

Original Research

Fabrication and Catalytic Property of an Ordered Terpyridine Pd(II)/Ni(II) Catalytic Monolayer for Suzuki Coupling Reactions

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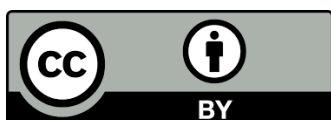
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Abstract

Fabrication, arrangement, and controllable composition of ordered organometallic films are critical for designing a highly active catalyst and investigating the catalytic mechanism. In this paper, an organometallic terpyridine Pd(II)/Ni(II) monolayer linked on the silicon substrate surface (denoted as **Si-Tpy-Pd₁/Ni₁**) was prepared and characterized using water contact angle, ultraviolet spectra, X-ray diffraction, scanning electron microscopy, and X-ray photoelectron microscopy. **Si-Tpy-Pd₁/Ni₁** exhibited high catalytic activity, substrate applicability, and reusability after 5 runs. During recycling, the deactivation was induced by the aggregation of active Pd/Ni nanoparticles. The catalytic mechanism was heterogeneous and occurred on the **Si-Tpy-Pd₁/Ni₁** monolayer surface; the mechanism was confirmed using hot filtrate, poison test, and a three-phase experiment. The real active center was Pd^{δ-}/Ni^{δ+} and was formed in situ on the organometallic monolayer surface, which acted as a precursor



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with a synergistic effect between Pd and Ni. The electron density of Pd became more negative because of electron transfer from Ni to Pd, which facilitated the oxidative addition reaction.

Keywords

Palladacycle; self-assembled monolayer; Pd/Ni bimetallic catalyst; Suzuki coupling reaction; synergistic effect

1. Introduction

Palladium (Pd)-catalyzed cross-coupling is a useful tool in organic synthesis [1]. Hetero-multimetallic catalysts exhibit unique properties because of the synergistic effects between different metals [2]. Hetero-bimetallic nano-catalysts, including Pd-based or nickel-based catalysts, were widely applied in synthesis because of their high activity, stability, and recyclability [3-6]. However, the active sites easily aggregate, with the changes in active sites being difficult to detect during catalysis [7], leading to difficulty in elucidating the true mechanism underlying heterogeneous catalysis [8].

The ordered multi-organometallic monolayer has been widely developed in catalytic systems, retaining most of the performances as precursors [9, 10]. The self-assembly method can offer desired design, control the orientation, and facilitate easy recycling in the forms of films or monolayers [11-13]. The surface properties of organometallic catalytic monolayers, such as Langmuir–Blodgett (LB) films [14-16] and self-assembled films supported on solid supports, can be easily characterized, identified, and evaluated using various scientific techniques [17]. Such studies can provide deep insights into catalytic behavior at the molecular level, such as ligands containing certain functional groups (e.g., Schiff bases) exhibiting excellent performance in heterogeneous catalysis.

Studies have demonstrated that the catalytic activity of the mono- or bi-organometallic catalytic monolayers can be improved by quantifying film morphology, tuning the composition of different metals, elucidating the relative distributions of electrons (which are related to the electrical characteristics of the ligand), and modifying the support and synergy of hetero-bimetals [18-35]. Appropriate supports, such as silicon with a greater flat surface, can result in a high dispersion and reproducibility of ordered organometallic catalytic monolayers [21-23, 25, 36-38]. Pd-based catalysts doped with other metals not only have less amount of Pd but also have high catalytic activity enhanced by the adjustment of the distance between Ni and Pd and the distribution and electronic structure of active sites [25, 27, 31]. Application of Pd catalysts exhibiting catalyst poisoning is restricted and is a major challenge [1]. Nickel (Ni) has the same chemical property as Pd [39]. Ni is non-expensive and more nucleophilic because of its smaller size compared with Pd, a characteristic critical in Suzuki coupling reaction; moreover, the catalytic performances of Ni and Pd vary [40, 41]. Therefore, the combined use of Pd and Ni in the catalysis of the Suzuki cross-coupling reaction has attracted much attention [42-44]. For this, the development of a regular, cost-effective, and eco-friendly film to enhance the catalytic property and elucidate synergy is warranted [45-47].

In this paper, an organometallic compound containing a terpyridine group acting as the binding site for Pd and Ni and its terpyridine Pd/Ni catalytic monolayer grafted onto the surface of silicon

substrate was fabricated through self-assembly (SA). The compound was characterized, and its catalytic property in the Suzuki coupling reaction, the structure of the active sites, and the synergistic effect were explored.

2. Materials and Methods

2.1 Reagent, Instruments, and General Procedure

Chemical reagents were obtained from chemical companies. Solvents were treated and distilled before use.

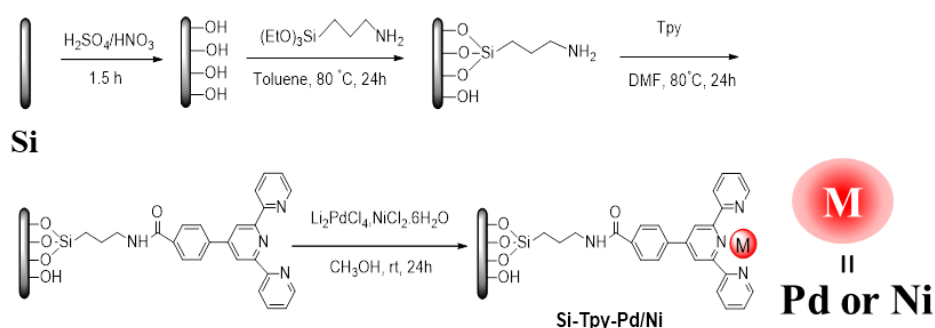
X-Ray diffraction was performed using a PAN analytical X-Pert PRO. The water contact angle (WCA) was recorded using a HARKE-SPCX1 (Beijing). UV-vis spectra were recorded using a Lambda 35 (UV-vis) spectrophotometer (Perkin Elmer Inc., USA). An SPM-9500J3 (Shimadzu Corporation, Japan) was employed for atomic force microscopy (AFM) measurements in the air under ambient conditions. Scanning electron microscopy images were measured using a Hitachi S-4800 instrument. X-ray photoelectron spectroscopy images were measured using an ESCALab220i-XL electron spectrometer (VG Scientific, 300 W Al K α radiation).

The Pd and Ni content in the catalysts before and after the cross-coupling reactions was measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES) with an ICAP 6000 Series (Thermo Scientific).

^1H NMR and ^{13}C NMR spectra were recorded using a Bruker Avance III 400 MHz spectrometer in CDCl_3 solution with tetramethyl silane as an internal standard. A VERTEX 70 V spectrometer (Bruker Optik, Ettlingen, Germany) at 293 K, with a spectral resolution of 4 cm^{-1} and a scanner velocity of 10 kHz, was used for monitoring the coupling reaction of 4-bromotoluene with phenylboronic acid.

2.2 Fabrication of Si-Tpy-Ni/Pd

This work combined two organometallics in a monolayer on supports by using self-assembly to improve the activity of active sites. The bi-organometallic catalytic monolayer was designed and prepared (Scheme 1).



Scheme 1 Fabricating route of a catalytic monolayer on a silicon wafer (Si-Tpy-Pd/Ni).

Silicon and quartz substrates ($3\text{ cm} \times 1\text{ cm} \times 0.1\text{ cm}$) were sonicated in ethanol (30 mL) and deionized water (30 mL) for 15 min. Subsequently, the quartz slide or silicon wafer was immersed in $\text{H}_2\text{SO}_4/\text{HNO}_3$ (1:1; v:v) solution at $90\text{ }^\circ\text{C}$ or in “piranha” solution ($\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$, 1:2; v:v) at $80\text{ }^\circ\text{C}$ for 1.5 h to remove any organic residues and to create silanol groups on the surfaces (Si-OH). The

cleaned slides were rinsed extensively with water (50 mL), ethanol (30 mL), and acetone (30 mL), followed by drying in a stream of nitrogen.

The freshly prepared hydroxyl silicon or quartz (**Si-OH**) (3 cm × 1 cm × 0.1 cm) surfaces were placed in a solution containing 0.5 mL of 3-aminopropyl triethoxysilane (1.1 mmol) and 10 mL of toluene. After treatment at 80 °C for 24 h, the surfaces were washed with toluene (50 mL), methanol, water, and acetone, followed by drying in a nitrogen stream (**Si-APTES**). The amino-functionalized substrates were immersed in 10 mL of dried DMF, containing 4-([2,2':6',2''-Terpyridin]-4'-yl) benzoic acid (**Tpy**, 1.2 mmol), 2-dimethylaminopyridine (DMAP, 1.2 mmol), and 1-Ethyl-(3-dimethylaminopropyl) carbodiimide salt (EDC-HCl, 1.5 mmol) at 80 °C for 24 h. The resulting substrates were removed and rinsed with ethanol (50 mL), deionized water (50 mL), and acetone (50 mL) to obtain the modified surfaces (**Si-Tpy**).

Si-Tpy (3 cm × 1 cm × 0.1 cm) was immersed in 30 mL of EtOH (anhydrous) and sonicated for 0.5 h. Subsequently, a mixture with a certain mole ratio of Ni to Pd was added at 40 °C and incubated for 12 h. **Si-Tpy-Pd/Ni** was removed and washed with methanol (50 mL), ethyl acetate (50 mL), and ethanol (50 mL), followed by vacuum drying at 40 °C for 24 h.

The real atomic ratios in the prepared **Si-Tpy-Pd/Ni** (3 cm × 1 cm × 0.1 cm) were further determined using ICP-AES. For sample treatment, the sample was broken down through nitrolysis with concentrated nitric acid (5 mL). Subsequently, the solution was transferred into a 10 mL volumetric flask to fix its quantity in water.

2.3 Procedure for Suzuki Reaction and Recycling

Si@Tpy-Pd/Ni (3 cm × 1 cm × 0.1 cm), a base (0.2 mmol), and a reactant (aryl halide derivatives, 0.10 mmol; arylboronic acid derivatives, 0.15 mmol) were added to a 10 mL round-bottom flask with 7 mL solvent (H₂O: EtOH, v:v = 1:5). The reaction was performed in an oil bath at 80 °C for 12 h, with the subsequent separation of catalysts from the reaction mixture. The residue solution was concentrated, and the cross-coupling product was separated using silica gel chromatography with ethyl acetate as eluent. The product was then purified two times using chromatography.

The recycling experiments were performed under the aforementioned conditions. The used catalyst was recovered from the reaction mixture after each run. The catalyst was reused in sequential runs after washing with ethyl acetate (20 mL), methyl alcohol (20 mL), and water (30 mL) three times.

3. Results and Discussion

3.1 Characterization of **Si@Tpy-Pd/Ni**

The fabricating processes were characterized. First, the water contact angle (WCA) was used to measure the wettability of functionalized surfaces [48, 49]. The silicon wafer surface was hydrophilic because of the hydroxyl groups formed (2.0°) after treatment with the “piranha” solution (Figure 1). The WCA increased to 38° after treatment with APTES and further increased to 54° when treated with terpyridine derivative because of the introduced aryl groups. The WCA of the modified silicon was 45° when Pd₂LiCl₄ and NiCl₂ were added to **Si-Tpy**. The significant changes in the WCAs of the modified surfaces varied during the fabrication step because of the surface configuration of the catalytic monolayer.

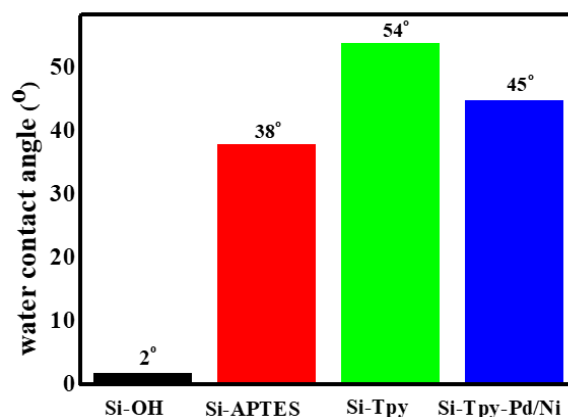


Figure 1 Changes in the silicon surface WCA in the fabrication process (**Si-OH**, **Si-APTES**, **Si-Tpy**, and **Si-Tpy-Pd/Ni**).

UV spectra of the fabricating processes of **Si-Tpy-Pd/Ni** monolayer modified on quartz were measured (Figure 2). Hydrophilic quartz (called **Si-OH**, black line) had no peak, and the absorption at approximately 200 nm increased gradually because of the introduced amine (**Si-APTES**, red line). An absorption at 290 nm for the terpyridine group appeared after modification with the terpyridine derivative (**Si-Tpy**, blue line). Two new peaks at 223 and 237 nm appeared, indicating coordination with Li_2PdCl_4 and NiCl_2 , respectively (green line and pink line). After **Si-Tpy** coordination with a mixture of Li_2PdCl_4 and NiCl_2 , the characteristic peak at 290 nm for terpyridine shifted to 282 nm (yellow-green line) because of the ordered monolayer. The vicinal terpyridine complex had a face-to-face configuration, indicating the interaction between the molecules and regular packing.

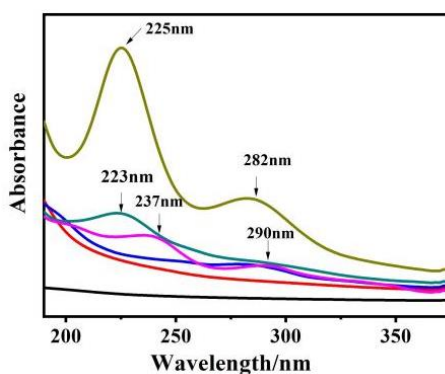


Figure 2 The UV-vis spectra of the fabrication self-assembly processes of **Si-Tpy-Pd/Ni** (**Si-OH**, black line; **Si-APTES**, red line; **Si-Tpy**, blue line; **Si-Tpy-Pd**, green line; **Si-Tpy-Ni**, pink line; and **Si-Tpy-Pd/Ni**, yellow-green line).

Low-angle X-ray diffractograms (LAXD) of the **Si-Tpy-Pd/Ni** preparation process on the silicon surface were measured (Figure 3). A characteristic peak at 1.02° for **Si-OH** was observed (Figure 3A), which shifted to 1.05° after APTES grafting (Figure 3B). The same peak slightly shifted to 1.03° after a terpyridine derivative was grafted (Figure 3C). The diffraction peak of the monolayer self-assembled with Pd and Ni was also observed approximately at the same position (Figure 3D), indicating coordination between terpyridine group metals to form **Si-Tpy-Pd/Ni**. Therefore, the ordered hetero-bimetallic self-assembled catalytic monolayer was fabricated on the silicon surface.

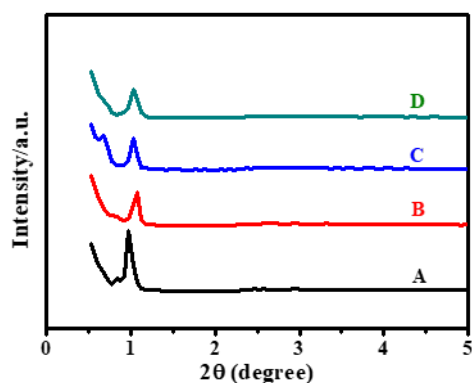


Figure 3 Low X-ray diffraction patterns of **Si-Tpy-Pd/Ni**. (A) **Si-OH**, (B) **Si-APTES**, (C) **Si-Tpy**, (D) **Si-Tpy-Pd/Ni** in the assembly processes.

SEM images of **Si-OH**, **Si-APTES**, **Si-Tpy**, and **Si-Tpy-Pd/Ni** were measured (Figure 4). The surface of the silicon substrate after hydrophilic treatment was smooth and without defects (Figure 4A). Uniform domains on the surface after silanization with APTES were observed (Figure 4B), and similar domains were observed in the image after terpyridine group grafting (Figure 4C). Finally, the uniform monolayer was fabricated after coordination with a mixture of Pd and Ni salts, indicating the formation of the ordered organometallic Pd/Ni monolayer (Figure 4D).

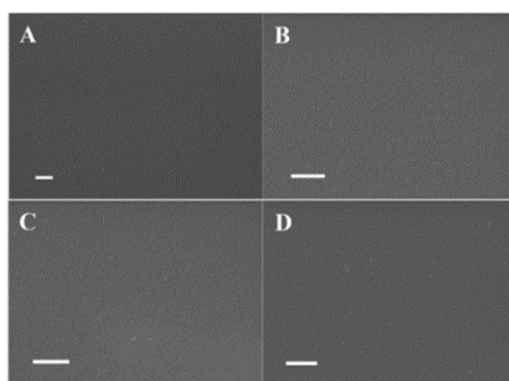


Figure 4 SEM images of the assembly processes of **Si-Tpy-Pd/Ni** (A), **Si-OH** (B), **Si-APTES** (C), **Si-Tpy**, and **Si-Tpy-Pd/Ni** (D) (white bar: 200 nm).

The chemical elements on the surface in the fabrication processes of **Si-Tpy-Pd/Ni** were analyzed using X-ray photoelectron spectroscopy (Figure 5). The peak at 399.1 eV was attributed to N1s (NH₂), and Si 2p (C-Si) was detected in Si-APTES (Figure 5A, black line). Peaks at 401.5 eV and 399.5 eV were attributed to N1s (CONH) and N1s (C = NH); the peaks were observed after terpyridine grafting in **Si-Tpy** (Figure 5A, red line). Peaks for Pd 3d and Ni 2p were detected after complexing Pd and Ni. Compared with **Si-Tpy**, in **Si-Tpy-Pd/Ni**, the HR-XPS of Ni 2p revealed characteristic peaks at 337.92 eV and 343.22 eV, which were attributed to the BE of Pd(II) (Figure 6A). The peaks at 855.67 eV, 861.57 eV (Sat peak), and 873.47 eV were attributed to the BE of Ni(II) (Figure 6B).

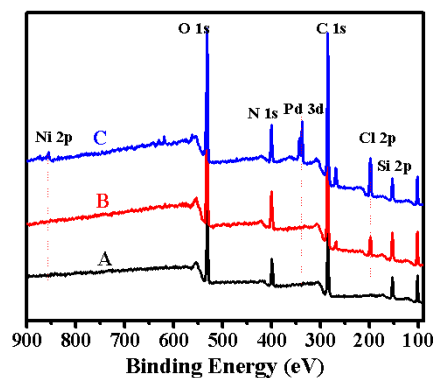


Figure 5 XPS spectra of the self-assembly process of **Si-Tpy-Pd/Ni** (A), **Si-APTES** (B), **Si-Tpy** (C), and **Si-Tpy-Pd/Ni**.

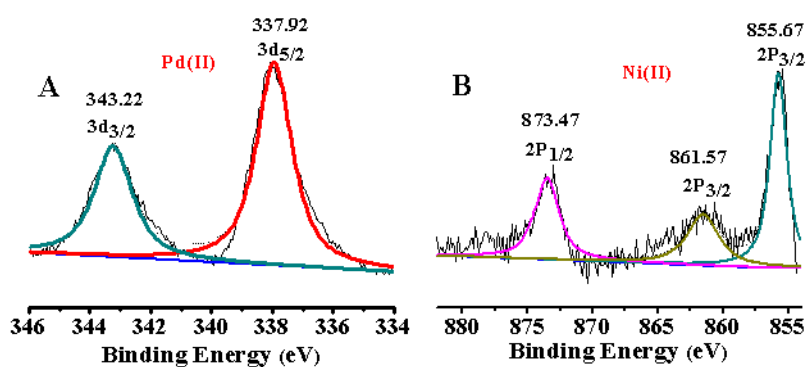


Figure 6 High resolution XPS spectra of (A) Pd 3d and (B) Ni 2p.

The contents of Pd and Ni in **Si-Tpy-Pd/Ni** as measured using ICP-AES were $1.12 \times 10^{-6} \text{ mmol}\cdot\text{cm}^{-2}$ and $9.30 \times 10^{-8} \text{ mmol}\cdot\text{cm}^{-2}$, respectively. In **Si-Tpy-Pd**, the content of Pd was $4.69 \times 10^{-6} \text{ mmol}/\text{cm}^2$, whereas, in **Si-Tpy-Ni**, the content of Ni was $3.82 \times 10^{-6} \text{ mmol}/\text{cm}^2$.

AFM images in fabrication processes were also measured (Figure 7). The surface of the silicon substrate exhibited a clear morphology, with arrays having a roughness average (Ra) of 0.49 nm (Figure 7A). Ordered surfaces with a Ra of 2.55 nm (Figure 7B) were observed after APTES grafting. Subsequently, the images exhibited a homogeneous surface with a Ra of 0.83 nm, except for a few defects after terpyridine group grafting (Figure 7C); this indicated that a monolayer may has formed. The surface image of the **Si-Tpy-Pd** monolayer (Figure 7D) exhibited high-density arrays, with a Ra of 1.19 nm, indicating that the coordination of Pd^{2+} with **Si-Tpy** resulted in morphology changes.

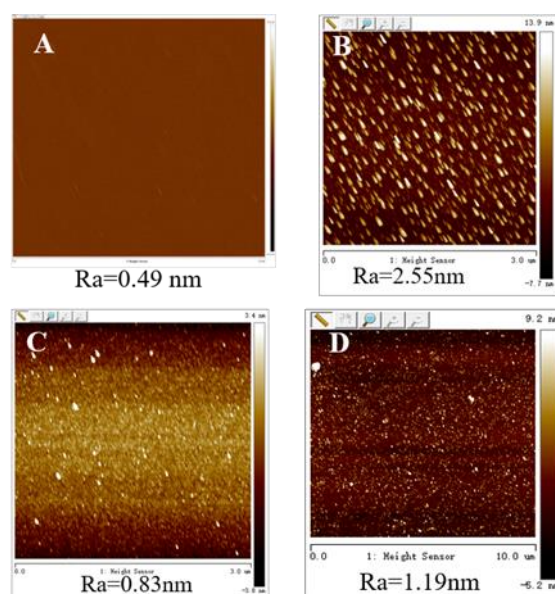


Figure 7 AFM images of a hydrophilic silicon wafer (A) (**Si-OH**), salinization (B) (**Si-APTE**), terpyridine grafting (C) (**Si-Tpy**), terpyridine (D) (**Si-Tpy-Pd**), and terpyridine Pd (II) grafting.

Characterizations mentioned above confirmed the oriental self-assembly of the **Si-Tpy-Pd/Ni** monolayer on the silicon wafer surface.

3.2 Catalytic Property of **Si-Tpy-Pd/Ni**

3.2.1 Evolution of **Si-Tpy-Pd/Ni** Catalytic Property

The optimization of reaction conditions in the Suzuki cross-coupling reaction was initially explored, and the results are listed in Table 1. Lower yields were obtained with different solvents (entries 1–6), whereas higher yields were achieved using H₂O/EtOH (v/v = 1:5) (entries 7–9). The effects of various bases were investigated, and the highest yield (95%) was obtained using K₂CO₃ (entries 9–13). With a decrease in temperature and time, yield decreased (entries, 14–19), and increased substrate loading resulted in low yields because of the limited amount of catalyst used. The optimized conditions were K₂CO₃, H₂O/EtOH (v/v = 1:5), 4-bromotoluene (0.10 mmol), 80 °C, and 12 h; these conditions were used in further investigation.

Table 1 Optimization of Suzuki–Miyaura reaction conditions^a.

Entry	Base	Solvent	T(°C)	Time (h)	Yield (%) ^b
1	K ₂ CO ₃	H ₂ O	80	12	46
2	K ₂ CO ₃	EA	80	12	25
3	K ₂ CO ₃	THF	80	12	trace
4	K ₂ CO ₃	DMF	80	12	17
5	K ₂ CO ₃	Toluene	80	12	trace
6	K ₂ CO ₃	EtOH	80	12	39
7	K ₂ CO ₃	H ₂ O: EtOH=1:1	80	12	83

8	K ₂ CO ₃	H ₂ O: EtOH=1:3	80	12	71
9	K ₂ CO ₃	H ₂ O: EtOH=1:5	80	12	96
10	Na ₂ CO ₃	H ₂ O: EtOH=1:5	80	12	79
11	NaOH	H ₂ O: EtOH=1:5	80	12	47
12	K ₃ PO ₄	H ₂ O: EtOH=1:5	80	12	73
13	NaHCO ₃	H ₂ O: EtOH=1:5	80	12	36
14	K ₂ CO ₃	H ₂ O: EtOH=1:5	30	12	39
15	K ₂ CO ₃	H ₂ O: EtOH=1:5	60	12	46
16	K ₂ CO ₃	H ₂ O: EtOH=1:5	60	24	58
17	K ₂ CO ₃	H ₂ O: EtOH=1:5	100	12	95
18	K ₂ CO ₃	H ₂ O: EtOH=1:5	80	8	69
19	K ₂ CO ₃	H ₂ O: EtOH=1:5	80	10	81
20	K ₂ CO ₃	H ₂ O: EtOH=1:5	80c	12	33

^a Reaction condition: 4-Bromotoluene (0.10 mmol), PhB(OH)₂ (0.15 mmol), base (0.20 mmol), solvent (7.0 mL), **Cat**: Pd: 1.34×10^{-5} , Ni: 1.11×10^{-6} . ^b Isolated yield. ^c 4-bromotoluene (0.20 mmol), PhB(OH)₂ (0.30 mmol), base (0.4 mmol), **Cat**: Pd: 1.34×10^{-5} , Ni: 1.11×10^{-6} , solvent (7.0 mL).

3.2.2 Effect of Composition on Si-Tpy-Pd_x/Ni_{1-x} Catalytic Activity

The influence of different ratios of Pd/Ni on **Si-Tpy-Pd_x/Ni_{1-x}** was explored under the optimized conditions, and the results are presented in Table 2. Among the six compositions used, **GO-Tpy-Pd₁/Ni₁** provided the highest yield of up to 96%. The yield of **GO-Tpy-Ni** and **GO-Tpy-Pd** were up to 61% and 86%, respectively, indicating the high activity of Ni and Pd complexes. In the case of Pd doped with Ni at a proper ratio, the activity was significantly enhanced. This was because the proper ratio of Pd/Ni effectively supplied favorable active sites on the catalytic monolayer surface to enhance the catalytic activity through a “cooperative effect” [27, 50]. Therefore, the novel structure of active sites efficiently came in contact with reactants, thereby ensuring a prompt reaction.

Table 2 Catalytic activity of **Si-Tpy-Pd_x/Ni_{1-x}** with different ratios of Pd/Ni in the Suzuki coupling reaction ^a.

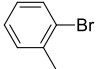
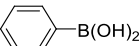
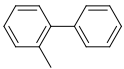
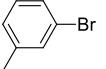
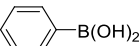
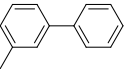
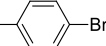
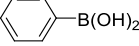
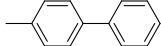
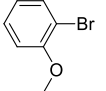
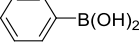
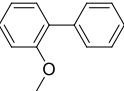
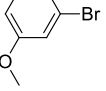
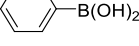
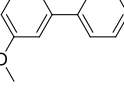
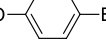
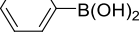
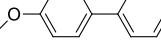
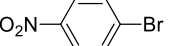
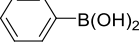
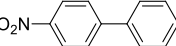
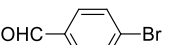
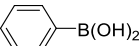
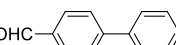
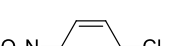
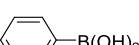
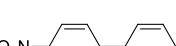
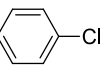
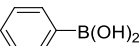
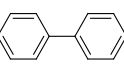
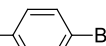
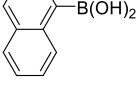
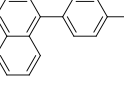
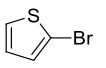
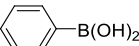
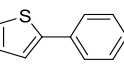
Catalyst	(mmol)	nPd: nNi ≈)	Yield/% ^b	TON
Si-Tpy-Pd	Pd: 5.62×10^{-5}	-	83	1474
Si-Tpy-Pd ₁ /Ni ₁	Pd: 1.34×10^{-5} Ni: 1.11×10^{-6}	1:0.08	96	7143
Si-Tpy-Pd ₁ /Ni ₅	Pd: 2.91×10^{-5} Ni: 4.05×10^{-6}	1:0.14	90	3086
Si-Tpy-Pd ₁ /Ni ₁₀	Pd: 5.34×10^{-5} Ni: 7.5×10^{-6}	1:0.15	81	1517
Si-Tpy-Pd ₁ /Ni ₂₀	Pd: 5.01×10^{-5} Ni: 2.38×10^{-5}	1:0.47	74	1475
Si-Tpy-Ni	Ni: 4.58×10^{-5}	-	61	1331

^a Reaction condition: 4-Bromotoluene (0.10 mmol), PhB(OH)₂ (0.15 mmol), base (0.20 mmol), **Cat**: 3 cm × 1 cm × 0.1 cm, solvent (7.0 mL), 80 °C. ^b Isolated yield.

3.2.3 Screening of Substrates Catalyzed by Si-Tpy-Pd₁/Ni₁

The Suzuki coupling reaction catalyzed by **Si-Tpy-Pd₁/Ni₁** in the presence of aryl halides and arylboronic acid derivatives was conducted under optimized conditions, and the results are summarized in Table 3. High yields of coupling products were achieved using both electron-donating and electron-withdrawing substituted aryl bromide and arylboronic acids (Table 3, entries 1–8). However, low yields were obtained for aryl chlorides (entry 9, 10) because of the high binding energy of the C-Cl bond. Cross-coupling compounds were also at higher yields by using benzyl bromide with naphthylboronic acid (entry 11). However, lower yields were obtained in the reaction of thiophene derivative with arylboronic acids because of its poison property of thiophene (entry 12). The results confirmed the high activity of **Si-Tpy-Pd₁/Ni₁** in the synthesis of aromatic compounds with a high turnover number (TON) and turnover frequency (TOF) values.

Table 3 Suzuki coupling reaction of aryl halides with different arylboronic acids ^a.

Entry	Ar-X	Ar'-B(OH) ₂	Product	Yield (%) ^b	TON	TOF (h ⁻¹)
1				85	6324	527
2				91	6771	564
3				96	7143	595
4				83	6175	515
5				87	6473	539
6				98	7292	608
7				97	7217	601
8				96	7143	595
9				37	2753	229
10				21	1563	130
11				80	5952	496
12				33	2455	205

^a Reaction condition: 0.10 mmol of substrate, 0.15 mmol of Ar-B(OH)₂, 0.20 mmol of base, 80 °C, Cat: Pd: 1.34 × 10⁻⁵, Ni: 1.11 × 10⁻⁶ mmol, solvent (7.0 mL). ^b Isolated yield.

3.2.4 Effects of Supports and Fabrication

Control experiments were performed to investigate the effect of different supports, such as glass, gel, silicon, and homogeneous Pd/Ni, on their catalytic activities (Table 4).

Table 4 Effect of different supports on the catalytic properties in Suzuki coupling reaction.

Catalyst	Pd loading (mmol)	Ni loading (mmol)	Molar ratio (Pd/Ni)	Yield/% ^b	TON
Silicon/glass/Gel	-	-	-	0	0
NiCl ₂ /Li ₂ PdCl ₄	2.41×10 ⁻⁶	3.38×10 ⁻⁷	1: 0.14	10	4149
Tpy/Pd/Ni	2.42×10 ⁻⁶	3.39×10 ⁻⁷	1: 0.14	8	3305
Si-Tpy-Pd	5.62×10 ⁻⁵	-	-	83	1474
Si-Tpy-Ni	-	4.58×10 ⁻⁵	-	61	1331
Si-Tpy-Pd ₁ /Ni ₁	1.34×10 ⁻⁵	1.11×10 ⁻⁶	1: 0.08	96	7143
Gel-Tpy-Pd/Ni	1.77×10 ⁻⁵	2.81×10 ⁻⁵	1: 1.58	75	4237
Glass-Tpy-Pd/Ni	1.19×10 ⁻⁵	2.75×10 ⁻⁵	1: 1.45	55	4850

^a Reaction condition: 0.1 mmol of substrate, 0.15 mmol of Ar-B(OH)₂, 0.2 mmol of base, 80 °C, 12 h, **Cat**: 3 cm × 1 cm, solvent (7.0 mL). ^b Isolated yield.

Cross-coupling compounds were not detected when silicon, glass, or gel was used (entry 1). A yield of 10% was obtained after mixing Li₂PdCl₄ with NiCl₂ (entry 2). When terpyridine derivative was mixed with Li₂PdCl₄/NiCl₂ as a catalyst without supports, only 8% yield was obtained (entry 3). In the case of **Si-Tpy-Ni**, **Gel-Tpy-Pd/Ni**, and **Glass-Tpy-Pd/Ni**, low yields were obtained (entries 5, 7, 8), indicating their poor activity compared with those of **Si-Tpy-Pd** (entry 4), **Si-Tpy-Ni** (entry 5), and **Si-Tpy-Pd₁/Ni₁** (entry 6). **Si-Tpy-Pd₁/Ni₁** also exhibited a higher activity than **Si-Tpy-Pd** and **Si-Tpy-Ni**, although the content of Pd in **Si-Tpy-Pd₁/Ni₁** was half of **GO-Tpy-Pd**. Therefore, the activity of **bi-organometallic Pd/Ni** was enhanced because of the ordered orientation of organometallic compounds in monolayer and synergy between Pd and Ni [51-55].

The catalytic properties of **Si-Tpy-Pd₁/Ni₁** were also compared with those reported by studies (Table 5). The results indicated that supports selection, ligand structure, formation and composition of metals, and orientation could efficiently affect catalytic activity.

Table 5 Comparison of **Si-Tpy-Pd₁/Ni₁** with Ni-based or Pd-based catalysts in the Suzuki reaction.

No	Catalyst	Pd/Ni loading(mol %)	Reaction condition	Yield (%)	TOF (based on Pd)	Ref.
1	Si-Tpy-Pd ₁ /Ni ₁	1.34×10 ⁻⁹ Pd 1.11×10 ⁻¹⁰ Ni	EtOH/H ₂ O, 80°C	96	595	This work
2	GO@Tpy-Pd ₁ /Ni ₁₀	1.82×10 ⁻⁵ Pd	EtOH/H ₂ O, 35 °C	93	1916	[31]

		2.93×10 ⁻⁵ Ni				
2	Pd ₁ Ni ₂	4.0 Ni	DMF,	91	5	[3]
3	Ni _{0.9} Pd _{0.1}	0.2 Pd1.8 Ni	EtOH/H ₂ O, 50 °C	71	15	[4]
4	Pd-Ni alloy	2.0 Pd2.0 Ni	1,4-dioxane, 100 °C	92	3.8	[52]
5	Ni _{0.20} Pd _{0.05} /CB	0.1 Pd0.4 Ni	EtOH/H ₂ O, 30 °C	88	1333	[53]
6	NPFNP-2	0.3 pd0.24 Ni	EtOH/H ₂ O, 50 °C	93	270	[54]
7	Pd ₁ Ni ₄ /CNF	1.25×10 ⁻³ Pd 5.1×10 ⁻³ Ni	EtOH/H ₂ O, 80 °C	99	263	[45]
8	Ni _{0.99} Pd _{0.01} alloy	0.02 Pd1.98 Ni	EtOH/H ₂ O, 50 °C	72	3600	[47]
9	G-Ni/Pd (Ni/Pd = 3/2)	0.91 Pd1.37 Ni	DMF/H ₂ O, 110 °C	78	171	[51]

3.3 Stability and Recycling Ability

Recycling tests were performed to investigate the recyclability of **Si-Tpy-Pd₁/Ni₁** (Figure 8). A significant loss in recyclability was not observed after the fourth run; however, a low yield was obtained after the fifth run (51%). When the reaction time was increased to 24 h at the seventh run, an yield of 60% was obtained, suggesting deactivation in the recycling process [27-34]. The contents of Pd and Ni reused at the fourth and fifth runs were also measured, with the values being 1.34×10^{-7} (fresh: 2.43×10^{-6}) mmol/cm² and 1.48×10^{-8} (fresh: 3.38×10^{-7}) mmol/cm², respectively. Therefore, the loss of Pd and Ni was responsible for the activity loss.

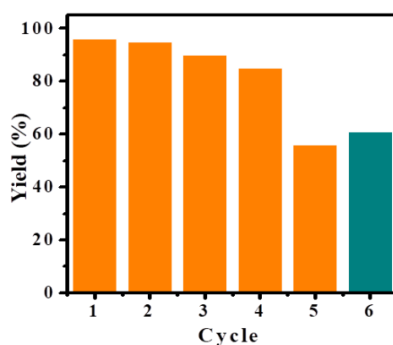


Figure 8 Recycling of **Si-Tpy-Pd₁/Ni₁** in the Suzuki coupling reaction.

The stability of **Si-Tpy-Pd₁/Ni₁** was investigated and compared with that of **Si-Tpy-Pd** (Figure 9). When **Si-Tpy-Pd₁/Ni₁** and **Si-Tpy-Pd** were exposed for 1 week at ambient conditions, 87% yield was obtained, and 61% yield of **Si-Tpy-Pd** was obtained in the model reaction. Subsequently, 90% and 48% yield was achieved by **Si-Tpy-Pd₁/Ni₁** and **Si-Tpy-Pd** in the second run after exposure for 2 weeks, indicating that **Si-Tpy-Pd₁/Ni₁** exhibited more stability than **Si-Tpy-Pd** because of Ni doping.

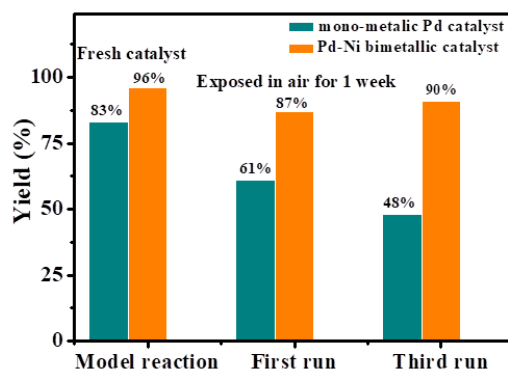


Figure 9 Investigation of **Si-Tpy-Pd₁/Ni₁** and **Si-Tpy-Pd** stability in the Suzuki coupling reaction.

The catalytic activity of **Si-Tpy-Pd₁/Ni₁** was also compared with commercial Pd/C under optimized conditions because Pd/C is a promising catalyst in Suzuki cross-coupling reactions (Figure 10) [56, 57]. A little cross-coupling product (yield of less than 3%) was detected using Pd/C as a catalyst with a lower TOF value (Figure 10a), indicating the higher catalytic activity of **Si-Tpy-Pd₁/Ni₁**. In recycling tests, **Si-Tpy-Pd₁/Ni₁** had higher stability than commercial Pd/C even after reusing three times (Figure 10b). The effect of temperature on TOFs of **Si-Tpy-Pd₁/Ni₁** and Pd/C was also investigated (Figure 10c), with the results indicating similar catalytic performance. In addition, catalytic performances of **Si-Tpy-Pd₁/Ni₁** and Pd/C at different substrate concentrations were explored. The results indicated that **Si-Tpy-Pd₁/Ni₁** exhibited higher activity with decreasing substrate concentration. Therefore, the orientation, arrangement, and composition of the catalyst, as well as the selected support, had a stronger effect on the catalytic performances and stability.

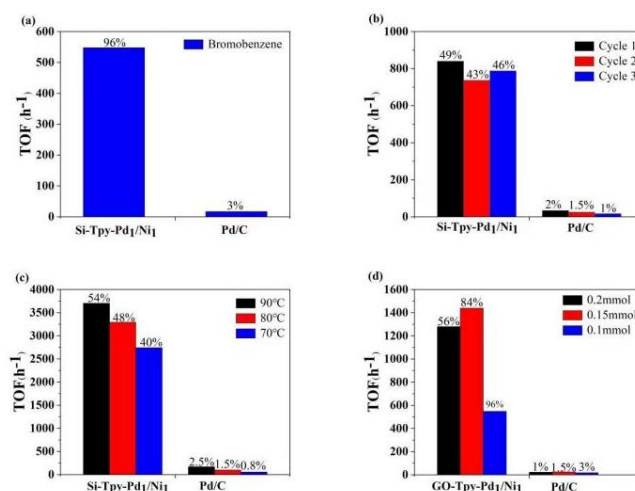


Figure 10 Yields per Pd atom of **Si-TpyPd₁/Ni₁** compared with commercial Pd/C in the Suzuki cross-coupling reaction. Reaction condition: (a) PhB(OH)₂ (0.15 mmol), 4-bromotoluene (0.1 mmol), K₂CO₃ (0.2 mmol), **Si-TpyPd₁/Ni₁**, solvent (H₂O:EtOH = 1:5 (1 mL + 5 mL)) at 80 °C for 12 h. (b) PhB(OH)₂ (0.15 mmol), 4-bromotoluene (0.10 mmol), K₂CO₃ (0.20 mmol), **Si@TpyPd₁/Ni₁**, solvent (H₂O:EtOH = 1:5 (1 mL + 5 mL)) at 80 °C for 4 h.

3.4 Exploration of the Catalytic Mechanism

3.4.1 Hot Filtration Experiment

The differentiation of heterogeneous from homogeneous catalysts is crucial [56]. The results of the hot filtration experiment indicated that the yield gradually increased before 8 h, followed by almost no change after 12 h (Figure 11, black line). A yield of 96% was obtained after 12 h. To investigate whether Pd leaching occurred during the catalytic process, **Si-Tpy-Pd₁/Ni₁** was separated from the catalysis system at 4 h. The yields remained constant (approximately 50%, Figure 11, red line), indicating Pd and Ni leaching did not occur during the catalytic process [26, 29].

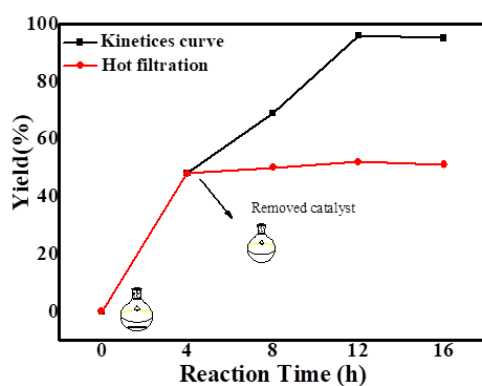


Figure 11 Hot filtration experiment of **Si-Tpy-Pd₁/Ni₁** in the Suzuki coupling reaction.

3.4.2 Poison Experiments

To investigate the active center on the catalytic monolayer surface, poison tests were performed (Table 6). A low yield of 17% was obtained by the addition of a drop of mercury into the reaction mixture before reaction initiation. The active center formed on the surface was partially coordinated with less Hg because of its poor dispersibility (entry 2). In the case of thiophene additives added with less than 1.0 aequivaler, significant deactivation was observed because of its stronger coordination with active sites, such as Pd, resulting in a decrease in active sites [58]. Therefore, the catalytic reaction mainly occurred on the surface of **Si-Tpy-Pd₁/Ni₁** (entry 4).

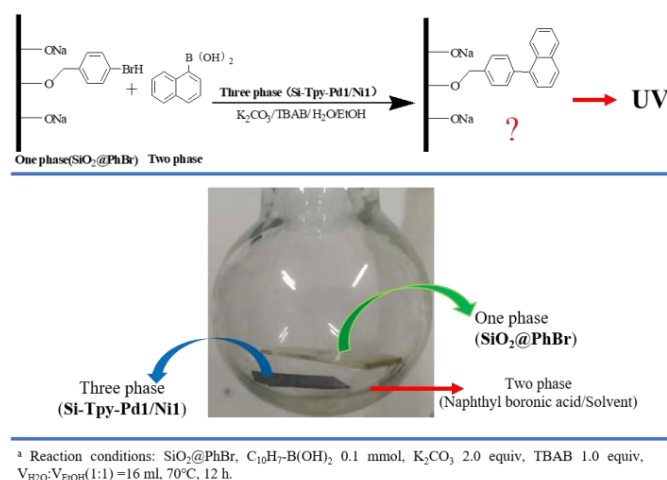
Table 6 Poison experiments of **Si-Tpy-Pd₁/Ni₁** catalyst ^a.

$\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{Br} + \text{C}_6\text{H}_5-\text{B}(\text{OH})_2 \xrightarrow[\text{poisoning additive}]{\text{Si-Tpy-Pd}_1/\text{Ni}_1} \text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_5$		
Entry	poisoning additive	Isolated yield (%) ^e
1	—	96
2b	Hg	17
3c	PPh ₃	48
4d	Thiophene	11

^a Reaction condition: 4-Bromotoluene (0.1 mmol), PhB(OH)₂ (0.15 mmol), base (0.2 mmol), **Cat**: Pd: 1.34×10^{-5} , Ni: 1.11×10^{-6} mmol. Solvent (7.0 mL). ^b One drop of Hg. ^c 0.5 equiv of PPh₃ (per metal atom). ^d 0.5 equiv of thiophene (per metal atom). ^e Isolated yield.

3.4.3 Three-Phase Test

The three-phase test is an effective method to determine the presence of heterogeneous catalysis [30, 55]. The experiment design is depicted in Scheme 2 and was performed as described in Figure 12.



Scheme 2 Three-phase experiment.

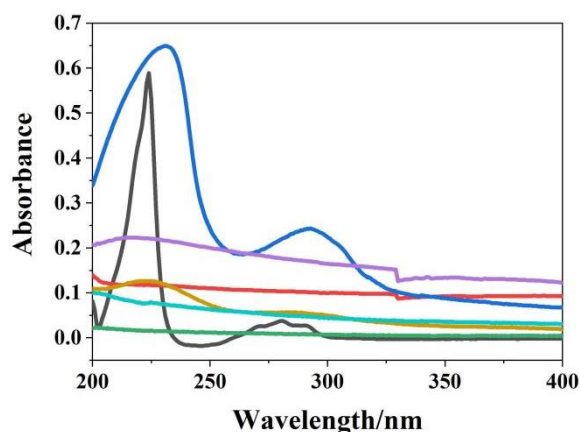


Figure 12 UV spectra of $\text{SiO}_2@\text{PhBr}$ in the three-phase test. Treatment: washing solvent (DCM, EtOH, and MeOH) and ultrasonic (naphthybromic acid, black; $\text{SiO}_2@\text{PhBr}$, red; $\text{SiO}_2@\text{PhBr}$ [add Si-Tpy-Pd₁N₁ without wash], blue; $\text{SiO}_2@\text{PhBr}$ [add washed Si-Tpy-Pd₁N₁], green; $\text{SiO}_2@\text{PhBr}$ [add washed and ultrasonicated Si-Tpy-Pd₁N₁], purple; $\text{SiO}_2@\text{PhBr}$ [no cat and unwashed], yellow; $\text{SiO}_2@\text{PhBr}$ [no cat, and washed] water).

For the three-phase test, 4-chlorobenzyl bromide was covalently anchored on a quartz surface as one phase as described in a previous report (denoted as $\text{SiO}_2@\text{PhBr}$) [30] (Figure 12).

Another soluble reagent (naphthyl boronic acid) was dissolved in a mixture solvent as the second phase to detect even a low amount of the naphthyl group with UV. The mixture was subjected to a reaction in the presence of a catalyst immobilized on the silicon as the third phase ($\text{Si-Tpy-Pd}_1\text{N}_1$). UV spectra of $\text{SiO}_2@\text{PhBr}$ and naphthyl boronic acid in ethanol were measured (Figure 12, red and black line), and the characteristic peak at 210 nm for $\text{SiO}_2@\text{PhBr}$ and at 225, 271, 280, and 291 nm for naphthyl boronic acid were observed. Because of the adsorption of naphthylboronic acid on one

phase (**SiO₂@PhBr**), designs were also presented under the reaction conditions. Reactions proceeded under the optimized conditions without **Si-Tpy-Pd₁Ni₁**. After the removal of **SiO₂@PhBr** without washing, UV was measured (Figure 12, yellow line). The characteristic peaks of naphthylboronic acid at 236, 296, and 300 nm were observed, indicating the adsorption of naphthylboronic acid. However, UV spectra of **SiO₂@PhBr** washed with DCM, EtOH, and MeOH or after ultrasonic treatment revealed no characteristic peaks (Figure 12, pink and green crimson line), indicating that adsorbed naphthylboronic acid was removed from **SiO₂@PhBr** surface. If the active Pd species from **Si-Tpy-Pd₁Ni₁** leached into the solution, the anchored reactant (one phase) may be converted to coupling compounds with naphthylboronic acid. Subsequently, **SiO₂@PhBr** was carefully treated after reaction with **Si-Tpy-Pd₁Ni₁** and analyzed under UV. A stronger broad peak for naphthylboronic acid (Figure 12, bright green line) and a gradual decrease after treatment with solvent and ultrasonication were observed (Figure 12, crimson and light blue line), indicating that the naphthyl boronic acid was absorbed on **SiO₂@PhBr** surface through intermolecular interaction. No coupling reaction occurred on **SiO₂@PhBr** surface. Therefore, the leaching of Pd active species into solution from **Si-Tpy-Pd₁Ni₁** did not occur. Moreover, the leaching of Pd active species into solution from **Si-Tpy-Pd₁Ni₁** did not occur. These results confirmed the presence of heterogeneous catalysis.

3.4.4 WCA Analysis

Wettability, a crucial property of solid materials, is governed by both surface chemical composition and the geometrical structure, and optimal wettability can enhance the catalytic activity [48, 49]. Figure 13 depicts the WCA changes in **Si-Tpy-Pd/Ni** during catalysis. The WCAs of **Si-Tpy-Pd/Ni** were 44° before catalysis, which changed from 44° (0 h) to 48° (1 h), 50° (2 h), 54° (4 h), 46° (8 h), and 43° (12 h), demonstrating that catalysis occurred on the **Si-Tpy-Pd/Ni** monolayer surface; moreover, substrate absorption, intermediate formation, and desorption of product occurred because the **Si-Tpy-Pd/Ni** monolayer surface almost recovered after catalysis. This phenomenon was investigated using XPS analysis.

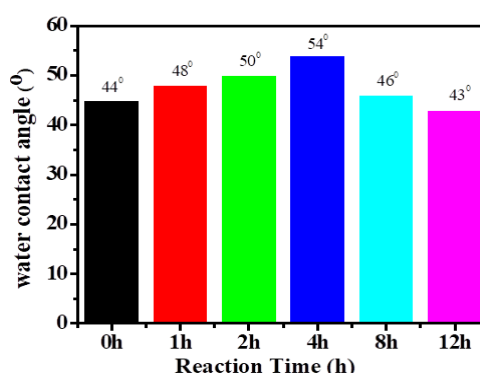


Figure 13 Changes of WCA in Suzuki coupling reaction catalyzed by **Si-Tpy-Pd₁/Ni₁** at 0, 1, 2, 4, 8, and 12 h.

3.4.5 Low X-ray Diffraction (LXRD) of Si-Tpy-Pd₁/Ni₁ During Catalysis.

The LXRD patterns of **Si-Tpy-Pd₁/Ni₁** used for catalysis at different times were measured (Figure 14). The LXRD pattern at 1.1° for **Si-Tpy-Pd₁/Ni₁** proved its regular structure, and the diffraction

peak shifted from a high to a low angle. Moreover, the pattern type remained unchanged during catalysis (from 1 to 12 h), indicating that the thickness of the catalyst monolayer decreased and increased and finally retained its original thickness. Therefore, the structure of the catalyst was not damaged before and after catalysis, demonstrating that the hetero-bimetallic catalyst was durable and could maintain its orientation under the optimized conditions.

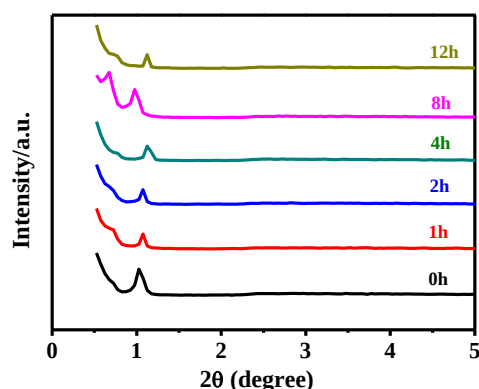


Figure 14 XRD of **Si-Tpy-Pd₁/Ni₁** in Suzuki coupling reaction at 0, 1, 2, 4, 8, and 12 h.

3.4.6 UV Spectra of Si-Tpy-Pd₁/Ni₁ During Catalysis.

Changes in **Si-Tpy-Pd₁/Ni₁** UV spectra were investigated during catalysis, and the results are displayed in Figure 15. The peak at 275 nm for **Si-Tpy-Pd₁/Ni₁** shifted to 218 nm after 1 h, indicating that substrate adsorption led to the high density of monolayer. The adsorption became instant at 2, 4, and 8 h, thereby demonstrating the equivalence. Finally, it recovered at 12 h, demonstrating the stability of the catalytic monolayer.

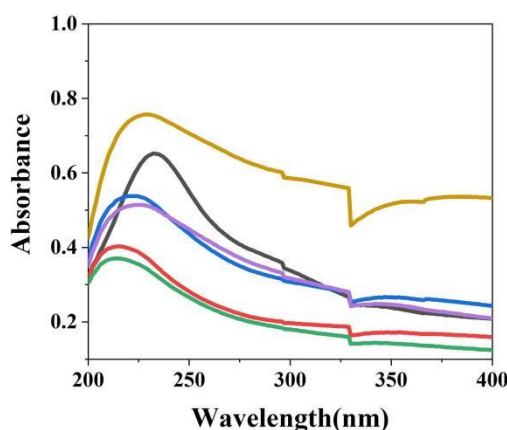


Figure 15 UV spectra of **Si-Tpy-Pd₁/Ni₁** during catalysis (0 h, black line; 1 h, red line; 2 h, blue line; 8 h, purple line; 12 h, yellow line).

3.4.7 SEM Images of SiTpy-Pd₁/Ni₁ During Catalysis

To investigate the changes on the surfaces, SEM images at different reaction times were obtained (Figure 16). SEM revealed a regular surface before catalysis (Figure 16A), and the morphology of the catalytic surface changed at 1 h (Figure 16B), indicating that the adsorption of substrates occurred on the catalytic monolayer surface. Extreme changes occurred on the catalyst surfaces at 2 and 4 h

(Figures 16C and 16D), indicating the automatic agglomeration of coupling compounds because of the higher adsorption rate, which was the key factor in the catalytic process. As observed in Figure 16E, the image became smooth at 8 h. This indicated that a violent reaction occurred, which was accompanied by a sequential process, including the adsorption of substrate and formation of intermediates and compounds on the catalytic surface. The morphology of the catalytic surface was more ordered at 12 h than at 2, 4, and 8 h (Figure 16F). The significant changes in the catalytic surface may be because of the in situ formation of Pd on the catalytic surface. The catalytic process included adsorption, synergism, and desorption. More time was required for catalysis because of the covered active sites, adsorption, and desorption rate of substrate or product affecting the catalytic process.

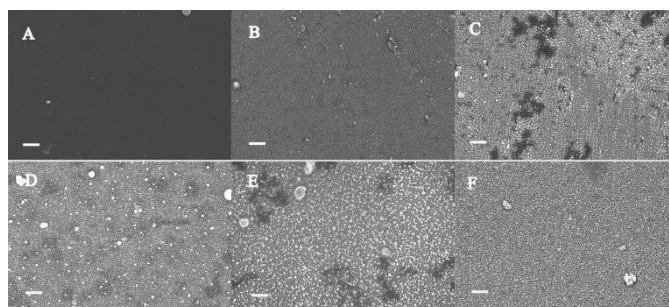


Figure 16 SEM images of **Si-Tpy-Pd₁/Ni₁** at (A) 0 h, (B) 1 h, (C) 2 h, (D) 4 h, (E) 8 h, and (F) 12 h (white bar: 200 nm).

The **Si-Tpy-Pd₁/Ni₁** surface morphology became random with some particles after the 1st, 2nd, 3rd, 4th, 5th, and 6th run (Figure 17). After the 1st run, some larger particles were observed, which might be the substrates or coupling products adsorbed on the catalytic monolayer surface (Figure 17A). As the recycling proceeded, much more large particles were obtained, especially after five or six runs (Figures 17B, C, D, E, and F). This may be the main reason for deactivation attributable to the aggregation of the active species forming Pd/Ni clusters through the migration of active atoms and coupling with each other [58]. Therefore, the prepared **Si-Tpy-Pd₁/Ni₁** was stable during catalysis.

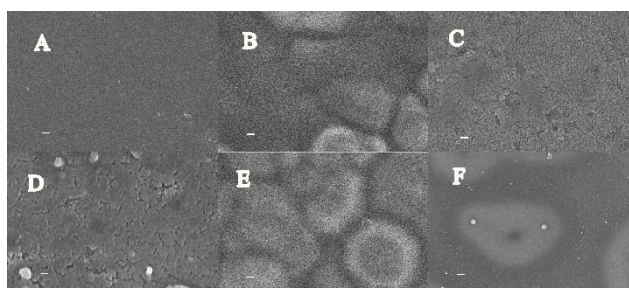


Figure 17 SEM images of **Si@Tpy-Pd₁/Ni₁** reused. (A) 1st run, (B) 2nd run, (C) 3rd run. (D) 4th run, (E) 5th run, (F) 6th run. (white bar: 200 nm).

3.4.8 XPS Analysis of GO-Tpy-Pd₁/Ni₁ During Catalysis

The HR-XPS of Pd 3d, Br 3d, and N 1s during catalysis was measured (Figure 18). During the catalytic process, the peaks at 399.89 eV for N 1s (Figure 18A) shifted to 399.99 eV (1 h), 400.14 eV

(2 h), 399.99 eV (4 h), 400.04 eV (8 h), and 400.19 eV (12 h). The peak position of N 1s changed during the catalytic process because of the electron transfer to or electron acceptance from the different valence states of Pd and Ni coordinated with the ligand. The peaks at 340.54 eV and 335.24 eV for Pd 3d_{3/2} and Pd 3d_{5/2} were assigned to Pd(0) and appeared at 1 h (Figure 18B). The intensity of the two peaks of Pd(0) gradually increased with increasing catalysis time, and the intensity of the peaks for Pd(II) gradually decreased with time, indicating that the real active site Pd(0) was formed in situ by Pd(II) reduction. The peak of Br 3d was observed at 8 and 12 h (Figure 18C). Therefore, the basic elements of the catalyst and substrates appeared and changed during catalysis, implying the oxidation of benzyl bromide with metal to produce an oxidative intermediate on the surface. The oxidative intermediate reacted with phenylboronic acid to form a transmetalation intermediate, which yielded cross-coupling compounds through elimination reduction, and finally desorbed from the surface.

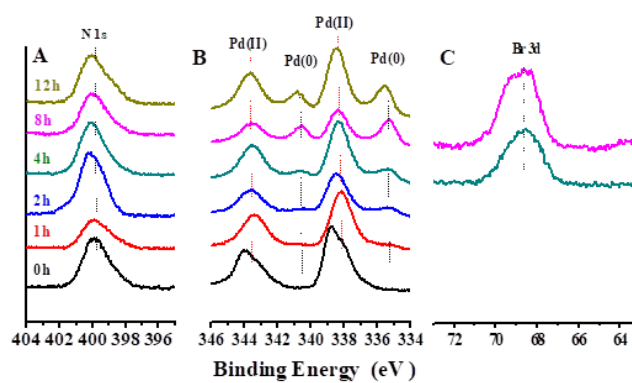


Figure 18 HR-XPS spectra of Pd 3d, N 1s, and Br 3d at 0, 1, 2, 4, 8, and 12 h.

In addition, the changes in the bonding energy of Ni 2p during catalysis were analyzed (Figure 19). Peaks at 855.67, 861.57, and 873.47 eV were attributed to N 2p_{3/2} and N 2p_{1/2}, indicating the existence of Ni²⁺ (Figure 19A). The binding energy of Ni 2p increased to 856.14 eV after 4 h, indicating the loss of electrons in Ni (Figure 19B); it decreased to 854.24 eV after 8 h, indicating electron acceptance by Ni (Figure 19C). Finally, the bonding energy gradually returned to the original state at 855.77 eV at 12 h, indicating that Ni(II) was reduced to Ni(0) (Figure 19D). The HR-XPS of Pd revealed that Pd(0) quantity increased with increasing catalytic time (Figure 18B). This may be attributed to the electron transfer from Ni to Pd, which facilitated the oxidation step because of more negative charge in the Pd active center (Ni^{δ+}/Pd^{δ-}/Pd(0)) formed during the catalysis process (Scheme 3). Ni^{δ+}/Pd^{δ-}/Pd(0) surrounded by appropriate Pd(II)/Ni(II) played a crucial role in catalysis because of the synergistic effect between Pd and Ni linked as a “guest” to a “host” in the entity, thereby modifying the electronic properties of its active center [45, 59-61] and increasing the activity. The catalytic film was regarded as an infinite “pool” of organometallic compounds containing a few active species on its surface [62]. This indicated the importance of catalysis surface modification by organometallic compounds to tune the catalytic activity.

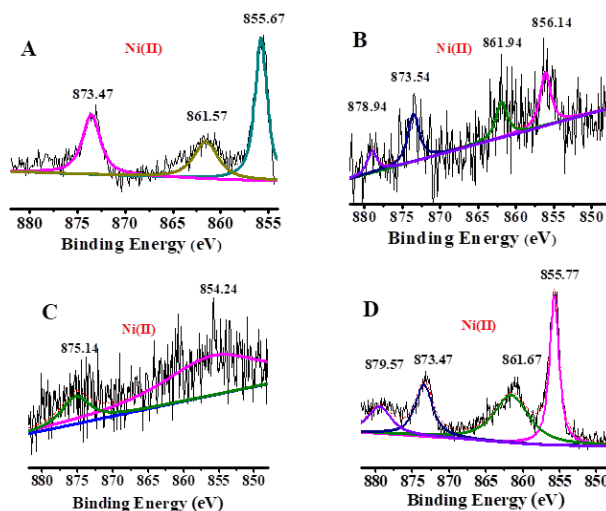
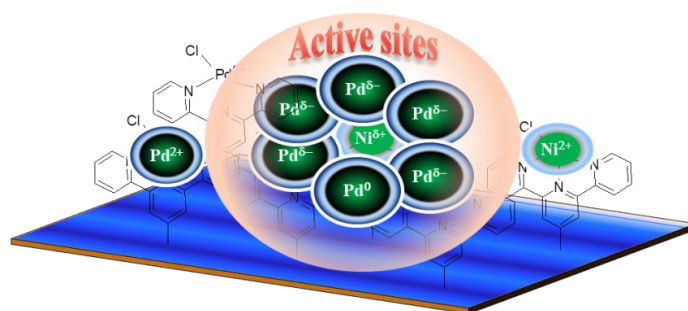
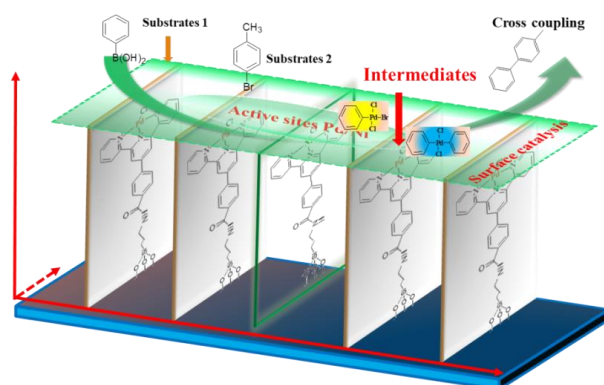


Figure 19 High resolution XPS of Ni 2p at different times: (A) 0 h, (B) 4 h, (C) 8 h, and (D) 12 h.



Scheme 3 Proposal of active center in Ni(II)/Pd(0) formed in situ during catalysis.

On the basis of the aforementioned results, a hypothetical catalytic mechanism was proposed (Scheme 4). An “induced step” was the adsorption of one or more substrates on the organometallic monolayer surface during the catalytic process. Pd(0) adsorbed *p*-bromotoluene to form the oxidative insertion intermediate. Pd(II) or Ni(II) in the vicinity of active Pd(0) adsorbed phenyl boronic acid, which transmetalated with the oxidative insertion intermediate, followed by the formation of a coupling compound through elimination reduction. Finally, coupling compounds diffused from the catalytic monolayer surface.



Scheme 4 Supposed catalytic mechanism and synergy on the self-assembled organometallic framework film (OMFF) surface.

Bi-organometallic catalytic monolayer exhibits higher activity than the mono-organometallic catalytic monolayer because of the synergistic effect existing on the catalytic surface, such as the electron distribution of active species. Moreover, active metals or nonactive metals in active sites simultaneously joined in the catalytic process, as described in Scheme 3 [63-66]. The results indicated that the morphology, catalyst orientation, ligand design, support selection, the rational combination of different metals, and the ratio of multi-metals were crucial factors for achieving a highly active and stable catalyst.

4. Conclusions

A new organometallic terpyridine Ni/Pd self-assembled catalytic monolayer supported on a silicon wafer surface (denoted as **Si-Tpy-Ni₁/Pd₁**) was fabricated and characterized. The monolayer exhibited high catalytic activity, substrate applicability, and recyclability after 5 runs, and the deactivation was induced by Pd aggregation during recycling. The catalytic mechanism on the surface of **Si-Tpy-Pd₁/Ni₁** was heterogeneous. The synergistic mechanism between Ni and Pd was investigated in detail, and the real active species was Pd/Ni, which was formed in situ. The electron density of Pd increased because of electron transfer from Ni to Pd, which was the crucial factor for the initial oxidation step. These results indicated that the high activity of a catalyst could be achieved through optimal ligand designing, support selection, catalyst arrangement, and a suitable combination of bi-organometallics.

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Author Contributions

Prof. Tiesheng Li designed, analysis and writing; Wei Wang and Huanhuan Li for synthesis and measurement; Sa Bi for synthesis.

Competing Interests

The authors have declared that no competing interests exist.

References

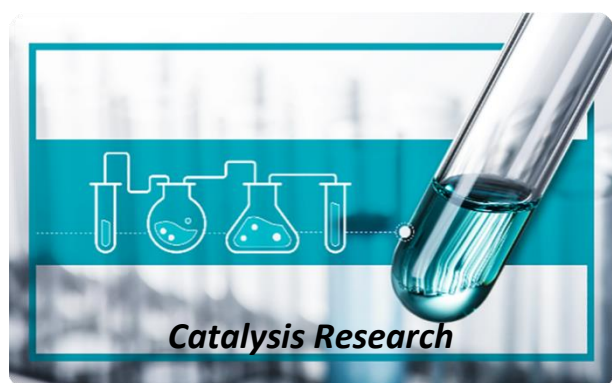
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