

Tungstophosphoric acid embedded magnetic chitosan as a green catalyst for the synthesis of N-cyclohexyl-3-aryl quinoxaline-2-amines

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ABSTRACT

In the present study, a novel catalyst was well designed by incorporating the tungstophosphoric acid into the magnetic chitosan, as highly stable composite, in which the iron oxides were used the strong super-magnetic core. The prepared composite was characterized by several methods, including FTIR, XRD, SEM, TEM and EDS and its catalytic activity was examined in a facile, green and highly efficient one-pot reaction for the synthesis of N-cyclohexyl-3-aryl-quinoxaline-2-amines with o-phenylenediamine, benzaldehyde and cyclohexyl isocyanide in water, under reflux conditions. This heterogeneous catalytic system was separated easily by an external magnet and was reused at least in four runs without pre-activation and appreciable loss in its activity.

Keywords: Magnetic chitosan; Heteropoly acid; Multicomponent reactions; Green synthesis.

1. Introduction

Heteropoly acids are important class of compounds built up from a specific combination of oxygen and many acidic hydrogen atoms with special kind metals such as tungsten, molybdenum or vanadium, called as addenda atoms, as well as an element which in general placed in the p-block of the periodic table, like arsenic, silicon and phosphorus which usually called as hetero atoms [1]. Polyoxometalates (POMs) are the corresponding conjugate anions of a heteropoly acid. Due to the possibilities of different combinations of addenda atoms and hetero atoms, several kinds of heteropoly acids are existed, including Keggin ($H_nXM_{12}O_{40}$), Dawson ($H_nX_2M_{18}O_{62}$) and Preyssler ($H_{14}NaP_5W_{30}O_{110}$) structures. HPAs, their corresponding POMs and their hybrid systems possess exceptional properties, such as high thermal stability, redox potential, strong Bronsted acidity, non-corrosiveness, reusability and sensitivity to electricity and light [2] and have make a wide variety of applications. More importantly, they showed highpotency a catalyst [3] and oxidant in organic

transformations as well as being involved in photocatalytic processes [4,5]. HPAs have been used as acid catalysts in several large scale industrial processes [6-9].

In spite of all aforementioned merits, the high solubility of HPAs in polar solvents and their low surface area influence their catalytic performance and make some challenges in their separation from the reaction mixture [10]. To circumvent this problem, HPAs have been frequently immobilized on various solid supports with high surface area, such as silica [3,11], carbon nanotube [12] and titania [12,13], in order to make them applicable as heterogeneous catalysts being easily separated and recycled.

In this line, in spite of several advantages and merits, the supporting of the catalysts on the magnetic supports such as magnetite nanoparticles (Fe_3O_4), has attracted much attention, since their active surface area increases and also can be easily separated from the reaction mixture using an external magnet without any inherent problems of leaching [14,15]. In spite of high improvement in supported HPAs catalysts, the design of stable magnetic solid acid catalysts in harsh catalytic conditions is a big challenge, yet [16].

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In recent years, magnetic chitosan based catalysts have received considerable attention for different kinds of reaction such as oxidation, C–C coupling, multi-component reactions and etc. [17,18]. Chitosan, as the most abundant natural biopolymer, has a special set of intrinsic properties such as availability, chemical stability, non-toxicity, low immunogenicity, biocompatibility, biodegradability and antibacterial properties [19]. The amino and hydroxyl groups in the repeating glycosidic residue of chitosan provide coordination sites for a variety of chemical modifications and synthesis of magnetic composites [20] and the iron oxides are the most commonly used magnetic core due to its strong superparamagnetic behavior, facile synthesis and low toxicity [21,22].

In spite of stimulating properties of magnetic chitosan, there is a very limited report on their application as support for HPAs [23]. Recently, Kong et al. applied the magnetic chitosan as support for tungstophosphoric acid, a recyclable catalyst [24] and Tanhaei et al. introduced a supported Preyssler HPA on magnetic chitosan, as an efficient methyl orange adsorbent [21]. Therefore, it is desirable to extend it to other HPAs as emerging catalyst in different organic transformation. Multicomponent reactions (MCRs) are by far the most fruitful class of strategies resulting in high structural diversity and molecular complexity via a one-pot single transformation. Nowadays a plethora of new three- and four-component reactions have already been reported [25-27]. Several, examples of “higher-order” MCRs where five or even more components are involved in a one-pot reaction can also be found in the literature [28].

Isocyanide-based multicomponent reactions (IMCRs) are particularly fascinating as they have been found more adaptable than other MCRs [29]. Isocyanides have been used as privileged synthons in the synthesis of various heterocyclic particularly via multicomponent reactions. The MCRs involving isocyanides usually have easy bond forming procedures, functional group tolerance, and also show high levels chemo-stereo and regioselectivity. Thus multicomponent reactions involving isocyanides are considered as powerful tools for the synthesis of wide range and diverse compounds [30].

Among the various classes of nitrogen-containing heterocyclic compounds, Quinoxalines, as nitrogen

containing exhibit a wide range of biological activity [31]. Thus they have caused enormous changes in combinatorial and parallel synthesis, and high-throughput screening, all of which have facilitated the discovery of novel lead compounds [32]. Quinoxalines are frequently considered as a basic framework for the design of several antibiotics such as actinomycin, and leromycin. They inhibit the growth of gram-positive bacteria, and are active towards a number of transplantable tumors [33].

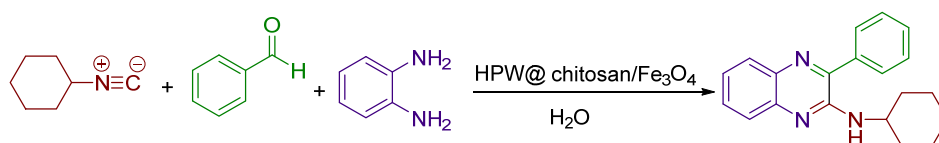
The quinoxaline ring is present in several biologically active compounds such as insecticides, fungicides, and anthelmintic [34]. They are also a component of several dyes [35] and electron luminescent compounds [36].

Very recently, we have reported the synthesis of N-cyclohexyl-3-aryl-quinoxaline-2-amines in the presence of Ferric perchlorate, as catalyst [37]. In continuation of our interest in using nanocatalyst [15] in multi-component reactions under green conditions [38,39], herein, we wish to report a facile and highly efficient strategy for the synthesis of N-cyclohexyl-3-aryl-quinoxaline-2-amines in the presence of H₃PW₁₂O₄₀ supported on chitosan/Fe₃O₄ catalyst (HPW@chitosan/Fe₃O₄), in water under reflux conditions (Scheme 1).

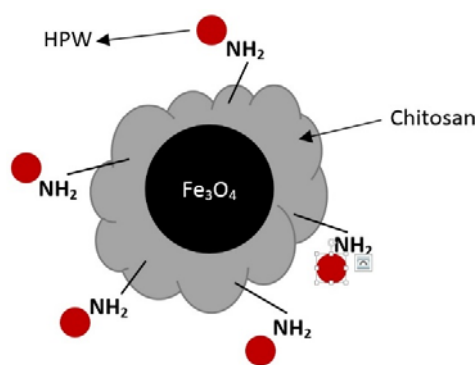
2. Experimental

2.1. Catalyst preparation

The catalyst was synthesized according to the recently reported procedure by Tanhaei et al. [21]. For this aim, 0.5 g of iron oxide nanoparticles (Sigma Aldrich) was added to the 50 mL of a solution of chitosan (Sigma Aldrich) in acetic acid (10 g mL⁻¹), sonicated and heated to 40 °C. Then, 12 mL glutaraldehyde (Sigma Aldrich, diluted to 4 wt%) was added to the suspension, dropwise, under mechanical agitation and stirred for 1 h at 40 °C and 1 h at 60 °C, respectively. Finally, 33 mL of H₃PW₁₂O₄₀ (Sigma Aldrich) solution with the concentration of 0.045 g mL⁻¹ was added to the cross-linked chitosan–Fe₃O₄, under stirring at 60 °C. The dark brown products were separated using a magnet, washed several times with deionized water and ethanol and dried in vacuum oven at 60 °C. The schematic of prepared composite is shown in Scheme 2.



Scheme 1. Synthesis of N-cyclohexyl-3-aryl-quinoxaline-2-amines in the presence of HPW@chitosan/Fe₃O₄ catalyst.



Scheme 2. The schematic structure of prepared composite.

2.2. Instruments

The catalyst was characterized by the X-ray diffractometer (XRD, D8 ADVANCE, Germany) operating at 40 kV and 40 mA using Cu K_{α} radiation and Ni filter. The scanning rate was 4 $^{\circ}$ min $^{-1}$ in the 2θ range from 15-100 $^{\circ}$. The VERTEX-70 infrared spectrometer was used for Fourier transform infrared (FT-IR) spectrum using ATR method in the range 400–4000 cm^{-1} . Also, the catalyst was analyzed using Hitachi S-4800 ultra-high resolution scanning electron microscope (SEM) to analyze the morphology and size of the products. It was equipped with EDAX analysis for the determination of elemental analysis. The EDAX model and its detector type were S4800 (I) and 7747/17-ME, respectively.

Melting points were measured by using the capillary tube method with an electrothermal 9200 apparatus. ^1H NMR spectra were obtained on a Bruker AQS AVANCE-300 MHz spectrometer using TMS as an internal standard (CDCl_3 solution). IR spectra were recorded on KBr disk on the FT-IR Bruker Tensor 27. All commercially available chemicals were used as received without further purification.

2.3 General procedure for catalyzed synthesis of *N*-cyclohexyl-3-aryl-quinoxaline-2-amines

A solution of an aromatic aldehyde (1 mmol), *o*-phenylenediamine (1 mmol), cyclohexyl isocyanide (1 mmol) and HPW@chitosan/ Fe_3O_4 (0.03 g) in H_2O (3 ml) was stirred under heating at reflux condition for indicated time. The progress of the reaction was monitored by TLC using Ethyl acetate and *n*-Hexan (2:8) as eluent. Upon the completion of reaction, the mixture was cooled to room temperature and the catalyst was easily separated by an external magnet. It was re-used in the model reaction for 4 times without appreciable catalytic activity and reused without any special treatment. The precipitated solid in reaction mixture was filtered off and washed with water and further purified by re-crystallization from CH_2Cl_2 .

3. Results and Discussion

3.1. Catalyst characterization

3.1.1. FTIR analysis

The FTIR spectroscopy was to obtain information regarding the binding of HPW molecules on the surface of chitosan/ Fe_3O_4 . The FTIR spectra of Fe_3O_4 NPs, chitosan and HPW@chitosan/ Fe_3O_4 core-shell composite are shown in Fig. 1. As it can be seen, the characteristic band in the magnetic iron oxide NPs at 568 cm^{-1} is related to the Fe-O bonds in the crystal lattice of iron oxide [40]. The chitosan spectrum, showed the characteristic peaks in the range of 400-2000 cm^{-1} . They are: 1659 cm^{-1} (assigned to the amide band I), 1591 cm^{-1} (assigned to the amide II band, N-H stretch) and 1378 cm^{-1} (assigned to the CH_3 symmetrical angular deformation) [41]. HPW is a well-known Keggin type heteropoly acid containing a cage of tungsten atoms linked by oxygen atoms with a phosphorus atom as hetero atom placed at the center of the tetrahedron [42]. Thus the oxygen atoms form four characteristic infrared peaks are as follows: 1080 cm^{-1} assigned to the stretching vibrational mode between phosphorus and oxygen atoms at the center of the structure (P-O_a), 800 and 890 cm^{-1} attributed to the bond between the tungsten atoms and Oxygen atoms at the corners (W-Ob-O) and oxygen atoms along the edges (W-Oc-W), respectively, and 980 cm^{-1} is due to the asymmetric stretching of the terminal double-bonded oxygen atoms (W=Od) [43].

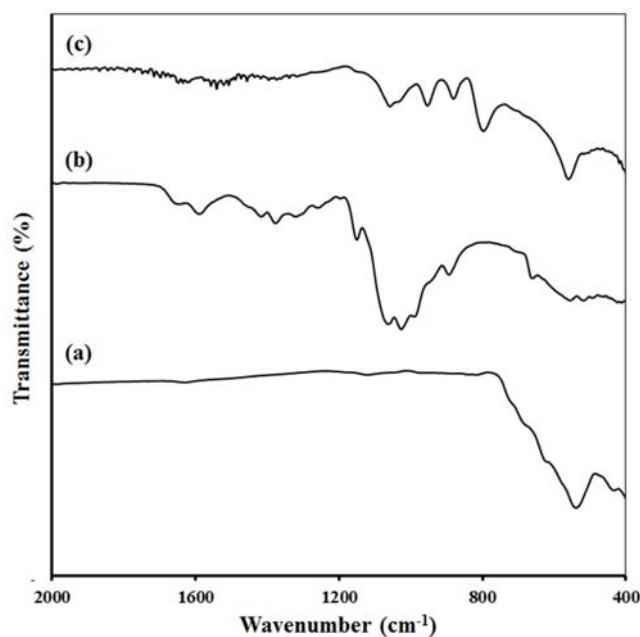


Fig. 1. The FTIR Spectra of (a) Fe_3O_4 nanoparticles, (b) chitosan and (c) HPW@chitosan/ Fe_3O_4 .

In the FT-IR spectrum of HPW@chitosan/Fe₃O₄, these peaks can be seen at 1060, 959, 878 and 795 cm⁻¹ which approve the modification of composite by the HPW molecules and the shift observed are attributed to the bending the HPW to the surface of chitosan/Fe₃O₄. The presence of a peak at 568 cm⁻¹ related to Fe-O, confirms that the cross-linked Fe₃O₄ particles on the chitosan surface with glutaraldehyde as cross-linker has been successfully occurred [44].

3.1.2. XRD analysis

In order to obtain more information about their crystallographic features of the prepared composite, the Fe₃O₄ nanoparticles and HPW@chitosan/Fe₃O₄ composite were characterized by XRD. The obtained data is shown in Fig. 2. Both XRD patterns have six peaks in 2θ of 35.1, 41.4, 50.5 and 62.9 and 67.2 which are related to their corresponding indices (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) of Fe₃O₄ lattice structure with typical face-centered cubic structure, respectively, which are indicating presence of magnetite NPs in the prepared composite [45]. However, the intensity of peaks reduced, due to the loading of chitosan on the Fe₃O₄ nanoparticles. It also clearly shows the weak, broad diffraction hump in the 2θ-range ~20° to 30°, is typically originating from an amorphous material, which in this case corresponds to the amorphous HPW chitosan phase [46].

3.1.3. SEM and TEM Analysis

The morphology of samples was studied by SEM analysis and shown in Fig. 3 in two magnifications. The SEM images clearly revealed the structure of the HPW modified magnetic catalyst. It showed that the magnetic Fe₃O₄ NPs were in a spherical shape with a diameter about 50 nm [21], but the prepared composite

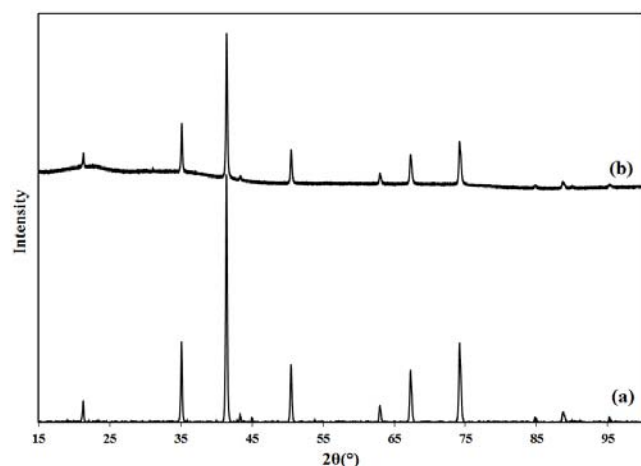


Fig. 2. The XRD patterns of (a) Fe₃O₄ nanoparticle, and (b) prepared HPW@chitosan/Fe₃O₄.

shows the irregular agglomeration of semi-hexagonal particles in the range of 20 -500 nm. For certainty, we obtained the TEM images which are shown in Fig. 4. As can be seen, in spite of the confirmation of the SEM results showing the cubic and semi-hexagonal particles in size of 100-200 nm.

3.1.4. EDAX

The EDX analysis (Fig. 5) was employed to determine the elemental composition of prepared HPW@chitosan/Fe₃O₄. It confirms the presence of C, N, Fe, and O, as well as, W in the structure of the composite and shows 9.71, 14.65, 25.23, 14.51 and 24.53 wt.% for each element, respectively. Although, these amounts are not precise percentages, due to the presence of Al and C in the tape and holder of the sample. This implied that magnetic chitosan polymer surface was excellently modified by HPW heteropoly acid molecules.

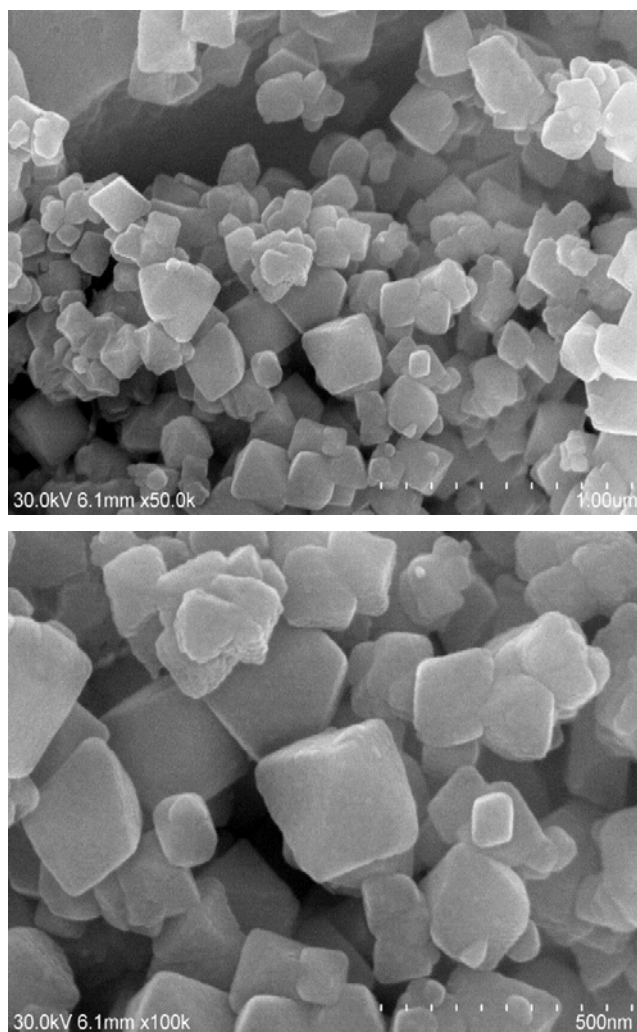


Fig. 3. The SEM images of prepared HPW@chitosan/Fe₃O₄ composite.

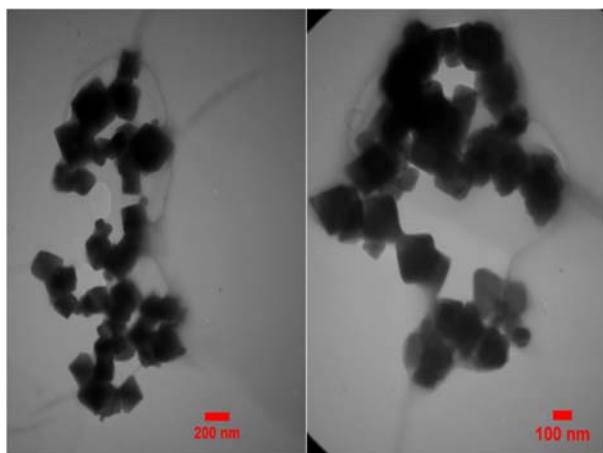


Fig. 4. TEM images of prepared HPW@chitosan/Fe₃O₄ composite.

3.2. Catalytic synthesis

Initially, in order to find the optimal conditions, the reaction of *o*-phenylenediamine (1 mmol), benzaldehyde (1 mmol), and cyclohexyl isocyanide (1 mmol) in the presence of various amount of HPW@chitosan/Fe₃O₄ in various solvents was performed as a model reaction. (Table 1). The reaction in the presence of 0.03 g of HPW@chitosan/Fe₃O₄ in water was complete within 1 h to afford N-cyclohexyl-3-aryl-quinoxaline-2-amines in good yields (Table 1).

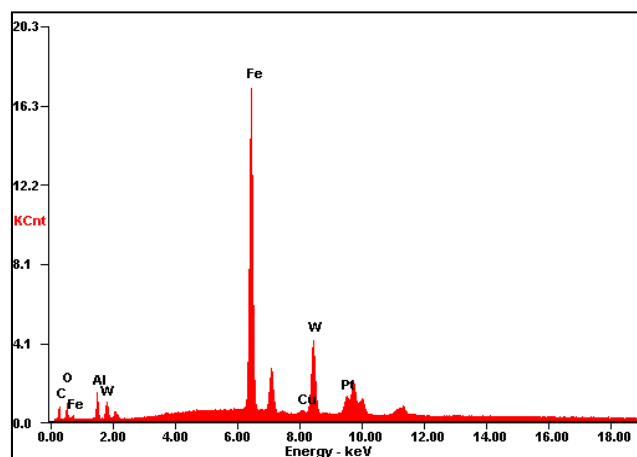


Fig. 5. EDAX pattern of prepared HPW@chitosan/Fe₃O₄ composite.

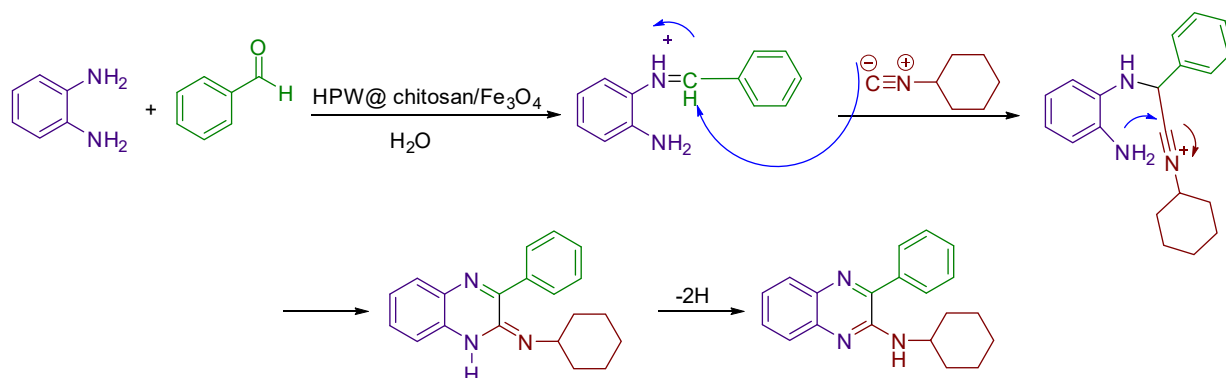
The yields of the reactions increased as the reaction temperature was raised, and refluxing conditions were found to be optimum. The observed catalytic activity was higher than some conventional catalysts in term of the yields of products and reaction times. The reaction mechanism is quite descriptive (Scheme 3).

The synthesis of a wide range of substituted N-cyclohexyl-3-aryl-quinoxaline-2-amines was achieved under optimized conditions. The results are summarized in Table 2.

Table 1. Optimization of the reaction conditions under refluxing conditions in 1 h.

Entry	Catalyst	Solvent	Yield(%) ^a
1	HPW@chitosan/Fe ₃ O ₄	CH ₃ COOH	60
2	HPW@chitosan/Fe ₃ O ₄	DCM	78
3	HPW@chitosan/Fe ₃ O ₄	CH ₃ CN	91
4	HPW@chitosan/Fe ₃ O ₄	EtOH	90
5	HPW@chitosan/Fe ₃ O ₄	H ₂ O	96

^aYields are related to the isolated pure products.



Scheme 3. Plausible mechanism for the synthesis of N-cyclohexyl-3-aryl-quinoxaline-2-amines.

Table 2. Synthesis of N-cyclohexyl-3-aryl-quinoxaline-2-amines using a variety of aromatic aldehydes

Entry	Aldehyde	Time(h)	Yield(%) ^a	m.p. (°C)	
				Found	Reported ^a
1	C ₆ H ₅ O	1	96	185-186	187
2	4-NO ₂ -C ₆ H ₄ O	1	93	208-210	209
3	4-MeO-C ₆ H ₄	0.8	94	179-180	179
4	4-OH-C ₆ H ₄ O	1.5	92	176-178	176
5	4-Cl-C ₆ H ₄ O	1	92	191-193	192
6	3-NO ₂ -C ₆ H ₄	1.1	91	195-196	195
7	4-Me-C ₆ H ₄ O	1	93	201-202	201

^aAll from Ref. [37].

3.3. Recycling of the catalyst

It is noteworthy to mention that the catalyst is recyclable and could be reused without significant loss of activity. The reusability of the catalysts was also studied. After completing of the model reaction, the catalyst was removed by an external magnet and washed with acetone. The recycled catalyst could be subjected to a second or even another reaction. The FTIR spectra of the catalyst before the reaction and after four runs are shown in Fig. 6, demonstrating that the structure of composite did not change after at least four times being reused. In the case of the model reaction, after three runs, the catalytic activity of catalysts (Yields were 96, 94 and 91%) was almost the same as those of the freshly used catalysts (Yield= 96%).

4. Conclusion

In summary, we have demonstrated an elegant protocol for the synthesis of substituted N-cyclohexyl-3-aryl-quinoxaline-2-amines using HPW@chitosan/Fe₃O₄, which proceeds efficiently in H₂O under heating conditions. Also, the use of green, non-toxic, inexpensive and reusable catalyst, HPW@chitosan/Fe₃O₄, renders this method eco-friendly, with a very simple isolation procedure that entails the filtration of the precipitated products.

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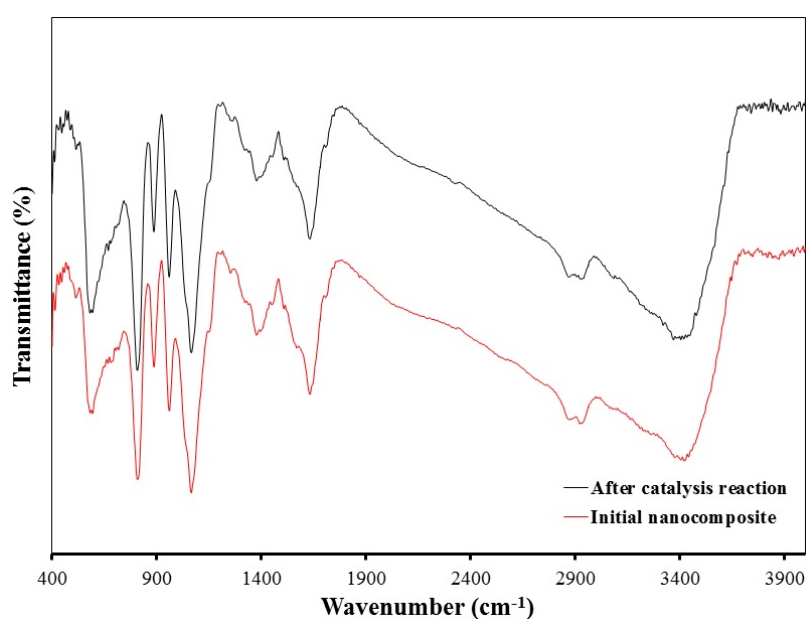


Fig. 6. FT-IR spectra of catalyst before reaction and after 4 runs.

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