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Nanomaterial Catalysed Environmental Benign Synthesis of Polyfunctionalized Tetrahydro-Benzopyrans and its Derivatives: A Review on Recent Update

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Abstract

Polyfunctionalized tetrahydro-benzopyrans known as important oxygen-containing privileged heterocyclic scaffolds offers wide range of useful applications in medicinal chemistry, biochemistry, and pharmacology. Owing to its pronounced pharmacological and biological applications, a wide range of catalysts including homogeneous and heterogeneous have been explored for efficient and environmental benign synthesis of polyfunctionalized tetrahydro-benzopyranes. Among the various types of catalyst, nanomaterials-based catalyst seems to be an exceptionally effective catalysts for various types of organic transformations as they offer advantages like large surface area-to-volume, broad functional group tolerance, milder reaction conditions, high yields, reusability, recyclability, simple and easy fabrications, etc. In this review, we have described an overview of different nanomaterial-based catalysts for environmental benign synthesis of polyfunctionalized tetrahydro-benzopyrans. In this article, we provide special emphasis on functionalized magnetic nano catalysts and composite based nanomaterials for synthesis of tetrahydro-benzopyrans and derivatives. Additionally, we have described design, fabrication, and characterization of interesting nanomaterials along with their reaction mechanism for synthesis of tetrahydro-benzopyrans heterocyclic scaffolds.

Keywords

Tetrahydro-benzopyran, Multicomponent reaction, Nanoparticles, Magnetic nanoparticles

Introduction

Multi component reactions (MCRs) involves three or more components (reactants) in same pot to generate product containing all starting material atoms in target product framework [1-4]. These reactions offer several advantages such as mild conditions, high convergence, excellent efficiency, atom and step economy and environmental benign reaction condition, synthesis of complex molecule in single step, etc. MCR can generate useful small heterocycles motifs which further play important role in natural product synthesis [5], medicinal chemistry [4], agro-chemistry, chemistry, polymer chemistry, and drug delivery program [6]. It is well known that MCRs have capability to address various challenge associated with several chemical reaction in an eco-friendly manner. To reduce chemical waste and improve efficiency of chemical transformations, several advancements in multi component reactions are carried out. Among the various advancements, use of economic and environmentally friendly catalysts in MCR are one of the important factors to enhance the efficiency of MCRs. Several categories of catalyst have been reported in literature which include homogeneous, heterogeneous, inorganic, organo-catalyst, endo selective catalyst and nano catalyst, etc., [7, 8].

It was observed that among all these catalysts, homogeneous catalysts are widely utilized in industries for better selectivity and high yield but possibility of agglomeration and aggregation of homogeneous catalysts and weak stability make them inferior choice. To avoid aggregation and agglomeration of catalyst and increase the stability of catalyst, size of catalyst is reduced to nano scale which not only increase stability but also enhanced selectivity and activity of catalyst [9, 10]. The research on nano catalysis undergone a sharp growth during last few decades in heterogeneous and homogeneous catalysis because nanomaterial have large surface-to-volume ratio. Nanoparticles of different metals, metal oxides, and composite nanomaterials have been widely used for many MCRs. The advantages like minimum economic friendly, chemical waste, improved chemical stability, improved selectivity and activity of catalysts, and cost effective are some of features of nano catalyst that made them attractive candidates in catalytic chemistry. Among the various types of nanomaterials-based catalysts such as graphene-based nano catalysts, Schiff-based nano catalysts, thin-film nano catalysts, magnetic nano catalysts, mixed metal oxide nano catalysts, and core-shell nano catalysts were successfully employed in various MCRs which results improved yield and eliminating the use of solvent. Additionally, these nanomaterials can be reused in reaction without significant decrease in their catalytic activities Some representative drugs containing benzopyran scaffolds were shown in Figure 1.

In view of potent applications of tetrahydro-benzopyrans scaffolds in diverse areas, several methods have been attempted for synthesis of benzo-pyrans and its derivatives. It was found that most of these methods suffer from different drawbacks like low yield, decomposition of product, harsh reaction conditions, use of hazardous solvents, multi-step synthetic procedure, etc. Nanomaterials catalyzed synthesis of tetrahydro-benzopyrans and its derivatives via single pot MCR where condensation of an aldehyde with malononitrile and dimedone results excellent yields under environmentally friendly conditions [11]. Thus, this review article offers an overview of

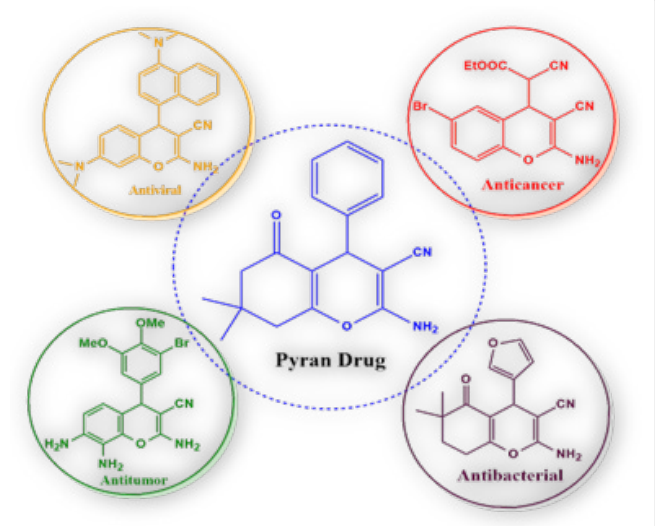


Figure 1: Few representative drug molecules containing benzopyrane scaffolds.

number of nano catalyst that has been recently used to synthesize benzopyrans and its derivatives. The already reported review articles on nanomaterial-catalyzed synthesis of heterocyclic ring systems explained on synthesis of several diverse heterocyclic scaffolds rather than considering single heterocyclic moiety. The examples described here were arranged under sections of metal-based nanoparticles and non-metal-based nanoparticle catalyzed synthesis of tetrahydro-benzopyran derivatives with brief discussion on synthesis of nanomaterials and advantages of chemical transformation thereof.

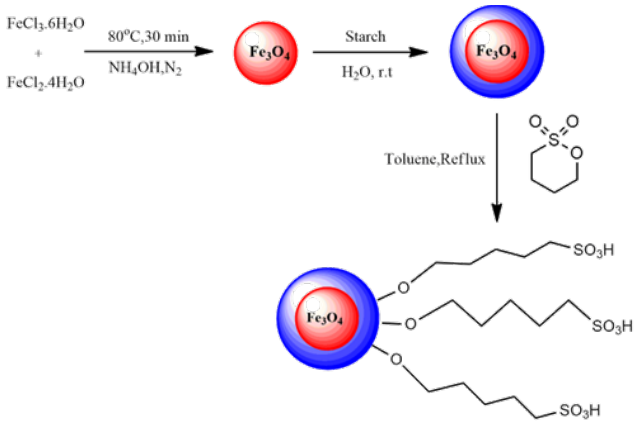
Magnetic nanoparticles (MNPs) have been explored expansively in last few years as efficient nano catalyst or catalyst-supported material specially for organic transformation because of their specific characteristics. In general, MNPs are capable to produce the target products in large-scale production possess because of its high mechanical and thermal stability. Moreover, their insolubility in most of solvents and exceptional paramagnetic nature permit their easy and effective separation from reaction mixtures by an external magnet which make this methodology more sustainable. Furthermore, minimal amount of waste generation during synthesis and easy workup procedures adequately satisfies the needs of green chemistry principles. However, it was found that aggregation of MNPs during organic transformation is major concern. The suitable coating and surface modifications of MNPs may prevent from aggregation and make them stable and more efficient for wide range of application such as heterocyclic synthesis, bioimaging, medicinal chemistry, etc. Easily recoverable nano catalysts have extensively used for synthesis of tetrahydro-benzopyran and derivatives. For example, Kiasat et al. reported Fe_3O_4@SiO_2/1,4-Diazabicyclo [2.2.2] octane) catalyzed synthesis of a series of pyran annulated compounds in aqueous medium at 80 °C, via one pot three-component reaction of substituted aldehydes 1, 3-diketone and malononitrile. The formation of reported catalyst was confirmed by X-ray diffraction (XRD), atomic force microscope (AFM), thermogravimetric analysis (TGA), field emission scanning electron microscope (FE-SEM), and fourier-transform infrared spectroscopy (FT-IR) spectroscopy. The high product yield (84 - 90%), reusable up to six cycles, short reaction time were some advantages of reported methodology [12] (Table 1).

Behrouz and his group developed carbon-based solid acid (C–SO_3H) containing Fe_3O_4 nanoparticles as shown in Scheme 1. The structure of reported catalyst was examined by different characterization techniques. This catalytic activity of synthesized catalyst was further examined for synthesis of tetrahydro-benzopyran derivatives. It was found that reported catalyst successfully carried out the formation of 2-amino-3-cyano-4H-pyrans via reactions of malononitrile, benzaldehyde , and dimedone. The excellent yield, recyclable, shorter reaction time, and use of green solvent like water were some advantages of this methodology [13] (Table 1).

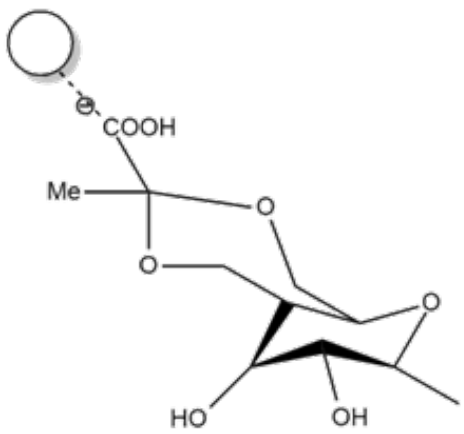
Synthetic route of Fe_2O_3@C-SO_3H nanoparticles was made by mixing $FeCl_2.4H_2O$, and $FeCl_3.6H_2O$ in 1:2 ratio followed by grafting of xanthan gum as shown in Scheme 2. The catalytic efficiency of Fe_3O_4@xanthan gum was monitored by the reaction of dimedone, aldehydes, and malononitrile to make 2-amino-3-cyano-4H-pyrans. This reaction was com-

Table 1: Different nanomaterials-based catalyst used for synthesis of tetrahydro-benzopyran and its derivatives.

S. No.	MNPs	Solvent	Temperature °C	Time (min)	Yield (%)	References
1.	Fe_3O_4@SiO_2/DABCO	Water	80	25 - 45	84 - 92	[12]
2.	Fe_3O_4@C-SO_3H	Water	60	30 - 70	80	[13]
3.	Fe_3O_4@Xanthan Gum	Ethanol	25	4 - 20	80	[14]
4.	Fe_3O_4/SiO_2-Met	Ethanol/ Water	25		85 - 92	[15]
5.	NH_2@SiO_2@Fe_3O_4	Solvent free	25	2	96	[16]
6.	Fe_3O_4@g-C_3N_4	Ethanol	60	30 - 180	97	[7]
7.	Fe_2O_3@SiO_2@VB_1	Ethanol: Water (1:4)	50	15	90	[8]
8.	Fe_3O_4@SiO_2@TiO_2	Solvent free	100	6 - 20	93 - 97	[17]
9.	Fe_3O_4@SiO_2@R-NMe_2	Ethanol	70	240	92	[18]
10.	([Y-Fe_2O_3@HApSi$(CH_2)_3$AMP])	Water	25	10	80 - 87	[19]
11.	Fe_3O_4@SiO_2-imd-PMA	Water	reflux	7 - 20	94 - 96	[20]
12.	PPY/Fe_3O_4/CNT	Solvent free	90	10	97	[21]
13.	Fe_3O_4@SiO_2@RF–SO_3H	Solvent free	40	15	>98	[22]
14.	n-Fe_3O_4@TDI@TiO_2	Solvent free	70	1 - 4	80 - 94	[23]
15.	Fe_3O_4–MDI-Gn	Water: Ethanol (1: 1)	25	10	95	[24]
16.	ZnO	Ethanol	25	10	75 - 95	[25]
17.	ZnS/$CuFe_2O_4$/Agar	Ethanol	25	3 - 15	97	[26]
18.	Nano ZnO 10 mol%	Water: Ethanol (1:1)	25	180	86 - 90	[27]
19.	$ZnFe_2O_4$@alginic acid	Ethanol	25	10	93	[28]
20.	SiO_2	Ethanol	25	20 - 30	86 - 98	[29]
21.	Ag/Fe_3O_4@Starch	Ethanol	50	9 - 17	84 - 95	[30]
22.	$CuFe_2O_4$@Starch	Ethanol	25	20 - 50	84 - 96	[31]
23.	[Co (MCG) $(H_2O)_3$] (5 mol%)	Water: Ethanol (1:1)	25	10 - 20	86 - 95	[6]
24.	$MnFe_2O_4$@SiO_2NHPhNH_2–PTA	Solvent free	80	30	95	[9]
25.	n-Pd	Acetonitrile	reflux	300	87	[32]
26.	TiO_2	Solvent free	reflux	35	92	[33]
27.	PbO	Solvent free	25	9 - 12	88 - 91	[34]
28.	$CoFe_2O_4$	Water: Ethanol (1: 3)	60	4 - 8	87 - 96	[35, 36]



Scheme 1: Synthetic route of Fe_2O_3@C-SO_3H nanoparticles.

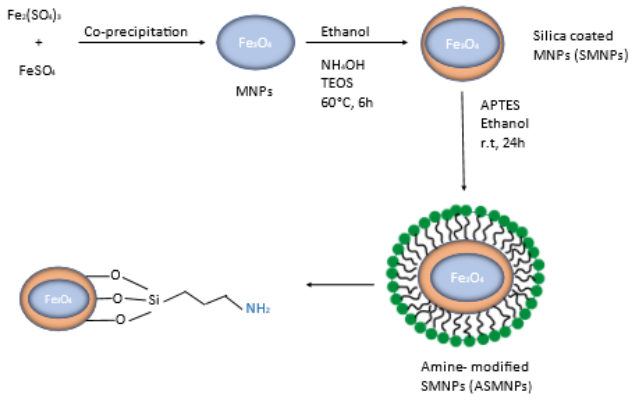


Scheme 2: Monomer unit of Fe_3O_4@xanthan gum.

pleted within 45 min in the presence of Fe_3O_4 and yielded 30% yield. Fe_3O_4@xanthan gum was shown to be more effective (80% yield, 4 - 20 min in ethanol) than Fe_3O_4 at activating carbonyl groups via hydrogen bonding [14] (Table 1).

(Fe_3O_4/SiO_2-Met) for facile preparation of pyran derivative in aqueous medium through reactions between dimedone, aldehydes, and malononitrile. In addition, they reported that Fe_3O_4/SiO_2-Met could be used in the nitroaldol processes. The high stability, excellent activity, high yield, and reusability of Fe_3O_4/SiO_2-Met, mild reaction conditions were some advantages of this process [15] (Table 1).

Satish K. Awasthi and his group reported amine-functionalized silica MNPs (NH_2@SiO_2@Fe_3O_4) as depicted in Scheme 3. The formation of catalyst was confirmed by different spectroscopic and other tools like FT-IR, energy-dispersive X-ray spectroscopy (EDX), vibrating-sample



Scheme 3: Synthesis of $NH_2@SiO_2@Fe_3O_4$.

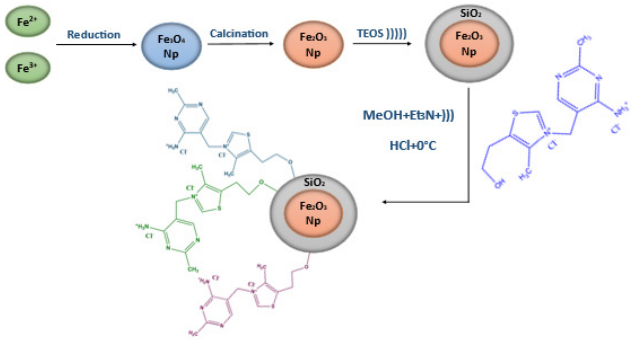
magnetometer (VSM), SEM, XRD, and transmission electron microscopy (TEM). Catalytic performance of reported ($NH_2@SiO_2@Fe_3O_4$) catalyst was examined for synthesis of 2-amino-4H-benzo[b]pyrans. Authors found that product was synthesized by grinding of different aromatic aldehydes, malononitrile, and dimedone at room temperature with excellent yields without using any solvent. The synthesized catalyst exhibits fascinating advantages like durability, reusability, improved yield, broad functional group tolerance, cost effectiveness, simple work up procedures, short reaction time, and milder reaction conditions. The synthesis of $NH_2@SiO_2@Fe_3O_4$ catalyst was depicted in Scheme 3 [16] (Table 1).

In another report, Najmedin Azizi et al. developed truly recyclable magnetite-supported graphitic carbon nitride catalyst ($Fe_3O_4@g\text{-}C_3N_4$) as shown in Scheme 4. The catalytic activity of reported $Fe_3O_4@g\text{-}C_3N_4$ nanocomposite was investigated in a one-pot synthesis of 4H-benzopyran by condensation of malononitrile, benzaldehyde, and dimedone as model reactants. The magnetically recoverable catalyst, simple experimental procedure, inexpensive catalyst, easy purification methods by simple crystallization, and use of environmental benign solvents were some key advantages of this protocol [7] (Table 1).

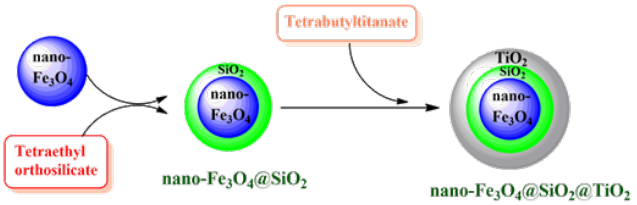
A vitamin B1 functionalized $Fe_2O_3@SiO_2@VB1$ nanoparticles was developed by Ridaphun Nongrum et al. by immobilization of SiO_2 core on Fe_2O_3 nanoparticles followed by vitamin B1 functionalization as depicted in Scheme 5. The reported catalyst was well characterized by FT-IR, SEM, TEM, powder XRD, and EDX. To examine efficiency of catalyst, benzo[b]pyrans were synthesized with excellent yields. Nano catalyst ($Fe_2O_3@SiO_2@VB_1$ nanoparticles) was magnetically recycled and retrieved. The beneficial features associated with this protocol were convenient mild reaction condition, easy catalyst recovery, work-up procedure, use of green solvents, and shorter reaction time [8] (Table 1).

Ardeshir Khazaei and his group developed one-pot three component condensation reaction between dimedone, different aldehydes, and malononitrile method for successful preparation of tetrahydro-benzopyran derivatives using ($Fe_3O_4@SiO_2@TiO_2$) nanoparticles at 100 °C as shown in Scheme 6. The ($Fe_3O_4@SiO_2@TiO_2$) were synthesized by interaction of nano Fe_3O_4 with tertbutyl and titanate tetraethyl orthosilicate. The reported catalyst was characterized by XRD, FE-SEM, TEM, and EDX analysis [17] (Table 1).

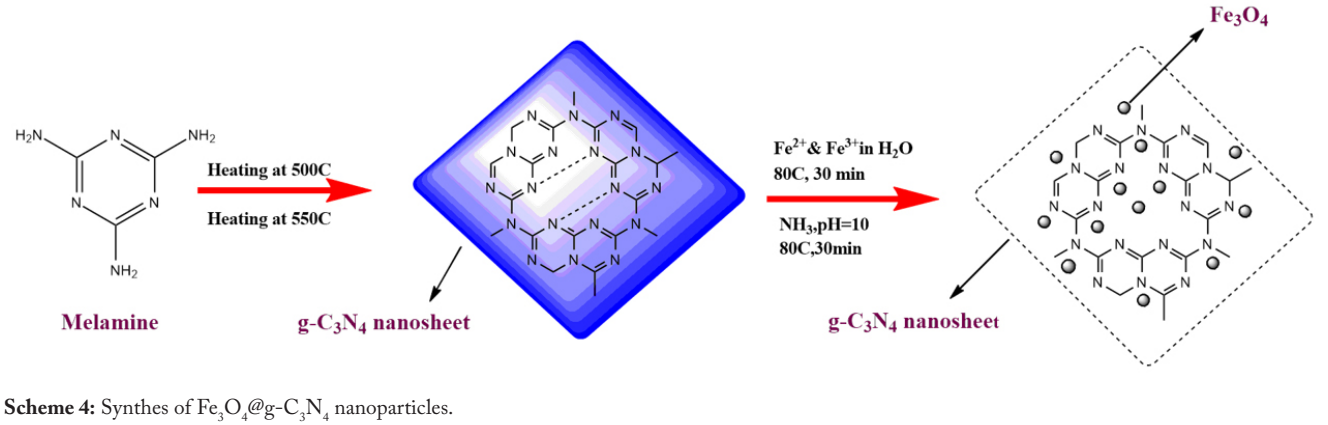
Mohammad Mehdi Eskandari and his group developed novel nanomagnetic material containing a dimethyl amino tag nano $Fe_3O_4@SiO_2@R\text{-}NMe_2$ as per Scheme 7. The nanoma-



Scheme 5: Synthesis of $Fe_2O_3@SiO_2@VB1$.



Scheme 6: Preparation of $Fe_3O_4@SiO_2@TiO_2$.



Scheme 4: Synthes of $Fe_3O_4@g\text{-}C_3N_4$ nanoparticles.

terial was well characterized and catalytic performance was then investigated in the synthesis of 2-amino-4H-benzo[b] pyrans from malononitrile, arylaldehydes, and dimedone [18] (Table 1). The advantages of this protocol include high selectivity, efficacy, wide scope, magnetic recyclability, and simple purification of the products.

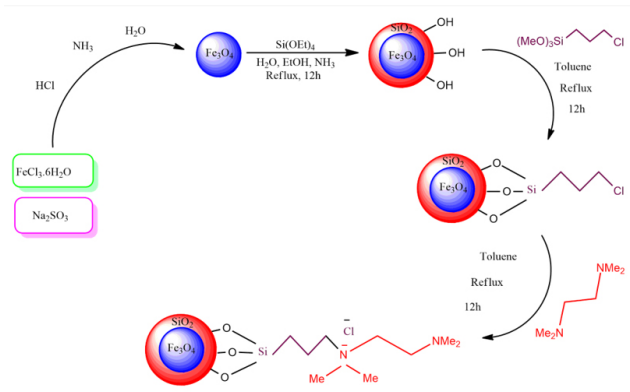
Abbas Shafiee synthesized inorganic–organic hybrid magnetic nano catalyst supported on hydroxyapatite encapsulated (ϒ-Fe_2O_3@HApSi $(CH_2)_3$AMP) as per Scheme 8. The reported novel magnetically immobilized organo-catalyst was prepared by covalently anchoring (2-aminomethyl) phenol moiety on surface of hydroxyapatite encapsulated maghemite nanoparticles as shown in Scheme 8 (Table 1). The synthesized inorganic–organic hybrid nano catalyst was confirmed TEM, SEM, FT-IR, TGA, XRD, BET (Brunauer–Emmett–Teller) and VSM, which reveal of superparamagnetic nature of catalyst. The synthesized nano catalyst provides a green protocol to obtain 4H-benzo[b]pyrans in aqueous solution. The synthesized catalyst exhibits easy synthesis, easy storage, recovered by application of external magnet, water-resistant and reused conveniently [19].

Similarly, E. Mohsen and his group designed and synthesized another versatile silica coated magnetic nano catalyst Fe_3O_4@SiO_2-imd-PMA from reaction of Fe_3O_4@SiO_2 with PMA^n in acetonitrile solution. The synthesized catalyst was characterized by different characterizations. The performance of synthesized nano catalyst was evaluated successfully to produce tetrahydro-benzopyran derivatives. The catalyst offers advantages like high yield, mild reaction condition, short reaction time, functional group tolerance, and use of green solvent [20] (Table 1).

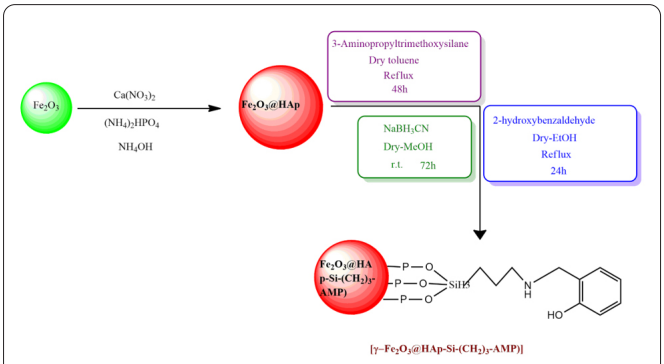
In another report, Ali Akbar and group developed polymer nanocomposites PPY/Fe_3O_4/CNT utilizing potassium persulfate as an oxidant and oxidative polymerization of pyrrole monomers in the presence of Fe_3O_4 nanoparticles and carbon nanotubes (CNTs) as the charge-balancing dopant in the polymer. The synthesized catalyst was characterized by various advanced characterization tools. The reported catalyst was successfully carried out the formation of benzopyran derivatives. The easy recoverability, mild reaction conditions, recyclable, and high yield were some advantages of this protocol [21] (Table 1).

Aliyeh Barzkar and his group designed and developed in situ spherical core@double-shell SO_3H supported nano catalyst (Fe_3O_4@SiO_2@RF–SO_3H) (Scheme 9) and well characterized using FT-IR, XRD, VSM, TGA, TEM, and SEM. To evaluate the acidity of Fe_3O_4@SiO_2@RF–SO_3H core–shell nano catalysts, concentration of hydrogen ion loaded on reported catalyst was examined which was found to be 1.3 mmol g/L. The well-characterized nano catalyst exhibited recyclability up to 10 cycles, high stability and catalytic activity for synthesis of tetrahydro-benzopyran derivatives through three compontent reaction of different aldehyde, dimedone, and malononitrile [22] (Table 1).

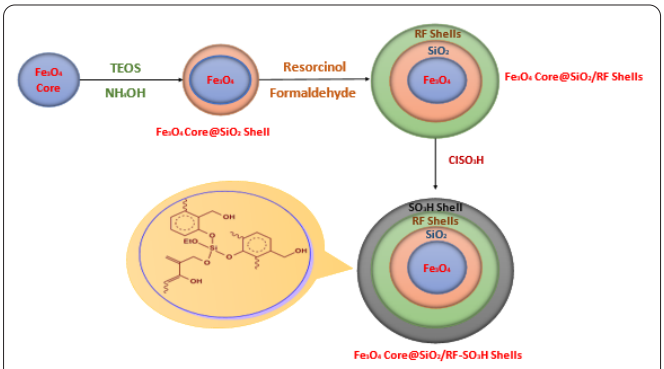
Elham Tabrizian and Ali Amoozadeh synthesized magnetically recyclable nano catalysts by grafting of TiO_2 and



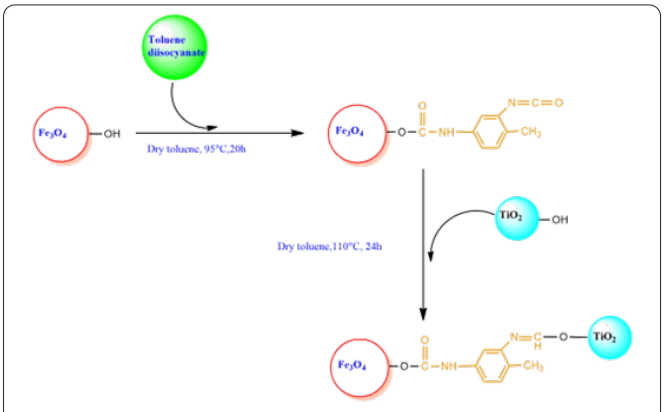
Scheme 7: The preparation of Fe_3O_4@SiO_2@R-NMe_2.



Scheme 8: Synthesis of hydroxyapatite encapsulated Fe_2O_3 supported (2-aminomethyl)phenol ([e_2O_3@HApSi$(CH_2)_3$AMP]).



Scheme 9: Synthesis of Fe_3O_4@SiO_2@RF–SO_3H.



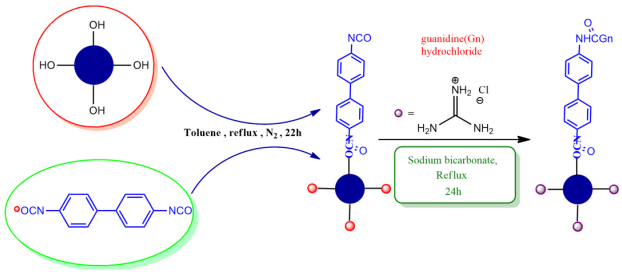
Scheme 10: Synthesis of Fe_3O_4@TDI@TiO_2.

Fe_3O_4 nanoparticles using reactive linker like 2,4-toluene diisocyanate as shown in Scheme 10. The structure of reported nano catalysts was investigated by FT-IR, FE-SEM, XRD, TGA, and VSM. The catalytic activity of synthesized nano-catalyst was investigated for synthesis of tetrahydro-benzopyran with high yields. Furthermore, catalyst can be easily recycled and used up to 6 times [23] (Table 1).

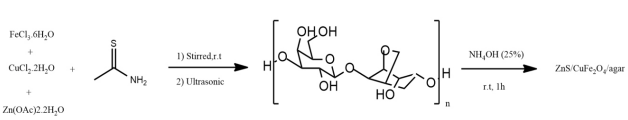
In another report, Eskandar Kolvari synthesized an interesting guanidine (Gn) supported on Fe_3O_4–4,4′-MDI MNPs using 4,4′-Methylene diphenyl diisocyanate as a coupling reagent and guanidine hydrochloride as a feasible amination reagent as depicted in Scheme 11. The synthesized nano catalyst was well characterized and catalyst activity was monitored through Knoevenagel–Michael-cyclocondensation reactions for synthesis of tetrahydro-benzopyran derivatives. It was observed that reaction time was remarkably shortened and nano catalyst was separated by magnetic decantation and reused at least seven times without significant loss of its catalytic activity [24] (Table 1).

The ZnO nanoparticles exhibit Lewis base–Lewis acid properties that can be employed as interesting heterogeneous catalyst to promote various acid/base catalyzed organic transformations. ZnO nanoparticles also successfully employed for synthesis of different tetrahydro-benzopyran derivatives. For example, Zavar and his team synthesized organic solvent soluble ZnO nanoparticles from zinc nitrate and used as catalyst for the production of 2-amino-4H-chromenes within 10 min with yield of 75 - 95% (Table 1) [25]. Similarly, Shahrzad Bahrami and team designed and developed rod-like magnetic biocompatible $ZnS/CuFe_2O_4$/agar organometallic hybrid catalyst using natural agar through facile method using nontoxic and inexpensive substances as shown in Scheme 12. The synthesis of catalyst was confirmed by FT-IR, EDX, SEM, TEM, VSM, TGA, and XRD. The catalytic application of reported catalyst was assessed in reaction of different substituted aromatic aldehydes, malononitrile, and dimedone for the synthesis of 2-amino-tetrahydro-4H-chromene-3-carbonitrile derivatives. This methodology offers advantages like environmentally benign catalyst, easy preparation of catalyst, high products yields, reusable up to five sequential runs, and short reaction times [26] (Table 1). A novel protocol was designed for synthesis of 4H-pyrans from coupling reaction of 1,3-diketo compound, substituted aldehyde and malononitrile in presence of ZnO nanoparticles in semi aqueous medium. It was found that wide spectrum of functional groups was tolerated in reported protocols with remarkable yield [27] (Table 1).

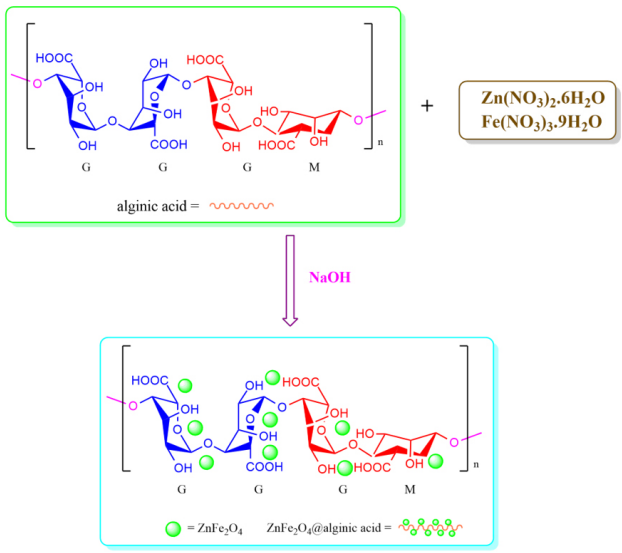
Ali Maleki et al. designed and synthesized $ZnFe_2O_4$@alginic acid nanocomposite by a facile synthetic procedure as depicted in Scheme 13. In this nanocomposites, alginic acid, a linear polysaccharide was utilized because of its already established role of a green catalyst in different organic transformation. The specific features such as biodegradability, renewability and reactivity make polysaccharide as environmental benign organo-catalyst. The synthesized $ZnFe_2O_4$@alginic acid nanocomposite was used in synthesis of 2-amino-3-cyano-4H-pyran derivatives from the reaction between various malononitrile, dimedone, and aromatic aldehydes. The present protocol offers beneficial features like simple procedure, mild



Scheme 11: Synthesis of Fe_3O_4–MDI-Gn.



Scheme 12: Synthesis of $ZnS/CuFe_2O_4$/agar.



Scheme 13: Synthesis of $ZnFe_2O_4$@alginic acid.

reaction conditions, green catalyst, rapid reaction, high yield, and easy workup. The magnetic properties of reported catalyst leads easy separation without considerable loss of catalytic activity [28] (Table 1).

The SiO_2 nanoparticles can easily synthesized from inexpensive and easily available materials at room temperature. These nanoparticles exhibit high stability at elevated temperature, biocompatibility, and neutrality. Along with above characteristics, excellent selectivity, and higher reactivity of SiO_2 nanoparticles encourage scientist to explore its full potential in MCRs (Scheme 14). In this connection, Subhash Banerjee et al. reported SiO_2 nanoparticles-catalyzed synthesis of 2-amino-3-cyano tetrahydro benzo[b]pyrans from the reaction between 3,3-dimethyl-1,3-cyclohexanedione, malononitrile, and aldehydes in ethanol high yields [29] (Table 1).

Amin Mohammadzadeh and his group synthesized Ag/Fe_3O_4@starch nano catalyst. The structure of this nano catalyst was confirmed by different analytical techniques including, FT-IR, XRD, TGA VSM, EDX, and TEM. The efficiency of Ag/Fe_3O_4@starch were examined from synthesis of 4H-pyrans using condensation reaction of different aldehydes,

1,3-diketoesters or cyclic 1,3-diketones and malononitrile. It was observed that reported magnetic nano catalysts was reused up to five runs and easily recovered [2, 30] (Table 1).

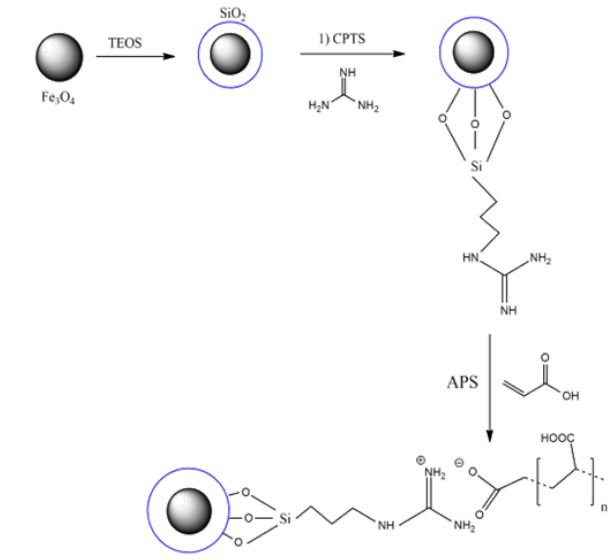
Maryam Kamalzare and group developed an interesting heterogeneous bio-nano catalysts by combining starch with MNPs as depicted in Scheme 15. The morphology of $CuFe_2O_4$@starch was specified by using FT-IR, VSM, SEM, XRD, EDX, and thermal analysis. The catalytic behavior of $CuFe_2O_4$@starch was evaluated by synthesize of 4H-pyran derivatives. Additionally, environmentally benign synthetic procedure, easy work-up, mild condition, non-toxicity, and low cost were few advantages of this protocol [31] (Table 1).

In another report, an improved three-component reaction of carbonyl compounds with aryl aldehydes and malononitrile in aqueous media for synthesis of benzopyran by using nano-structured coumarin-based cobalt complex as catalyst was reported by Hashem Sharghi and group as depicted in Scheme 16. The study reported improved protocol, which include high yields, easy isolation of products, simple procedure, rapid reaction and reusable up to five times. In addition, biological impact assessments of synthesized complex were carried out by eukaryotic cell toxicity measurement and DNA cleavage ability assay which revealed low cell toxicity [6] (Table 1).

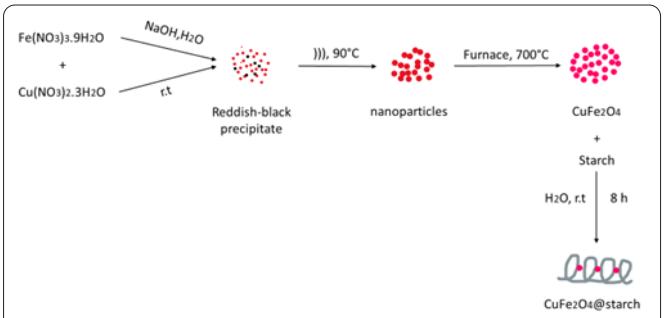
A magnetic phosphotungstic acid supported $MnFe_2O_4$ nanoparticles ($MnFe_2O_4$@SiO_2@$NHPhNH_2$–phosphotungstic acid) was prepared by Roya Mozafari et al. by the reaction of heteropoly acid ($H_3PW_{12}O_{40}$) with diamine-modified silica coated manganese ferrite nanoparticles as depicted in Scheme 17. The synthesis of this catalyst was confirmed by different spectroscopic techniques which include FT-IR, XRD, EDX, TEM, SEM, etc. The reported MNPs was evaluated as catalyst for preparation of tetrahydro-benzopyran under solvent-free heating condition. This reported protocol offers various advantages including low reaction times, high yield, simple workup procedure, easy recovery, and reused for at least six successive times [9] (Table 1).

In recent times, palladium nanoparticles have received substantial attention as nano catalyst in various organic transformation because palladium nanoparticles exhibit size-induced quantum- size effects. For example, Mithu Saha et al. reported ligand free, palladium nanoparticles catalyzed formation of tetrahydro benzo pyranes. The advantages of this reported protocol lie in its, simplicity, low catalyst loading easy to handle and cost effectiveness [32] (Table 1).

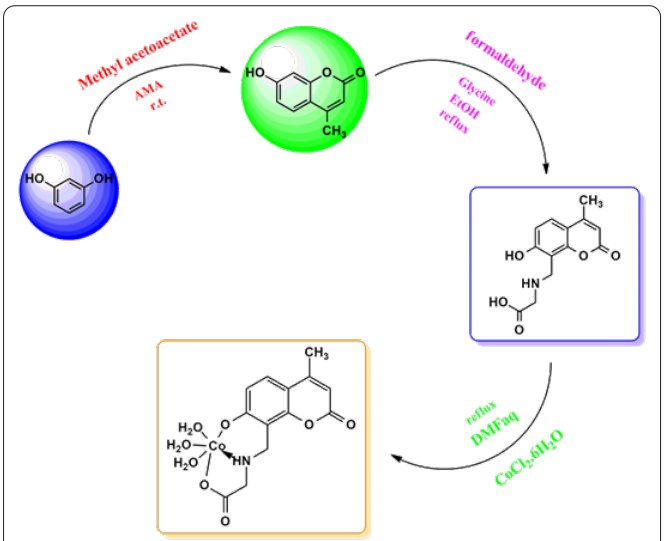
Titanium oxides (TiO_2) is exceptional adsorbents for numerous organic compounds and increases reactivity of reactants. In addition, TiO_2 is known as one of the most important metal oxides because of its non-toxicity, mesoporous structure, reusability, and moisture stability. In view of the special characteristic, TiO_2 is of great interest to many scientists as an effective catalyst in environmentally friendly organic transformation. For example, Priyanka L. Anandgaonker et al. reported TiO_2 nanoparticle catalyzed synthesis of tetrahydro-benzopyran derivative using three components reaction of dimedone, aromatic aldehyde, and malononitrile at room temperature in a solvent free condition [33] (Table 1). In another report, PbO nanoparticles were employed as a catalyst for solvent free synthesis of tetrahydro-benzopyran using green chemistry approach. This protocol was found to be eco-friendly, highly efficient, and recyclable [34] (Table 1). Similarly, a green and simple protocol was developed by Jaspreet Kaur et al. for the synthesis of tetrahydro-benzopyran derivatives in high yield using $CoFe_2O_4$ nanoparticles as catalyst in aque-



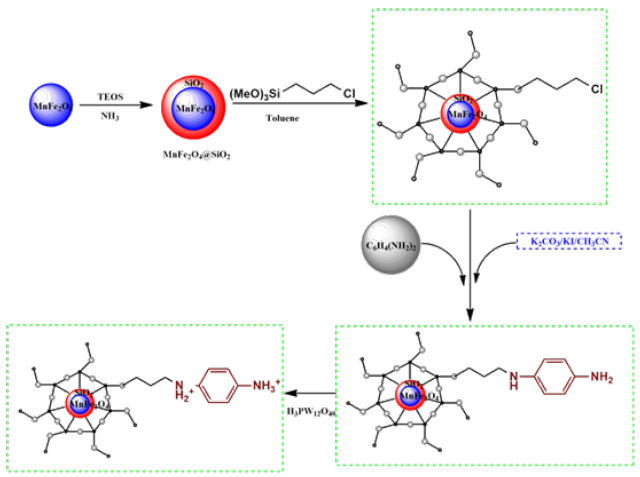
Scheme 14: Synthesis of silica magnetic nano particle.



Scheme 15: Synthesis of ferrite MNP followed by starch.



Scheme 16: Synthesis of [Co (MCG) $(H2O)_3$].



Scheme 17: ($MnFe_2O_4$@SiO_2@NHPhNH$_2$–phosphotungstic acid.

ous medium. The $CoFe_2O_4$ nanoparticles was synthesized by a simple co-precipitation method followed by ultrasonication. It was found that $CoFe_2O_4$ nanoparticles have small size (2–8 nm) and high surface area (140.9 m^2 g^{-1}). The reported catalytic protocol offers high yield, use of aqueous medium, short reaction times, economical catalyst, and easy recovery. Additionally, authors observed catalyst can be easily recovered and used for multiple cycles [35, 36] (Table 1).

Conclusion

Tetrahydro-benzopyran and its derivatives are important heterocyclic scaffolds offers various applications in biochemistry, pharmaceutical chemistry, high-energy materials research, and many other fields. There are several limitations are associated with synthesis of tetrahydro-benzopyran and its derivatives utilizing standard homogeneous and heterogeneous catalytic systems which include long reaction times, moderate yields, use of hazardous solvents, tedious workup procedure, and difficult purification. In view of all these limitations, synthetic chemists from all over the world, are trying to develop an efficient and environmentally favored catalytic systems for synthesis of tetrahydro-benzopyran derivatives with goals of high yield, minimal by-products, reusable catalyst, low temperature, and cost-effective and environmentally friendly methodology. Detail literature survey revealed that different nanomaterial-derived catalytic systems are proved to be an efficient and environmentally friendly catalyst for different organic transformation. This review article explained synthetic methodology of nano catalyst and its benefits in the synthesis of tetrahydro-benzopyran and its derivatives. In addition, we also focused on detail synthetic procedure, functionalization and advantages of these nanomaterials based catalytic system. We believe that this article will be helpful for chemists in designing and development of eco-friendly methodologies for tetrahydro-benzopyran and its derivatives while considering environmental and chemical industrial concerns, and that the field of nanomaterials-derived tetrahydro-benzopyran synthesis will continue to grow.

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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