

Palladium nanoparticles in poly(ethyleneglycol): the efficient and recyclable catalyst for Heck reaction

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Abstract

Palladium nanoparticles with narrow size distribution were prepared by applying poly(ethyleneglycol) (PEG) and Pd(OAc)₂ in the absence of other chemical agents. PEG appeared to act as both reducing agent and stabilizer. The results of XRD show that the concentration of precursor played the key role to the development of palladium nanoparticles. The reduction of Pd²⁺ to nano Pd was sensitive to the chain length of the PEG, and the larger chain length PEG such as PEG 2000 exhibited higher reduction reactivity. The as-prepared palladium nanoparticles were found to be a highly stable and reusable catalyst for Heck reaction.

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Keywords: Palladium nanoparticles; Heck reaction; Poly(ethyleneglycol); Catalyst

1. Introduction

Heck reaction is one of the most versatile and useful tools in organic synthesis [1,2]. From the corresponding alkene and aryl compounds, the Heck reaction provides a direct route to synthesize the important olefins. Heck reaction is normally carried out in the presence of phosphine ligands and base under an inert atmosphere. Advantages of Heck reaction include the high selectivity, the tolerance of various substrates, and the mild reaction conditions [3–5].

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. The removal of ligands derived from palladium homogeneous catalyst often complicates workup and product isolation. In addition, phosphine-freed reaction conditions are highly desired due to the environmental effects associated with phosphine [6–8]. To address these concerns, heterogeneous palladium catalysts have been developed over the past decades [9–14]. Ying

and coworkers reported on highly dispersed palladium in the mesoporous silica [9,10]. Although this solid catalyst was characterized by excellent activity, its recycling was hampered due to the collapse of mesopores. Reetz et al. described the formation of palladium nanoparticles stabilized by surfactant and it was claimed that a true heterogeneous catalyst was functioning [11,12]. Very recently, dendrimers [15–17], fluoros ligands [18], ionic liquids [19–21], block copolymer [22], and polyvinylpyridine [23] have been introduced to stabilize the nanosized palladium species and were applied as catalysts active for carbon–carbon coupling reactions.

Among the preparations of nano-Pd particles, the chemical reduction of palladium salt in an aqueous or organic solution by suitable reducing agents such as hydrazine [24], hydrogen [25,26], and sodium borohydride [27] has been widely adopted, even though there are questions regarding the toxicity of some of these reducing agents. The employment of polymers in these systems was mainly involved with the protection of the nanosized palladium from aggregation. The report of other properties about the polymer such as reducing properties was extremely rare. PEGs are inexpensive polymers and widely applied as the promising soluble polymeric supports [28–32]. Herein, we report a novel and facile

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route for preparation of nano-Pd by exploiting PEG, which was found to act as both reducing agent and stabilizer. The average molecular weight of PEG influences the fabrication of Pd⁰. It was noted that as-prepared nano-Pd provides the active and recyclable heterogeneous catalysts for the Heck-type carbon–carbon bond formation reaction in the absence of phosphine ligands. The reaction was insensitive to the air and moisture with high yields, and Pd-PEG can be readily recycled more than six times without obvious deactivation.

2. Experimental

2.1. Preparation of nano-Pd

The nano-Pd preparation process is “green” and very simple. Palladium(II) acetate 0.05 g (0.22 mmol) was added into the PEG (molecular weight: 2000, 4 g, 2 mmol) at 80 °C by magnetic stirring. The resulting light yellow homogeneous solution was further stirred for 2 h at the same temperature. During this process the color of the solution turned from light yellow to gray dark, indicating the formation of nano-Pd. The mixture of PEG and palladium nanoparticles solidified when cooling to room temperature. The as-prepared nano-Pd can be preserved for months without changes of properties.

2.2. Characterization

The X-ray diffraction patterns of Pd nanoparticles were recorded by a Bruker D8 Advance X-ray diffractometer (Cu K α). The average size of crystallites was calculated from the peak broad (1 1 1) by using the Debye–Scherrer equation [33]. The transmission electron micrographs and selected area electron diffraction (SAED) patterns were obtained by employing JEM-2010 microscopes under 200 kV. Samples for observation of TEM were prepared by placing 3 drops of CH₂Cl₂ colloidal Pd/PEG solution onto a carbon-coated copper grid. UV–vis spectroscopy measurements (300–700 nm) were performed on a Jena SPECORD 200 using quartz cells. 0.57 mM palladium solution of CH₂Cl₂ was used for UV–vis measurements. GC–MS was performed on a HP5973 apparatus.

2.3. Catalysis properties

The as-prepared nano-Pd (PEG: Pd(OAc)₂ = 4: 0.05 g, Pd(OAc)₂ 0.22 mmol, 4.5 mmol% related to aryl halides) was used as the catalyst in a solution of toluene and ethanol (9:1) and 5 mmol aryl halide, 7.5 mmol olefin, 7.5 mmol triethylamine was added. The mixture was stirred at 100 °C for the indicated time. After the reaction, toluene and ethanol was removed in a rotavapor and the residue was extracted with cold ether (5 × 15 ml). The combined ether solution was taken for GC or ICP analyses. The solution was concentrated and purified by column chromatography (silica gel) to afford the products. The recycle experiment was carried out under the same condition by exploiting the residue after the extraction.

The conversion of the Heck reaction was determined with a gas chromatograph (HP 5989B) equipped with a SE-30 column and a flame ionization detector. Palladium content in the extractant was analyzed using an inductively coupled plasma-atomic emission spectrometer (ICP-AES).

3. Results and discussion

The preparation of nano-Pd was very straightforward. Pd(OAc)₂ was added into the PEG at 80 °C in a flask by magnetic stirring. The resulting homogeneous solution was maintained at 80 °C with further stirring for 2 h. This resulted in conversion of transparent solution to the characteristic gray black color of nano Pd. Pd⁰ diffraction lines at $2\theta = 40.039, 46.581, 68.047^\circ$ are well recorded by X-ray diffractogram (Fig. 1), illustrating the formation of Pd⁰. The broadening of the diffraction peaks as compared to that of bulk Pd indicates the formation of the palladium nanoparticles. With the increase of Pd(OAc)₂ content, the reflections of crystalline palladium became stronger and narrower, illustrating that highly crystalline palladium nanoparticles were developed. It was manifest that the concentration of Pd(OAc)₂ in the PEG had an influence on the formation of palladium nanoparticles. The average diameter of the palladium particles calculated from Scherrer's equation demonstrated that the denser PEG solution of Pd(OAc)₂ facilitates the formation of larger nano-Pd particles.

Transmission electron microscope (TEM) analysis visualized the presence of narrow size distributed palladium nanoparticles. Fig. 2 presents the TEM images of palladium nanoparticles prepared at 80 °C and 120 °C using PEG 2000 and PEG 4000. It is seen that the average dimensions of nano-Pd fabricated at different temperatures deviated little. Both samples show the average size around 5 nm, even though the separation of palladium nanoparticles prepared at 80 °C was more widely than those prepared at 120 °C. This may be a consequence of the good stability effect of PEG to the palladium nanoparticles. The large number of oxygen in the

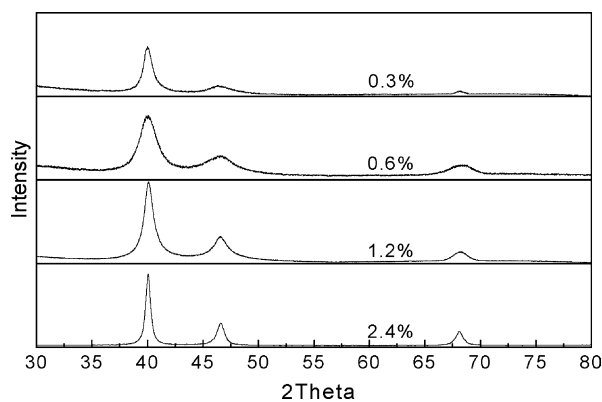


Fig. 1. XRD patterns of nano-Pd prepared in PEG 2000 with different amount of Pd(OAc)₂ (wt.%) at 80 °C for 2 h.

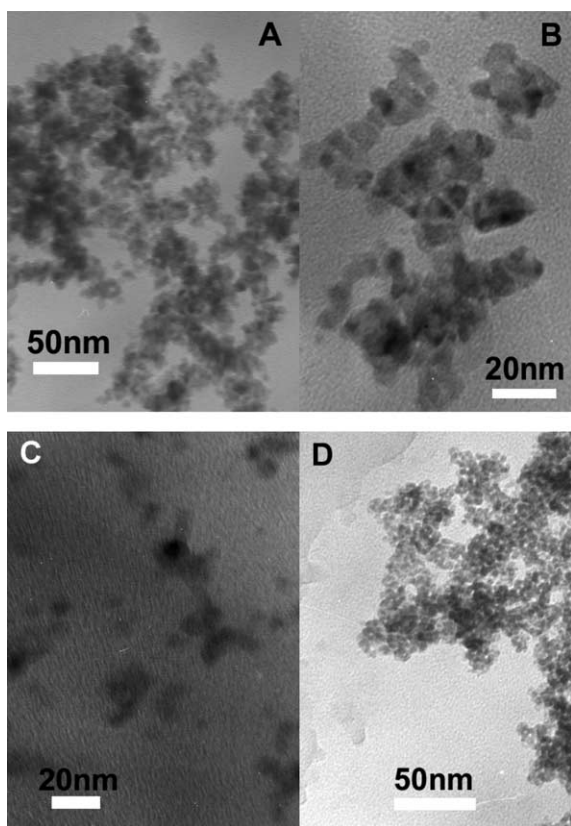


Fig. 2. TEM images of palladium nanoparticles prepared at different temperatures for 2 h by PEG (PEG:Pd(OAc)₂ = 4:0.05 g). (A) PEG 2000, 80 °C; (B) PEG 2000, 120 °C; (C) PEG 4000, 80 °C; (D) PEG 4000, 120 °C.

long PEG chains provided coordinative saturation of dangling bonds on the surface of the nanoparticles and hence assisted in their stabilization at high temperatures.

The formation of palladium nanoparticles by heating the metal salt in PEG in the absence of any other reducing agent may occur through the oxidation of the hydroxyl group in PEG. The analysis of PEG after the reaction by ¹H NMR revealed that a new peak appeared at $\delta = 9.75$, which could be attributed to the formation of the aldehyde during the reduction of Pd(II).

It is interesting that the reactivity of PEG is very sensitive to its average molecular weight. Fig. 3 displayed the experimental UV–vis spectra of the palladium nanoparticles by using different molecular weight PEG as reducing agent at 100 °C for 1 h. The amount of PEGs in all of the experiments was the same (4 g). No reaction was observed for ethylene glycol and PEG 200 at this condition. A weak decrease of the absorbance intensity using PEG 600 was observed at 400 nm, showing that palladium nanoparticles were developed at a relatively low concentration. The intensity of this peak further decreased when PEG with larger chain length was applied. In the cases of using PEG 4000, the peak at 400 nm was disappeared, revealing that full conversation of Pd(II) to nano-Pd. The behavior of different molecular weight PEG is indicative of rapid reduction of Pd(II) to palladium particles with larger

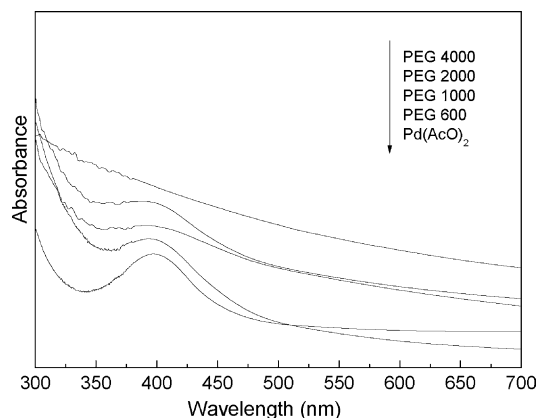


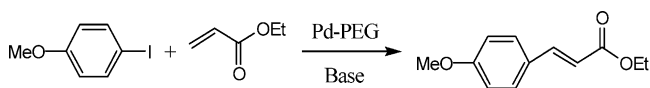
Fig. 3. UV–vis absorption spectra of the palladium nanoparticles using different PEG at 100 °C for 1 h.

polymer chain length PEG. It is clear that the reducing reactivity of PEG was markedly increased with the enhancement of its average molecular weight. The precise mechanism for this change is unclear but might be related to the formation of metal complexes. It is reported that metal complexation stabilizes the metal cation against reduction [34]. A decreasing of chain in PEG might facilitate the more effective coordination of PEG with metal ions, and hence inhibit the electron transfer involved in the reduction of metal ions. Another explanation for the poor activity of shorter chain PEG was envisaged in the possibility of easier nucleation in the pseudo random coil conformation of larger chain length PEG.

The catalytic reactivity of as-prepared nano-Pd to Heck reaction involving the cross-coupling of aryl halides with styrene and ethyl acrylate was tested. The reactions were performed in Pd-PEG by using 4.5 mmol% of the palladium related to aryl halide. All of the coupling reactions of aryl halide with diverse olefins were performed in the absence of any phosphine ligand. The product was easily extracted by ether, and the residue was employed as the catalyst of recycling reaction.

We first screened a number of bases for the reaction. The base showed the different effect to the various catalysis systems of Heck reaction [17,36]. In the Heck reaction using Pd supported on activated carbon by Heidenreich et al. [42], sodium acetate showed the higher activity than the other bases like amines. Zhao et al. [37] disclosed that the concurrent use of inorganic and organic base could increase the rate of the Heck reaction catalyzed by Pd/SiO₂ and Pd/C. The scope of the Pd-PEG catalyst for Heck reaction was examined with use of iodobenzene at 100 °C for 8 h. All the reaction went to completion and there was no difference between various bases. To determine the reactivity of the catalyst in various bases, the relatively less active 4-iodoanisole was chosen as the initial coupling partner in combination with ethyl acrylate as a model reaction for investigation of the optimal reaction conditions (Table 1). The catalyst of Pd-PEG was prepared by using 4 g PEG 2000 and 0.05 g Pd(OAc)₂ at 80 °C for 2 h with magnetic stirring. Employing the catalyst generated

Table 1
Heck reaction of 4-iodoanisole with ethyl acrylate catalysed by Pd-PEG



Entry	Temperature	Base	PEG	Conversion ^{a,b} (%)
1	100	Na ₂ CO ₃	PEG 2000	92
2	100	DBU	PEG 2000	23
3	100	KOH	PEG 2000	15
4	100	NaOAc	PEG 2000	87
5	100	N(Et) ₃	PEG 2000	90
6	100	K ₃ PO ₄	PEG 2000	95
7	120	K ₃ PO ₄	PEG 2000	94
8	80	K ₃ PO ₄	PEG 2000	87
9	120	K ₃ PO ₄	PEG 4000	94
10	100	K ₃ PO ₄	PEG 4000	86
11	100	K ₃ PO ₄	PEG 1000	50
12	120	K ₃ PO ₄	PEG 1000	72

^a The reactions were carried out at indicated conditions for 8 h. The amount of nano-Pd was 4.5 mmol% relative to the amount of aryl halides.

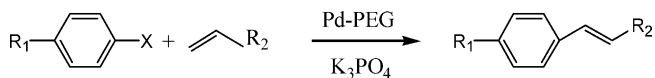
^b Conversion of 4-iodoanisole was obtained by GC analysis.

from Pd(OAc)₂ with Na₂CO₃ as base at 100 °C delivered 92% of the expected product (Table 1, entry 1), while exchanging the base to DBU or KOH under the same conditions gave the low yields (entries 2 and 3). The bases of NaOAc, N(Et)₃, and K₃PO₄ were also evaluated and all the reactions examined led to some conversion with K₃PO₄ giving the best results. In addition, the reaction was sensitive to temperature. Low conversion occurred at 80 °C (entry 8), while temperatures higher than 100 °C afforded good conversions and yields (entries 6 and 9).

Toluene was often used as solvent in the Heck reaction catalyzed by supported palladium and there was almost no leaching detected in the Heck reaction performed in toluene in some cases [35]. In our experiment, however, a light yellow extraction solution at the end of reaction was obtained in the coupling of iodobenzene with acrylate when toluene was used as solvent, illustrating the higher leaching of palladium. The combination of toluene and ethanol (9:1) remarkably reduced the leaching, and the conversion of the product was not influenced by the replacement of toluene with the mix solvent.

As we discussed above that the PEG with different chain length had effect on the conversion of Pd(II) to Pd⁰. The larger chain length PEG was more favorable to the fabrication of palladium nanoparticles. However, it was found that PEG 2000 showed the best reactivity to the Heck reaction. When PEG 4000 was applied as the reaction medium, the conversion was decreased slightly (entry 12). The decline of the conversion for PEG 4000 may rise from the fact that PEG 4000 was more viscous than PEG 2000 at 100 °C, which resulted the less efficiency of stirring. When the temperature was increased to 120 °C, high conversion was obtained with

Table 2
Heck reactions of aryl halide with olefins catalyzed by Pd-PEG



Entry	R ¹	R ²	X	Time	Yields ^{a,b}
1	–NO ₂	–CO ₂ Et	I	8	85
2	–Cl	–CO ₂ Et	I	8	92
3	–H	–CO ₂ Et	I	8	93
4	–OMe	–CO ₂ Et	I	8	90
5	–NO ₂	–C ₆ H ₅	I	8	89
6	–Cl	–C ₆ H ₅	I	8	90
7	–H	–C ₆ H ₅	I	8	95
8	–OMe	–C ₆ H ₅	I	8	91
9	–CHO	–CO ₂ Et	Br	10	90 ^c
10	–CHO	–C ₆ H ₅	Br	10	88 ^c
11	–COCH ₃	–CO ₂ Et	Br	10	80 ^c
12	–COCH ₃	–C ₆ H ₅	Br	10	85 ^c
13	–H	–C ₆ H ₅	Br	14	35
14	–H	–CO ₂ Et	Br	14	30

^a Isolated yield. All the reactions were carried out at 100 °C for 8–14 h. The amount of nano-Pd was 4.5 mmol% relative to the amount of aryl halides.

^b All of the products were isolated as *trans*-isomers.

^c Sodium acetate as base.

PEG 4000. The conversion by exploiting PEG 1000 was obviously reduced, which could be attributed to the less stabilizing effect to nano-Pd and lower reducing reactivity of short chain length PEG to Pd(II).

Extension of the reaction to other substituted aryl iodides afforded the high yields as shown in Table 2. It was found that there was no difference between electron withdrawing substituents (nitro, chloride) and electron donating group (methoxy) (Table 2, entries 1–4). Displacement of ethyl acrylate to styrene gave excellent yields (entries 5–8). All of the obtained products were *trans*-isomers, which were identified by GC and ¹H NMR. When activated aryl bromides were used as starting materials, good conversion was also obtained with NaOAc as the base (Table 2, entries 9–12). However, the as-prepared nano-Pd was less efficient in catalyzing the coupling of deactivated aryl bromide (entries 13–16).

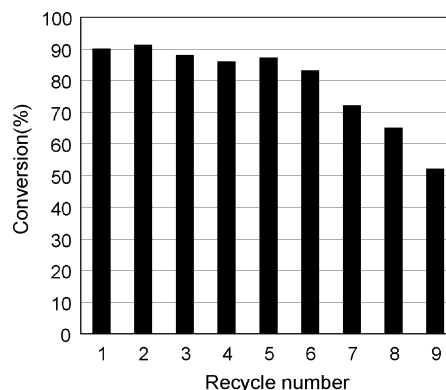


Fig. 4. Conversion of the recycle experiments by using Pd-PEG 2000 as catalyst in the coupling of 4-iodoanisole with ethyl acrylate.

Table 3
Evaluation of palladium leaching in the recycling experiments

Recycle number	1	2	3	4	5	6	7
Concentration ($\mu\text{g/ml}$)	0.08	2.33	0.30	0.30	0.30	0.30	0.30
Pd leaching (%)	0.017	0.48	0.064	0.064	0.064	0.064	0.064

The coupling of iodobenzene with ethyl acrylate was taken as the model reaction. The amount of nano-Pd was 4.5 mmol% relative to the amount of iodobenzene.

The lifetime is an important point concerning the use of the catalysts, especially in industrial and pharmaceutical applications. Our results presented above demonstrated that Pd-PEG was an efficient catalyst system for the Heck reaction. In order to investigate the recovery and reuse of the catalyst, the Pd-PEG catalysts after the treatment of ether were used for the same reactions under the similar conditions. $\text{N}(\text{Et})_3$ was proven to be more efficient in the recycle of the catalyst as a base, albeit K_3PO_4 provided the best conversion in the first run. The Pd-PEG was readily reused after the treatment of ether in the recycle experiments and the reuse experiments were repeated until lower yield was observed. Fig. 4 presented the results of recycle efficient of the catalyst system with the coupling of 4-iodo-anisole with ethyl acrylate. It is seen that the Pd-PEG had been reused six times without significant loss in activity. Ionic liquid systems were suitable for catalyst recycling, and ionic liquids were applied recently as the reaction medium of Heck reaction in the absence or presence of phosphine ligands [38,39]. It was reported that the recycling reaction yield decreased after 4 runs using PdCl_2 ionic liquid without phosphine ligand [40] and the recycling reaction could be performed without loss in the reaction yield at least 12 runs when using the phosphapalladacycle compound [41]. Our results demonstrated that Pd-PEG was an efficient and recyclable catalyst system for the Heck reaction in the absence of phosphine ligands.

Obviously, PEG had played an important role to the properties of the nano-Pd. It is well known that the nanosized metal particles are effective catalysts for chemical transformations. However, the metal nanoparticles are unstable and go through aggregation in most cases, which leads to the loss of the catalytic reactivity and the catalyst recycling is often hampered by early formation of palladium black. Stabilizers, such as polymer, surfactants, or ligands, are therefore applied in the preparation on nanoparticles to prevent the aggregation. In some cases the stabilizers are too effective to strongly absorb on the surface of the nanoparticles, which also makes the nanoparticles inactive. Although some of the supported nanopalladium catalysts exhibited high activity with the coupling of deactivated aryl bromides and chlorides, the reactivity of as-prepared Pd-PEG was analogous with the most colloidal palladium catalysts reported, which was effective with aryl iodides and activated aryl bromides. The results show that PEG provides the protection to the palladium nanoparticles, but with some surface deactivation.

Involving nano-palladium particles, the process of the heterogeneous catalysts mediated the Heck reaction may thoroughly different. Blackmond [46] and Reetz [47] reported that the reaction occurred at the surface of the catalysts. On

the other hand, the studies by Biffis [44] and Arai [48] showed that the activity was proportional to the leached palladium, implying that the catalytic reactions actually performed at homogeneous phase. In order to ascertain the situations in Pd-PEG system, the coupling of iodobenzene with ethyl acrylate was carried out for the Heck reaction using the Pd-PEG as catalyst at 100°C . The experiment was terminated after 3 h, and the conversion was found to be 25%. The reaction mixture was cooled to 0°C and the Pd-PEG were separated by filtration. The reaction was continued with the filtrate for an additional 5 h, and the conversion almost remained unchanged, indicating that the palladium in Pd-PEG was only active. This showed that the reaction proceeded most possibly on the heterogeneous surface of the nano-palladium.

The leaching of active species is a serious problem for supported metal catalysts, which prohibits the catalyst separation and recycling. The leaching of supported palladium catalyst in the presence of ligands or some solvents was much more pronounced [42–44]. Previous studies about the leaching of Heck reaction catalyzed by supported palladium indicated that many factors influenced the palladium leaching during and after the reaction, which including solvent, base, substrate and product, the surface nature of supports, and so on [37,42,44,45]. We studied the leaching of Pd-PEG systems at the recycle experiments by determination of the Pd content in the extraction solution at the end of the reaction. The leaching of palladium in the recycling of the Pd-PEG was detected by ICP-AES and the result was presented in Table 3. The subsequent ICP-AES analysis of the crude product (obtained by extraction of Pd-PEG by ether) showed that palladium levels were around 0.3 ppm corresponding to 0.064% leaching of the original Pd content. This indicated that the extent of leaching of the palladium species was extremely low. The results are especially significant for product purification and economic synthesis.

4. Conclusion

In summary, an easy mild novel method for preparing nano-Pd was described by exploiting PEG containing no other reducing agent for the first time. Both XRD and TEM reveal that nanosized palladium was not only fabricated by reducing of PEG under mild conditions, but was stabilized suitably by PEG. The as-prepared nanosized palladium particles have a narrow size distribution and the concentration of palladium(II) acetate influences the crystalline of palladium. The as-prepared Pd-PEG systems exhibited a high activity towards the Heck reaction without use of toxic ligands or

activation. The catalysts can be easily recycled to six times without significant loss in reactivity, which are of great importance to the practical applications.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [10.1016/j.molcata.2004.10.039](https://doi.org/10.1016/j.molcata.2004.10.039).

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