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A self-assembled bisoxazoline/Pd composite microsphere as an excellent catalyst for Suzuki-Miyaura coupling reaction

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Palladium complex based on a novel oxazoline, a solid microsphere catalyst, was successfully prepared. The structure and composition of the solid catalyst were characterized by SEM, \textsuperscript{1}H NMR, TGA and FT-IR. This catalyst exhibits high catalytic activity for Suzuki-Miyaura cross-coupling reactions of various aryl halides and arylboronic acids in aqueous media. Moreover, the catalyst shows outstanding stability and reusability, can be recovered simply and effectively and reused eight times without any activity decrease.

Introduction

Palladium-catalyzed Suzuki-Miyaura (SM) cross-coupling reactions that lead to the formation of new C-C bonds are of strategic importance in synthetic organic chemistry because of the broad functional group tolerance of this catalytic process.\textsuperscript{1} It is one of the most powerful tools for the preparation of unsymmetrical biaryl derivatives that are structural elements of numerous natural products, agrochemicals, pharmaceuticals, and polymers.\textsuperscript{2,3} In general, Suzuki-Miyaura (SM) reaction was usually performed in the presence of Pd-phosphine complexes.\textsuperscript{6-9} However, phosphane ligands are usually toxic, unrecoverable, thermally unstable, and their synthesis are difficult.

In order to avoid mentioned disadvantages, there are growing interests in using phosphine free palladium catalyzed Suzuki-Miyaura coupling reactions in past years. A number of phosphine-free ligands for the Suzuki-Miyaura reaction had been reported in numerous literature such as N-heterocyclic carbenes,\textsuperscript{10-11} diimines,\textsuperscript{12-13} diaminos,\textsuperscript{14-15} and N,O ligands.\textsuperscript{16-18} However, the homogeneous catalysts can easily lead to a giant heat release effect and a serious reactor fouling in the slurry process of olefin polymerization. Thus the application of these catalysts in a continuous process is difficult. In general, the way to solve these problems is to immobilize palladium complexes on various supports to create heterogeneous catalysts.\textsuperscript{19-25} However, some heterogeneous palladium catalysts show lower reactivity than homogeneous ones due to leaching of palladium from the supports.\textsuperscript{26-28} In fact, the leached palladium species is responsible for the catalytic activity in most of the cases. Thus, there is a need to design of new heterogeneous catalysts that can retain the activities and selectivities of homogeneous catalysts.

Recently, metal-organic polymerization catalysts through the formation of “self-assembled” is a promising strategy to realize heterogenization of the homogeneous catalysts or precursors.\textsuperscript{29} Compared with other methods, the self-assembled strategy can produce heterogeneous catalysts without using any supports with high density of catalytically active units. \textbf{(Scheme 1)} Our hypothesis takes advantage of the self-assembled strategy, and it could also be conceptually possible to generate self-assembled catalysts or catalyst precursors. However, the catalysts could be recovered heterogeneously.

![Scheme 1](https://example.com/scheme1.png)

\textbf{Scheme 1} The principle of self-assembled catalysis.

![Scheme 2](https://example.com/scheme2.png)

\textbf{Scheme 2} Suzuki-Miyaura coupling reaction catalysed by self-assembled bisoxazoline/Pd composite microsphere

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\textsuperscript{d} Footnotes relating to the title and/or authors should appear here.
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/s0000000x

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Driven by these results, herein, we report the synthesis of a novel self-assembled bisoxazoline/Pd composite microsphere, and investigate the catalytical property for Suzuki-Miyaura coupling reaction under mild and environmental friendly conditions (Scheme 2).

**Results and Discussion**

**Preparation and characterization of the catalyst**

As illustrated in Scheme 3, the synthesis of the ligand (C) is a straightforward process starting from 4,4'-oxybisbenzoyl chloride and 2-aminoethanol, which are inexpensive. 4,4'-oxybisbenzoyl chloride (A) was treated with ammonium sulfocyanide in the presence of PEG-400 in CH$_2$Cl$_2$, followed by the addition of 2-aminoethanol, to obtain 4,4'-oxybis(N-((2-hydroxyethyl)carbamothioyl)benzamide) (B) in good yields (85%). This intermediate can be used to implement the intramolecular cyclization in the presence of DCC to obtain the corresponding 4,4'-oxybis(N-(4,5-dihydrooxazol-2-yl)benzamide)(C) as the ligand in excellent yields (98%). By means of the self-assembled coordination, Pd(OAc)$_2$ was added into the solution of the ligand in acetonitrile, and then the pale yellow powder was obtained as the catalyst (D). After washing with solvent (DMF) thoroughly and drying, the solid remains pale yellow. However, the complex between ligand and palladium acetate was synthesized without using any deprotonating base.

The catalyst has a high melting point of above 200 °C, and it was observed to be insoluble in the polar solvents (DMF, methanol, ethanol), which enable the catalyst to be a solid catalyst for organic reaction.

The structure of the synthesized palladium complex was characterized using different techniques such as $^1$H NMR, TGA, IR, and SEM. $^1$H NMR spectra difference between the novel oxazoline ligands and their metal complexes is one of the important methods for characterization of complexes in the literature.$^{30,31}$ However, it is difficult to distinguish the $^1$H NMR spectra difference between the novel bisoxazoline ligands and its metal complexes owing to its poor solubility in DMSO-D$_6$. Therefore, we focused on the synthesis of N-(4,5-dihydrooxazol-2-yl)benzamide(E), and prepared the its Pd complex (F) to confirm successful chelation of ligand to Pd (Scheme 4). It is worth to note that, the $^1$H NMR spectra of the ligand (E) in DMSO-D$_6$ and its palladium complex (F) is similar, but the protons of oxazoline in the complex are shifted downfield relative to the protons of the ligand, which results from the complexation of N,O ligands and Pd. In addition, the protons of N-H in the ligand(E) disappeared(Fig. 1). This result is accordant to our previous work.$^{32}$

![Scheme 3 Preparation of the self-assembled bisoxazoline/Pd composite microsphere](image1)

![Scheme 4 Preparation of the N-(4,5-dihydrooxazol-2-yl)benzamide/Pd (F)](image2)

![Fig. 1 the comparison of $^1$H NMR spectra between the ligand(E) and its palladium complex (F)](image3)

![Fig. 2 FT-IR spectra of the ligand(C) and palladium complex (D)](image4)
FT-IR spectra of the ligand shows that the strong peak at 1638 cm\(^{-1}\) could be due to the asymmetric and symmetric stretching vibrations of C=O, and that the broad peak at 3310 cm\(^{-1}\) could be due to N-H vibrations. However, there are not absorption peaks of the C=O and N-H in palladium complex. Thus, the above results indicate that the ligand was successfully coordinated with palladium via coordination bond.

The stability of the ligand and palladium complex was compared by the thermogravimetric (TG) analysis (Fig. 3). The TG curve indicates that the decomposition temperature of the ligand was about 246.3 °C, which is lower than that of palladium complex (291.1 °C). This fact indicates the palladium complex is not a physical mixture of the ligand with palladium, but a metal complex.

Fig. 4 SEM of bisoxazoline/Pd composite microsphere catalyst(D)

Fig. 4 depicts the scanning electron microscopy (SEM) images of the bisoxazoline/Pd composite microsphere catalyst(D), the catalyst presents with a monodispersed, uniform spherical morphology with the glabrate outer surface. The particle diameter is ranging from 0.53 to 0.55 μm. EDAX analysis offers both quantitative and qualitative information. The qualitative results are those “maps” or images which indicate the distribution of chemical elements in a sample (Fig. 5).

In the beginning, we investigated the catalytic activity of bisoxazoline/Pd composite in the SM reaction of p-bromoanisole and phenylboronic acid. Since water solvent endows the reaction with green and safe properties, we focused on the use of water to replace organic solvents, and the results are summarized in Table 1. We found that the coupled product was obtained in 15%, 29 %, 10 %, 18% and 8% isolated yield after 2 h in pure water when Na\(_2\)CO\(_3\), K\(_2\)CO\(_3\), NaHCO\(_3\), NaOAc and TEA were used as base respectively (Table 1, Entry 1-5). However, no significant improvement was observed when the reaction time was enhanced. Remarkably, it seemed K\(_2\)CO\(_3\) is the best base in the reaction. The addition of ethanol enhanced the yield of the coupled product (Table 1, Entries 6-8). With the raise of the ethanol ratio, the yields increase accordingly. However, the yield of the coupling reaction in pure ethanol was unsatisfied (Table 1, Entry 9). It

**Table 1 The effect of solvents and bases\(^a\)**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Base</th>
<th>Time(h)</th>
<th>Yield(%)</th>
</tr>
</thead>
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<td>Na(_2)CO(_3)</td>
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<td>10</td>
</tr>
<tr>
<td>4</td>
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<td>NaOAc</td>
<td>2</td>
<td>18</td>
</tr>
<tr>
<td>5</td>
<td>H(_2)O</td>
<td>TEA</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
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<td>41</td>
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<tr>
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<td>65</td>
</tr>
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<tr>
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<td>Toluene</td>
<td>K(_2)CO(_3)</td>
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<td>DMF</td>
<td>K(_2)CO(_3)</td>
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<td>7</td>
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<td>H(_2)O:PEG-400 (5:1)</td>
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<tr>
<td>14</td>
<td>H(_2)O:PEG-400 (8:1)</td>
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<td>84</td>
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<td>15</td>
<td>H(_2)O:PEG-400 (10:1)</td>
<td>K(_2)CO(_3)</td>
<td>2</td>
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<td>H(_2)O:PEG-400 (10:1)</td>
<td>K(_2)CO(_3)</td>
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<td>93</td>
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<td>H(_2)O:PEG-400 (10:1)</td>
<td>K(_2)CO(_3)</td>
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<td>98</td>
</tr>
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\(^a\) Reaction conditions: bisoxazoline/Pd microsphere containing 0.1mol% Pd, 1 mmol of p-bromoanisole, 1 mmol of phenylboronic acid, 2 mmol of base, 5 ml of solvent , 70 °C in air.

\(^b\) Isolated yield.
seemed that the presence of water increases solubility of the bases, which is responsible for the activation of boronic acid resulting in enhancing the rate of the reaction in aqueous medium.\textsuperscript{34} We also investigated other organic solvents, such as toluene, DMF and dioxane, but the obtained results were less than satisfactory (Table 1, Entries 10-12). To our delight, the addition of PEG-400 into H\textsubscript{2}O, the yield was improved remarkably (Table 1, Entries 13-15). Even if the amount of PEG-400 decreased from 20\% to 10\%, the reaction still proceeded smoothly. PEG-400 can play an important role as phase transfer catalyst (PTC).\textsuperscript{35} Finally, it was found that the best condition in this reaction is the combination of K\textsubscript{2}CO\textsubscript{3} as base and a mixture of water and PEG-400 (H\textsubscript{2}O:PEG-400= 10:1) as solvent. With the increase of the time of reaction, the yields were also improved (Table 1, Entries 16-17).

With the optimum reaction conditions, a range of substituted aryl bromides and iodides with electron-donating and electron withdrawing groups were investigated to check the feasibility of this protocol whose results are tabulated in Table 2. It is worthwhile to note that the electronic effects of either coupling partner produced no significant impact on the reaction yields (Table 2, Entries 1-10). These results suggest that bisoxazoline/Pd microsphere was a very effective catalyst for this coupling reaction. However, ortho-substituted aryl bromides and aryloboronic acids were coupled in very lower yields (Table 2, entry 11). This fact indicates that the steric hindrance of coupling partners definite influence on this coupling reaction. Even if the reaction time was extended, the yield was not improved. Highly sterically hindered di-ortho substituted biphenyls cannot be synthesized under the same conditions (Table 2, entry 12). In order to show the effect of the ligand in this reaction, we performed a reaction of bromobenzene and phenylboronic acid in the absence of the ligand. The results showed that in the absence of the ligand, the reaction was sluggish and only 47\% yield was obtained (Table 2, entry 13). From these studies we can predict that this catalyst can be applied to a wide range of aryl iodides and bromides. Aryl chlorides are usually cheaper but less active than aryl bromides. Their reluctance to perform the oxidative addition to palladium makes the coupling procedure difficult.\textsuperscript{35,36} Unfortunately, the coupling of aryloboronic acid cannot proceed smoothly under the same condition. When the reaction temperature was raised to 100 °C and the catalyst loading was increased to 0.4 mol\%, the corresponding coupling products can be obtained in moderate yields. However, the coupling of aryl iodides with phenylboronic acid can completed withing the shorter time (Table 2, Entries 16, 17).

### Table 2: Suzuki-Miyaura cross-coupling catalyzed by bisoxazoline/Pd microsphere\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>ArX</th>
<th>ArB(OH)\textsubscript{2}</th>
<th>Time(h)</th>
<th>Yield(%a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Br</td>
<td>B(OH)\textsubscript{2}</td>
<td>4</td>
<td>98</td>
</tr>
<tr>
<td>2</td>
<td>Br</td>
<td>Cl</td>
<td>4</td>
<td>97</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction conditions: bisoxazoline/Pd microsphere containing 0.1 mol\% Pd, 1 mmol of aryl halide, 1 mmol of phenylboronic acid, 2 mmol of base, 5 mL of H\textsubscript{2}O/PEG-400 (10:1), 70 °C, in air.

\textsuperscript{b} Isolated yield.

0.4 mol\% Pd was used.

Generally, a hot filtration test can determine if the catalysis was derived from the bisoxazoline/Pd composite microsphere or from leaching palladium.\textsuperscript{37} Thus, we chose 4-bromoanisole with phenylboronic acid as model reaction to investigate the fact. After the reaction was carried out for 20 min. (the conversion of 4-bromoanisole reached 42\%, and the yield of the crude cross coupling product is almost 42\%), the catalyst was separated by a hot rapid filtration. No further reaction was observed by GC analysis, and no palladium could be detected in the hot liquid mixture by atomic absorption spectrometry (AAS)\textsuperscript{c} The detection limit of the AAS experiment is 11μg/L. These facts demonstrate that the palladium atom remains into the ligand during the reaction.

The recyclability of a catalyst is a prominent feature of
heterogeneous catalysis reactions. In another investigation, the reusability of the catalyst was examined upon the reaction of 4-bromoanisole (1 mmol) with phenylboronic acid (1 mmol). In detail, the catalyst particles were collected simply and effectively by centrifugation and then the recovered catalyst particles were reused in the next round of coupling reaction by mixing them with new substrate, base, and solvent. It is noteworthy that the catalytic activity was maintained at least until the eighth use, with almost the excellent yield of biphenyl in each run (Fig. 6). Furthermore, according to the IR shown in Fig. 7 the used bisoxazoline/Pd microsphere catalyst can retain its structure, indicating a good stability and durable structure of bisoxazoline/Pd microsphere in liquid reaction. The palladium content of the catalyst was determined by AAS after eight consecutive runs and no appreciable change was observed. All of the facts show that the catalyst was very promising and encouraging from a practical point of view.

Conclusions

By the self-assembly of the bisoxazoline and Pd(AcO)₂, a novel and non-phosphine solid palladium catalyst, bisoxazoline/Pd composite microsphere, was successfully prepared. The synthesized bisoxazoline/Pd composite microsphere exhibits high catalytic activity for Suzuki-Miyaura cross-coupling reactions of various aryl halides and arylboronic acids in aqueous media. Moreover, the catalyst shows outstanding stability and reusability, can be recovered simply and effectively and reused eight times without any activity decrease.

Experimental Section

General information

Melting points were determined on a Perkin-Elmer differential scanning calorimeter and were uncorrected. The IR spectra were run on a Nicolette spectrometer (KBr). NMR spectra were recorded at 400 (1H) and 100 (13C) MHz, respectively, on a Varian Mercury plus-400 instrument using CDCl₃ as solvent and TMS as the internal standard. Scanning electron microscopy (SEM) was performed on a FEI Quanta 450 FEG FESEM instrument. High resolution mass spectra (HRMS) were obtained on an Agilent LC-MSD-Trap-XCT spectrometer with micromass MS software using electrospray ionisation (ESI). All the solvents used were strictly dried according to standard operation and stored on 4 Å molecular sieves.

All other chemicals (AR grade) were commercially available and used without further purification.

Synthesis of bisacylthiourea B

To a solution of 4,4’-Oxybisbenzoyl chloride A (2 mmol) in CH₂Cl₂ (10 mL) was added ammonium thiocyanate (2.6 mmol) and PEG-400 (0.2 mmol). The mixture was then stirred at room temperature for 60 min and cooled to 0°C, and the solution of 2-aminoethanol (1.8 mmol) in CH₂Cl₂ (2 mL) was added. The mixture was continuously stirred for 60 min. After the completion of the reaction, the solvent was removed by distillation, and water (10 mL) was added to obtain a white solid. The analytical sample was produced by flash chromatography (acetone and petroleum ether) to give a white solid B. Yield: 85%. Spectral data: IR (KBr) (cm⁻¹): ν 3337, 2944, 1670, 1531. ¹H NMR (400 MHz, DMSO) δ 11.35 (s, 2H), 11.05 (s, 2H), 8.02 (d, J = 8.8 Hz, 4H), 7.17 (d, J = 8.8 Hz, 4H), 4.98 (s, 2H), 3.83-3.44 (m, 8H). ¹³C NMR (100 MHz, DMSO) δ 180.71, 167.65, 159.87, 131.68, 128.22, 118.95, 58.75, 47.97, 40.38, 40.17, 39.96, 39.75, 39.54. HR-MS: m/z calcd for C₂₀H₁₃N₄O₃S (M+1): 433.0892; found: 433.0892.

Synthesis of bisoxazoline C

To a solution of compound B (1 mmol) in DMF (5 mL) was added dicyclohexylcarbodiimide (DCC) (1 mmol) and TEA (1 mmol). The mixture was stirred for 2 h at 80°C, and cooled to room temperature. After the addition of water (5 mL), the white solid was obtained by distillation, and to 10 mL of H₂O was added dicyclohexylcarbodiimide (DCC) (1 mmol) and TEA (1 mmol). The mixture was continuously stirred for 60 min. After the completion of the reaction, the solvent was removed by distillation, and water (10 mL) was added to obtain a white solid. The analytical sample was produced by flash chromatography (acetone and petroleum ether) to give a white solid C. Yield: 98%. Spectral data: IR (KBr) (cm⁻¹): ν 3300, 2921, 1638, 1548. ¹H NMR (400 MHz, DMSO) δ 9.61 (s, 2H), 8.28 – 7.99 (m, 4H), 7.20 – 6.98 (m, 4H), 4.47 (t, J = 8.6 Hz, 4H), 3.78 (t, J = 8.6 Hz, 4H). ¹³C NMR (100 MHz, DMSO) δ 180.71, 167.65, 159.87, 131.68, 128.22, 118.95, 58.75, 47.97, 40.38, 40.17, 39.96, 39.75, 39.54. HR-MS: m/z calcd for C₂₀H₁₃N₄O₃S (M+H⁺): 395.1395; found: 395.1355.

Synthesis of catalyst D

To a solution of compound C (1 mmol) in DMF (5 mL) was added dicyclohexylcarbodiimide (DCC) (1 mmol) and TEA (1 mmol). The mixture was stirred for 2 h at 80°C, and cooled to room temperature. After the addition of water (5 mL), the white solid was obtained by filtration. The solid was added into CH₂CN (5 mL) to be dissolved, followed by the filtration and concentration to afford the target compound C. Yield: 98%. Spectral data: IR (KBr) (cm⁻¹): ν 3330, 2921, 1638, 1548. ¹H NMR (400 MHz, DMSO) δ 9.61 (s, 2H), 8.28 – 7.99 (m, 4H), 7.20 – 6.98 (m, 4H), 4.47 (t, J = 8.6 Hz, 4H), 3.78 (t, J = 8.6 Hz, 4H). ¹³C NMR (100 MHz, DMSO) δ 180.71, 167.65, 159.87, 131.68, 128.22, 118.95, 58.75, 47.97, 40.38, 40.17, 39.96, 39.75, 39.54. HR-MS: m/z calcd for C₂₀H₁₃N₄O₃S (M+H⁺): 395.1395; found: 395.1395.
bisoxazoline/Pd microsphere catalyst is 20.01 wt% (1.8 mmol/g) measured by atomic absorption spectroscopy (AAS).

General Experimental Procedures for Suzuki-Miyaura Couplings

In a typical experiment, the bisoxazoline/Pd microsphere catalyst (0.005 mmol of Pd) was added to a mixture of aryl halide (1.0 mmol), arylboronic acid (1.0 mmol), PEG-400(0.1 mmol) and K₂CO₃ (2.0 mmol) in water (5.0 mL), and the reaction mixture was stirred at reflux. After the reaction was monitored to be complete by TLC analysis, the catalyst was removed by filtration, washed with ethanol (3 × 3 mL), and dried under vacuum for the next run. The organic fractions were then concentrated on a rotary evaporator to afford the desired biaryl in excellent yield. The crude products were further purified by recrystallization. All of the products are known compounds, and their ¹H NMR data were identical to those reported in literature.

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Notes and references

A self-assembled bisoxazoline/Pd composite microsphere as an excellent catalyst for Suzuki-Miyaura coupling reaction

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Graphical Abstract