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Palladium nanoparticles supported on cucurbit [6]uril: an efficient heterogeneous catalyst for the Suzuki reaction under mild conditions

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A new NC palladacycle was synthesized and supported on cucurbit[6]uril (CB[6]). The CB[6]-supported palladium was used as an efficient nanocatalyst for the Suzuki reaction. In these reactions various aryl halides were reacted with arylboronic acids in H₂O–EtOH at both room temperature and 40 °C. The obtained Pd nanocatalyst exhibited excellent reactivity and stability in C–C bond formation, which confirms that the catalyst is a completely active heterogeneous species. The Pd nanocatalyst was characterized using X-ray diffraction, scanning electron microscopy and transmission electron microscopy. Copyright © 2014 John Wiley & Sons, Ltd.

Keywords: Pd nanoparticles; Suzuki reaction; heterogeneous catalyst; green solvents

Introduction

Cyclopalladated complexes derived from N-donor ligands have received much attention due to their extremely high catalytic activity in various C-C coupling reactions including Heck, Suzuki and Sonogashira reactions.^[1–4] The most important organic reactions have been performed with homogeneous palladium catalysts, these catalysts possessing many merits, such as high turnover number, high reaction rate and efficient selectivity.^[5-10] However, one of the great drawbacks of such catalysis is that the products might be contaminated by metal, which is unacceptable for the production of pharmaceutical and fine chemicals. Additionally, expensive materials might be lost and bring about environmental pollution. A popular strategy is facilitating the recovery of expensive ligands and complexes by immobilization of various complexes on support surfaces.^[11] To reach this goal, heterogeneous catalysts have been prepared using many supports, such as poly(ethylene glycol), TiO₂, SiO₂, MgO, zeolites, clays, polymers, capsules, and alkali and alkaline earth salts.^[12–19]

Cucurbit[6]uril (CB[6]) is one of a family of macrocyclic molecules that can act as both support and capping agents (Fig. 1). This family of macrocyclic molecules have two identical portals lined by carbonyl groups that provide two negative fringes of bonding to the surface of metals or nanomaterials.

The Suzuki reaction of aryl halides with arylboronic acids in the presence of Pd nanocatalysts is one of the most important methods for the construction of C–C bonds and plays an important role in pharmaceutical and organic synthesis.^[20–24] Palladium catalysts are generally irreplaceable choices for cross-coupling reactions. Tamami and Ghasemi have reported the effectiveness of a palladium catalyst based on modified crosslinked polyacrylamide for the Suzuki reaction in DMF.^[17] He and Cai have proposed a polymer-supported macrocyclic Schiff base palladium complex for the Suzuki reaction in the presence of 0.1 mol% Pd in DMF–H₂O.^[18] In our previous work, polymer-supported palladium nanoparticle catalysts were successfully used for the Suzuki reaction and showed lower levels of palladium leaching during cross-coupling.^[14]

Costa *et al.* have described the preparation of supported palladium nanoparticles stabilized by pendant phosphine groups. This catalyst was used for the Suzuki reaction in toluene at 100 °C.^[25] Moreover, Jamwal *et al.* have developed a successful Suzuki reaction and aerobic oxidation of benzyl alcohols catalysed by a reusable nano-palladium(0) supported on cellulose.^[26] Although all the methods provide good yields, some of the reactions suffer from long reaction times, need for heating, need for toxic solvents or leaching of Pd nanoparticles from the support.

In this work we report a simple and environmentally friendly route for the preparation of CB[6]-supported Pd nanoparticles (CB[6]-Pd NPs). Furthermore, we investigated the catalytic activity of the nanocatalyst for the Suzuki reaction in non-toxic solvents (H₂O–EtOH). Finally, it was found that CB[6]-Pd NPs was a highly re-usable catalyst for repeat cycles.

Experimental

General

All reactants were purchased from Merck Chemical Company and Aldrich and were used as received. Solvents were used without further purification or drying.

Fourier transform infrared (FT-IR) spectra were obtained in KBr pellets with a Jasco FT/IR 680 plus instrument. NMR spectra were measured with a Bruker spectrometer at 400.13 MHz (¹H). UV–visible spectra were recorded with a JASCO V-750 spectrophotometer. Elemental analysis was performed using a LECO CHNS-932 apparatus. Scanning electron microscopy (SEM) studies were conducted with a Philips (model XL-30) instrument. Transmission electron microscopy (TEM) was carried out with a Philips (model

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Figure 1. Structure of cucurbit[6]uril.



Scheme 1. Preparation of NC palladacycle.

CM30) instrument. Palladium content of the catalyst was measured by inductively coupled plasma optical emission spectrometry (ICP-OES; PerkinElmer 7300DVspectrometer). X-ray diffraction (XRD) patterns were measured using a Scintag X-ray diffractometer with X-ray wavelength of 1.54 Å (Cu K α radiation source). Conversions were monitored using an Agilent Technologies 6890 N gas chromatograph equipped with a flame ionization detector and an HB-50⁺ column (length = 30 m, inner diameter = 320 μ m, and film thickness = 0.25 μ m). Products were identified by comparison with authentic samples.

Preparation of Palladium Complex

Pd(OAc)₂ (1 mmol, 0.224 g) was dissolved in 20 ml of toluene and 1 mmol (0.174 g) of 3-(dimethylaminomethyl)indole was added to the solution. The mixture was stirred in a round-bottom flask equipped with condenser at 60 °C for 24 h. After this time, toluene was vaporized and the dinuclear complex was precipitated from CH₂Cl₂ and *n*-hexane. The five-membered NC palladacycle [(Pd{ κ^2 (N,C)-(3-(dimethylaminomethyl)indole)} μ -OAc)₂] with a reaction yield of 61% (0.207 g) was prepared and dried.

UV-visible (CH₂Cl₂, λ_{max} , nm): 291 (ε = 41 700 M⁻¹ cm⁻¹), 240 (ε = 61 400 M⁻¹ cm⁻¹). FT-IR (KBr, v_{max} , cm⁻¹): 3429 s (NH),



Scheme 2. Preparation of CB[6]-Pd NPs.^[31,32]

1577vs, 1413s (CO). ¹H NMR (400 MHz, CDCl₃, *δ*, ppm): 1.96 (3H, s, MeCO₂), 2.31 (3H, s, Me), 2.29 (3H, s, Me), 2.99 (2H, s, CH₂), 5.93 (1H, s, NH), 7.28–7.38 (4H, m, C₆H₄). ¹³C[¹H} NMR (CDCl₃, *δ*, ppm): 23.79 (MeCO₂), 40.00 (Me), 41.37 (CH₂), 124.18 (C₁), 115.91 (C₂), 128.70 (C₃), 129.96 (C₄), 117.85, 118.88, 118.93, 129.93 (C_{aromatic}). Anal. Calcd for C₂₆H₃₄N₄O₅Pd₂ (%): C, 44.91; H, 4.93; N, 8.06. Found (%): C, 44.43; H, 4.97; N, 7.63.

Preparation of Glycoluril and CB[6]

Glycoluril and CB[6] were prepared according to previous reports.^[27,28]



Figure 2. Powder XRD pattern of CB[6]-Pd NPs.



Figure 3. SEM images of CB[6]-Pd NPs.



Figure 4. TEM images of (a) fresh CB[6]-Pd NPs and (b) CB[6]-Pd NPs after the fifth run.

Preparation of CB[6]-Pd NPs

CB[6]-Pd NPs catalyst was prepared according to the literature method.^[29] For this purpose, 0.1 mmol (0.068 g) of [(Pd{ κ^2 (N,C)-(3-(dimethylaminomethyl)indole)} μ -OAc)₂] and 0.1 mmol (0.099 g) of CB[6] were mixed in 10 ml of water at room temperature. The mixture was stirred for 30 min until a brown uniform suspension was formed. After this, freshly prepared NaBH₄ in ethanol (1 mmol (0.037 g) in 10 ml) was rapidly added to the reaction mixture and the reduction occurred instantaneously. The reduction was characterized by a colour change from brown to black. The

mixture was stirred for another 3 h. The final reaction product was separated by centrifugation and washed three times with aqueous ethanol (1:1 v/v) to remove excess salt. CB[6]-Pd NPs was dried at 70 °C for 10 h in air.

General Procedure for Suzuki Reaction

A round-bottomed flask was equipped with a stir bar and was charged with aryl halide (0.25 mmol), arylboronic acid (0.5 mmol), Na₂CO₃ (1.25 mmol) and CB[6]-Pd NPs (0.05 mol% of Pd) in 6 ml of EtOH-H₂O (1:1). The flask was placed in an oil bath, and the mixture was stirred and heated at 40 °C for 30 min. The reaction was monitored using GC.

Recycle Procedure for CB[6]-Pd NPs

The Suzuki reaction of bromobenzene with phenylboronic acid was used to test the recycle ability of CB[6]-Pd NPs. After the first run was complete, the CB[6]-Pd NPs catalyst was separated by centrifugation and was washed with ethanol and water to remove adsorbed organic substrates and salt. The catalyst was dried overnight at 70 °C prior to being reused. Then the catalyst was used for the second run without further activation and the same process was repeated for the next run.

Results and Discussion

Synthesis and Structure of Dinuclear Palladacycle

The reaction of 3-(dimethylaminomethyl)indole with $Pd(OAc)_2$ in a 1:1 molar ratio was carried out in toluene at 60 °C for

Table 1. Optimizing of reaction conditions for Suzuki reaction of bromobenzene with phenylboronic acid ^a								
B(OH) ₂ + Br - Catalyst solvent Base, T, t								
Entry	Solvent	Catalyst (mol% Pd)	Base	Temperature (°C)	Time (min)	Conversion (%) ^a	TON ^b	TOF $(h^{-1})^{c}$
1	DMSO-H ₂ O (1:1)	0.05	Na ₂ CO ₃	40	60	93	1860	1860
2	EtOH-H ₂ O (1:1)	0.05	Na ₂ CO ₃	40	30	93	1860	3720
3	EtOH-H ₂ O (1:2)	0.05	Na ₂ CO ₃	40	60	90	1800	1800
4	EtOH-H ₂ O (1:4)	0.05	Na ₂ CO ₃	40	60	85	1700	1700
5	THF-H ₂ O (1:1)	0.05	Na ₂ CO ₃	40	120	95	1900	950
6	H ₂ O	0.05	Na ₂ CO ₃	40	120	80	1600	800
7	EtOH	0.05	Na ₂ CO ₃	40	120	60	1200	600
8	DMF	0.05	Na ₂ CO ₃	40	210	31	620	177.1
9	CH₃CN	0.05	Na ₂ CO ₃	40	30	72	1440	2880
10	MeOH	0.05	Na ₂ CO ₃	40	60	75	1500	1500
11	EtOH-H ₂ O (1:1)	0.05	K ₂ CO ₃	40	180	93	1940	646.6
12	EtOH-H ₂ O (1:1)	0.05	КОН	40	60	55	1100	1100
13	EtOH-H ₂ O (1:1)	0.05	K ₃ PO ₄ .3H ₂ O	40	75	97	1940	1686.9
14	EtOH-H ₂ O (1:1)	0.05	CH₃COONa	40	120	50	1000	500
15	EtOH-H ₂ O (1:1)	0.025	Na ₂ CO ₃	40	120	93	3720	1860
16	EtOH-H ₂ O (1:1)	0.05	Na ₂ CO ₃	Room temp.	300	95	1900	380
17	EtOH-H ₂ O (1:1)	0.05	Na ₂ CO ₃	40	30	88 ^d	1760	3520

^aReaction conditions: bromobenzene (0.25 mmol), phenylboronic acid (0.5 mmol), base (1.25 mmol), solvent (6 ml), catalyst (0.05 mol% Pd), 40 °C, in air. The reactions were monitored using GC.

^bTON = mmol of products/mmol of catalyst.

^cTOF = TON/time.

^dReaction was carried out in the presence of Pd(OAc)₂ supported on CB[6].

24 h to produce five-membered NC palladacycle [(Pd{ κ^2 (N,C)-(3-(dimethylaminomethyl)indole)} μ -OAc)₂] (Scheme 1).

The FT-IR spectrum of complex **1** shows characteristic bands at 1577 and 1413 cm⁻¹ belonging to the bridging acetato ligand.^[30] The ¹H NMR spectrum of complex **1** displays two well-separated sets of signals at 2.29 and 2.31 ppm corresponding to the *N*-methyl protons. A singlet signal attributed to the pyrrole hydrogen of indole is observed at 5.93 ppm. Acetatomethyl and methylene protons are located at 1.96 and 2.99 ppm as two singlet signals, respectively. The ¹³C{H} NMR spectrum of complex **1** shows aliphatic and aromatic regions and the carbon signal of CO is absent. The UV-visible spectrum of the ligand in CH₂Cl₂ has two absorption peaks at 238 and 272 nm. In the spectrum of the complex, these bands are shifted to higher value (240 and 291 nm). The d–d bands from the spectrum of complex **1** having low intensities appear at 511–631 nm. The elemental analysis of the prepared compound is in good agreement with the calculated values.

Synthesis and Characterization of CB[6]-Pd NPs

Simple methods were used for synthesis of CB[6]-Pd NPs. To achieve this goal, glycoluril and CB[6] were prepared in water, and Pd nanoparticles were dispersed on CB[6] in green solvents, namely water and ethanol (Scheme 2).

Previous studies show that carbonyl groups on the surface of CB[6] have an affinity for metal ions and can act as a switch through varying the chemical environment.^[33,34] However, the palladium ions can bind to carbonyl groups at the portal of CB [6] before reducing agent (NaBH₄) is added to the reaction mixture. Perhaps electrostatic interaction between the surface atoms of Pd and CB[6] can effectively prevent the Pd nanoparticles from agglomerating.

The XRD pattern of the fresh Pd nanocatalyst exhibits a broad reflection belonging to CB[6] and also shows peaks at 40°, 46° and 68° corresponding to (111), (200) and (220) crystallographic planes of the Pd(0) nanoparticles that are reflections of the face-centred cubic Pd lattice. This is in good agreement with previous results.^[35] The size of the Pd-NPs is estimated from the XRD pattern (Fig. 2) using the Scherrer equation and is found to be close to the size observed in TEM images.

The SEM images confirm the uniform distribution of Pd NPs onto CB[6] (Fig. 3). According to the TEM images, the Pd nanoparticles are formed and well dispersed through the support surface. The Pd(0) particle sizes of fresh CB[6]-Pd NPs are between 1.12 and 8.92 nm (Fig. 4(a)). The TEM images after the fifth run are also shown in Fig. 4(b). The Pd(0) particle sizes in CB[6]-Pd NPs after use are in the range 0.74–5.40 nm. Also the TEM images show that aggregation of Pd-NPs does not occur even after the fifth run.

Table 2. Suzuki reactions of various aryl halides with arylboronic acids							
$\begin{array}{c} & & \\ R_1 \end{array} \longrightarrow B(OH)_2 + X \longrightarrow \begin{array}{c} & \\ R_2 \end{array} \xrightarrow{\begin{array}{c} Catalyst \\ EtOH:H_2O(1:1) \\ Na_2CO_3, T, t \end{array}} \begin{array}{c} & \\ R_1 \end{array} \xrightarrow{\begin{array}{c} \\ R_2 \end{array} \xrightarrow{\begin{array}{c} \\ R_2 \end{array}} \begin{array}{c} \\ R_2 \end{array} \xrightarrow{\begin{array}{c} \\ R_2 \end{array} \xrightarrow{\begin{array}{c} \\ R_2 \end{array}} \begin{array}{c} \\ R_2 \end{array} \xrightarrow{\begin{array}{c} \\ R_2 \end{array} \xrightarrow{\begin{array}{c} \\ R_2 \end{array}} \begin{array}{c} \\ R_2 \end{array} \xrightarrow{\begin{array}{c} \\ R_2 \end{array} \xrightarrow{\begin{array}{c} \\ R_2 \end{array}} \begin{array}{c} \\ R_2 \end{array} \xrightarrow{\begin{array}{c} \\ R_2 \end{array} \xrightarrow{\begin{array}{c} \\ R_2 \end{array} \xrightarrow{\begin{array}{c} \\ R_2 \end{array}} \begin{array}{c} \\ R_2 \end{array} \xrightarrow{\begin{array}{c} \\ R_2 \end{array} \xrightarrow{\begin{array}{c} \\ R_2 \end{array} \xrightarrow{\begin{array}{c} \\ R_2 \end{array} \xrightarrow{\begin{array}{c} \\ R_2 \end{array}} \begin{array}{c} \\ R_2 \end{array} \xrightarrow{\begin{array}{c} \\ \\ \\ R_2 \end{array} \xrightarrow{\begin{array}{c} \\ \\ \\ R_2 \end{array} \xrightarrow{\begin{array}{c} \\ \\ \\ \\ R_2 \end{array} \xrightarrow{\begin{array}{c} \\ \\ \\ \\ \\ R_2 \end{array} \xrightarrow{\begin{array}{c} \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$							
Entry	R ₁	R ₂	Х	Conversion (%) ^a	Conversion ^b (yield) ^c (%)	TON ^b	$TOF (h^{-1})^{b}$
1	Н	Н	I	98	94 (92)	1880 (1840) ^c	3760 (3680) ^c
2	Н	<i>m</i> -CH₃	I.	88	89	1780	3560
3	Н	<i>p</i> -CH₃CO	I.	94	93	1860	3720
4	Н	p-NO ₂	I.	100	98 (96)	1960 (1920) ^c	3920 (3840) ^c
5	Н	Н	Br	95	93 (92)	1860 (1840) ^c	3720 (3680) ^c
6	Н	<i>p</i> -CH₃CO	Br	50	46	920	1840
7	Н	o-CH₃CO	Br	48	82	1640	3280
8	Н	<i>m</i> -CH₃	Br	78	50	1000	2000
9	Н	p-NO ₂	Br	75	50 (45)	1000 (900) ^c	2000 (1800) ^c
10	Н	o-Py	Br	35	8	160	320
11	Н	1-Naphthalene	Br	91	64	920	1840
12	Н	<i>p</i> -CHO	Br	100	97 (94)	1940 (1880) ^c	3880 (3760) ^c
13	Н	o-CHO	Br	74	65	1300	2600
14	Н	Н	Cl	40	30	600	1200
15	Н	p-NO ₂	Cl	21	21	420	840
16	Н	p-NH ₂	Cl	31	42	840	1680
17	<i>p</i> -OMe	Н	I.	100	100	2000	4000
18	<i>p</i> -OMe	Н	Br	100	97	1940	3880
19	<i>p</i> -OMe	p-CHO	Br	100	100 (96)	2000 (1920) ^c	4000 (3840) ^c
20	<i>p</i> -OMe	1-Naphthalene	Br	82	85	1700	3400
21	<i>p</i> -OMe	m-CH ₃	Br	77	64	1280	2560
22	<i>p</i> -OMe	Н	н	35	28	560	1120
23	<i>p</i> -OMe	Н	p-NO ₂	49	41	820	1640

^aReaction conditions: aryl halides (0.25 mmol), arylboronic acid (0.5 mmol), Na₂CO₃ (1.25 mmol), EtOH–H₂O (1:1) (6 ml), catalyst (0.05 mol% Pd), room temperature, 5 h, in air. Reactions were monitored using GC.

^bReaction conditions: aryl halides (0.25 mmol), arylboronic acid (0.5 mmol), Na₂CO₃ (1.25 mmol), EtOH–H₂O (1:1) (6 ml), catalyst (0.05 mol% Pd), 40 °C, 30 min, in air. Reactions were monitored using GC.

^cAccording to isolated yields.



CB[6]-Pd NPs Catalyse the Suzuki Reaction

CB[6]-Pd NPs catalyst was tested for the Suzuki reaction of aryl halides with arylboronic acids. For this purpose we initially used various solvents for the coupling reaction of bromobenzene with phenylboronic acid to optimize the reaction conditions at 40 °C. Table 1 summarizes the Suzuki reaction results. All reactions give 100% selectivity to the biphenyl coupling product. Solvents have marked effects on C-C bond formation. As a result, in the presence of Na₂CO₃ and CB[6]-Pd NPs (0.05 mol% Pd), EtOH-H₂O mixture with 1:1 ratio is the best choice (Table 1, entry 2). However, it is clear that a suitable amount of water is very important for dissolving the base and improving the reactivity of Suzuki reactions. Therefore other mixtures of solvents such as DMSO-H₂O (1:1) and THF-H₂O (1:1) were tested and show very good results (Table 1, entries 1 and 5). Therefore, we evaluated the bases Na₂CO₃, CH₃COONa, K₃PO₄·3H₂O, KOH and K₂CO₃ (Table 1, entries 2, 11-14), and Na₂CO₃ was selected as the base for Suzuki reactions (Table 1, entry 2). Also, lowering of the amount of CB [6]-Pd NPs from 0.05 to 0.025 mol% Pd leads to a longer period of reaction (Table 1, entry 15). For further investigation, Pd(OAc)₂ was also supported on CB[6] and, in comparison with the present catalyst (CB[6]-Pd NPs), lower turnover number (TON) and turnover frequency (TOF) are obtained (Table 1, entries 2 and 17). In comparison with results of previous studies, this catalytic system provides higher TON and TOF.^[16,18]

In addition, the reaction was tested at room temperature and gives very good yield with a longer reaction time (Table 1, entry 16). The excellent yield under such extremely mild conditions inspired our further exploration of the catalytic effect of CB[6]-Pd NPs on Suzuki reactions of various aryl halides. To this end, we tested the reactions of various aryl halids with arylboronic acids under optimized conditions at both room temperature and 40 °C. The results are listed in Table 2. Both temperatures show good results. Without heating the reaction mixture, more time is required; but in order to save energy and prevent global warming, room temperature Suzuki reactions are suggested.

As evident from Table 2, various aryl halides were tested containing either electron-donating or electron-withdrawing groups such as -Me, -OMe, $-NO_2$ and -CHO. Generally, electron-withdrawing groups afford the corresponding product very efficiently (Table 2, entries 4, 12, 13 and 19). However, in our catalytic system, for aryl iodides, all strongly electron-withdrawing or electron-donating groups such as $-NO_2$ and $-CH_3$ afford the corresponding products in very high yields (Table 2, entries 1–4). The reactions of substituted bromobenzene and chlorobenzene with *p*-NO₂ group are slower than that of bromobenzene in both temperatures (Table 2, entries 9 and 15). The reasons for this are not clear. In addition, aryl halides with *ortho* substitution are poor substrates, which is because of steric hindrance. This rule is seen in the case of 2-bromobenzaldehyde (Table 2, entry13). The coupling between aryl halides and phenylboronic acid containing an electron-donating group (OMe) also proceeds readily to afford the corresponding products in good yields with high TOF (Table 2, entries 17–23).

The catalytic activity of complex **1** was also studied in the Suzuki reaction of various aryl halides with phenylboronic acid using the optimized heterogeneous Suzuki reaction conditions. As presented in Table 3, in these homogeneous systems, different aryl halides react with phenylboronic acid to give the corresponding biaryls. In comparison with the homogeneous system, Suzuki reactions in the presence of CB[6]-Pd NPs (heterogeneous system) can be considered as efficient and versatile catalytic reactions for the C–C cross-coupling reaction under mild conditions.

Thus this catalytic system provides a simple and green method for the Suzuki reaction of aryl halides in low temperatures and in air. Compared to previous research,^[12,29] this catalytic system requires a very small amount of catalyst loading and can be run under relatively mild reaction conditions.



Figure 5. Recyclability test for catalyst in Suzuki reaction.

Table 4. Comparison with reported results for Suzuki reaction using supported Pd catalysts							
Entry	Catalyst ^a	Reaction conditions (solvent/base/temp./time)	Yield (%) ^b	TOF (h^{-1})	Ref.		
1	Pd/bentonite (0.06)	MeOH/K ₂ CO ₃ /25 °C/5 h	95	320	[36]		
2	Polymer-supported macrocyclic Schiff base palladium complex (0.1)	DMF–H ₂ O/K ₂ CO ₃ /25 °C/0.5 h	99	1980	[18]		
3	Polymeric Pd catalyst (0.1)	DMF/K ₂ CO ₃ /80 °C/1 h	85	850	[17]		
4	Fe ₃ O ₄ @PUNP (0.1)	H ₂ O/K ₂ CO ₃ /90 °C/1 h	95	950	[37]		
5	Pd NPs/PS (0.5)	DMF-H ₂ O/Na ₂ CO ₃ /110 °C/12 h	80	160	[14]		
6	CB[6]-Pd NPs (0.05)	EtOH-H ₂ O/Na ₂ CO ₃ /40 °C/0.5 h	92	3680	This work		
^a Data in parentheses indicate mol% of Pd used. ^b Based on bromobenzene yields.							

Recycle of CB[6]-Pd NPs

After the catalytic reactions, the recovery and reusability of the CB [6]-Pd NPs were initially investigated in the Suzuki reaction of bromobenzene with phenylboronic acid as model substrates. The recycle method is simple: the CB[6]-Pd NPs catalyst was used for reaction and recovered after reaction completion by centrifugation and was washed with ethanol and water. The catalyst, which is highly reusable, was used for five cycles and retains its catalytic activity in these repeat cycles (Fig. 5). TEM images of the recycled CB [6]-Pd NPs show that, after the fifth run, Pd nanoparticles do not agglomerate on the surface of CB[6] (Fig. 4(b)). This is an interesting result and confirms the good catalytic activity of CB[6]-Pd NPs even after five cycles. ICP-OES analysis shows that the palladium content of fresh CB[6]-Pd NPs is 11.8 wt% and palladium leaching of used CB[6]-Pd NPs after five runs is negligible, which confirms the heterogeneous character of the catalytically active species, improved reusability of the nanocatalyst and decreased pollution caused by the catalyst. For further investigation of Pd leaching during the Suzuki reaction, a hot-filtration experiment was run. The catalyst was removed after a certain time (10 min) and the resulting filtrate was monitored after additional reaction time under identical reaction conditions (30 min). The filtrate gives no coupling product after the removal of catalyst from the reaction mixture, as analysed using GC. This result suggests that the catalytic process occurs on the surface of Pd NPs and it is a heterogeneous reaction pathway.

Comparison with Other Studies

The catalytic performance of the CB[6]-Pd NPs catalyst for the Suzuki reaction was compared with some previously reported results using various types of supports. As evident from Table 4, comparing with other supported palladium catalysts, the CB[6]-Pd NPs catalyst exhibits comparable yields with low catalyst loading in short reaction times with high TOF. Also, the preparation process of the CB[6]-Pd NPs catalyst is very simple and environmentally friendly.

Conclusions

We have reported the synthesis of a new dimeric NC palladacycle and a simple method for dispersing it onto the surface of CB[6]. CB[6]-Pd NPs preparation reaction was carried out in green solvents (H₂O and EtOH). The introduced Pd nanocatalyst was used in the coupling reactions of various aryl halides with arylboronic acids in H₂O–EtOH (1:1) and excellent results were obtained. Using green solvents, total separation of CB[6]-Pd NPs from the reaction products, short reaction times for the Suzuki reaction, performance at room temperature and recyclability of the catalyst for at least five times without reduction in catalytic activity can also be regarded as advantages of this method.

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References

- [1] I. Omae, Coord. Chem. Rev. 2004, 248, 995.
- I. P. Beletskaya, A. V. Cheprakov, J. Organometal. Chem. 2004, 689, 4055.
 D. S. Ryabukhin, V. N. Sorokoumov, E. A. Savicheva, V. P. Boyarskiy,
- I. A. Balova, A. V. Vasilyev, *Tetrahedron Lett.* **2013**, *54*, 2369. [4] K. Karami, N. Rahimi, M. Bahrami Shehni, *Tetrahedron Lett.* **2012**, *53*, 2428.
- [5] M. Beller, Chem. Ing. Tech. 2006, 78, 1061.
- [6] N. Selander, K. J. Szabo, Chem. Rev. 2011, 111, 2048.
- [7] C. E. Tucker, J. G. De Vries, Top. Catal. 2002, 19, 111.
- [8] B. M. Bhanage, M. Arai, Catal. Rev. Sci. Eng. 2001, 43, 315.
- [9] S. J. Sabounchei, M. Ahmadi, Z. Nasri, E. Shams, M. Panahimehr, Tetrahedron Lett. 2013, 54, 4656.
- [10] C. Liu, Q. Ni, F. Bao, J. Qiu, Green Chem. 2011, 13, 1260.
- [11] K. Komura, H. Nakamura, Y. Sugi, J. Mol. Catal. A 2008, 293, 72.
- [12] K. Karami, M. Bahrami Shehni, N. Rahimi, Appl. Organometal. Chem. 2013, 27, 437.
- [13] A. Biffis, M. Zecca, M. Basato, J. Mol. Catal. A 2001, 173, 249.
- [14] K. Karami, M. Ghasemi, N. Haghighat Naeini, *Catal. Commun.* **2013**, *38*, 10.
- [15] K. Karami, Z. Karami Moghadam, M. Hosseini-Kharat, Catal. Commun. 2014, 43, 25.
- [16] F. Durap, M. Rakap, M. Aydemir, S. Ozkar, Appl. Catal. A 2010, 382, 339.
- [17] B. Tamami, S. Ghasemi, J. Mol. Catal. A 2010, 322, 98.
- [18] Y. He, C. Cai, Catal. Commun. 2012, 12, 678.
- [19] S. V. Ley, C. Ramarao, R. S. Gordon, A. B. Holmes, A. J. Morrison, I. F. McConvey, I. M. Shirley, S. C. Smith, M. D. Smith, *Chem. Commun.* 2002, *10*, 1134.
- [20] N. Miyaura, Metal-Catalyzed Cross Coupling Reactions, 2nd edn, Wiley-VCH, Weinheim, 2004.
- [21] N. Miyaura, A. Suzuki, Chem. Rev. 1995, 95, 2457.
- [22] A. Suzuki, J. Organometal. Chem. **1999**, 576, 147.
- [23] D. Astruc, F. Lu, J. R. Aranzaes, Angew. Chem. Int. Ed. 2005, 44, 7852.
- [24] W. Han, C. Liu, Z. L. Jin, Org. Lett. 2007, 9, 4005.
- [25] N. J. S. Costa, P. K. Kiyohara, A. L. Monteiro, Y. Coppel, K. Philippot, L. M. Rossi, J. Catal. 2010, 276, 382.
- [26] N. Jamwal, R. KourSodhi, P. Gupta, S. Paul, Int. J. Biol. Macromol. 2011, 49, 930.
- [27] F. Diederich, P. J. Stang, R. R. Tykwinski (Eds). Modern Supramolecular Chemistry: Strategies for Macrocycle synthesis, Wiley-VCH, Weinheim, 2008.

- [28] K. Jansen, H. J. Buschmann, A. Wego, D. Dopp, C. Mayer, H. J. Drexler, H. J. Holdt, E. Schollmeyer, J. Incl. Phenom. Macrocyclic Chem. 2001, 39, 357.
- [29] M. Cao, Y. Wei, S. Gao, R. Cao, Catal. Sci. Technol. 2012, 2, 156.
- [30] Y. Fuchita, H. Tsuchiya, A. Miyafuji, *Inorg. Chim. Acta* **1995**, *233*, 91.
- [31] W. A. Freeman, W. L. Mock, N.-Y. Shih, J. Am. Chem. Soc. 1981, 103, 7367.
- [32] J. W. Lee, S. Samal, N. Selvapalam, H.-J. Kim, K. Kim, Acc. Chem. Res. 2003, 36, 621.
- [33] H.-J. Buschmann, E. Cleve, L. Mutihac, E. Schollmeyer, J. Incl. Phenom. Macrocyclic Chem. 2009, 65, 293.
- [34] A. L. Koner, C. Márquez, M. H. Dickman, W. M. Nau, Angew. Chem. Int. Ed. 2011, 50, 545.
- [35] S. Martinez, A. Vallribera, C. L. Cotet, M. Popovici, L. Martin, A. Roig, M. Moreno-Manas, E. Molins, New J. Chem. 2005, 29, 1342.
 - [36] G. Ding, W. Wang, T. Jiang, B. Han, Green Chem. **2013**, *15*, 3396.
- [37] J. Yang, D. Wang, W. Liu, X. Zhang, F. Bian, W. Yu, Green Chem. 2013, 15, 3429.

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