Cellulose supported palladium(0) catalyst for Heck and Sonogashira coupling reactions

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Abstract

Cellulose supported palladium(0) catalyst was prepared and applied for the Heck and Sonogashira coupling reactions by treating aryl iodides with alkenes and phenylacetylene, respectively, to afford corresponding coupled products in good to excellent yields. The catalyst was recovered by simple filtration and reused for several cycles.
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1. Introduction

Heterogeneous catalysis for the synthesis of fine chemicals is particularly attractive as it allows production and ready separation of large quantities of products with the use of a small amount of catalyst [1]. Majority of the reported supports for catalytic applications are based on pure inorganic materials or functional polymers in which the synthesis of the supports involves either high temperature calcinations or polymerization of petrochemical feed stocks. In recent years, the emphasis of science and technology is shifting more towards environmentally friendly and sustainable resources and processes, in this regard biopolymers are attractive candidates to explore for supported catalysis [2,3].

Several interesting features of the biopolymers for example, high sorption capacity, stability of metal anions, and physical and chemical versatility make them attractive to use as supports. Moreover, the polymers can be moulded in different forms, flakes, gel beads, membranes, fibers, hollow fibers, sponge or supported on inert materials. In recent years, efforts have been devoted to use several biopolymers, for example alginate [4], gelatin [5], starch [6] and chitosan [7] derivatives as supports for catalytic applications.

Cellulose is the most common biopolymer represents about 1.5×10^{12} tons of the total annual biomass production. Cellulose and its derivatives are produced on an industrial scale and used for coatings, laminates, optical films as well as for property-determining additives in building materials, pharmaceuticals, foodstuffs and cosmetics [8]. However, its use as a support for catalytic applications is not well explored. Recently, Choplin and co-workers reported cellulose as the support for water soluble $Pd(OAc)_2$/5 TPPTS system in Trost Tsuji allylic alkylation reaction [9]. Similarly cellulose supported Pd-metal complexes are used for hydrogenations reactions [10]. Li et al. utilized the cellulose-supported tetraethylenepentamine as a catalyst for the Knoevenagel condensation of aromatic aldehydes with active methylene compounds [11]. Here we wish to report a ligand free and copper free process for the Heck and Sonogashira coupling reactions using cellulose supported palladium(0) as a catalyst (CELL-Pd(0)).

2. Experimental

2.1. Materials

Microcrystalline cellulose was purchased from S.D. Fine chemicals Ltd., India and is used as such. All the aryl halides, olefins and palladium chloride are purchased from Aldrich.

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2.2. Catalyst preparation

To a solution of 0.1 M (0.443 g) of $PdCl_2$ in methanol (25 mL), microcrystalline cellulose (5 g) is suspended and stirred for 15 min. Then, hydrazine hydrate (80%, 1 mL) is added drop wise for 15 min and stirred for 12 h at room temperature. The black coloured solid formed is filtered, washed several times with methanol and finally with acetone and dried under vacuum resulting cellulose supported Pd(0) catalyst (CELL-Pd(0)) in quantitative yield.

2.3. Characterization

X-ray powder diffraction (XRD) data was collected on a Siemens/D-5000 diffractometer. The elemental contents of palladium in the supported catalyst were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using Thermo electron corporation make, IRIS Intrepid 11 XDL instrument. X-ray photoelectronic spectrographs (XPS) are recorded on a KRATOS AXIS 165 instrument. ^{1}H NMR of the products was characterized using Varian-Unity 400 MHz NMR Spectrophotometer. The particle size and external morphology of the samples were observed on a JEOL JEM-100CX transmission electron microscopy (TEM).

2.4. Reaction procedures

2.4.1. General procedure for Heck/Sonogashira coupling of aryl iodides with olefins/phenylacetylene

To a mixture of aryl iodide (1.0 mmol), triethylamine (2.0 mmol) and olefin/phenylacetylene (1.2 mmol) in acetonitrile (3 mL), CELL-Pd(0) catalyst (0.05 g) was added and stirred under reflux. After a stipulated period, the reaction mixture was filtered and wash with acetonitrile. The solvent was evaporated under vacuum and ethyl acetate was added and washed with distilled water. The organic layer was separated and dried over Na_2SO_4 and the solvent was removed under vacuum. The resultant mixture was purified by column chromatography (ethyl acetate:hexane) to get the desired product, which gave satisfactory ^{1}H NMR and mass spectral data.

3. Results and discussion

The catalyst CELL-Pd(0) is prepared by simple in situ reduction of methanolic solution of palladium chloride in the presence of microcrystalline cellulose support. The X-ray diffraction pattern of CELL-Pd(0) catalyst clearly indicates the presence of Pd (1 1 1) and Pd (1 1 0) phases which are attributed to Pd(0) (Fig. 1) [12]. Further, the high-resolution XPS narrow scan [Fig. 2(a)] of the fresh CELL-Pd(0) catalyst shows two peaks at 335.4 eV of Pd $3d_{5/2}$ which is attributed to Pd(0) and 336.5 of Pd $3d_{5/2}$ which is attributed to Pd(II) [13]. Metal content in CELL-Pd(0) catalyst was analyzed by ICP-AES, which shows the presence of 4.94% (w/w) of palladium. TEM image (Fig. 3(a)) shows the formation of palladium particles in the range of 10–20 nm.

Preliminary testing for Heck reaction is carried out by treating iodobenzene with methyl acrylate in acetonitrile. All reactions
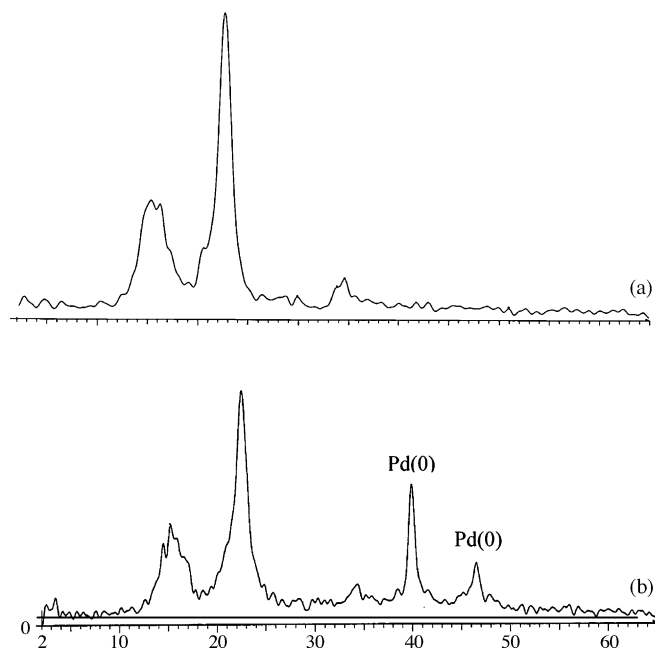

Fig. 1. X-ray diffraction spectra of (a) microcrystalline cellulose and (b) CELL-Pd(0) catalyst.
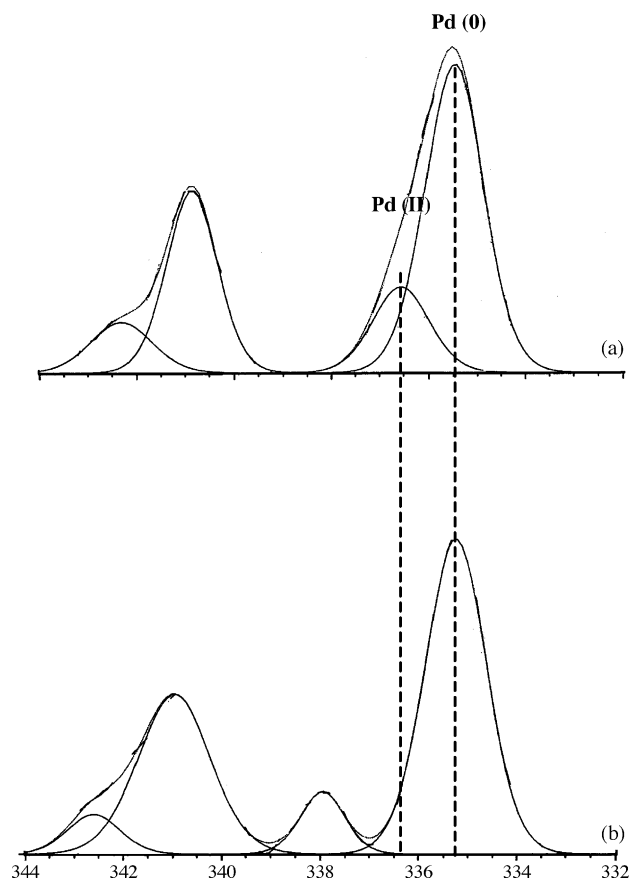

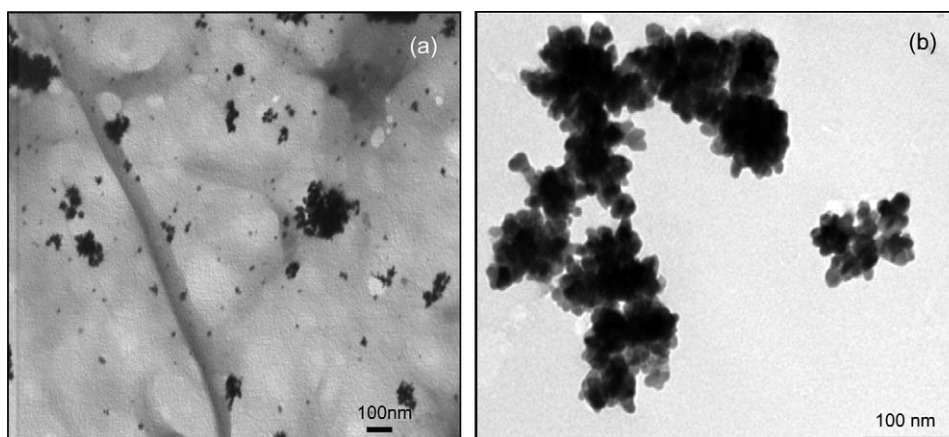Fig. 2. XPS spectra of (a) fresh and (b) used CELL-Pd(0) catalyst.

Fig. 3. TEM photographs of (a) fresh and (b) used CELL-Pd(0) catalysts.

Scheme 1.

are performed at reflux conditions by taking with 1.9 mol% of catalyst loading (Scheme 1) and the results are as shown in Table 1.

Among the various bases screened, triethylamine and K_2CO_3 provided 100% and 80% conversions, respectively (Table 1, entries 1 and 3), on the other hand no product formation is observed with KO^{t}Bu. Various solvents have been screened and acetonitrile provided high conversions where as MeOH, ^{i}PrOH and toluene resulted in trace amount of product formation (Table 1, entries 3–6). We observed good conversions with activated iodobenzenes in acetonitrile as the solvent (Table 1, entry

7), however for the deactivated iodobenzene derivatives, the conversions are very poor even at longer reaction time (Table 1, entry 8). The temperature of the reaction plays an important role, increasing the temperature to 120 °C utilizing the DMF as the solvent provided higher conversions with deactivated iodobenzene derivatives (Table 1, entries 9 and 10). Further improvements in conversions are obtained by increasing the amount of catalyst as well as duration of the reaction (Table 1, entries 11–14). Quantitative conversions are obtained for the reactions of methyl acrylate with 4-iodoanisole and 4-iodoacetophenone (Table 1, entries 11 and 12), whereas 2-iodoanisole resulted in

Table 1
CELL-Pd(0) catalyzed Heck reaction of aryl iodides with methyl acrylate[a]

Entry	R	Solvent	Temperature (°C)	Base	Time (h)	Yield (%)[b]
1	H	CH_3CN	Reflux	K_2CO_3	12	80
2	H	CH_3CN	Reflux	KO^{t}Bu	12	–
3	H	CH_3CN	Reflux	Et_3N	12	100 (98)[c], 98[d]
4	H	^{i}PrOH	Reflux	Et_3N	12	<5
5	H	CH_3OH	Reflux	Et_3N	12	–
6	H	$PhCH_3$	Reflux	Et_3N	12	17
7	p-NO_2	CH_3CN	Reflux	Et_3N	12	100
8	p-OCH_3	CH_3CN	Reflux	Et_3N	24	30
9	p-OCH_3	DMF	120	Et_3N	24	55
10	p-CH_3	DMF	120	Et_3N	24	60
11	p-OCH_3	DMF	120	Et_3N	24	100[e], 98[d]
12	p-$COCH_3$	DMF	120	Et_3N	24	100[e]
13	o-OCH_3	DMF	120	Et_3N	24	80[e]
14	3,5-Dimethyl	DMF	120	Et_3N	24	100[e]
15	H	DMF	120	Et_3N	12	100[f]
16	p-OCH_3	DMF	120	Et_3N	24	90[f], 88[d]

[a] Reaction conditions: aryl halide (1 mmol), olefin (1.2 mmol), base (2 mmol), CELL-Pd(0) 0.05 g, solvent (3 mL).
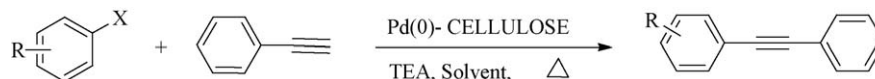[b] Yields based on NMR.
[c] Isolated yield.
[d] Yield after 4th cycle.
[e] With 0.1 g of CELL-Pd(0).
[f] Reactions with styrene.

Scheme 2.

lower conversion (Table 1, entry 13), which is due to the steric effect of the *ortho*-substitution. However, we have not observed any steric effect in the reaction of 3,5-dimethyliodobenzene with methyl acrylate, because steric influence is low at 3,5-position (Table 1, entry 14). Reactions of iodobenzene and 4-iodoanisole with styrene afforded very good conversions (Table 1, entries 15 and 16).

In order to explore the activity of the catalyst further, we tested the CELL-Pd(0) catalyst for the Sonogashira coupling (Scheme 2) of various structurally and sterically diverse aryl halides with phenylacetylene and the results are tabulated in Table 2.

Among the different solvents screened, CH_3CN was effective (Table 2, entries 1–3). Similarly, various bases such as KO^tBu, K_2CO_3 and triethylamine were screened, of which triethylamine was found to be an efficient base (Table 2, entries 4–6). Under the optimized conditions, various substituted aryl iodides were subjected to react with phenylacetylene. Reaction of 4-nitroiodobenzene with phenylacetylene afforded the coupled product in 95% yield (Table 2, entry 7), on the other hand reaction of 4-iodoanisole with phenylacetylene resulted in lower yield (Table 2, entry 8). However, there is a substantial improvement in the yield for the reaction of 4-iodoanisole with phenylacetylene when the temperature and reaction time are increased using DMF as solvent (Table 2, entry 9). Similarly, the reaction of 4-iodoacetophenone with phenylacetylene afforded higher yield of the product (Table 2, entry 10). Whereas under the same reaction conditions, 4-iodotoulene and 2-iodoanisole with phenylacetylene resulted in 42% and 75% of the coupled products, respectively (Table 2, entries 11 and 12).

Table 2
CELL-Pd(0) catalyzed Sonogashira reaction of aryl iodides with phenylacetylene[a]

Entry	R	Solvent	Temperature (°C)	Base	Time (h)	Yield (%)[b]
1	H	^iPrOH	Reflux	Et_3N	12	<8
2	H	CH_3OH	Reflux	Et_3N	12	–
3	H	$PhCH_3$	Reflux	Et_3N	12	52
4	H	CH_3CN	Reflux	K_2CO_3	12	30
5	H	CH_3CN	Reflux	KO^tBu	12	17
6	H	CH_3CN	Reflux	Et_3N	12	96, 93[c]
7	p-NO_2	CH_3CN	Reflux	Et_3N	12	95, 92[c]
8	p-OCH_3	CH_3CN	Reflux	Et_3N	24	50
9	p-OCH_3	DMF	120	Et_3N	24	98, 95[c]
10	p-$COCH_3$	DMF	120	Et_3N	24	90
11	p-CH_3	DMF	120	Et_3N	24	42
12	o-OCH_3	DMF	120	Et_3N	24	75

[a] Reaction conditions: aryl halide (1 mmol), phenylacetylene (1.2 mmol), base (2 mmol), CELL-Pd(0) 0.05 g, solvent (3 mL).
[b] Isolated yield.
[c] Yield after 4th cycle.

3.1. Reusability of the catalyst

The catalyst was recovered by simple filtration and washed with acetone and oven dried. The recovered catalyst was reused for Heck and Sonogashira coupling reactions with different aryl halides and methyl acrylate (Table 1, entries 3 and 11), styrene (Table 1, entry 16) and phenylacetylene (Table 2, entries 3, 7 and 10) respectively. These results indicate that the CELL-Pd(0) catalyst can be used for several cycles successfully with minimal loss of activity. ICP-AES results indicate leaching of 1.11% of palladium in the case of Heck reaction and 2.22% in Sonogashira reaction after the fourth cycle.

We have observed very low conversions (<20%) for Heck and Sonogashira reactions with bromobenzene upon treatment with methyl acrylate or phenylacetylene, respectively. However, the activity of the present CELL-Pd(0) catalyst for Heck coupling reactions are comparable with the recently reported Nafion–Teflon bimembrane-supported palladium catalyst [14]. Nature of the support plays a very important role for the activity of the catalyst. For example, Macquarrie and co-workers [15] observed higher activity with modified chitosan-based biopolymer supported palladium catalyst for Suzuki and Heck reactions. Similarly, from our group, it was observed that palladium catalyst supported on layered double hydroxides (LDH's) [16] shows higher activity, which is attributed to the more basic nature of the support and the large surface area associated with palladium nanoparticles. Lower activity of the present system for bromo- and chloro-derivatives may be because of either less basic nature of the support or non-uniform distribution of the particles as observed from TEM image (Fig. 3). TEM analysis of fresh CELL-Pd(0) catalyst [Fig. 3(a)] shows the presence of smaller palladium nanoparticles along with some larger aggregates. More agglomeration of the particles is observed in the used catalyst [Fig. 3(b)]. However, the consistent activity of the catalyst from the recycle experiments clearly reveals that particle agglomeration has less influence on the reactivity.

4. Conclusion

In conclusion, we have utilized the biopolymer, cellulose to prepare supported palladium(0) catalyst which was successfully applied for the Heck and Sonogashira coupling reactions to afford corresponding coupled products in good to excellent yields. The catalyst was recovered by simple filtration and reused for several cycles.

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