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Short Communication

Polyethylene glycol-supported recyclable NC palladacycle catalyst for Heck cross-coupling reactions

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ABSTRACT

Palladium nanoparticles with narrow size distribution were easily prepared by applying polyethylene glycol (PEG 1000 and 15000) and NC palladacycle in the absence of other chemical agents. The Pd-PEG catalysts were fully characterized by a variety of techniques including X-ray diffraction (XRD), transmission electron microscopy (TEM), UV–vis and Fourier transform infrared (FT-IR) spectroscopy. TEM micrographs of Pd/PEG 15000 show that palladium nanoparticles have mostly very well-defined geometrical shapes. Also Pd/PEG 15000 was relatively an efficient catalyst system for the Heck reaction, affording a diverse range of products in moderate to good yields.

1. Introduction

The palladium-catalyzed Heck reaction developed in the early 1970s was a milestone in modern organic chemistry [1,2]. Heck reaction is normally carried out in the presence of phosphine ligands and base under an inert atmosphere. However, the relatively high price of the palladium complex has greatly limited the industrial application of homogeneous Heck reaction, and some of the phosphine ligands are sensitive to air and moisture [3,4]. Most of the problems related to homogeneous catalysts can be solved by immobilizing the catalyst or catalyst precursor on polymer supports with good solvation attributes [5].

Palladium (Pd) nanoparticles are a unique class of heterogeneous catalysts that is widely used and effective for a variety of organic reactions due to its high surface-to-volume ratio. These catalysts can be based on either supported palladium nanoparticles or supported palladium complexes on various supports, such as, carbon [6], silica [7], resin [8], chitosan [9], alumina [10], zeolite [11], and organic polymer supports [12,13].

On the other hand, palladacycles have been known as well-defined catalysts or precatalysts in cross-coupling reactions [14–16]. They can be easily prepared, show high stability under atmospheric conditions and can be anchored to different solid supports. Supported palladacycles are increasingly investigated by several research groups and being used in various organic transformations. Najera and Alacid [17,18] performed Heck and Suzuki cross-couplings using polystyrene supported oxime palladacycle in water as solvent. Luo et al. [19], used polystyrene-supported soluble palladacycle as an excellent and recyclable catalyst for Heck, Suzuki and Sonogashira reactions. The activity and stability of the PEG-anchored oxime palladacycle in coupling reactions have been also reported by Corma et al. [20].

Among polymer supported nanoparticles, polyethylene glycol (PEG) is a promising candidate which is inexpensive, nontoxic and its properties can be tuned by simply changing molecular weight [21]. Herein, in continuation of our studies in developing new supported catalysts [22,23], we report a simple and environmentally friendly route for the preparation of PEG supported NC palladacycle (Scheme 1). To the best of our knowledge, the present work is the first example of the heterogeneous nanocatalyst based on amine NC palladacycle supported on PEG. We also investigated the application of the prepared catalyst in the Heck cross-coupling reaction which was carried out in the absence of phosphine ligands under air.

2. Experimental

2.1. Instruments and reagents

All chemicals and solvents were purchased from Merck and Aldrich and used without further purification or drying. Conversions were monitored using an Agilent 6890N gas chromatograph equipped with a capillary HP-5^{+} column, based on aryl halides. Electronic absorption spectra were recorded on a JASCO 7580 UV–vis–NIR spectrophotometer. Infrared spectra were recorded on a FT-IR JASCO 680 spectrophotometer in the spectral range 4000–400 cm^{-1} using the KBr pellets technique. X-ray powder diffraction data were collected on an XD-3A diffractometer using Cu Kα radiation. Transmission electron microscopy analyses were performed by PHILIPS (model CM120) electron microscope.

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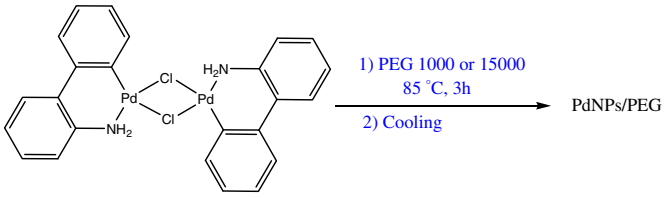


Scheme 1. Preparation of supported palladium nanoparticles (PdNPs) using different PEGs.

Palladium content of the catalyst was measured by Inductively Coupled Plasma (ICP-OES) analyzer (PerkinElmer 7300DV spectrometer). Dimeric NC palladacycle was obtained using procedure described earlier [24].

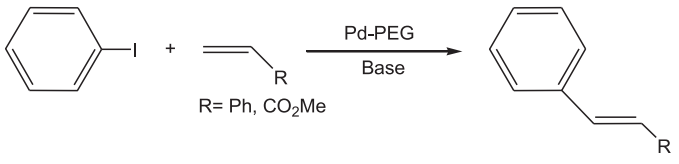
2.2. Preparation of Pd-PEG catalyst

Dimeric NC palladacycle (0.22 mmol, 0.136 g) was added into PEG (2 mmol) with different molecular weights (1000 or 15000) in a 25-mL round-bottomed flask. The mixture was heated in a water bath at 85 °C under vigorous, continuous stirring for 3 h. During this stage, the red-brown color of the solution turned to dark gray, indicating the formation of Pd nanoparticles. The mixture of Pd nanoparticles in PEG solidified upon cooling at room temperature.

2.3. General procedure for Heck reaction

A mixture of aryl halide (1.0 mmol), olefin (1.5 mmol), Et_3N (1.5 mmol), toluene (9 mL), ethanol (1 mL) and catalyst (4.5 mmol% related to aryl halides) was stirred at 80–120 °C for the time given in Tables 1 and 2. After the reaction, toluene and ethanol were removed in a rotavapor and the residue was extracted with cold ether (5 × 15 mL). The combined ether solution was taken for GC analyses.

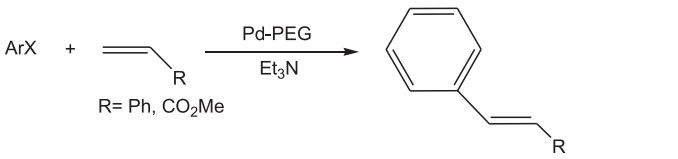
Table 1
Heck coupling of iodobenzene with styrene and methyl acrylate: Reaction conditions study.



Entry	Olefin	Base	Temp (°C)/time (h)	Yield[a] (%)
1	Methyl acrylate	Na_2CO_3	80/8	Trace
2	Methyl acrylate	NaOAc	80/8	Trace
3	Methyl acrylate	KOH	80/8	Trace
4	Methyl acrylate	$K_3PO_4{\cdot}3H_2O$	80/8	Trace
5	Methyl acrylate	Et_3N	80/8	7
6	Methyl acrylate	Na_2CO_3	100/8	Trace
7	Methyl acrylate	NaOAc	100/8	Trace
8	Methyl acrylate	KOH	100/8	Trace
9	Methyl acrylate	$K_3PO_4{\cdot}3H_2O$	100/8	Trace
10	Methyl acrylate	Et_3N	100/8	17
11	Methyl acrylate	Et_3N	120/8	21
12	Methyl acrylate	Et_3N	100/16	40
13	Styrene	Na_2CO_3	100/8	4
14	Styrene	Et_3N	80/8	12
15	Styrene	Et_3N	100/8	43
16	Styrene	Et_3N	100/16	80
17	Styrene	Me_3N	100/16	9
18[b]	Styrene	Et_3N	100/16	50
19	Methyl acrylate	Et_3N	100/24	48

Reaction conditions: iodobenzene 1 mmol, olefin 1.5 mmol, base 1.5 mmol, Toluene 9 mL, ethanol 1 mL, catalyst (4.5 mmol% relative to the amount of iodobenzene).
[a] Isolated yields determined by GC, based on iodobenzene.
[b] Using Pd/PEG 1000.

Table 2
Heck coupling of aryl halides with styrene and methyl acrylate catalyzed by Pd/PEG 15000.



Entry	Ar	X	R	Yield[a] (%)
1	C_6H_5	I	C_6H_5	80
2	m-$CH_3C_6H_4$	I	C_6H_5	40
3	p-$CH_3C_6H_4$	I	C_6H_5	53
4	p-$CH_3OC_6H_4$	I	C_6H_5	68
5	C_6H_5	Br	C_6H_5	61
6	C_6H_5	Br	CO_2Me	27
7	C_6H_5	I	CO_2Me	40
8	m-$CH_3C_6H_4$	I	CO_2Me	19
9	p-$CH_3C_6H_4$	I	CO_2Me	27
10	p-$CH_3OC_6H_4$	I	CO_2Me	67

Reaction conditions: aryl halide 1 mmol, olefin 1.5 mmol, Et_3N 1.5 mmol, toluene 9 mL, ethanol 1 mL, catalyst (4.5 mmol% relative to the amount of aryl halides) at 100 °C, 16 h.
[a] Isolated yields determined by GC, based on aryl halide.

3. Results and discussion

3.1. Catalysts characterization

The crystalline structure of supported Pd-catalyst was obtained using powder XRD. The typical patterns of catalysts prepared using NC palladacycle in PEG (1000 and 15000) are presented in Fig. S1 (Supporting information). As shown in the XRD patterns, two peaks at about 19.2° and 23.4° indicated the presence of pure PEG polymer [12]. Also, broad weak peak near $2\theta = 40°$ is detected, which can be indexed to the characteristic reflection (111) plane for face-centered-cubic Pd(0) with another weak peak around $2\theta = 43°$, consistent with the (200) crystalline plane (JCPDS card no. 87-641). The broadening of the diffraction peaks as compared to that of bulk Pd indicates the formation of the palladium nanoparticles. The intensity of palladium peaks slightly increases in the case of using PEG 15000, which related to the different degrees of chemical reduction of NC palladacycle in PEGs. The crystallite size was calculated using Scherer's equation, and the values corresponding to the refection planes (111) were found to be 14.8 nm and 13.2 nm for Pd/PEG 1000 and 15000, respectively. The same result was also obtained for the XRD pattern of the Pd/PEG 15000 after its use in the Heck reaction for several cycles. This reveals the excellent stability and recovery of the catalyst.

Fig. S2 (Supporting information) displayed the UV–vis spectra of dimeric NC palladacycle before and after the reduction with different molecular weight PEGs as a reducing agent. As can be seen, the UV–vis spectrum of dimer shows absorption maximum at around 330 nm. After the reaction of Pd(II) ions with different molecular weight PEGs, the peak observed at 330 nm has strongly decreased, indicating the conversion of Pd(II) to Pd(0) nanoparticles. Also, the intensity of this peak further decreased when PEG with larger chain length was applied.

Fig. 1 presents the TEM images of palladium nanoparticles prepared at 85 °C using PEG 15000. The average dimension of Pd nanoparticles is around 2–12 nm, in good agreement with the crystallite size calculated from XRD data. As shown in Fig. 2(a), palladium nanoparticles derived from PEG 15000 have interestingly very well-defined geometrical shapes including triangle, rhombohedral, pentagonal and unidentified. Comparing to the previously reported catalysts (from various starting materials of palladium) [13,20], this typical catalyst exhibits such a distinguished shapes.