Proceedings of the World Congress on New Technologies (NewTech 2015)
Barcelona, Spain – July 15 - 17, 2015
Paper No. 334

Preyssler Heteropolyacid Supported on Silica Coated Ni0.5Zn0.5Fe2O4 Nanoparticles; Synthesis and Characterization

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Abstract **-**A novel magnetic acidic catalyst comprising Preyssler ($H_{14}[NaP_5W_{30}O_{110}]$) heteropoly acid supported on silica coated nickel zinc ferrite nanoparticles ($Ni_{0.5}Zn_{0.5}Fe_2O_4@SiO_2$) was prepared. The catalyst was characterized by FT-IR, TEM and particle size measurement. Its catalytic activity was investigated for the synthesis of polyhydro quinoline derivatives by the Hantzsch reaction. With the catalyst, the reactions occurred in less than 1 h with good to excellent yields. More importantly, the catalyst was easily separated from the reaction mixture by an external magnet and reused at least four times without degradation in the activity.

Keywords**:** Preyssler, Nickel zinc ferrite nanoparticles, Magnetically green catalyst, Polyhydroquinolines

1. Introduction

In recent decades, magnetic nanoparticles (MNPs) have been widely studied for various biological and medical applications. They have been shown to be promising supports for the immobilization of catalysts because magnetic catalysts can be easily separated from the reaction medium by an external magnet, which provides a simple separation of the catalyst without the need for filtration, centrifugation, or other tedious workup processes (Polshettiwar et al., 2011). This separation technique has a special importance for nano-sized catalyst supports where filtration methods result in the loss of catalyst particles and product contamination. Apart from an easy separation, an interesting property of MNPs is that an appropriate surface modification provides a wide range of magnetic-functionalized catalysts that show equal and sometimes higher activity than their homogeneous catalysts in organic transformations.

In recent years, MNPs as catalyst or catalyst support have been widely used in a variety of important organic reactions such as C-C coupling (Li et al., 2012), reduction (Rossi et al., 2007), oxidation (Oliveira et al., 2010) and multicomponent reactions (Karimi et al., 2013) with high activity.

Recently, the synthesis of silica coated Fe_3O_4 MNPs for immobilizing heteropolyacids (HPAs) were reported (Wang et al., 2013). Their synthesized catalyst was a magnetically separable catalyst and after completion of the reaction, it was easily separated by an external magnet. Also, another silica coated MNPs with the formula $Fe_2O_3@SiO_2$ for supporting tungstophosphoric acid and phosphomolybdic acid were reported (Rafiee et al., 2013).They showed good catalytic activity by these catalysts.

In addition to Fe_3O_4 and Fe_2O_3, there are other iron oxides with the ferrite structure and general formula (AFe_2O_4), where A can be Mn, Co, Ni, Cu, and Zn (Hou et al., 2010). Ni-Zn ferrites are one of the most versatile magnetic materials with a high saturation magnetization, chemical stability, and relatively high permeability, and because of these magnetic properties it can be used as a magnetic source (Gabal et al., 2012).

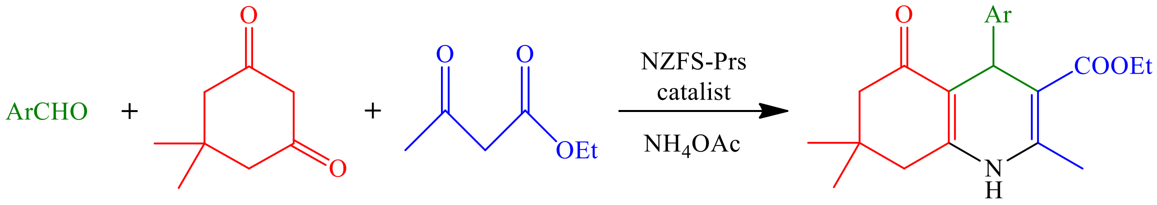
The Preyssler ($H_{14}NaP_5W_{30}O_{120}$) is a HPA which has significant advantages, such as 14 acidic protons, safety, high thermal and hydrolytic stability. Owing to the low surface area (7–10 m2/g) and high solubility of HPAs in polar solvents, it is preferable to use them in supported form. Preyssler can be supported on neutral solids, such as silica, activated carbons, or zeolites and acidic ion exchange resins (Hafizi et al., 2014). Recently, we supported Preyssler HPA on silica and used this supported catalyst for various reactions (Javid et al., 2012a).

Several advantages of using supported HPAs compared to the homogeneous catalyst include easier recovery and recycling after reaction and easier product separation. However, the separation and recovery of the immobilized Preyssler on silica is usually performed by filtration or centrifugation, which are not eco-friendly processes.

The immobilization of this HPA on silica-coated MNPs with a new structure ($NiFe_2O_4$) can be employed to develop a novel heterogeneous catalyst system which is magnetic that possesses both a high separation efficiency and a relatively high surface area to maximize catalyst loading and activity.

In a continuation of our achievements in the preparation of novel catalysts (Javid et al., 2012b) and based on our previous success in the preparation of MNPs as catalysts (Eshghi et al., 2015), in this study, we supported Preyssler HPA on $Ni_{0.5}Zn_{0.5}Fe_2O_4@SiO_2$ (denoted NZFS-PRS). After the characterization of this novel magnetically recoverable catalyst, its catalytic activity was tested in the synthesis of polyhydroquinoline derivatives by the Hantzsch reaction.

The synthesis of these products occurred from the condensation of aldehydes, ethyl acetoacetate, dimedone, ammonium acetate and catalyst in ethanol. This is a simple, green, and efficient synthesis method with these reactions using NZFS-PRS as a heterogeneous and highly active acidic catalyst (Fig. 1).



1(a-f) **2** **3** **4(a-f)**

Fig. 1. Synthesis of polyhydroquinolines using NZFS-Prs as a nano magnetic catalyst

2. Experimental

Preparation of NZFS-Prs: The core-shell silica nickel zinc ferrite (NZFS) was synthesized same as similar reports [Girgis et al., 2011]. Afterwards, for the immobilization of Preyssler HPA on the NZFS, 0.75 g of Preyssler was dissolved in 5 mL of water. This solution was added drop wise to a suspension of 1.0 g of NZFS in water (50 mL). The mixture was stirred for 12 h at room temperature under vacuum. After stirring for the specified time, the solvent was evaporated off and the supported catalyst collected by a permanent magnet and dried in a vacuum overnight. After the drying, the supported nano catalyst was calcined at 250 °C for 2 h.

Synthesis of polyhydroquinoline derivatives: The NZFS-Prs catalyst (0.02 g) was added to a solution of aldehyde (1.0 mmol), ethyl acetoacetate (1.0 mmol), dimedone (1.0 mmol), ammonium acetate (1.0 mmol), in ethanol (15 mL) and refluxed for 60 min. Upon completion, the reaction mixture was allowed to cool to room temperature and the NZFS-Prs was separated from the reaction mixture by an external magnet and thoroughly washed and dried to be reused in the next run. Cold water (20 mL) was added to the reaction mixture (without a catalyst) and after stirring for a few minutes, the solid product formed was filtered off and washed several times with cold ethanol and water. The resulting crude product was recrystallized from ethanol and gave compounds **5a**–**5f** in high yields.

3. Result and Discussion

Characterization of NZFS-Prs: The Preyssler HPA was supported on the silica coated MNPs to give the corresponding Preyssler HPA supported on the magnetic nanoparticles (NZFS-Prs). The catalyst was characterized by FT-IR, TEM, and particle size measurement. The FT-IR spectra of NFS, Preyssler and NFS-PRS are shown in Fig. 2. NZFS exhibited highly intense absorption peaks at 1200 and 1100 cm^{-1}. These peaks are assigned to the longitudinal and transverse stretching vibration modes of the Si–O–Si asymmetric bond. Additional bands at 812 and 470 cm^{-1} were identified as the characteristic peaks of the Si–O–Si bond. The other peak observed at 950 cm^{-1} assigned to the SiO_3^{2-} vibrations indicated the existence of nonbridging oxygen ions. Preyssler HPA displayed vibrations at 1162, 1090, and 1025 cm^{-1} for the P–O stretching in the Preyssler structure, 980 and 906 cm^{-1} for W–O–W stretching, 802 cm^{-1} for W=O stretching, and 522 cm^{-1} for P–O bending (Hafizi et al., 2014). There was also a highly intense absorption peak at 1630 cm^{-1}, which was attributed to adsorbed water (Wang et al., 2013). In the NZFS-Prs, the peaks in the regions of 3563, 1090, 960, 913, 794, and 566 cm^{-1} confirmed the successful immobilizing of the Preyssler HPA on the surface of the silica coated nickel zinc ferrite NPs.

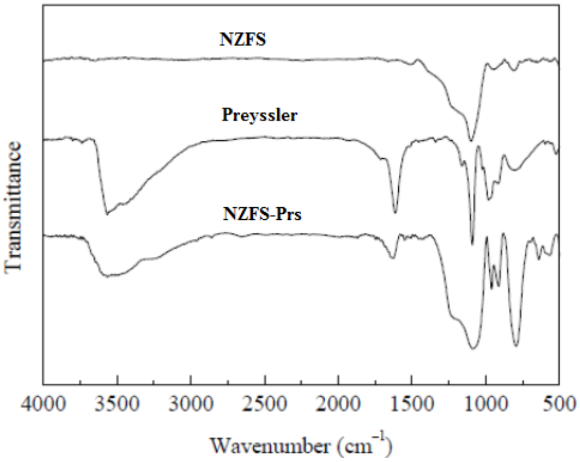


Fig. 2. FT-IR spectra of NZFS, Preyssler HPA, and NZFS-Prs.

Fig. 3 shows TEM images of the synthesized NZFS and NZFS-Prs. In the NZFS-PRS, the darker parts proved good immobilizing of Preyssler HPA on the NZFS. Also, the particle size distribution of the NZFS showed that these MNPs have a size between 25 to 97 nm.

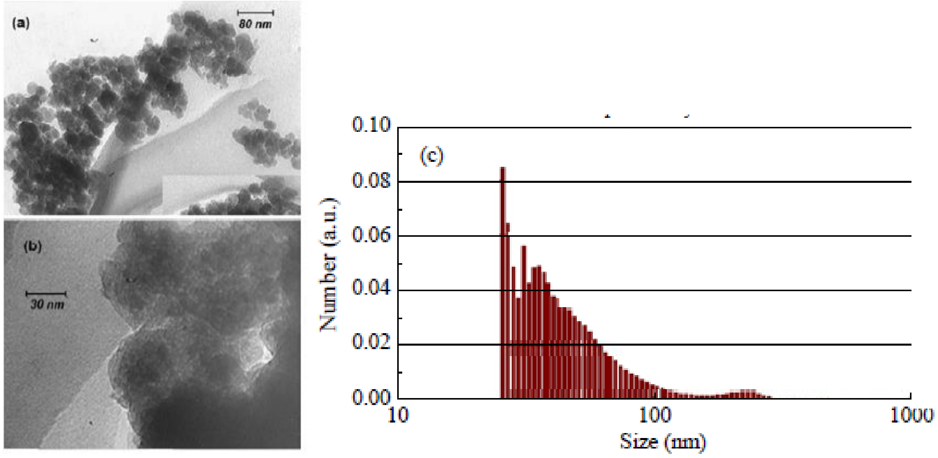


Fig. 3. TEM images of NZFS (a) and NZFS-Prs (b) and particle size distribution of NZFS (c).

Table 1. Effect of catalysts, solvents and temperature in the preparation of polyhydroquinoline of benzaldehyde

Entry	Catalyst	Reaction conditions	Time (min)	Yield[1] (%)
1	$H_4SiW_{12}O_{40}$	EtOH/Reflux	120	31
2	$H_3PW_{12}O_{40}$	EtOH/Reflux	120	40
3	$H_{14}NaP_5W_{30}O_{120}$	EtOH/Reflux	90	66
4	NZFS-Prs	CH_3CN/Reflux	120	trace
5	NZFS-Prs	H_2O/Reflux	120	52
6	NZFS-Prs	EtOH/r.t.	120	no reaction
7	NZFS-Prs	EtOH/Reflux	60	91

1. Reaction of benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol), Dimedone (1 mmol), ammonium acetate (1 mmol) and catalyst (0.03 mmol)

The reusability of the catalysts is an important benefit and makes them useful for commercial applications. Thus, the recovery and reusability of NZFS-Prs were investigated. The separated catalyst was reused after washing with ethanol and drying at 150°C. The catalyst was recovered in excellent yields and catalyst was used in the mentioned reaction for four times, it showed the same activity such as fresh catalyst without any considerable loss of its activity (Table 2).

Table 2. Recovery of NZFS-Prs catalyst in the preparation of polyhydroquinoline of benzaldehyde

Number of recycles	Yield[1] (%)
fresh	91
2	90
3	90
4	88

1. Reaction of benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol), Dimedone (1 mmol), ammonium acetate (1 mmol) and NZFS-Prs (0.03 mmol) in ethanol reflux condition after 1 h.

Finally, we prepared a range of polyhydroquinoline derivatives. In all cases, aromatic aldehydes containing electron-donating and electron-withdrawing groups reacted successfully and gave the expected products in good to excellent yields and short reaction times (Table 3).

Table 3. One-pot Hantzsch synthesis of polyhydroquinolines in the presence of NZFS-Prs catalyst

Entry	Ar	Product	Yield[1] (%)	m.p. (°C)
1	C_6H_5	4a	91	201-204
2	4-MeOC_6H_4	4b		256-258
3	4-OHC_6H_4	4c		227-230
4	4-MeC_6H_4	4d		259-262
5	4-ClC_6H_4	4e		245-247
6	4-$NO_2C_6H_4$	4f		203-206

1. Reaction of aldehyde (1 mmol), ethyl acetoacetate (1 mmol), Dimedone (1 mmol), ammonium acetate (1 mmol) and NZFS-Prs (0.03 mmol) in ethanol reflux condition after 1 h.

4. Conclusion

In conclusion, we have reported an efficient, versatile and convenient method for one-pot multicomponent Hantzsch synthesis of polyhydroquinoline derivatives using NZFS-Prs as a novel magnetic catalyst, reusable, non-toxic, non-corrosive and heterogeneous catalyst. The Preyssler HPA provided adequate acidic sites to give the excellent catalytic activity of NZFS-PRS. The method offers advantages such as clean reaction, high yields of products, short reaction times and use of various substrates, which makes it a useful and attractive strategy for the synthesis of polyhydroquinoline derivatives.

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