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FULL PAPER

Cyclodextrin-supported palladium complex: A highly active and recoverable catalyst for Suzuki–Miyaura cross-coupling reaction in aqueous medium

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A water-soluble, cyclodextrin-supported palladium complex (DACH-Pd-β-CD) catalytic system was designed and synthesized, which can efficiently catalyze Suzuki–Miyaura cross-coupling reactions between aryl halides and arylboronic acid in water under mild conditions. The catalyst was successfully characterized using the methods of transmission electron microscopy, energy-dispersive X-ray spectrometry, X-ray diffraction, thermogravimetric analysis, and Fourier transform infrared and NMR spectroscopies. Furthermore, the catalyst can be easily separated from the reaction mixture and still maintain high catalytic activity after ten cycles. No leaching of palladium into the reaction solution occurred. The advantages of green solvent (water), short reaction times (2–6 h), low catalyst loading (0.001 mol%), excellent yields (up to 99%) and reusability of the catalyst mean it will have potential applications in green chemical synthesis.

KEYWORDS

Cyclodextrin, green catalysis, palladium, Suzuki–Miyaura cross-coupling reaction

1 | INTRODUCTION

Carbon–carbon cross-coupling reactions catalyzed by transition metals play an important role in modern synthetic chemistry for the synthesis of complex molecules.[1] In particular, the Suzuki–Miyaura coupling reaction has a wide range of applications from the synthesis of natural products and pharmaceutical intermediates to functional materials with mild reaction conditions, use of low-toxicity organic boron reagents, stability and a wide range of substrates.[2] It is reported that palladium (Pd) catalysts are most frequently used in Suzuki–Miyaura coupling reactions and often lead to high reaction rates and yields.[3] With its great advantages, the Pd-catalyzed Suzuki–Miyaura coupling reaction made a significant contribution to the 2010 Nobel Prize in Chemistry.[4] However, the Suzuki–Miyaura coupling reaction also has some drawbacks, such as the difficulty of recycling and separating precious metals, expensive ligands and pollution to the environment.[5] As a result, the disadvantages are conflicting with the conception of green chemistry. Thus, a large number of researchers, who have recently been interested in the Suzuki–Miyaura coupling reaction, have focused their attention on three issues: (1) endeavoring to minimize the quantity of precious metal catalysts; (2) improving the recovery and recycling efficiency; and (3) using environmentally friendly and cheap solvents.[6]

With these issues in mind, various carriers have been employed to immobilize Pd catalysts, such as magnetic nanoparticles,[7] Pd/C,[8] silica,[9] carbon nanotubes,[10] glycosyls,[11] other polymers[12] and nanomaterials.[13] Most of the carriers were functionalized with amine,[14] phosphorus[15] and sulfydryl groups[16] so as to form stable complexes with Pd catalysts. On the one hand, the Pd complexes are very easy to recycle and reuse. On the other hand, the quantities of Pd catalysts required are minimal and the solvents are environmentally friendly, such as water and ethanol.

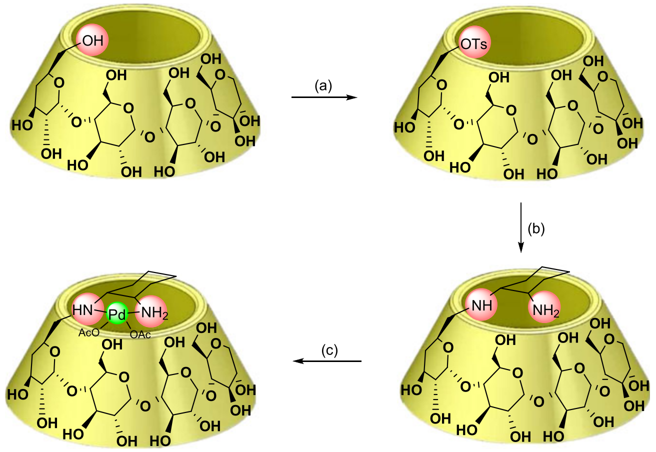
Cyclodextrin (CD)-supported Pd catalytic systems recently have attracted much attention for green Suzuki–Miyaura coupling reactions.[17] CD is a kind of cyclic oligosaccharide and consists of (α-1,4)-linked α-D-glucopyranose units which possess a special structure of lipophilic central cavity and hydrophilic outer surface. The special structure endows it with various functions, such as drug delivery,[18] catalysis in water[19] and selective recognition.[20] The superb catalytic performance of CD in water is probably due to organic substances being able to spontaneously form inclusion complexes with CD and the organic reactions may happen in the central lipophilic cavity.[21] In recent years, a few functionalized CD ligands were synthesized for Suzuki–Miyaura coupling reactions which were usually grafted with amine and phosphorus groups.[22] For example, Pd supported by triazolyl β-cyclodextrin[23] and tetraphosphine α-cyclodextrin[24] showed wonderful catalytic properties in Suzuki–Miyaura coupling reactions in neat water and also showed high turnover numbers and turnover frequencies. However, the synthesis of CD-based ligands in most reports involved complex multi-steps and the reusability of the catalysts was not studied. Moreover, metal leaching experiments were not considered. Hence, we hypothesized that it would be meaningful to use a simple and cheap CD-based water-soluble catalyst to accomplish Suzuki–Miyaura coupling reactions in water. In addition, it will be better if the catalyst has both high catalytic activity and shows easy catalyst separation/reuse in aqueous media without significant catalyst leaching.

In our previous report, a type of cheap CD-based water-soluble catalyst, namely DACH-Pd-β-CD (where DACH is 1,2-cyclohexanediamine), was used to catalyze the reduction of nitroarenes in water.[25] In the present paper, we report the synthesis and characterization of DACH-Pd-β-CD and its application in other Suzuki–Miyaura reactions in water. The ligand is cheap and can be easily synthesized with the most common β-CD derivative (Tos-β-CD) and DACH, which may significantly increase its application in industry. In addition, the excellent catalytic activity, recycling performance, metal leaching and catalytic mechanism were studied.

2 | RESULTS AND DISCUSSION

2.1 | Preparation of DACH-Pd-β-CD catalyst

The DACH-Pd-β-CD catalyst was prepared following the procedure shown in Scheme 1. At first, 6-O-monotosyl-β-CD was synthesized with a frequently used method in our groups. Then, DACH was grafted on 6-*O*-monotosyl-β-CD according to previous methods.[26] Finally, $Pd(OAc)_2$ and DACH-β-CD were added in toluene and stirred at room temperature for 24 h. The pure DACH-Pd-β-CD catalyst was obtained as a light yellow powder. Moreover, the catalyst is soluble in water to form a light yellow clear solution. The palladium content of DACH-Pd-β-CD is 0.1625 mmol g^{-1} (determined using inductively coupled plasma optical emission spectrometry (ICP-OES)) and the amount of catalyst in this study has been calculated based on the Pd content of DACH-Pd-β-CD.



SCHEME 1 Synthesis of DACH-Pd-β-CD. Reaction conditions: (a) TosCl, NaOH, CH_3CN, H_2O; (b) DMF, 80°C; (c) $Pd(OAc)_2$, toluene, room temperature, 24 h

2.2 | Characterization of DACH-Pd-β-CD catalyst

NMR spectroscopy is a useful way to demonstrate the formation of ligand and catalyst. The NMR spectra of DACH-β-CD and DACH-Pd-β-CD are shown in Figure 1. As illustrated in Figure 1, the characteristic peaks of DACH appear from 3.0 to 1.0 ppm. This result demonstrates the formation of DACH-β-CD. Comparing the spectrum of DACH-β-CD with that of DACH-Pd-β-CD, the peak of acetyl in DACH-Pd-β-CD is extremely obvious and it could provide probable evidence that the DACH-Pd-β-CD catalyst has been synthesized. High-resolution (HR)-MS was used to confirm the successful synthesis of DACH-β-CD (Fig. S4; m/*z* calcd for $[C_{48}H_{82}N_2O_{34}]$ 1230.47, found 1231.4848 $[M + H]^+$, 1253.4670 $[M + Na]^+$). The NMR and HR-MS results indicate that the degree of substitution of DACH-β-CD is 1.

The X-ray diffraction (XRD) patterns of DACH-β-CD and DACH-Pd-β-CD are presented in Figure 2. Compared with each other, it is obvious that DACH-β-CD (the red curve) and DACH-Pd-β-CD (the black curve) are both amorphous and show a strong and wide characteristic diffraction peak at 2θ of 15–30°. In addition, the new peaks in the XRD pattern of DACH-Pd-β-CD at 2θ of 39.6° and 47.1°, corresponding to 110 and 200 crystalline planes of Pd^2, indicate the existence of Pd in DACH-Pd-β-CD. As a result, the XRD patterns demonstrate that the catalyst had been synthesized without damaging the crystal structure of the DACH-β-CD ligand and Pd is present in the DACH-Pd-β-CD catalyst.

Transmission electron microscopy (TEM) images of DACH-β-CD and DACH-Pd-β-CD and HR-TEM image of DACH-Pd-β-CD are shown in Figure 3. The sample was put on a piece of copper grid and dried at room temperature under vacuum. Comparing Figure 3(A) and (B), the main difference is that many black spots are apparent in the latter, but

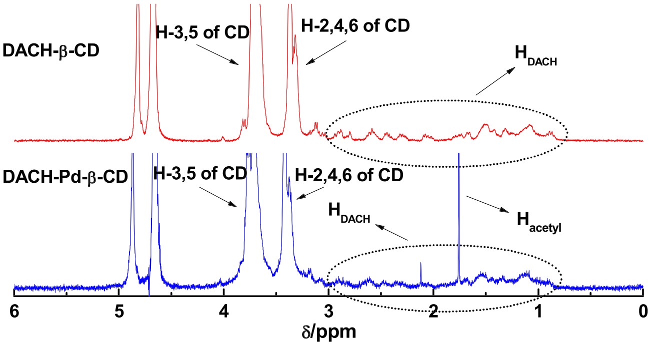


FIGURE 1 ^{1}H NMR spectra of DACH-β-CD and DACH-Pd-β-CD

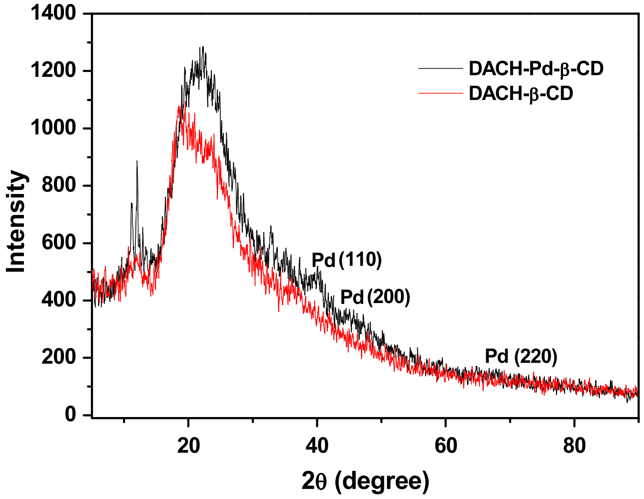


FIGURE 2 XRD patterns of DACH-β-CD and DACH-Pd-β-CD

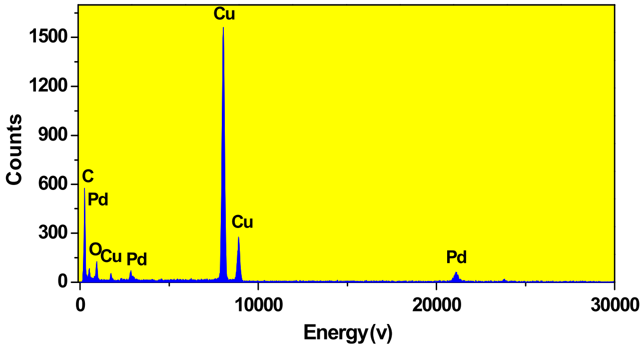


FIGURE 3 TEM images: (A) DACH-β-CD at 100 nm; (B) DACH-Pd-β-CD at 200 nm; (C) DACH-Pd-β-CD at 50 nm. (D) HR-TEM image of DACH-Pd-β-CD at 5 nm

not in the former. When the image is enlarged to 50 nm in Figure 3(C), the black spots become much clearer. The black spots are likely to be Pd atoms. In order to further demonstrate the presence of Pd, a HR-TEM image of DACH-Pd-β-CD was obtained (Figure 3D). From Figure 3(D), the average interplanar distance of DACH-Pd-β-CD is measured to be *ca* 0.22 nm, which corresponds well to the plane of Pd. In addition, energy-dispersive X-ray spectrometry (EDS) was used to study the elementary composition of DACH-Pd-β-CD (Figure 4). Ignoring the peaks of the Cu grid, DACH-Pd-β-CD consists of O, C, N and Pd. All the results show the presence of Pd in the DACH-Pd-β-CD catalyst.

2.3 | Catalytic performance studies

The catalytic performance of DACH-Pd-β-CD for the Suzuki–Miyaura coupling reaction was evaluated with the model reaction of 4-bromoacetophenone and phenylboronic acid. As is known, base has a significant influence on the Suzuki–Miyaura coupling reaction. Hence, seven bases were chosen to test the catalytic activity and the results are summarized in Table 1. Except for the different bases, the other reaction conditions are identical. In the absence of base, the yield is only about 3% (entry 1). Therefore, the presence of base is required for the reaction to occur. The coupling reaction yields using the seven bases were very good, from 82 to 93% (entries 2–8). However, using the base Cs_2CO_3, the product is very clean and without any other byproducts. Moreover, the isolated yield is up to 93%. All the results in Table 1 indicate that Cs_2CO_3 is the optimal base.

The temperature and the mount of catalyst are very significant to the catalytic performance. The screening results are listed in Table 2. As is evident, the Suzuki–Miyaura coupling reaction can occur at room temperature with a yield of 32% (entry 1). With the temperature rising from 50 to 80°C, the yields gradually increase to 93% (entries 2 and 3). In addition, at higher temperature, the yields show nearly no change (entries 4 and 5). As a result, 80°C is the optimum temperature. Considering the amount of catalyst, the quantity of DACH-Pd-β-CD was selected from 0 to 0.1 mol%.

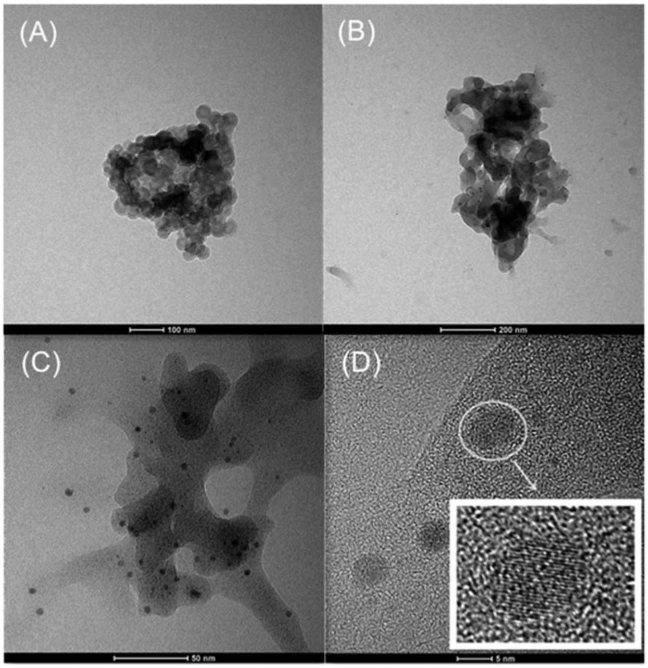


FIGURE 4 EDS pattern of DACH-Pd-β-CD

TABLE 1 Optimization of base[a]

Entry	Base	Yield (%)[b]
1	—	3
2	Na_2CO_3	82
3	K_2CO_3	85
4	$NaHCO_3$	78
5	**Cs_2CO_3**	**93**
6	NaOH	92
7	K_3PO_4	89
8	Et_3N	82

[a] Reaction conditions: aryl halide(1.0 mM), arylboronic acid (1.5 mmol), H_2O (2 ml), DACH-Pd-β-CD (1×10^{-3} mol%), base (1.5 eq.), 80°C, 2 h.

[b] Isolated by column chromatography.

TABLE 2 Optimization of temperature and catalyst loading[a]

Entry	Temperature (°C)	Catalyst (mol%)	Yield (%)[b]
1	r.t.	0.001	32
2	50	0.001	68
3	**80**	**0.001**	**93**
4	100	0.001	92
5	110	0.001	93
6	80	0	—
7	80	0.1	92
8	80	0.01	93
9[c]	80	0.001	—
10[d]	80	0.001	—
11[e]	80	0.001	6

[a] Reaction conditions: aryl halide (1.0 mM), arylboronic acid (1.5 mmol), Cs_2CO_3 (1.5 eq.), H_2O (2 ml), DACH-Pd-β-CD, 2 h.

[b] Isolated by column chromatography.

[c] β-CD was used to instead of DACH-β-Pd-CD.

[d] DACH-β-CD was used to instead of DACH-β-Pd-CD.

[e] β-CD was used to instead of DACH-β-CD, $Pd(OAc)_2$ (0.001 mmol%).

TABLE 3 Suzuki–Miyaura coupling reactions between aryl halides and arylboronic acid using DACH-Pd-β-CD[a]

Entry	R^1	X	R^2	Time (h)	Yield (%)[b]
1	H	I	H	1	99
2	H	Br	H	1	98
3	4-$COCH_3$	Br	H	2	93
4	4-OCH_3	Br	H	2	96
5	4-CHO	Br	H	4	95
6	2-CHO	Br	H	24	65
7	4-$COCH_3$	Br	4-CH_3	2	96
8	4-OCH_3	Br	4-CH_3	2	98
9	4-CHO	Br	4-CH_3	4	95
10	4-$COCH_3$	Br	3-CH_3	6	94
11	4-OCH_3	Br	3-CH_3	6	96
12	4-OCH_3	I	3-CH_3	3	97
13	4-CHO	Br	3-CH_3	6	95
14	2-OCH_3	I	4-F	4	76
15	4-$COCH_3$	Br	4-F	6	96
16	4-OCH_3	Br	4-F	6	97
17	3-NO_2	Br	4-F	8	90
18	4-CHO	Br	4-F	6	96
19	4-CH_3	I	4-F	4	94
20	4-CH_3	I	4-$COCH_3$	8	95

[a] Reaction conditions: aryl halide (1.0 mmol), arylboronic acid (1.5 mmol), Cs_2CO_3 (1.5 mmol), H_2O (2 ml), DACH-Pd-β-CD (1×10^{-3} mol%), 80°C.

[b] Isolated by column chromatography.

Entry 6 reveals that the DACH-Pd-β-CD catalyst is quite important and the coupling reaction cannot happen without catalyst. Furthermore, the yield for the minimum quantity (0.001 mol%) of DACH-Pd-β-CD is very good and shows the same performance with higher quantities (entries 7 and 8). In addition, considering the influence of CD itself, β-CD and DACH-β-CD were used to test their catalytic activity (entries 9 and 10), no product being detected. However, when we added β-CD and $Pd(OAc)_2$ to replace the DACH-Pd-β-CD catalyst (entry 11), the yield is reduced to 6%.

In order to investigate the generality of this cross-coupling reaction, various arylboronic acids were used to react with aryl halides (iodide or bromide) under the optimized conditions. The catalytic results are summarized in Table 3. Overall, the catalyst shows good catalytic activity leading to excellent yields in the Suzuki–Miyaura coupling reactions. As indicated in entries 1 and 2, simple aryl halides, such as iodobenzene and bromobenzene, have a high reactivity with boronic acid and the reactions are quickly completed in 1 h. Moreover, the yields of diphenyl are up to 98–99%. Comparing the reactions between various aryl bromides (entries 3–6) and boronic acid, it turns out that the yields of *para*-substituted aryl bromides (entries 3–5) are much higher than that of *ortho*-substituted aryl bromide (entry 6). In particular, for entries 5 and 6, the yields of the same substituent of —CHO, respectively at *para*-position and *ortho*-position, are quite different. This may be due to the regioselectivity of DACH-Pd-β-CD. Because of the constant cavity size of DACH-Pd-β-CD, the *para*-substituted aryl bromides probably combine more easily with Pd than *ortho*-substituted aryl bromides. Therefore, the yield of 2-phenylbenzaldehyde is only 65%. In addition, a series of arylboronic acid derivatives (entries 7–13) was also studied. Regardless of using 4-methylphenylboronic acid and 3-methylphenylboronic acid, all the yields are very good at about 96–98%. The only difference was the time of the coupling reactions; 4-methylphenylboronic acid took less time. Furthermore, *para*-substituted aryl halides were also tested with 4-fluorophenylboronic acid and excellent yields are obtained (entries 14–19). The presence of F in the products was characterized using ^{19}F NMR spectroscopy. For the coupling reactions of other substrates, we used 3-nitrobromobenzene (entry 17) to study the catalytic activity of *meta*-substituted aryl bromide and the yield is up to 90%. In conclusion, the DACH-Pd-β-CD catalyst possesses excellent catalytic activity in Suzuki–Miyaura coupling reactions. Substituents (electron-withdrawing or electron-donating groups) have a slight influence on the yields. Also, DACH-Pd-β-CD shows a regioselectivity to aryl halides, the strength of the regioselectivity being: *para*-substituted aryl halides and *meta*-substituted aryl halides > *ortho*-substituted aryl halides. The detailed reasons for the regioselectivity are still under investigation by our groups.

2.4 | Recyclability of DACH-Pd-β-CD

It is well known that the main advantage of metal catalysts is their high catalytic efficiency, but unfavorable factors, such as high price, difficulty in recycling and pollution to the environment, seriously limit their applications in industry. Therefore, in order to expand the applications of DACH-Pd-β-CD, the recycling of the catalyst was carried out. The general procedure for recycling the catalytic system is described in Figure 5. Furthermore, the reaction was conducted with the optimum reaction conditions: 4-bromoacetophenone (1.0 mmol), phenylboronic acid (1.5 mmol), DACH-Pd-β-CD (1×10^{-3} mol%), Cs_2CO_3 (1.5 mmol), 80°C and H_2O (2.0 ml). After completion of each cycle, 3 × 5 ml of ethyl acetate was added to separate the organic phase and the aqueous phase was used in the next run without changing the reaction conditions. The recycling results are shown in Figure 6. In the first cycle, the yield is 93% and the DACH-Pd-β-CD catalyst still shows high catalytic activity giving a yield of 88% after ten cycles. Moreover, after ten cycles, the Pd in the TEM image of DACH-Pd-β-CD is still obvious (Figure 7).

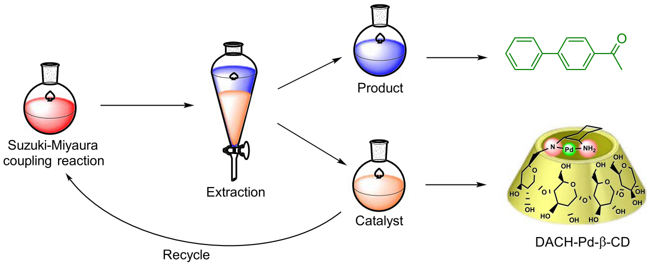


FIGURE 5 Recycling procedure for DACH-Pd-β-CD

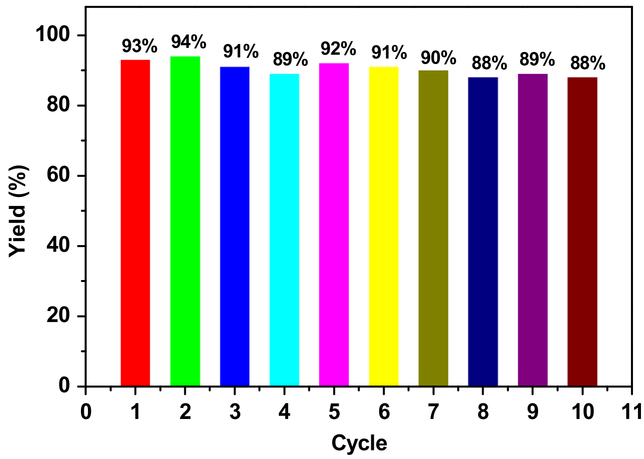


FIGURE 6 Recycling of DACH-Pd-β-CD

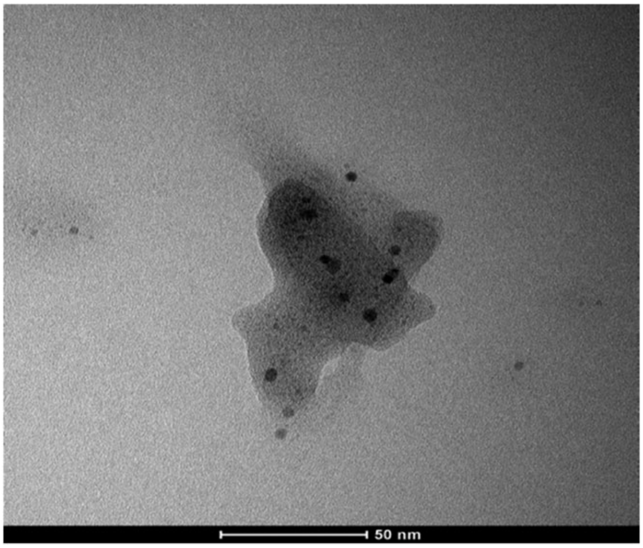


FIGURE 7 TEM image of DACH-Pd-β-CD after ten cycles

The content of Pd in the product was determined using ICP-OES and no leaching of Pd is detected. The excellent reusability of the catalyst could be due to the strong binding capacity between Pd and DACH-β-CD.

2.5 | Proposed mechanism for Suzuki–Miyaura coupling reaction

Given the results of this work and previous literature, a possible catalytic mechanism is proposed as shown in Figure 8. The mechanism is the same as reported previously and involves three sequential steps: oxidative addition, transmetalation and reductive elimination.[27] We studied the two-dimensional ROESY spectrum (Fig. S7). The results indicate that the spectrum shows a correlation between the aromatic protons of 4-bromoacetophenone and internal DACH-Pd-β-CD protons (H-3 and H-5 of CD), which

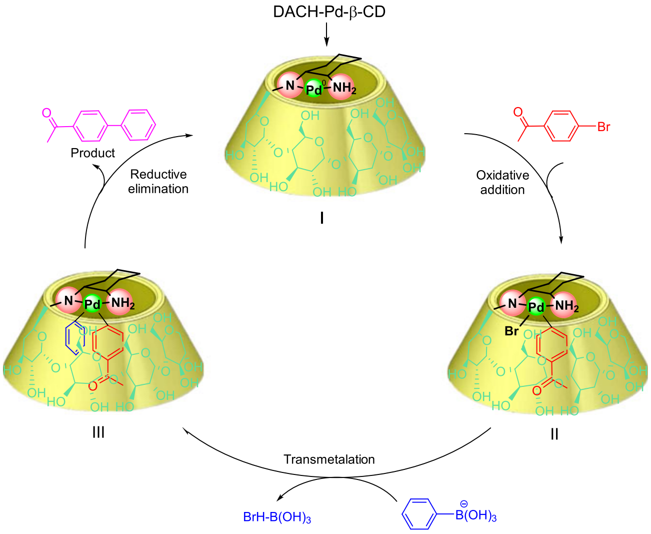


FIGURE 8 Possible catalytic mechanism of Suzuki–Miyaura cross-coupling reaction using DACH-Pd-β-CD

implies that the DACH-Pd-β-CD catalyst is able to recognize the substrate and insert it into the cavity of β-CD. Hence, the catalyst can probably recognize the substrate in water and promote the Suzuki reaction to occur in its cavity. At first, DACH-Pd-β-CD is activated to Pd(0) and the aryl halide reacts with the active DACH-Pd-β-CD (oxidative addition) to produce the intermediate II. The coordinated halide ion is weak, and then activated arylboronic acid forms the diaryl complex with the progress of transmetalation. Finally, the desired reductive elimination product is released from the cavity. Afterward, the catalytic cycles can be repeated.

3 | CONCLUSIONS

In this study, a new kind of water-soluble, macromolecular Pd complex catalyst, DACH-Pd-β-CD, for Suzuki–Miyaura coupling reactions was successfully prepared and characterized using NMR spectroscopy, XRD, TEM, HR-TEM and EDS. The catalyst showed excellent activity in the Suzuki–Miyaura cross-coupling reaction and the yields of most desired products ranged from 88 to 99%. The advantages of this catalyst are mainly divided into the following several aspects. Firstly, the catalytic efficiency was strongly enhanced by the minimum catalyst amount of 0.001 mol%. Secondly, the reaction solvent of water is very beneficial to the environment. Thirdly, after the reaction finished, a simple operation of extraction is used to get the desired products. Fourthly, the catalytic performance is still very good and without catalyst loss after ten cycles. In conclusion, the advantages of the DACH-Pd-β-CD catalyst fully meet the requirements of green chemistry.

4 | EXPERIMENTAL

4.1 | Materials

β-CD (AR, 98%, MW = 1134.98), DACH (AR, 99%, MW = 114.19), $Pd(OAc)_2$ (metals basis, 99.9%, MW = 224.51) and *p*-toluenesulfonyl chloride (AR, 99%, MW = 190.65) were purchased from Aladdin Industrial Corporation, Shanghai, China. NaOH, dimethylformamide (DMF) and CH_3CN were purchased from Tianjin Fengchuan Chemical Reagent Technologies, China. Aryl halides and arylboronic acid (AR) were obtained from Macklin Biochemical Technology Co. Ltd. All experiments were carried out in ultrapure water and all chemicals were used without further purification.

4.2 | Instrumentation

XRD patterns were obtained using a PHI 5000 VersaProbe II with Cu Kα radiation ($k = 1.5460$ Å, 40 kV, 100 mA), at a scanning rate of 5° min^{-1}. Powder samples were mounted on a vitreous sample holder and scanned with a step size of $2\theta = 0.02°$ between $2\theta = 5°$ and 90°. TEM and EDS were conducted using a Tecnai G^2 TF30 S-Twin. NMR spectra were obtained with a Bruker Avance DRX spectrometer at 500 MHz, with tetramethylsilane as internal reference, 298 K, at Yunnan University, Kunming, China. ICP-OES was carried out with an Agilent 5100 instrument. Thermogravimetric measurements were performed with a Netzsch STA449F3 instrument, at a heating rate of 10° C min^{-1} from room temperature to 450°C in a dynamic nitrogen atmosphere (flow rate = 100 ml min^{-1}).

4.3 | Synthesis of DACH-β-CD ligand

6-*O*-Monotosyl-β-CD was synthesized according to procedures in the literature.[26] 6-*O*-Monotosyl-β-CD (3.22 g, 2.5 mmol) and DACH (1.14 g, 10.0 mmol) were dissolved in anhydrous DMF. The mixture was stirred for 12 h at 80° C. Then, the reaction solution was added dropwise in acetone (3 × 500 ml) to remove the excess DACH. The final pure DACH-β-CD was dried overnight in vacuum at 50°C. Yield: 82%.

4.4 | Synthesis of DACH-Pd-β-CD catalyst

$Pd(OAc)_2$ (0.0225 g, 0.1 mM) was dissolved in toluene (15 ml) and DACH-β-CD (0.369 g, 0.3 mM) was added. The suspension was stirred at room temperature for 24 h. Then, the precipitate was washed three times with a large amount of acetone (300 ml) to remove the tiny amounts of free $Pd(OAc)_2$. Then, the catalyst was dried in vacuum at 50°C for 24 h, and a light yellow powder was obtained.

4.5 | General procedure for Suzuki–Miyaura coupling reaction

Aryl halide (1.0 mM), arylboronic acid (1.5 mmol), DACH-Pd-β-CD (1×10^{-3} mol%) and Cs_2CO_3 (1.5 mmol) were added in a sealed tube with 2.0 ml of water. The mixture was stirred at 80°C for a few hours and monitored by TLC. After the reaction completed, the aqueous phase was extracted with ethyl acetate (3 × 5 ml). Then the combined organic layers were dried using anhydrous $MgSO_4$ and further purified by column chromatography.

4.6 | Separation of catalyst and recycling procedure

Once each Suzuki–Miyaura reaction was finished, ethyl acetate (3 × 5 ml) was added to separate the organic phase and the aqueous phase was used in the next run with the optimum reaction conditions.

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