



An efficient and magnetically separable heteropoly acid catalyst for the synthesis of β -amino carbonyl compounds under solvent-free conditions

Zahra Maleki, Nahid Rasouli*, Maryam Movahedi, Zahra Sadeghi

Department of Chemistry, Payame Noor University, PO Box 19395-3697, Tehran, Iran

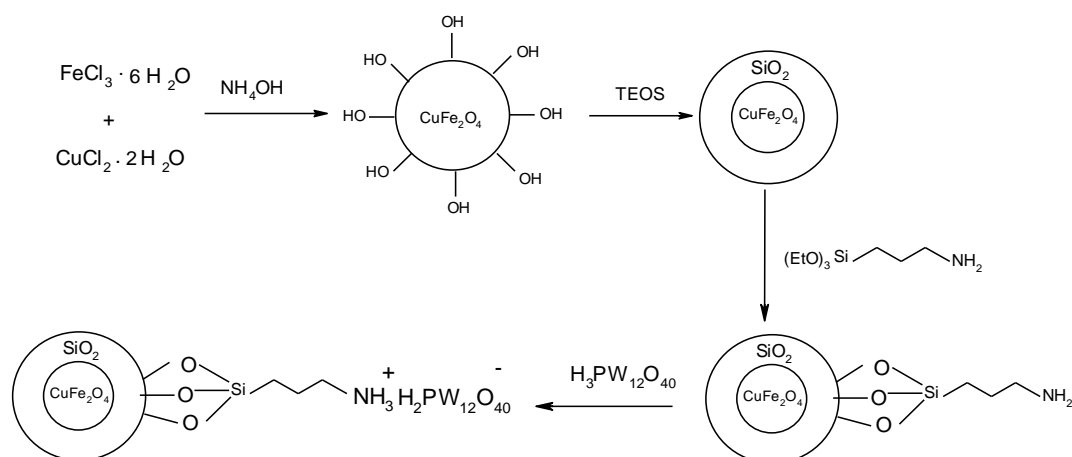
Abstract This paper reports a facile synthesis method of magnetically separable heteropoly acid, ($\text{CuFe}_2\text{O}_4\cdot\text{SiO}_2\cdot\text{NH}_2\cdot\text{H}_3\text{PW}_{12}\text{O}_{40}$) consisting of phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) immobilized on amine functionalized silica coated magnetic copper–ferrite nanoparticles ($\text{CuFe}_2\text{O}_4\cdot\text{SiO}_2\cdot\text{NH}_2$). The synthesized catalyst was characterized by Fourier transform infrared (FT-IR), scanning electron microscopy (SEM), powder X-ray diffraction (XRD), energy dispersive X-ray analysis (EDAX) and transmission electron microscopy (TEM). The immobilized phosphotungstic acid have been used as an efficient heterogeneous catalyst for the synthesis of β -aminocarbonyl compounds using one-pot three-component coupling reaction of aldehydes, amines and ketones at room temperature and under solvent free conditions. The different electrons withdrawing and electrons donating substrates show an excellent yield of desired products with the advantage of magnetic separation of ($\text{CuFe}_2\text{O}_4\cdot\text{SiO}_2\cdot\text{NH}_2\cdot\text{H}_3\text{PW}_{12}\text{O}_{40}$) catalyst.

Keywords Organic compounds, Magnetic properties, Spectroscopy, Catalytic properties

Introduction

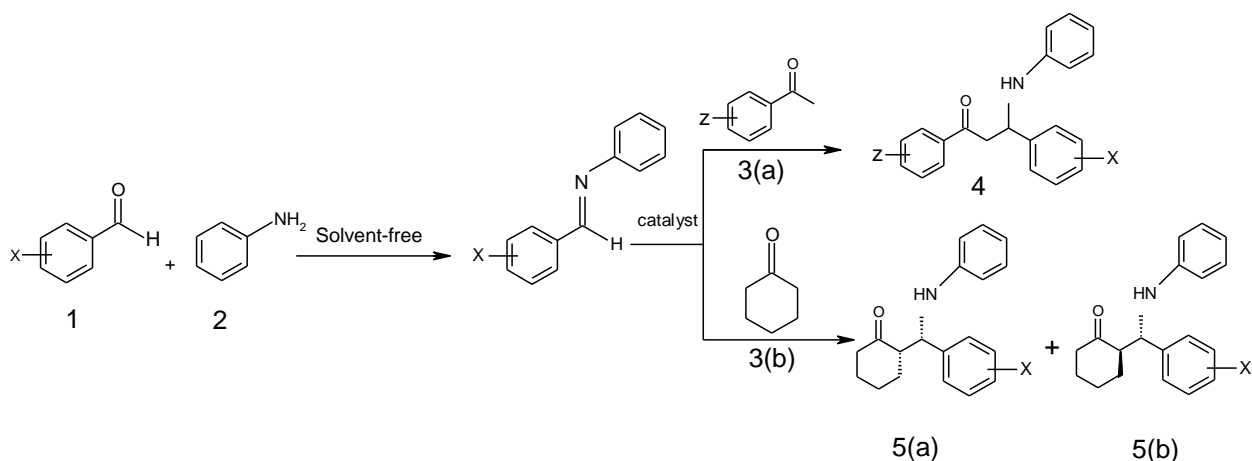
One of the most important reactions in organic synthesis is carbon–carbon bond forming that known as Mannich reaction [1-4]. The β -amino carbonyl compounds as intermediate in the synthesis of pharmaceuticals compounds are of particular importance [5]. In Mannich reaction an amine and two carbonyl compounds in the presence of organic or inorganic acids are used to produce β -amino carbonyl compounds [6-12]. However, Mannich reaction using these catalysts are associated with disadvantages like longer reaction time, low yield, use of toxic organic solvents and separation of catalyst-product. So, it is necessary that an efficient catalyst used for the synthesis of β -amino carbonyl compounds. Recently, Keggin type heteropoly acids with features such as multi-electron oxidants or strong acids used as catalyst in organic synthesis reactions [13,14]. But, there are some disadvantages about catalysis with heteropolyacid catalysts such as high solubility in polar solvents and low surface area. Therefore the separation of products and reuseability of catalyst become difficult. In this regard, immobilization of heteropolyacid catalysts on solid supports are important because they can easily be separated from reaction mixtures and reused [15,16]. Recent studies show that magnetic nanoparticles are excellent supports for various catalysts [17,18], that can be separated and recycled from the products by an external magnet. For this purpose, the surface of magnetic nanoparticles modified by organic or inorganic materials such as polymers, biomolecules, silica, etc used at various reactions including oxidation, epoxidation, esterification, hydration, hydrogenation, enantioselective acylation, nitroaldol condensation, coupling reaction, cycloaddition, photocatalysis [19,20]. To the best of our knowledge, a few reports were related to immobilization of heteropolyacid compounds on magnetic nanoparticles [21, 22]. In this work, a facile method for immobilization of phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) on the surface of copper-ferrite modified with amine and silica ($\text{CuFe}_2\text{O}_4\cdot\text{SiO}_2\cdot\text{NH}_2\cdot\text{H}_3\text{PW}_{12}\text{O}_{40}$) (Scheme.1) is reported and for the first time evaluate.





Scheme 1: Synthetic pathways of $(\text{CuFe}_2\text{O}_4\text{-SiO}_2\text{-NH}_2\text{-H}_3\text{PW}_{12}\text{O}_{40})$

Then, its catalytic activity in the synthesis of β -amino carbonyl compounds in Mannich-type reaction (Scheme.2).



Scheme 2: The Mannich reaction catalyzed by $(\text{CuFe}_2\text{O}_4\text{-SiO}_2\text{-NH}_2\text{-H}_3\text{PW}_{12}\text{O}_{40})$

Experimental

Synthesis of copper-ferrite nanoparticles (CuFe_2O_4)

CuFe_2O_4 magnetic nanoparticles were prepared by simple chemical co-precipitation of Fe^{3+} and Cu^{2+} ions with a molar ratio of 2:1 [23]. In this way, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (21.6 mmol) and $\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$ (10.8 mmol) were dissolved in 100 ml deionized water at 80°C . Then, 10 ml of 25% NH_4OH was entered into the reaction mixture, stirred for 30 min and then cooled to room temperature. The obtained black precipitate was washed three times with distilled water and 0.02 M solution of NaCl. The synthesized CuFe_2O_4 nanoparticles were magnetically separated.

Synthesis of copper-ferrite nanoparticles covered with silica ($\text{CuFe}_2\text{O}_4\text{-SiO}_2$)

According to the method reported by Stöber method (Yamaura et al. 2004), 0.58 g of copper-ferrite CuFe_2O_4 was dispersed in mixture of 40 ml ethanol, 24 ml deionized water and 12 ml concentrated ammonia aqueous solution by ultrasonication for 30 min. Subsequently, 1.6 ml of tetraethylorthosilicate (TEOS) was added and stirred for 24 h at room temperature. Finally, the produced solid was separated magnetically, washed with water and ethanol and then dried at 60°C .

Synthesis of silica modified copper-ferrite with 3-aminopropyltriethoxysilane ($\text{CuFe}_2\text{O}_4\text{-SiO}_2\text{-NH}_2$)

0.05 g of $\text{CuFe}_2\text{O}_4\text{-SiO}_2$ was dispersed in 10 ml of ethanol and ultrasonicated for 30 min. Then, 3 ml of 3-aminopropyltriethoxysilane was added into the dispersion and ultrasonicated for 15 min. The mixture was refluxed at 50°C under constant stirring for 2 h. The obtained product was separated magnetically, washed with ethanol and then dried at 60°C .



Synthesis of amine and silica modified copper-ferrite with phosphotungstic acid ($\text{CuFe}_2\text{O}_4\text{-SiO}_2\text{-NH}_2\text{-H}_3\text{PW}_{12}\text{O}_{40}$)

In this procedure, 0.3 g of $\text{CuFe}_2\text{O}_4\text{-SiO}_2\text{-NH}_2$ was dispersed in 50 ml of acetonitrile and ultrasonicated for 30 min. Then, a solution of phosphotungstic acid $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 6\text{H}_2\text{O}$ (0.3 g) in 20 ml deionized water was added dropwise into the solution, ultrasonicated for 30 min and the mixture was stirred for 24 h at room temperature. Finally, the produced $\text{CuFe}_2\text{O}_4\text{-SiO}_2\text{-NH}_2\text{-H}_3\text{PW}_{12}\text{O}_{40}$ was separated magnetically and washed twice with water and dried at 60 °C.

General procedure for the synthesis of β -amino carbonyl compounds

To the mixture of cyclohexanone (3.0 mmol), aromatic aldehyde derivatives (1.0 mmol), aniline (1.0 mmol) and ($\text{CuFe}_2\text{O}_4\text{-SiO}_2\text{-NH}_2\text{-H}_3\text{PW}_{12}\text{O}_{40}$) as catalyst (0.01 g, 0.4 mol %) was stirred under solvent-free conditions at room temperature for appropriate time indicated in Table.1, until the reaction was completed as monitored by TLC (*n*-hexane/EtOAc=80/20). After completion of the reaction, hot ethanol was added to the reaction mixture to dissolve the product and catalyst was recovered by an external magnet. The reaction procedure for acetophenone is similar to the above protocol with the ratio of aromatic aldehyde derivatives (1.0 mmol): aniline (1.0 mmol): acetophenone derivatives (3 mmol): catalyst (0.01 g) (Scheme.2) and the appropriate reaction times as indicated in Table.1. All of the products are known and were characterized by $^1\text{H-NMR}$ and melting points.

Characterization

The size and morphology of synthesized compounds were determined using transmission electron microscopy (Phillips-CM10 operating at 100 kV with a Cu grid); the FT-IR spectra were recorded by a Fourier transform Infrared Spectroscopy (JASCO FT/IR-4200, Japan), the X-ray diffraction measurement was recorded on a X-ray diffractometer Bruker, D8 ADVANCE [(Germany) using $\text{Cu K}\alpha$ radiation ($\lambda=0.1540$ nm)] and the EDX spectra was recorded by Energy-dispersive X-ray spectroscopy (EDX) (Philips XL 30).

Results and Discussion

FT-IR analysis

In order to demonstrate the formation of 3-aminopropyltriethoxysilane layer and phosphotungstic acid on the surface of CuFe_2O_4 , FT-IR spectroscopy was used. Fig. 1 shows the FTIR spectrum in the skeletal region of 4000–400 cm^{-1} . The primary structure of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ could be identified by four characteristic IR bands appearing at 1080 cm^{-1} (P-O band), 982 cm^{-1} (W=O band), 892 and 791 cm^{-1} (W-O-W bands) [23,24]. In the case of $\text{CuFe}_2\text{O}_4\text{-SiO}_2\text{-NH}_2\text{-H}_3\text{PW}_{12}\text{O}_{40}$ (Fig.1), typical FT-IR spectrum show characteristic vibration peaks of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ at 1096 cm^{-1} , 990 cm^{-1} , 889 cm^{-1} and 807 cm^{-1} , respectively in which attributed to stretching vibration modes of P-O, W=O and W-O-W bonds of the Keggin heteropoly acid.

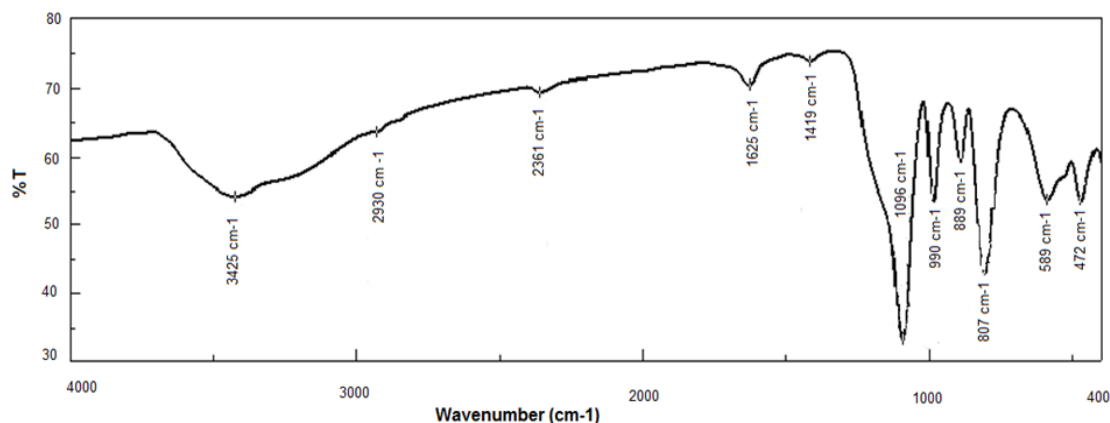


Figure 1: FT-IR spectrum of $\text{CuFe}_2\text{O}_4\text{-SiO}_2\text{-NH}_2\text{-H}_3\text{PW}_{12}\text{O}_{40}$

In Fig. 1 for the CuFe_2O_4 , two characteristic peaks observed at around 472 and 589 cm^{-1} corresponds to octahedral-metal stretching and stretching vibrations of the metal at the tetrahedral site, respectively [25]. Compared to the starting Keggin heteropolyacid, the peak at 1096 cm^{-1} overlap with Si-O-Si stretching vibration of silica, indicating that $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was anchored to the surface of $\text{CuFe}_2\text{O}_4\text{-SiO}_2\text{-NH}_2$ successfully.



XRD Analysis

The crystalline structure of CuFe_2O_4 nanoparticles and $\text{CuFe}_2\text{O}_4\cdot\text{SiO}_2\cdot\text{NH}_2\text{-H}_3\text{PW}_{12}\text{O}_{40}$, were identified with XRD technique (Fig. 2a and Fig. 2b). For CuFe_2O_4 , diffraction peaks with $2\theta = 18.4^\circ, 30.2^\circ, 35.6^\circ, 43.2^\circ, 53.6^\circ, 57.1^\circ$ and 62.6° are indicative of a cubic structure of the CuFe_2O_4 . As shown in Fig. 2b, the XRD pattern of $\text{CuFe}_2\text{O}_4\cdot\text{SiO}_2\cdot\text{NH}_2\text{-H}_3\text{PW}_{12}\text{O}_{40}$ displayed diffraction peaks of CuFe_2O_4 indicating the formation of CuFe_2O_4 phase. In the XRD pattern of $\text{CuFe}_2\text{O}_4\cdot\text{SiO}_2\cdot\text{NH}_2\text{-H}_3\text{PW}_{12}\text{O}_{40}$, the characteristic peaks of CuFe_2O_4 did not change after being modified with $\text{H}_3\text{PW}_{12}\text{O}_{40}$.

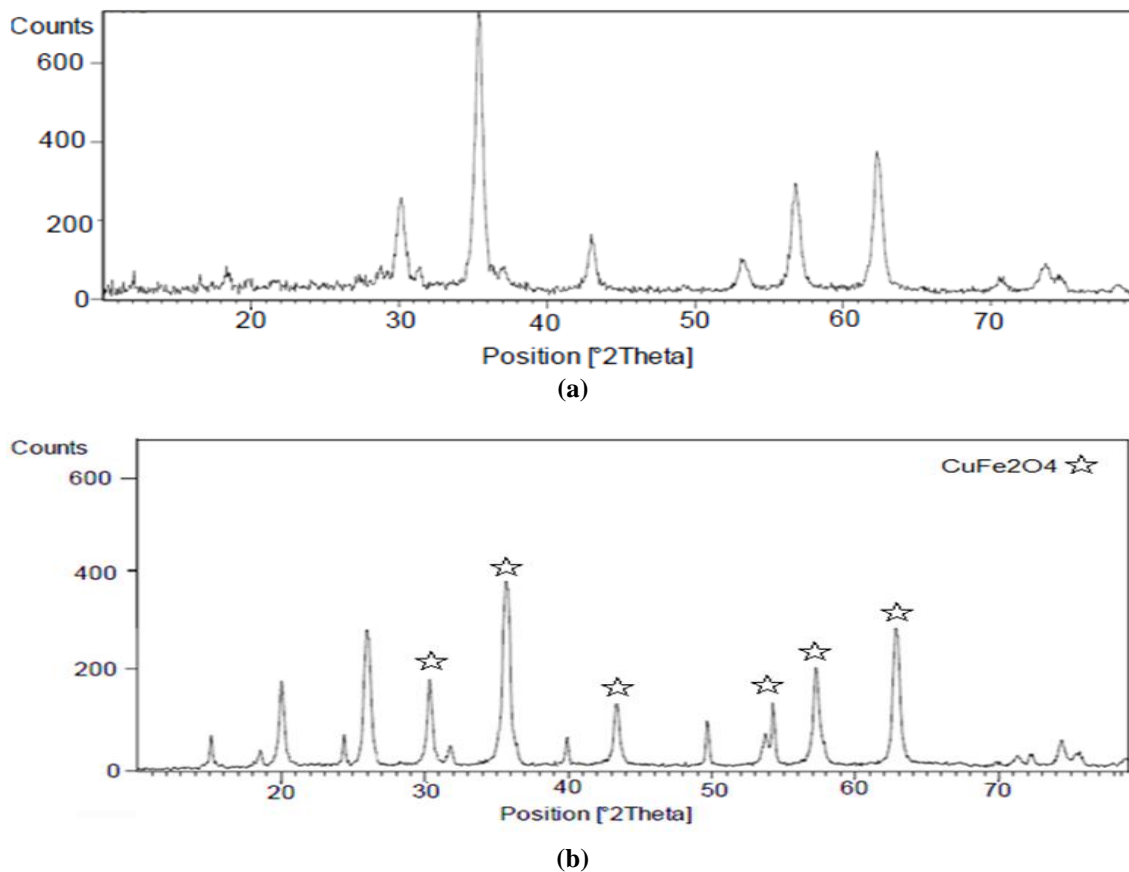


Figure 2: The XRD patterns of (a) CuFe_2O_4 (b) $\text{CuFe}_2\text{O}_4\cdot\text{SiO}_2\cdot\text{NH}_2\text{-H}_3\text{PW}_{12}\text{O}_{40}$

SEM, EDAX and TEM Analysis

Fig. 3a and 3b show the SEM images of $\text{CuFe}_2\text{O}_4\text{-SiO}_2$ and $\text{CuFe}_2\text{O}_4\cdot\text{SiO}_2\cdot\text{NH}_2\text{-H}_3\text{PW}_{12}\text{O}_{40}$. The obtained $\text{CuFe}_2\text{O}_4\text{-SiO}_2$ nanoparticles are uniform size with spherical shape (Fig. 3a).

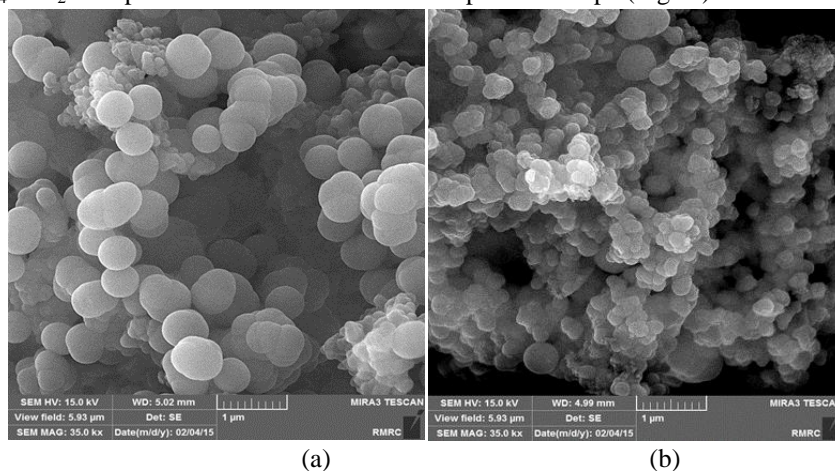


Figure 3: The SEM images of (a) $\text{CuFe}_2\text{O}_4\text{-SiO}_2$ (b) $\text{CuFe}_2\text{O}_4\cdot\text{SiO}_2\cdot\text{NH}_2\text{-H}_3\text{PW}_{12}\text{O}_{40}$



In comparison with the Fig.3a the morphology of the obtained catalyst $\text{CuFe}_2\text{O}_4\cdot\text{SiO}_2\cdot\text{NH}_2\text{-H}_3\text{PW}_{12}\text{O}_{40}$ shows that the preferred catalyst is formed. In order to obtain some information on the elemental composition of $\text{CuFe}_2\text{O}_4\cdot\text{SiO}_2$ and $\text{CuFe}_2\text{O}_4\cdot\text{SiO}_2\cdot\text{NH}_2\text{-H}_3\text{PW}_{12}\text{O}_{40}$, the EDAX analysis were performed and presence of Fe, O, Si, C, N, P, W were detected (Fig.4).

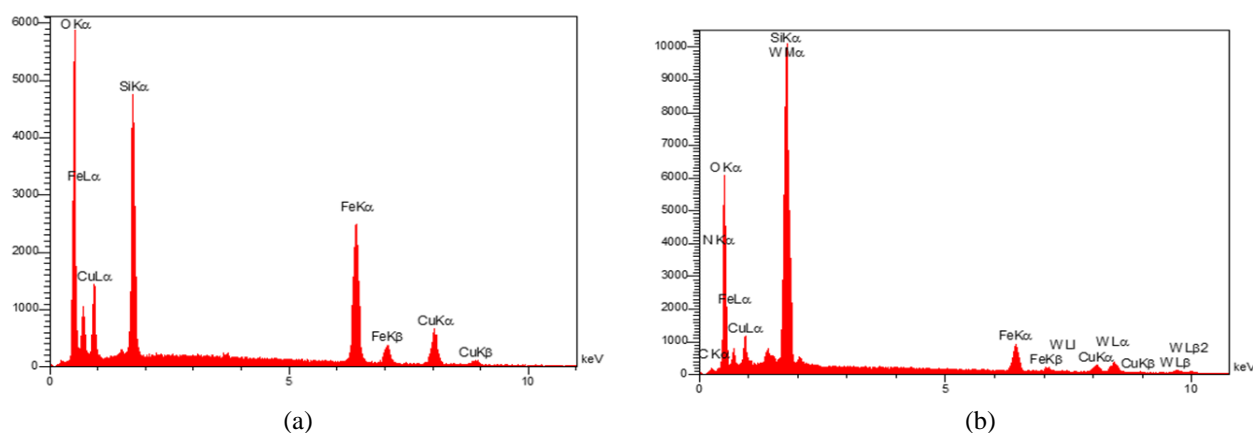


Figure 4: Energy Disperse X-ray Analysis spectrum of (a) $\text{CuFe}_2\text{O}_4\cdot\text{SiO}_2$ (b) $\text{CuFe}_2\text{O}_4\cdot\text{SiO}_2\cdot\text{NH}_2\text{-H}_3\text{PW}_{12}\text{O}_{40}$. Based on the above results, it is demonstrated that $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was supported on the surface of modified CuFe_2O_4 nanoparticles. Fig. 5 (a) shows the TEM image of $\text{CuFe}_2\text{O}_4\cdot\text{SiO}_2$. The mean diameter determined from the TEM image is about 20 nm. Fig. 5(b) shows TEM image of $\text{CuFe}_2\text{O}_4\cdot\text{SiO}_2\cdot\text{NH}_2\text{-H}_3\text{PW}_{12}\text{O}_{40}$. The average size of nanoparticles in Fig 5(b) 30 nm is larger than that of 20 nm Fig 5(a), because two layers of 3-aminopropyltriethoxysilane and phosphotungstic acid were added to the surface of silica-coated nanoparticles ($\text{CuFe}_2\text{O}_4\cdot\text{SiO}_2$).

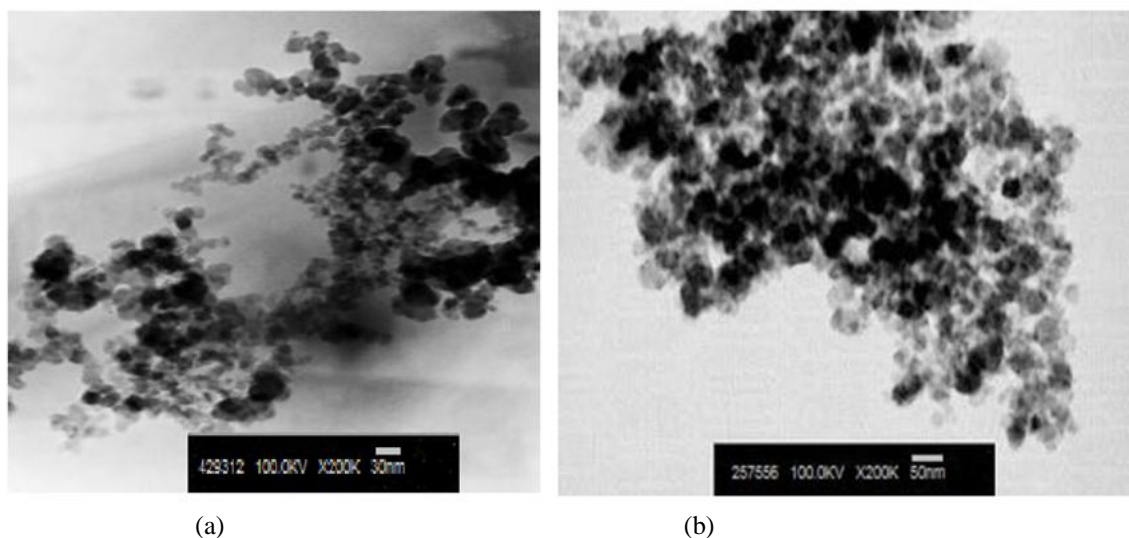


Figure 5: transmission electron image of (a) $\text{CuFe}_2\text{O}_4\cdot\text{SiO}_2$ (b) $\text{CuFe}_2\text{O}_4\cdot\text{SiO}_2\cdot\text{NH}_2\text{-H}_3\text{PW}_{12}\text{O}_{40}$

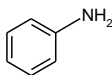
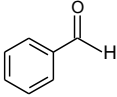
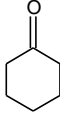
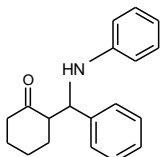
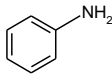
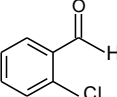
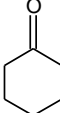
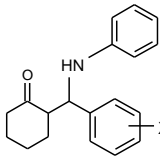
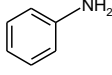
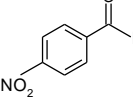
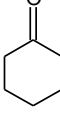
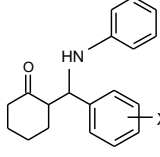
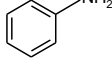
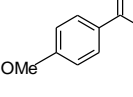
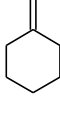
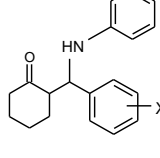
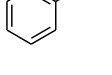
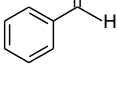

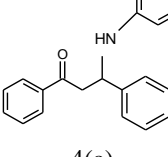
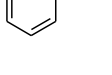
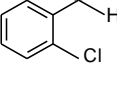

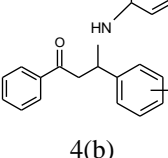
Catalytic Activity of the synthesized catalyst

The catalytic activity of the $\text{CuFe}_2\text{O}_4\cdot\text{SiO}_2\cdot\text{NH}_2\text{-H}_3\text{PW}_{12}\text{O}_{40}$ was investigated in the reaction of aniline, benzaldehyde and cyclohexanone as a model reaction. The reaction was monitored to optimize the reaction conditions for synthesis of 1,3-diphenyl-3-(phenylamino) propane-1-one. The reaction progress was monitored by thin layer chromatography. As can be seen, 0.01 g catalyst, time of 25 min and temperature of 25 °C were suitable for this synthesis reaction (Table 1, entry 1). Also, in order to obtain the effect of different substitution groups on the yield of the reaction, several reactions were carried out in the same conditions (Table.1, entry 2-4). The obtained results show that the phosphotungstic acid magnetic nanoparticles considerably produces β -aminocarbonyl compounds. Also, the one-pot solvent free Mannich synthesis of β -aminocarbonyl compounds was run in the absence of the catalyst and it was found that the reaction proceeds only 5% which shows the

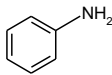
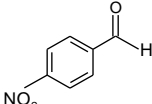
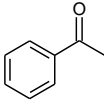
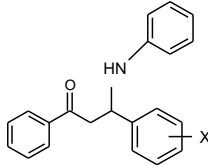
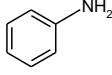
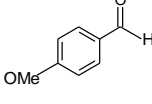
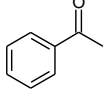
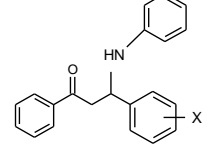
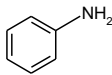
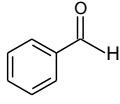
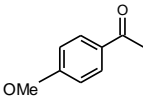
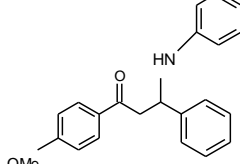
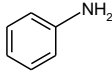
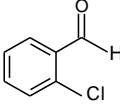
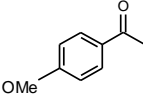
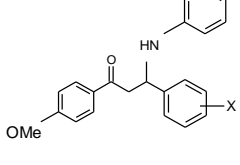
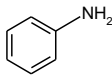
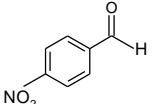
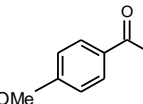
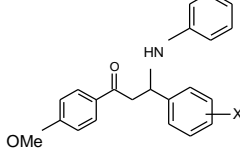
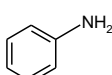
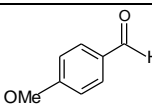
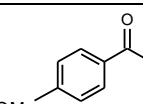
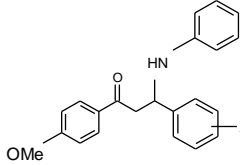
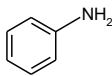
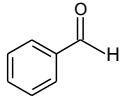
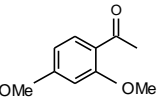
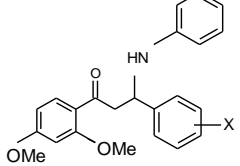


importance of the catalyst for the reaction completion. Moreover, we have examined bare CuFe_2O_4 , silica-coated CuFe_2O_4 , neat $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{CuFe}_2\text{O}_4\cdot\text{SiO}_2\cdot\text{NH}_2\cdot\text{H}_3\text{PW}_{12}\text{O}_{40}$ for the model reaction. The bare CuFe_2O_4 showed relatively good activity as catalyst (40% yield), however CuFe_2O_4 loses its catalytic activity after coating with silica. The neat $\text{H}_3\text{PW}_{12}\text{O}_{40}$ shows much lower catalytic activity compared with $\text{CuFe}_2\text{O}_4\cdot\text{SiO}_2\cdot\text{NH}_2\cdot\text{H}_3\text{PW}_{12}\text{O}_{40}$ (35% yield). The effect of time, the amount of catalyst and various substitution groups on the rate of the reaction were studied (Table 1).

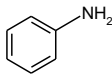
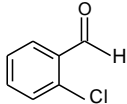
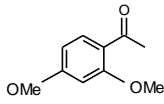
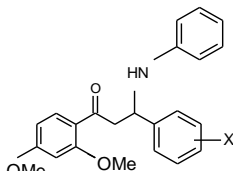
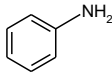
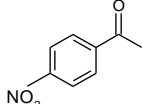
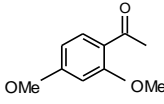
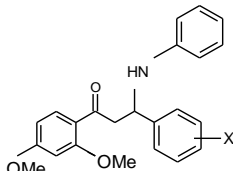
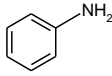
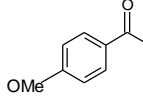
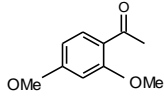
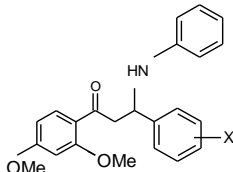
Table 1: Synthesis of β -aminocarbonyl compounds catalyzed by $\text{CuFe}_2\text{O}_4\cdot\text{SiO}_2\cdot\text{NH}_2\cdot\text{H}_3\text{PW}_{12}\text{O}_{40}$ at room temperature^a

Entry	Amine	Aldehyde	Ketone	Product ^a	Time (min)	Yield (%) ^b	[ref]
1				 5(c)	25	100 (Syn/Anti) ^b (15/85)	[26]
2				 5(d)	60	100 (Syn/Anti) ^b (25/75)	[26]
3				 5(e)	90	90 (Syn/Anti) ^b (45/55)	[26]
4				 5(f)	40	100 (Syn/Anti) ^b (27/73)	[27]
5				 4(a)	30	100	[26]
6				 4(b)	60	90	[28]



7				 4(c)	100	80	[29]
8				 4(d)	70	100	[30]
9				 4(f)	40	80	[30]
10				 4(g)	80	90	[30]
11				 4(h)	80	80	[30]
12				 4(i)	30	100	[30]
13				 4(j)	40	100	[30]



14					80	90	[30]
15					80	80	[30]
16					80	100	[30]

^aThe structures of all the products were characterized by ¹HNMR and melting point.

^bIsolated yields.

Effect of Reaction Time

The effect of reaction time on the yield was also investigated. An increase in yield was observed as the reaction time increased (Table.1). A different in the time of the reaction is probably due to the presence of electron-donating and electron-withdrawing groups on the aldehyde or ketone component which cause the the aldehyde or ketone to be active or inactive.

Effect of Different Amounts of Catalyst

The catalytic activity of the CuFe₂O₄.SiO₂.NH₂-H₃PW₁₂O₄₀ was investigated in the reaction of aniline, benzaldehyde and cyclohexanone as a model reaction to evaluate the effect of the amount of catalyst on product yield. In general, the amount of CuFe₂O₄.SiO₂.NH₂-H₃PW₁₂O₄₀ catalyst could improve the rate of reaction significantly. The reaction rate and yield of three component coupling of cyclohexanone, benzaldehyde and aniline are enhanced along with increasing in amounts of catalyst (Table.2). By raising the amount of catalyst from 0.03 mol to 0.4 mol the product yield increased significantly from 15 to 100 %. In the presence of catalyst (0.4 mol%), the reaction produced the corresponding β-aminocarbonyl compounds in excellent yield, so the optimized amount of catalyst was chosen 0.4 mol % for Mannich reaction (Table.2, entry 4).

Table 2: Mannich reaction of cyclohexanone, benzaldehyde and aniline catalyzed by different amounts of catalyst^a

Entry	CuFe ₂ O ₄ .SiO ₂ .NH ₂ -H ₃ PW ₁₂ O ₄₀ (mol %)	Time (min)	Yield ^b (%)
1	0.03	120	15
2	0.06	90	30
3	0.15	45	30
4	0.4	25	100

^aAll reaction were carried out at room temperature under solvent free conditions.

^bIsolated yields.



Separation and recyclability

Recycling experiments were performed via a one-pot three-component reaction of aniline, benzaldehyde and cyclohexanone under solvent free condition at room temperature. At the end of the reaction, the catalyst that could be recovered by a applied magnetic field and washed with ethanol and subjected to a second run of the reaction process. In Table.3, the comparison of efficiency of catalyst for three consecutive cycles is reported. As shown in Table.3, the first reaction using recovered catalyst afforded the 100% yield that is similar to that obtained in the first run. In the second and third runs, the yields were gradually decreased from 90 to 50%.

Table 3: Reusability of the $\text{CuFe}_2\text{O}_4\cdot\text{SiO}_2\cdot\text{NH}_2\text{-H}_3\text{PW}_{12}\text{O}_{40}$ for synthesis of β -amino carbonyl compound

No. of cycles	Run (1)	Run (2)	Run (3)
Yield (%) ^a	100	90	50
Time (min)	35	45	90

^aIsolated yield

The ¹H-NMR of Selected Products

1,3-Diphenyl-3-(phenylamino)propan-1-one (4a): ¹H NMR (500 MHz, TMS, CDCl_3), 3.44 (d, J = 6.2 Hz, 1H), 3.50 (d, J = 6.2 Hz, 1H), 5.03 (m, 1H), 6.54 (d, J = 7.8 Hz, 2H), 6.62–6.68 (m, 1H), 7.05–7.09 (m, 2H), 7.23 (d, J = 6.4 Hz, 1H), 7.29–7.34 (m, 2H), 7.42–7.55 (m, 5H), 7.89 (d, J = 7.8 Hz, 2H), m.p= 170-172 °C.

3-(4-Nitrophenyl)-1-phenyl-3-(phenylamino)propan-1-one (4h): ¹H NMR (500 MHz, TMS, CDCl_3), 3.54 (d, J = 6.1 Hz, 2H), 5.17 (t, J = 6.1 Hz, 1H), 6.77 (d, J = 6.9 Hz, 2H), 6.92 (t, J = 6.8 Hz, 1H), 7.15 (t, J = 7.8 Hz, 2H), 7.47 (t, J = 7.4 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.69 (t, J = 8.5 Hz, 2H), 7.91 (d, J = 7.8 Hz, 2H), 8.20 (d, J = 8.5 Hz, 2H), m.p= 114-116 °C.

2-(phenyl(phenylamino) methyl) cyclohexanone (5c): ¹H-NMR (500 MHz, TMS, CDCl_3), 1.55-2.00 (m, 6H), 2.20-2.50 (m, 2H), 2.65-2.85 (m, 1H), 4.2 (br, 1H), 4.60 (d, J=4.8 Hz, 1H), 6.55-6.70 (m, 3H), 6.95-7.10 (m, 2H), 7.15-7.5 (m, 5H), m.p= 137-139 °C.

2[(4-Nitrophenyl)(phenylamino)methyl]cyclohexanone (5e): ¹H-NMR (500 MHz, TMS, CDCl_3), 1.60-2.25 (m, 6H), 2.20-2.50 (m, 2H), 2.75-2.90 (m, 1H), 4.5 (br, NH), 4.75 (d, J=4.8 Hz, 1H), 6.55 (2, 2H), 6.6-6.7 (m, 1H), 6.95-7.15 (m, 2H), 7.45-7.60 (m, 2H), 8.2 (d, J=7.7 Hz, 2H, m.p= 264-267 °C.

Conclusion

In this study, synthetic processes for phosphotungstic magnetic nanoparticles catalyst $\text{CuFe}_2\text{O}_4\cdot\text{SiO}_2\cdot\text{NH}_2\text{-H}_3\text{PW}_{12}\text{O}_{40}$ induces significant possibilities for the synthesis of magnetically recoverable catalysts. Separation of catalyst by external magnetic field is an environmentally eco-friendly method. We have synthesized a highly active catalyst for the first time. The results of XRD, EDAX and TEM confirms the formation of $\text{CuFe}_2\text{O}_4\cdot\text{SiO}_2\cdot\text{NH}_2\text{-H}_3\text{PW}_{12}\text{O}_{40}$ catalyst. The synthesized catalyst can be used as an efficient catalyst for the synthesis of β -amino carbonyl compounds in Mannich-type reaction under solvent free reaction. This method offers several advantages including high yield, low reaction times, low amount of catalyst, simple recyclability and avoidance of organic toxic solvents.

Acknowledgments

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