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PII:	\$0277-5387(19)30087-7
DOI:	https://doi.org/10.1016/j.poly.2019.01.065
Reference:	POLY 13738
To appear in:	Polyhedron
Received Date:	31 December 2018
Revised Date:	22 January 2019
Accepted Date:	27 January 2019



Please cite this article as: R. Mozafari, F. Heidarizadeh, Phosphotungstic acid supported on $SiO_2@NHPhNH_2$ functionalized nanoparticles of $MnFe_2O_4$ as a recyclable catalyst for the preparation of tetrahydrobenzo[b]pyran and indazolo[2,1-b]phthalazine-triones, *Polyhedron* (2019), doi: https://doi.org/10.1016/j.poly.2019.01.065

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Phosphotungstic acid supported on SiO₂@NHPhNH₂ functionalized nanoparticles of MnFe₂O₄ as a recyclable catalyst for the preparation of tetrahydrobenzo[b]pyran and indazolo[2,1-b]phthalazine-triones

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MnFe₂O₄@SiO₂@NHPhNH₂- phosphotungstic acid was synthesized by the reaction of diamine-modified silica coated manganese ferrite nanoparticles with H₃PW₁₂O₄₀, the Keggintype heteropoly acid. This is the first time that H₃PW₁₂O₄₀ supported on diamine functionalized MnFe₂O₄ nanoparticles has been reported. The synthesized catalyst was characterized by various techniques, including Fourier Transform Infrared Spectroscopy (FTIR), Transmission electron-microscopy (TEM), X-ray Powder Diffraction (XRD), Scanning Electron Microscope (SEM), Energy Dispersive X-Ray Spectroscopy (EDX), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), Thermogravimetric Analysis (TGA), and Vibrating Sample Magnetometer (VSM). The synthesized nanoparticle was examined as the heterogenous nanocatalyst for the synthesis of tetrahydrobenzo-[b]pyran derivatives and 2H-indazolo-[2, 1-b]-phthalazine-triones under the solvent-free heating or ultrasonic irradiation conditions. This method offers several advantages including high yield, low reaction times, and the simple work-up procedure due to the presence of the magnetic nanoparticles in this catalyst, so that, it can be easily recovered and reused for at least six successive times without the loss of its high catalytic activity, suggesting its great Potential for industrial applications.

Keywords: phosphotungstic acid, Keggin-type heteropoly acid, ferrite nanoparticles, 2H-indazolo-[2, 1-b]-phthalazine-triones, tetrahydrobenzo-[b]-pyran

1. Introduction

The magnetic nanoparticles (MNPs) have attracted great interest because of their magnetic and electrical properties, and the tremendous surface area-to-volume ratio which make a unique compound with wide applications in drug delivery system, targeted gene therapy, magnetic resonance imaging, biosensors, ion exchange separation, magnetic data storage and environmental remediation and catalysis [1].

The utilizing of an efficient support, could significantly improve the activity, selectivity, recycling, and reproducibility of the catalyst systems [2]. In recent years, MNPs have appeared as attractive solid supports for immobilization of homogeneous catalysts [3]. Furthermore, the magnetic nanoparticles can be well dispersed in the reaction mixtures and after the completion of the reaction can be isolated efficiently from the product solution through a simple magnetic separation process [4]. The MNPs have been grafted onto inorganic and organic materials supports to amend their stabilization and recycling ability. magnetic nanoparticles can be used in a wide range of the catalytic reactions including condensation, oxidation, esterification, acylation, epoxidation, hydration, and hydrogenation [5]. Among the various magnetic nanoparticles, Fe₃O₄ presents the most interesting magnetic substance as the catalyst support; however, Fe₃O₄ is quite chemically unstable [6]. On the contrary, manganese ferrite (MnFe₂O₄) which is a typical ferromagnetic oxide has high thermal constancy, moderate magnetization, mechanical rigidity, and the significant chemical stability [7].

More recently, polyoxometalate functionalized magnetic nanoparticles have emerged much broadly and been widely used as active species in organic reactions catalysis [8].

Polyoxometalate, with the molecular formula of $[XM_{12}O_{40}]^{n-}$, where $X = P^{5+}$, As^{5+} , Si^{4+} , or Ge^{4+} and $M = Mo^{6+}$, or W^{6+} , have been utilized as catalysts for various organic reactions due to their unique physicochemical properties [9]. Lately, the phosphotungstic acid (PTA), has been attracted the considerable attention because of its super strong Brønsted acidity and also its ease of preparation. However, it should be immobilized on the proper support to eliminate its very low surface area, and instability in polar solvents [10]. The supported PTA has a greater number of surface acid sites than its bulk form and therefore show higher catalytic activity [11]. On the other hand, most of the acidic protons of the bulk phosphotungstic acid are in the interior of the solid which are inaccessible for catalysis of non-polar hydrocarbon reactions [12]. This kind of keggin-type heteropoly acid has more properties such as high thermal stability, ease of handling, stronger acidity properties compared to the homogeneous acid catalysts, low toxicity, capability of the clean technologies development and low cost [13]. Pyran derivatives have received significant attention due to their important biological and pharmacological properties [14]. Among the pyrans, the substituted tetrahydrobenzeno-[b]-pyran have a special importance among the 6-membered oxygen containing heterocycles as they have been utilized in the synthesis of blood anticoagulant [15]. In addition, they have been used as anticancer and antimicrobial agents [16], and the photoactive materials [17].

Moreover, phthalazine and its derivatives are very useful compounds in various fields of chemistry, biology and pharmacology [18]. Some of these compounds exhibit antimicrobial [19], anticonvulsant [20], antifungal [21], anticancer [22], and anti-inflammatory activity [23] and can be incorporated for hypertensive treatment. The photophysical properties of some selected derivatives have also been studied showing medium to strong optical behaviour [24]. Therefore, several methods have been reported for improving the preparation of these compounds, but most of these methods suffer from some drawbacks [25]. Consequently, to

overcome these drawbacks, a great deal of efforts is directed to develop an efficient catalytic system for the synthesis of these compounds.

Followed by the efforts done by this research group to utilize the green condition in organic synthesis, MnFe₂O₄@SiO₂@NHPhNH₂-PTA was synthesized and used as a magnetic hereocatalyst for the synthesis of tetrahydrobenzo-[b]-pyrans and 2H-indazolo-[2,1-b]-phthalazine-triones from the simple and easily available starting materials under a very simple condition.

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2. Experimental

2.1. Materials and methods

All the chemicals were of analytical grade and used without further purification. Manipulation and reactions were carried out in air without the protection of inert gas. Phosphotungstic acid was synthesized according to the literature. Fourier transform infrared (FT-IR) spectra were obtained using potassium bromide pellets in the range of 400–4000 cm¹ with a FT BOMEM MB102 spectrophotometer. ¹H NMR and ¹³C NMR spectra were recorded on a Brucker spectrometer at 400 MHz and 100 MHz, respectively, with tetra methylsilane as an internal standard. X-ray diffraction (XRD) patterns of the synthesized samples were taken with a Philips X-ray diffractometer (modelPW1840) over a 20 range from 10 to 80° using Cu K α radiation($\lambda = 1.54056$ A°). The FESEM images were obtained using a Hitachi Japan S4160 scanning electron microscope. The magnetic proper-ties of the fabricated MnFe₂O₄@SiO₂@NHPhNH₂-PTA composite as well as other samples were studied using vibrating sample magnetometer (VSM) of Meghnatis Daghigh Kavir Company. The TGA curve of the MnFe₂O₄@SiO₂@NHPhNH₂-PTA was recordedon a BAHR, SPA 503 at heating rates of 10 °C min⁻¹. The surface properties of the samples were determined by nitrogen adsorption/ desorption isotherms at - 197°C using a micromeritics ASAP 2000 instrument and the surface area and the pore size distribution were investigated by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) analysis. The content of metal in the catalyst was measured by inductively coupled plasma-optical emission spectrometry (ICP-OES). The thermal behavior was studied by heating 1-3 mg of samples in aluminum-crimped pans under airflow, over the temperature range of 25-800 °C.

2.2. Synthesis of MnFe₂O₄

First, the mixture of MnSO₄ (11.24 g, 0.02 mol) and FeSO₄ (2.77 g, 0.01 mol) was dissolved in 100 ml deionized water and magnetically stirred. Sodium hydroxide (10%) solution was added dropwise under constant stirring to raise pH to 10. Then, the mixture was stirred for 30 minutes. 1 g of Polyvinylpyrrolidone (PVP) was add to the liquid precipitate and it was brought to reaction temperature of 100 °C and stirred for 2 h. Synthesized nano MnFe₂O₄ (dark brown precipitate) was separated by a permanent magnet from the reaction media and

washed with distilled water-ethanol mixture solution several times to remove impurities. Finally, the product (light brown powder) was dried at 80 $^{\circ}$ C for 12 h.

2.3. Synthesis of diamine-functionalized modified silica coated manganese ferrite nanoparticles (MnFe₂O₄@SiO₂@NHPhNH₂)

1 g of magnetic $MnFe_2O_4$ was dispersed in a mixture of 84 mL ethanol, 24 mL deionized water, and 25 mL concentrated ammonia aqueous solution (25%) by stirring for 30 min. Subsequently, 2 mL of tetraethyl orthosilicate (TEOS) was added dropwise. After being stirred for 24 h at room temperature, the resulted solid was magnetically separated, washed twice with water and twice with ethanol, and then dried at 100 °C for 2 h.

Then for the linkage of 3-chloropropyl unit to the surface of the obtained support, 0.7 g of $MnFe_2O_4$ were dispersed in 100 mL anhydrous toluene, with ultrasonication for 25 min and 1 mL of 3-chloropropyltrimethoxysilane was added dropwise into the dispersion and ultrasonicated for 15 min. Subsequently, the mixture was refluxed at 110 °C under constant stirring for 24 h. The products were magnetically separated and washed two times with toluene and two times with ethanol and then dried at 60 °C.

The prepared MnFe₂O₄@SiO₂-Cl (0.7 g) was dispersed into 70 mL of acetonitrile and ultrasonicated for 20 min. Then, KI (7 mmol, 1.162 g) and K₂CO₃ (7 mmol, 0.967 g) were added into the dispertion and ultrasonicated for 20 min. Subsequently 1,4-phenylenediamine (20 mmol, 2.16 g) was added to a solution and the mixture was stirred under reflux condition for 24h. The obtained solid was then magnetically collected from the solution and washed abundantly with water/ethanol and dried at 60 °C. The attachment of 1,4-phenylenediamine group onto the surface of Manganese ferrite was confirmed according to FT-IR spectra.

2.4. Synthesis of diamine modified silica coated manganese ferrite polyoxometalte nanoparticles(MnFe₂O₄@SiO₂@NHPhNH₂PTA)

0.3 g of $MnFe_2O_4@SiO_2@NHPhNH_2$ was dispersed in 50 mL of deionized water and ultrasonicated for 25 min. Then, a solution of $H_3PW_{12}O_{40}.6H_{20}$ (0.42 mmol, 1.254 g) in 20 mL deionized water was added dropwise into the solution and ultrasonicated for 25 min and the mixture was stirred for 24h at room temperature. Finally, the formed ($MnFe_2O_4@SiO_2@NHPhNH_2$ -PTA) was magnetically separated and washed twice with water and dried at 60 °C.

2.5 General procedure for the synthesis of 2H-indazolo[2,1b]phthalazine-triones

In a 5 ml round-bottom flask, to a mixture of dimedone (1 mmol), phthalhydrazide (1 mmol), aldehyde (1mmol) and MnFe₂O₄@SiO₂@NHPhNH₂-PTA (0.030 g) was heated under solvent –free conditions at 80 °C or under sonicated at 80 °C in presence of H₂O for an appropriate period of time as indicated in Table 2. After the reaction was completed (monitored by TLC), the catalyst separated by an external magnet. Finally, the obtained organic layer was extracted with ethyl acetate to afford the pure [b]pyrans derivatives by removing solvent in

good to high yield. The desired pure product(s) was characterized by comparison of their physical data with those of known 2H-indazolo[2,1-b]phthalazine-triones.

2.6 General procedure for the synthesis of tetrahydrobenzo[b]pyrans

In a typical experiment, to a mixture of the aromatic aldehyde (1 mmol), malononitrile (1.2 mmol), dimedone (1 mmol), and MnFe₂O₄@SiO₂@NHPhNH₂-PTA (0.040 g) was heated under solvent–free conditions at 80 °C or under sonicated at 80 °C in presence of H₂O as a green solvent for the time specified in Table 4. After complete consumption of starting material as judged by TLC (n-hexane/ethyl 10:5), 5 mL EtOAc was added and the magnetic catalyst was concentrated on the sidewall of the reaction vessel using an external magnet. The solid residue was isolated with EtOAc (10 ml) and dried with anhydrous Na₂SO₄. After evaporation of EtOAc the crude product was by recrystallization in hot EtOH. The desired pure product(s) was characterized by comparison of their physical data with those of known 4H-benzo[b]pyrans. The residual catalyst in the reaction vessel was washed and dried and then subjected to the next run directly.

2.7 Selected spectral data

3,4-Dihydro-3,3-dimethyl-13-(3-flourophenyl)-2-H-indazolo[2,1-b]phthalazine1,6,11(13H)-trione (Table 3, entry 7)

IR (KBr) v (cm⁻¹): 2957, 2877, 1663, 1629, 1603, 1471, 1357, 1314, 1271, 1142, 778, 701, 684. ¹H NMR (DMSO-*d6*, 400 MHz): δ = 1.11 (s, 3H), 1.13 (s, 3H), 2.27 (s, 2H), 3.18 (AB system, dd, 1H, J = 19.1 Hz and J = 2.2 Hz), 3.33 (AB system, d, 1H, J = 19.2 Hz), 6.31 (s, 1H), 7.08–7.12 (pt, 1H), 7.31–7.39 (m, 3H), 7.96–7.98 (m, 2H), 8.01–8.12 (m, 1H), 8.26–8.29 (m, 1H). ¹³C NMR (DMSO-*d6*, 100.6 MHz): δ = 28.3, 28.4, 34.7, 37.7, 50.7, 64.3, 114.7, 115.2, 117.0, 124.1, 127.5, 129.0, 129.7, 130.5, 134.2, 135.0, 140.8, 152.9, 154.3, 155.9, 161.3, 163.7, 192.3

3,4-Dihydro-3,3-dimethyl-13-(4-hydroxyphenyl)-2-H-indazolo[2,1-b]phthalazine1,6,11 (13H)-trione (Table 3, entry 9)

IR (KBr) v(cm⁻¹): 3363(OH), 2960, 1674, 1657, 1634, 1362, 1271, 847, 704

¹H NMR (DMSO-*d6*, 400 MHz): $\delta = 1.10$ (s, 3H), 1.14 (s, 3H), 2.27 (d, 2H), 3.16 (AB system, dd, 1H, J = 17.8 Hz and J = 2.0 Hz), 3.32 (AB system, d, 1H, J = 17.2 Hz), 6.20 (s, 1H), 6.86 (d, 2H), 7.22 (d, 2H), 7.94–7.99 (m, 2H), 8.10–8.12 (m, 1H), 8.25–8.27 (m, 1H), 9.47 (br, 1HOH). ¹³C NMR (DMSO-*d6*, 100.6 MHz): $\delta = 28.4$, 28.5, 34.7, 37.7, 50.8, 64.4, 115.2, 115.3, 118.0, 127.1, 127.9, 128.1, 129.2, 129.4, 134.1, 134.9, 151.4, 154.0, 155.8, 157.7, 192.4.

3,4-Dihydro-3,3-dimethyl-13-(4-nitrophenyl)-2-H-indazolo[2,1-b]phthalazine-1,6,11(13H)-trione (Table 3, entry 4)

IR (KBr) v(cm⁻¹): 2973, 1697, 1617, 1660, 1525, 1368, 1148, 1102, 858, 701

¹H NMR (DMSO-*d6*, 400 MHz): $\delta = 1.10$ (s, 3H), 1.14 (s, 3H), 2.27 (s, 2H), 3.20 (AB system, dd, 1H, J = 18.8 Hz and J = 2.0 Hz), 3.32 (AB system, d, 1H, J = 18.8 Hz), 6.44 (s, 1H), 7.79–7.82 (m, 2H), 7.96–8.01 (m, 2H), 8.09–8.12 (m, 4H). ¹³C NMR (DMSO-*d6*,

100.6 MHz): δ = 28.3, 28.4, 34.8, 37.7, 50.6, 64.2, 116.8, 123.8, 127.2, 128.0, 128.9, 129.2, 129.7, 134.3, 135.0, 145.3, 147.6, 152.3, 154.4, 155.9, 192.3.

2-Amino-3-cyano-4-(2-chlorophenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8tetrahydrobenzo [b]pyran (Table 5, entry 3)

IR (KBr) υ (cm⁻¹): 1150, 1414, 1645, 1688, 2230, 2963, 3327, 3390.

¹H NMR (CDCl₃, 400 MHz) δ (ppm): 1.08, 1.13 (s, 6H, 2CH₃), 2.20 and 2.26 (2H, CH₂), 2.43 and 2.49 (2H, CH₂), 4.63 (bs, 1H, CH), 7.14-7.33 (m, 4H, CHAr), 7.35 (bs, 2H, NH₂). ¹³C NMR (100 MHz, DMSO-*d*6) δ : 27.7, 33.1, 36.7, 40.4, 50.0, 62.0, 113.0, 120.0, 126.0, 129.4, 131.4, 143.5, 159.15, 161.5, 193.0

2-Amino-3-cyano-4-(4-methylphenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo [b]pyran (Table 5, entry 2)

IR (KBr) υ (cm⁻¹): 1414, 1470, 1603, 1681, 1683, 2199, 2875, 2959, 3197, 3330, 3471.

¹H NMR (DMSO, 400 MHz) δ (ppm): 0.99 (s, 6H, 2CH₃), 1.98 (1H, CH₂), 2.03, (1H, CH₂), 2.47 (2H, CH₂), 2.94 (bs, 3H, CH₃), 4.479 (s, 1H, CH), 7.62-7.94 (m, 4H, CHAr), 7.21 (bs, 2H, NH₂). ¹³C NMR (100 MHz, DMSO-*d*6) δ : 23.2, 29.2, 29.2, 30.7, 36.0, 40.4, 53.2, 56.7, 113.8, 120.2, 126.0, 131.8, 134.6 141.0, 159.2, 163.0, 198.8

2-Amino-3-cyano-4-(3-nitrophenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8tetrahydrobenzo [b pyran (Table 5, entry 4)

IR (KBr) υ (cm⁻¹): 1349, 1374, 1599, 1595, 1661, 1679, 2186, 2871, 2956, 3202, 3336, 3431. ¹H NMR (400 MHz, DMSO-*d*6) δ : 1.03 (s, 3H, CH₃), 1.08 (s, 3H, CH₃), 2.4 (2H, CH₂), 2.7 (2H, CH₂), 4.7 (dd, 1H, CH), 7.2 (s, 2H, NH₂), 7.2-7.34 (m, 4H, CHAr) ¹³C NMR (100 MHz, DMSO-*d*6) δ : 28.5, 30.7, 37.0, 46.6, 50.0, 60.2, 113.0, 119.6, 122.5, 126.0, 130.8,135.1 145.9, 159. 9, 163.0, 198.1

2-Amino-3-cyano-4-(2-nitrophenyl)-7,7-dimethyl-5-oxo-4*H*-5,6,7,8-tetrahydrobenzo[b]pyran (Table 5, entry 9)

IR (KBr) υ (cm⁻¹): 1380, 1518, 1595, 1647, 1683, 2196, 2957, 3257, 3311.

¹H NMR (DMSO-*d6*, 400 MHz) δ (ppm): 1.03 (s, 6H, 2CH₃), 2.03 and 2.21, (2H, CH₂), 2.83 (2H, CH₂) 4.83 (bs, 1H, CH), 7.14-7.33 (m, 4H, CHAr), 7.21 (bs, 2H, NH₂). ¹³C NMR (100 MHz, DMSO-*d6*) δ : 28.2, 28.7, 32.6, 36.0, 40.4, 58.7, 61.0, 113.0, 117.8, 120.04, 126.0, 130.4,131.4 143.5, 159. 5, 162.6, 194.2

3 Results and discussion

In order to design and synthesize of a new and highly efficient catalyst system, The manganese ferrite -polyoxometalate hybrid nanomaterials, $MnFe_2O_4@SiO_2@NHPhNH_2$ -PTA, were fabricated via a straight forward four-step procedure.(Scheme 1) Manganese ferrite, as the magnetic core of the composite, was made by the co-precipitation of Mn^{2+} , and Fe^{3+} ions in the basic solution leading to the formation of $MnFe_2O_4$ magnetic nanoparticles [26], and then coated with a thin layer of silica. The treatment of the silanol group of $MnFe_2O_4@SiO_2$ with 3-Chloropropyltrimethoxysilane (CPTMS) afforded $MnFe_2O_4@SiO_2$ -Cl. $MnFe_2O_4@SiO_2$ -NHPhNH₂ was carried out by the reaction of 1, 4-phenylenediamine

with chloropropyl-grafted $MnF_2O_4@SiO_2$. The final step involved the reaction of $MnFe_2O_4@SiO_2@NHPhNH_2$ amine groups with $H_3PW_{12}O_{40}$ to yield $MnFe_2O_4@SiO_2@NHPhNH_2$ -PTA. Protonation of diamine group yields the positively charged cations which bounds electrostatically to the heteropolyanions. It has been proven that the heteropoly anion salts of the organic cations are generally insoluble in water [27]. Thus, the excess heteropoly acids can be removed by washing the resulting materials with water.



Scheme. 1 Step-by-step synthesis of MnFe₂O₄@SiO₂@NHPhNH₂-PTA

3.5 Catalyst characterization

The obtained MnFe₂O₄@SiO₂@NHPhNH₂-PTA catalyst has been characterized by FT-IR, XRD ,FESEM, TEM, TGA, EDX, ICP-AES and VSM techniques.

Fig. 1 represents the results of field emission scanning electron micrograms (FESEM) in order to investigate the particle shape, surface morphology and architecture of the MnFe₂O₄, MnFe₂O₄@SiO₂ and MnFe₂O₄@SiO₂@NHPhNH₂-PTA. Also, FESEM images of the particles showed spherical core–shell structured magnetic nanocomposite with nano dimension ranging under 50 nm. As shown in Fig. 3, grafting heteropoly acid onto the nanoparticle shell did not lead to the significant change in the structure and morphology of nanoparticles, indicating that the magnetic core remained intact during the immobilization and functionalization process on the surface of nanocomposite.



 $\label{eq:Fig.1.} \textbf{Fig. 1.} SEM image of MnFe_2O_4 (a), MnFe_2O_4 @SiO_2 (b), and MnFe_2O_4 @SiO_2 @NHPhNH_2-PTA (c) \\$

In order to obtain some information on the elemental composition and distribution on the surface of the sample, $MnFe_2O_4@SiO_2@NHPhNH_2$ -PTA was characterized by using EDX analysis and Mn, Fe, O, Si, C, N, P, W were detected (Fig. 2). Based on the above results, it is demonstrated that $H_3PW_{12}O_{40}$ was immobilized onto the surface of the phenylenediamine functionalized $MnFe_2O_4$ nanoparticles. Also, the loading of PTA in $MnFe_2O_4@SiO_2@NHPhNH_2$ -PTA was calculated by the ICP-AES atomic emission spectroscopy technique. The exact amount of PTA loaded onto the diamine functionalized

silica coated $MnFe_2O_4$ was found to be 0.77 mmol g⁻¹. The amount of Mn and Fe was checked by ICP-AES analysis and their 2:1 ratio was confirmed. The amount of H⁺ in the $MnFe_2O_4@SiO_2@NHPhNH_2$ -PTA determined by acid-base titration was 0.88 mmol g⁻¹.



Transmission electron-microscopy (TEM) studies of the of MnFe₂O₄@SiO₂@NHPhNH₂-PTA organic–inorganic composites (Fig. 3) confirmed that the particles have almost spherical morphology .The images indicate that MnFe₂O₄ (dark spots) was encapsulated by silica, amine and heteropoly acid, and particles exhibit a size distribution of 26 nm, similar to the sizes obtained from the FESEM measurements.



Fig. 3 TEM image of MnFe₂O₄@SiO₂@NHPhNH₂-PTA

The XRD patterns of MnFe₂O₄, MnFe₂O₄@SiO₂ and MnFe₂O₄@SiO₂@NHPhNH₂-PTA are displayed in Fig. 4. The diffraction peaks related to Bragg's reflections from (2 2 0), (3 1 1), (4 0 0), (4 2 2), and (3 3 3) planes correspond to the standard spinel structure of MnFe₂O₄ (JCPDS 02-8517) with a space group of Fd3m (Fig. 4A)[28]. The crystallite size of MnFe₂O₄ nanoparticles was about 27nm, as measured by using the well-known Debye–Scherrer formula 29. After coating with silica, an additional weak peak in the XRD pattern of MnFe₂O₄@SiO₂ at 20 = 20 is attributed to the amorphous silica shell formed around the magnetic core (Fig. 4B). In the XRD pattern of MnFe₂O₄@SiO₂@NHPhNH₂-PTA, the characteristic peaks of MnFe₂O₄ did not change, but some peaks related to phosphotungstic acid have been added. (Fig. 4C)



Fig. 4. XRD patterns of MnFe₂O₄(A), MnFe₂O₄@SiO₂(B), MnFe₂O₄@SiO₂@NHPhNH₂-PTA(C)

The FT-IR spectrum of MnFe₂O₄ shows two peaks at 400 cm⁻¹ and 505 cm⁻¹ which are attributed to Fe-O stretching in the tetrahedral and octahedral sites of MnFe₂O₄, respectively (Fig. 5a) [29]. The bands located at 1091 cm⁻¹ and 798 cm⁻¹ in the spectrum of MnFe₂O₄@SiO₂, are ascribed to the symmetrical and asymmetrical vibration modes of the Si-O-Si bonds in SiO₂ (Fig. 5b) [30]. C–H stretching vibrations appeared at 2925 cm⁻¹ and 2846 cm⁻¹ confirming the presence of the anchored propyl group of MnFe₂O₄@SiO₂-Cl nanoparticles (Fig 5c). Fig. 5d, shows the peaks in the range of 1400 to 1634 cm⁻¹ assigned to the phenylenediamine ring and also N-H bending at 3400 cm⁻¹ for the synthesized MnFe₂O₄@SiO₂@NHPhNH₂ clearly observed [31]. the is In case of MnFe₂O₄@SiO₂@NHPhNH₂-PTA nanoparticles, typical FT-IR spectra of H₃PW₁₂O₄₀ show four characteristic vibration peaks at 1081 cm⁻¹, 985 cm⁻¹, 897 cm⁻¹, and 803 cm⁻¹, attributed

to the stretching vibration modes of P-O, W-O and W-O-W bonds of the Keggin unit, respectively (Fig. 5e) [32]. As compared to the starting Keggin unit, the peak at 1080 cm⁻¹ overlapped the Si–O–Si stretching vibration, however, new peaks and non-overlapped bands at 980 cm⁻¹, 896 cm⁻¹ and 809 cm⁻¹ are observed in the FT-IR spectra of MnFe₂O₄@SiO₂@NHPhNH₂-PTA, indicating that H₃PW₁₂O₄₀ was successfully anchored to MnFe₂O₄@SiO₂@NHPhNH₂.





 $MnFe_{2}O_{4}@SiO_{2}@NHPhNH_{2}(d), and MnFe_{2}O_{4}@SiO_{2}@NHPhNH_{2}-PTA(e)$

the thermogravimetric analysis (TGA) curves of, $MnFe_2O_4$, $MnFe_2O_4@SiO_2$ and $MnFe_2O_4@SiO_2@NHPhNH_2$ -PTA nanocatalyst indicates the weight loss of the organic material as they decompose upon heating (Fig. 6). The first weight loss of 4.6% below 180 °C which might be due to the loss of the adsorbed water as well as dehydration of the surface

OH groups. The weight loss of 5.28% about 180– 410 °C attributed to the decomposition of the organic species, i.e. diamine group. The weight loss of 7.60% in around 480 was due to the break down and decomposition of $H_3PW_{12}O_{40}$ structure. On the basis of this result, the well grafting of organic and inorganic groups on the MnFe₂O₄ is verified.



Fig. 6. The TGA curves of MnFe₂O₄(a), MnFe₂O₄@SiO₂ (b) and MnFe₂O₄@SiO₂@NHPhNH₂-PTA(C)

Magnetic properties of MnFe₂O₄@SiO₂@NHPhNH₂-PTA and MnFe₂O₄@SiO₂@NHPhNH₂-PTA were investigated using a vibrating sample magnetometer (VSM) with a field of -10000 Oe to 10000 Oe at room temperature. As shown in (Fig. 7), the M(H) hysteresis loop for the sample was completely reversible, which indicated their superparamagnetic characteristics. The catalyst MnFe₂O₄@SiO₂@NHPhNH₂-PTA demonstrated saturation magnetization values of 20 emu. g⁻¹, while the MnFe₂O₄ nanoparticle had the value of 78.98 emu. g⁻¹. The reason may be attributed to the grafting of silica, diamine groups and H₃PW₁₂O₄₀ over MnFe₂O₄. However, the lower value of (Fig 7b) is still enough to ensure the readily recovery of the catalyst from reaction mixture using external magnetic force.



Fig. 7. Magnetization curves for MnFe₂O₄(a) and MnFe₂O₄@SiO₂@NHPhNH₂-PTA (b) at room temperature

Fig. 8 represent the low temperature nitrogen adsorption–desorption isotherms and pore volume and pore size distribution of $MnFe_2O_4@SiO_2@NHPhNH_2$ -PTA sample which exhibit a type III curve with a hysteresis loop. Type III isotherms correspond to a mesoporous material. According to the report in Table 1 about Brunauer–Emmett–Teller (BET) surface area, pore volume and pore size of (BET: 19.64 m²/g, pore volume: 6.99 cm³/g and pore size: 29 nm), decrease in surface area, pore volume and pore diameter after loading Phosphotungstic acid on MnFe₂O₄@SiO₂@NHPhNH₂ is due to this fact that the PTA unites were immobilized dispersed on the surface of MnFe₂O₄@SiO₂.



Fig. 8. pore size distributions (left) and Nitrogen adsorption-desorption isotherms (right) of MnFe₂O₄@SiO₂@NHPhNH₂-PTA

Table 1 Specific surface area (BET), diameter pore and total pore volume of MnFe₂O₄@SiO₂@NHPhNH₂-PTA

Sample	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
MnFe ₂ O ₄ @SiO ₂ @NHPhNH ₂ - PTA	19.64	6.99	29

3.2. Catalytic studies

Due to the ability of MnFe₂O₄@SiO₂NHPhNH₂-PTA as a mild and efficient acid catalyst, in this study, it was decided to apply this catalyst for the synthesis of phthalazine (Scheme 2) and pyran (Scheme 4) derivatives. At the first stage, to obtain the best reaction conditions, the reaction of dimedone, benzaldehyde and phthalhydrazide in the presence of 0.03 g of MnFe₂O₄@SiO₂NHPhNH₂-PTA as a model reaction at 80 °C and under the solvent-free conditions and a variety of solvents such H₂O, EtOH, EtOAc, CH₂Cl₂ and CH₃CN was examined. The represented data in Table 2, showed that the reaction proceeded efficiently under the solvent-free conditions at 80 °C and resulted in high yields of the desired product (Table 2, entry 9). This three-component condensation was also accomplished in protic solvent such as EtOH and H₂O under the reflux condition and gave the corresponding product in 90% yield after a longer time (Table 2, entries 1 and 6). Moreover, aprotic solvents such as CH₂Cl₂, EtOAc, CH₃CN afforded the desired product in lower yields and longer reaction times (Table 2, entries 2, 3and 4). Then the best amount of catalyst under the solvent-free conditions at 80 °C was checked and the best result was obtained in the presence of 0.03 g of catalyst. The effect of temperature was also studied by carrying out the model reaction under the solvent-free condition and 0.03 g of catalyst at room temperature, 60 °C, and 80 °C. The yield increased when the reaction temperature was increased (Table 2, entry 9). The reaction was also checked in the absence of the catalyst in which the reaction did not proceed even after 3 hours (Table 2, entry 5). These observations established the crucial role of MnFe₂O₄@SiO₂NHPhNH₂-PTA for the expedition of the reaction time and the product yield.

For the investigation of the ultrasonic irradiation ability for the acceleration of the organic reactions, the model reaction under the ultrasonic irradiation at 80°C in the presence of H_2O as a green solvent and various amounts of catalyst was examined. The excellent yield of the three-component coupling product was obtained under the optimized condition using 0.03 g of catalyst in water as the solvent in 8 minutes.



Scheme 2 Preparation of indazolo [2,1-b] phthalazine-triones by MnFe₂O₄@SiO₂NHPhNH₂-PTA

Entry	Catalyst	Solvent	Condition	Time(min)	Yield(%) ^b

	amount(g)		-		
1	0.03	EtOH	reflux	60	87
2	0.03	CH_2Cl_2	reflux	100	30
3	0.03	CH ₃ CN	reflux	100	35
4	0.03	EtOAc	reflux	100	45
5	None	-	reflux	180	trace
6	0.03	H_2O	reflux	60	90
7	0.03	Solvent free	rt	100	60
8	0.03	Solvent free	60	45	80
9	0.03	Solvent free	80	25	96
10	0.025	Solvent free	80	25	93
11	0.015	Solvent free	80	35	88
12	None	H_2O	Sonication/ rt	25	tace
13	0.015	H_2O	Sonication/ 80	18	65
14	0.025	H_2O	Sonication/ 80	14	89
15	0.03	H_2O	Sonication/80	8	95

^aReaction Conditions: bezaldehyde(1mmol), dimedone(1 mmol), phthalhydrazide (1 mmol), under solvent-free

, MnFe₂O₄@SiO₂NH-NH₂-PTA(0.03 g) or water(5ml, ultrasonic irradiation)

^b Yields isolated product.

After optimizing the reaction conditions, the generality of this catalytic system was confirmed by employment of a series of aldehydes. The results are summarized in Table 3.

Table	3	Synthesis	of	derivatives	of	2H-indazolo[2,1-b]phthalazine-1,6,11(13H)-trione	derivatives	in	the
preser	ice o	of MnFe ₂ O	4@5	SiO2@NH-N	H_2 -	PTA ^a			

	Solvent- free/80 °C	C	Ultrasonic /H2O/80 °C		
Entry Aldehyde Product	Time	Yield	Time	Yield	M.p. °C Found/ Reported
	25	94	8	92	208-209 (203205) [33]





^aReaction Conditions: bezaldehyde(1mmol), dimedone(1 mmol), phthalhydrazide (1 mmol), under solvent-free

, MnFe₂O₄@SiO₂NH-NH₂-PTA(0.03 g) or water(5ml, ultrasonic irradiation)

As shown in Table 3, the aldehydes with both electron donating and withdrawing groups were participated in the condensation reaction with the equal efficiency and excellent yields without the formation of any byproducts. The meta-substituted aromatic aldehydes (Table 3, entry 4) as well as the sterically hindered ortho-substituted aromatic aldehydes (Table 3, entry 3), both undergo the condensation reactions without any difficulties.

A proposed mechanism for the synthesis of indazolo[2,1-b]phthalazine-triones is was outlined in Scheme 3 .Based on this mechanism, as shown theintermediate (1) is produced upon initial condensation of aldehyde with dimedone under the catalytic activity of $MnFe_2O_4@SiO_2@NHPhNH_2$ -PTA. Subsequent nucleophilic addition of phthalhydrazide the intermediate (1) followed successively by intramolecular cyclization to the intermediate (2),and rearrangement to furnish the corresponding product.



Scheme. 3 Proposed mechanism for the synthesis of indazolo[2,1-b]phthalazine-triones

The reusability of the catalyst is an important benefit especially for commercial applications. Thus, the activity constancy of the catalyst, catalytic reusability of $MnFe_2O_4@SiO_2@NHPhNH_2$ -PTA was investigated for synthesis of 2H-indazolo[2,1-b] phthalazine-1,6,11(13H)-trione under the optimized reaction conditions in the model reaction (Fig.9).



Fig. 9 Recycl ability of $MnFe_2O_4@SiO_2@NHPhNH_2$ -PTA in the synthesis of 2H-indazolo[2,1-b]phthalazine-1,6,11(13H)-trione

Encouraged by these results, the phthalylhydrazide with malonitrile was replaced, in order to explore its further applications toward the synthesis of the tetrahydrobenzo-[b]-pyrans derivatives. Initially, the reaction conditions were optimized. For this purpose, the reaction of benzaldehyde, malonitrile and dimedone was chosen as a model reaction and then the model reaction was carried out under the solvent-free conditions at 80 °C in the presence of 0.04 g of MnFe₂O₄@SiO₂NHPhNH₂-PTA and the variety of solvents such H₂O, EtOH, EtOAc, CH₂Cl₂ and CH₃CN were examined. The results are summarized in Table 4. The best result in terms of the reaction time (30 min) and the yield (95%) was obtained when the reaction time carried out under the solvent-free condition at 80 °C (Table 4, entry 8).

In addition, the model reaction in the presence of 0.04 g catalyst at 60 °C was examined and the corresponding product was formed in longer reaction time and lower yield (Table 4, entries 7).

It was found that in the absence of nanomagnetic acid catalyst, only a trace of the desired product was observed on the Thin Layer Chromatography (TLC) plate even after 3 hours of heating (Table 4, entry 5). The result clearly showed that the catalyst is effective for this transformation and in its absence, the reaction did not take place even after the higher reaction time.

Scheme. 4 General scheme for the of synthesis tetrahydrobenzo-[b]-pyrans by MnFe₂O₄@SiO₂NHPhNH₂-PTA

MnFe ₂ O ₄	@SiO ₂ NH	PhNH ₂ -PTA ^a				
	Entry	Catalyst amount(g)	Solvent	Condition	Time(min)	Yield(%) ^b
	1	0.04	EtOH	reflux	60	73
	2	0.04	CH_2Cl_2	reflux	100	40
	3	0.04	CH ₃ CN	reflux	90	48
	4	0.04	EtOAc	reflux	100	69
	5	0.04	None	rt	180	trace
	6	0.04	H_2O	reflux	60	90
	7	0.04	Solvent free	60	40	85
	8	0.04	Solvent free	80	30	95
	9	0.03	Solvent free	80	35	91
	10	None	H ₂ O	Sonication/ rt	30	tace

Table	4	Optimization	of	various	parameters	for	the	synthesis	of	tetrahydrobenzo[b]pyran	by
MnFe ₂	$O_4@$	SiO ₂ NHPhNH	2-PT	A ^a							

11	0.02	H ₂ O	Sonication/ 80	25	78
12	0.03	H_2O	Sonication/ 80	20	89
13	0.04	H ₂ O	Sonication/80	10	94

^aReaction Conditions: bezaldehyde(1mmol), dimedone(1 mmol), malononitrile (1.2 mmol), under solvent-free , MnFe₂O₄@SiO₂NH-NH₂-PTA (0.04 g) or water (5ml, ultrasonic irradiation)

^aIsolated yields.

The optimum conditions were applied to a series of aromatic aldehydes carrying either electron-donating or electron-withdrawing substitutions in the ortho, meta, and para positions. The results are shown in Table 5.

			Solven-free/ 80°C	P	Ultrasoni H2O/80°C	c/ 2	-
Entry	Ar	Product	Time	Yield	Time	Yield ^a	M.p. °C Found/ Reported
1	CHO	CN CN NH ₂	30	95	10	92	235-237 (236-239)[41]
20	CHO HO Me		35	86	12	85	210-212 (214-216)[41]
3	CHO		30	91	10	90	214-216 (212-213)[42]



^aReaction Conditions: bezaldehyde(1mmol), dimedone(1 mmol), malononitrile (1.2 mmol), under solvent-free , MnFe₂O₄@SiO₂NH-NH₂-PTA (0.04 g) or water (5ml, ultrasonic irradiation)

^aIsolated yields.

It was observed that the electron-withdrawing groups gave rise to the excellent yields of products under both the solvent-free condition at 80 °C and the ultrasonic irradiation. The structures of products were determined from their analytical and spectral [IR, ¹H and ¹³C, Nuclear Magnetic Resonance (NMR)] data and by direct comparison with authentic samples. The formation of the products were also confirmed by the comparison of their melting points with the products prepared by the previously reported methods. As can be seen from Tables 3 and 5, the catalytic system worked exceedingly well in both phthalazine-triones and tetrahydrobenzo-[b]-pyran and the expected products were obtained in short times and in good to high yields.

A plausible reaction mechanism for the synthesis of tetrahydrobenzo-[b]-pyran is shown in Scheme 5. Initially, both aldehyde and malononitrile were activated in the presence of MnFe₂O₄@SiO₂NHPhNH₂-PTA. After condensation and elimination of a water molecule, the product reacts with dimedone via Michael addition to afford the desired tetrahydrobenzo[b]pyran derivative. The mechanism clearly explains the role of heteropolyacid active sites.



Scheme 5 Proposed mechanism for the synthesis of tetrahydrobenzo[b]pyran

The reusability of catalysts is one of the most important benefits of heterogeneous catalytic systems from economic, and environmentally point of view. The recyclability of nanocatalyst was investigated for the one-pot three-component reaction between aldehyde, malononitrile and dimedone by carrying out six consecutive cycles using the same reaction conditions. run, recovered without After each the catalyst was filtration since the MnFe₂O₄@SiO₂NHPhNH₂-PTA was rapidly concentrated as soon as an external magnet was set close to the sidewall of the reaction vessel, then washed with EtOH (10 mL), CH_2Cl_2 (10

mL). The solid catalyst dried under vacuum after each cycle, and then reused for the next reaction (Fig. 10).



Fig. 10 Recycl ability of MnFe₂O₄@SiO₂@NHPhNH₂-PTA in the synthesis of 2-amino-5-oxo-5,6,7,8-tetrahydro-4-H-benzo[b]pyran

It was observed that the MnFe₂O₄@SiO₂@NHPhNH₂-PTA indicated excellent activity for the three-component reaction even after the six run. TGA, XRD, BET, FT-IR and TEM analyses of reused catalyst after six run indicated that no detectable changes of the catalyst occurred during the reaction the recycling stages (Fig. 11)



Fig. 11 TGA, XRD, BET, FT-IR and TEM analyses of reused catalyst after six run

A comparison for the efficiency of the catalytic activity of MnFe₂O₄@SiO₂NHPhNH₂-PTA for the synthesis of indazolo-[2, 1-b]-phthalazine-triones (Table 6, entries 1–7) and tetrahydrobenzo-[b]-pyran condensation (Table 6, entries 8–13), with several previously reported methods is presented. The results show that this method is superior to some previously reported methods in terms of yields, reaction times, the amount of the reagent used, and the avoidance of toxic catalysts, organic volatile solvents and the easy separation of the catalyst.

Table 6 Comparison of the efficacy of $MnFe_2O_4@SiO_2@NH-NH_2-PTA$ catalyst with some various catalysts in the synthesis of 3,4-Dihydro-3,3-dimethyl-13-(4-chlorophenyl)-2H-indazolo[2,1-b]phthalazine-1,6,11(13H)-trione (1) and 2-Amino-4-(4-chlorophenyl)-5-oxo-5,6,7,8-tetrahydro-4H chromene-3-carbonitrile condensation (2).

Enty	Catalyst	product	Catalyst	Time	Condition	Yield	Ref.
			loading	(min)		(%)	
1	Fe ₃ O ₄ @silica sulfuric acid	1	0.075 g	35	solvent-	88	[40]
					free,100 ° C		
2	Ceric ammonium nitrate	1	0.027 g	120	solvent-	94	[45]
					free,50 °C		
3	β -CD (β -Cyclodextrin) /	1	15mol%	26	80 ° C	85	[33]
	H ₂ O.						
4	Citric acid	1	0.03mol%	20	solvent-	92	[46]
		\sim			free,80 ° C		
5	[Dsim][HSO ₄]	1	15 mol%	20	solvent-	93	[47]
					free,100 °C		
6	MnFe ₂ O ₄ @SiO ₂ NH-NH ₂ -	1	0.03 g	20	solvent-	95	This work
	РТА				free,80 ° C		
7	MnFe ₂ O ₄ @SiO ₂ NH-NH ₂ -	1	0.03 g	8	Sonication/	95	This work
	РТА				H ₂ O 80 ° C		
8	H ₂ PO ₄ -SCMNPs	2	0.03 g	20	solvent-	89	[48]
	1				free,80 ° C		
9	Fe ₃ O ₄ @Ph-SO ₃ H	2	0.2 mol%	25	Sonication/	90	[49]
					$H_2O.$		
10	Nano ZnO	2	10 mol%	30	80 ° C	95	[50]
11	Fe ₃ O ₄ /SiO ₂ /Met	2	0.03 g	60	Reflux	78	[51]
12	MnFe ₂ O ₄ @SiO ₂ NH-NH ₂ -	2	0.04	25	solvent-	95	This work
	PTA				free,80 ° C		
13	MnFe ₂ O ₄ @SiO ₂ NH-NH ₂ -	2	0.04	8	Sonication/	94	This work
	PTA				H ₂ O 80 ° C		

In view of the leaching problems observed with tungsten supported on heteropoly acid catalyst, quantitative analysis using AAS was employed to determine the amount of metal in

the reaction. The heterogeneity of the $MnFe_2O_4@SiO_2NHPhNH_2$ -PTA catalyst was examined by carrying out a hot filtration test using dimedone, malononitrile and benzaldehyde as model substrates. No tungsten could be detected in the liquid phase using AAS and, more significantly, after hot filtration, the reaction of the residual mixture was completely stopped.

4 Conclusions

In Conclusion, an easy, green methodology and highly efficient method was developed for the synthesis of 2H-indazolo-[2,1-b]-phthalazine-triones and tetrahydrobenzo-[b]-pyran derivatives via one-pot three-component reaction in the presence of $MnFe_2O_4@SiO_2@NHPhNH_2$ -PTA nanoparticles as the efficient and magnetic catalyst under the solvent-free condition at 80 °C or the ultrasonic irradiation conditions in water.

This method gives notable advantages such as easy preparation, heterogeneous nature, clean and simple procedure, thermal stability and the easy separation of the catalyst, easy product separation and purification, excellent yields, short reaction time, lower loading of the catalyst compared with the other methods, and avoidance of using hazardous organic solvents that makes this method an instrumental alternative to the previous methodologies for the scale up of these one-pot three-component reactions. Furthermore, the catalyst is magnetically separable and eliminates the requirement of catalyst filtration after the completion of the reaction, which represents a major advantage for reactions from an economic and environmental point of view.

Acknowledgements

This work was supported by the Research Council at the Shahid Chamran University of Ahvaz.

References

[1] M. Esmaeilpour, J. Javidi, F. Nowroozi Dodeji and M. Mokhtari Abarghoui, Transition Met. Chem. 39 (2014) 797.

- [2] J. Mondal, T. Sen, A. Bhaumik, Dalton Trans. 4 (2012) 6181.
- [3] (a) S. Shylesh, V. Schunemann, W.R. Thiel, Angew. Chem. Int. Ed. 49 (2010) 3428.

(b) C.W. Lim, I.S. Lee, Nano Today. 5 (2010) 412.

[4] J. Govan, Y. Gun'ko, Nanomaterials. 4 (2018) 222.

[5] (a) Y. Zhu, L.P. Stubbs, F. Ho, R. Liu, C.P. Ship, J.A. Maguire, N.S. Hosmane, ChemCatChem. 2(2010) 365. (b) P. Wang, H. Liu, J. Niu, R. Li, J. Ma, Catal. Sci. Technol. 4

(2014) 1333.(c) R.B. Nasir Baig, R.S. Varma, Chem. Commun.49 (2013) 752.(d) T. Cheng, D. Zhang, H. Li, G. Liu, Green Chem. 16 (2014) 3401.

[6] A. Kong, P. Wang, H. Zhang, F. Yang, S.P. Huang, Y. Shan, Appl. Catal. A. 417 (2012) 183

[7] B. JansiRani, M. Ravina, B. Saravana kumar, G. Ravi, V. Ganesh, S. Ravichandran, R. Yuvakkumar, Nano-Structures & Nano-Objects. 14 (2018) 84.

[8] O, Makrygenni, E. Secret, A. Michel, D. Brouri, V. Dupuis, A. Proust, J.M. Siaugue, R. Villanneau, Journal of Colloid and Interface Science 514 (2018) 4.

[9] (a) A.M.I. lnicka, E. Bielanska, L.L. Dobrzynska, A. Bielanski, Appl. Catal. A. 421-422
(2012) 91; (b) A. Ciftci, D. Varisli, C.K. Tokay, N.A. Sezgi, T. Dogu, Chem. Eng. J. 207–208 (2012) 85; (c) A. Kumar, P. Singh, S. Kumar, R. Chandra, S. Mozumdar, J. Mol. Catal. A: Chem. 276 (2007) 95.

[10] T. Jihuai, L. Tingting, Zh.Jinwen, X. Bingxue, Ch.Muhua, Zh. Xinbao, Journal of the Taiwan Institute of Chemical Engineers. 000 (2018) 1.

[11] (a) L. T.Aany Sofia, A. Krishnan, M. Sankar, N. K. Kala Raj, P. Manikandan, P. R. Rajamohanan and T.G. Aithkumar, J. Phys. Chem. 113 (2009) 21114; (b) J. Javidi, M. Esmaeilpour and F. Nowroozi Dodeji, RSC Adv. 5 (2015) 308; (c) M. Esmaeilpour, J.Javidi, F. Nowroozi Dodeji, New J. Chem. 38 (2014) 5453.

[12] A. Khodadadi Dizaji, B. Mokhtarani, H. R, Mortaheb, Fuel. 236 (2019) 717.

[13] (a) M. A. Schwegler, H. Bekkum, N. Munck, Appl. Catal. A. 74 (1991) 191; (b) E. Rafiee, N. Nobakht, Journal of Molecular Catalysis A: Chemical. 398 (2015) 17; (c) Y. Wei, Y. Chen, R. Wang, Fuel Processing Technology 178 (2018) 262.

[14] A.T. Khan, M. Lal, S. Ali, M.M. Khan, Tetrahedron Lett. 52 (2011) 5327.

[15] (a) B. Karami, S. Khodabakhshi, K. Eskandari, Tetrahedron Lett. 53 (2012) 1445; (b)C.Wiener, C. H. Schroeder, B. D. West and K. P. Link, J. Org. Chem. 27 (1962) 3086.

[16] (a) Z. Chen, Q. Zhu, W. Su, Tetrahedron Lett. 52 (2011) 2601; (b) A. Hasaninejad, M. Shekouhy, N. Golzar, A. Zare, M.M. Doroodmand, Appl. Catal.A: Gen. 402 (2011) 11.

[17] S. F Hojati, M. Moosavifar, T. Ghorbanipoor, Comptes Rendus Chimie. 5 (2017) 520.

[18] R.G. Vaghei, R.K. Nami, Z.T. Semiromi, M. Amiri, M. Ghavidel, Tetrahedron. 67 (2011) 1930.

[19] R. Tayebee, M. Fattahi Abdizadeh, B. Maleki, E. Shahri, Journal of Molecular Liquids. 241 (2017) 447.

[20] F. M. Awadallah, W. I. EI-Eraky, D. O. Saleh, European Journal of Medicinal Chemistry, 52 (2012)14.

[21] P. Sagar Vijay Kumar, L. Suresh, G. V. P. Chandramouli, Journal of Saudi Chemical Society 3 (2017) 306.

[22] K. Kong, J. Zhang, P. Zhao, H. Lu, Y. Chen, Tetrahedron 48 (2017) 6742.

[23] Da-Ch. Liu,G-H. Gong, Ch-X. Wei, X-J. Jin, Zh-Sh. Quan, Bioorganic & Medicinal Chemistry Letters. 6 (2016) 1576.

[24] D. S. Raghuvanshi, K. N. Singh, Tetrahedron Letters. 52 (2011) 5702.

[25] (a) G. Shukla, R.K. Verma, G.K. Verma, M.S. Singh, Tetrahedron Lett. 52 (2011) 7195;

(b) G. Karthikeyana, A. Pandurangan, J. Mol. Catal. A: Chem. 361-362 (2012) 58.

[26] I. Malaescu, A. Lungu, C. N. Marin, P. Vlazan, P. Sfirloaga, G. M. Turi, Ceramics International. 15 (2016) 16744.

[27] I.V. Kozhevnikov, Catalysis for Fine Chemicals, Catalysis by Polyoxometalates, vol. 2, Wiley, Chichester, (2002) 175 pp.

[28] G. Singh, S. Chandra, International Journal of Hydrogen Energy. 43 (2018) 4058.

[29] K. Ashwini, H. Rajanaika, K.S. Anantharaju, H. Nagabhushanad, P. Adinarayana Reddy, K. Shetty, K.R. Vishnu Mahesh, Materials Today: Proceedings 4 (2017) 11902.

[30] M. Arshad, M. Abbas, S. Ehtisham-ul-Haque, M. Akhyar Farrukh, M. Iqbal, Journal of Molecular Structure. 1180 (2019) 244.

[31] Y. Lin, H. Chen, K. Lin, B. Chen, C. Chiou, J. Environ. Sci. 23 (2011) 44.

[32] F. Mahmoudi, S. Farhadi, P. Machek, M. Jarosova, Polyhedron 158 (2019) 423.

[33] A. V. Chate, P. K. Bhadke, M. A. Khande, J. N. Sangshetti, Ch. H. Gill, Chinese Chemical Letters. 7 (2017) 1577.

[34] R. Tayebee, M. Jomei, B. Maleki, M. Kargar Razi, H. Veisi, M. Bakherad, Journal of Molecular Liquids. 206 (2015) 119.

[35] M. Abedini, F. Shirini, J. M, Alinejad Omran, Journal of Molecular Liquids. 212 (2015) 405.

[36] B. Afzalian, J. T.Mague, M. Mohamadi, S. Y. Ebrahimipour, B. Pouramiri, E. Tavakolinejad Kermani, Chinese Journal of Catalysis.7 (2015) 1101.

[37] F. Shirini, M. Safarpoor, N. Langarudi, O.Goli-Jolodar, Dyes and Pigments. 123 (2015) 186.

[38] M. Saha, S. Phukan, R. Jamatia, S. Mitra, A.K. Pal, RSC Adv. 3 (2013) 1714.

[39] H.R. Shaterian, S. Sedghipour, E. Mollashahi, Res. Chem. Intermed. (2014)

[40] A.R. Kiasat, J. Davarpanah, Journal of Molecular Catalysis A: Chemical. 373 (2013) 46.

[41] M. Rastgoo Yousefi, O. Goli-Jolodar, F. Shirini, Bioorganic Chemistry. 81 (2018) 326.

[42] S. M. Baghbanian, N. Rezaeia and H. Tashakkorian, Green Chem. 15 (2013) 95.

[43] B. Maleki and S. S.Ashrafi, RSC Adv. 4 (2014) 42873.

[44] A. r Hasaninejada, N. Golzar, M. Beyrati, A. Zare, M. M. Doroodmand, Journal of Molecular Catalysis A: Chemical 372 (2013) 137.

[45] K. Mazaahir, C. Ritika, J. Anwar, Chin. Sci. Bull. 57 (2012) 2273.

[46] M. A. Zolfigol, M. Mokhlesi, Sh. Farahmand, J IRAN CHEM SOC. 10 (2013) 577.

[47] F. Masihpour, A. Zare, M. Merajoddin, A.r. Hasaninejad, Journal of Chemical Technology and Metallurgy, 54 (2019) 23.

[48] H.R. Saadati-Moshtaghin, F.M. Zonoz ,Materials Chemistry and Physics 199 (2017) 159.

[49] D. Elhamifar, Z. Ramazani, M. Norouzi, R. Mirbagheri, Journal of Colloid and Interface Science 511 (2018) 392.

[50] M. Hosseini-Sarvari, S. Shafiee-Haghighi, Chem. Heterocycl. Compd. 48 (2012) 1307.

[51] A. Alizadeh, M. M. Khodaei, M. Beygzadeh, D. Kordestani, M. Feyzi, Bull. Korean Chem. Soc. 33 (2012) 2546.

Graphical Abstract - Synopsis

The present work describes the synthesis of a new ionic compound based on polyoxometalate anion supported on silica coated nanoparticle MnFe₂O₄ as a novel scaffold for the preparation of tetrahydrobenzo[b]pyran and indazolo[2,1-b]phthalazine-triones. The structure and composition ofthe nanocomposite was performed by different methods and analyzed by FT-IR, FE-SEM, TEM, TGA, XRD, BET, ICP and VSM. This catalyst show high activity and give excellent yields. The catalyst can be easily separated from the reaction mixture and reused several time. The results show that the particles are mostly spherical in shape and have an average size of approximately <30 nm.