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Reusable biomacromolecule-Pd complex catalyzed C–C cross-coupling reactions via C–S cleavage of disulfide

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ABSTRACT

A well-defined heterogeneous palladium catalyst, natural wool supported $Pd(OAc)_2$-complex was found to be an effective catalyst [illegible] the C–S bonds cleavage and C–C bonds formation from 1,2-di(pyrimidin-2-yl)disulfane derivatives with arylboronic acids or terminal alkynes, giving the desired coupling products in moderate to excellent yields. The novel catalyst, which is stable and easy handling in experiment, was characterized by XPS, IR, SEM and ICP analysis. Subsequent analysis of the used catalyst after reaction revealed its negligible metal leaching and at least 10 rounds of recycled catalyzing capacity and wide range of substrate tolerance.

1. Introduction

Heterogeneous catalysis, a recent focus of research among the organic synthesis, as a method of catalyst reuse has attracted much attention not only from academe,[1–[illegible]] but it was also largely applied in the industrial production.[11–[illegible]] Among the catalytic organic synthesis, it has always been the subject to investigate on the bonds cleavage and formation that catalyzed by transition metal on one side, and also the transition-metal complexes[18–26] for the other, which both achieved dramatic progress recently.

Many organic molecules were used as substrates in organic synthesis to construct new structures. Among various organosulfur compounds, disulfides, [illegible] existed in biosphere, can be used as a valuable material and intermediate for the organic synthesis. Efforts in this field [illegible] the C[illegible] S–S bonds cleavage of the disulfides bred plenty of publications.[27–39] Among our recent observations towards the palladium and cuprous-catalyzed desulfurative C–C cross-coupling reactions,[40–43] progress was also made for the conversion of disulfides via C–S bonds cleavage with arylboronic acids and terminal alkynes as nucleophiles.[41] But in these reactions, large quantities of transition metal as palladium and copper were used as catalyst and cast off as waste thereafter. Continuous efforts were made in our laboratory to improve those catalytic systems in consideration of environmental protection as well as materiel economy. And the heterogeneous catalysis was thereupon incorporated in our speculations for her virtues as recyclability, easy separation, and non-residue of catalytic metal such as palladium.

As a matter of fact, plenty organic (mainly organic polymers), inorganic (silica, zeolites, metal oxides, etc.) and hybrid organic–inorganic (mainly grafted silica) supported palladium nanoparticles have been used as catalysts for chemical transformations.[44–57] However, a serious defects that reduces the activity of heterogeneous catalyst is the palladium-leaching. This would mainly rest on the size of palladium, and the formation of inactive large particles (even bulk Pd) during the catalytic reactions.[58]

In the past decade, natural biomacromolecules as chitosan,[59,60] cellulose,[61] wool,[62–65] etc. were reported as supporters for the palladium catalysts and applied in several important reaction processes. In our previous studies, a biomacromolecule-$PdCl_2$ complex catalyst was prepared via simple methods.[66–68] This wool-anchored palladium catalyst was successfully used in multiple catalytic processes like Suzuki, Sonogashira, Heck, photocatalysis and photodegradation coupling reactions. Wool fibre, natural biopolymer of ordered amino acids that were cross-linked by S–S

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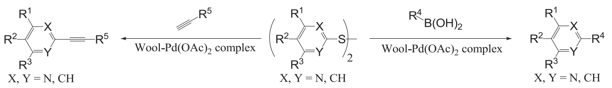
bonds, is covered with many hybrid pores on the surface. This feature anchors a high dispersion of palladium particles and prevents the aggregation of palladium-black. Due to their biodegradability, biocompatibility, ready availability, and low cost, wool attracted growing interest as environment friendly substitutes for classical organic inorganic and polymer supports. But still, this catalyst remains the practical drawbacks like low TONs and low-activity for the heteroaromatic compounds. In reply to these problems, we prepared a new generation of wool-Pd(OAc)$_2$ complex catalyst.

So far, this biomacromolecule-Pd(OAc)$_2$ complex catalyst, remains spaces unexplored, can be applied as excellent catalyst for the C–C cross-coupling reactions under Suzuki conditions and for the desulfurative coupling reactions. In this paper, therefore, as a part of our ongoing research in desulfurative C–C coupling reactions, we introduce the similar processes of disulfides catalyzed by a recyclable wool supported Pd(OAc)$_2$ complex catalyst (Scheme 1). Notably, the preparation of this novel heterogeneous catalyst is easy to operate, with the wool-Pd(OAc)$_2$ produced as a stable complex with high catalytic activities (the total TONS is 916). Subsequent analysis indicated negligible palladium leaching of the catalyst, which can be reused in cyclicity for at least 10 rounds recovered.



Scheme 1. Wool-Pd(OAc)$_2$ catalyzed C–C coupling reactions of disulfides.

2. Results and discussion

2.1. Synthesis and characterization of the catalyst

The typical route of wool-Pd(OAc)$_2$ complex synthesis: [illegible]0 g the treated-wool pieces prepared in our laboratory[66] (a, Fig. 1) and 0.2 g Pd(OAc)$_2$ were dipped in 30 mL of de-ionized water, the mixture was stirred at rt for 3 h until the white wool pieces were changed to brownish yellow. Then the wool-Pd(OAc)$_2$ complex catalyst was filtered and washed with de-ionized water (3×20 mL) and acetone (3×20 mL), dried in a vacuum oven at 50 °C for 4 h ([illegible] Fig. [illegible]). The palladium content in Wool-Pd(II) complex was determined by means of inductively coupled plasma equipped with atomic emission spectrometry (ICP-AES) and amounted to [illegible]1.56 wt % (0.1[illegible]mol/g).

Fig. 1. (a) Wool an[illegible] wool-Pd(OAc)$_2$ complex catalyst.

The detailed electronic configurations of wool-Pd(OAc)$_2$ complex was examined by means of X-ray photoelectron spectroscopy (XPS) measurements (Table 1). It was realized that Pd_{3d} peaks are consisted of two components with binding energy at 343.75 eV ($Pd_{3d3/2}$) and 338.38 eV ($Pd_{3d5/2}$) in Pd(OAc)$_2$, and 343.08 eV ($Pd_{3d3/2}$) and 337.71 eV ($Pd_{3d5/2}$) in wool-Pd(OAc)$_2$ complex, respectively, which are originated from $Pd_{3d3/2}$ and $Pd_{3d5/2}$ of Pd(II). The difference of Pd_{3d} binding energy features the electron density increase as Pd_{3d} binding energy changes (Fig. [illegible]). Similarly, the peak at 400.37 eV is assigned to the binding energy of $-NH_2$ (N_{1s}) in wool; it was found to be 0.54 eV higher than that in wool-Pd(OAc)$_2$. The difference between –NH–CO– in wool and –NH–CO– in the catalyst is 0.32 eV (Fig. [illegible]). Furthermore, there are four major peaks with binding energies at 16[illegible]63 eV, 168.18 eV, 165.05 eV, and 163.80 eV in wool, corresponding to $-SO_x-$, –S–S–, and –SH, respectively.[69,70] The change of $-SO_x-$ binding energy in wool and in complex are 0.55 eV and 0.22 eV. The difference of S_{2p} binding energy between –S–S– in wool and wool–Pd(OAc)$_2$ complex is 0.72 eV, and that of –SH is 0.47 eV (Fig. 4). Likewise, little change of the binding energy of the O_{1s} was observed. The results show O is uncreative, and the coordination or ionic bonds were formed in Pd(OAc)$_2$ with $-NH_2$, –NH–CO–, $-SO_x-$, –S–S– and –SH in wool.

Table 1
XPS date of the Pd(OAc)$_2$, wool and wool-Pd(OAc)$_2$ complex[a]

XPS peaks		Binding energy (eV)			ΔE_b(eV)
		Pd(OAc)$_2$	Wool	Wool-Pd complex	
Pd_{3d}	$Pd_{3d\ 3/2}$	343.75		343.08	−0.67
	$Pd_{3d\ 5/2}$	338.38		337.71	−0.67
N_{1s}	$-NH_2$		400.37	399.83	−0.54
	–NH–CO–		400.05	399.73	−0.32
S_{2p}	$-SO_x-$		169.63	169.08	−0.55
			168.18	167.96	−0.22
	–S–S–		165.05	164.33	−0.72
	–SH		163.8	163.33	−0.47
O_{1s}			531.93	532.08	0.15

[a] The binding energy is referre[illegible]84.80 eV.

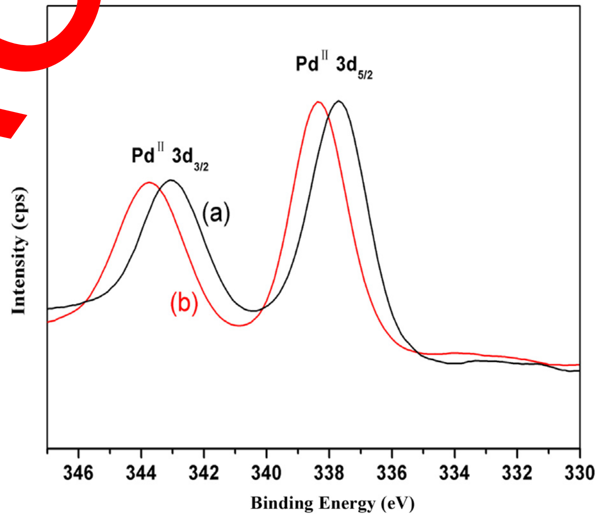


Fig. 2. XPS spectra of (a) wool-Pd(OAc)$_2$ complex, (b). Pd(OAc)$_2$.

In order to further investigate the chemical structural changes from wool to wool-Pd(OAc)$_2$, Fourier transform infrared spectroscopy (FT-IR) measurements was performed (Fig. 5). In Fig. 5 (a), the absorption bands at 1689 and 1510 cm^{-1} are attributed to C=O stretching and $-CH_3$ bending vibration of Pd(OAc)$_2$, respectively. In the wool, the peak at 3410 cm^{-1} can be assigned to the characteristic the –NH stretching vibration bands of $-NH_2$, and the bands at 1529 cm^{-1} and 1648 cm^{-1} can be attributed to the –NH and C=O bending vibration of –NH–CO–. And in wool-Pd(OAc)$_2$, the –NH stretching vibration bands of $-NH_2$ has shifted to a higher wave number (3423 cm^{-1}), indicating a decrease in the $-NH_2$ group fraction. Furthermore, the –NH bending vibration bands of –NH–CO– has moved from 1529 cm^{-1} to 1514 cm^{-1}. Therefore, it can be confirmed in further that in the wool-Pd(OAc)$_2$ complex,