Journal of Molecular Catalysis A: Chemical 347 (2011) 38–45

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

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

Solvent-free Mizoroki–Heck reaction catalyzed by palladium nano-particles deposited on gelatin as the reductant, ligand and the non-toxic and degradable natural product support

Habib Firouzabadi*, Nasser Iranpoor*, Arash Ghaderi

Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran

ARTICLE INFO

Article history:
Received 18 April 2011
Received in revised form 15 June 2011
Accepted 8 July 2011
Available online 20 July 2011

Keywords:
Nanoparticles
Palladium
Gelatin
Mizoroki–Heck reaction
Solvent-free

ABSTRACT

Gram-scale synthesis of uniform nano-particles of palladium supported on gelatin, as a reductant and ligand is described. These particles were prepared under green conditions without addition of any external reducing agent and ligand. No complicated work up process was needed for the isolation of the nano-particles. Full characterization of the supported palladium particles on gelatin was performed by UV–Vis spectra and also by SEM, TEM and AFM images. The amount of palladium particles on gelatin was determined by induced coupled plasma (ICP) analysis and atomic absorption spectroscopy (AAS) to be 0.09 mmol of Pd per gram of the gelatin. The supported nano-particles of palladium on gelatin were applied successfully as the catalyst in Mizoroki–Heck reaction. The reaction was conducted under solvent-free conditions using tri(*n*-propyl) amine as a base at 140 °C. This system showed high catalytic activity for the reaction of aryl iodides and aryl bromides with *n*-butyl acrylate and styrene. In the case of the reaction of aryl iodides with *n*-butyl acrylate, incredible reaction rates were observed which is unique in comparison with the other methods reported in the literature. The catalyst was recovered and recycled for ten consecutive runs. We have also checked the effect of one of the generated base adduct on the reaction rate.

1. Introduction

In recent years, the design and preparation of green catalysts have attracted much attention in academia and industries [1]. For this mean, heterogenization of the catalysts to solid supports is one of the interesting choices to prevent wasting the catalyst. In addition, the supports usually have a great effect on the activity of the catalyst. Particle size, surface area and pore structure are important parameters of the support. The support can have an effect on the catalytic activity of the supported metal either by creating reactive sites at the metal surface or by enhanced release of the metal into the solution by leaching [2]. In addition, recoverability of the catalyst increases the overall output and economic profitability of chemical transformations [3].

The immobilization methods to deposit the palladium metal into heterogeneous solid beds have been studied extensively and diverse supports such as clay [4], carbon nanofiber [5], montmorillonite [6], magnetic mesoporous silica [7], zeolite [8] and metal oxides [9] have been investigated. However, less attention has been paid to bioorganic polymers, which are ecofriendly degradable materials and are abundant in nature. In addition, they are not expensive and toxic [10].

Gelatin is a colorless, fragile, translucent, nearly tasteless solid. It is commonly used as a gelling agent in food, pharmaceuticals, photography, and cosmetic manufacturing. It is a water soluble protein and is an irreversibly hydrolyzed form of collagen [11]. Attractive properties of gelatin, such as elasticity, low immunogenicity, adhesiveness and low price, make it suitable for practical use in many areas of science [12]. Gelatin contains free carboxyl groups on its backbone and has the potential for chelating and reducing transition metals [10]. Therefore, using gelatin as a support for palladium species has two advantages; first it has the ability to reduces Pd(II) to Pd(0) *via* its available free carboxyl groups by liberation of CO_2 gas and the second is to act as a highly functionalized support, which stabilizes the reduced form of the palladium particles by ligation.

Recent progress in palladium catalysis has revealed that Pd in nanoparticle forms can catalyze numerous reactions such as Suzuki–Miyaura [13], Sonogashira–Hagihara [14], Stille [15] and Mizoroki–Heck [16] reactions.

By consideration of Mizoroki–Heck coupling reaction, which is one of the most powerful tools for building up the carbon–carbon bond, considerable attention has been focused on improving the

* Corresponding authors. Tel.: +98 711 228 4822; fax: +98 711 228 0926.
E-mail addresses: firouzabadi@chem.susc.ac.ir (H. Firouzabadi), iranpoor@chem.susc.ac.ir (N. Iranpoor).

1381-1169/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2011.07.008

efficiency of the catalyst from different views. Even though palladium has widespread utility for this reaction, it has some limitations such as being expensive and also some precautionary measures should be taken into account such as air-sensitivity, toxicity of some of its salts and also the amount of Pd leaching, which contaminates the terminal product. In order to overcome these problems, heterogenization of the catalyst and using nanoparticles of palladium are good options. It was reported that palladium nanoparticles of different origins have been used in this reaction [17]. However, the design and generation of new nanoparticles, on easily available, cheap, and nontoxic naturally occurring beds are of great values from different aspects.

In recent years, we have paid attention to the use of transition metal catalyst in different naturally compatible media for C–C and C–X bond formation [18]. In the current work, we have established a simple approach to gram-scale preparation of palladium nanoparticles supported on gelatin, as an edible, ecofriendly, degradable in nature and cheap protein. The supported nanoparticles have been successfully applied for solvent-free Mizoroki–Heck reaction as a recyclable catalyst.

2. Experimental

2.1. General

All chemicals were purchased from Merck, Fluka or Acros Chemical Companies and used without any further purification. NMR spectra were recorded with a Bruker Avance DPX-250 spectrometer (^{1}H NMR 250 MHz and ^{13}C NMR 62.9 MHz) in pure deuteriated chloroform with tetramethylsilane (TMS) as the internal standard. UV spectra (PerkinElmer, Lambda 25, UV/Vis spectrometer) were used to ensure the complete conversion of Pd(II) to Pd(0). Scanning electron micrographs were obtained by SEM (SEM, XL-30 FEG SEM, Philips, at 20 kV). Transmission electron microscope, TEM (Philips CM10) was also used to obtain TEM images. Atomic force microscope, AFM (DME, Dual ScopeTM DS 95-200-E) was also used to obtain AFM images. The amount of palladium nanoparticles supported on gelatin was measured by ICP analyzer (Varian, Vista-pro) and atomic absorption spectroscopy.

2.2. Large scale synthesis of palladium nanoparticles supported on gelatin

Gelatin (1 g) was first dissolved in water (100 mL) at room temperature. To this solution was added a solution of $PdCl_2$ (100 mL, 1 mM) and diluted with water (100 mL). Then, the solution was refluxed for 5 h to ensure the complete conversion of Pd(II) to Pd(0). The solution was cooled down to room temperature. Evaporation of the solvent was performed under a flow of air over night and dried in vacuum for 24 h to give a dark grayish solid material.

2.3. General procedure for Mizoroki–Heck reaction using Pd-nanoparticles supported on gelatin

Aryl halide (1 mmol) and alkene (1.5 mmol) were added to a flask containing gelatin supported Pd-nanoparticles (0.05 g of the gelatin-catalyst, contains 0.0045 mmol of palladium) and ^{n}Pr$_3$N (1.5 mmol, 0.29 mL) in the absence of solvent. The mixture was stirred at 140 °C in the air. After completion of the reaction (monitored by TLC or GC), ethyl acetate (15 mL) was added to the reaction vessel. The catalyst was separated by simple filtration. Water (3× 15 mL) was added to the ethyl acetate phase and decanted. Then the organic phase was dried over anhydrous Na_2SO_4. Evaporation of the solvent gave the desired products in excellent yields (Table 2).

2.4. Reusability of the catalyst

After completion of the reaction in the first run, ethyl acetate (5 mL) was added to the reaction mixture to extract the organic compounds. The ethyl acetate phase was removed by a syringe and the catalyst was dried under nitrogen flow. After complete drying, the catalyst was charged into another vessel containing the starting materials. The consecutive reaction was performed under the same conditions as discussed in the preceding general procedure. The recycling was repeated for ten cycles with success.

2.5. Spectral data

(3a): [18e] ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm): 0.90 (t, 3H, J = 7.5 Hz), 1.37 (sex, 2H, J = 7.7), 1.65 (quint, 2H, J = 7.5), 4.17 (t, 2H, J = 6.75 Hz), 6.53 (d, 1H, J = 16 Hz), 7.60 (d, 2H, J = 8.75), 7.63 (d, 1H, J = 16.25), 8.18 (d, 2H, J = 8.75); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm): 13.69, 19.14, 30.66, 64.88, 122.59, 124.14, 128.59, 140.58, 141.55, 166.09.

(3b): [19] ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm): 0.87 (t, 3H, J = 7.25 Hz), 1.37 (sex, 2H, J = 7.5), 1.65 (quint, 2H, J = 6.5), 4.17 (t, 2H, J = 7 Hz), 6.40 (d, 1H, J = 14 Hz), 7.31–7.42 (m, 3H), 7.58–7.74 (m, 3H), 8.05 (d, 1H, J = 8.25 Hz), 8.40 (d, 1H, J = 15.75 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm): 13.81, 19.27, 30.84, 64.53, 120.93, 123.38, 124.45, 124.98, 125.44, 125.84, 126.20, 126.40, 126.60, 126.83, 128.72, 129.12, 130.46, 131.42, 131.81, 133.68, 141.56, 166.97.

(3c): [18e] ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm): 0.89 (t, 3H, J = 7.5 Hz), 1.35 (sex, 2H, J = 7.5 Hz), 1.61 (quint, 2H, J = 5 Hz), 3.76 (s, 3H), 4.13 (t, 2H, J = 6.7), 6.24 (d, 1H, J = 15 Hz), 6.83 (d, 1H, J = 5 Hz), 7.40 (d, 2H, J = 5 Hz), 7.56 (d, 1H, J = 16 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm): 13.75, 19.20, 30.80, 55.35, 64.25, 114.28, 115.76, 129.67, 144.19, 161.30.

(3d): [18e] ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm): 0.97 (t, 3H, J = 7.25 Hz), 1.45 (sex, 2H, J = 7.5 Hz), 1.67 (quint, 2H, J = 5 Hz), 4.23 (t, 2H, J = 7.5 Hz), 6.54 (dd, 1H, J = 16 Hz, J' = 6.2 Hz), 7.67 (m, 3H), 8.24 (m, 2H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm): 13.70, 19.15, 30.67, 64.90, 122.59, 124.15, 128.60, 140.58, 141.56.

(3e): [18e] ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm): 0.85 (t, 3H, J = 4.7 Hz), 1.32 (sex, 2H, J = 4.3 Hz), 1.56 (quint, 2H, J = 2.5 Hz), 2.24 (s, 3H), 4.09 (t, 2H, J = 5 Hz), 6.30 (dd, 1H, J = 16 Hz, J' = 5.9 Hz), 7.06 (m, 2H), 7.29 (m, 2H), 7.52 (dd, 1H, J = 18.2 Hz, J' = 5.5 Hz),); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm): 13.75, 19.21, 21.41, 30.80, 64.28, 117.16, 128.34, 129.57, 131.73, 140.55, 144.52, 167.22.

(3f): [18e] ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm): 0.85 (t, 3H, J = 2.5 Hz), 1.32 (sex, 2H), 1.57 (quint, 2H), 2.30 (s, 3H), 4.11 (t, 2H), 6.27 (dd, 1H, J = 15.9 Hz, J' = 4.8 Hz), 7.11 (m, 3H), 7.41 (m, 1H), 7.84 (dd, 1H, J = 13.7 Hz, J' = 4.3 Hz); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm): 13.76, 18.96, 19.74, 30.79, 64.36, 119.26, 126.31, 129.94, 130.75, 133.40, 137.56, 142.20, 167.09.

(3g): [18e] ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm): 0.89 (t, 3H, J = 7.25 Hz), 1.35 (sex, 2H, J = 7.5 Hz), 1.64 (quint, 2H, J = 6.7), 4.16 (t, 2H, J = 6.5 Hz), 6.48 (d, 1H, J = 16 Hz), 7.59, (m, 5H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm): 13.68, 19.12, 27.82, 30.64, 64.75, 113.27, 118.31, 121.84, 128.35, 132.58, 138.55, 142.03, 166.14.

(3h): [18e] ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm): 0.90 (t, 3H, J = 7.5 Hz), 1.39 (sex, 2H, J = 7.5 Hz), 1.61 (quin, 2H, J = 6 Hz), 4.17 (t, 2H, J = 5.5 Hz), 6.53 (d, 1H, J = 15 Hz), 7.52 (d, 1H, J = 15 Hz), 8.82 (s, 2H), 9.13 (s, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm): 13.68, 19.13, 30.63, 64.98, 122.49, 137.00, 155.55, 159.11, 165.71.

(3i): [19] ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm): 7.02–8.11 (m, 12H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm): 123.65, 123.81, 125.73, 125.86, 126.12, 126.72, 127.81, 128.07, 128.65, 128.78, 131.43, 131.79, 133.76, 135.04, 137.65.

(3j): [18e] ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm): 2.32 (s, 3H), 6.89 (d, 1H, J = 16.25), 7.06–7.29 (m, 7H), 7.40–7.52 (m, 3H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm): 19.99, 124.95,125.44, 126.28, 126.61,

126.63, 127.28, 127.62, 127.66, 128.75, 130.08, 130.47, 135.86, 136.47, 137.75.

(3k): [18e] ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm): 7.13 (d, 2H), 7.31 (m, 6H), 7.52 (m, 4H).

(3l): [18e] ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm): 2.26 (s, 3H), 6.91–7.64 (m, 9H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm): 21.30, 126.45, 126.48, 127.45, 127.74, 128.69, 129.44, 134.59, 137.55.

(3m): [18b] ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm): 6.89 (d, 1H, J = 16.5 Hz), 7.15 (d, 1H, J = 16.5 Hz), 7.25–7.47 (m, 5H), 8.77 (s, 2H), 9.12 (s, 1H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ (ppm): 121.08, 126.84, 128.83, 128.88, 130.99, 132.80, 135.95, 154.22, 157.17.

(3n): [18e] ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm): 6.98–7.57 (m, 9H), 8.14 (m, 2H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (ppm): 124.07, 124.95, 126.20, 126.93, 127.00, 128.08, 129.04, 129.93, 132.58, 133.25, 136.13, 143.82.

(3o): [18e] ^{1}H NMR ($CDCl_3$, 250 MHz): δ (ppm): 6.99 (d, 1H, J = 16.3), 7.13 (d, 1H, J = 16.5), 7.31–7.26 (m, 3H), 7.56–7.43 (m, 6H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ (ppm): 110.55, 119.06, 126.71, 126.86, 126.92, 128.65, 128.86, 132.39, 132.49, 136.27, 141.82.

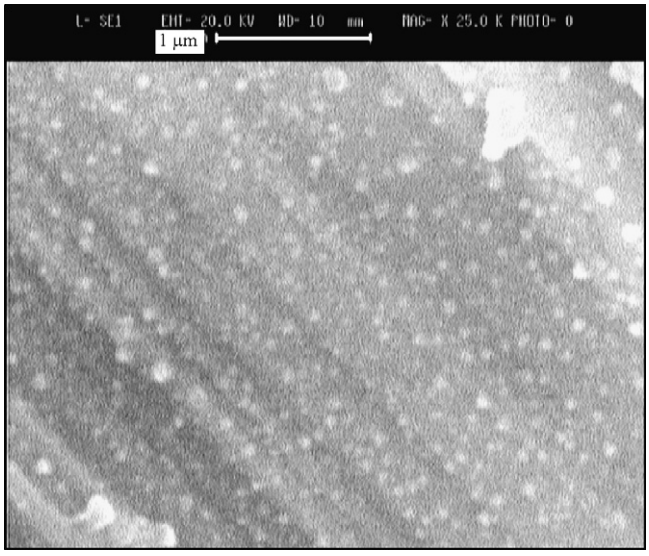


Fig. 2. SEM picture of the immobilized palladium on gelatin.

3. Results and discussion

We have recently reported the use of the sheets of edible gelatin as a support and reductant for palladium nanoparticles [20], which has been applied as the catalyst for Sonogashira–Hagihara reaction in molten TBAB and PEG. Now in this report, we have presented another highly useful catalytic application of gelatin supported palladium nanoparticles for Mizoroki–Heck reaction under solvent-free conditions in the absence of ligand.

Since the composition of gelatin is variable, depending on the source and its treatment, first we have determined the amount of water content and contamination of gelatin with traces of inorganic salts. The quantity of water content was determined by Karl–Fischer method to be 0.08 mL of water per gram of the gelatin. For determination of transition metal contaminants, ICP technique was employed. According to the analysis, there exist traces of Co (1.96×10^{-4} mmol), Cu (2.50×10^{-4} mmol), Fe (4.71×10^{-4} mmol), Ni (4.96×10^{-4} mmol) and Pd (1.31×10^{-4} mmol) in 1 g of the gelatin. This gelatin was used for our further studies.

The catalyst was prepared and characterized according to our previously reported protocol [20]. The resulting Pd supported nanoparticles were characterized by UV–Vis spectroscopy to ascertain the conversion of Pd(II) to Pd(0). This was supported by the disappearance of the peak at around 420 nm (Fig. 1). The process of reduction of Pd(II) to Pd(0) is performed by oxidation of $-CO_2H$ functional groups, which are accessible on the surface of gelatin molecules. The oxidation is accompanied by the liberation of CO_2 gas at the reflux temperature used for the preparation of the catalyst. Complexation and stabilization of the *in situ* generated Pd(0) particles may occur by the two-dentate amide groups available on the surface of gelatin. The SEM and the TEM images of the supported nanoparticles show the size of the particles to be in the range of less than 12 nm (Figs. 2 and 3a). In order to obtain more information about the topography of the surface of the prepared catalyst, we have also presented the AFM image of the catalyst (Fig. 4). The amount of palladium content supported on gelatin was determined by ICP and atomic absorption techniques to be 0.09 mmol of Pd per gram of the gelatin. This amount shows that the gelatin has a high ability to accommodate palladium nanoparticles in a good loading without aggregation of the metal particles.

In order to show the merit of application of these nanoparticles in organic synthesis, we applied them as the catalysts in the Mizoroki–Heck reaction. Initial studies were performed upon the reaction of iodobenzene with *n*-butyl acrylate as a model reaction and the effects of different solvents and bases were studied for this reaction (Table 1). The results showed that among the tested solvents, DMF and NMP were more efficient ones in which the desired product was obtained in shorter reaction times (20 and 25 min) than the other solvents under study. The results are shown in Table 1 (Entries 1 and 2). In the reactions employing toluene, ethanol and water as the solvents, the reactions did not progress efficiently and after 12 h, the desired product was obtained in only 15, 50 and 30% yields, respectively at their reflux temperatures (Table 1, Entries 3–5). Beyond of our imagination, when the model

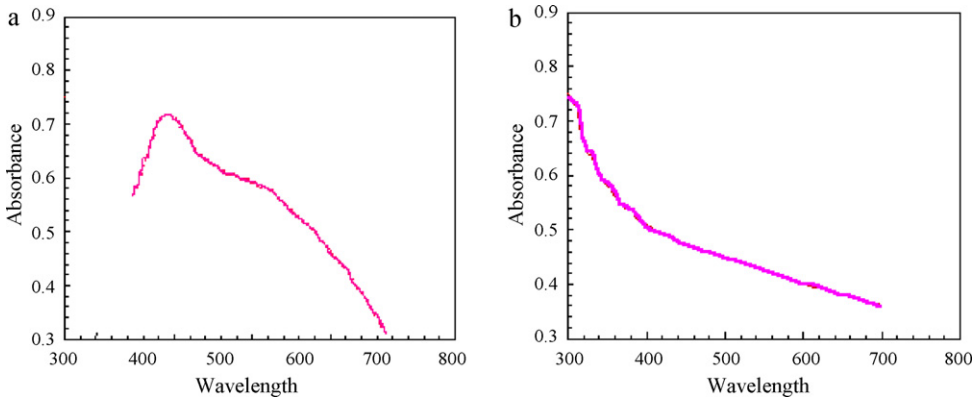


Fig. 1. UV–Vis spectra of (a) Pd(II) before reduction and (b) Pd(0) after reduction with gelatin.

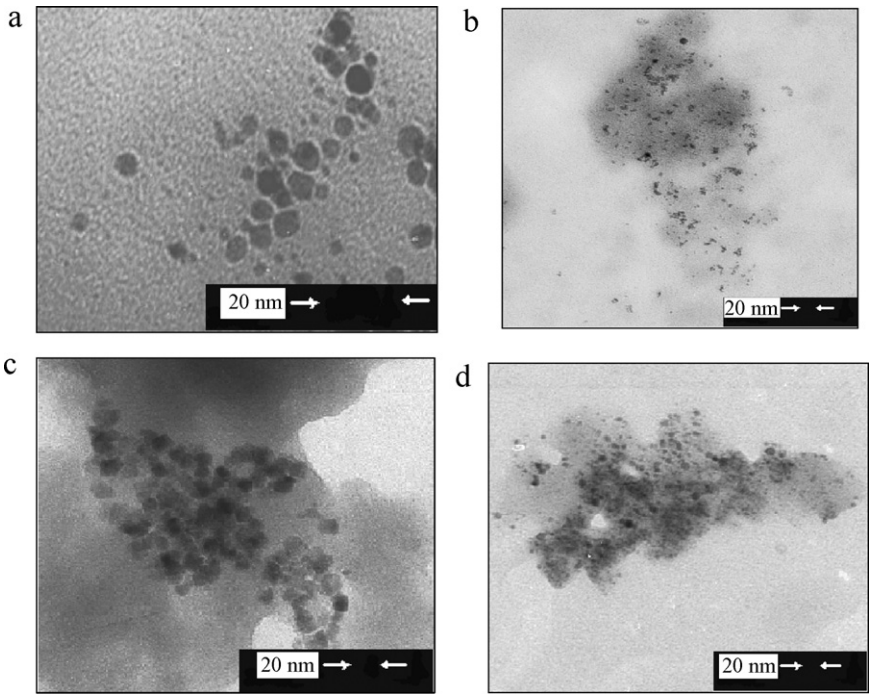


Fig. 3. TEM pictures of the palladium nanoparticles supported on gelatin used for the reaction of iodobenzene with *n*-butyl acrylate. (a) Before applying the catalyst for the reaction, (b) after the 1st run recycling of the catalyst, (c) after the 5th run of recycling of the catalyst and (d) after the 10th run recycling of the catalyst.

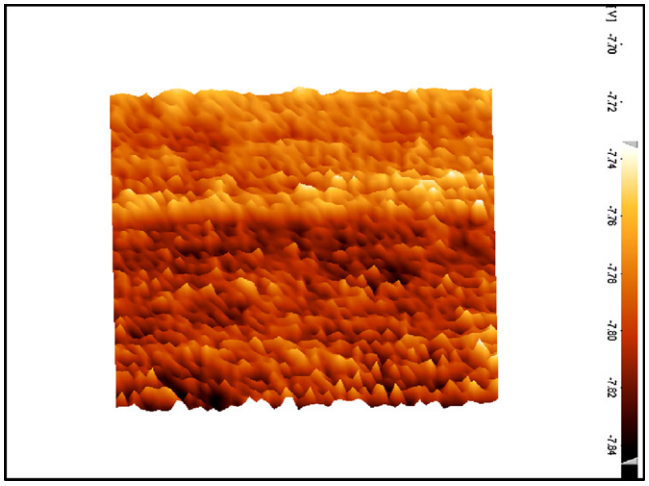


Fig. 4. 3D AFM image of the gelatin-supported palladium nanoparticles.

reaction was performed under solvent-free conditions at 140 °C, the desired product was obtained, in a highly short reaction time (2 min) with an excellent yield (92%) without observable byproduct production (Table 1, Entry 8). The reaction was also studied at temperatures 100 and 80 °C under non-solvent conditions. Lowering the temperature was accompanied by the elongation of the reaction times from 2 min to 45 min and 6.5 h with the production of the desired product in 81 and 70%, respectively. We have also investigated the effect of different bases upon the reaction. The results showed that, the inorganic bases were not as effective as the organic ones therefore, the rest of the reactions were conducted in the presence of tri-*n*-propyl amine. The entire results are presented in Table 1.

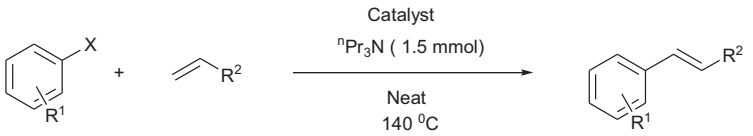
Study for optimization of the reaction with respect to the amounts of the starting materials and the catalyst, led us to aryl halide (1 mmol), alkene (1.5 mmol), $^{n}Pr_3N$ (1.5 mmol) and Pd-nanoparticles supported on gelatin (0.05 g, containing 0.0045 mmol of Pd) under solvent-free conditions at 140 °C. As shown in Table 2 , a range of aryl iodides and bromides reacted with *n*-butyl acrylate

Table 1
Comparison of the conditions used for the reaction of iodobenzene with *n*-butyl acrylate in the presence of palladium nanoparticles supported on gelatin in the presence of different bases and solvents.

Entry	Solvent	Temperature (°C)	Base	Time (min)	Isolated yield (%)
1	NMP	140	$^{n}Pr_3N$	20	88 (100)
2	DMF	140	$^{n}Pr_3N$	25	89 (100)
3	Toluene	Reflux	$^{n}Pr_3N$	12 h	15 (19)
4	EtOH	Reflux	$^{n}Pr_3N$	12 h	50 (57)
5	H_2O	Reflux	$^{n}Pr_3N$	12 h	30 (33)
6	None	80	$^{n}Pr_3N$	6.5 h	78 (100)
7	None	100	$^{n}Pr_3N$	45	81 (100)
8	None	140	$^{n}Pr_3N$	2	92 (100)
9	None	140	Et_3N	5	83 (100)
10	None	140	Morpholine	35	89 (100)
11	None	140	K_2CO_3	12 h	25 (30)
12	None	140	Cs_2CO_3	12 h	30 (40)
13	None	140	KOAc	12 h	10 (16)
14	None	140	NaOH	12 h	10 (15)

The data presented in the parenthesis refer to the conversion of iodobenzene.

Table 2
Mizoroki–Heck reaction of aryl halides (I, Br) with *n*-butyl acrylate or styrene in the presence of Pd nanoparticles supported on gelatin under solvent-free conditions.



1 **2** **3**

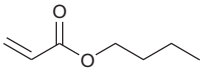
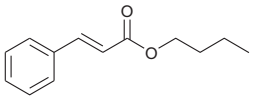
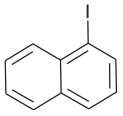
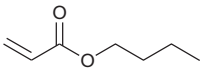
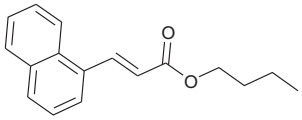
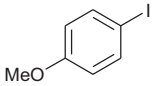
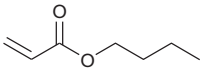
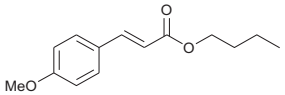
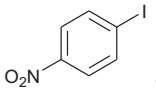
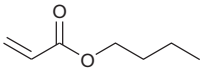
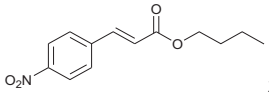
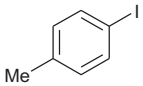
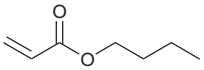
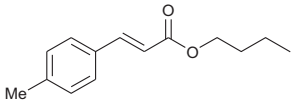
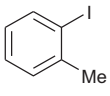
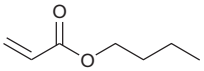
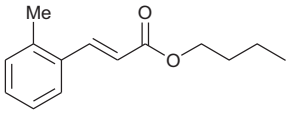
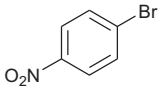
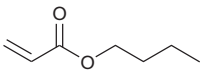
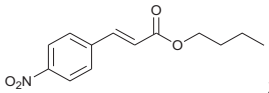
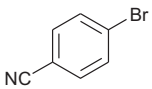
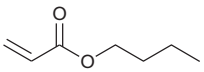
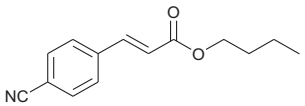
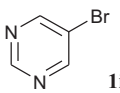
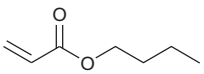
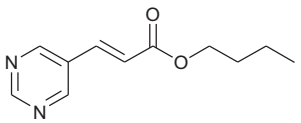
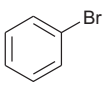
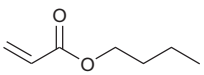
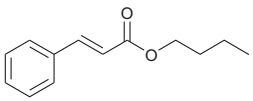
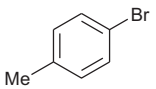
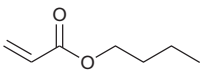
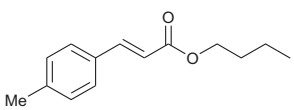
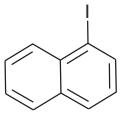
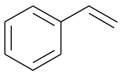
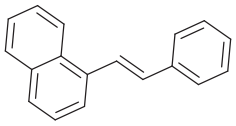
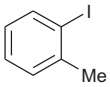
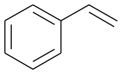
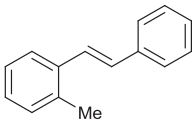
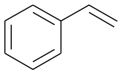
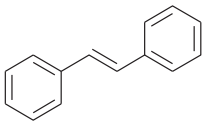
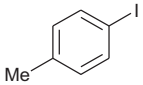
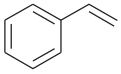
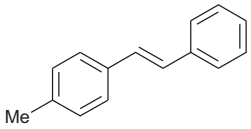
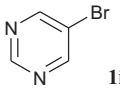
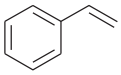
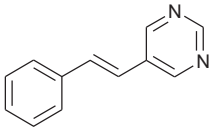
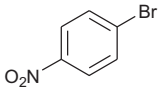
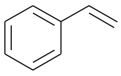
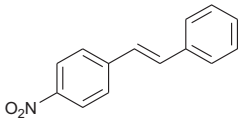
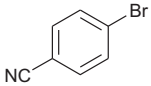
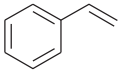
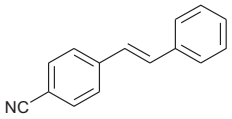
Entry	Aryl halide	Alkene	Product	Time (min)	Isolated yield (%)
1	 **1a**	 **2a**	 **3a**	2	92
2	 **1b**	 **2a**	 **3b**	10	95
3	 **1c**	 **2a**	 **3c**	5	95
4	 **1d**	 **2a**	 **3 d**	10	90
5	 **1e**	 **2a**	 **3e**	9	92
6	 **1f**	 **2a**	 **3f**	15	90
7	 **1g**	 **2a**	 **3 d**	30	94
8	 **1h**	 **2a**	 **3g**	60	98
9	 **1i**	 **2a**	 **3h**	100	91
10	 **1j**	 **2a**	 **3a**	12 h	70
11	 **1k**	 **2a**	 **3e**	18 h	75

Table 2 (*Continued*)

Entry	Aryl halide	Alkene	Product	Time (min)	Isolated yield (%)
12	 **1b**	 **2b**	 **3i**	240	84
13	 **1f**	 **2b**	 **3j**	75	90
14	 **1a**	 **2b**	 **3k**	20	88
15	 **1e**	 **2b**	 **3l**	30	89
16	 **1i**	 **2b**	 **3m**	200	85
17	 **1g**	 **2b**	 **3n**	150	73
18	 **1h**	 **2b**	 **3o**	240	70

or styrene to give the desired products plus tri-^{n}propylammonium iodide (^{n}Pr$_3$NHI) or tri-^{n}propylammonium bromide (^{n}Pr$_3$NHBr) as the base adducts. As we have noticed, the rate of the reaction of some aryl iodides with *n*-butyl acrylate in the presence of this catalyst was strangely fast (Table 2, Entries 1–6). As an example, in the case of the reaction of iodobenzene, the reaction proceeded in 2 min to completion (Table 2, Entry 1) whereas, similar reaction reported by Vallribera et al. using nanoparticles of palladium supported on a fluorinated hybrid material in acetonitrile at 130 °C went to completion in 24 h [21]. In addition, similar reaction catalyzed by nanoparticles of Pd in polyaniline in DMF at 130 °C after 36 h resulted the total yield of the product in 69% (*E*:*Z*, 75:25) [22]. While, this reaction in DMF, as we have observed, proceeded in the presence of the gelatin-supported Pd nanoparticles in only 25 min with the isolation of the final product in 89% yield (Table 1, Entry 2). The fastest reaction time for the similar reaction, has been reported by Calo et al. to be 5 min at 100 °C by the aid of nanosized palladium on chitosan in ionic liquids giving the desired product in 95% isolated yield [23].

Employing the optimized catalytic conditions, sterically hindered aryl iodides with *n*-butyl acrylate provided excellent yields of the desired products in very short reaction times (Table 2, Entries 2 and 6). Similarly, the reactions of activated aryl bromides as well as a heteroaryl bromide with *n*-butyl acrylate were also studied. The reaction of 1-bromo-4-nitrobenzene with *n*-butyl acrylate was completed within 30 min while, the similar reaction conducted in the presence of polyvinylpyridine-supported nanoparticles of palladium in NMP at 150 °C went to completion after 4 h [24]. The reaction of aryl halides with styrene was also studied. As shown in Table 2, the reaction of iodobenzene with styrene went to completion within 20 min to give *trans*-stilbene in 88% yield (Table 2, Entry 14). Steric hindrance also shows its effects upon the rates of the reactions. As the example, 4-iodotoluene reacted with styrene within 30 min with the isolation of the desired product in 89% (Table 2, Entry 16). Although, the similar reaction with 2-iodotoluene was performed in 75 min producing the final product in 90% yield (Table 2, Entry 13). The observed longer reaction time for the reaction of 1-iodo naphthalene with styrene is due to the hindrance imposed by the hydrogen atom located at 8 position of the neighboring fused ring (Table 2, Entry 12). Aryl chlorides did not react under these conditions.

There are many reports in the literature applying palladium particles deposited on various supports especially Pd supported on amine-modified silica for the Mizoroki–Heck reaction. Some studies have been investigated to compare the catalytic activity of these modified beds in the coupling reactions. Herein we wish to compare the previously reported systems in Mizoroki–Heck reaction with the system reported in this article. Stepnicka et al. reported the application of palladium deposited on SBA-15 functionalized with $\equiv Si(CH_2)_3NH(CH_2)_2NEt_2$ in the Mizoroki–Heck reaction of bromobenzene with *n*-butyl acrylate in the presence of NaOAc as a base in DMAc at 160 °C. Under these conditions, the reaction was completed within 4 h [25]. The same group observed that the mesoporous molecular sieves modified with the above mentioned

amine could be used as a suitable support for Pd(II) particles. This catalyst has been applied for the reaction of bromobenzene with *n*-butyl acrylate under the above conditions giving 73% conversion within 6 h [26]. Similar reaction under our optimized conditions gave the desired product within 12 h at 120 °C in 70% yield(Table 2, Entry 10). The preparation of MCM-41-supported Pd(II)-(S)-1-((6-(2-hydroxyphenyl) pyridine-2-yl)methyl)-*N*-methyl-*N*-(3-(triethoxysilyl)-propyl)pyrrolidine-2-carboxamide ligand has been reported. This complex has been applied as a catalyst in Mizoroki–Heck reaction of iodobenzene with *n*-butyl acrylate using a biphasic toluene/ethylene glycol mixture as solvent in the presence of potassium acetate under phosphine-free conditions giving 90% conversion of iodobenzene within 24 h at reflux [27]. While for the similar reaction, using the gelatin supported palladium nanoparticles the reaction was completed after only 2 min (Table 2, Entry 1). In another try, the Pd nanoparticles supported on functionalized mesoporous silica exhibited high catalytic activity for Mizoroki–Heck reaction. The reaction of iodobenzene with *n*-butyl acrylate in the presence of this catalyst proceeded to completion within 1 h in the presence of Et_3N in DMF as the solvent at 120 °C [28], whereas, the similar reaction, as mentioned above, went to completion within 2 min. We have also recently reported the application of amino-functionalized clay catalyst for the reaction of iodobenzene with *n*-butyl acrylate to perform the reaction to completion within 25 min [18e].

During this study, we have noticed, at the beginning of the reactions, the rate of the reactions was slow. However, when the reactions proceeded, a sudden increase in the rate of the reactions was observed. In order to explain this phenomenon, we studied the reaction of 1-bromo-4-nitrobenzene with *n*-butyl acrylate as a model reaction under the optimized conditions. The progress of the reaction was monitored by GC in 5-min intervals. We observed that only 20% conversion of the 1-bromo-4-nitrobenzene was detected after 15 min. As the reaction was performed for another 10 min, the conversion of the starting material was increased drastically to 88% (Fig. 5). We thought that, the *in situ* generated base adduct, tri-^{n}propylammonium bromide ($^nPr_3NHBr$), should have some important role in speeding up the reaction as its accumulation in the reaction mixture is increased, which may function as a co-catalyst in the reaction. In order to justify this observation, first, the reaction of 1-bromo-4-nitrobenzene with *n*-butyl acrylate was studied without extra addition of the base adduct, $^nPr_3NHBr$, to the reaction mixture, in the presence of Pd supported gelatin catalyst. Under this condition, the reaction was completed within 30 min (Table 2, Entry 7). Then, the similar reaction was conducted by the extra addition of the base adduct to the reaction mixture. We have

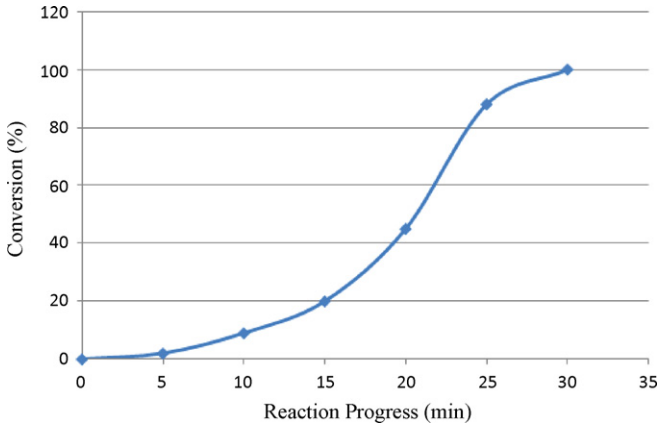


Fig. 5. Reaction progress *vs.* conversion of 1-bromo-4-nitrobenzene for the reaction with *n*-butyl acrylate under optimized conditions.

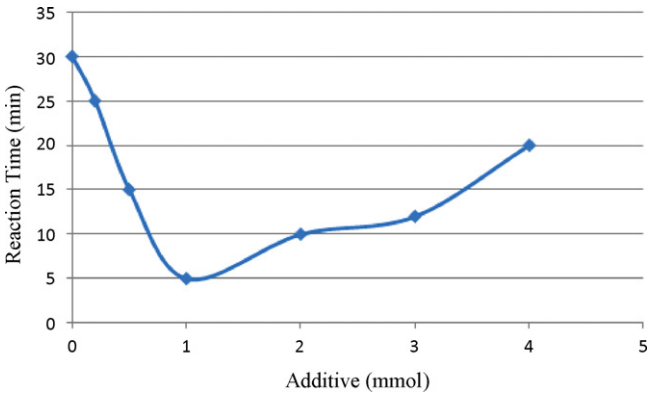


Fig. 6. The effect of the amount of the externally added base adduct ($^nPr_3NHBr$) to the reaction of 1-bromo-4-nitrobenzene with *n*-butyl acrylate under the optimized conditions.

observed that the increase in the rate of the reaction was dependent on the amounts of the added base adduct. For example, when we added 0.2 mmol of the base adduct to the reaction mixture, the reaction was completed within 25 min. When the amount of the base adduct was increased to 0.5 mmol, the reaction was performed to completion within 15 min. Finally, when the amount of the externally added base adduct was increased to 1 mmol the reaction was completed within 5 min (Fig. 6). The similar reaction in the presence of the external addition (1 mmol) of the base adduct ($^nPr_3NHBr$) in the absence of the catalyst under similar reaction condition was failed after 2 h. Therefore, we may conclude that, the accumulation of the base adduct in the reaction mixture shows a synergy effect upon the rate of the reaction.

The reusability of the catalyst was tested upon the reaction of iodobenzene with *n*-butyl acrylate employing 0.05 g of the catalyst in the presence of $^nPr_3N$ at 140 °C. At the first run, the reaction was completed within 2 min. Similarly, the reactions for the repeated runs were conducted after separation of the organic compounds from the reaction mixture by extraction and the recovered solid catalyst was recycled for another run. The recycling process was repeated for ten cycles with some decrease in the catalytic activity of the catalyst (Table 3). The amount of palladium leaching after the first run was determined by ICP analysis to be only 0.3%, and after 10 repeated recycling was 15%, which shows the average amount of leaching of palladium per cycle has been around 1.5%. The TEM pictures of the recovered nano catalyst after the 1st, 5th and the 10th runs showed that the aggregation of the particles has not been occurred significantly and the morphology and the size of the particles were not disturbed notably in comparison with the TEM picture of the catalyst before its application for the reaction (Fig. 3a–d).

In order to get more information about the leaching of palladium in different reactions, the reaction of 5-bromopyrimidine and bromobenzene with *n*-butyl acrylate as model reactions was studied. After completion of the reactions and the workup, the amount of leaching was determined by ICP analysis for the above mentioned reactions. For the reaction of 5-bromopyrimidine with *n*-butyl acrylate was 0.8% and for the reaction of bromobenzene with *n*-butyl acrylate was 2%.

Table 3
Recycling of the catalyst for the reaction of iodobenzene with *n*-butyl acrylate in the presence of $^nPr_3N$ and 0.05 g of the catalyst at 140 °C.

Run	1	2	3	4	5	6	7	8	9	10
Time (min)	2	4	5	6	8	9	11	16	20	25

The times indicated in this table is the completion time for the reaction.

In order to show that palladium nano-particles deposited on gelatin function as a heterogeneous catalyst, we have performed hot filtration test [29]. For this purpose, we studied the reaction of 1-bromo-4-nitrobenzene with *n*-butyl acrylate in the presence of Pd nanoparticles and $^{n}Pr_3N$ as the base in high coordinate solvent; *N*-methylpyrrolidone (NMP) at 140 °C. The heterogeneous palladium catalyst was removed by hot filtration when 20% conversion (15 min) of 1-bromo-4-nitrobenzene had been occurred. Then the resulting filtrate which contains also unreacted substrates was allowed to proceed under the mentioned reaction conditions. We observed that only 35% conversion of 1-bromo-4-nitrobenzene had been occurred after 48 h. This result showed that the palladium nano-particles deposited on gelatin act as a heterogeneous catalyst in the reaction mixture.

We have also shown that the catalyst was suitable for the large scale operation. For this purpose, we scaled-up the reaction of iodobenzene (10 mmol), *n*-butyl acrylate (15 mmol) gelatin supported Pd-nanoparticles (0.5 g of the gelatin-catalyst, contains 0.045 mmol of palladium) and $^{n}Pr_3N$ (15 mmol, 2.9 mL) in the absence of solvent. The reaction went smoothly to completion within 30 min to afford the desired product in 80% isolated yield.

We have also shown that the catalyst is stable towards air. For this aim, the freshly prepared catalyst was left in the air for a few months. Then, it was applied for the reaction of iodobenzene with *n*-butyl acrylate under the above mentioned conditions. The desired final product was obtained in 87% isolated yield within 20 min.

4. Conclusion

In this study, we have presented a green approach for the preparation and characterization of the uniform nanoparticles of palladium supported on gelatin without using any external reducing agent and ligand. The nanoparticles were characterized using SEM, TEM and AFM images and also by UV–Vis spectra. The palladium content of gelatin was determined by ICP and atomic absorption spectroscopy. The nanoparticles supported on the surface of gelatin are stable towards air and moisture and their handling does not need any precautionary measures. We have shown that the supported nanoparticles on gelatin are useful catalysts for solvent-free C–C bond formation *via* Mizoroki–Heck reaction using tri(*n*-propyl) amine as the base at 140 °C using different aryl halides (I and Br) and *n*-butyl acrylate and styrene. Astonishingly, some of the reactions proceeded in the presence of this catalyst under solvent-free conditions, are among the fastest ever reported in the literature. The catalyst was recyclable and has been recycled for ten successive runs with little loss of the catalytic activities. The amount of leaching of Pd for the first run of recycling to be only 0.3%. TEM images of the recycled catalyst after several runs showed no significant aggregation and agglomeration of the particles. Moreover, the catalyst was easily applied for the large scale operation. The kinetic study showed the important role of the *in situ* generated base adducts on the reaction rate.

Acknowledgments

The authors are thankful to TWAS Chapter of Iran based at ISMO and Shiraz University Research Council for their supports.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.07.008.

References

[1] R. Tao, S. Miao, Z. Liu, Y. Xie, B. Han, G. An, K. Ding, Green Chem. 11 (2009) 96–101.
[2] L. Yin, J. Liebscher, Chem. Rev. 107 (2007) 133–173.
[3] P. Barbaro, F. Liguori, Chem. Rev. 109 (2009) 515–529.
[4] K.K.R. Datta, M. Eswaramoorthy, C.N.R. Rao, J. Mater. Chem. 17 (2007) 613–615.
[5] J. Zhu, J. Zhou, T. Zhao, X. Zhou, D. Chen, W. Yuan, Appl. Catal. A: Gen. 352 (2009) 243–250.
[6] K.B. Sidhpuria, H.A. Patel, P.A. Parikh, P. Bahadur, H.C. Bajaj, R.V. Jasra, Appl. Clay Sci. 42 (2009) 386–390.
[7] J. Li, Y. Zhang, D. Han, Q. Gao, C. Li, J. Mol. Catal. A: Chem. 298 (2009) 31–35.
[8] M. Choi, D.H. Lee, R. Ryoo, Angew. Chem. Int. Ed. 48 (2009) 3673–3676.
[9] (a) F.Z. Su, Y.M. Liu, Y. Cao, K.N. Fan, Angew. Chem. Int. Ed. 47 (2008) 334–337; (b) U.R. Pillai, E. Sahle-Demessite, A. Baiker, Green Chem. 6 (2004) 161–165.
[10] Y. Hattori, E. Matijevic, J. Colloid Interface Sci. 335 (2009) 50–53.
[11] H. Hong, C. Liu, W. Wu, J. Appl. Polym. Sci. 114 (2009) 1220–1225.
[12] Y. Huang, S. Onyeri, M. Siewe, A. Moshfeghian, S.V. Madihally, Biomaterials 26 (2005) 7616–7627.
[13] A.J. Amali, R.K. Rana, Green Chem. 11 (2009) 1781–1786.
[14] S.G. Ryu, S.W. Kim, S.D. Oh, S.H. Choi, H.G. Park, Y.P. Zhang, Colloids Surf. A: Physicochem. Eng. Aspects 313–314 (2008) 224–229.
[15] V. Kogan, Z. Aizenshtat, R. Popovitz-Biro, R. Neumann, Org. Lett. 4 (2002) 3529–3532.
[16] V. Polshettiwar, A. Molnar, Tetrahedron 63 (2007) 6949–6976.
[17] (a) V. Calo, A. Nacci, A. Monopoli, P. Cotugno, Angew. Chem. Int. Ed. 48 (2009) 6101–6103;
(b) R. Bernini, S. Cacchi, G. Fabrizi, G. Forte, S. Niembro, F. Petrucci, R. Pleixats, A. Prastaro, R.M. Sebastian, R. Soler, M. Tristany, A. Vallribera, Org. Lett. 10 (2008) 561–564.
[18] (a) H. Firouzabadi, N. Iranpoor, M. Gholinejad, J. Mol. Catal. A: Chem. 321 (2010) 110–116;
(b) H. Firouzabadi, N. Iranpoor, M. Gholinejad, Tetrahedron 65 (2009) 7079–7081;
(c) H. Firouzabadi, N. Iranpoor, M. Gholinejad, J. Organomet. Chem. 695 (2010) 2093–2097;
(d) H. Firouzabadi, N. Iranpoor, M. Gholinejad, Adv. Synth. Catal. 352 (2010) 119–124;
(e) H. Firouzabadi, N. Iranpoor, A. Ghaderi, M. Ghavami, S.J. Hoseini, Bull. Chem. Soc. Jpn. 84 (2011) 100–109.
[19] X. Cui, Z. Li, C.-Z. Tao, Y. Xu, J. Li, L. Liu, Q.-X. Guo, Org. Lett. 8 (2006) 2467–2470.
[20] H. Firouzabadi, N. Iranpoor, A. Ghaderi, Org. Biomol. Chem. 9 (2011) 865–871.
[21] S. Niembro, A. Shafir, A. Vallribera, R. Alibes, Org. Lett. 10 (2008) 3215–3218.
[22] A. Houdayer, R. Schneider, D. Billaud, J. Ghanbaja, Lambert, J. Appl. Organomet. Chem. 19 (2005) 1239–1248.
[23] V. Calo, A. Nacci, A. Monopoli, A. Fornaro, L. Sabbatini, N. Cioffi, N. Ditaranto, Organometallics 23 (2004) 5154–5158.
[24] C. Evangelisti, N. Panziera, P. Perticib, G. Vitulli, P. Salvadori, C. Battocchio, G. Polzonetti, J. Catal. 262 (2009) 287–293.
[25] J. Demel, J. Cejka, P. Stepnicka, J. Mol. Catal. A. Chem. 329 (2010) 13–20.
[26] J. Demel, M. Lamac, J. Cejka, P. Stepnicka, ChemSusChem 2 (2009) 442–451.
[27] C. del Pozo, N. Debono, A. Corma, M. Iglesias, F. Sanchez, ChemSusChem 2 (2009) 650–657.
[28] P. Wang, Q. Lu, J. Li, Mater. Res. Bull. 45 (2010) 129–134.
[29] R.A. Sheldon, M. Wallau, I.W.C.E. Arends, U. Schuchardt, Acc. Chem. Res. 31 (1998) 485–493.