Short communication

Selective homocoupling of phenylboronic acid over supported Pd nanoparticle in biphase solvent

Shaodan Xu [a,b,*], Huadong Sheng [b], Shangfu Liao [b], Dan Hu [b], Deqing Yu [b], Tao Ye [b,c]

[a] Department of Chemistry, Zhejiang University, Hangzhou 310027, China
[b] Zhejiang Institute of Quality Inspection Science, Hangzhou 310018, China
[c] MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

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ABSTRACT

We reported an effective method to improve the biphenyl selectivity by employing a biphasic solvent of water-toluene mixture over hydrophilic Pd catalyst. The coupling reactions occurred in water, and the biphenyl product formed in water could be immediately extracted into the toluene, leading to the shift of reaction balance to the formation of biphenyl. By using a hydrophilic Pd catalyst, the conversion of phenylboronic acid and biphenyl selectivity could reach as high as 99.0 and 83.0%, respectively, which are much higher than those in mono-phase solvent under the same conditions. More importantly, the heterogeneous Pd nanocatalyst exhibited excellent recyclability.

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1. Introduction

One of the most important developments in the field of organic synthesis is the metal-catalyzed coupling reactions, which are widely used for the formation of C—C bonds [1–12]. The well-known coupling reactions (e.g. Suzuki [1,13–15], Heck [16–18] and Sonogashira reactions [18–20]) have attracted much attention in both laboratory research and industrial application. Conventionally, homogeneous Pd complex is employed as highly active catalyst for the coupling reactions [2,5, 20]. Notably, these homogeneous catalysts have difficulty in separation and regeneration from the reaction liquor, which makes it high-cost and environmentally unfriendly for wide applications [21]. Supporting Pd nanoparticles or complex on the solid support to synthesize heterogeneous catalyst is regarded as efficient method to solve the problem in catalyst separation [22,23,24]. However, in most of these cases, the soluble organic ligands are still necessary, making these processes are still unsatisfactory for further application. Therefore, developing efficient heterogeneous catalysts without using organic ligands is still challenging.

The aerobic homocoupling of phenylboronic acid has been regarded as an efficient strategy to synthesize biphenyl without using toxic halogen aromatics [25]. However, phenol by-product is usually formed in the homocoupling reactions, where the yield of desired biphenyl product is still unsatisfactory. Hindering the formation of phenol to improve the biphenyl selectivity in homocoupling is an attractive topic, but achieving this goal is difficult due to the easy formation of phenol from the coupling of aromatic intermediate and hydroxyl species. Additionally, it is worth noting that Au-based catalysts of Au^+-Shiff based complex [26], Au nanoparticles [25,27], and CeO_2 supported Au^{3+} and Au^+ species [28] have been found to be efficient catalysts for the homocoupling of phenylboronic acid. To the best of our knowledge, Pd nanoparticle catalysts, which have been industrially used for various reactions, are more beneficial for wide application than Au catalysts, but the Pd nanoparticles also have the problems in biphenyl selectivity. Therefore, developing efficient Pd catalysts for the homocoupling of phenylboronic acid with high selectivity to biphenyl is challenging.

In this work, we reported an effective strategy to improve the biphenyl selectivity by employing a biphasic solvent of water-toluene mixture over hydrophilic Pd catalyst. In this case, the coupling reactions occurred in water, and the biphenyl product formed in water could be immediately extracted into the toluene, leading to the shift of reaction balance to the formation of biphenyl. By using a hydrophilic mesoporous silica supported Pd catalyst, which has been widely studied in various reactions [29–32], the conversion of phenylboronic acid and selectivity of biphenyl could reach as high as 99.0 and 83.0%, respectively, which are much higher than those in mono-phase solvent under the same reaction conditions. More importantly, the heterogeneous Pd catalysts in the biphase solvent can be easily separated, exhibiting excellent recyclability in the aerobic homocoupling reactions.

* Corresponding author at: Department of Chemistry, Zhejiang University, Hangzhou 310027, China.
E-mail address: xushaodan6677@126.com (S. Xu).

2. Experimental

2.1. Sample preparation

All chemicals were commercially available and directly used without any treatment. MCM-41 was obtained from Xianfeng Nano Co. Ltd.

2.1.1. Synthesis of Pd/MCM-41

Organosilicon-modified MCM-41was prepared from the interaction between MCM-41 with KH-550. As a typical run, 0.3 g of MCM-41 was dried at 393 K under vacuum for 3 h, followed by addition of 10 mL of toluene pretreated and 0.5 g of KH-550. The mixture was refluxed overnight and collected by rotary evaporation, followed by washing with a large amount of ethanol. The organosilicon-modified MCM-41 was obtained. Pd/MCM-41 was prepared by addition of organosilicon-modified MCM-41 into Na_2PdCl_4 solution, stirring at room temperature for overnight, drying at 373 K under vacuum, reduction by $NaBH_4$ in anhydrous toluene, and washing with a large amount of ethanol and water. After calcining at 500 °C in oxygen to remove the organic species, Pd/MCM-41 was obtained. By ICP analysis, the Pd loading was established to be 1.5 wt%. The Au, Pt and Ru supported on MCM-41 were synthesized in the same method except changing the metal precursor.

2.2. Sample characterization

Powder X-ray diffraction patterns (XRD) were obtained with a Rigaku D/MAX 2550 diffractometer with Cu Kα radiation (λ = 0.1542 nm). The content of Pd was determined from inductively coupled plasma (ICP) with a Perkin-Elmer plasma 40 emission spectrometer. Transmission electron microscopy (TEM) experiments were performed on a JEM-3010 electron microscope (JEOL, Japan) with an acceleration voltage of 200 kV. Nitrogen isotherms at the temperature of liquid nitrogen were measured using a Micromeritics ASAP Tristar. The samples were outgassed for 10 h at 150 °C before the measurement. Pore-size distribution for mesopores was calculated using Barrett-Joyner-Halenda (BJH) model.

2.3. Catalytic tests

Aerobic homocoupling of phenylboronic acid was carried out in a high-pressure autoclave with a magnetic stirrer. Typically, the substrate, catalyst, and solvent were mixed in the reactor, then the reaction system was heated to a given temperature and oxygen was introduced and kept at desired pressure. After the reaction, the product was taken out from the reaction system and analyzed by gas chromatography (GC-2014 Shimadzu, using a flame ionization detector with a flexible quartz capillary column coated withOV-1 and FFAP). The conversion of phenylboronic acid and product selectivities were obtained from the product yields which was established by internal standard. The recyclability of the catalyst was tested by separating it from the reaction system by centrifugation, washing with large quantity of methanol and drying at vacuum for overnight.

3. Results and discussion

In order to obtain hydrophilic Pd catalyst, the KH-550 modified mesoporous silicate of MCM-41 (Scheme S1, Fig. S1) was employed to support Pd nanoparticles, denoted as Pd/MCM-41. In this case, the role of KH-550 is to modify the MCM-41 surface with amino groups, which benefits the distribution and formation of small-size metal nanoparticles in the mesoporous of MCM-41 [29,33,34]. Fig. 1A shows the small-angle XRD patterns of Pd/MCM-41, which exhibited peaks at 2.1, 3.7 and 4.2°, assigning to typical *p6mm* structure, similar to that of as-synthesized MCM-41. Fig. 1B shows the N_2 sorption isotherms of MCM-41 and Pd/MCM-41, which exhibit IV-type curves associated
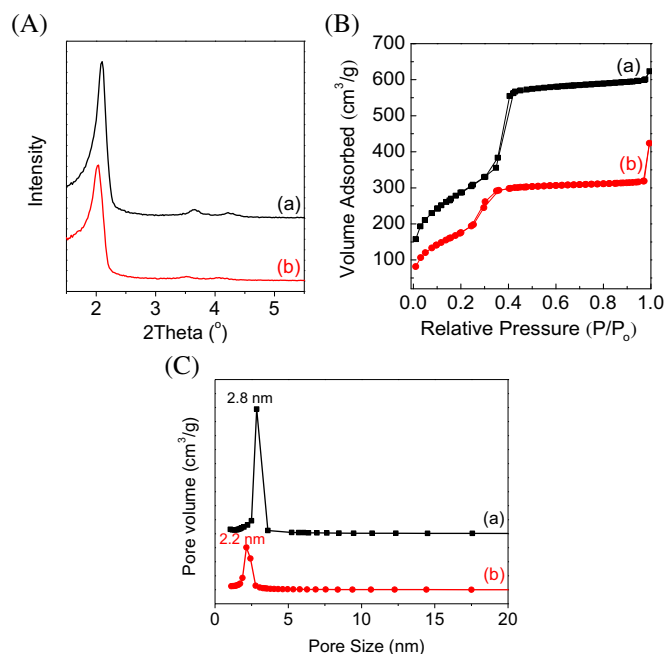
Fig. 1. (A) Small-angle XRD patterns, (B) N_2-sorption isotherms and (C) pore size distribution of (a) MCM-41 and (b) Pd/MCM-41.

with typical mesoporous structure. These results indicate the mesoporous structure of MCM-41 was well maintained during the synthesis of Pd/MCM-41. Notably, the surface area and mesopore diameter of Pd/MCM-41 (690 m^2/g and 2.2 nm) are smaller than those of as-synthesized MCM-41 (880 m^2/g and 2.8 nm), which suggest the successful grafting of organosilicon and loading of Pd nanoparticles in the mesopores (Fig. 1C, Table 1).

TEM gives direct observation of the Pd nanoparticles on Pd/MCM-41. As shown in Fig. 2A, the Pd nanoparticles are highly dispersed in the mesopores of MCM-41 support. By counting more than 80 nanoparticles, the Pd nanoparticle size distribution was established at 2–5 nm. The dispersion degree of Pd (mole ratio of Pd atoms on the surface/ total Pd atoms) was established at 39.3% by CO-adsorption test (Table 1). Additionally, water-droplet contact angle test was carried out to understand the wettability of Pd/MCM-41. It is well knows that silica (MCM-41) is superhydrophilic due to the rich hydroxyl groups. Notably, after loading Pd nanoparticles, the Pd/MCM-41 is still superhydrophilic with water droplet contact angle smaller than 5° (Fig. 2B).

The catalytic tests start from aerobic homocoupling of phenylboronic acid in various solvent at 80 °C (Figs. S2 and S3). Notably, oxygen was necessary in these reactions for regenerating the metal sites after the coupling step according to the mechanism in literature [25,35]. As summarized in Table 2, different solvents have obvious influences on the catalytic performances of Pd/MCM-41. In the solvents of toluene, NMP and THF, which are usually used in coupling reactions, the Pd/MCM-41 exhibit high selectivity of 80–90% to biphenyl and low phenylboronic acid conversion of 3.3–33.0% (entries 1–3 in Table 2). In comparison, when water was used as solvent, the conversion of phenylboronic acid

Table 1
Structural parameters of Pd/MCM-41 and MCM-41.

Samples	BET surface area (m^2/g)	Pore size (nm)	Pd loading (%)[a]	Dispersion degree of Pd (%)[b]
Pd/MCM-41	690	2.2	1.5	39.3
MCM-41	880	2.8	–	–

[a] By ICP analysis.
[b] By CO-adsorption test.
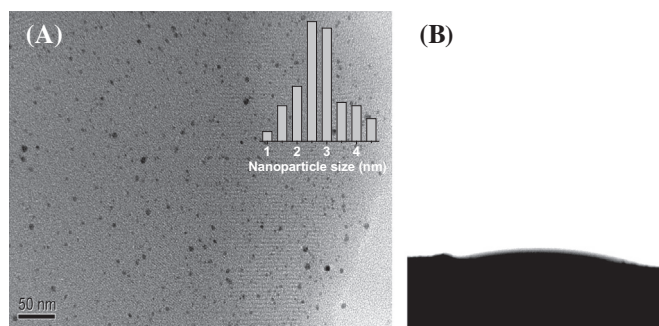
Fig. 2. (A) TEM image and (B) Water-droplet contact angle of Pd/MCM-41. Insert: size distribution of Pd nanoparticles.

Fig. 3. Catalytic data of Pd/MCM-41 in aerobic coupling of phenylboronic acid in biphase solvent with different water and toluene ratios. The reaction conditions are the same to those in Table 2.

could reach as high as 71.0%, but the biphenyl selectivity was extremely low at only 2.2% (entry 4 in Table 2). This phenomenon is because that the benzene intermedia could easily react with hydroxyl species in water to form phenol by-product. When a mono-phase mixture of water and THF was used as solvent, similar catalytic results to those in pure water solvent were obtained (entry 5 in Table 2). Interestingly, when a mixture of water and toluene (weight ratio at 2/3) was used, the phenylboronic acid conversion could reach as high as 99% with significantly enhanced biphenyl selectivity at 83.0% (entry 6 in Table 2). These results indicate the positive effect of the biphase solvent for the homocoupling of phenylboronic acid to biphenyl.

Furthermore, the influence of water/toluene ratio for the reaction was studied. As summarized in Fig. 3, the phenylboronic acid conversion was always very high in the biphase solvent. Notably, the biphenyl selectivity increases with the amount of toluene. Considering both the phenylboronic acid conversion and the biphenyl selectivity, the biphase water-toluene with weight ratio at 2/3 was employed as the biphase solvent. Moreover, various metals of Au, Pt, and Ru supported on MCM-41 was also used in the homocoupling reactions in biphase solvent (entries 7–9, Table 2), which exhibit lower activity or selectivity than the Pd/MCM-41 catalyst. These results indicate the excellent catalytic performances of Pd/MCM-41 in biphase water-toluene for the homocoupling reactions. Notably, this positive effect of biphase water-toluene solvent is not only limited to Pd/MCM-41 catalyst, but also can be extended to the other hydrophilic catalysts of Pd/TiO$_2$ and Pd/MgO. In the biphase solvent, Pd/TiO$_2$ and Pd/MgO exhibited high Ph-B(OH)$_2$ conversion and biphenyl selectivity, which is unachieved in the toluene solvent (Table S1).

In order to understand the unique catalytic performances of Pd/MCM-41 in the biphase solvent, the content of substrate and products

in water and toluene phase were analyzed separately. The contents of phenylboronic acid, biphenyl, and phenol in water and toluene phase before and after reaction were summarized in Table 3, before the reaction, most of the phenylboronic acids are presented in water phase containing Na$_2$CO$_3$ due to the high solubility in basic aqueous solution. After a 6-h conversion, all the phenylboronic acid was converted, and the biphenyl products are presented in toluene, while most of the phenol products are present in water. During the reaction process, the Pd/MCM-41 catalyst with superhydrophilicity was always present in the water phase. Based on these phenomena, it could be reasonably to propose that the conversion of phenylboronic acid occurred in water phase *via* two reaction routes to form biphenyl and phenol. During the reaction, the biphenyl product was immediately transferred into the toluene phase, while the phenol product was kept in water (Scheme 1). This biphase system could form high concentration of phenol and low concentration of biphenyl around the Pd/MCM-41 catalyst in water phase, thus shifting the reaction balance to the formation of biphenyl [35].

It is worth noting that the Pd/MCM-41 catalyst is recyclable. After each reaction run, the catalyst can be easily separated from the reaction system and reused in the next run. Even after using for five times, the catalyst still gave phenylboronic acid conversion at 92.0% and biphenyl selectivity at 79.5% (entry 10 in Table 2), which are comparable to those of the as-synthesized catalyst. These results indicate the good recyclability of Pd/MCM-41.

4. Conclusion

In summary, we report an efficient bi-phase water-toluene solvent for the aerobic homocoupling of phenylboronic acid to biphenyl. By employing superhydrophilic Pd/MCM-41 as catalyst, the selectivity to biphenyl could reach 83.0% with 99.0% conversion of phenylboronic acid, which are much higher than those in the conventional monophase solvent. The good catalytic performances are reasonably attributed to the synergistic effect of bi-phase water and toluene, which are favorable for shifting the reaction balance to the formation of biphenyl. This work

Table 2
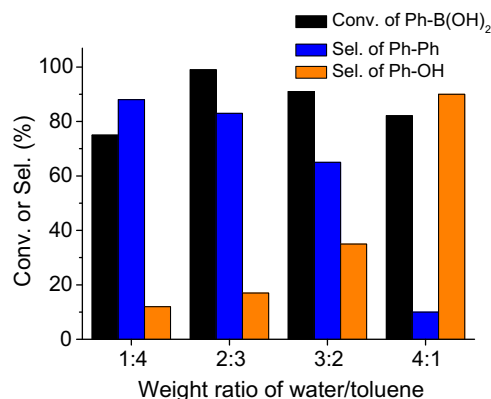Catalytic data in aerobic homocoupling of phenylboronic acid over Pd/MCM-41 in various solvents.[a]

Entry	Solvent	Catalyst	Conv. of Ph-B(OH)$_2$ (%)	Selectivity (%)	
				Ph-Ph	Ph-OH
1	Toluene	Pd/MCM-41	33.0	90.0	10.0
2	NMP	Pd/MCM-41	11.0	89.0	11.0
3	THF	Pd/MCM-41	3.3	80.0	20.0
4	H$_2$O	Pd/MCM-41	71.0	2.2	97.8
5	H$_2$O + THF[b]	Pd/MCM-41	4.4	5.9	94.1
6	H$_2$O + Toluene[c]	Pd/MCM-41	99.0	83.0	17.0
7	H$_2$O + Toluene[c]	Au/MCM-41	34.2	90.5	9.5
8	H$_2$O + Toluene[c]	Pt/MCM-41	4.0	10.2	89.8
9	H$_2$O + Toluene[c]	Ru/MCM-41	<1.0	–	–
10	H$_2$O + Toluene[c,d]	Pd/MCM-41	92.0	79.5	20.5

[a] Reaction conditions: 1 mmol of phenylboronic acid, 0.2 mmol of Na$_2$CO$_3$, 5 mL of solvent, 30 mg of Pd/MCM-41 catalyst, 1.5 MPa of O$_2$, 80 °C, 6 h.
[b] 2 g of water and 3 g of THF.
[c] 2 g of water and 3 g of toluene.
[d] In the fifth run.

Table 3
The content of phenylboronic acid, biphenyl, and phenol in biphase solvent.[a]

Distribution	Contents of various compounds (mmol)					
	Before reaction			After 6-h reaction		
	Ph-B(OH)$_2$	Ph-Ph	Ph-OH	Ph-B(OH)$_2$	Ph-Ph	Ph-OH
Total	1.00	–	–	0.01	0.82	0.17
In toluene	0.05	–	–	–	0.82	0.02
In water	0.95	–	–	0.01	–	0.15

[a] Reaction conditions: 1 mmol of phenylboronic acid, 0.2 mmol of Na$_2$CO$_3$, 2 g of water and 3 g of toluene, 30 mg of Pd/MCM-41 catalyst, 1.5 MPa of O$_2$, 80 °C, 6 h.
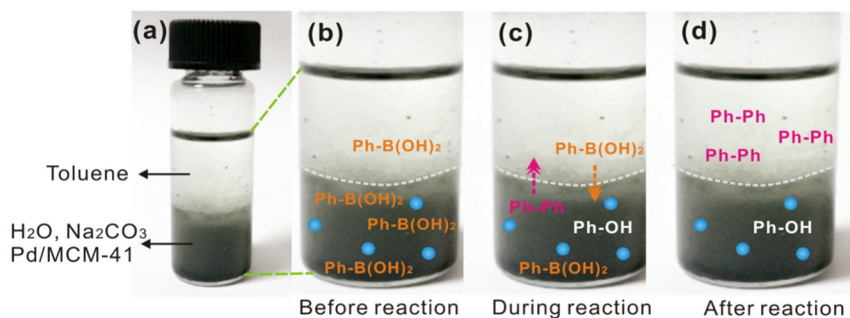
Scheme 1. Distribution of (a) Pd/MCMC-41 catalyst and (b)–(d) phenylboronic acid, biphenyl, and phenol in toluene and water phase (● = Pd/MCM-41).

would be helpful for developing more efficient strategies for coupling reactions in the future.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2016.11.003.

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