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1. Introduction

In homogeneous catalysis, the chemo-, regio-, and enantioselectivity of the catalyst is better but the difficulty of catalyst separation from the final product creates economic and environmental barriers. To overcome these drawbacks, chemists and engineers have investigated a wide range of strategies; the use of heterogeneous catalyst systems appears to be the best logical solution.¹ The vast majority of the novel heterogenized catalysts are based on silica supports, due to the fact that organic groups can be robustly anchored to the silica surface to provide catalytic centers.² The common structural feature of these materials is the anchoring of the catalytic molecule (dopant) in the pores of silica, a phenomenon that imparts unique chemical and physical properties to the resulting hybrid silica. A vast majority of the industrial, heterogeneous catalysts are high-surface area solids onto which an active component is dispersed or attached. Although attempts have been made to make all active sites on solid supports accessible for the reaction only, sites on the surface are available for catalysis, which decreases the overall reactivity of the catalyst system. To address this issue, the emerging area of nano-catalysis can ideally provide the solution as most of the catalyst surface is available for the reaction. Among them functionalized magnetic nanoparticles are very good alternatives to conventional materials as a robust, readily available, and a

Organic synthesis *via* magnetic attraction: benign and sustainable protocols using magnetic nanoferrites†

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Magnetic nano-catalysts have been prepared using simple modification of iron ferrites. The nm size range of these particles facilitates the catalysis process, as an increased surface area is available for the reaction; the easy separation of the catalysts by an external magnet and their recovery and reuse are additional beneficial attributes. Glutathione bearing nano-ferrites have been used as organocatalysts for the Paal–Knorr reaction and homocoupling of boronic acids. Nanoferrites, post-synthetically modified by ligands, were used to immobilize nanometals (Cu, Pd, Ru, *etc.*) which enabled the development of efficient, sustainable and green procedures for azide–alkynes-cycloaddition (AAC) reactions, C–S coupling, *O*-allylation of phenol, Heck-type reactions and hydration of nitriles.

high-surface-area heterogeneous catalyst support.³ They offer an added advantage of being magnetically separable, thereby eliminating the requirement of catalyst filtration after completion of the reaction. Engaged in the development of greener and sustainable pathways for organic transformations,^{4,5} nanomaterials,⁶ and nano-catalysis,⁷ herein, a simple and efficient synthesis of nano-ferrite-supported, magnetically recyclable, and inexpensive catalysts and their applications in organic synthesis are reported.

1.1. Magnetic nano-catalysts (MNC)

The applications of magnetic nano-catalysts are increasing steadily in the field of catalysis as they are designed at the nano-level, especially for heterogeneous catalysis. MNC can assist researchers in the design of catalysts with good activity, stability, selectivity and reusability by virtue of isolation using an external magnet; most heterogeneous systems require a filtration or a centrifugation step or a tedious workup of the final reaction mixture to recover the catalyst. These active magnetic nanocatalytic systems possess several advantages over conventional catalyst systems:

• Magnetic nanocatalysts are small in size and have an enormous surface area to volume ratio.

• Since the available surface area of the active component of the catalyst is large, the contact between the reactant molecules and the catalyst is enhanced to a great extent which facilitates the heterogeneous catalytic system; reaction rates closer to its homogeneous counterpart can be achieved.

• Easy control over size, shape, and morphology makes it possible to rationally design the materials that are specifically needed for a particular catalytic application; tuning the properties of metals is easily possible when working at the

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nanoscale, which would be impossible with their macroscopic counterparts.

• Magnetic nature allows them to be separated using external magnet thus facilitating recyclability and reusability.

2. Results and discussion

2.1 Design and synthesis of a magnetic nanoferritesupported glutathione catalyst

Organocatalysis has been extensively explored during the past decade but much remains to be accomplished, especially in the context of developing truly sustainable protocols. In view of our ongoing program in the development of greener and sustainable processes for organic synthesis and nano-catalysis,^{4–7} an approach is envisioned: (a) a magnetic nano-particle supported organocatalyst, (b) a totally benign aqueous protocol which does not involve the use of organic solvents, even in the work-up step, and (c) the use of glutathione as an organocatalyst.

The first step in the development of this concept was the selection of amino acids for the functionalization of magnetic nanoparticles. It was decided to explore the completely benign tripeptide glutathione, an essential component of plants and human cell systems, as an organocatalyst. An additional benefit of using glutathione is the presence of the highly reactive thiol group in the middle of the molecule, which can be used for anchoring to the nano-ferrite surfaces, keeping active sites free for catalysis. To the best of our knowledge, neither ubiquitous glutathione nor a magnetic nanoparticle-supported organocatalyst has been exploited previously for any organocatalytic reactions, despite the potential activity of such a system. The nano-organocatalyst (nano-FGT) was prepared in excellent yield using a post-functionalization method (Scheme 1).^{7a}

The crystalline structures of nano-FGT were determined by powder X-ray diffraction (XRD) (Fig. 1(a)); the diffraction

patterns and relative intensities of all the peaks matched well with those of magnetite (JCPDS card no. 00-002-1035). No other oxide or hydroxide phase was observed; the broad XRD peaks clearly indicate the nanocrystalline nature of the material. Transmission electron microscopy (TEM) analysis



Fig. 1 (a) Powder XRD pattern and (b) TEM image of nano-FGT. (c) FTIR spectra for glutathione; (d) FTIR spectra for the nano-FGT catalyst.



Scheme 1 Synthesis of nanoparticle-supported glutathione (nano-FGT)

(Fig. 1(b)) of the organocatalyst showed uniform-sized particles with spherical morphology with an average size range of 10–12 nm. Anchoring of glutathione on the surface of magnetic nanoparticles was confirmed by FT-IR spectroscopy (Fig. 1c and 1d).

2.2 MW-assisted Paal-Knorr reaction using magnetic nano-FGT catalyst

The Paal–Knorr reaction in which amines are converted to pyrrole in one step has gained great interest in the synthetic organic chemistry, as these heterocycles are intermediates for various pharmaceutical drugs.⁸ A range of clean protocols have been developed.^{9–14} However, most of the above methods involve the use of excess amounts of catalysts, toxic organic solvents, and tedious workup and cannot be considered as real green protocols. Hence, this glutathione-coated magnetic nanomaterial was explored as a nano-organocatalyst for Paal–Knorr reactions (Scheme 2).¹⁵ Reaction conditions were

$$R-NH_2$$
 + $MeO \longrightarrow OMe$ $Mano-FGT \longrightarrow R-N$

R= alkyl, aryl, heterocyclic etc

Scheme 2 Nano-FGT promoted Paal–Knorr reactions.

Table 1	Optimization of reaction conditions					
S.N.	Solvent	Temp. (°C)	Time (min)	Conversion ^a		
1	Toluene	120	30	>5%		
2	Toluene	140	30	>5%		
3	Toluene + water	140	30	80%		
4	Water	120	30	70%		
5	Water	140	20	92%		
6	Water	140	30	95%		

^a Reaction conditions: 1 mmol of benzyl amine, 25 mg of nano-FGT.

optimized for the Paal–Knorr reaction using benzylamine as a substrate and using nano-FGT under MW irradiation conditions (Table 1).

MW-assisted chemistry was used due to the efficiency of the interaction of microwaves with the polar nano-catalyst as they allow rapid heating of the reaction mixture to required temperatures with precise control.4,5,16 The reaction was first conducted using nano-FGT in toluene as a reaction medium at 120 °C; a poor conversion was observed. Increasing the reaction temperature to 140 °C provided no significant increase in conversion. Interestingly, when the reaction was carried out in a mixture of toluene and water, good conversion was achieved. Encouraged from this result, the reaction was carried out in pure water; 92% conversion was achieved in 20 min at 140 °C under MW irradiation. No product formation was observed when the reaction was tested with non-functionalized ferrites, which clearly confirms that supported glutathione is the catalytic species. Using these optimized reaction conditions, the scope of this catalyst was then investigated for the Paal-Knorr reaction of a variety of amines (Fig. 2).

The nano-FGT displayed high catalytic activity for Paal-Knorr reactions. A variety of amines reacted efficiently with tetrahydro-2,5-dimethoxyfuran to afford the desired pyrrole derivatives in good yields (Fig. 2). The rates were barely influenced by the aliphatic or aromatic nature of the amines, showing the high activity of the catalyst. Chiral (*S*)- α -methylbenzylamine and (*R*)- α -methylbenzylamine yielded the corresponding pyrroles without racemization. A heterocyclic and aliphatic amine also underwent the Paal–Knorr reaction to the corresponding pyrrole in good yield. This protocol is also suitable for acid hydrazide.

2.3 Homocoupling of arylboronic acids

Symmetrical biaryl motifs are present in a wide range of natural products, which have interesting properties. A number



Fig. 2 Synthesis of pyrroles using a magnetic nano-FGT catalyst.



Scheme 3 Nano-FGT catalysed homocoupling of aryl boronic acids



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of organic protocols including the Suzuki and Sonogashira cross coupling reactions as well as their homocoupling alternatives can synthesize this important family of compounds. Both types of reactions have generally been reported to be catalyzed with a variety of supported transition metals or transition metal complexes and oxidants under basic conditions in a range of solvents.¹⁷ The nano-FGT catalyst was tested for the homocoupling of aryl boronic acid (Scheme 3).¹⁸ Interestingly the catalyst works well with a wide range of substrates in aqueous media under microwave conditions (Fig. 3) and reused several times without losing its activity. The reaction works well under neutral conditions; however, a few drops of 0.1 N NaOH was added in order to facilitate the solubility of aryl boronic acid in water.

2.4 Recovery and reuse of nano-FGT catalyst

Separation of the catalyst and isolation of products are the main operations in aqueous organocatalysis.¹⁹ Catalyst recovery is often performed by filtration that reduces efficiency and extractive isolation of products requires large amounts of organic solvents. In the case of the Paal–Knorr reaction, because of the super-paramagnetic nature of the material, within a few seconds after stirring was stopped, the reaction mixture turned clear and the catalyst was deposited on the magnetic bar which was easily removed using an external magnet. It was observed that after completion of the reactions,

the phase separation of the desired product from the aqueous media occurred in most cases, thus facilitating the isolation of the crude product by simple decantation rather than tedious extraction processes. Consequently, the use of volatile organic solvents is reduced during product workup. In a few cases, the solid product precipitated out; the product could then be isolated by simple filtration.

To evaluate lifetime and level of reusability of the catalyst, the experiments were conducted using the recycled nano-FGT catalyst for the Paal–Knorr reaction of benzylamine. After the completion of the first reaction, the product layer was removed by decantation and the catalyst was recovered magnetically, washed with water and methanol, and dried. A new reaction was then conducted with fresh reactants under similar conditions. It was found that the developed catalyst could be used at least 5 times without any change in activity. Alternatively, the reaction could be carried out by simply removing the product layer and adding fresh benzylamine and tetrahydro-2,5-dimethoxyfuran, and similar results were obtained.

2.5 Design and synthesis of magnetic bimetallic nano-FGT-Cu catalyst

The first step in the accomplishment of this goal was the synthesis and functionalization of magnetic nanoparticles. The catalyst was prepared by sonicating nano-ferrites with glutathione (Scheme 4) in water for 2 h followed by the addition of



Nano-Fe₃O₄-FGT-Cu catalyst (nano-FGT-Cu(0))

Scheme 4 Synthesis of nano-ferrite supported glutathione-copper (nano-FGT-Cu(0)) catalyst.

CuCl₂ at a basic pH. Cu nanoparticles on the glutathione functionalized nano-ferrites, nano-Fe₃O₄-glutathione (nano-FGT-Cu), were separated using an external magnet, washed with water followed by methanol, and dried under vacuum at 60 °C for 8 h. The catalyst was characterized by X-ray diffraction (XRD) (Fig. 4b) and transmission electron microscopy (TEM) (Fig. 4a), which confirms the formation of single-phase Fe₃O₄ nanoparticles with spherical morphology and a size range of 10–25 nm. FT-IR confirms the anchoring of glutathione on ferrite surfaces. The signals pertaining to the copper metal were not detected by XRD (Fig. 4b) indicating that the Cu species is highly dispersed on ferrites. The weight percentage of copper in nano-FGT-Cu was found to be 1.57% by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis.

2.6 Triazole synthesis using nano-FGT-Cu copper catalyst

The 1,2,3-triazole family has shown interesting biological properties, such as anti-allergic,²⁰ anti-bacterial,²¹ and anti-HIV activity.²² Additionally, 1,2,3-triazoles are found in fungicides, herbicides, and dyes.²³ The recently discovered copper(1)



Fig. 4 (a) TEM of nano-FGT-Cu, (b) XRD of nano-FGT-Cu



Scheme 5 Screening of magnetic catalysts for cycloaddition of benzyl azide and phenyl acetylene.

catalysis of this transformation,²⁴ which accelerates the reaction up to 107 times, has placed it in a class of its own and has enabled many novel applications. To further improve the utility and user-friendliness of this process, a practical multicomponent variant was developed. Initially, experiments were performed to optimize the reaction conditions for cycloaddition of benzyl azide and phenylacetylene in aqueous media. First, the reaction was conducted using nano-Fe₃O₄ and nano-Fe₃O₄-glutathione (nano-FGT) in water under microwave (MW) irradiation at 120 °C, which furnished 1,4 and 1,5 cyclic adducts in 20% yield and in 1:1 ratio (Scheme 5, Table 2). In order to develop a magnetically recoverable catalyst for regio-selective cycloaddition of alkynes and azides, the reaction of iron oxide with Cu(0) at its surface,²⁵ *i.e.* using the nano-Fe₃O₄-Cu bimetallic catalyst, was performed. Though the rate of the reaction improved and 80% conversion was observed (10 min, MW, 120 °C, H₂O), the selectivity of the reaction was poor (3:1). To develop a highly active magnetically recoverable catalyst, the nano-FGT-Cu catalyst was then prepared by immobilizing Cu(0) on the nano-FGT surface (see Scheme 4) with a particle size of 10-25 nm, and tested for the cycloaddition of benzyl azide and phenyl acetylene. A very selective formation of the 1,4 adduct in quantitative yield was observed (Scheme 5, Table 2). After identifying the active nanomagnetic catalyst, its role as a catalyst was then explored for the Huisgen [3 + 2]-cycloaddition. Initially, the reactions of benzyl azide with a variety of alkynes under MW in water were examined (120 °C, MW, H₂O). MW-assisted chemistry was used due to the efficiency of the interaction of microwaves with the polar nano-catalyst as they allow rapid heating of the

 Table 2
 Screening of catalysts^a

Entry	Catalyst	Time	Yield	Selectivity
1 2 3	Fe ₃ O ₄ Fe ₃ O ₄ -glut Fe ₃ O ₄ -Cu Napo-EGT-Cu	10 min 10 min 10 min 10 min	20 20% 80 99%	1:1 1:1 3:1

^a Reaction conditions: 1.2 mmol of benzyl azide, 1.0 mmol of alkyne, 100 mg of nano-FGT-Cu catalyst. MW, 120 °C, power 100 Watt.

reaction mixture to required temperatures.^{26,27} The expeditious reaction was completed within 8 min to give very high yields of the corresponding 1,2,4 triazoles.^{28a} In the case of a highly electron withdrawing group present in the alkynes (entry 3, Table 3), the rate of the reaction was found to be relatively slow and required 12 min for completion whereas in all of the other cases (entries 1, 2, 4-6, Table 3) the reaction was completed within 8 min. Encouraged by the preliminary results, further studies were undertaken to make the reaction greener and more sustainable. It was decided to perform this reaction in one-pot via in situ azide generation followed by cycloaddition using a magnetically separable nano-FGT-Cu catalyst. At the starting point of the exploration, alkyl halides, aromatic alkynes, and sodium azide were suspended in water, together with the nano-FGT-Cu catalyst (Scheme 6), in a 10 mL sealed glass tube. After 10-15 min of irradiation and subsequent cooling to room temperature, the catalyst was separated magnetically. The triazole product often solidified from the mixture upon completion of the reaction and could be isolated

Table 3 Reaction of benzyl azide with alkyne catalyzed by a magnetic nano-FGT-Cu catalyst

Entry	Alkyl halide	Alkyne	Times	Product	Yield ^a
1	N ₃		8 min	Ph N=N	99%
2	N ₃		8 min	N=N Ph	97%
3	N ₃	0 ₂ N-	12 min	Ph NO ₂	86%
4	N ₃	MeO-	8 min	N=N N OMe	98%
5	N ₃	онс-	8 min	N=N N CHO	94%
6	N ₃	CI	8 min	Ph Cl	95%

^a Reaction conditions: 1.2 mmol of benzyl azide, 1.0 mmol of alkyne, 100 mg of nano-FGT-Cu catalyst. MW, 120 °C, power 100 Watt.

by simple filtration and purified by crystallization or by using a short column (Table 4). To check the regio-selectivity of the multicomponent reaction, the products formed from the reaction of benzyl bromide and phenyl acetylene were compared (Table 4, entry 1) with an authentic sample.

It was established that the triazole was formed in a completely regio-selective manner, with no contamination by the 1,5regioisomer. In almost all cases, the reactions proceeded smoothly to completion within 10 min, and the products were isolated in excellent yields and high purity (Table 4). The 4bromo butene (Table 4, entry 13) was found to be less reactive among other halides. However, the reaction was completed (as analyzed by TLC) within 15 min. In the case of alkynes, the reactions were over in 10 min except for the reaction of p-nitro phenylacetylene (Table 4, entry 6) which required 15 min. The presence of various functional groups (CHO, NO₂, halides, OMe, etc.) or a hetero ring in either of the substrates did not affect the product formation in the one-pot treatment of alkyl halides, alkynes, and sodium azide with a catalyst except for the reaction of 2-amino phenylacetylene (Table 4, entry 12), which gave the complex mixture of products. It is believed that the free amine may react with benzyl bromide along with sodium azide, which leads to the formation of multiple products. In order to synthesize the corresponding triazole with a free amine group, some changes were made in the sequence of addition of the reactants. First, benzyl bromide (1.2 mmol)

with NaN₃ (1.5 mmol) were treated in water, irradiated in an MW oven for 4 min at 120 °C followed by the addition of 2-amino phenylacetylene (1.0 mmol) and further subjected to MW irradiation for another 8 min. The reaction proceeded very cleanly and furnished the corresponding triazole in 87% yield (Table 4, entry 12). To further demonstrate the general applicability and versatility of the nano-FGT-Cu catalyst, the mixture of benzyl bromide, sodium azide, and aliphatic alkynes and catalyst (Table 5) were irradiated in water. In all of the cases (Table 5, entries 1-3), the reactions proceeded smoothly at 120 °C and required 12 min to afford the desired triazoles. In the case of ethyl propionate (Table 5, entry 4), the reaction gave a mixture of products. To minimize the formation of byproducts the reaction temperature was reduced to 80 °C, which led to an increase in the reaction time to 20 min (Table 5, entry 4) and furnished the corresponding triazole in 85% yield. Concurrently, Li et al. reported a magnetic copper-iron nanoparticle for the azide-alkyne cycloaddition reaction in water.^{28b}

2.7 Recovery and reusability of nano-FGT-Cu catalyst

The lifetime of the catalyst and its level of reusability are very significant factors. To determine recyclability of nano-FGT-Cu, a set of experiments was performed for the cycloaddition of benzyl azide and phenylacetylene using the recycled nano-FGT-Cu catalyst. After the completion of the first reaction, the catalyst was recovered magnetically, washed with methanol,

$$R_1$$
 Br + NaN₃ + R_2 \longrightarrow $H_2O, Nano-FGT-Cu$ R_1 $N=N$
MW 120 ^{0}C R_1 N R_2

Scheme 6 Synthesis of triazoles via a one-pot multi-component reaction.

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Table 4	Synthesis of	triazoles via	a one-pot mi	ulticomponent	reaction	catalyzed by a	a magnetic nano-l	GT-Cu catalyst

Entry	Alkyl halide	Alkyne	Times	Product	Yield ^a
1	Br		10 min	Ph_N=N	94%
2	Br	-<>-=	10 min	Ph_N=N	94%
3	Br	MeO-	10 min	Ph_N=N	92%
4	Br	CI-	10 min		88%
5	Br	онс-	10 min		86%
6	Br	0 ₂ N-	15 min	Ph_N=N	80%
7	Br		10 min		90%
8	O ₂ N_CI		10 min	O ₂ N N=N N_Ph	87%
9	O ₂ N Br		10 min	O ₂ N N=N N=N	89%
10	Br		10 min	N=N N_Ph	92%
11	F		10 min	F N=N N Ph	89%
12	Br	NH2	10 min	Ph N=N H ₂ N	87% ^b
13	Br		15 min		91%

^{*a*} Reaction conditions: 1.2 mmol of alkyl halides, 1.5 mmol of NaN₃, 1.0 mmol of alkyne, 100 mg of nano-FGT-Cu catalyst. MW, 120 °C, power 100 Watt. ^{*b*} (i) Reaction conditions: 1.2 mmol of benzyl bromide, 1.5 mmol of NaN₃, MW, 4 min, 120 °C, power 100 Watt. (ii) 1.0 mmol of alkyne, 100 mg of nano-FGT-Cu catalyst. MW, 8 min, 120 °C, power 100 Watt.

and dried at 60 °C for 30 min. A new reaction was then performed with fresh reactants, under the same conditions. The nano-ferrite-supported Cu catalyst could be reused at least three times without any change in activity (Table 6).²⁸

3. Application of nano-FeDOPACu in organic synthesis

3.1 Coupling of aryl halides with thiols

The carbon-sulfur cross-coupling reaction plays a significant role in organic synthesis and constitutes a key step in the synthesis of many molecules that are of biological and material interest.²⁹ Organosulfur compounds are used in diverse fields with various applications, such as treatment of diabetes, cancer, inflammation, Alzheimer's disease, and HIV.^{30–32} Traditionally, couplings were achieved under drastic conditions, such as high reaction temperatures with the use of toxic and high boiling polar solvents like quinoline, HMPA and *N*,*N*-dimethylacetamide (DMF). Organosulfur chemistry has been a beneficiary of the progress in transition metal catalysis but C–S cross-coupling reactions are underexplored as compared to C–N or C–O bond formation due to the deactivation of the metal catalyst by organosulfur compounds.³³

Entry	Alkyl halide	Alkyne	Times	Product	Yield ^a
1	Br	<i></i>	12 min	Ph_N=N	92%
2	Br	ОН	12 min	Ph N=N OH	84%
3	Br	ОН	12 min	Ph N=N OH	89%
4	Br		20 min		85% ^b

^{*a*} Reaction conditions: 1.2 mmol of benzyl bromide, 1.5 mmol of NaN₃, 1.0 mmol of alkyne, 100 mg of nano-FGT-Cu catalyst. MW, 120 °C, power 100 Watt. ^{*b*} Reaction conditions: 1.2 mmol of benzyl bromide, 1.5 mmol of NaN₃, 1.0 mmol of alkyne, 100 mg of nano-FGT-Cu catalyst. MW, 20 min, 80 °C, power 100 Watt.

 Table 6
 Recycling of the catalyst



Palladium catalyzed C–S cross-coupling reactions, using Pd $(PPh_3)_4$ as a catalyst,³⁴ require an additional ligand along with precious Pd and an inert atmosphere.³⁵ On the other hand, Co and Ni catalysts are associated with toxicity.^{36,37} Thus, the development of alternative, inexpensive, ligand-free, air and moisture insensitive, and recyclable catalysts for this useful reaction is highly desirable in the context of environmental and industrial concerns.

Initially, the experiments were performed to identify the appropriate catalyst for the coupling of thiophenols (1.2 equiv.) with 4-bromonitrobenzene (1.0 equiv.). First, the reaction was explored using nano- α -Fe₃O₄ and nano- α -Fe₃O₄dopamine (nano-FeDOPA) in DMF at reflux temperature using Cs₂CO₃ as a base, but no product formation occurred. The catalyst was modified using CuCl₂ with a particle size of 10–25 nm, termed nano- α -Fe₃O₄-dopamine copper (nano-FeDOPACu) (Scheme 7).³⁸ The coupling of thiophenols with 1-bromo-4-nitrobenzene using this catalyst afforded a selective formation of corresponding sulfides in 70% yield (Table 7).

In the context of optimization of solvent and base, the reaction did not proceed in water and in traditional solvents such as DMF, THF and CH_3CN gave coupled products in moderate yield (Table 8). The use of K_2CO_3 or Cs_2CO_3 did not significantly affect the outcome of the reaction. The observation that rapid formation of the corresponding disulfide takes place, which precluded the availability of free thiol for coupling after a certain reaction time, prompted the search for a reductive environment for the reaction. Isopropanol appeared to be the logical choice. The reaction in a THF-iPrOH (1:1) mixture at reflux temperature for 24 h showed a significant improvement but did not proceed to completion. To reduce the reaction time, the reaction was conducted under microwave (MW) irradiation conditions at 120 °C for 25 min, which afforded the corresponding coupled product in quantitative yield (Table 8, entry 14). The cross-coupling of a wide variety of commercially available aryl iodides and aryl bromides with thiophenols occurred neatly; the corresponding diaryl sulfides were obtained in good to excellent yields (Table 9). Electron withdrawing and donating substituents on aryl halides did not show a significant effect on the yield or the reaction time. Interestingly, as in the case of thiophenols, para-chlorothiophenol did not undergo self-coupling and gave the desired cross-coupled products (Table 9, entries 2, 4, 7, 9 and 11). The reaction of 4-nitrothiophenol, however, proceeded sluggishly and required 45 min for completion (Table 9, entry 5). Interestingly, unlike other copper catalytic systems,^{39,40} it was selective towards C-S bond formation and ineffective for C-O, C-N, and C-C bond coupling and cycloaddition reactions.

3.2 Recovery and reusability of nano-FeDOPACu catalyst

For practical applications of heterogeneous systems, the lifetime of the catalyst and its level of reusability are significant factors. To clarify this issue, the reaction of 1-bromo-4nitrobenzene with thiophenol using the recycled nano-FeDO-PACu catalyst was examined. After completion of the first reaction, the catalyst was recovered magnetically, washed with methanol, and dried at 60 °C for 30 min. A new reaction was then performed with fresh reactants, under the same conditions. The nano-ferrite supported Cu catalyst could be reused at least three times without any change in activity (Table 10). Metal leaching, as measured by ICP-AES analysis of the catalyst before and after the three reactions, showed Cu concentration to be 0.82% before the reaction and 0.81% after the reaction. The TEM image of the catalyst taken after the third cycle of the reaction does not show a significant change



Scheme 7 Synthesis of a nano-Fe₃O₄-DOPA-Cu (nano-FeDOPACu) catalyst.

$Br + HS - \frac{DMF}{I}$	$\frac{Cs_2CO_3}{Reflux}$ O_2N	.s
Catalyst	Times	Yield
Fe ₃ O ₄ Nano-FeDOPA Nano-FeDOPACu	24 h 24 h 24 h	0% 0% 70%
	$Br + HS - \underbrace{DMF}_{I}$ Catalyst Fe_3O_4 Nano-FeDOPA Nano-FeDOPACu	$\begin{array}{c c} & & & & \\ & & & \\ \hline & & & \\ \hline & & & \\ \hline \hline & & \\ \hline \hline & & \\ \hline & & \\ \hline \hline \\ \hline & & \\ \hline \hline \hline \\ \hline \hline \hline \\ \hline \hline \hline \\ \hline \hline \hline \hline \\ \hline \hline \hline \hline \hline \\ \hline \hline$

 Table 7
 C–S coupling of 1-bromo-4-nitro-benzene: screening of the catalyst

in the morphology and the size of the catalyst nanoparticles (10–25 nm), which indicates the retention of the catalytic activity after recycling.⁴⁴ No Cu metal was detected in the reaction solvent after completion of the reaction, which confirms the fact that dopamine provides enough binding sites on the surface of Fe_3O_4 nanoparticles and serves as a pseudo-ligand by coordinating with Cu. This strategy minimizes deterioration, prevents metal leaching, and enables efficient catalyst recycling.

4. Application of nano-FeDOPAPd in organic synthesis

4.1 O-Allylation of phenols

Allyl ethers are important starting materials for a wide range of organic reactions, including the 1,3-hydrogen shift, [3,3]-sigmatropic rearrangement, and polymerization reactions,⁴¹ in addition to being a popular protecting group for alcohols.⁴² The traditional method for the synthesis of allyl ethers is the Williamson-type ether synthesis, which involves the use of strongly basic metal alkoxide anions and highly active allyl halides or their equivalents.⁴³ Comparatively, the addition of oxygen nucleophiles to η^3 -allyl metal complexes of various transition metals^{44–47} provides an attractive mild alternative approach for their synthesis using much less reactive allyl alcohols, allyl esters, or allyl carbonates. However, most of the existing methods for transition metal catalyzed *O*-allylation *via* η^3 -allyl metal intermediates are accomplished using a non-recyclable homogeneous catalyst in various toxic solvents.^{44–47}

Entry	Solvent	Base	Temp	Times	Yield ^a
1	H ₂ O	NaOH	100 °C	24 h	
2	H ₂ O	K ₂ CO ₃	100 °C	24 h	_
3	H ₂ O	Cs ₂ CO ₃	100 °C	24 h	_
4	DMF	K ₂ CO ₃	153 °C	24 h	70%
5	DMF	Cs ₂ CO ₃	153 °C	24 h	70%
6	THF	K ₂ CO ₃	65 °C	24 h	65%
7	THF	Cs ₂ CO ₃	65 °C	24 h	66%
8	CH ₃ CN	K ₂ CO ₃	82 °C	24 h	63%
9	CH ₃ CN	Cs ₂ CO ₃	82 °C	24 h	65%
10	THF: iPrOH	K ₂ CO ₃	Reflux	24 h	77%
11	THF: iPrOH	Cs ₂ CO ₃	Reflux	24 h	76%
12	iPrOH	Cs_2CO_3	82 °C	24 h	79%
13	iPrOH	K ₂ CO ₃	82 °C	24 h	81%
14	iPrOH	K_2CO_3	120 °C	25 min	$98\%^{b}$

^{*a*} Reaction conditions: 1.2 mmol of thiophenol, 1.0 mmol of aryl halide, 100 mg of nano-FeDOPACu catalyst. ^{*b*} Reaction conditions: 1.2 mmol of thiophenol, 1.0 mmol of aryl halide, 100 mg of nano-FeDOPACu catalyst. MW, 120 °C, power 100 Watt.

Yield

In continuation of this work, nano-FeDOPAPd was explored for the aqueous *O*-allylation of phenols. A wide range of phenols undergo unprecedented allylic substitution reactions with various allylic acetates in air under refluxing aqueous media conditions within 3–10 h whilst in the presence of the nano-FeDO-PAPd catalyst; a mild base, sodium bicarbonate, is adequate to produce the allyl ethers (Scheme 8, Table 11) in good yields.⁴⁸

Table 10 Recycling of the catalyst



No. of cycles

1

2

3



Table 9 Syr	nthesis of diaryl sulfide				
Entry	Substrate	Thiophenols	Product	Times	Yield ^a
1	O ₂ N-Br	SH SH	O ₂ N-	25 min	98%
2	O ₂ N-Br	Cl—SH	O ₂ N-Cl	25 min	95%
3	— — I	SH	-<->-s-<->	25 min	95%
4	— — I	Cl—SH		25 min	63%
5		O ₂ N-SH		45 min	85%
6	Γ. I	SH	⟨ _ s-√ >	25 min	92%
7	Ϋ́-Ι	Cl—		25 min	94%
8	MeO	SH	MeO-S-S-	25 min	91%
9	MeO	Cl————————————————————————————————————	MeO-S-Cl	25 min	89%
10	O ₂ N	SH	S-S-	25 min	98%
11		Cl—		25 min	96%
12	Br	SH		30 min	88%
	U O				

^a Reaction conditions: 1.2 mmol of thiophenol, 1.0 mmol of aryl halide, 100 mg of nano-FeDOPACu catalyst. MW, 120 °C, power 100 Watt.

Paper



Scheme 8 O-Allylation of phenols with allylic acetates.

4.2 Heck-type arylation

The diaryliodonium salts are a class of hypervalent iodine reagents. They are trivalent iodine compounds with two carbon ligands. These salts are stable towards heat and oxygen, nontoxic, and non-explosive. The application of diaryliodonium salts in organic synthetic chemistry is ever

Table 11 O-A	llylation of phenols with allyli	c acetates ^a			
Entry	Phenols	Allylic acetates	Time (h)	Products	Yield ^b
1	OH	Ph ^{ron} OAc	6	O Ph	80%
2	OH C	Ph ^r OAc	5	O Ph	85%
3	OH	Ph ^{ron} OAc	5	O Ph	87%
4	OH	Ph ^{ron} OAc	5	O Ph	83%
5	OH	≫~OAc	10		90% ^c
6	OH CI	Ph ^A OAc	9	Cl Ph	79%
7	OH Br	Ph ^{ron} OAc	10	O Ph Br	85%
8	OH	Ph ^A OAc	3	OPh	75%
9	OH C	OAc	8		87%
10	OH	MeO	8	OMe	75%
11	OH	CI	8		73%
12	OH	NO ₂ OAc	8		76%
13	OH OH	OAc Ph	8	O Ph	81%

^a A mixture of phenol (1 mmol), allylic acetates (1 mmol), sodium bicarbonate (2 mmol) and Pd catalyst (50 mg, 4.8 mol%) in water (2.5 mL) was heated to reflux in air. ^b Yields refer to those of column purified isolated products. ^c The reaction mixture in DMF (2 mL) was heated at 90 °C.

Table 12 Heck type arylation of alkenes using diaryliodonium salts catalyzed by nano-FeDOPAPd

	OTf/OTs Ar Ar R	nano-FeDOPAPd PEG-400:H ₂ O(1:1)	
Entry	Ar	R	Product yield ^a
1	C_6H_5	$COCH_3$	90%
2	C_6H_5	CH ₂ OAc	88%
3	C_6H_5	CO ₂ <i>n</i> Bu	85%
4	C_6H_5	C_6H_5	78%
5	C_6H_5	$C_6H_5CH_2$	69%
6	C_6H_5	CH ₂ OH	45%
7	$4\text{-MeC}_6\text{H}_4$	CH ₂ OAc	82%
8	$3-NO_2C_6H_4$	CH ₂ OAc	80%
9	$3-NO_2C_6H_4$	COOMe	75%
10	$3-NO_2C_6H_4$	CO ₂ <i>n</i> Bu	81%
11	$2,4,6-(Me)_3C_6H_2$	COCH ₃	72%
12	4- t -BuC ₆ H ₄	CH_2OAc	82%
13	$4\text{-OMeC}_6\text{H}_4$	CH ₂ OAc	84%

^{*a*} Reaction conditions: 1.1 mmol of alkene, 1 mmol of diaryliodonium salt, and 50 mg (4.8 mol%) of [nano-FeDOPAPd] catalyst with aq. PEG-400 (1:1, v/v) subjected to ultrasonication (1 to5 min).

OH	Fe₃O₄-DOPAPd	O Ph
+ Ph ² OAc	NaHCO ₃ , H ₂ O Reflux, 5 h, air	
No. of cycles	Catalyst	Yield
1	Fe ₃ O ₄ -DOPAPd	85%
2	Fe_3O_4	84%
3	Fe_3O_4	85%
4	Fe_3O_4	83%
5	Fe_3O_4	82%
6	Fe_3O_4	82%

increasing.^{49–57} Recently, the iodonium salts have been employed in the Heck-type coupling, however, with limited substrate scope and yields.⁵⁷ We extended our ongoing studies on nano-FeDOPAPd as a catalyst for the Heck reaction using diaryliodonium salts. The Heck coupling of diaryliodonium salts with variety of alkenes (activated and non-activated) proceeded expeditiously (1–5 min) in aqueous PEG-400(1:1) without using any base under ultrasonication conditions (Table 12).⁵⁸

4.3 Recovery and reusability of nano-FeDOPAPd catalyst

For practical applications, the lifetime and the stability of the catalyst are very important. To clarify this issue, the reaction of p-cresol with cinnamyl acetate using a recycled nano-FeDO-PAPd catalyst was examined. After completion of the first reaction, the catalyst was recovered magnetically, washed with methanol, and dried at 60 °C for 30 min. A new reaction was then performed with fresh reactants, under the same

conditions. The nano-ferrite supported Pd catalyst could be reused at least six times (Table 13) without any change in activity. Metal leaching, as measured by ICP-AES analysis of the catalyst before and after the three reactions, showed Pd concentration to be 7.91% before the reaction and 7.85% after the reaction. No Pd metal was detected in the reaction solvent after completion of the reaction, which confirms the fact that dopamine provides enough binding sites on the surface of Fe₃O₄ nanoparticles and serves as a pseudo-ligand by coordinating with Pd. This strategy minimizes deterioration, prevents metal leaching, and enables efficient catalyst recycling.

5. Application of magnetically separable ruthenium catalyst in organic synthesis

Amides, an important class of compounds in the chemical and pharmaceutical industries, have been prepared by the hydration of nitriles, catalyzed by strong acids and bases. This strategy produced several by-products including carboxylic acids. Because of the use of strong reagents/catalysts and harsh conditions, sensitive functional groups on nitrile molecules could not be kept intact, consequently decreasing the selectivity of the reaction protocol. Several heterogeneous catalyst systems were developed to overcome the drawbacks of the homogeneous processes. However, the turnover numbers of these protocols were still small and the reusability of the catalyst was a challenge. A recently developed hydration method in pure water was a good attempt in terms of reaction conditions and product yields.⁵⁹ It required expensive ruthenium complexes as catalysts and needed traditional work-up using toxic organic solvents for isolation of the product. A greener and sustainable method for hydration of nitriles was successfully



Fig. 5 Synthesis of a magnetically separable nano-Ru(OH)_x catalyst.



developed by using a magnetic ruthenium hydroxide nanocatalyst under aqueous MW conditions.⁶⁰ Nano-Ru(OH)_x was prepared in two steps: (1) magnetic nanoparticles were functionalized by post-synthetic functionalization *via* sonication of nano-ferrites with dopamine in an aqueous medium and (2) ruthenium (Ru) chloride was added followed by hydrolysis using sodium hydroxide solution (Fig. 5). This ruthenium hydroxide coated nanomaterial was then explored as a heterogeneous catalyst for hydration of nitriles in an aqueous medium as a benign solvent under microwave (MW) irradiation conditions (Scheme 9).

 Table 14
 Optimization of reaction conditions^a

Entry	Catalyst	Temperature ^c	Time ^b	Conversion
1	Nano[Fe ₃ O ₄]	100	30	0%
2	Nano Fe ₃ O ₄	130	30	0%
3	Nano $[Fe_3O_4]$ - $[Ru(OH)_r]$	100	20	30%
4	Nano $[Fe_3O_4]$ - $[Ru(OH)_x]$	130	20	65%
5	Nano $[Fe_3O_4]$ - $[Ru(OH)_x]$	130	30	85%

 a Reactions were carried out with 1 mmol of benzonitrile, 100 mg of nanocatalyst, in water under MW irradiation. b Reaction temperature. c Reaction time.

Initially, experiments were performed to optimize the reaction conditions for hydration of benzonitrile as a substrate, in an aqueous medium (Table 14). The reaction was conducted using nanoferrites; hydration did not proceed at 100 °C or at 130 °C even after 30 min of MW exposure (Table 14, entries 1 and 2). Nanoferrite– $[Ru(OH)_x]$ was then

 Table 15
 Hydration of nitriles using nanoferrite--[Ru(OH)_x]^a



^{*a*} Reactions were carried out with 1 mmol of nitrile, 100 mg nanocatalyst at 130 °C for 30 min, in water under MW irradiation. ^{*b*} Isolated yield. ^{*c*} Reaction time 45 min.

tested as a catalyst at 100 °C for 20 min under MW irradiation where the low conversion of nitrile to amide (30%) was observed (Table 14, entry 3). However, when the reaction temperature was increased to 130 °C, the reaction proceeded expeditiously with 65% conversion within 20 min

(Table 14, entry 4), which was further increased to 85% by extending the reaction time by another 10 min (Table 14, entry 5).

Using the above optimized conditions, the scope of the nanoferrite- $[Ru(OH)_x]$ catalyst was then explored for hydration of a variety of nitriles (Table 15). Nanoferrite-[Ru(OH)_r] has shown high catalytic activity for hydration of activated, inactivated, and heterocyclic nitriles in pure water. A variety of benzonitrile derivatives (Table 15, entries 1 and 10) as well as aliphatic nitriles (Table 15, entries 11 and 12) were smoothly hydrated to the corresponding amides in excellent yield. The rates were barely influenced by the electronic effects of the substituents on the aromatic ring of benzonitriles. Interestingly, the hydration of *m*- and *p*-nitro benzonitriles (Table 15, entries 5 and 6) as well as 3- and 4-cyanopyridine (Table 15, entries 7 and 8) proceeded with a similar rate, without any difference in reactivity, which shows negligible influence of substituent's position on the reaction rate. However, hydration of isonicotinonitrile N-oxide does not yield the corresponding isonicotinoamide N-oxide, instead isonicotinoamide was obtained (Table 15, entry 9). Hydration of the benzo[1,3-d]dioxole-5-carbonitrile proceeded only at the cyano group to afford the corresponding amide, while keeping the dioxole ring intact (Table 15, entry 10).

Although this catalyst works well, it suffers from the requirement of an elaborate and tedious procedure for their synthesis that involves three steps: (i) synthesis of nanoferrite, (ii) postsynthetic modification *via* anchoring of ligands which may be toxic and, (iii) immobilization of the ruthenium metal. To overcome this drawback and to avoid the use of toxic ligands and reagents, a one-step procedure was developed for the synthesis of magnetic silica supported ruthenium as a magnetically retrievable catalyst (Scheme 10).⁶¹ The scope of the magnetic silica supported ruthenium catalyst Nano-Fe@SiO₂Ru was then demonstrated for the hydration of a variety of nitriles.⁶¹ The catalyst displayed high activity for hydration of activated, inactivated, aliphatic, and heterocyclic nitriles in pure water. It also displayed high activity for a



Scheme 10 One-pot synthesis of a nano-Fe@SiO₂Ru catalyst.

variety of benzonitrile derivatives as well as aliphatic nitriles that were smoothly hydrated to the corresponding amides in excellent yield.

6. Conclusion

In conclusion, varieties of magnetic nano-ferrites modified with various ligands have been synthesized. Glutathione bearing nano-ferrites have been used as organocatalysts for the Paal–Knorr reaction and homocoupling of boronic acids. A variety of other nanoferrites, post-synthetically modified by ligands, were used to immobilize nanometals (Cu, Pd, Ru, *etc.*) which enabled the development of efficient, sustainable and green procedures for azide–alkynes-cycloaddition (AAC) reactions, C–S coupling, *O*-allylation of phenol, Heck-type reactions and hydration of nitriles. Because of their reduced size, in the nm range, most of the catalyst surface is now available for the reaction. An additional salient feature is that the catalyst can be easily separated, recycled and reused several times using an external magnet without any loss in activity.

7. Experimental section

7.1 Synthesis of magnetic nano-ferrites

FeSO₄·7H₂O (13.9 g) and Fe₂(SO₄)₃ (20 g) were dissolved in 500 mL water in a 1000 mL beaker. Ammonium hydroxide (25%) was added slowly to adjust the pH of the solution to 10. The reaction mixture was then continually stirred for 1 h at 60 °C. The precipitated nanoparticles were separated magnetically, washed with water until the pH reached 7, and then dried under vacuum at 60 °C for 2 h. Ferrite was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). This magnetic nano-ferrite (Fe₃O₄) was then used for further chemical modification.

7.2 Surface modification of nano-ferrites with glutathione

Nano-Fe₃O₄ (0.5 g) was dispersed in water (15 mL) and methanol (5 mL) and sonicated for 15 min. Glutathione (reduced form) (0.2 g) dissolved in water (5 mL) was added to this solution and again sonicated for 2 h. The glutathione-functionalized nanomaterial (nano-organocatalyst) was then isolated by centrifugation, washed with water and methanol, and dried under vacuum at 50–60 °C.

7.3 Surface modification of nano-ferrites with dopamine

Nano- $[Fe_3O_4]$ (2 g) was dispersed in 25 mL water by sonication for 30 min. Dopamine hydrochloride (2 g) dissolved in 5 mL of water was added to this solution and again sonicated for 2 h. The amine-functionalized nanomaterial was then precipitated using acetone, isolated by using an external magnet, and dried under vacuum at 50 °C for 2 h.

7.4 Synthesis of nano-FGT-Cu catalyst

Glutathione-functionalized nano-Fe₃O₄ (1 g) was dispersed in a water-methanol mixture (1:1). CuCl₂·2H₂O (100 mg) solution in water was added to the reaction mixture. Hydrazine monohydrate solution in water was added dropwise to bring the pH of this mixture to 9, followed by the addition of 0.1 g of NaBH₄. The reaction mixture was then stirred for 24 h at room temperature. The product was allowed to settle, washed several times with water and acetone, and dried under vacuum at 60 °C for 2 h. Catalyst characterization by X-ray diffraction (XRD) (Fig. 4b) and transmission electron microscopy (TEM) (Fig. 4a) confirms the anchoring of Cu nanoparticles on ferrite surfaces. The weight percentage of Cu in the catalyst was found to be 1.57% by ICP-AES analysis.

7.5 Synthesis of nano-ferrite-dopamine-metal (Cu and Pd) catalyst

Amine-functionalized nano-Fe₃O₄ (1 g) was dispersed in water and metal salt solution in water was added to the mixture. Hydrazine monohydrate solution in water was added dropwise to bring the pH of this mixture to 9 followed by the addition of 0.1 g of NaBH4. The reaction mixture was then stirred for 24 h at room temperature. The product was allowed to settle, washed several times with water and acetone, and dried under vacuum at 60 °C for 2 h. The weight percentage of metals (Cu and Pd) in the catalyst was determined using ICP-AES analysis.

7.6 Synthesis of nanoferrite- $[Ru(OH)_x]$ catalyst

Amine-functionalized nano-[Fe₃O₄] (2 g) was dispersed in water. A RuCl₃ solution in water (60 mL, 8.3×10^{-3} M) was then added to it and stirred for 20 min. An aqueous solution of sodium hydroxide (1 m) was added dropwise to bring the pH of this mixture to 13. The resulting slurry was stirred for 36 h at room temperature. The product was separated magnetically, washed several times with water and methanol, and dried under vacuum at 50 °C for 2 h. The weight percentage of Ru in the catalyst was found to be 3.22% by ICP-AES analysis.

7.7 Synthesis of magnetic silica supported ruthenium hydroxide nanoparticles

FeSO₄·7H₂O (2.78 g) and Fe₂(SO₄)₃ (4.0 g) were dissolved in 200 mL water in a 500 mL beaker. Ammonium hydroxide (25%) was added slowly to adjust the pH of the solution to 10. The reaction mixture was then continually stirred for 1 h at 50 °C. The reaction mixture was cooled down to room temperature. To this solution, tetraethyl orthosilicate (TEOS, 10 mL) was added and vigorous stirring was continued for 18 h under ambient conditions. To this solution, RuCl₃ (600 mg) was added; the pH of the solution was adjusted to ~10 using ammonium hydroxide solution (25%) and stirring continued for another 24 h. Magnetic silica supported Ru-hydroxide nanoparticles were separated using an external magnet, washed with water, followed by acetone, and dried under vacuum at 50 °C for 8 hours. The catalyst was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The weight percentage of Ru was found to be 3.96% and Si 6.85% by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis.

7.8 Paal-Knorr reaction of amines using nano-FGT

The (1 mmol), tetrahydro-2,5-dimethoxyfuran amines (1.1 mmol), and nano-FGT (25 mg) were placed in a 10 mL crimp sealed thick-walled glass tube equipped with a pressure sensor and a magnetic stirrer. Water (2 mL) was added and the reaction mixture was thoroughly mixed. The reaction tube was then placed inside the cavity of a CEM Discover focused MW synthesis system, operated at 140 °C (temperature monitored by a built-in infrared sensor) with a power of 50-250 W, and a pressure of 50-180 psi for 20 min. After completion of the reaction, the phase separation of the desired product from the aqueous medium occurred, facilitating the isolation of the crude product by simple decantation, which was further purified by simply passing through a short silica column.

7.9 Synthesis of triazole from benzyl azide and alkyne

Benzyl azide (1.2 mmol), alkyne (1.0 mmol), and nano-FGT-Cu catalyst (100 mg) were placed in a crimp-sealed thick-walled glass tube equipped with a pressure sensor and a magnetic stirrer. Water (4 mL) was added to the reaction mixture. The reaction tube was placed inside the cavity of a CEM Discover focused microwave synthesis system, operated at 120 °C (temperature monitored by a built-in infrared sensor), 100 Watts, and 10–60 psi for 8–12 min. After completion of the reaction, the catalyst was easily removed from the reaction mixture using an external magnet. After separation of the catalyst, the solid product was filtered off or extracted with ethyl acetate and recrystallized.

7.10 Synthesis of triazoles *via in situ* generation of alkyl azides

Alkyl halides (1.2 mmol), NaN₃ (1.5 mmol), alkyne (1.0 mmol), and nano-FGT-Cu catalyst (100 mg) were placed in a crimpsealed thick-walled glass tube equipped with a pressure sensor and a magnetic stirrer. 4 mL of water was added to the reaction mixture. The reaction tube was placed inside the cavity of a CEM Discover focused microwave synthesis system, operated at 120 °C (temperature monitored by a built-in infrared sensor), 100 Watts, and 10–60 psi for 10–20 min. After completion of the reaction, the catalyst was easily removed from the reaction mixture using an external magnet. After separation of the catalyst, the solid product was filtered off or extracted with ethyl acetate and recrystallized or purified by column chromatography.

7.11 Synthesis of diaryl sulfides

Aryl halide (1.0 mmol), thiophenol (1.2 mmol), and nano-FeDOPACu catalyst (100 mg) were placed in a crimp-sealed thick-walled glass tube equipped with a pressure sensor and a magnetic stirrer. Isopropanol (5 mL) was added to the reaction mixture. The reaction tube was placed inside the cavity of a CEM Discover focused microwave synthesis system, operated at

120 °C (temperature monitored by a built-in infrared sensor), 100 Watts, and 10–60 psi for 25–45 min. After completion of the reaction, the catalyst was easily removed from the reaction mixture using an external magnet. After separation of the catalyst, the solid product was filtered off or extracted with ethyl acetate and purified by column chromatography.

7.12 *O*-Allylation of phenols by allylic acetates using nano-FeDOPAPd catalyst

A mixture of phenol (1 mmol), allylic acetate (1 mmol), NaHCO₃ (2 mmol), and Pd catalyst (50 mg, 4.8 mol%) was added to 2.5 mL of water. The aqueous reaction mixture was heated to reflux for the required time as indicated in Table 9. The progress of the reaction was monitored by TLC. Standard work-up with ethyl acetate followed by simple column chromatography provided the pure product.

7.13 Heck-type arylation using nano-FeDOPAPd catalyst

The diaryliodonium salt (1 mmol), alkene (1.1 mmol), and 50 mg (4.8 mol%) of nano-FeDOPAPd catalyst with aqueous PEG-400 (1:1, v/v, 3 mL) are subjected to ultrasonication (1–5 min) (cycle: 20 s pulse and 10 s pause) in a high intensity sonicator. Upon completion of the reaction, as indicated by TLC, the catalyst is separated using an external magnet. The reaction mixture is diluted with water and the crude product is extracted using ethyl acetate. The organic layer is dried over anhydrous Na_2SO_4 and purified by passing through a silica gel column. The recovered magnetic catalyst was washed with acetone, dried under vacuum, and reused for the next batch of the reaction. All the synthesized compounds have been reported in the literature and characterized by comparing their spectral data.

7.14 Hydration of nitriles using nanoferrite- $[Ru(OH)_x]$ catalyst

1 mmol of nitrile and 100 mg of nanoferrite-[Ru(OH)_x] (0.003 mole% of Ru) catalyst were placed in a crimp-sealed thick-walled glass tube equipped with a pressure sensor and a magnetic stirrer. 5 mL of water was then added to the reaction mixture. The reaction tube was placed inside the cavity of a CEM Discover focused microwave synthesis system, operated at 130 °C (temperature monitored by a built-in infrared sensor) with a power of 50 to 140 Watt and a pressure of 10-60 psi for 30 min (Table 14, entry 5). After completion of the reaction, the reaction mixture turned clear and the catalyst was deposited on the magnetic bar within 30-45 s, which was easily removed from the reaction mixture using an external magnet. After separation of the catalyst, the clear liquid was cooled slowly resulting in analytically pure crystals of benzamides, which can be isolated from the water medium by simple decantation/filtration.

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