

Gelatin as a bioorganic reductant, ligand and support for palladium nanoparticles. Application as a catalyst for ligand- and amine-free Sonogashira–Hagihara reaction†

Habib Firouzabadi,* Nasser Iranpoor* and Arash Ghaderi

Received 14th June 2010, Accepted 15th October 2010

DOI: 10.1039/c0ob00253d

Palladium nanoparticles were deposited and reduced by gelatin as a safe edible, naturally occurring and cheap support. No extra reducing agents were used for the generation of Pd(0) nanoparticles from the Pd(II) salt. The nanoparticles of Pd supported on gelatin were characterized by SEM, TEM and AFM images, UV-Vis and XRD spectra and the amount of palladium entrapped in the gelatin was measured by ICP and atomic absorption analysis. The nanoparticles showed high catalytic activity for the Sonogashira–Hagihara coupling reaction of various aryl iodides, bromides and chlorides as well as heteroaryl halides and also β -bromo styrene with phenylacetylene under copper-, ligand- and amine-free conditions. The reactions were carried out at 100 °C in molten tetrabutylammonium bromide (TBAB) or polyethylene glycol (PEG400) in the presence of potassium acetate as a base in argon atmosphere. Dimerization of phenylacetylene applying similar conditions in air is also described.

Introduction

Gelatin is a water soluble edible protein derived from partially denatured collagen.¹ Collagen occurs extensively in nature and is insoluble in water, but the gelatin derived from it is freely soluble in hot water. Eye-catching properties of gelatin, such as flexibility, adhesiveness, low immunogenicity, promotion of cell adhesion and growth, and low cost, make it suitable for practical use in many areas of science.² Gelatin contains free carboxyl groups on its backbone and has the potential for chelating and reducing transition metals.³ Therefore, using gelatin as a support for important transition metals such as palladium has two advantages, it reduces Pd(II) to Pd(0) without using any extra reducing agent and also acts as a highly functionalized support to catch and stabilize the nanoparticles of palladium. In comparison with other reducing agents employed for the generation of palladium nanoparticles, such as NaBH₄, gelatin is a weak reductant which generates and deposits Pd(0) nanoparticles from Pd(II) very gently, which causes the size of the particles to be smaller and the distribution of the particles on the surface of gelatin to be more dispersed.

Palladium metal nanoparticles are employed in a diversity of catalytic reactions including Mizoroki–Heck,⁴ Suzuki–Miyaura,⁵ Stille⁶ and Sonogashira–Hagihara reactions.⁷ To date, various supports have been investigated to stabilize palladium nanoparticles and prevent their aggregation.^{8,9} Chemical methods such as the reduction of transition metal salts are the most convenient ways to deposit the metallic nanoparticles onto supports. A literature survey shows that, in the presence of a suitable support,

a wide variety of reducing agents such as NaBH₄,⁸ citric acid,¹⁰ hydrazine,¹¹ HCOOH,¹² ethyleneglycol,¹³ ethanol¹⁴ *etc.* have been used for the reduction of transition metal salts to produce metal nanoparticles.

Despite significant advances in the synthesis of palladium nanoparticles, the development of special supports which are cheap, non-hazardous, environmentally friendly and naturally degradable remains a subject of scientific interest and of vital industrial significance. One of the choices which may be efficient in this theme is using bioorganic materials for supporting palladium nanoparticles which are readily available in nature and are not expensive.³ To expand the use of naturally occurring materials in the synthesis of nanoparticles, we decided to search for bioorganic polymers with a potential reducing ability. For this aim, we have chosen gelatin as a bed for the synthesis of palladium nanoparticles.

One of the most successful methods for the formation of a sp–sp² carbon–carbon bond is Sonogashira–Hagihara reaction.¹⁵ The traditional procedure for the Sonogashira–Hagihara reaction employs a Pd-complex of phosphines as a catalyst and copper iodide salt as a co-catalyst. However, using copper salts as co-catalysts sometimes leads to the homo-coupling reaction of terminal alkynes (Glaser-type reaction) upon exposure of the copper-acetylide intermediate to air or other oxidizing agents.¹⁶ Therefore, numerous improved methodologies were reported to eliminate the copper co-catalyst from the Sonogashira–Hagihara reaction.¹⁷ For instance, the complex PdClMe(bisimidazole) has been demonstrated to be an efficient and recoverable catalyst for the reaction.¹⁸ A copper-free Sonogashira–Hagihara reaction was reported for coupling of vinyl tosylates and alkynes using the Pd(OAc)₂/PPh₃ catalytic system.¹⁹ The reaction was also performed in the presence of heterogeneous palladium supported on a zeolite surface.²⁰ Moreover, there are some other reports available in the literature in which the reaction has been performed in the absence of any copper salts.²¹

Department of Chemistry, College of Sciences, Shiraz University, Shiraz, 71454, Iran. E-mail: firouzabadi@chem.susc.ac.ir, iranpoor@chem.susc.ac.ir; Fax: +98 711 2280926; Tel: +98 711 2284822

† Electronic supplementary information (ESI) available: General experimental details for starting materials and instruments and also elemental analysis, spectral data of all compounds and literature references for known compounds. See DOI: 10.1039/c0ob00253d

Table 1 ICP analysis results to show the amounts of traces of metal salts in gelatin

Metals	Cobalt	Copper	Iron	Nickel	Palladium
mmol of metals per 1 g of gelatin	1.96×10^{-4}	2.50×10^{-4}	4.71×10^{-4}	4.96×10^{-4}	1.31×10^{-4}

Using palladium nanoparticles as catalyst in a Sonogashira–Hagihara reaction in the ionic liquid [bmim]BF₄ was reported in the presence of triethyl amine as a base at ambient temperature under ultrasonic irradiation.²² In this report, aryl iodides worked well and the desired coupling products were obtained in high isolated yields. In the case of aryl bromides, only activated ones reacted to give the product in moderate yields. Reusable palladium nanoparticles supported on PVP as a catalyst for Sonogashira–Hagihara reaction of aryl halides and terminal acetylenes at 80 °C is also reported.²³

In addition, the homo-coupling of terminal acetylenes is an important approach towards the synthesis of conjugated enynes to form building blocks of biologically active compounds, natural products, electronic and optical materials. A number of transition metal complexes have been employed for alkyne dimerization reactions.²⁴ In the most reported protocols, a mixture of regio- and stereoisomeric products were obtained. Selective reaction proceeds only under carefully controlled conditions. For example, head to head dimerization of phenylacetylene has been obtained selectively when (η^3 -allyl-PdCl)₂ and TDMPP were used in the presence of Et₂NH.²⁵

In order to advance the successful results obtained by using TBAB as a solvent or additive in the Mizoroki–Heck reaction²⁶ and Suzuki–Miyaura²⁷ cross coupling, now we want to release our results using molten TBAB and PEG as media and employing gelatin supported nanoparticles of palladium as the catalyst for a ligand- and amine-free Sonogashira–Hagihara reaction and dimerization of phenylacetylene.

Results and discussion

In this study, we have used edible gelatin as a support and reductant for palladium nanoparticles. Since gelatin is a natural product its composition is variable, depending on the source and its treatment, so we have first determined the water content and amount of contamination of gelatin with traces of inorganic salts. The water content in the gelatin sample used for this study was determined, using the Karl-Fischer method, to be 0.08 ml of water per 1 gram of gelatin. According to ICP analysis, there exist traces of cobalt, copper, iron, nickel and palladium salts in the gelatin. The results are presented in Table 1.

The gelatin supported palladium nanoparticles were prepared on a gram-scale by dissolving the above mentioned gelatin (1 g) in water at room temperature. To the resulting solution, PdCl₂ (100mL, 1 mM) in water was added and refluxed for five hours. The obtained dark-grey solution was cooled to room temperature and evaporation of the solvent under air flow resulted a dark green-greyish solid. Our initial efforts were focused on the characterization of the resulting solid material, which would be used as the catalyst in the further studies for C–C bond formation. First, we established the oxidation state of Pd on the surface of gelatin by UV-Vis spectra which confirmed the conversion

of Pd(II) to Pd(0) by the disappearance of the peak at 420 nm⁸ (Fig. 1). The SEM image of the gelatin revealed the regularly dispersed Pd-particles on the surface of the gelatin (Fig. 2) and its TEM pictures showed the average size of the particles entrapped in gelatin framework to be around 4–7 nm (Fig. 3 and Figure S1†). The AFM image also showed and confirmed the regularity of the deposited particles on the gelatin (Fig. 4).

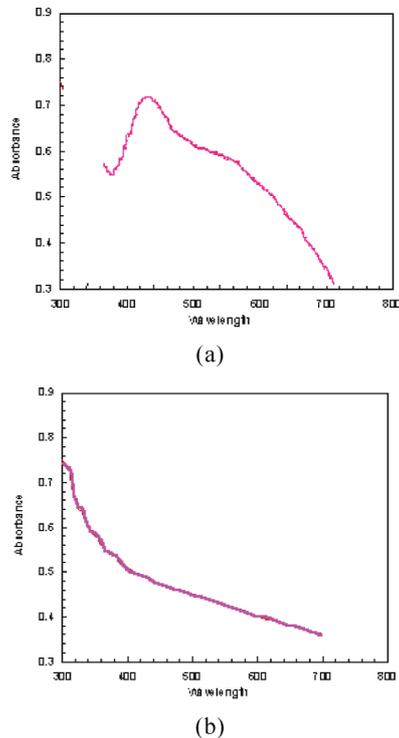


Fig. 1 UV-Vis spectra of (a) Pd(II) before reduction and (b) Pd(0) after reduction with gelatin.

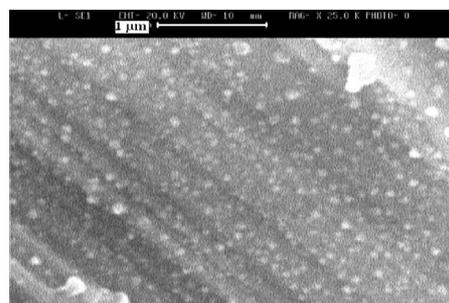


Fig. 2 SEM picture of the immobilized palladium nanoparticles on gelatin.

X-ray diffraction (XRD) analysis did not show any peaks related to a crystalline structure, indicating that the particles are amorphous and the usual *fcc* structure of palladium metal does not exist in these particles.²⁸ The amount of palladium content deposited on the surface of gelatin was determined by ICP and atomic absorption analysis to be 0.09 mmol of palladium per gram of gelatin. This amount and also SEM, TEM and AFM pictures show that the gelatin has a high capacity to entrap palladium in a good quantity without bulk aggregation of the metal.

Table 2 Optimization conditions in Sonogashira–Hagihara reaction between 1-bromo-4-nitrobenzene and phenylacetylene (**2**) in the presence of Pd-nanoparticles at 100 °C under argon atmosphere

Entry	Solvent	Base	<i>T</i> /°C	Time/h	Conversion (%)
1	H ₂ O	KOAc	100	24	22
2	H ₂ O/TBAB	KOAc	100	24	70
3	TBAB	KOAc	100	2	100
4	TBAB	NaOAc	100	5	100
5	TBAB	none	100	24	18
6	none	KOAc	100	24	40
7	TBAB	Cs ₂ CO ₃	100	7	100
8	TBAB	NaOH	100	24	—
9	TBAB	NaOH	120	24	34
10	TBAB	morpholine	100	7	100
11	TBAB	KOAc	80	24	87
12	DMSO	KOAc	100	19	100
13	DMSO	NaOH	100	24	trace
14	DMSO	Et ₃ N	100	24	trace
15	DMSO/H ₂ O	NaOH	100	24	13
16	DMSO/H ₂ O	Cs ₂ CO ₃	100	24	—
17	NMP	KOAc	100	24	—
18	none	ⁿ Pr ₃ N	100	12	9
19	PEG400	KOAc	100	2	100
20	PEG400	NaOH	100	24	11
21	PEG400	Cs ₂ CO ₃	100	24	—

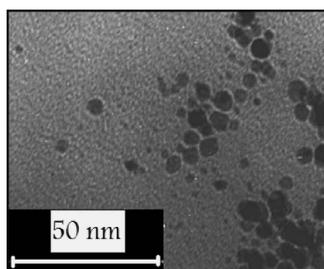


Fig. 3 TEM picture of the supported palladium nanoparticles on gelatin.

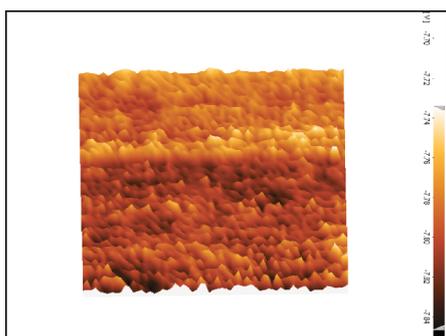


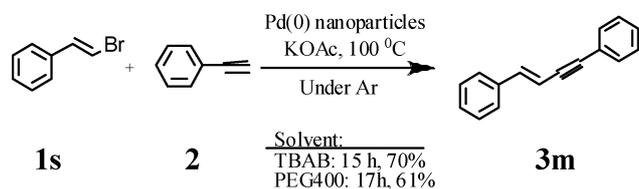
Fig. 4 3D AFM image of the gelatin-supported palladium nanoparticles.

In order to show the merit of gelatin supported palladium nanoparticles as a catalyst in organic synthesis, we first applied the gelatin loaded palladium for important Sonogashira–Hagihara reaction.

Preliminary screening to compare different systems in the Sonogashira–Hagihara reaction was performed by using different

solvents and bases as well as changing the reaction temperature upon the reaction of 1-bromo-4-nitrobenzene with phenylacetylene as a benchmark. First, we tried to conduct the reaction in aqueous media. As shown in Table 2, the catalyst was not efficient when the reaction was performed in water using KOAc as a base at 100 °C. Addition of TBAB (1 mmol) as a phase transfer agent made a good impact on the progress of the reaction. This observation motivated us to check TBAB as a reaction medium in its melt form (100 °C) instead of water. Switching the solvent from water to TBAB in combination with KOAc as the base achieved complete conversion of the starting material within 2 h. We also investigated the effect of different kinds of bases in molten TBAB. For instance, in the presence of NaOAc, Cs₂CO₃ and morpholine, 100% conversion of the starting material within 5, 7 and 7 h, respectively, has been observed. To show the merit of the molten TBAB/KOAc system, we left out TBAB or KOAc periodically from the reaction media. The reaction in the absence of KOAc gave only 18% conversion after 24 h and when TBAB was omitted from the reaction mixture, 40% conversion of the starting material was observed by GC after the same reaction time. A similar reaction was also studied in DMSO at 100 °C using different bases. The results of this study showed that KOAc was also the most proper base for the reaction of 1-bromo-4-nitrobenzene with phenylacetylene in DMSO which gave the desired product in 100% conversion (GC) within 19 h. We have also used NMP as a solvent in the presence of KOAc for the similar reaction, which was not successful at all. In order to expand our studies, we conducted a model reaction in polyethylene glycol (PEG400). We observed that PEG400 was also a suitable medium for the reaction in the presence of KOAc as a base to complete the reaction within 2 h.

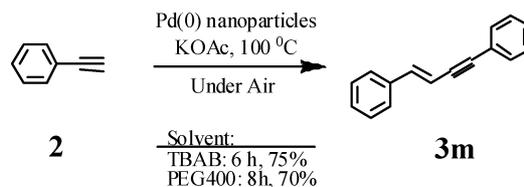
As shown in Table 3, a range of aryl iodides, bromides and chlorides reacted with phenylacetylene to give the desired products in high yields. As expected, the reaction of aryl iodides bearing electron donating groups went to completion in longer reaction times (Table 3, Entries 2, 3). Also, *ortho*-substituted aryl iodides reacted in longer reaction times (Table 3, Entries 4, 5). 1-Iodo naphthalene **1g**, reacted smoothly to give the desired product in 88% conversion within 5 h in molten TBAB while, when the reaction was conducted in PEG400 at 100 °C, the desired product was obtained in 90% isolated yield within 5.5 h (Table 3, Entry 7). The coupling reaction of sterically hindered iodomesitylene **1f**, did not give the product even after 24 h and the starting materials remained intact in these reaction conditions showing the strong effect of steric hindrance in this reaction (Table 3, Entry 6). The coupling reaction of phenylacetylene with both electron-releasing and electron-withdrawing aryl bromides afforded products in high yields. Heterocyclic bromides such as 3-bromopyridine, 5-bromopyrimidine and 3-bromothiophene led to the corresponding bi-functionalized acetylene in desirable yields (Table 3, Entries 12–14). The catalytic system effect was also manifested for the reaction of aryl chlorides with phenylacetylene. In these cases, prolonged reaction times to 24 h were required to give the expected products in good yields (Table 3, Entries 15–17). We also made an effort to activate the strong C–F bond and study the coupling reaction of aryl fluorides. Unfortunately, the reaction of 2,4-dinitro-fluorobenzene with phenylacetylene failed. However, the starting material of 2,4-dinitro-fluorobenzene was consumed and a mixture of unidentified products was observed by TLC. In order to show the wide applicability of our catalytic system, we applied our protocol for the reaction of β -bromostyrene, a vinylic bromide, and phenylacetylene under similar reaction conditions. The reaction proceeded well within 15 h (70%) in molten TBAB and 17 h (61%) in PEG400 (Scheme 1).



Scheme 1 Coupling reaction of β -bromostyrene with phenylacetylene catalyzed by Pd-nanoparticles supported on gelatin.

We have also investigated the homocoupling reaction of phenylacetylene as a model compound in the air under ligand- and amine-free conditions in molten TBAB which resulted the homocoupled product in 75% isolated yield at 100 °C in 6 h. Similar reaction in PEG 400 at 100 °C gave the desired product in 70% isolated yield in 8 h. As it is evident from $^1\text{H NMR}$ of the products, the reaction in both media proceeded with high regio- and stereoselectivity producing the homo-coupled *E*-enynes product (Scheme 2).

The recoverability of the catalyst was examined for the reaction of 1-bromo-4-nitrobenzene with phenylacetylene. After completion of the reaction, the mixture was cooled to room temperature and EtOAc was added to the reaction mixture. Addition of EtOAc dissolves organic materials and TBAB as well, and the gelatin-based catalyst remains intact at the bottom of the vessel. This was employed for the subsequent reaction. This catalyst was recycled



Scheme 2 Dimerization of phenylacetylene catalyzed by Pd-nanoparticles supported on gelatin.

and reused three times which was accompanied by the loss of its catalytic activity. According to ICP analysis, 31% leaching of the catalyst into molten TBAB was observed after the third run. SEM pictures of the recovered palladium nanoparticles after the first and the second runs showed aggregation of the metal particles (Fig. 5). However, when this catalyst is used for the similar reaction in PEG400, the leaching of the catalyst into PEG400 was reduced drastically to 12% after the third run, which was determined by ICP analysis. We believe that the strong ionic character of molten TBAB can easily remove the particles of Pd from the surface of gelatin. The results are summarized in Table 4.

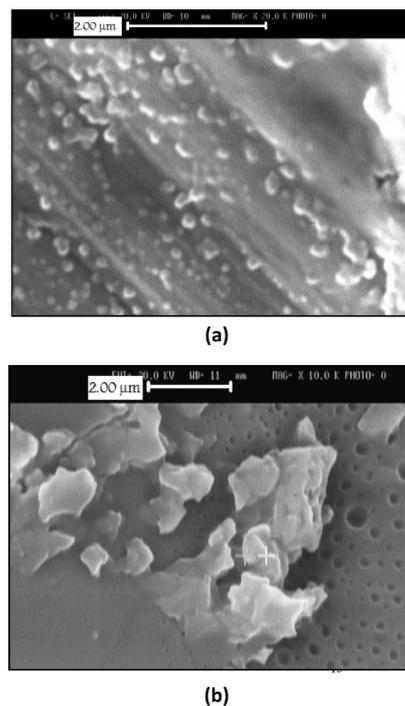


Fig. 5 SEM pictures of the recovered Pd-nanoparticles supported on gelatin after the reaction of 1-bromo-4-nitrobenzene with phenylacetylene in TBAB (a) after the first run, (b) after the second run.

Conclusions

In conclusion, we have described a clean, eco-friendly and green one-pot method to synthesize uniform nanoparticles supported on gelatin as a cheap and available protein without using any special reducing agents, in water. The synthesized palladium nanoparticles were characterized using SEM, TEM, AFM, ICP, UV-Vis and atomic absorption techniques. These particles showed excellent catalytic activities in a Sonogashira–Hagihara reaction of various aryl iodides, bromides and chlorides as well as heteroaryl

Table 3 Sonogashira-Hagihara reaction of aryl halides with phenylacetylene in the presence of Pd-nanoparticles in molten TBAB or PEG400 under Ar atmosphere

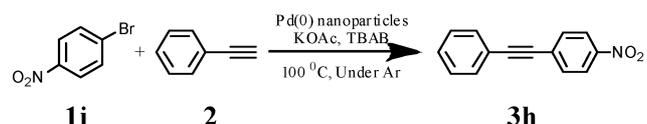
Entry	Aryl halide	Product	Time/h ^a	Isolated Yield (%) ^a
1	 1a	 3a	45 min (1)	90 (94)
2	 1b	 3b	4.5 (5)	85 (80)
3	 1c	 3c	1.25 (1.5)	93 (93)
4	 1d	 3d	4 (4.25)	93 (91)
5	 1e	 3e	2 (2)	90 (91)
6	 1f	 3f	24	—
7	 1g	 3g	5 (5.5)	88 (90)
8	 1h	 3a	5.5 (6)	80 (74)
9	 1i	 3c	6 (6.5)	75 (72)

Table 3 (Contd.)

Entry	Aryl halide	Product	Time/h ^a	Isolated Yield (%) ^a
10	 1j	 3h	2 (2)	81 (85)
11	 1k	 3i	24 (24)	80 (78)
12	 1l	 3j	2 (2.25)	77 (75)
13	 1m	 3k	8 (9)	75 (74)
14	 1n	 3l	21 (24)	81 (75)
15	 1o	 3a	24 (24)	74 (53)
16	 1p	 3h	24 (24)	70 (58)
17	 1q	 3c	24 (24)	60 (60)
18	 1r	Mixture of unidentified products	24	Starting material was consumed

^a The data indicated in parentheses refer to the reactions conducted in PEG400

Table 4 Recycling of Pd-nanoparticles supported on gelatin for the reaction of 1-bromo-4-nitrobenzene with phenylacetylene



Run	1 ^a	2 ^a	3 ^a
Time for completion of the reaction/h	2 (2)	6 (5)	15 (8)

^a The data shown in parentheses refer to the reaction times in PEG400

bromides with phenylacetylene in molten salt of TBAB or PEG400 in the presence of KOAc as base at 100 °C. We have also presented the catalytic activity of the catalyst upon a dimerization reaction of phenylacetylene as a model compound. The catalyst can be easily recovered and recycled for at least three runs in the reaction. This catalytic system is also suitable for large-scale operations.

Further studies on the applications of the catalyst to the other reactions such as Mizoroki–Heck and Suzuki–Miyaura reactions are in progress in our laboratory and will be published elsewhere.

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

Experimental

General procedure for Sonogashira–Hagihara reaction catalyzed by palladium nanoparticles supported on gelatin in TBAB:

Aryl halide (1 mmol) and terminal acetylene (2 mmol) were added to a flask containing Pd-nanoparticles (0.05 g of the catalyst) and KOAc (1.5 mmol) in the presence of tetrabutyl ammonium bromide (TBAB) (1 g) as solvent. The mixture was stirred at 100 °C under argon atmosphere. After completion of the reaction (monitored by TLC or GC) the products were isolated by column chromatography. Evaporation of the solvent gave the desired pure products in high yields.

General procedure for Sonogashira–Hagihara reaction catalyzed by palladium nanoparticles supported on gelatin in PEG400:

Aryl halide (1 mmol) and terminal acetylene (2 mmol) were added to a flask containing Pd-nanoparticles (0.05 g of the catalyst) and KOAc (1.5 mmol) in the presence of polyethylene glycol 400 (PEG400) (2 ml) as solvent. The mixture was stirred at 100 °C under argon atmosphere. After completion of the reaction (monitored by TLC or GC) water (10 ml) and ethyl acetate (10 ml) was added to the reaction mixture and decanted and the products were purified by column chromatography. Evaporation of the solvent gave the desired pure products in high yields.

Large-scale Sonogashira–Hagihara reaction catalyzed by palladium nanoparticles supported on gelatin in TBAB:

1-bromo-4-nitrobenzene (5 mmol) and phenylacetylene (8 mmol) were added to a flask containing Pd-nanoparticles (0.3 g of the catalyst) and KOAc (7 mmol) in the presence of tetrabutyl ammonium bromide (TBAB) (4 g) as solvent. The mixture was stirred at 100 °C under argon atmosphere for 3 h. After completion of the reaction (monitored by TLC) the products were isolated by column chromatography. Evaporation of the solvent gave the desired pure products in 75% yield.

Reusability of the catalyst:

After completion of the reaction in the first run, ethyl acetate (5 × 10 ml) was added to the reaction mixture to extract the organic compounds. The ethyl acetate solution was removed by filtration and the catalyst, which is insoluble in ethyl acetate, was dried under nitrogen flow. After complete drying, the catalyst was charged again into the vessel containing starting materials and the reaction was performed under the same conditions.

Typical procedure for dimerization of phenylacetylene catalyzed by palladium nanoparticles supported on gelatin:

Phenylacetylene (2 mmol) was added to a flask containing Pd-nanoparticles (0.05 g of the catalyst) and KOAc (1.5 mmol) in the presence of tetrabutyl ammonium bromide (TBAB) (1 g) as solvent. The mixture was stirred at 100 °C under air atmosphere. After completion of the reaction (monitored by TLC) the products were isolated by column chromatography. Evaporation of the solvent gave the desired pure product in high yield.

Notes and references

- H. Hong, C. Liu and W. Wu, *J. Appl. Polym. Sci.*, 2009, **114**, 1220.
- Y. Huang, S. Onyeri, M. Siewe, A. Moshfeghian and S. V. Madihally, *Biomaterials*, 2005, **26**, 7616.
- Y. Hattori and E. Matijevic, *J. Colloid Interface Sci.*, 2009, **335**, 50.
- V. Polshettiwar and A. Molnar, *Tetrahedron*, 2007, **63**, 6949.
- A. J. Amali and R. K. Rana, *Green Chem.*, 2009, **11**, 1781.
- V. Kogan, Z. Aizenshtat, R. Popovitz-Biro and R. Neumann, *Org. Lett.*, 2002, **4**, 3529.
- S. G. Ryu, S. W. Kim, S. D. Oh, S. H. Choi, H. G. Park and Y. P. Zhang, *Colloids Surf., A*, 2008, **313**, 224.
- K. K. R. Datta, M. Eswaramoorthy and C. N. R. Rao, *J. Mater. Chem.*, 2007, **17**, 613.
- J. Zhu, J. Zhou, T. Zhao, X. Zhou, D. Chen and W. Yuan, *Appl. Catal., A*, 2009, **352**, 243; F. Z. Su, Y. M. Liu, Y. Cao and K. N. Fan, *Angew. Chem., Int. Ed.*, 2008, **47**, 334; U. R. Pillai, E. Sahle-Demessite and A. Baiker, *Green Chem.*, 2004, **6**, 161.
- S. Yang, Y. Wang, Q. Wang, R. Zhang and B. Ding, *Colloids Surf., A*, 2007, **301**, 174.
- M. Ojeda, S. Rojas, M. Boutonnet, F. J. Perez-Alonso, F. J. Garcia-Garcia and J. L. G. Fierro, *Appl. Catal., A*, 2004, **274**, 33.
- S. V. Ley, C. Mitchell, D. Pears, C. Ramarao, J. Q. Yu and W. Zhou, *Org. Lett.*, 2003, **5**, 4665.
- W. Wang, B. Zhao, P. Li and X. Tan, *J. Nanopart. Res.*, 2008, **10**, 543.
- Z. Wang, B. Shen, Z. Aihua and N. He, *Chem. Eng. J.*, 2005, **113**, 27.
- R. Chinchilla and C. Najera, *Chem. Rev.*, 2007, **107**, 874; H. Doucet and J.-C. Hierso, *Angew. Chem., Int. Ed.*, 2007, **46**, 834.
- J.-H. Li, Y. Liang and Y.-X. Xie, *J. Org. Chem.*, 2005, **70**, 4393; F. Yang, X. Cui, Y. Li, J. Zhang, G. Ren and Y. Wu, *Tetrahedron*, 2007, **63**, 1963; P. Siemsen, R. C. Livingston and F. Diederich, *Angew. Chem., Int. Ed.*, 2000, **39**, 2632.
- X. Wang, W. Qin, N. Kakusawa, S. Yasuike and J. Kurita, *Tetrahedron Lett.*, 2009, **50**, 6293; J. Z. Jiang and C. Cai, *J. Colloid Interface Sci.*, 2007, **307**, 300; J. C. Hierso, J. Boudon, M. Picquet and P. Meunier, *Eur. J. Org. Chem.*, 2007, 583; T. Suzuka, Y. Okada, K. Ooshiro and Y. Uozumi, *Tetrahedron*, 2010, **66**, 1064.
- S. B. Park and H. Alper, *Chem. Commun.*, 2004, 1306.
- X. Fu, S. Zhang, Y. Yin and D. Schumacher, *Tetrahedron Lett.*, 2002, **43**, 6673.
- L. Djakovitch and P. Rollet, *Tetrahedron Lett.*, 2004, **45**, 1367.
- S. Liu and J. Xiao, *J. Mol. Catal. A: Chem.*, 2007, **270**, 1.
- A. R. Gholap, K. Venkatesan, R. Pasricha, T. Daniel, R. J. Lahoti and K. V. Srinivasan, *J. Org. Chem.*, 2005, **70**, 4869.
- P. Li, L. Wanga and H. Li, *Tetrahedron*, 2005, **61**, 8633.
- C. Yang and S. P. Nolan, *J. Org. Chem.*, 2002, **67**, 591.
- M. Rubina and V. Gevorgyan, *J. Am. Chem. Soc.*, 2001, **123**, 11107.
- V. Calo, A. Nacci, A. Monopoli and P. Cotugno, *Angew. Chem., Int. Ed.*, 2009, **48**, 6101.
- J. H. Li, J. L. Li, D. P. Wang, S. F. Pi, Y. X. Xie, M. B. Zhang and X. C. Hu, *J. Org. Chem.*, 2007, **72**, 2053.
- T. Z. Ren, Z. Y. Yuan and B. L. Su, *Chem. Commun.*, 2004, 2730.