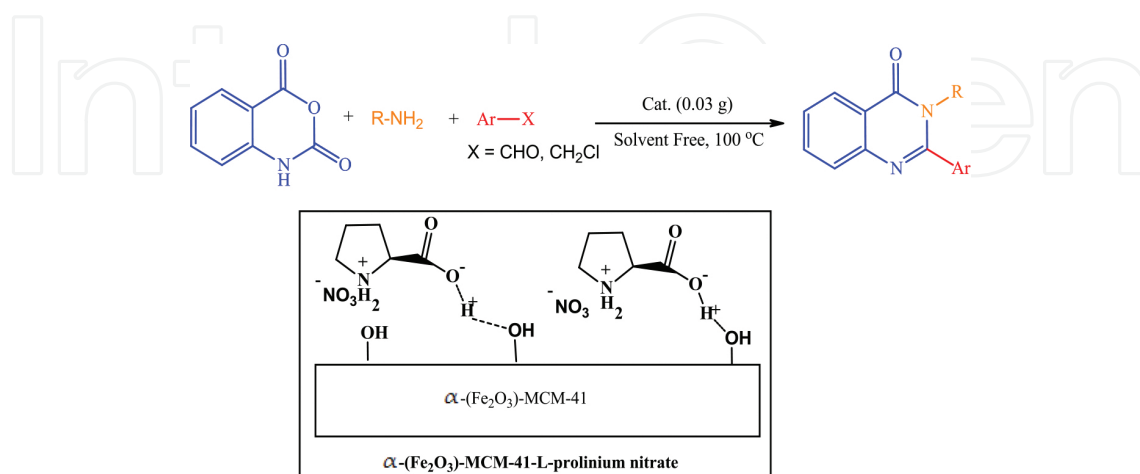
Table 3. MNP-1-PW-A catalyzed aldol reaction of different aldol donors^a.

A suitable approach has been improved for preparation of retrievable Pd catalyst using immobilization of palladium nanoparticles on magnetic nanoparticles modified with functional ionic liquid [16]. The amine functionalized ionic liquid immobilized Pd nanoparticles in the Pd/IL-NH₂/SiO₂/Fe₃O₄ catalyst demonstrates great catalytic activity for a wide diversity of aryl iodides and bromides in the Suzuki coupling reactions at ambient temperature (**Scheme 12**). Furthermore, the catalyst is able to be good distributed in the reaction media, simply retrieved from the reaction mixture by using a magnet, and reused for several times with no significant loss in activity. Because of all these advantages, this procedure is a green and appropriate for other important reactions catalyzed with metal.



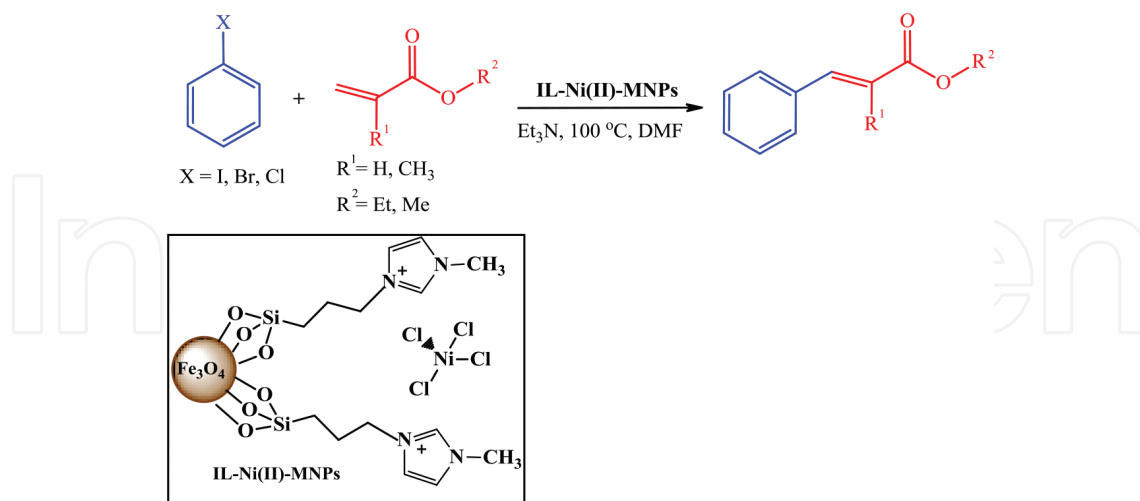
Scheme 12. The Suzuki coupling reactions of aryl iodides and bromides by Pd/IL-NH₂/SiO₂/Fe₃O₄ catalyst.

α -Fe₂O₃-MCM-41 immobilized with amino acid ionic liquid was prepared as a retrievable catalyst for synthesizing quinazolin-4(3*H*)-ones at ambient temperature in short reaction times under oxidant and solvent-less conditions (**Scheme 13**). It is supposed that the L-prolinium nitrate in the mesochannels of (α -Fe₂O₃)-MCM-41 might enhance the strength of Brønsted acid and oxidation power of catalytic system [17].



Scheme 13. (α -Fe₂O₃)-MCM-41-L-prolinium nitrate for the synthesis of quinazolin-4(3*H*)-ones.

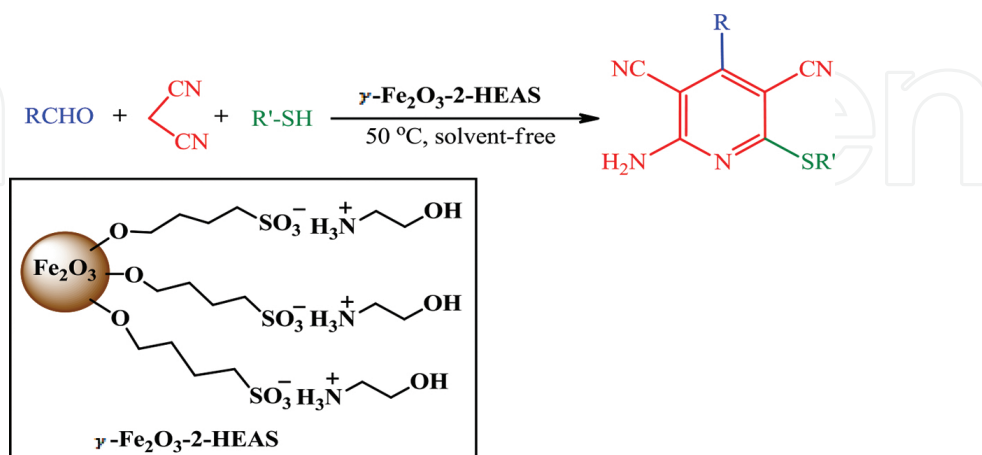
Moreover, there is a report on synthesis of magnetic nanoparticles immobilized with Ni²⁺ ion-containing 1-methyl-3-(3-trimethoxysilylpropyl) imidazolium chloride ionic liquid as a recoverable nanocatalyst for the Heck reaction at 100°C, and it can be applied after washing with no loss in activity (**Scheme 14**) [18].



Scheme 14. Heck reaction catalyzed by IL-Ni(II)-MNPs.

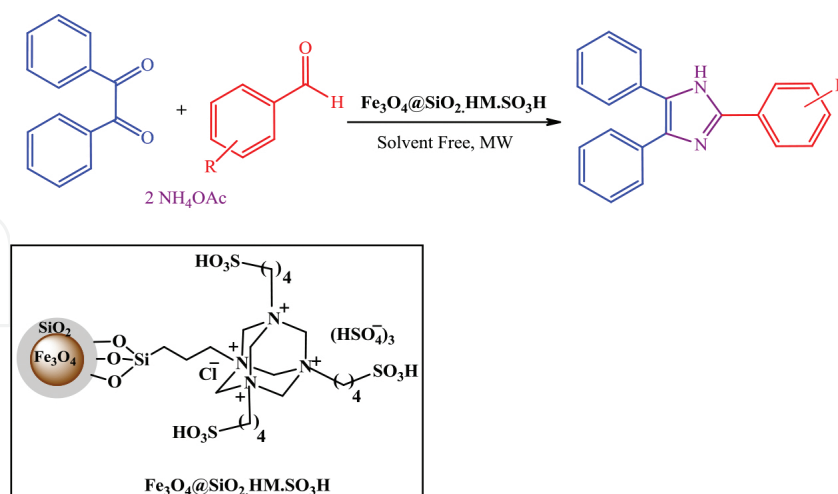
γ -Fe₂O₃ nanoparticles immobilized with 2-Hydroxyethylammonium sulphonate (γ -Fe₂O₃-2-HEAS) were prepared through the reaction of n-butylsulfonated γ -Fe₂O₃ with ethanolamine [19]. Here, the catalyst effectively increases the condensation of both aliphatic and aromatic

aldehydes and thiols with malononitrile resulting in 2-amino-3,5-dicarbonitrile-6-thio-pyridines in good to excellent efficiency under solvent-less conditions (**Scheme 15**). Separating the product and recycling the catalyst are easily performed using a suitable external magnet. The catalyst can be reused for five times with no significant loss in its catalytic activity.



Scheme 15. Synthesis of 2-amino-3,5-dicarbonitrile-6-thio-pyridines catalyzed using $\gamma\text{-Fe}_2\text{O}_3$ MNPs.

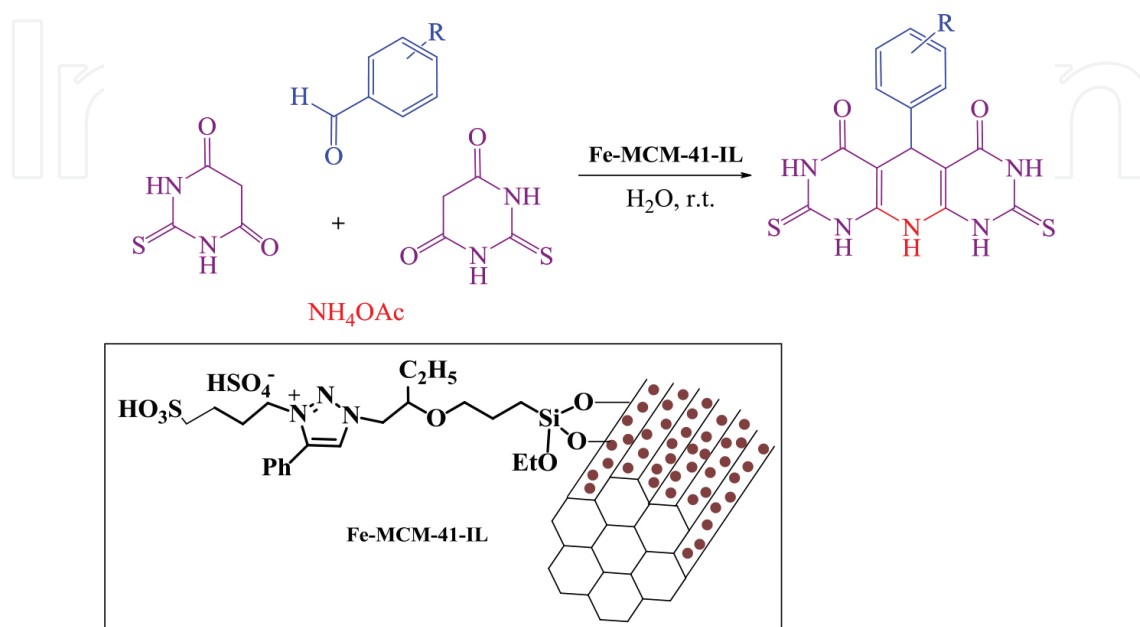
An effective synthesis of 2,4,5-trisubstituted imidazoles is achieved by silica-coated magnetite nanoparticles immobilized with multi- SO_3H functionalized acidic ionic liquid (**Scheme 16**). Because of high performance, recoverability, short reaction times, efficiency of products and operational simplicity, this process is an attractive substitute for the green synthesis of 2,4,5-trisubstituted imidazoles as biological and pharmaceutical-related substances [20].



Scheme 16. Synthesis of 2,4,5-trisubstituted imidazoles catalyzed by $\text{Fe}_3\text{O}_4@\text{SiO}_2.\text{HM}.\text{SO}_3\text{H}$.

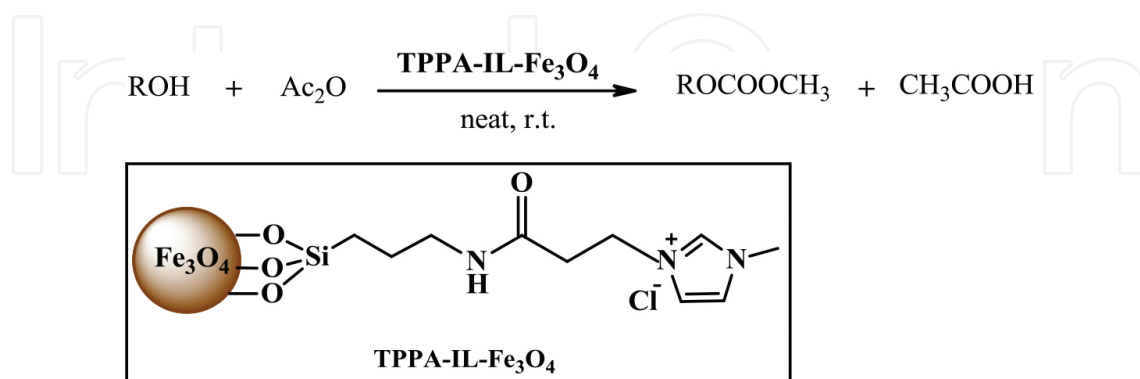
An ionic liquid stabilized iron-containing mesoporous silica nanoparticles (Fe-MCM-41-IL) was synthesized by fixing a triazolium ionic liquid on Fe-coated MCM. The pyrimidine derivatives were synthesized through one-pot method in the presence of Fe-MCM-41-IL as an

effective heterogeneous acidic IL catalyst from aldehydes, 2-thiobarbituric acid and ammonium acetate under moderate condition in excellent efficiencies (**Scheme 17**). This procedure is greener compared with other reported methods because of its moderate conditions of reaction, excellent efficiencies and simple recycling of the catalyst [21].



Scheme 17. One-pot synthesis of pyrido[2,3-d:6,5-d]dipyrimidines catalyzed by Fe-MCM-41-IL.

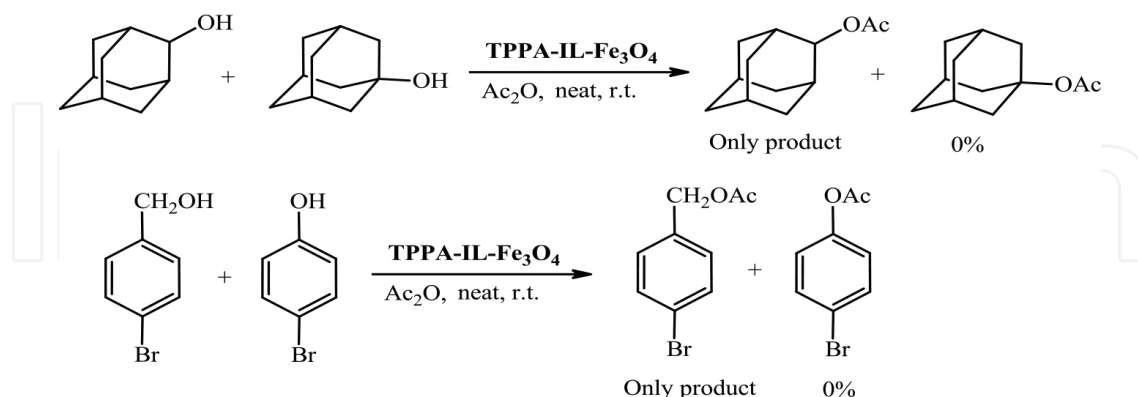
A simple and effective process has been reported for synthesizing 3-((3-(trisilyloxy)propyl)propionamide)-1-methylimidazolium chloride ionic liquid supported on magnetic nanoparticles (TPPA-IL-Fe₃O₄) [22]. The TPPA-IL-Fe₃O₄ assessed as a recoverable heterogeneous catalyst for the alcohols acetylation with acetic anhydride under moderate conditions at ambient temperature with high efficiencies (**Scheme 18**).



Scheme 18. Acetylation of alcohols catalyzed by TPPA-IL-Fe₃O₄.

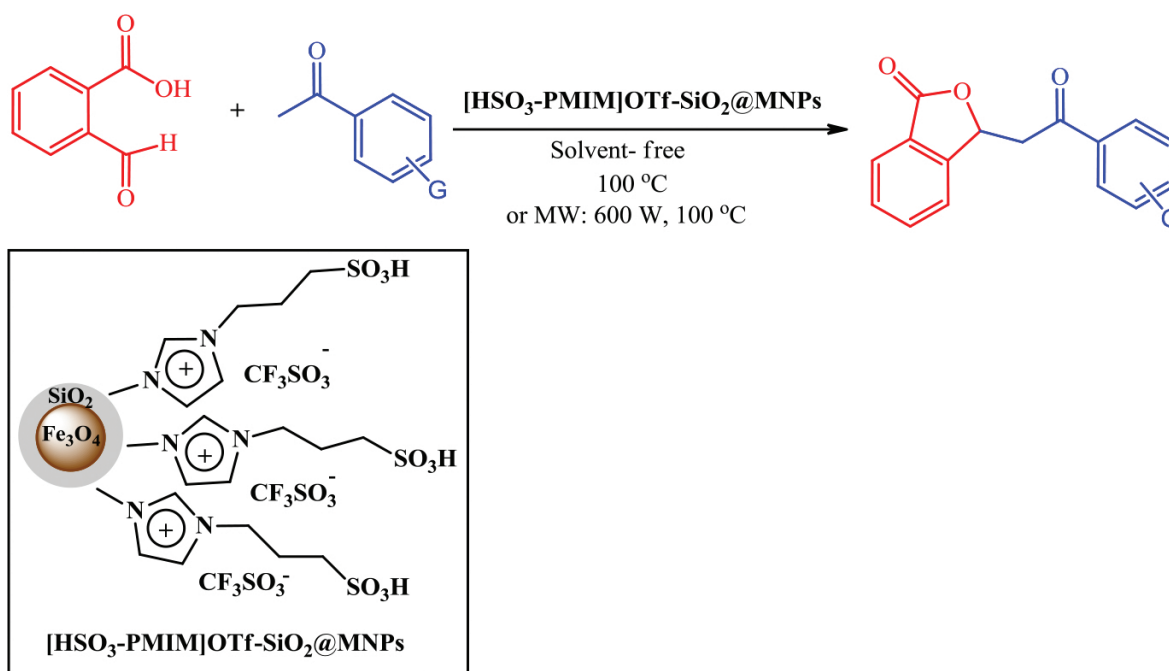
The hydroxyl groups were chemoselectively acetylated in the existence of other reactive groups by using the synthesized catalyst. The acetylation of 4-bormobenzyl alcohol did occur

selectively in the presence of 4-bromophenol, and the hydroxyl group of phenol was intact during this reaction (**Scheme 19**).



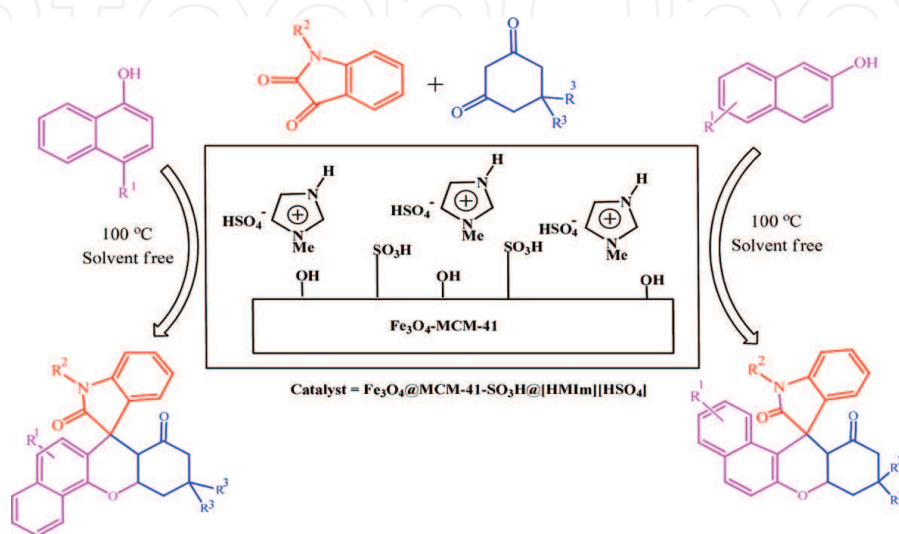
Scheme 19. Chemoselectivity of the acetylation hydroxyl groups in the presence of TPPA-IL-Fe₃O₄.

An ecologically friendly technique has been improved for preparing isobenzofuran-1(3*H*)-ones in the existence of [HSO₃PMIM]OTf-SiO₂@MNPs as a highly retrievable catalyst under solvent-less thermal conditions and MW irradiation [23]. Mono- and bis-isobenzofuran-1(3*H*)-ones was effectively synthesized in the presence of this catalyst under thermal conditions and MW irradiation. The considerable advantages of this procedure for the synthesis of isobenzofuran-1(3*H*)-ones are its simplicity, excellent yields, short times of reaction, eco-friendly and simple recycling of the catalyst (**Scheme 20**).



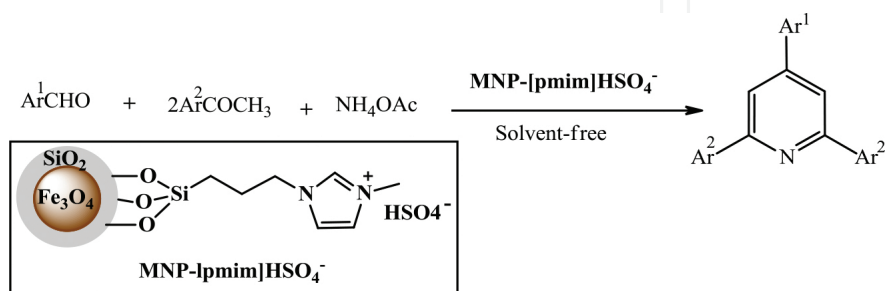
Scheme 20. Synthesis of isobenzofuran-1(3*H*)-ones catalyzed using [HSO₃PMIM]OTf-SiO₂@MNPs.

The $\text{Fe}_3\text{O}_4@\text{MCM-41-SO}_3\text{H}@\text{[HMIm][HSO}_4\text{]}$ efficiently catalyzed the one-pot three-component condensation of α or β naphthol, cyclic 1,3-diketone and isatin derivatives for the synthesis of spiro[benzoxanthene-indoline]diones (**Scheme 21**) [24]. This active catalyst was thermally stable, green, recyclable and easy to prepare. In addition, its separation of the reaction mixture is easy and it could be retrieved up to five times with no significant influence on its activity or the reaction efficiency.



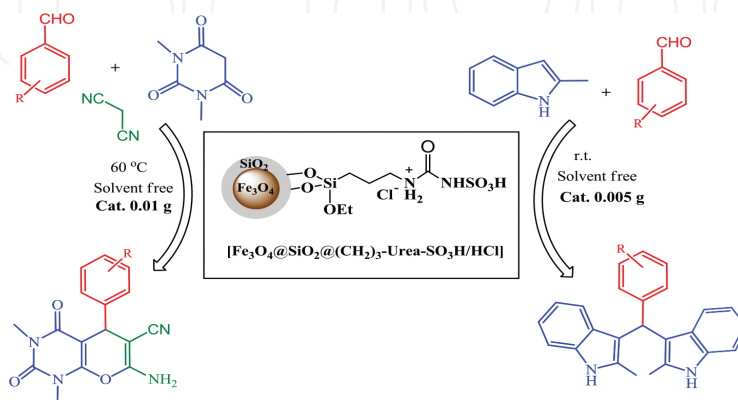
Scheme 21. Synthesis of spiro[benzoxanthene-indoline]diones catalyzed by $\text{Fe}_3\text{O}_4@\text{MCM-41-SO}_3\text{H}@\text{[HMIm][HSO}_4\text{]}$.

The silica-coated magnetic particles immobilized with 1-methyl-3-(triethoxysilylpropyl) imidazolium chloride provided the corresponding supported ionic liquid. Substituting the Cl^- anion through treatment with H_2SO_4 resulted in Bronsted ionic liquid 1-methyl-3-(triethoxysilylpropyl) imidazolium hydrogensulfate (MNP-[pmim]HSO_4) [25]. The activity of the immobilized ionic liquid was studied as a catalyst for synthesizing the polysubstituted pyridines using condensation of aromatic aldehydes with acetophenones and ammonium acetate in modest to excellent efficiency under solvent-less conditions (**Scheme 22**). The recycling of the catalyst can be simply performed using an external magnet, and it can be reapplied for at least seven times with no change in its activity.



Scheme 22. Synthesis of triarylpyridines catalyzed by MNP-[pmim]HSO_4^- .

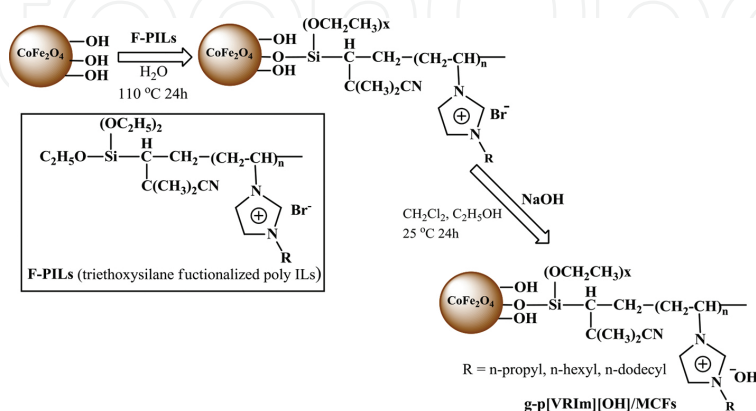
Silica-coated Fe_3O_4 magnetic nanoparticles immobilized with urea-based ionic liquid $[\text{Fe}_3\text{O}_4@\text{SiO}_2@(\text{CH}_2)_3\text{-Urea-SO}_3\text{H/HCl}]$ have been prepared [26]. The catalyst was studied for the synthesis of bis(indolyl)methane derivatives through the reaction between 2-methylindole and aldehydes at ambient temperature under solvent-free conditions. In addition, pyrano[2,3-d]pyrimidinones were synthesized in the presence of the catalyst through the one-pot condensation reaction of 1,3-dimethylbarbituric acid, aldehydes and malononitrile under solvent-less conditions at 60°C (Scheme 23).



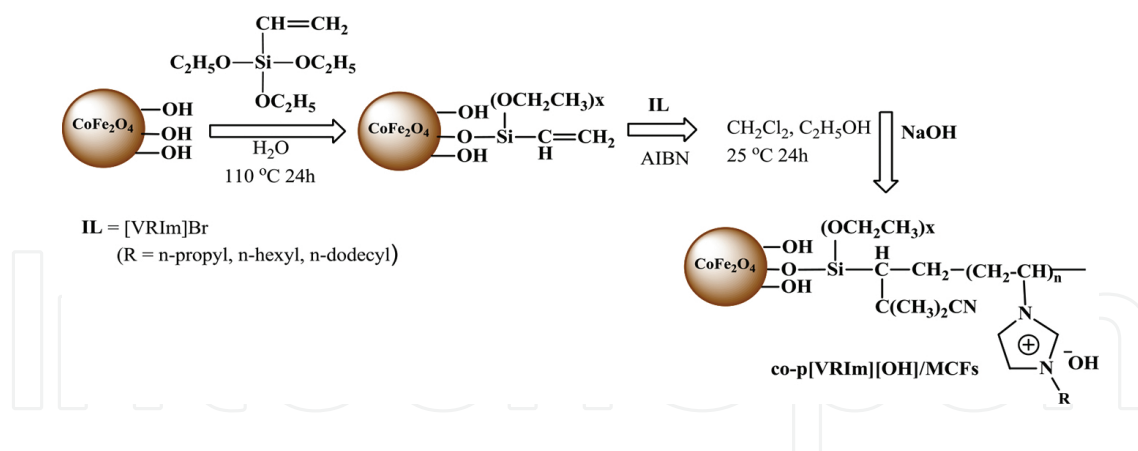
Scheme 23. Synthesis of bis(indolyl)methanes and pyrano[2,3-d]pyrimidinones catalyzed by MNPs@ILs.

3. Polymeric ionic liquids immobilized on magnetic nanoparticles

The successful synthesis of magnetic CoFe_2O_4 nanoparticles coated with basic poly(ionic liquids) was carried out, and the catalyst synthesized using the surface grafting technique (*g*-*p*[VRIm][OH]/MCFs) (Scheme 24) had a better stability, greater loading of ionic liquids and good paramagnetism compared with that synthesized through the conventional copolymerization technique (*co*-*p*[VRIm][OH]/MCFs) (Scheme 25) [27].

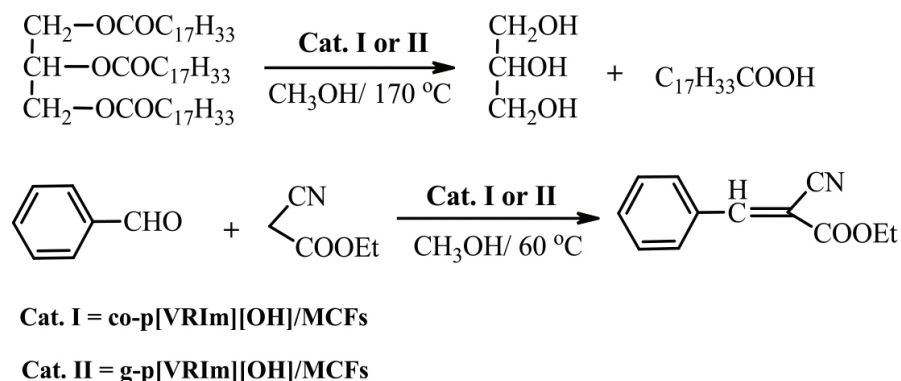


Scheme 24. The procedure for preparation of *g*-*p*[VRIm][OH]/MCFs.



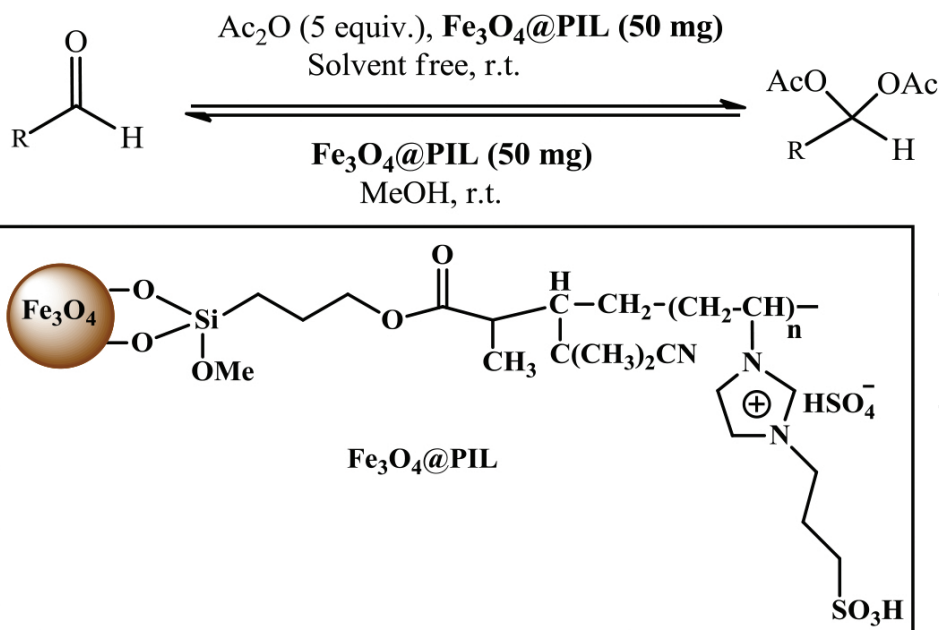
Scheme 25. The procedure for preparation of co-p[VRIm][OH]/MCFs.

The activities of the catalysts were studied for the Knoevenagel condensation reaction of benzaldehyde with ethyl cyanoacetate and for the transesterification of glycerol trioleate (TG) with methanol (**Scheme 26**). The results showed that in contrast to the sample synthesized by the copolymerization technique, the catalysts had a good catalytic efficiency.



Scheme 26. The transesterification of glycerol trioleate (TG) and the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate.

Because of the influence of steric hindrance and active sites, g-p[VDoIm][OH]/MCFs showed a higher catalytic activity than co-p[VDoIm][OH]/MCFs. The conversion of benzaldehyde was around 97% for g-p[VDoIm][OH]/MCFs higher than 72.5% for co-p[VDoIm][OH]/MCFs that was in accordance with the reaction of transesterification. Moreover, *N*-propyl-sulfonic acid bonded onto magnetic nanoparticle coated with poly(ionic liquid) ($\text{Fe}_3\text{O}_4\text{@PIL}$) catalyst was successfully synthesized through polymerizing functionalized vinylimidazolium in the existence of magnetic nanoparticles with modified surface [28]. The obtained catalyst is indicated to be an effective heterogeneous acidic nanocatalyst for synthesizing 1,1-diacetal from aldehydes under solvent-less conditions and ambient temperature in a good efficiency. In addition, the catalyst demonstrates an excellent activity for the deprotection reaction of acetals (**Scheme 27**). The catalyst has an excellent thermal stability and reusability because the surface of the magnetic nanoparticles is coated with polymer layers.



Scheme 27. Acetylation of aldehydes and their deprotection using $\text{Fe}_3\text{O}_4\text{@PIL}$ as catalyst.

4. Summary and outlook

According to this chapter, there are some interesting new advancements in ionic liquids supported on magnetic nanoparticles. There is a clear procedure including silica coating of magnetic nanoparticle core followed by functionalization using proper alkoxy silane derivatives. Easy modification of the magnetic iron oxide surfaces with organic ligands increases the adsorption of catalytically active metal nanoparticles, as highlighted with palladium-mediated C-C coupling and Pt-catalyzed hydrogenation reactions. The high dispersity of the MNPs in different solvents is another advantage, when it exposes the surface-bound active reaction sites for the reactants in an optimized way. This lets diffusion restriction to be dominated, which is generally found in microporous or mesoporous heterogenized solids. Clearly, the unique magnetic properties of the superparamagnetic particles lead to recyclable magnetic nanoparticles immobilized with ionic liquids for several times using a suitable magnet with no significant loss in their catalytic activity. The sustainable synthesis of magnetically retrievable ionic liquids using readily available reactants will also make this field of research green. Additional interesting improvement is the poly(ionic liquids) stabilized magnetic nanoparticles as a new group of heterogeneous catalyst that is mainly attractive in organic synthesis practiced in an ecologically friendly way. In the end, future efforts for more efficient protocols will still focus on the stability, sustainability, environmental impact and considerable cost and energy savings due to the growing needs of industry. These attempts will permit a wide diversity of industrial usages for ionic liquids immobilized on magnetic nanoparticles in the future.

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