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β-cyclodextrin-capped palladium nanoparticle-catalyzed ligand-free Suzuki and Heck couplings in low-melting β-cyclodextrin/NMU mixtures

Xiaohua Zhao[a]*, Xiang Liu[b] and Ming Lu[b]

Low-melting β-cyclodextrin/*N*-methylurea (NMU) mixture, an efficient catalytic system for ligand-free Suzuki and Heck couplings in the presence of fresh native β-CD-capped Pd^0 nanoparticles, has been successfully reported. This natural and convenient system can be performed in air and could afford the corresponding cross-coupled products in good to excellent isolated yields after a simple workup under every low Pd loading (0.05 mol%). Remarkably, the catalytic system can be recycled and reused without loss of catalytic activity. Copyright © 2014 John Wiley & Sons, Ltd.

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Keywords: β-CD-capped Pd^0 nanoparticles; β-cyclodextrin/*N*-methylurea mixture; ligand-free

Introduction

Since the discovery of Suzuki – Miyaura and Heck reactions, both cross-couplings have attracted widespread attention and find important industrial application as one of the most important methods of forming C–C bonds.[1–6] It is well known that the use of phosphine ligands in homogeneous systems has proven to be efficient for these kinds of cross-couplings, but they are highly sensitive to air and moisture owing to the physical characteristics of the ligands. Moreover, they are comparatively difficult to prepare and tend to be expensive.[7–11] Consequently, the development of cheap and facile ligand-free palladium catalyst to overcome these difficulties is considered to be one of the most challenging fields in organic chemistry.[12–15]

Another major concern is the uses of organic solvents because of their associated environmental hazards. The main disadvantages are their pyrophoric nature, volatility and poor recovery. To circumvent some of these issues, attempts have been made to develop solvent-green chemistry.[16] Among them, solvent-free reactions have been successful for a few transformations.[17,18] However, in performing most organic reactions, solvents play a critical role in making the reaction homogeneous and allowing molecular interactions to be more efficient. In principle, water is the ideal solvent, being non-toxic, cheap and readily available, but its use is limited because most organic compounds do not dissolve in pure water and many reactive substrates or reagents decompose in water.[19,20] In recent years, ionic liquids have received a lot of attention as green solvents for their excellent properties: no measurable vapor pressure, stability over a wide temperature range and recyclability.[21] In addition, various publications and reviews have already appeared, including their application in metal-catalyzed cross-coupling.[22–25] Even though ionic liquids offer some advantages, the tedious preparation of ionic liquids (and raw materials for ionic liquids) and their environmental safety are still debated. To date, available liquid polymers or low-melting polymers, e.g. PEGs,[26–29] have been used successfully as solvents in various different reactions. B. König and co-workers[30] reported organic transformations in low-melting mixtures consisting of sugars, urea and inorganic salts as a solvent. In 2011, a paper about the synthesis of dihydropyrimidinones in low melting tartaric acid–urea mixtures was reported by B. Koenig and co-workers.[31] In this communication, we have contributed to this field and present the use of low-melting mixtures of native β-cyclodextrin/*N*-methylurea for Suzuki – Miyaura and Heck reactions. The novel medium consists only of non-toxic compounds from readily available commercial resources and has, like ionic liquids, a low vapor pressure. To the best of our knowledge, there is no report on the utility of this novel system for metal palladium-catalyzed coupling reaction. Moreover, no toxic and air-sensitive ligands need to be utilized during the entire cross-coupling process. To our delight, this system exhibited outstanding catalytic activity, stability and excellent recyclability in the presence of fresh native β-cyclodextrin-supported Pd^0 nanoparticles.

Experimental

General Information

All chemicals were reagent grade. Both β-cyclodextrin and *N*-methylurea (NMU) were purchased from Aladdin Chemistry Co. Ltd. Field emission scanning electron microscopy (SEM) analyses

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* Correspondence to: Xiaohua Zhao, School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, China. E-mail: zhao12_19@163.com

a School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, China

b School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

were performed with a JEOL JSM-7001F instrument. IR spectra were recorded in KBr disks with a Shimadzu IR Prestige-21 FT-IR spectrometer. TG was performed on a DSC 204 differential scanning calorimeter. ^{1}H NMR spectra were measured with a Bruker Avance III 500 analyzer. GC-MS analyses were performed on a Saturn 2000 GC-MS instrument.

Preparation of β-Cyclodextrin-Capped Palladium Nanoparticles (β-CD-supported Pd nanoparticles)

The procedure used in this work to prepare β-CD-supported Pd nanoparticles was reported previously.[32] In a typical preparation, 146.8 mg Na_2Cl_4Pd and 100 mg native β-cyclodextrin were dissolved in 80 ml DMF. This solution was then divided into four parts. 300 mg $NaBH_4$ was dissolved in 80 ml DMF under N_2 atmosphere. The reaction was continued overnight. DMF was then removed by centrifugation. The residue was washed four times with 100 ml DMF and subsequently with 100 ml ethanol/water (90/10) mixed solvent. The final product was redissolved in 5 ml pure water in a 100 ml round-bottom flask and freeze-dried to yield a deep-brown powder.

General Procedure for Suzuki Cross-Coupling Reactions

Under air atmosphere, a round-bottomed flask was charged with aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (2.0 mmol), β-CD/NMU (3:7) (1 g), a catalytic amount of water (no more than 3 drops: approximately 0.06 ml) and β-CD-supported Pd nanoparticles (0.05 mol%). The mixture was heated to 85°C for the indicated time and reaction progress was monitored by thin-layer chromatography (TLC). After the reaction completed, water (10 ml) and hexane (20 ml) were added while the mixture was still hot. The organic layer was separated, dried over Na_2SO_4 and evaporated. The crude product obtained was purified by flash chromatography with PE/EtOAc as eluent to afford the corresponding products. The remainder was dried under vacuum for the next cycle.

General Procedure for Heck Cross-Coupling Reactions

Under air atmosphere, a round-bottom flask was charged with aryl halides (1.0 mmol), terminal olefins (2.0 mmol), Et_3N (2 mmol), β-CD/NMU (3:7) (1 g) and β-CD-supported Pd nanoparticles (0.05 mol%). The mixture was heated to 85°C for the indicated time and reaction progress was monitored by TLC. After the reaction completed, water (10 ml) and hexane (20 ml) were added while the mixture was still hot. The organic layer was separated, dried over Na_2SO_4 and evaporated. The crude product obtained was purified by flash chromatography with PE/EtOAc as eluent to afford the corresponding products. The remainder was dried under vacuum for the next cycle.

Results and Discussion

Cyclodextrins (CDs) are a class of naturally occurring receptors which are cyclic oligosaccharides constituted of six (in α), seven (in β) or eight (in γ) D-glucopyranose residues joined by α-1,4 linkages. Indeed, CD derivatives have commonly been applied successfully in various organic reactions, especial involving green chemistry. Among these, CDs have attracted a wide interest in the synthesis and stabilization of transition metal nanoparticles for carbon–carbon bond formation.[33–35] Furthermore, Matt *et al.* showed that cavity-shaped ligands could bring an added value to the efficiency of Suzuki–Miyaura coupling.[36] In this report, we discovered that β-CD/NMU could provide a clear viscose melt at 80°C, while the addition of *N*-methylurea was necessary to achieve such low melting temperature (Fig. 1). To evaluate the thermal stability of the mixture it was analyzed through three heating–cooling cycles, which showed similar melting points (78, 81 and 80°C, respectively). In addition, the mixture was heated for 4 h to 90°C without any evident decomposition. The novel medium was prepared easily and had a small vapor pressure, just like ionic liquid. It was hence tempting and logical to study its potential for Pd-catalyzed coupling reactions.

At the outset, application of the novel system was first investigated using palladium(II) in the Suzuki reaction, which could also give the desired product in 45% yield (Table 1, entry 11). According to the widely accepted mechanism of Suzuki coupling, the real catalyst is palladium(0) species. Ligands are used to support the active palladium(0) species, thus preventing it from deactivation. Native CDs prove to be insufficiently reactive to reduce Pd(II) to Pd(0) under mild conditions.[37] It is worth mentioning that previously Yao *et al.* proposed a mechanism in which the acetate anion acted as a ligand in the rate-determining oxidative addition step.[38] Compared to this mechanism, it appears that the dramatic effect of NMU is due to the formation of *N,O*-bidentate complex (Fig. 2). To some extent, NMU plays a very important part in the coupling reaction, just like the ligand. Moreover, urea compounds were reported to be effective alternatives for phosphine ligands in Pd-catalyzed processes.[39,40]

Metal nanoparticles (NPs) have appeared as a very promising approach to efficient catalysis under mild, environmentally benign conditions because of their large surface-to-volume ratio. Ligand-free Heck reactions, Suzuki reactions and Sonogashira reactions catalyzed by modified cyclodextrin-capped Pd nanoparticles in water have been reported.[41–45] However, in contrast to a wide variety of traditional organic solvents or green media such as low-melting polymers, the availability of water is rather limited. The reactants and products of these reactions tend to be rather insoluble in aqueous media. The CD-capped PdNPs also slowly decomposed to Pd black in water at high temperature, which is not catalytically active. To the best of our knowledge, there are few examples employing cheaper native β-CD-capped metal nanoparticles as catalyst for C–C coupling in a low-melting mixture system – in particular, the Miyaura–Suzuki reactions.

The procedure used in this work to prepare β-CD/Pd nanoparticles was reported previously.[32] Native β-CD-supported Pd nanoparticles were prepared by $NaBH_4$ reduction of Na_2Cl_4Pd in

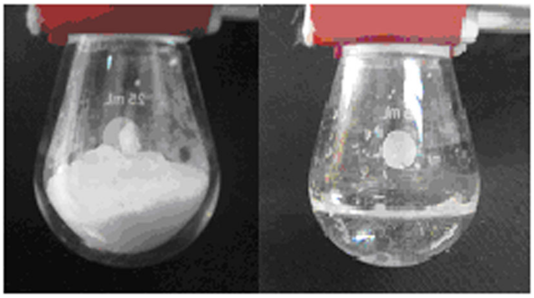
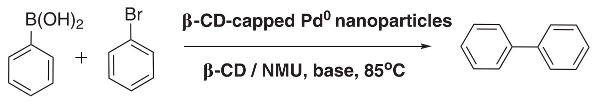


Figure 1. Mixture of β-cyclodextrin/N-methylurea (3/7) at room temperature (left) and at 80°C (right).

Table 1. Suzuki reaction of benzeneboronic acid with bromobenzene in low-melting β-cyclodextrin/NMU mixtures[a]



Entry	Base	Pd (mol%)	Time[b] (h)	Yield[c] (%)
1	KF	0.05	2	77
2	KOH	0.05	2	80
3	NaOAc	0.05	4	55
4	Et_3N	0.05	2	82
5	Na_2CO_3	0.05	2	76
6	K_2CO_3	0.05	2	90
7	K_2CO_3	0.05	2	95[e]
8	K_2CO_3	0.05	2	95[f]
9	K_2CO_3	0.01	6	68
10	K_2CO_3	0.05	2	86
11	K_2CO_3	0.1	1.5	95
12	K_2CO_3	0.05	6	45[d]

[a] Reaction conditions: bromobenzene (1.0 mmol), phenylboronic acid (1.2 mmol), base (2.0 mmol), β-CD/NMU (3:7) (1 g).
[b] The reaction was monitored by TLC.
[c] Isolated yield.
[d] $Pd(OAc)_2$ was used as catalyst.
[e] A catalytic amount of water was added (no more than 3 drops, approximately 0.06 ml).
[f] α-CD/NMU (3:7, melting point 75°C).

DMF solution, leading to the isolation of dark precipitates. Field emission SEM images of the isolated palladium nanoparticles (Fig. 3), obtained as depicted in the Experimental section, show spherical nanoparticles (with a size range of 20–30 nm). In an attempt to probe the native β-CD-supported Pd nanoparticles, further characterization was conducted. Interestingly, the FT-IR spectra of capped palladium nanoparticles and β-CD were very similar. It seemed plausible that the primary structure of β-CD is not involved in the reduction process but does play a role in particle stabilization (Fig. 4). These conclusions agree with previous observations.[37,46] The concentration of Pd loaded onto the catalyst was calculated based on elemental analysis and TG data, which indicated approximately 6% (w/w) of mean palladium content.

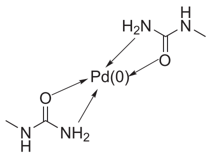


Figure 2. Proposed *N,O*-bidentate intermediates using Pd(0) species as catalyst in reported novel medium.

Having gained insight into the nature of the Pd nanoclusters stabilized by native β-CD, we proceeded to evaluate the catalytic performance of these nanoparticles in C–C cross-coupling reactions. Our investigation of the activity of Suzuki–Miyaura cross-coupling reaction was employed in this novel media using native β-CD-supported Pd nanoparticles as catalyst and

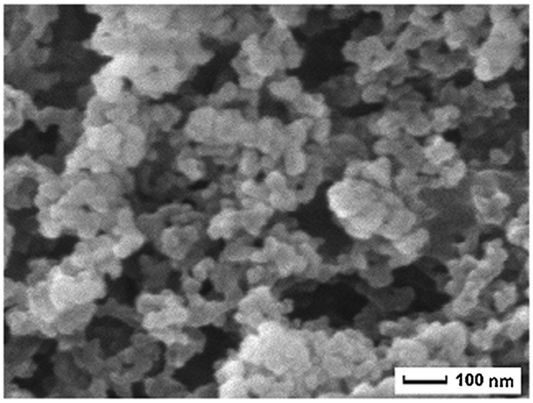


Figure 3. A typical SEM image of β-CD-supported Pd nanoparticles.

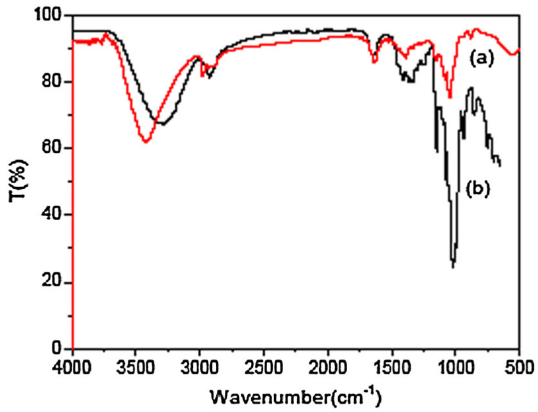


Figure 4. (a) Native β-CD; (b) β-CD-supported Pd nanoparticles.

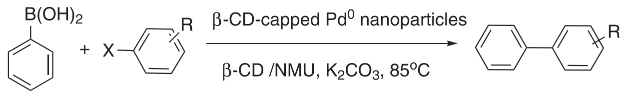
optimizing the conditions in terms of bases, temperature (Table 1) and the amount of catalyst. The coupling between bromobenzene and benzeneboronic acid was chosen as a model reaction, and the results are summarized in Table 1. As demonstrated in the table, the best yield was not obtained until the Suzuki reaction was carried at 85°C in low-melting β-CD/NMU mixture using K_2CO_3 as base and 0.05 mol% Pd. It is worth noting that a catalytic amount of water is necessary to improve the reaction (Table 1, entry 7). It is possible that in neat low-melting β-CD/NMU mixture Pd nanoparticles were overly stabilized and that the substrates were unable to compete effectively with the catalyst. The addition of water may lead to opening up of active sites on the catalyst surface. Under the same conditions as described above, the result showed there was not a significant beneficial effect on the performance of other cyclodextrins during the model reaction with lower-melting mixture as solvent (α-CD/NMU 3/7, melting point 75°C; Table 1, entry 8).

With the optimized reaction conditions in hand, we next examined the application of the cross-coupling of a variety of aryl halides with several arylboronic acids in the novel media. As expected, aryl iodides as the substrate under the same conditions could afford excellent yields and the conversion rates were faster than with other aryl halides, which were reflected in the shorter reaction time (Table 2, entries 1–3). It was found that both electron-rich and electron-deficient aryl bromides delivered the desired products with high yields in approximately 2 h. Furthermore, the catalytic system could tolerate a broad range of functional groups, such as NO_2, NH_2, OMe and CN (Table 2, entries 4–7). It was worth noting that the coupling of 4-bromochlorobenzene with phenylboronic acid gave exclusively 4-chlorobiphenyl in 93% yield, showing good chemoselectivity (Table 2, entry 10). To our delight, aryl chlorides gave the corresponding product in moderate yields – in particular, activated electron-deficient aryl chlorides – although a prolonged reaction time and increased usage of β-CD-supported Pd nanoparticles were required (Table 2, entries 11–14).

Encouraged by the success for Suzuki coupling, we further extended the application of the novel media to Heck coupling, which is another most important palladium-catalyzed C–C bond-forming reaction. Initially, we explored the conditions for the Heck reaction using iodobenzene and methyl acrylate (Table 3, entry 9) as the reactants. When no base was used in this reaction, only a trace amount of the desired product was detected. The results in Table 3 also demonstrated that Et_3N as the base was the best choice for the cross-coupling reaction, other bases such as KOH, Na_2CO_3 and K_2CO_3 being less effective. Many aryl iodides including electron-poor and electron-rich substrates could react with terminal olefins within a short time (approximately 2 h) and the yields of corresponding coupling products were very satisfactory (Table 3, entries 1–9). Compared to aryl iodides, poorer yields of coupling products were obtained when aryl bromides were used as substrates, even if longer reaction time and higher amounts of catalyst were required. (Table 3, entries 10–13).

The reusability of the catalyst or catalyst system is a very important theme, especially for commercial application. The advantage of the novel catalyst system (β-CD-supported Pd nanoparticles/β-CD/NMU) lies not only in the high catalytic activity attributed to the formation of C–C bond, but also in the ease of separation and recyclability. Recycling experiments were carried out for the cross-coupling of bromobenzene and benzeneboronic acid under the conditions described in Table 1. After the reaction was finished, water was added to the reaction mixture while still hot and the desired product was isolated with hexane. Water was removed from the aqueous phase by applying reduced pressure and the residue containing the Pd

Table 2. Suzuki reaction of aryl halides with phenylboronic acid in low-melting β-cyclodextrin/NMU mixtures[a]



Entry	X	R1	Time [b] (h)	Yield [c] (%)
1	I	4-NO_2	1	98
2	I	H	1	98
3	I	4-OCH_3	1	96
4	Br	4-NO_2	2	97
5	Br	4-NH2	2	96
6	Br	4-OCH_3	2	91
7	Br	4-CN	2	90
8	Br	H	2	95
9	Br	4-F	2	92
10	Br	Cl	2	93
11	Cl	4-NO_2	18	82[d]
12	Cl	4-CHO	18	76[d]
13	Cl	H	30	74[d]
14	Cl	4-CH_3	40	46[d]

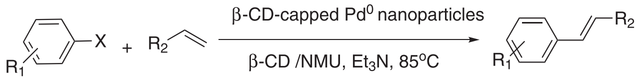
[a] Reaction conditions: bromobenzene (1.0 mmol), phenylboronic acid (1.2 mmol), base (2.0 mmol), β-CD/NMU (3:7) (1 g), catalytic amount of water (no more than 3 drops, approximately 0.06 ml).

[b] The reaction was monitored by TLC.

[c] Isolated yield.

[d] Pd was 0.5 mol%.

Table 3. Heck reaction of various aryl halides with terminal olefins in low-melting β-cyclodextrin/NMU mixtures[a]



Entry	R_1	R_2	X	Time[b] (h)	Yield[c] (%)
1	3-F	Ph(4-F)	I	2	95
2	4-CH_3	Ph(4-F)	I	2	96
3	4-OCH_3	Ph(4-F)	I	2	93
4	4-Cl	Ph(4-F)	I	2	95
5	H	Ph(4-F)	I	2	92
6	3-F	Ph(4-Cl)	I	2	90
7	4-OCH_3	Ph(4-Cl)	I	2	94
8	4-Cl	Ph(4-Cl)	I	2	95
9	H	COOMe	I	2	94
10	H	COOMe	Br	10	66[d]
11	H	COOEt	Br	10	71[d]
12	4-NO_2	COOMe	Br	10	55[d]
13	4-NO_2	COOEt	Br	10	76[d]

[a] Reaction conditions: ArX (1.0 mmol), terminal olefins (2.0 equiv.), Et_3N (2.0 equiv.), β-CD/NMU (3:7) (1 g), Pd (0.05 mol%), 85°C (external).
[b] The reaction was monitored by TLC.
[c] Isolated yield.
[d] Pd (0.5 mol%); the temperature was 110°C.

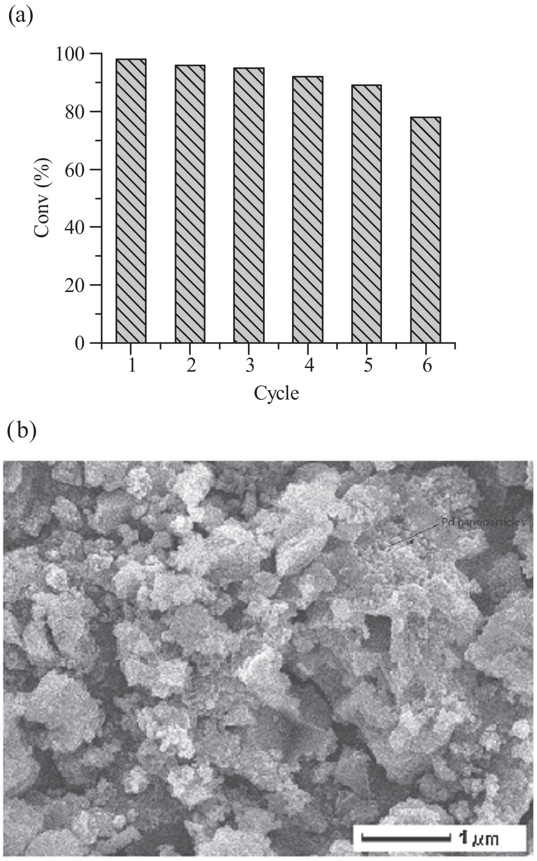


Figure 5. (a) Catalytic activity of the recycled β-CD-supported Pd nanoparticles/β-CD/NMU mixture; (b) SEM image of the sixth reused native β-CD-supported Pd nanoparticles.

nanoparticles was loaded with reactants and base. It is noted that a little water in the residue would not adversely affect the cross-coupling reaction, as previous researchers discovered that water could promote this typical reaction effectively. As shown in Fig. 5(a), the catalytic activity of the recovered β-CD-supported Pd nanoparticles/β-CD/NMU was consistent with efficient stability after four runs. More agglomeration of the real catalyst Pd nanoparticles was observed in the used catalyst (Fig. 5b). As a result, a decrease in catalytic activity was observed in the fifth and sixth recycling experiments, which indicated that particles size had a clear correlation with catalytic activity during the cycles. The conclusion is also consistent with the well-established finding.[37]

Conclusion

In summary, we have presented the use of a low-melting mixture of β-cyclodextrin/*N*-methylurea (NMU) as reaction media for Suzuki–Miyaura and Heck reaction in the presence of β-CD-supported Pd nanoparticles without any ligand. The advantages of our new method include mild reaction conditions, ease of workup, high yields, stability and easy isolation of the compounds. In addition, the non-toxic reaction media could be applied to organic transformations as a substitute for ionic liquids. Currently, further studies are underway in our laboratory, addressing extension of the system to other palladium-catalyzed transformations.

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