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REVIEW

Catalytic Applications of Vitamin-Supported Nanoparticles in Organic Chemistry

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Abstract—Considering the green nature, biocompatibility, novelty, ease of preparation, and unique properties of vitamin-functionalized nanocatalysts, various vitamins have been supported on various nanosupports to be utilized as heterogeneous catalysts. Due to the novelty and synergistic effect of nanocatalysis and organocatalysis, vitamin-functionalized nanocatalysts have been used in various organic reactions, including C–C coupling, oxidation, multicomponent reactions, etc. These heterogeneous nanocatalysts provide chemists with various advantages such as low catalyst loading, nontoxic and easy-to-handle catalyst, shorter reaction time, high yield, elimination of by-products, avoidance of hazardous organic solvents, and easy workup.

Keywords: vitamins, immobilization, vitamin B_1, vitamin B_3, supported nanocatalysts, catalysis

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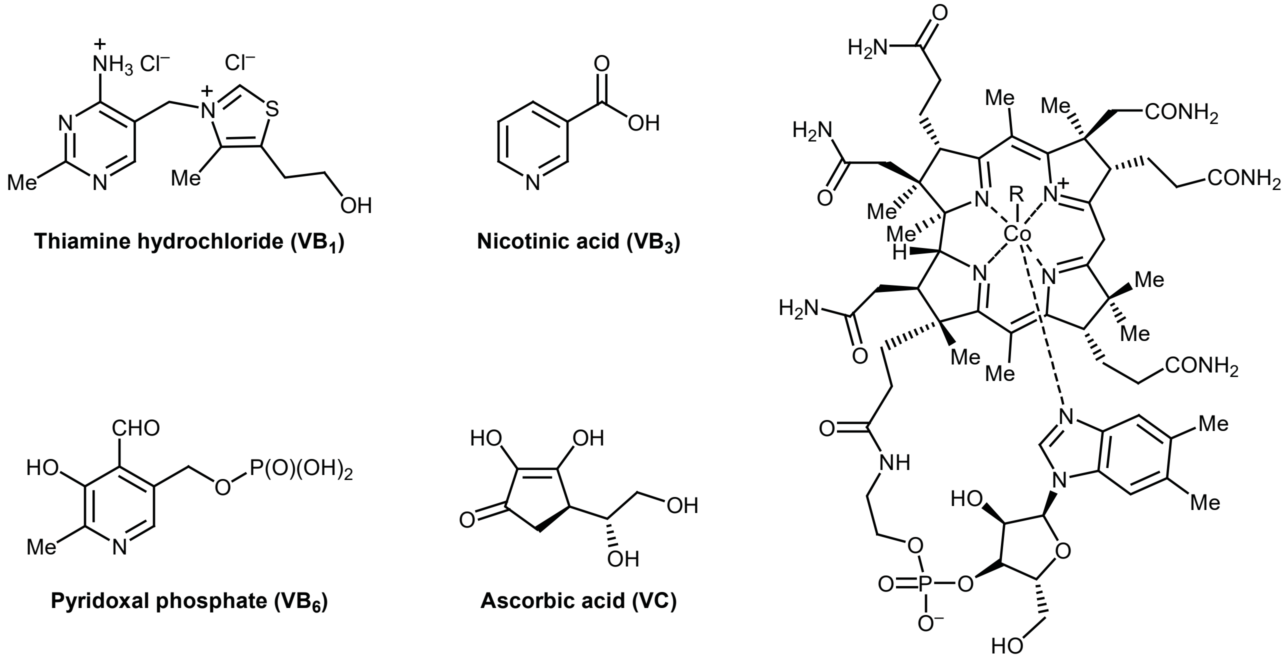
INTRODUCTION

One of the most important principles of green chemistry is the use of smart catalytic systems. Environmental protection, cost effectiveness, energy saving, increasing the production of desired products, and preventing the formation of by-products are the advantages of using catalysts in the synthesis of organic compounds [1–3]. A desirable catalyst in any organic reaction must be environmentally benign, easily recoverable, inexpensive, effective, and highly efficient in moderate conditions. Over the past few years, the use of environmentally friendly small molecules called organocatalysts has been one of the



Thiamine hydrochloride (VB_1) **Nicotinic acid (VB_3)** **Pyridoxal phosphate (VB_6)** **Ascorbic acid (VC)** **Cobalamin (VB_{12})**

Fig. 1. Structure of selected vitamins.

most interesting and powerful tools in the field of catalysis in organic synthesis [4–10].

Organocatalysis provides many opportunities for more economical and greener methods for synthesizing organic compounds. Many pure organic enantiomeric catalysts are readily available from natural sources. Organic catalysts are divided into 4 main groups: Lewis acids, Lewis bases, Brønsted acids, and Brønsted bases [11–17]. The aim of this review article is to study the catalytic efficiency of vitamins supported on nanoparticles as organocatalysts in the synthesis of organic compounds. Over the past few years, due to the destructive effects of corrosive protic acids and toxic Lewis acids on the environment, the use of organocatalysts have gained interest as one of the most interesting and powerful tool for synthesizing organic compounds [18–24]. According to the advantages of organic catalysts in terms of availability, low cost, low sensitivity to moisture and oxygen, and also low toxicity over the traditionally used transition metal catalysts, many researchers have focused on this area [25–31]. The organocatalysts discussed in this article are mostly based on the vitamin B family and vitamin C (Fig. 1) which are considered as potential green catalysts due to their nontoxicity, low cost, water solubility, ease of operation, and climate compatibility [32–38]. Regardless of their efficiency, the main problem with the use of organocatalysis is the difficulty concerning the recovery of homogeneous organic molecules from the reaction mixture [39–42]. Greener fabrication of organic nanocatalysts by immobilizing organic catalysts on magnetic solid supports provides advantages including exploitation of the catalytic activity of organic catalysts in heterogeneous medium, easy preparation and surface modification, significant catalytic activity, reduction of environmental hazards, low cost, and reusability [43–47]. Various nanoparticles have been utilized as supports for the immobilization of organocatalysts; meanwhile, magnetic nanocatalysts due to their advantage of easy separation from the reaction mixture via an external magnet have gained more attention. Typically, the surface of magnetic nanoparticles can be modified by various functional materials such as carbon [48, 49], silica [50, 51], and polymers such as starch [52, 53] via a simple procedure, which stabilizes the prepared magnetic nanoparticles (MNPs) [54]. In addition, immobilization of vitamins on the surface of nanoparticles could be considered as a solution to reduce the problems of using harsh mineral or solid acids [55–58]. Accordingly, due to numerous advantages of using supported vitamins in catalysis, including green nature, biocompatibility, versatility, availability, selectivity, non-toxicity, reusability, stability, and facile work-up, we were motivated to review recent catalytic applications of vitamin-supported catalysts especially in organic chemistry (Table 1).

Table 1. Vitamins supported on various nanomaterials

Entry no.	Vitamin	Catalyst	Reaction or product	Characterization	Reference
1	B_1	γ-Fe_2O_3@SiO_2@Vitamin B_1	Acylation of phenols	FT-IR, XRD, SEM, VSM, TG/DTA	[59]
		Fe_2O_3@SiO_2@VB_1	4*H*-benzo pyranes	FT-IR, TEM, EDS, XRD	[60]
		CN-Pr-VB_1	Quinoxalines	FT-IR, XRD, SEM, TG/DTA., EDX	[61]
		Fe_3O_4@SiO_2@VB_1	Silylation of a wide range of alcohols and phenols	FTIR, XRD, SEM, TGA, EDX, DTG-TGA	[62]
		Fe_3O_4@SiO_2@GMSI-VB_1	2,3-Dihydroquinazolin-4(1*H*)-ones	FTIR, XRD, SEM, TGA, EDX, DTG-TGA	[63]
		GO-VB_1	2-Substituted benzimidazoles	FTIR, XRD, SEM, TGA, EDX, TGA, AFM	[64]
		Fe_3O_4@VitB_1–Ag (I)	Propargylamines	FT-IR, XRD, SEM, TGA, VSM, EDX, DFT	[65]
		SiO_2@VB_1-Pd	Suzuki cross-coupling	FT-IR, XPS, FE-SEM, TEM, EDX, XRD, VSM, TGA, ICP-AES	[66]
		Fe_3O_4@vitamin B_1 MNPs	Trisubstituted thiazole derivatives	TEM, VSM, FTIR, XRD, SEM, TGA	[67]
		SCMNPs@PC/VB_1-Zn	Pyrano[2,3-*c*]pyrazoles and 1,8-dioxooctahydroxanthene derivatives	FTIR, XRD, VSM, EDX, TGA, SEM	[68]
2	B_3	Fe_3O_4@Nico@Ag	Hydrogenation of 4-nitrophenol and 4-nitroaniline	FTIR, XRD, VSM, TGA, SEM, UV-Vis	[69]
		Fe_3O_4 @ niacin	2-Amino-3-cyanopyridine derivatives	FT-IR, XRD, SEM, VSM, UV–Vis, DLS, EDS	[70]
		Pd(II)NA_2@SMNP	Suzuki cross coupling	FT-IR, TGA, XPS, EDS, ICP-AES. TEM	[71]
		Fe_3O_4@nicotinic acid@sulfonic acid	1-Carbamatoalkyl- 2-naphthols	FE-SEM, EDX, TGA, XRD, FT-IR	[72]
		Fe_3O_4@SiO_2@$Si(CH_2)_3Cl$@NA	Chromeno[3,4-*b*]quinoline derivatives	FT-IR, EDS, XRD, FESEM, HRTEM	[73]
		[NicTC]HSO_4@MNPs	Mono- and bis-4*H*-pyrimido[2,1-*b*]benzothiazoles	FT-IR, SEM, EDX, TEM, TGA/DTG, XRD	[74]
		Fe_3O_4@nicotinic acid@sulfonic acid	3,4-Dihydropyrimidin-2(1*H*)-ones	FE-SEM, EDX, TGA, XRD, FT-IR	[75]
3	B_6	Fe_3O_4@vitaminB_6-Pd (II)	Cross-coupling	SEM, TEM, TGA, EDS, ICP, FTIR, VSM, XRD	[76]
4	B_{12}	Vit-B_{12}/MCM-41.	Oxidation of a number of organic substrates	GC, GC mass, XRD, FT-IR, BET,	[77]
		GO-vitamin B_{12}	Oxidation of alcohols	FT-IR, TGA, XRD, FESEM, ICP-OES	[78]
5	C	Cu/AA@MNPs	Cross-linking reactions	FT-IR, TGA, SEM, XRD, TEM	[79]
		TiO_2-AA-Cu(II)	Oxidation of benzylic alcohols	FT-IR, XPS, ICP-AES, TGA and TEM	[80]

2. VITAMIN B-SUPPORTED NANOPARTICLES

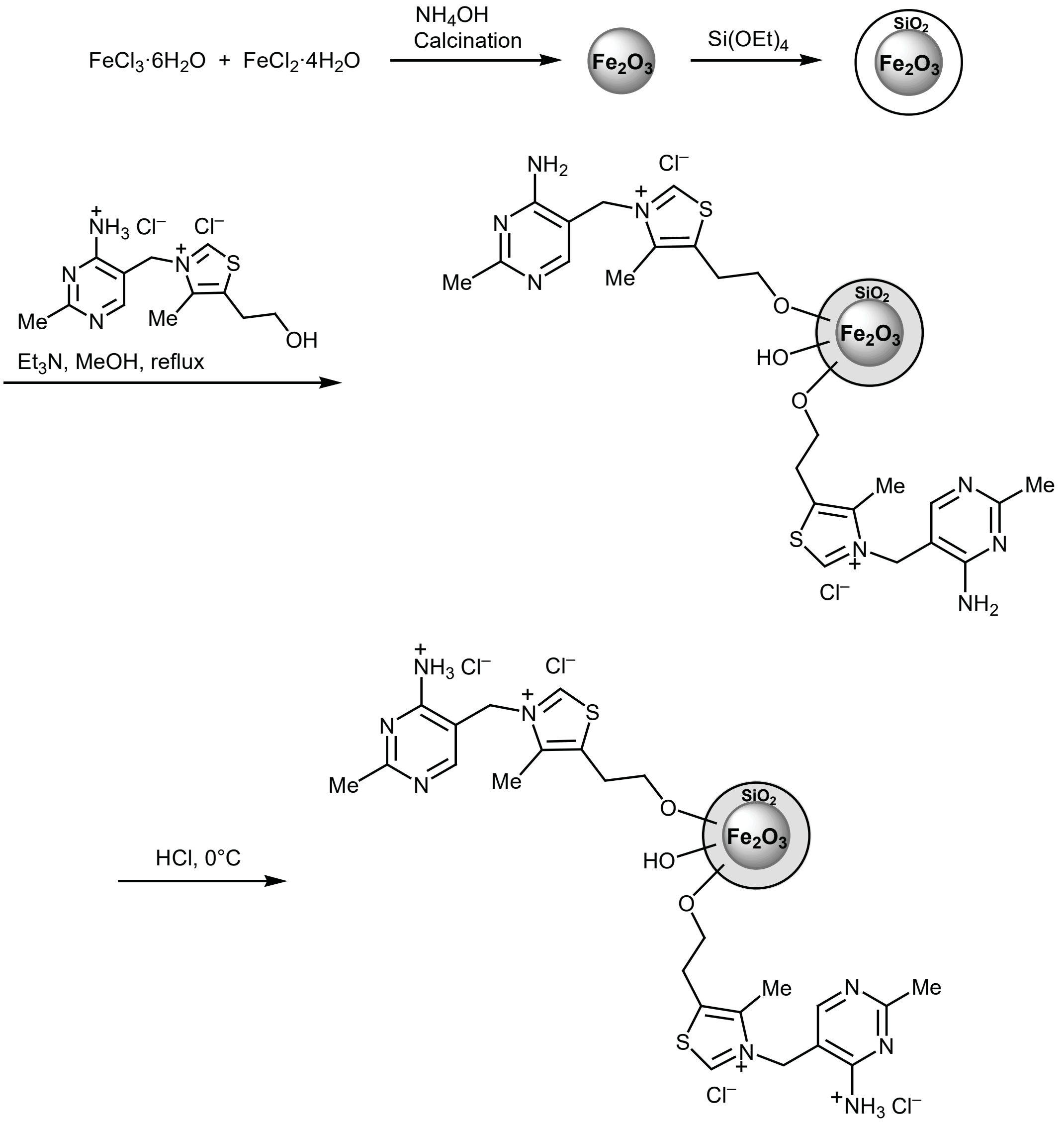
2.1. Vitamin B_1 (Thiamine)-Supported Nanoparticles

Azizi et al. [59] presented a new magnetic catalyst with immobilization of vitamin B_1 (thiamine hydrochloride) on the surface of γ-Fe_2O_3 nanoparticles encapsulated with silica for the acylation of alcohols and phenols with acetic anhydride under solvent-free conditions. Some advantages of this methodology were easy separation and reuse of the catalyst for 5 times without loss of efficiency and good performance for product synthesis (Scheme 1).

Due to several advantages of magnetic supports, including facile separation by external magnet, magnetic nanoparticles (MNPs) have gained a lot of attention recently. Since MNPs lack stability in harsh media especially acidic medium, their surface is coated with a layer of silica to enhance their stability and facilitate functionalization.

Nongrum et al. [60] offered the use of vitamin B_1 as an organic catalyst based on silica-supported ferrite nanoparticles (**Fe_2O_3@SiO_2@VB_1**) for the synthesis of 4*H*-benzopyranes. Good performance, easy catalyst recovery, short reaction time, mild reaction conditions,

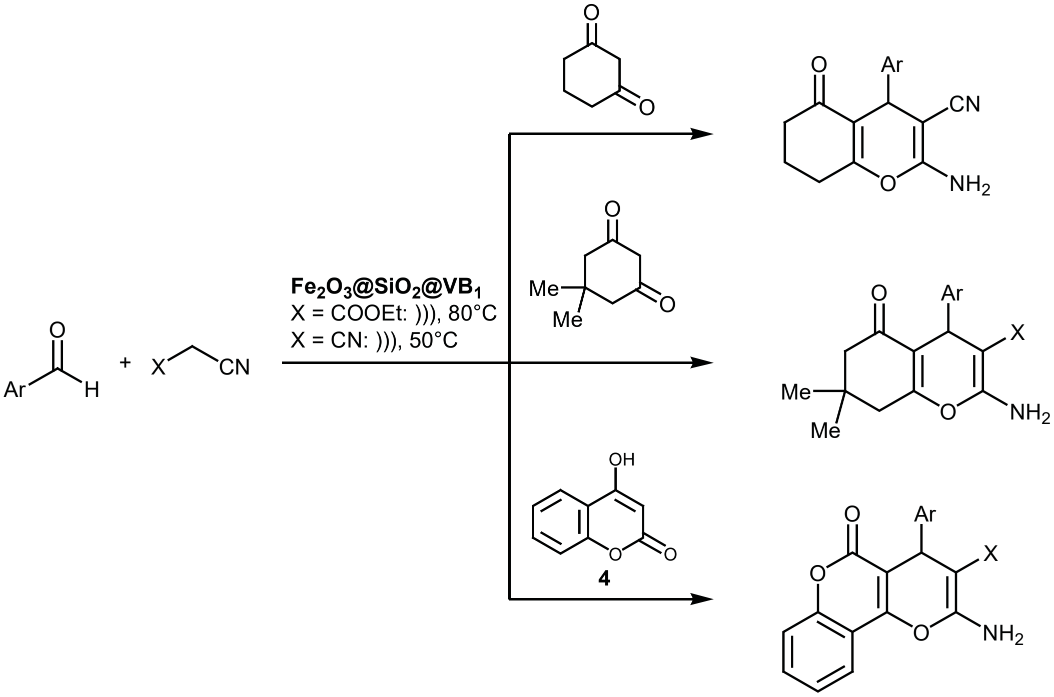
Scheme 1.



Fe_2O_3@SiO_2@VB_1

$$\text{ROH} \xrightarrow{\text{Ac}_2\text{O},\ \mathbf{Fe_2O_3@SiO_2@VB_1},\ \text{r.t.}} \text{ROAc} + \text{AcOH}$$

Scheme 2.

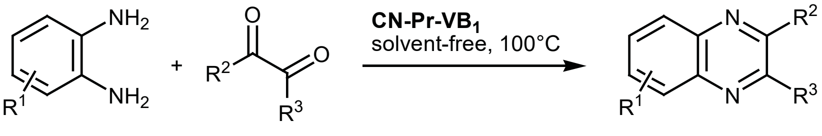


and use of green solvents are the positive features of this protocol. In addition, it was found that, considering the ease of catalyst recovery and its reuse in mild reaction conditions, ultrasonic activation helps to reduce the reaction time and improve the performance of the product. This protocol can be used for various synthetic approaches related to the formation of C–C and C–O bonds (Scheme 2).

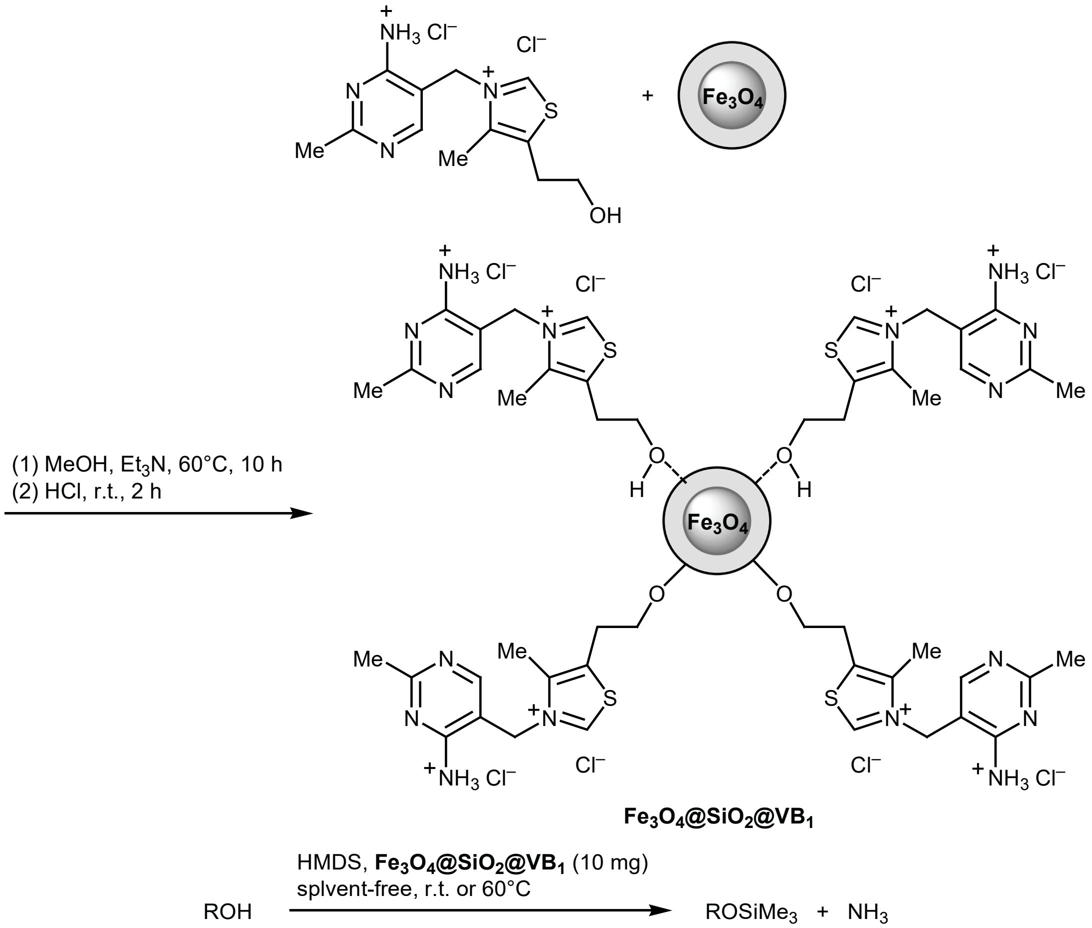
Rashidizadeh et al. [61] synthesized vitamin B$_1$-functionalized graphitic carbon nitride nanosheets (**CN-Pr-VB$_1$**) as a novel catalyst for the preparation of quinoxaline derivatives by condensation of benzene-1,2-diamines and 1,2-dicarbonyl derivatives. Among two-dimensional (2D) nanofoil materials, graphitic carbon nitride has unique properties due to its electronic structure and high chemical and thermal stability. Covalent functionalization of g-C_3N_4 can be a fundamental step in changing its stability and significantly improving its properties. To achieve this end, a new strategy for the covalent functionalization of *n*-plate g-C_3N_4 (**CN**) with vitamin B$_1$ (**VB$_1$**) using 1,3-dibromopropane as a covalent bond linker was proposed. The application of **CN-Pr-VB$_1$** as a heterogeneous catalyst for the synthesis of quinoxaline derivatives under solvent-free conditions was investigated. The target products were isolated with high purity. In addition, the catalyst can be easily recycled and reused for seven consecutive runs without noticeable reduction in catalytic activity (Scheme 3). It should be mentioned that the authors have claimed that the reaction of *o*-phenylenediamine (1.0 mmol) and benzil (1.0 mmol) did not proceed in the absence of the catalyst in the optimized reaction conditions (solvent-free, 100°C) even after 24 h, while in the presence of 15 mg of the catalyst at the same reaction conditions, the product was prepared in 3 min [61].

Thiamine-functionalized magnetic nanoparticles (**Fe$_3$O$_4$@ SiO$_2$@VB$_1$**) were reported by Abbasi and coworkers [62] as a catalyst for the silylation of a wide range of alcohols and phenols with hexamethyldisilazane. The catalyst was prepared in three steps. First, magnetite nanoparticles were prepared by co-precipitation from an iron source solution. Second, SiO_2 coating with tetraethyl orthosilicate (TEOS) was performed, and finally thiamine (VB$_1$) was anchored on the surface. The catalytic activity of **Fe$_3$O$_4$@SiO$_2$@VB$_1$** was

Scheme 3.



Scheme 4.



evaluated by protecting alcohols and phenols via trimethylsilylation in mild reaction conditions and short reaction times. In addition, the proposed nanocatalyst was easily separated using an external magnet and reused with almost constant efficiency. The advantages of this method are the use of recyclable organic catalyst with good performance, simple synthesis procedure, and gentle reaction conditions [62] (Scheme 4).

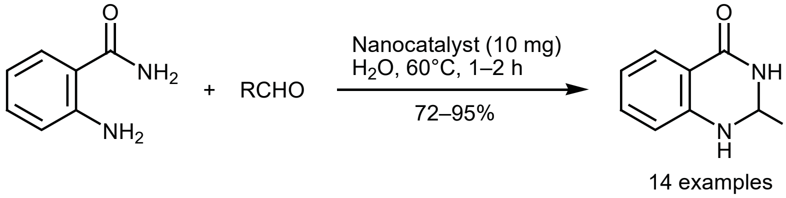
Azizi et al. [63] introduced a VB_1-grafted magnetic nanocatalyst (**Fe_3O_4@SiO_2@GMSI-VB_1**) for the efficient synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones in water from 2-aminobenzamide and carbonyl compounds (aldehydes or ketones). Covalent anchoring of VB_1 was performed by (3-glycidyloxypropyl)trimethoxysilane (GMSI) as a linker on the silica-modified Fe_3O_4. High efficiency, low reaction time, excellent durability, and low catalyst toxicity along with easy work-up using external magnets and low catalyst loading are the outstanding advantages of this methodology [63] (Scheme 5).

Ghafuri et al. [64] reported VB_1 covalently modified graphene oxide (**GO-VB_1**) as a useful catalyst for the synthesis of 2-substituted benzimidazole derivatives via condensation of phenylenediamines with substituted aldehydes in mild reaction conditions in ethanol at room temperature with yields of 85–95% (Scheme 6). In the absence of the catalyst, long reaction time was required to obtain the product [64].

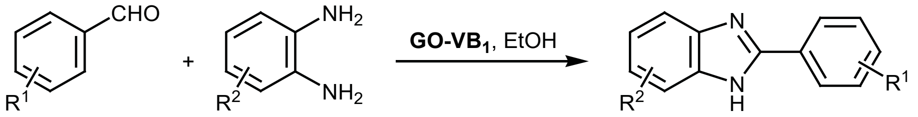
Esfandiary et al. [65] reported a novel superparamagnetic nanocatalyst, **Fe_3O_4@VB_1-Ag(I)**. Vitamin B_1 was utilized to activate the surface of Fe_3O_4 nanoparticles and facilitate the subsequent immobilization of Ag(I). This catalyst was efficiently used in the synthesis of propargylamines from alkynes, aldehydes, and amines via an A^3-coupling reaction. Solvent-free conditions, the absence of side reactions such as aldehyde–alkyne cyclization, and no base or other cocatalysts required were important features of this protocol (Scheme 7).

Rafiee et al. [66] synthesized an efficient and ecofriendly Pd nanocatalyst (**Fe_3O_4@SiO_2@VB_1-Pd**) for

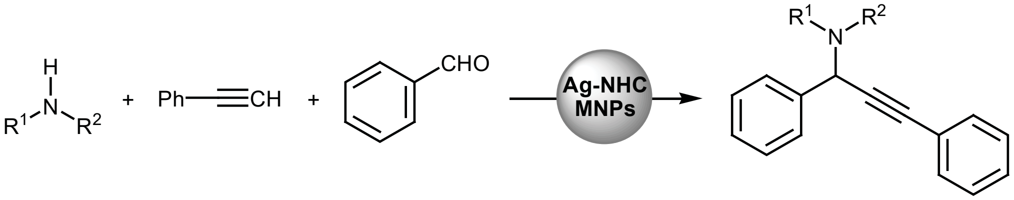
Scheme 5.



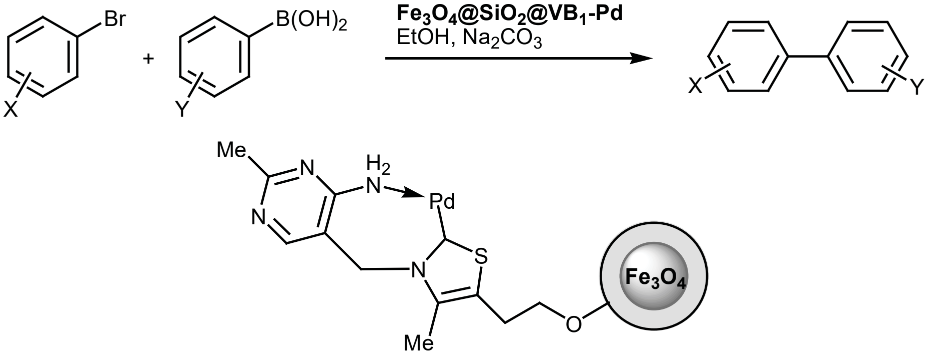
Scheme 6.



Scheme 7.



Scheme 8.



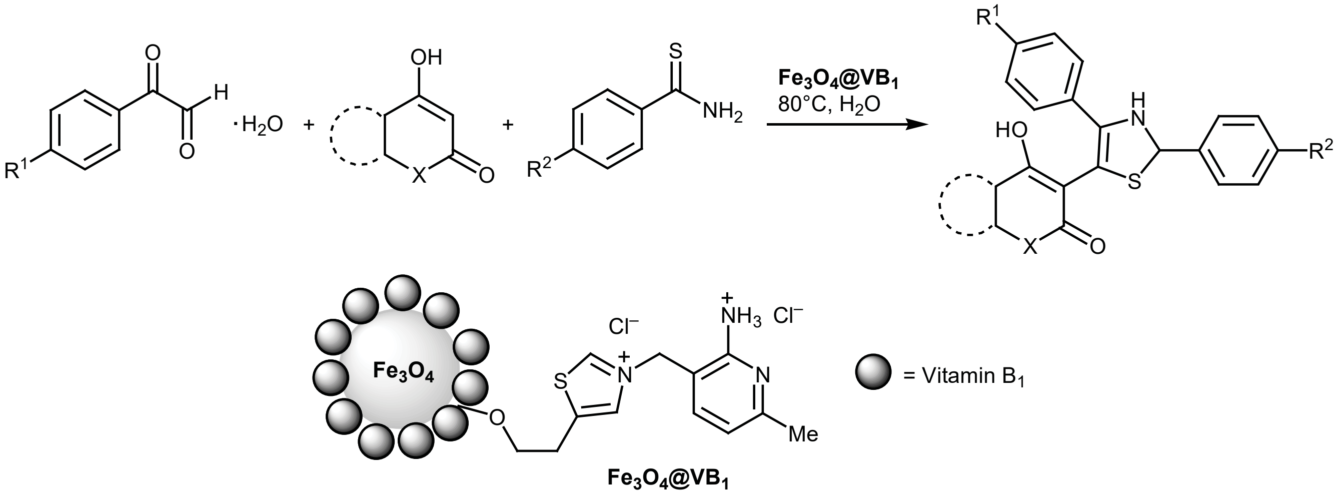
$Fe_3O_4@SiO_2@VB_1$-Pd

the Suzuki reaction of various aryl halides with phenylboronic acids. $Fe_3O_4@SiO_2$ nanoparticles were prepared by hydrolysis of TEOS in the presence of Fe_3O_4 nanoparticles that were synthesized through coprecipitation procedure. Then, thiamine hydrochloride (VB_1) was covalently linked to silica to provide a biodegradable, nontoxic, and cheap *N*-heterocyclic carbene (NHC) ligand for the encapsulation of complex with palladium. Excellent efficiency, short reaction times, easy recovery and reusability for 5 times with good performance, stability of the catalyst against air and humidity, and low loading of the catalyst in the reaction are the advantages of using this procedure (Scheme 8).

Shaterian et al. [67] synthesized **$Fe_3O_4@VB_1$** MNPs as an efficient nanocatalyst for the one-pot preparation of trisubstituted 1,3-thiazole derivatives via the three-component reaction of arylglyoxal monohydrate, cyclic 1,3-dicarbonyl compunds and thiobenzamides in aqueous medium at 80°C. The catalyst can be recovered using an external magnet and reused up to 4 times without loss in efficiency. Highlights of this catalyst are short reaction time, simple procedure, environmental friendliness, and cost efficiency in accordance with some green chemistry protocols (Scheme 9).

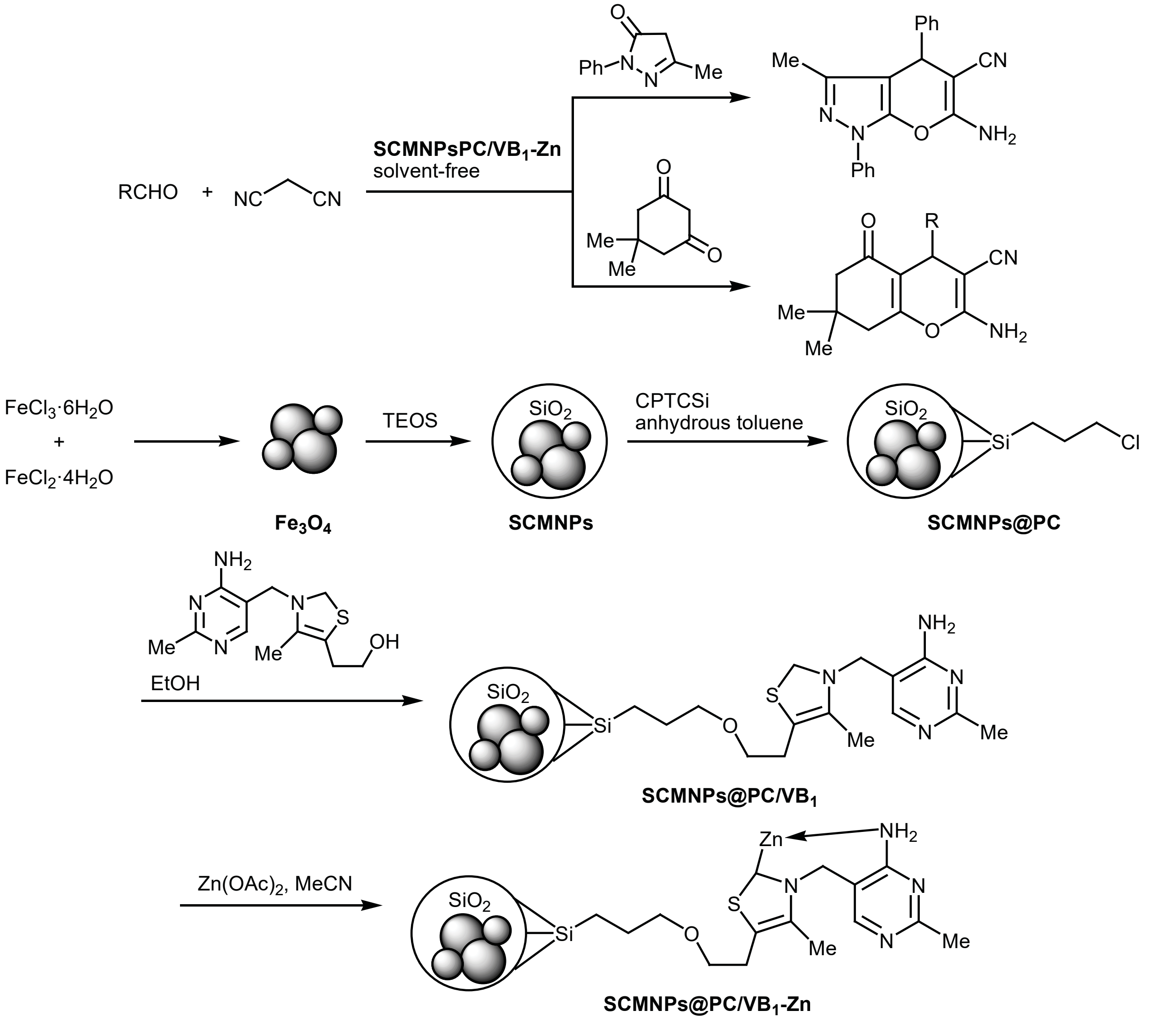
Hou et al. [68] invented silica-coated magnetic nanoparticles functionalized with 3-chloropropyl(triethoxy)silane (**SCMNPs@PC/VB_1-Zn**) for the one-pot synthesis of pyrano[2,3-*c*]pyrazoles and 1,8-dioxooctahydroxanthene derivatives. Vitamin B_1 was anchored on the surface of the nanoparticles by S_N2 reac-

Scheme 9.



R^1 = H, OMe; R^2 = F, Br , OMe, H; X = O, NMe, CH_2.

Scheme 10.



tion of OH functional group of VB_1 and the grafted 3-chlopropylsilyl linker. Subsequently, zinc acetate was added to prepare the nanocatalyst. In addition to positive features such as short reaction time, excellent efficiency, and simple separation, this magnetic nanocatalyst can be used 6 times without reducing performance (Scheme 10).

2.2. Nicotinic Acid (B_3)-Supported Nanoparticles

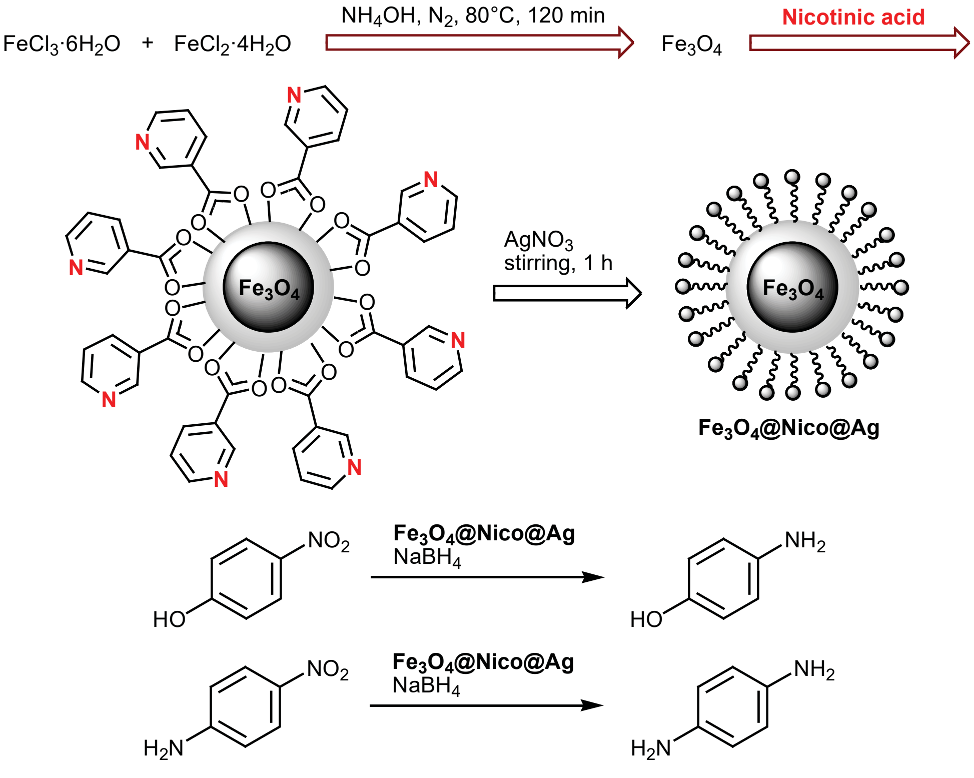
Kurtan et al. [69] synthesized a recyclable magnetic nanocatalyst (**Fe_3O_4@Nico@Ag**) for the hydrogenation of 4-nitrophenol and 4-nitroaniline. The catalyst was synthesized using a combination of reflux and reduction methods. The magnetic nanocatalyst **Fe_3O_4@Nico@Ag** was a good catalyst for reducing 4-nitrophenol to 4-aminophenol and of 4-nitroaniline to *p*-phenylenediamine at room temperature using $NaBH_4$ as the reducing agent. The reaction followed pseudo-first order kinetics. This nanocatalyst, in addition to good stability, can be reused for 4 runs without loss in efficiency (Scheme 11).

Afradi et al. [70] reported **Fe_3O_4@Niacin** as a reusable green biocatalyst for the one-pot preparation of 2-amino-3-cyanopyridines through four-component condensation reaction between aldehydes, ketones, malononitrile, and ammonium acetate under microwave irradiation in water. This environmentally friendly catalyst can be reused 6 times, and it presented other features such as low catalyst loading, nontoxicity, high yield, short reaction time, reusability of the catalyst, the absence of by-products, and no hazardous organic solvents (Scheme 12).

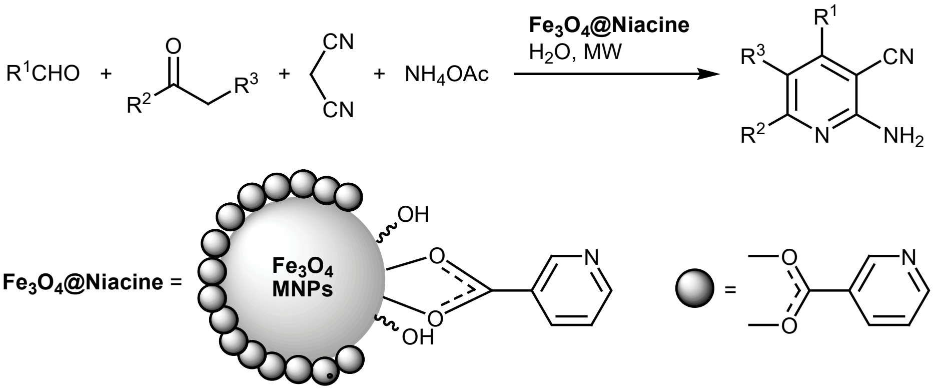
Rezapour et al. [71] reported starch-coated maghemite nanoparticles functionalized with palladium niacin complex (**Pd(II)NA_2@SMNP**) as a magnetically recoverable catalyst for the cross-coupling reactions such as Ullmann, Sonogashira, and Suzuki reaction. The catalyst was characterized by FT-IR, TGA, XPS, EDS, ICP-AES, TEM, and VSM. The catalyst provided satisfactory results in terms of yield and reaction time [71] (Scheme 13).

Khazaei et al. [72] synthesized Fe_3O_4@nicotinic acid @sulfonic acid nanoparticles as a recoverable catalyst for the synthesis of 1-carbamatoalkyl-2-naphthols. The catalyst was synthesized in two steps. In the first step, Fe_3O_4@nicotinic acid was prepared by refluxing iron (II) and iron (III) salts and nicotinic acid, followed by the addition to aqueous ammonia. In the second step, Fe_3O_4@nicotinic acid was functionalized with $ClSO_3H$ to produce Fe_3O_4@nicotinicacid@sulfonic acid. Simple operation, excellent efficiency in a short time, and easy catalyst recovery are some of the advantages of using this method (Scheme 14).

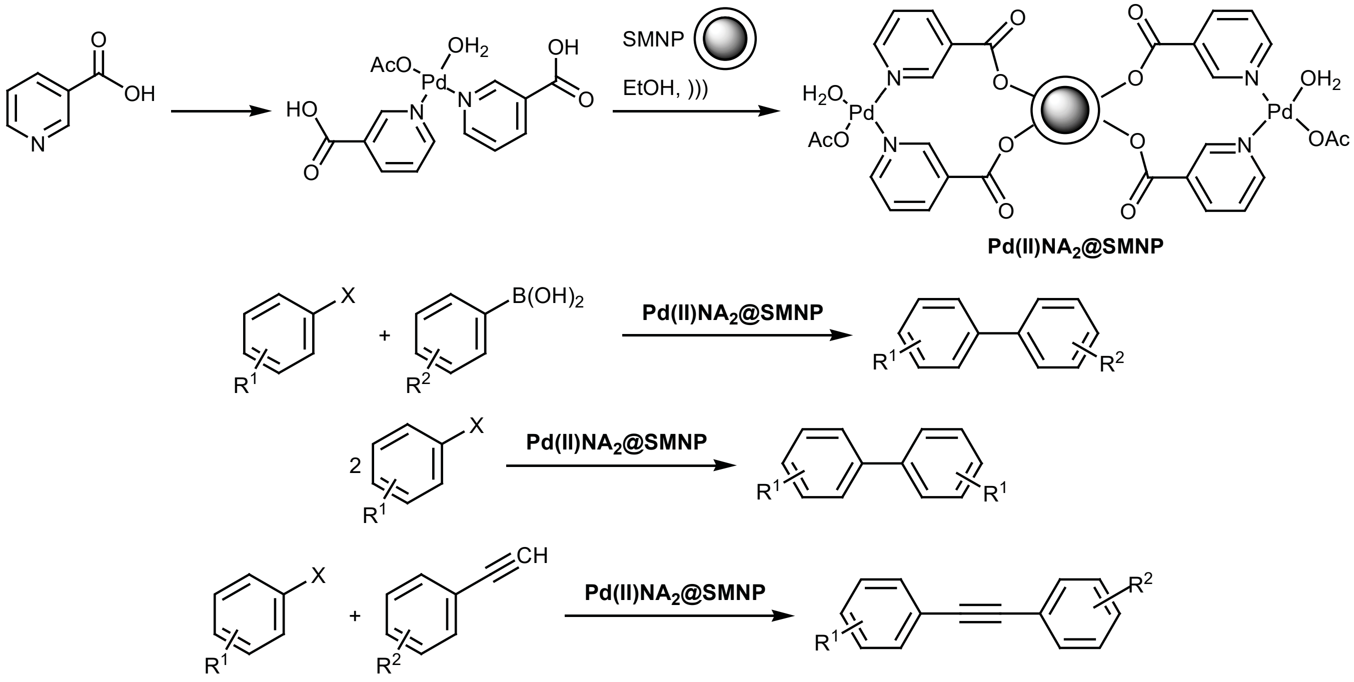
Scheme 11.



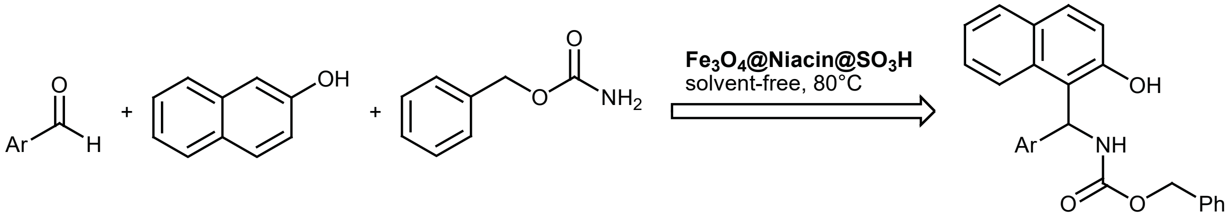
Scheme 12.



Scheme 13.



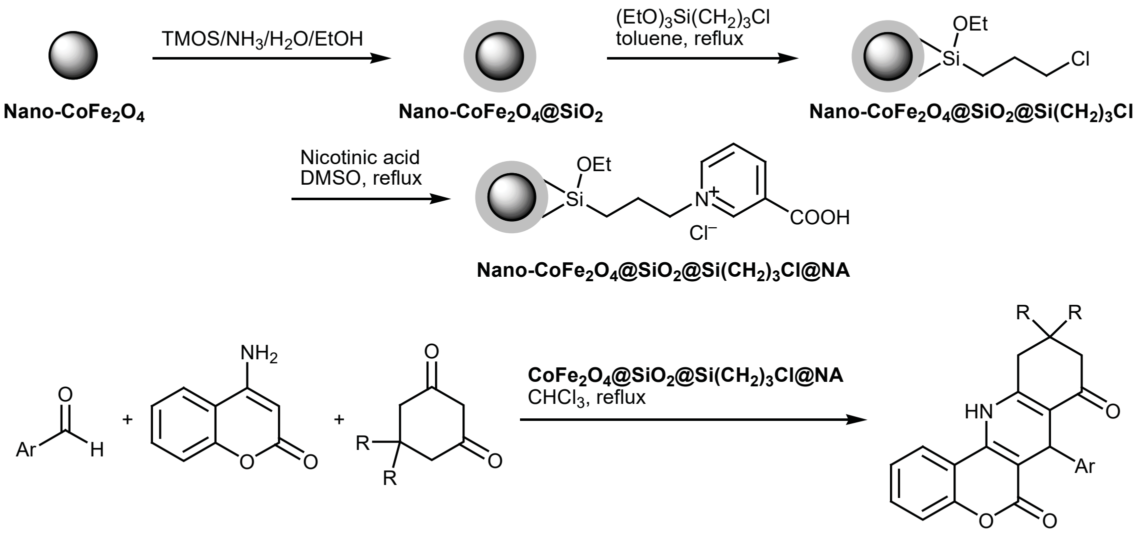
Scheme 14.



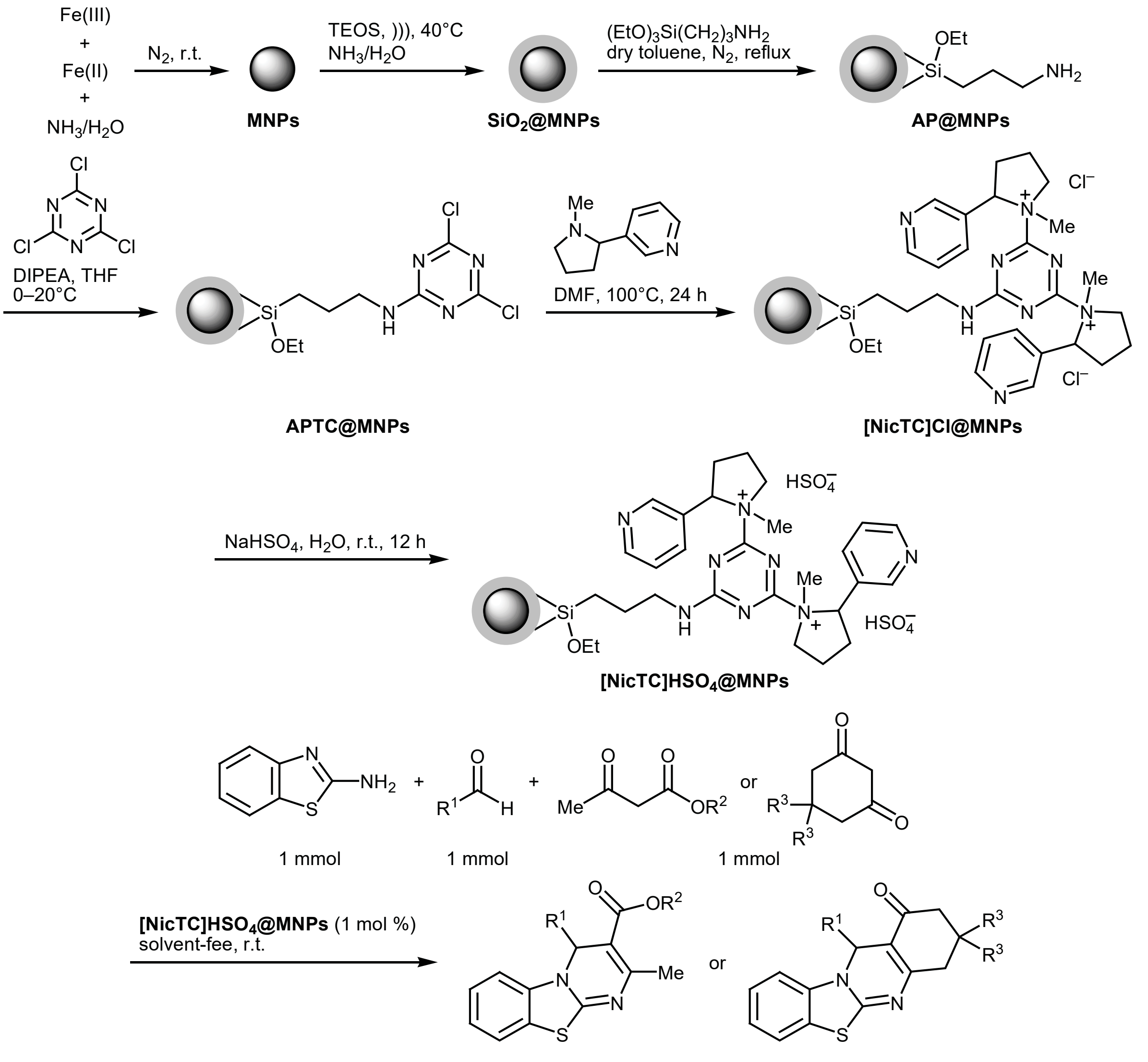
Quite recently, Foroughi and coworkers [73] presented for the first time nicotinic acid supported on cobalt ferrite [**Fe_3O_4@SiO_2@Si-$(CH_2)_3$@NA**] as a recyclable magnetic nanocatalyst for the one-pot synthesis of chromeno[3,4-*b*]quinoline derivatives by the reaction of aldehydes, dimedone or cyclohexane-1,3-dione, and 4-aminocoumarin. While cobalt ferrite is utilized as a magnetic support, silica shell is used to stabilize and protect the cobalt ferrite and also provide further functionalization and immobilization of nicotinic acid as the outermost component which acts as organocatalyst (Scheme 15).

Mohammadpoor-Baltork research group recently presented a nicotine-containing supported organocata-

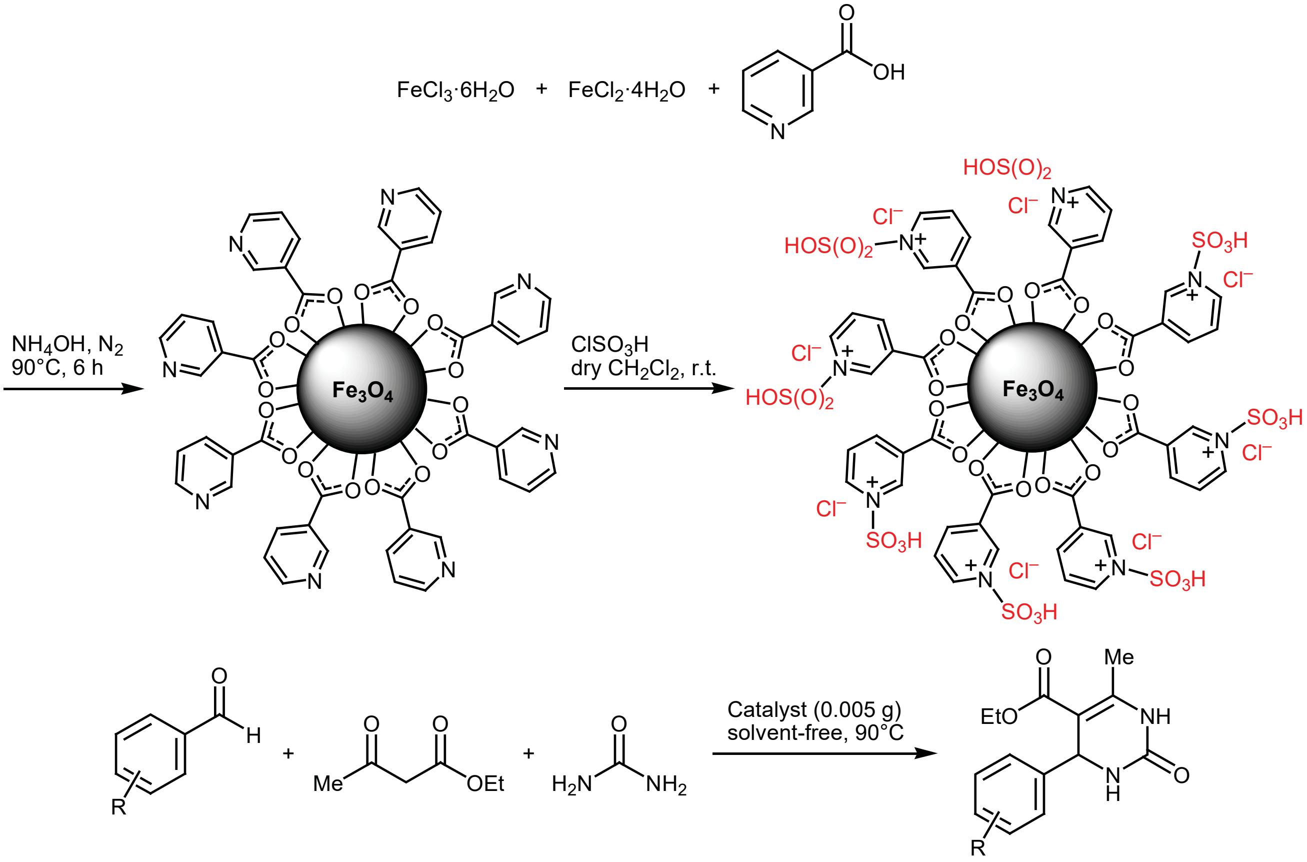
Scheme 15.



Scheme 16.



Scheme 17.



lyst (**[NicTC]HSO$_4$@MNPs**) for the synthesis of novel mono- and bis-4*H*-pyrimido[2,1-*b*][1,3]benzothiazoles under solvent-free conditions. The immobilization of nicotine was performed via cyanuric chloride (Scheme 16) [74].

Khazaei et al. [75] introduced Fe_3O_4-bonded pyridinium-3-carboxylic acid-N-sulfonic acid chloride as an efficient catalyst for the one-pot multicomponent synthesis of some 3,4-dihydropyrimidin-2(1*H*)-ones by the reaction of urea, ethyl acetoacetate, and various aldehydes under solvent-free conditions. The catalyst was synthesized as follows. In the first step, Fe_3O_4@nicotinic acid was prepared by refluxing iron(II), iron(III), and nicotinic acid, followed by treatment with aqueous ammonia. In the second step, Fe_3O_4@nicotinic acid was reacted with $ClSO_3H$ to produce Fe_3O_4@Niacin@sulfonic acid as a reusable magnetic catalyst (Scheme 17).

2.3. Vitamin B_6-Supported Nanoparticles

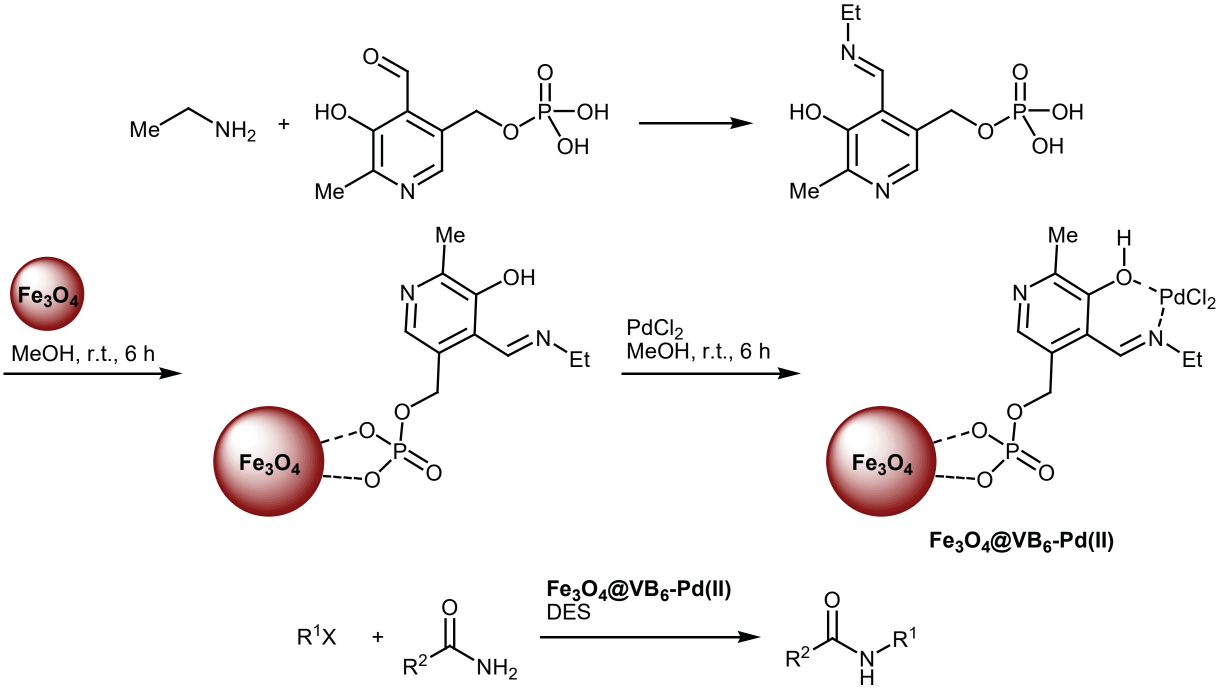
The synthesis of vitamin B_6-Pd(II) immobilized on magnetic nanoparticles was proposed by Bagheri et al. [76] for the C–X cross-coupling reactions with aryl halides in deep eutectic solvents (DES). Good catalyst stability and performance, and simple recovery and reusability of the catalyst (up to 5 times) are some of the advantages of this procedure (Scheme 18).

2.4. Vitamin B_{12}-Supported Nanoparticles

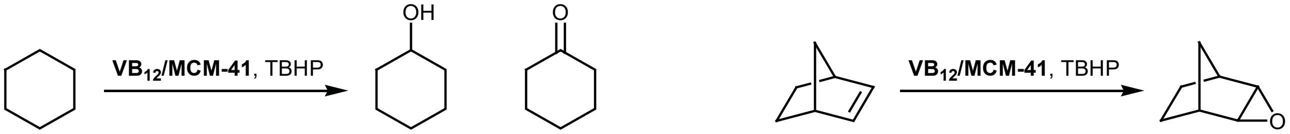
Immobilization of vitamin B_{12} (VB_{12}) within Mobil Composition of Matter no. 41 (MCM-41) nanopores has been performed to obtain an efficient catalyst for the oxidation of a number of organic substrates. The results showed that *tert*-butyl hydroperoxide (TBHP)-mediated oxygen transfer was successfully catalyzed by **VB$_{12}$/MCM-41**. Norbornene was thus oxidized to the corresponding epoxide. Furthermore, cyclohexane and cyclohexanol were converted to the corresponding alcohol and ketone. On the other hand, styrene underwent oxidative decomposition with the formation of benzaldehyde and benzoic acid [77] (Scheme 19).

Shaabani et al. [78] synthesized vitamin B_{12} supported on graphene oxide (**GO-VB$_{12}$**) as a bio-based catalyst for the selective aerobic oxidation of alcohols in accordance with the green chemistry principles. The results indicated that **GO-VB$_{12}$** as a green and reusable

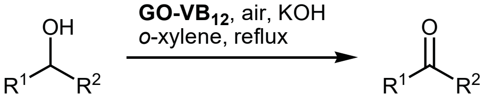
Scheme 18.



Scheme 19.



Scheme 20.



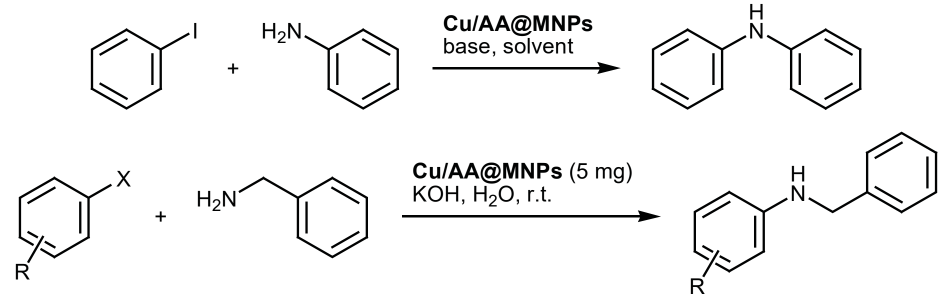
catalyst effectively catalyzed aerobic oxidation of a wide range of primary and secondary alcohols to the corresponding aldehydes and ketones (Scheme 20). Due to the simplicity and safety of **GO-VB$_{12}$**, it is hoped that this catalyst may be useful for a variety of other reactions.

3. VITAMIN C-SUPPORTED NANOPARTICLES

Hajipour et al. [79] reported magnetic nanoparticle-supported ascorbic acid (**MNP@AA**) as an alternative to the usually used silica layer coating. It was then used to immobilize copper nanoparticles to produce **Cu/AA@MNPs** catalyst. The hydrocarbon tails containing hydroxy group derived from the reaction of ascorbic acid and MNPs can help stabilize transition metal catalysts as well as prevent their accumulation. The catalyst was utilized for the C–N crosslinking reactions of organic halides (including aryl chlorides) and benzylamine, aniline, imidazole, or aliphatic amines. Moreover, C–O cross-coupling reaction of aryl halides with phenols was also reported (Scheme 21). The results showed that the use of this protocol is very safe, efficient, and environmentally friendly and that the catalyst can be easily separated by an external magnet to speed up the recovery process. The catalyst was reused for six runs without reducing performance.

Pourmorteza et al. [80] recently immobilized $Cu(OAc)_2$ onto ascorbic acid-coated TiO_2 nanoparticles under ultrasonic irradiation to obtain an active photocatalyst for the selective oxidation of benzylic alcohols. The main feature of this green method is the use of atmospheric oxygen along with TEMPO as an oxidizer under visible light and solvent-free conditions. Easy recovery and reuse of the catalyst is a prominent feature of this protocol (Scheme 22).

Scheme 21.



Scheme 22.

4. OTHER APPLICATIONS OF VITAMINS

4.1. Application of Vitamins in Drug Delivery

Suksiriworapong et al. [81] reported the grafting of nicotinic acid and *p*-aminobenzoic acid (PABA) on poly(ε-caprolactone)-poly(ethylene glycol)-poly(ε-caprolactone), which was performed by Huisgen 1,3-dipolar cycloaddition, also known as click chemistry. Because of the difference in molecular structure between PABA and nicotinic acid, the physicochemical properties (surface charge and particle size) of the bonded copolymer nanoparticles were entirely different. As the molar ratio of the bonded units increased, the particle size of the blank nanoparticles tended to gain, resulting in an enhancement in the hydrophobic components of the bonded copolymer. Ibuprofen was selected as a model drug to appraise the interaction of grafted copolymers and loaded drug. After loading with ibuprofen, the particle size of the nanoparticles loaded from both bonded copolymers increased compared to the empty nanoparticles. Significant differences in loading capacity between nicotinic acid and PABA bonded copolymer nanoparticles were clearly demonstrated. Presumably, this is the result of different adaptability between each bonded compound and ibuprofen, including hydrogen bond interaction, π–π interaction, and steric hindrance [81].

The same authors [82] reported a method for the preparation of nanoparticles for the purpose of monitoring particle size and optimizing drug loading capacity by grafting nicotinic acid on copolymers [poly(ε-caprolactone)]$_2$-poly(ethylene glycol). Ibuprofen and indomethacin with two different molecular characteristics were selected as model drugs to be bound to nanoparticles. As particle diffusion characteristics, increasing nicotinic acid bond values increases the particle size as a result of increasing the hydrophobicity of the copolymer. The presence of grafted nicotinic acid increases the loading capacity for both drugs compared to nanoparticles without nicotinic acid. It was shown that nicotinic acid grafting affects the loading capacity and diffusion properties of the nanoparticles.

Thepphankulngarm et al. [83] reported a successful method for designing a new targeted cisplatin (CDDP) delivery system based on VB_{12}-conjugated porous silica nanoparticles. Vitamin B_{12} was grafted to the cobalt center on drug carriers (PSNs) as an active targeting unit through coordination. The system consisted of carboxy group-modified porous silica nanoparticles (PSNs-C) as a drug carrier, cisplatin (CDDP) as an anticancer drug, and vitamin B_{12} as an active targeting unit for tumor cells. Porous silica nanoparticles were prepared by co-condensation of TEOS and carboxyethylsilane (CES) using CTAB as the structure-directing agent. Vitamin B_{12} was then successfully decorated on the drug-loaded particles through coordination to cobalt. Vitamin B_{12} “could control the drug release by serving as a gatekeeper to hinder prevent drug leaching during circulation.” In addition, vitamin B_{12} could help to regulate drug secretion, which in turn can reduce side effects and increase efficiency [83].

4.2. Application of Supported Vitamins in Wastewater Treatment

Amir et al. [84] proposed an easy way to destroy chemically and biologically resistant azo dyes using Fe_3O_4@Nico@Cu magnetic nanocatalyst. The results of the UV-Vis studies indicated a good decolorization potential of the newly synthesized magnetic nanocatalyst Fe_3O_4@Nico@Cu in the degradation of azo dyes in wastewater. In particular, the nanocatalysts could easily reduce azo compounds (Methyl Orange, Methylene Blue, Eosin Y, and Rhodamine B) in the presence of $NaBH_4$. Easy and fast preparation and separation from the reaction mixture, low cost, and insensitivity to moisture make the catalyst an excellent, superior, and stable compared to other nanocatalysts.

It should also be mentioned that not only vitamins but also enzymes [85], other organic molecules (organocatalysts) [86], and DNA [87] have been supported on various nanomaterials. Enzymes immobilized on nanomaterials were used to design biocatalysts [88] and for biofuel production [89], along with other applications.

5. CONCLUSIONS

Over the past few years, in order to achieve more economical and greener methods for the synthesis of organic compounds, environmentally friendly organocatalysts have attracted much attention. Accordingly, utilization of vitamins as natural organocatalysts with excellent catalyst activity in both homogeneous and heterogeneous media have gained interest. Immobilization of vitamins on nanomaterials not only increases their catalytic activity but also makes them recyclable. Therefore, supported vitamins have been used in several organic reactions including cross-coupling reactions, oxidations, reductions, cyclizations, and multicomponent reactions. It should also be noted that vitamins are gaining more interest in other fields of study such as water treatment and analytical, medicinal, polymer, and materials chemistry.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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