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Short Communication

An efficient ligand- and copper-free Sonogashira reaction catalyzed by palladium nanoparticles supported on pectin

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ABSTRACT

A novel and green procedure for synthesis of Palladium nanoparticles (2–6 nm) supported on pectin, as a reductant and ligand is described. The synthesized catalyst was further successfully explored in copper, ligand- and amine-free Sonogashira–Hagihara coupling of various aryl iodides, bromides and chlorides as well as heteroaryl halides with phenylacetylene under aerobic conditions. It was found that the catalyst exhibited a high activity and selectivity for the Sonogashira–Hagihara reaction. The catalyst can be recovered and recycled by a simple filtration of the reaction solution with some decrease in catalytic activity.

1. Introduction

Palladium catalyzed methods for formation of carbon–carbon bonds have been widely studied because of the usefulness and wide applicability to various substrates [1,2]. In recent years, investigators have focused their attention to reduce the cost of the reaction either by replacing palladium with cheap metals [3] or by using palladium nanoparticles immobilized on solid supports [4,5]. In this regard, immobilization of the catalysts to organic [6] or inorganic [7] supports has gained much attention because they offer several advantages such as easy separation, low waste and low cost.

In the last few years, immobilization of the palladium nanoparticles on solid supports to prepare active and stable catalytic systems is an interesting topic, and various supports have been employed to stabilize the nanoparticles, such as silica [8], carbon nanotube [9], metal oxides [10], polymers [11], magnetic-material [12], dendrimer [13] and ionic liquid [14]. Despite significant advances in the use of new supports with various ability for stabilized of palladium nanoparticles, less attention has been paid to bioorganic polymers [15–18] such as carbohydrate-based materials. Carbohydrate-based materials such as polysaccharides are attracting growing interest as substitutes for classical inorganic and organic supports for environmentally friendly catalysts. Along this line, Pd/chitosan [19,20] and Pd/starch [21] have been prepared using polysaccharides as the bed. In addition, they are cheap, non-toxic, environmentally friendly and readily available in the nature.

Pectin is a polysaccharide that is found extensively in all plant primary cells. It is a natural polymer which extensively employed in food industry, as a thickener or stabilizing agent. Pectin is a linear chain of 1,4-linked α-D-galacturonic acid residues in which some of the carboxyl groups are methyl esterified (Fig. 1). Eye-catching properties of pectin, such as flexibility, biodegradability, non-toxicity, low price and carrying freely available hydroxyl groups make it suitable and ideal candidate for many practices in different areas of science [22,23]. Pectin contains free carboxyl groups on its backbone which can form complexes with Pd(II) ions in solution and reduce them to Pd(0) without using any extra reducing agent such as $NaBH_4$, hydrazine or molecular hydrogen. This slow rate in situ reduction of Pd(II) to Pd(0) causes the formation of small size and well distributed palladium nanoparticles on the surface of pectin.

Recent development in Pd-catalyzed reactions has revealed that palladium nanoparticles can catalyze various C – C coupling reactions including Mizoroki–Heck, Suzuki–Miyaura and Sonogashira–Hagihara reactions [24]. The Sonogashira–Hagihara coupling reaction is often used as a key step in the $sp–sp^2$ carbon–carbon bond forming reactions [25]. The Sonogashira coupling reaction of terminal alkynes and aryl or alkenyl halides provides an efficient method to the synthesis of aryl alkynes [26]. This reaction is performed in the presence of catalytic amounts of a palladium complex and copper(I) iodide in the presence of a base [27]. Using copper iodide as the co-catalyst sometimes lead to the homo-coupling reaction of terminal alkynes [28]. In order to solve this problem, copper-free systems for this reaction were reported [29]. In this paper, we report a ligand- and copper-free Sonogashira reaction catalyzed by palladium nanoparticles stabilized by pectin as biopolymer support under aerobic conditions.

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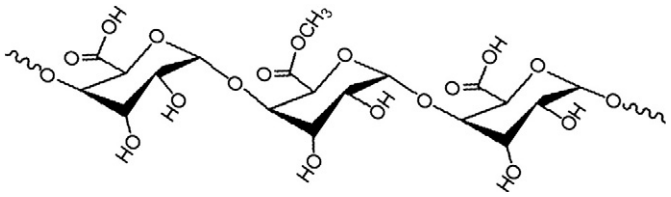


Fig. 1. Chemical structure of pectin.

2. Experimental

2.1. Gram-scale preparation of palladium nanoparticles supported on pectin

Pectin (1 g) was dissolved in water (100 mL) at ambient temperature. To this solution was added a solution of $PdCl_2$ (100 mL, 1 mM) and diluted with water (100 mL). The reaction mixture was refluxed at 100 °C for 4 h. The mixture was cooled down to room temperature and the solvent was evaporated. The obtained dark gray composite was dried by the flow of air over night and then under vacuum for 24 h.

2.2. General procedure for the Sonogashira–Hagihara reaction in the presence of the nanocatalyst

Into a conical flask, a mixture of pectin supported Pd nanoparticles (0.05 g of the composite, contains 0.0028 mmol of Pd), aryl halide (1 mmol), terminal acetylene (2 mmol), KOAc (1.5 mmol) and DMF (2 mL) were stirred at 100 °C under aerobic conditions. After completion of the reaction (monitored by TLC or GC), water (10 mL) and ethylacetate (10 mL) was added to the reaction mixture and decanted. The organic layer was dried over anhydrous Na_2SO_4. After evaporation of the solvent, the products were purified by column chromatography. Finally, evaporation of the solvent gave the desired pure products in good yields.

3. Results and discussion

The palladium nanoparticles supported on pectin were prepared by addition of aqueous solution $PdCl_2$ (100 mL, 1 mM) to pectin (1 g dissolved in 100 mL water) without using any extra reducing agent. This solution was refluxed for 4 h giving a dark gray solution. Evaporation of the solvent followed by drying gave a dark gray solid.

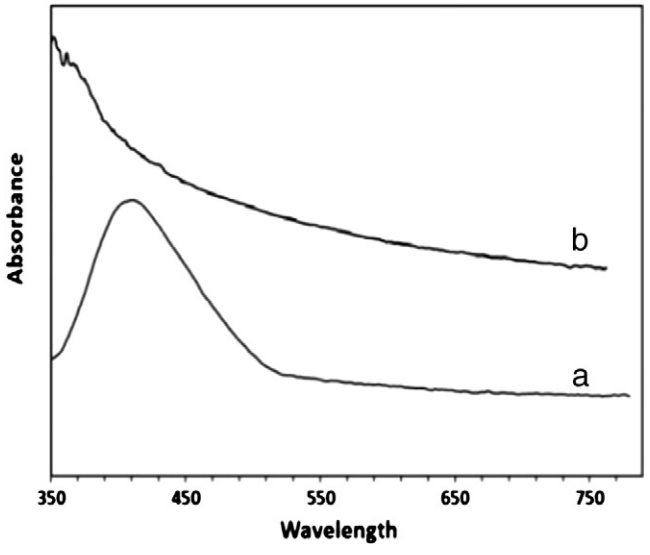


Fig. 2. UV–vis spectra of (a) Pd(II) before reduction and (b) Pd(0) after reduction with pectin.

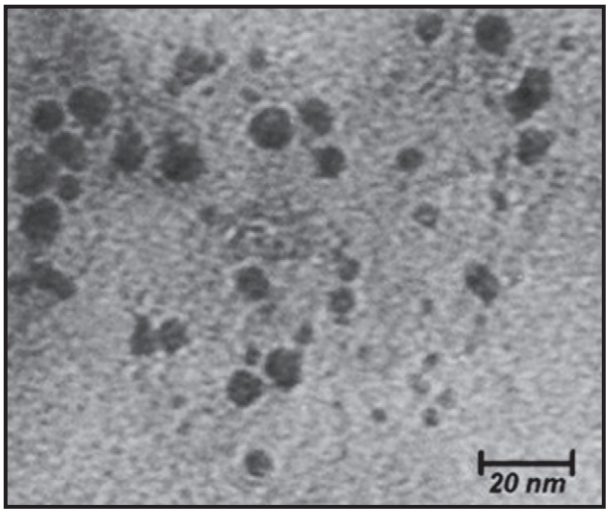


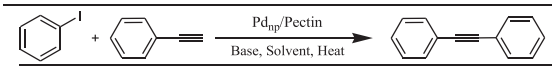
Fig. 3. TEM image of palladium nanoparticles supported on pectin.

Our initial efforts were focused on the characterization of the resulting Pd supported nanoparticles. The UV–Vis spectroscopy of the resulted material showed the complete conversion of Pd(II) to Pd(0) which was proved by the disappearance of the peak at around 430 nm (Fig. 2). The presence of palladium in the obtained material was confirmed by energy dispersive X-ray analysis (EDX) and its loading amount was measured to be 0.61% w/w. The EDX spectrum also shows other elements, including C and O, which are present in the pectin substrate (Supporting information, Fig. 1S). The X-ray diffraction (XRD) spectroscopy of the resulted material shows four peaks at (111), (200), (220) and (311) crystallographic planes related to the formation of Pd(0) (Supporting information, Fig. 2S).

The transmission electron microscopy (TEM) image shows that the average size of the Pd nanoparticles entrapped by pectin is around 2–6 nm (Fig. 3). The amount of palladium content deposited on the surface of pectin was detected by ICP and EDX. According to the ICP results the amount of palladium to be 0.056 mmol per gram of the pectin. Energy dispersive X-ray (EDX) results showed that the amount of palladium to be 0.057 mmol per gram of the pectin.

After characterization of the composite, the catalytic activities of Pd_{np}/Pectin were examined in the Sonogashira reaction. Initially, the optimum conditions were investigated for the reaction of iodobenzene with phenylacetylene in the presence of the nanocatalyst (Table 1). The effect of solvents and bases was studied upon the reaction at different

Table 1
Optimization conditions in Sonogashira reaction between iodobenzene and phenylacetylene in the presence of Pd_{np}/Pectin.



Entry	Solvent	Base	Temperature (°C)	Time	Conversion (%)
1	H_2O	KOAc	100	5 h	Trace
2	H_2O/TBAB	KOAc	100	3 h	20
3	TBAB	KOAc	100	50 min	91
4	TBAB	NaOAc	100	2 h	73
5	PEG	KOAc	100	70 min	82
6	DMF	KOAc	60	4 h	Trace
7	DMF	KOAc	80	4 h	78
8	**DMF**	**KOAc**	**100**	**25 min**	**100**
9	DMF	NaOAc	100	65 min	60
10	DMF	DABCO	100	55 min	81
11	DMF	K_2CO_3	100	85 min	52
12	DMF	Et_3N	100	3 h	Trace
13	DMF	n-Pr_3N	100	3 h	15