Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Phospha-Michael addition of diethyl phosphite to α , β -unsaturated malonates catalyzed by nano γ -Fe₂O₃-pyridine based catalyst as a new magnetically recyclable heterogeneous organic base



Sara Sobhani*, Mahboobeh Bazrafshan, Amin Arabshahi Delluei, Zahra Pakdin Parizi

Department of Chemistry, College of Sciences, University of Birjand, Birjand 414, Iran

ARTICLE INFO

Article history: Received 21 October 2012 Received in revised form 30 December 2012 Accepted 10 January 2013 Available online xxx

Keywords: β-Phosphonomalonates Nanoparticles Heterogeneous catalyst Pyridine Iron oxide

1. Introduction

In recent years, extensive efforts have been made to introduce convenient and efficient methods for the synthesis of phosphonates. Direct P-C bond formation is the most versatile and powerful tools for the synthesis of phosphonates. Within the methods for P–C bond formation, phospha-Michael addition has evoked remarkable attention by organic chemists [1-17]. Synthesis of β-phosphonomalonates by this method are most commonly promoted by BrØnsted/Lewis acids [1-3], bases [4-10], transition metals [11,12], radical initiators [13,14], microwaves [15] or ionic liquid [17]. Even though, phospha-Michael addition could proceed by these methods, many of these reagents cannot be reused, and in many instances, long reaction time, drastic reaction conditions and sometimes, according to the nature of the catalyst, tedious work-up is needed. Therefore, the development of a new method to overcome these short comings still remains an ongoing challenge for the synthesis of these significant scaffolds.

In the past decades, much attention has been paid to research dedicated to the development of environmentally compatible processes. Along with this awareness; industries have started implementing safer practices such as waste prevention using new catalysts. In this view, the design of environmentally benign, an

ABSTRACT

Nano γ -Fe₂O₃-pyridine based catalyst as a new magnetically recyclable heterogeneous organic base was synthesized. The synthesized odorless pyridine based catalyst was used as a new catalyst for the efficient synthesis of β -phosphonomalonates by the reaction of diethyl phosphite with α , β -unsaturated malonates. The catalyst was easily isolated from the reaction mixture by a magnetic bar and reused at least 10 times without significant degradation in the activity.

© 2013 Elsevier B.V. All rights reserved.

economical and practical efficient process for catalyst separation and reuse have been attracted much attention as a central focus area in the green chemistry research in 21st century. Heterogenization of homogeneous catalysts by their immobilization on various insoluble supports simplifies the catalyst removal and minimizes the amount of waste formed. However, although heterogeneous catalysts can be recovered by filtration or centrifugation methods, these methods are time consuming and may cause loss of the catalyst. Moreover, a substantial decrease in the activity and selectivity of the immobilized catalyst is frequently observed due to the heterogeneous nature of support materials in reaction media, steric and diffusion factors [18,19]. Therefore, to maintain economic viability, a suitable heterogeneous system must not only minimize the production of waste, but should also exhibit activity and selectivity comparable or superior to existing homogeneous routes. In an attempt to resolve such problems, nanoparticles (NPs) have been used as alternative matrix for supporting homogeneous catalysts. When the size of the support materials is decreased to the nanometer scale, the surface area of the NPs might be increased. As a consequence, NPs could have a higher catalyst loading capacity and a higher dispersion than many conventional support matrices, leading to an improved catalytic activity of the supported catalysts. However, conventional separation methods may become inefficient for support particle sizes below 100 nm. The use of magnetic NPs (MNPs) such as iron oxide as supporting materials offers a solution to this problem [20-22]. MNPs are easily separated by an external magnet. The magnetic separation of MNPs is simple,



^{*} Corresponding author. Tel.: +98 561 2502065; fax: +98 561 2502065. E-mail addresses: sobhanisara@yahoo.com, ssobhani@birjand.ac.ir (S. Sobhani).

⁰⁹²⁶⁻⁸⁶⁰X/\$ - see front matter © 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.apcata.2013.01.009



Scheme 1. γ -Fe₂O₃-pyridine based catalyst 1.

economical and promising for industrial applications. It is also typically more effective than filtration or centrifugation as it prevents loss of the catalyst.

Pyridine is a well-known liquid organic base, which is used as an active catalyst in organic syntheses. However, its separation from homogeneous reaction mixtures requires neutralization by acidic conditions which lead to worthless pyridinium salts. The best way to avoid the harmful effect of acidic work-up is supporting pyridine on a solid surface [23]. Supporting provides the reusability of pyridine and eliminates the unpleasant fish-like odor of pyridine.

Due to the importance of the synthesis of supported pyridine on the solid surface and characteristic properties of nano magnetic iron oxides as supporting material, in this paper, we have synthesized nano γ -Fe₂O₃-pyridine based catalyst **1** (Scheme 1) as a new odorless pyridine based catalyst. We have also used it as a magnetically recyclable heterogeneous basic catalyst for the synthesis of β -phosphonomalonates *via* Michael addition of dialkyl phosphites to α , β -unsaturated malonates.

2. Experimental

2.1. Large scale synthesis of nano γ -Fe₂O₃-pyridine based catalyst **1**

The γ -Fe₂O₃ nanoparticles were synthesized by a reported chemical co-precipitation technique of ferric and ferrous ions in alkali solution with minor modifications [24–26]. FeCl₂·4H₂O (3.68 g) and FeCl₃·6H₂O (10 g) were dissolved in deionized water (300 mL) under Ar atmosphere at room temperature. A NH₄OH solution (25%, 100 mL) was then added drop wise (drop rate = 1 mL min⁻¹) to the stirring mixture at room temperature to reach the reaction pH to 11. The resulting black dispersion was continuously stirred for 1 h at room temperature and then heated to reflux for 1 h to yield a brown dispersion. The magnetic nanoparticles were then purified by a repeated centrifugation (1730–3461 g, 20 min), decantation, and redispersion cycle 3 times. The as-synthesized sample was heated in air at 2 °C min⁻¹ up to 200 °C and then kept in the furnace for 3 h to give a reddish-brown powder.

Concentrated solution of ammonia was then added to the dispersed γ -Fe₂O₃ nanoparticles (8.5%, w/w, 20 mL) in methanol (80 mL) and the resulting mixture was stirred at 40 °C for 30 min. Subsequently, tetraethyl orthosilicate (TEOS, 1.0 mL) was charged to the reaction vessel, and the mixture was continuously stirred at 40 °C for 24 h. The silica-coated nanoparticles (γ -Fe₂O₃@SiO₂) were collected by a permanent magnet, followed by washing 3 times with EtOH and diethyl ether and dried at 100 °C in vacuum for 24 h.

A mixture of γ -Fe₂O₃@SiO₂ (2 g) in toluene (40 mL) was sonicated for 30 min. 3-Mercaptopropyl trimethoxysilane (0.5 mL) was added to the dispersed γ -Fe₂O₃@SiO₂ in toluene and slowly heated to 105 °C and stirred at this temperature for 20 h. The resulting mercapto-functionalized γ -Fe₂O₃@SiO₂ was separated by an external magnet and washed 3 times with methanol, ethanol and CH₂Cl₂ and dried under vacuum. 3-(Chloromethyl)pyridine hydrochloride (0.15 g) and triethylamine (0.13 mL) were added to mercapto-functionalized γ -Fe₂O₃@SiO₂ (1.7 g) in dry toluene (15 mL), and the

mixture was refluxed for 18 h. The solid material was then filtered, washed with water, methanol, CH_2Cl_2 and dried at room temperature in vacuum to afford nano γ -Fe₂O₃-pyridine based catalyst **1**.

2.2. Back titration analysis of catalyst 1

HCl solution (10 mL, 0.1 M) was added to the catalyst (100 mg) in an Erlenmeyer flask. Excess amount of the acid was neutralized by addition of NaOH solution (0.1 M) to the equivalence point of titration. The required volume of NaOH to this point was 9.76 mL. The amount of pyridine functionalized on γ -Fe₂O₃@SiO₂ is evaluated to be 0.24 mmol g⁻¹.

2.3. General procedure for Michael addition of diethyl phosphite to α , β -unsaturated malonates catalyzed by nano γ -Fe₂O₃-pyridine based catalyst **1**

Catalyst **1** (5 mol%) was added to a mixture of α , β -unsaturated malonate (5 mmol) and diethyl phosphite (10 mmol). The mixture was stirred at 70 °C for the appropriate time (Table 2). The catalyst was separated by a magnetic bar from the cooled mixture, washed with EtOH, dried 30 min at 110 °C and reused for a consecutive run under the same reaction conditions. Evaporation of the solvent of the remaining solution under reduced pressure gave the crude products. The pure products (**2–18**, Table 2) were isolated by chromatography on silica gel eluted with *n*-hexane:EtOAc (1:2).

2.4. Typical procedure for the use of nano γ -Fe₂O₃-pyridine based catalyst **1** in multiple sequential synthesis of β -phosphonomalonate **2**

Catalyst **1** (5 mol%) was added to a mixture of benzylidenmalononitrile (5 mmol) and diethyl phosphite (10 mmol). The mixture was stirred at 70 °C for 1 h. New samples of benzylidenemalononitrile (5 mmol) and diethyl phosphite (10 mmol) were added to the reaction mixture (ten times) and each time the reaction mixture was stirred at 70 °C for 1 h. After separation of the catalyst from the cooled mixture by a magnetic bar, the solvent was evaporated to give a crude product. The pure product **2** was isolated in 83% yield by chromatography on silica gel eluted with *n*-hexane:EtOAc (1:2).

3. Results and discussion

3.1. Synthesis of nano γ -Fe₂O₃-pyridine based catalyst **1**

At first, γ -Fe₂O₃ NPs were synthesized by a chemical coprecipitation technique of ferric and ferrous ions in alkali solution [24–26]. Fig. 1 shows the XRD pattern of γ -Fe₂O₃ NPs. Diffraction peaks at around 2θ = 30.4°, 35.8°, 43.6°, 53.7°, 57.6°, 63.2° corresponding to the (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0) are readily recognized from the XRD pattern. The observed diffraction peaks agree with the cubic structure of maghemite (JCPDS file No 04-0755) with a unit cell dimension of 0.835 nm and the space group of P4132 (213). The average crystallite size was calculated to be 13.1 nm using the Scherrer equation in which *K* = 0.9 and λ = 0.154 nm.

Ultimately, sonication of γ -Fe₂O₃ NPs suspension in an alkaline solution of tetraethyl orthosilicate (TEOS) caused coating of the magnetic cores with silica shells. The outer shell of silica not only improves the dispersibility but also provides suitable sites (Si-OH groups) for further surface functionalization. The resulting silica-coated γ -Fe₂O₃ NPs (γ -Fe₂O₃@SiO₂) were then allowed to react with an appropriate concentration of 3-mercaptopropyl trimethoxysilane to give mercapto-functionalized silica-coated



Fig. 1. XRD pattern of γ -Fe₂O₃ NPs.

 γ -Fe₂O₃. To this end, the obtained mercapto-functionalized γ -Fe₂O₃@SiO₂ was subjected to react with 3-(chloromethyl)pyridine hydrochloride to obtain nano γ -Fe₂O₃-pyridine based catalyst **1**.

3.2. SEM and HRTEM

The size and structure of nano γ -Fe₂O₃-pyridine based catalyst 1 were evaluated using scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HRTEM). The SEM image of the supported catalyst showed uniformity and spherical morphology of nanoparticles (Fig. 2). The aggregation gives rise to increase the size of observed nanoparticles with an average diameter of *ca*. 63 nm. Fig. 3 shows HRTEM of nano γ -Fe₂O₃-pyridine based catalyst 1 which further confirmed an assembly of the catalyst and its size is less than 13 nm. HRTEM image of the catalyst demonstrates the core-shell structure of the particles and confirms the presence of the silica coating (Fig. 3b). This observation is in agreement with reducing surface area calculated by BET method for catalyst **1** (56 m² g⁻¹) compared with γ -Fe₂O₃ (91 m².g⁻¹). It is worth to note that reducing surface area is also a consequence of incorporation of organic spacer containing pyridine groups onto the surface of nanoparticles.

3.3. FT-IR spectra

In the FT-IR spectra of catalyst **1** (Fig. 4), characteristic absorption bands due to the ring stretching vibrations of C=C and C=N are observed at $1325-1436 \text{ cm}^{-1}$. An absorption band at 2624 cm^{-1} is observed in the FT-IR spectra of mercapto-functionalized



Fig. 2. SEM image of catalyst 1.

 γ -Fe2O3@SiO2. This band which is related to the stretching vibration of S–H bonds is disappeared in the spectra of catalyst **1**. The peaks placed at 626 and 1062 cm⁻¹ are related to the stretching vibrations of Fe–O and Si–O bonds, respectively. These two peaks are also observed in the FT-IR spectra of γ -Fe₂O₃@SiO₂ and mercapto-functionalized γ -Fe2O3@SiO2. The strong and broad band in the range of 3147–3504 cm⁻¹ corresponds to the hydrogen bonded Si–OH groups and adsorbed water. Another broad band at 1612 cm⁻¹ is also due to the OH vibration of adsorbed water.

3.4. Thermo-gravimetric analysis (TGA)

The thermal behavior of nano γ -Fe₂O₃-pyridine based catalyst **1** is shown in Fig. 5. A significant decrease in the weight percentage of catalyst **1** at about 150 °C is related to desorption of water molecules from the catalyst surface. This was evaluated to be ~0.07% according to the TG analysis. Another decreasing peak started at 279 °C and exhibits high thermostability of the catalyst. The organic parts decomposed completely at around 800 °C. According to the TGA, the amount of pyridine functionalized on γ -Fe₂O₃@SiO₂ calculated to be 0.25 mmol g⁻¹. These results are in agreement with back titration and elemental analysis (N=0.35 and C=2.5%). The average number of pyridine attached to one NP evaluated to be 2.27 × 10⁻¹⁸ mmol per one NP [27]. It was calculated using surface area (obtained from BET method), the amount of pyridine



Fig. 3. HRTEM images of catalyst 1.

Entry	Catalyst	Molar ratio (%)	Reaction temperature (°C)	Reaction time (h)	Yield of product 2 ^a (%)
1	Catalyst 1	5	70	1	85
2	Catalyst 1	3	70	1.5	70
3	Catalyst 1	1	70	3	70
4	Catalyst 1	5	r.t.	6	40
5	-	-	70	24	60
6	γ -Fe ₂ O ₃ @SiO ₂	5	70	24	65

Michael addition of diethyl phosphite to benzylidenmalononitrile under different conditions.

^a Isolated yield. Conditions: benzylidenmalononitrile (1 mmol), diethyl phosphite (2 mmol).

functionalized on catalyst **1** (obtained from TGA) and average dimeter of nanoparticles (obtained from HRTEM image).

3.5. Catalytic activity of nano γ -Fe₂O₃-pyridine based catalyst **1** for the synthesis of β -phosphonomalonates

As part of our efforts directed toward the development of new methods for the synthesis of phosphonate derivatives, we have recently introduced micellar solution of sodium stearate



Fig. 4. FT-IR spectra of γ -Fe₂O₃@SiO₂, mercapto-functionalized γ -Fe₂O₃@SiO₂ and catalyst **1**.



[28], heterogeneous catalysts {H₃PMo₁₂O₄₀ [29], HClO₄/SiO₂ [30], nano *n*-propylsulfonated γ -Fe₂O₃ (NPS- γ -Fe₂O₃) [31]} and 5hydroxypentylammonium acetate (5-HPAA) [32] as an ionic liquid for the synthesis of β -phosphonomalonates. In these reactions, due to the use of acidic or neutral conditions, malodorous trialkyl phosphite was used as the phosphorus compound. In one report, we have synthesized β -phosphonomalonates using aminopropylated silica (AP-SiO₂) [33] as a basic catalyst in the presence of dialkyl phosphite as an odorless phosphorus nucleophile. In this connection, in order to show the merit of synthesized nano γ -Fe₂O₃-pyridine based catalyst **1** as magnetically recyclable heterogeneous catalyst in organic synthesis, we have studied Michael addition of dialkyl phosphites to α , β -unsaturated malonates in the presence of this newly synthesized organic base.

At first, reaction of diethyl phosphite to benzylidenmalononitrile was chosen to optimize the reaction conditions such as temperature and molar ratio of the catalyst (Scheme 2, Table 1). We found that in the presence of 5 mol% of nano γ -Fe₂O₃pyridine based catalyst **1**, the best yield of the corresponding β -phosphonomalonate was obtained at 70 °C (Entry 1). In order to show the role of the catalyst, similar reactions in the absence of the catalyst and in the presence of nanomagnetic γ -Fe₂O₃@SiO₂ were also examined. Under these conditions, the reactions led to the formation of the desired product in low yields after a long reaction time (Entries 5 and 6). A reaction of banzaldehyde, malononitrile and diethyl phosphite in the presence of catalyst **1** (5 mol%) at 70 °C produced the desired product in 20% yield after 1 h.

The reaction of diethyl phosphite with different α , β unsaturated malonates in the presence of nano γ -Fe₂O₃-pyridine based catalyst **1** under the best reaction conditions was then investigated. The results of this study are depicted in Table 2.

As indicated in Table 2, phospha-Michael addition of diethyl phosphite with benzylidenemalononitriles substituted with different electron-donating and electron-withdrawing groups proceeded well and the corresponding β -phosphonomalonates in 71-96% yields were obtained (Entries 1-11). The catalyst was compatible with functional groups such as Cl, Br and O-Me. No competitive nucleophilic methyl ether cleavage was observed for the substrates which possessed an aryl-O-Me group (Entries 2 and 3), despite the strong nucleophilicity of phosphites. The reaction of diethyl phosphite with α , β -unsaturated malonates substituted with heteroaromatic groups worked well to produce the desired products in good to high yields (Entries 12 and 13). The method is also applicable for the synthesis of β -phosphonomalonates from the reaction of diethyl phosphite with β , β -disubstituted malonates (Entries 14 and 15). The applicability of this method was also studied for the phospha-Michael addition to some other



Fig. 5. TGA diagram of catalyst 1.

Scheme 2. Michael addition of diethyl phosphite to benzylidenmalononitrile.

Table 1

S. Sobhani et al. / Applied Catalysis A: General 454 (2013) 145-151

Table 2

Synthesis of different β -phosphonomalonates catalyzed by nano γ -Fe₂O₃-pyridine based catalyst **1**.

Entry [Ref]	Substrate	Product	Reactiontime (h)	Yield of the product ^a (%)
1 [9]	CN	2	1	85
2	MeO CN	3	2	82
3 [9]	MeO	4	4	78
4	HO	5	3	71
5 [9]	Me	6	2.5	92
6 [9]	O ₂ N CN	7	2.5	95
7 [34]	CI CN CN	8	1.5	95
8 [9]	CI CN CN	9	1.5	96
9 [9]	CI CN	10	0.75	94
10	Br CN CN	11	1.5	93
11	Br	12	1.5	91
12	CN CN	13	1.5	98
13 [10,34]	CN O CN	14	3	78
14		15	1	73
15		16	4	72
16 [9]	CO ₂ Et	17	3	75 ^b

Table 2 (Continued)

Entry [Ref]	Substrate	Product	Reactiontime (h)	Yield of the product ^a (%)
17 [35]	CO ₂ Et CO ₂ Et	18	3	65

^a Yields refer to isolated pure products which were identified by their physical and spectral data compared with the authentic samples. Conditions: α , β -unsaturated malonates (1 mmol), diethyl phosphite (2 mmol), catalyst **1** (5 mol%), 70 °C. ^b d.r. = 50:50, according to NMR.

Table 3

Phospha-Michael addition of various phosphite esters to benzylidenemalononitrile catalyzed by **1**.

Entry	Phosphite	Reaction time (h)	Yield of the product ^a (%)
1	HP(O-iso-Pr) ₂	0.5	98
2	P(OMe) ₃	0.5	94
3	P(OEt) ₃	1	95
4	P(O-iso-Pr) ₃	3	73

 a Isolated yield. Conditions: benzylidenmalononitrile (1 mmol), phosphite (2 mmol), catalyst 1 (5 mol %), 70 $^\circ$ C.

activated alkenes such as ethyl cyanocinnamate, benzylidenemalonate, nitrostyrene and acrylonitrile. Within the examined activated alkenes, the reaction of ethyl cyanocinnamate and benzylidenemalonate with diethyl phosphite worked well and the desired products were isolated in 75 and 65% yields, respectively (Entries 16 and 17). Any product was not formed with the other activated alkenes even after 24 h.

We have also evaluated the generality of the method for the phospha-Michael addition of different phosphite esters to benzylidenemalononitrile under the present reaction conditions (Table 3).

As it is obvious from Table 3, the catalytic phospha-Michael addition of di-*iso*-propyl/trimethyl/triethyl/tri-*iso*-propyl phosphite with benzylidenmalononitrile worked well and the desired products isolated in 73–98% yields.

It is important to note that the magnetic property of nano γ -Fe₂O₃-pyridine based catalyst **1** facilitates efficient recovery of the catalyst from the reaction mixture during work-up procedure. The catalyst was separated by a magnetic bar from the reaction mixture (Fig. 6b), washed with EtOH, dried 30 min at 110 °C and reused without any significant deactivation for the synthesis of β -phosphonomalonate **2** even after ten runs (Fig. 7). The comparison of HRTEM images of used catalyst **1** (Fig. 8) with fresh catalyst showed the fact that the structure

and morphology of the catalyst remained intact after ten times recovering. This reusability demonstrates the high stability and turnover of the catalyst under the employed conditions. Furthermore, the recovered heterogeneous catalyst was found to contain 0.25 mmol g^{-1} of pyridine (according to the elemental analysis), which indicates that any amount of pyridine did not leach during ten reaction cycles.

We have also found that nano γ -Fe₂O₃-pyridine based catalyst **1** was reusable at least 10 times in multiple sequential reactions by the addition of new samples of benzylidenemalononitrile and diethyl phosphite to the reaction mixture. This protocol was also easily amenable to scale-up. For example, Michael reaction of diethyl phosphite with benzylidenemalononitrile in a semi scale-up procedure (10 times) was carried out successfully and produced the desired product in 83% yield.

In order to show the unique catalytic behavior of nano γ -Fe₂O₃pyridine based catalyst **1** in these reactions, we have performed the





Fig. 6. (a) Reaction mixture, (b) separation of catalyst **1** from the reaction mixture by a magnetic bar.

Fig. 7. Reusability of γ -Fe₂O₃-pyridine based catalyst 1 for the synthesis of β -phosphonomalonate 2.



Fig. 8. HRTEM image after 10 times reuses of catalyst 1.

Table 4

Comparison of the catalytic efficiency of nano $\gamma\mbox{-}Fe_2O_3\mbox{-}pyridine based catalyst 1 with various catalysts.$

Entry	Catalyst	Reaction time (h)	Yield of product 2^{a} (%)
1	Catalyst 1	1	85
2	Sodium Stearate	24	80
3	HPA	24	61
4	HClO ₄ -SiO ₂	24	55
5	NPS- γ -Fe ₂ O ₃	24	62
6	AP-SiO ₂	24	72
7	5-HPAA	24	56
8	Pyridine	1	86

 $^a\,$ Isolated yield. Conditions: benzylidenmalononitrile (1 mmol), diethyl phosphite (2 mmol), catalyst (5 mol%), 70 $^\circ$ C.

reaction of benzylidenemalononitrile in the presence of a catalytic amount of solid catalysts (5 mol%) including sodium sterarate, BrØnsted acids (H₃PMo₁₂O₄₀, HClO₄/SiO₂ and NPS- γ -Fe₂O₃), basic catalyst (AP-SiO₂) and an ionic liquid (5-HPAA) (Table 4). As is evident from Table 4, nano γ -Fe₂O₃-pyridine based catalyst 1 is the most effective catalyst for this purpose leading to the formation of β -phosphonomalonate **2** in good yield. Pyridine catalyzed a similar reaction as well as nano γ -Fe₂O₃-pyridine based catalyst **1** (Entry 8). This observation showed that the catalylic activity of pyridine did not changed after its supporting on the surface of nanoparticls.

4. Conclusions

In summary, in this paper, the synthesis of nano γ -Fe₂O₃pyridine based catalyst as a new odorless pyridine based catalyst was described. This newly synthesized catalyst was used as a magnetically recyclable heterogeneous organic base for the efficient synthesis of β -phosphonomalonates by the reaction of diethyl phosphite with α , β -unsaturated malonates under solventfree conditions. Good to high yields of the products, use of dialkyl phosphite instead of malodorous trialkyl phosphite, simple work-up, ease of catalyst recovery and its reusability without appreciable loss of activity make this protocol environmentally benign and a useful contribution to the present methodologies.

Acknowledgement

We are thankful to University of Birjand Research Council for their support on this work and Dr. R. Malakooti for her assistance.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2013.01.009.

References

- [1] K. Green, Tetrahedron Lett. 30 (1989) 4807-4810.
- [2] R.R. Hindersinn, R.S. Ludington, J. Org. Chem. 30 (1965) 4020-4025.
- [3] Z. Jiang, Y. Zhang, W. Ye, C.H. Tan, Tetrahedron Lett. 48 (2007) 51-54.
- [4] A.N. Pudovik, I.V. Konovalova, Synthesis 2 (1979) 81-96.
- [5] D. Enders, A. Saint-Dizier, M.I. Lannou, A. Lenzen, Eur. J. Org. Chem. (2006) 29-49.
- [6] R.C. Miller, J.S. Bradley, L.A. Hamilton, J. Am. Chem. Soc. 78 (1956) 5299-5303.
- [7] R. Bodalski, K. Pietrusiewicz, Tetrahedron Lett. 13 (1972) 4209-4212.
- [8] D. Simoni, F.P. Invidiata, M. Manferdini, I. Lampronti, R. Rondanin, M. Roberti, G.P. Pollini, Tetrahedron Lett. 39 (1998) 7615–7618.
- [9] M. Hosseini-Sarvari, S. Etemad, Tetrahedron 64 (2008) 5519-5523.
- [10] M.A. Kulkarni, V.R. Pandurangi, U.V. Desai, P.P. Wadgaonkar, C. R. Chim. 15 (2012) 745–752.
- [11] M.O. Shulyupin, M.A. Kazankova, I.P. Beletskaya, Org. Lett. 4 (2002) 761-763.
- [12] Q. Xu, L.B. Han, Org. Lett. 8 (2006) 2099-2101.
- [13] D. Semenzin, G. Etemad-Moghadam, D. Albouy, O. Diallo, M. Koenig, J. Org. Chem. 62 (1997) 2414–2422.
- [14] L.B. Han, C.Q. Zhao, J. Org. Chem. 70 (2005) 10121-10123.
- [15] R.A. Stockland, R.I. Taylor, L.E. Thompson, P.B. Patel, Org. Lett. 7 (2005) 851-853.
- [16] M.R. Mahran, W.M. Abdou, Heteroat. Chem. 3 (1992) 93-99.
- [17] S.R. Kolla, Y.R. Lee, Tetrahedron 68 (2012) 226-237.
- [18] N.E. Leadbeater, M. Marco, Chem. Rev. 102 (2002) 3217-3274.
- [19] S. Minakata, M. Komatsu, Chem. Rev. 109 (2009) 711-724.
- [20] A. Hu, G.T. Yee, W. Lin, J. Am. Chem. Soc. 127 (2005) 12486-12487.
- [21] R. Abu-Reziq, H. Alper, D. Wang, M.L. Post, J. Am. Chem. Soc. 128 (2006) 5279-5282.
- [22] C.O. Dalaigh, S.A. Corr, Y. Gun'ko, S.J. Connon, Angew. Chem. Int. Ed. 46 (2007) 4329–4332.
- [23] C. Mukhopadhyay, S. Ray, Tetrahedron 67 (2011) 7936–7945.
- [24] R. Massart, E. Dubois, V. Cabuil, E. Hasmonay, J. Magn. Magn. Mater. 149 (1995)
- 1-5.
 [25] B.Z. Tang, Y. Geng, J.W.Y. Lam, B. Li, X. Jing, X. Wang, F. Wang, A.B. Pakhomov, X.X. Zhang, Chem. Mater. 11 (1999) 1581–1589.
- [26] K.M. Ho, P. Li, Langmuir 24 (2008) 1801-1807.
- [27] Number of NP in 1g catalyst **1**=Surface area/Average surface area of one NP=56 m².g⁻¹/4(3.14)(6.5×10^{-9} m)² = 0.11 × 10¹⁸ g⁻¹ Average number of pyridine attached to one NP=The amount of pyridine functionalized on 1g of catalyst **1**/Number of NP in 1g of catalyst **1**=0.25 mmol.g⁻¹/0.11 × 10¹⁸ g⁻¹ = 2.27 × 10⁻¹⁸ mmol per one NP.
- [28] S. Sobhani, Z. PakdinParizi, Tetrahedron 67 (2011) 3540-3545.
- [29] S. Sobhani, S. Rezazadeh, J. Iran. Chem. Soc. 8 (2011) 198–203.
- [30] S. Sobhani, S. Rezazadeh, Synlett (2010) 1485-1488.
- [31] S. Sobhani, Z. Pakdin Parizi, Appl. Catal. A: Gen. 409 (2011) 162–166.
- [32] S. Sobhani, M. Honarmand, J. Iran. Chem. Soc. 9 (2012) 661–669.
- [33] S. Sobhani, Z. Pakdin Parizi, S. Rezazadeh, J. Organomet. Chem. 696 (2011) 813–817.
- [34] A.A. Fahmy, N.A. Ismail, T.S. Hafez, Phosphorus Sulfur Silicon Relat. Elem. 66 (1992) 201–205.
- [35] B.E. Ivanoy, L.A. Kudryavtseva, T.G. Bykova, Bull. Acad. Sci. USSR Div. Chem. Sci. 18 (1969) 807-811.