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"Click" magnetic nanoparticle-supported palladium catalyst: a phosphine-free, highly efficient and magnetically recoverable catalyst for Suzuki–Miyaura coupling reactions

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A novel magnetic nanoparticle-supported nano-palladium catalyst was successfully prepared *via* a "click" route. The as-prepared catalyst was well characterized and evaluated in Suzuki–Miyaura coupling in terms of activity and recyclability in aqueous ethanol. It was found to be highly efficient for the reactions of various aryl bromides with arylboronic acids under phosphine-free and low Pd loading (0.2 mol%) conditions. Moreover, the catalyst could be easily separated from the reaction system by an external magnet and reused several times without a remarkable loss of its activity.

Introduction

The palladium-catalyzed cross-coupling of aryl halides with arylboronic acids, known as Suzuki–Miyaura coupling, has been recognized as one of the most powerful tools for the construction of unsymmetrical biaryl units,[1] and extensively used in the synthesis of natural products, pharmaceuticals and functional materials.[2] Although, a variety of homogeneous palladium catalysts, such as palladium–phosphine complexes,[3] oxime-carbapalladacycles,[4] or palladium–*N*-heterocyclic carbene complexes,[5] have been proved to be highly active and selective in this transformation, separation of the catalyst from the product is often problematic in these homogeneous systems. Moreover, catalyst recovery is highly desirable, in particular, if expensive noble metal catalysts are used in large-scale synthesis due to environmental and economic concerns.

Heterogenization could be an attractive solution to these problems since the Pd catalyst immobilized on a support could be easily separated from the product and effectively reused. A lot of organic and inorganic supports, including microporous polymers,[6] carbon materials,[7] amorphous or mesoporous silica,[8] metal oxides,[9] and molecular sieves,[10] have been explored in Pd-mediated catalysis, in which Pd complexes or nanoparticles are involved as active species. Although significant efforts have been made to develop recoverable Pd catalysts, some supported Pd catalysts suffered from lower efficiency in comparison with their analogues in homogeneous systems, owing to limitations related to the diffusion of the reactants through the pores of the supports. Alternatively, ligand-free Pd catalysts were developed by entrapment or adsorption of Pd salts on porous solids. Meanwhile, Pd leaching could be found in such systems.[11]

Nanoparticles (NPs) have recently emerged as robust alternatives for the immobilization of homogeneous catalysts due to their high surface area and low porosity caused by their nanoscale dimensions.[12] This makes the active catalytic sites on the surface well accessible to the reactants. And the NP-supported catalysts can be readily dispersed in the reaction system, where the catalytic sites seem to be soluble, thus the catalytic NPs can be considered as quasi-homogeneous catalysts. However, they still suffer from the problem of catalyst separation and recovery due to their colloidal nature. This could be solved by using magnetic nanoparticles (MNPs), which can be simply removed from the reaction system by magnetic separation. Over the past few decades, a series of MNP-supported Pd catalysts have been designed by anchoring strategies.[13] Recently, Thiel *et al.* have reported a successful example of immobilizing a Pd(II)–phosphine complex on MNPs for Suzuki reaction.[14] Li and his co-workers developed an efficient MNP-supported Pd catalyst for Suzuki and Heck reactions.[15] Wang's group also prepared another MNP-supported Pd–phosphine complex for various C–C coupling reactions.[16] Among them, phosphines were the most employed ligands. However, phosphine ligands are often extremely expensive, air-sensitive, and virulent, which limit their wide use in large-scale application.[17] In addition, high Pd loadings were generally required for reasonable catalytic results. Therefore, it is still highly desirable to develop phosphine-free

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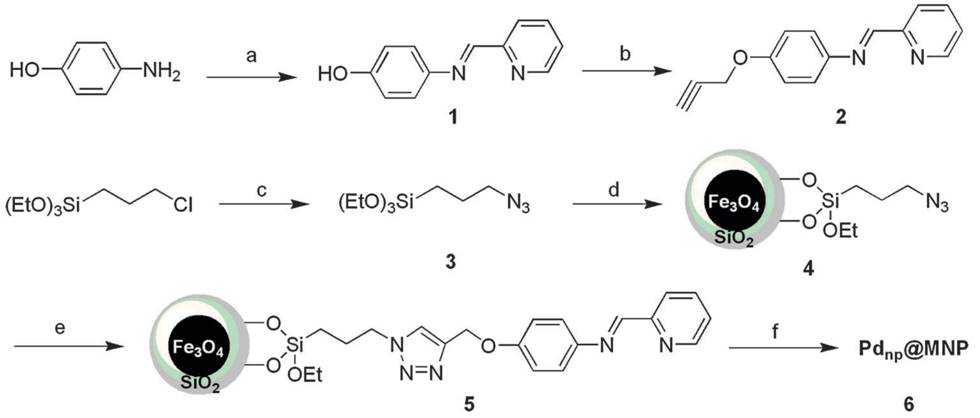


Scheme 1 Synthesis of magnetic nanoparticle-supported nano-palladium catalyst **6**. Reaction conditions: (a) MeOH, pyridine-2-carbaldehyde, reflux, 3 h; (b) K_2CO_3, acetone, propargyl bromide, 50 °C, 18 h; (c) NaN_3, CH_3CN, TBAB, reflux, 24 h; (d) silica-coated Fe_3O_4 nanoparticles, toluene, reflux, 24 h; (e) **2**, CuI, DIPEA, DMF/THF, r.t., 3 d; (f) $Na_2Pd_2Cl_6$, MeOH, 60 °C, 24 h, then AcONa, r.t., 1 h.

MNP-supported Pd catalysts with high activity, excellent stability and low cost.

The copper-catalyzed azide–alkyne cycloaddition (CuAAC) reaction known as ''click chemistry'' strategy has been proved to be a powerful tool for conjugation between azides and alkynes owing to its high efficiency, simple procedure, mild conditions and absence of byproducts.[18] More recently, the 1,2,3-triazole unit has drawn much attention for catalyst immobilization as a highly stable linker or/and a chelator, and many metal catalysts, such as Au,[19] V,[20] and Pd,[21] have been successively explored. Inspired by its attractive features, we tried to develop a new ''click'' MNP-supported catalyst incorporating a 1,2,3-triazole moiety for the fusion of linker functionality and a MNP backbone.

In continuation of our efforts in designing greener supported catalysts,[22] we herein present the preparation of a novel MNP-supported Pd catalyst (Pd_{np}@MNP) *via* the copper-catalyzed ligation of an alkynlated imino-pyridine ligand with azide functionalized silica-coated Fe_3O_4 nanoparticles (Scheme 1), and its application in Suzuki–Miyaura reactions.

Results and discussion

The magnetic nanoparticle-supported Pd catalyst was prepared following the procedure shown in Scheme 1. The imino-pyridine ligand **1** was firstly synthesized by a simple condensation of 4-aminophenol with pyridine-2-carbaldehyde, then it underwent direct propargylation to afford compound **2** in an almost quantitative yield. Secondly, the silica-coated Fe_3O_4 nanoparticles (SiO_2@Fe_3O_4) were prepared according to our previous methods[22b] and chosen as the magnetic nano-support. The azide group was then introduced into the SiO_2@Fe_3O_4 through a simple procedure and verified by the appearance of the N_3 band at 2104 cm^{-1} in FT-IR spectra (Fig. 1). Meanwhile, the loading of the azide group was determined to be 0.40 mmol g^{-1} by elemental analysis of the nitrogen content.

Reaction of the azide-functionalized MNP **4** with an excess of compound **2** using CuI and *N*,*N*-diisopropylethylamine (DIPEA) as a typical ''click'' catalytic system[23] led to nearly complete conversion of all azide groups. FT-IR spectra show a strong absorption band at 2104 cm^{-1} (N_3 vibrations), which disappears upon formation of the 1,2,3-triazole linker during the ''click'' reaction. In addition, the typical bands at around 1590 cm^{-1} (C=N vibration) and 1500 cm^{-1} (C=C vibration of the aryl ring) are observed (Fig. 1). The above results indicate that the imino-pyridine ligand was successfully grafted onto SiO_2@Fe_3O_4.

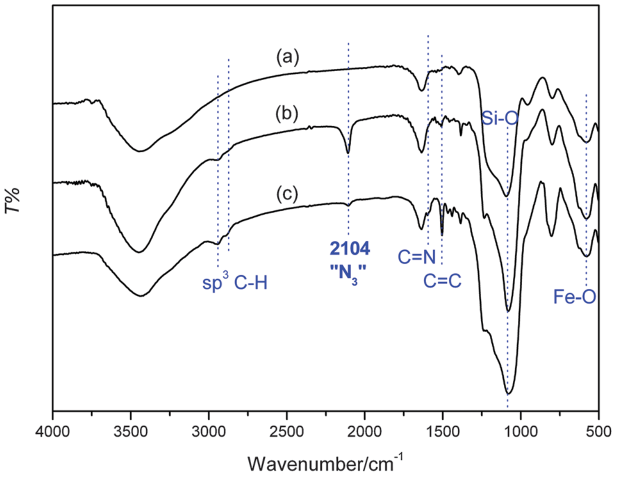


Fig. 1 FT-IR spectra of SiO_2@Fe_3O_4 (a), azide-functionalized MNP **4** (b), imino-pyridine ligand-functionalized MNP **5** (c).

Ultimately, the resulting functionalized MNP **5** was treated with a methanolic solution of $Na_2Pd_2Cl_6$ under reflux conditions[24] to provide the desired solid catalyst Pd_{np}@MNP **6.** The amount of Pd measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) was 1.18%. X-Ray reflective diffraction (XRD) and transmission electron microscopy (TEM) were then carried out to get detailed information about the structure and morphology of the as-prepared catalyst.

The high-angle XRD pattern of the novel catalyst exhibits diffraction peaks corresponding to the standard Fe_3O_4 sample

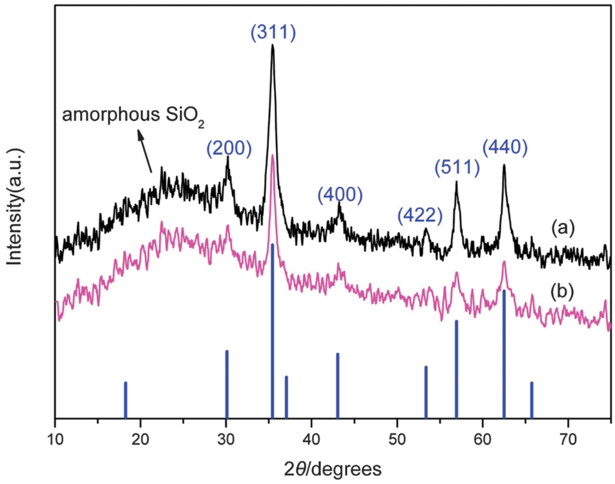


Fig. 2 XRD patterns of $SiO_2@Fe_3O_4$ (a), MNP-supported Pd catalyst **6** (b). The bottom row of tick marks indicates the reflection positions for a standard magnetite pattern (JCPDS no. 19-0629).

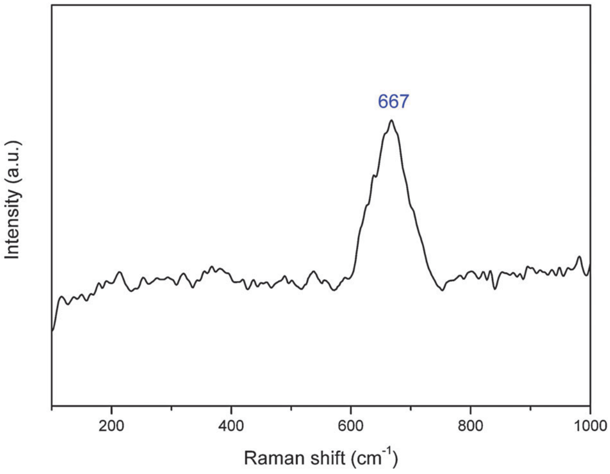


Fig. 3 Raman spectrum of the as-synthesized magnetic catalyst.

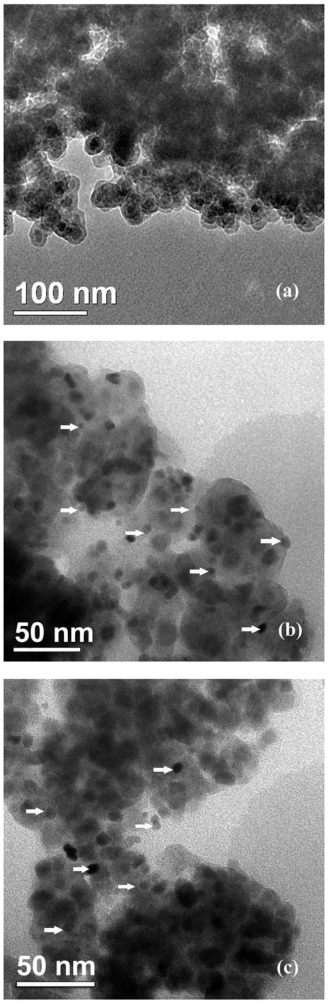


Fig. 4 TEM images of $SiO_2@Fe_3O_4$ (a), MNP-supported Pd catalyst **6** (b), six-times reused catalyst (c). The arrows indicate some of the Pd nanoparticles.

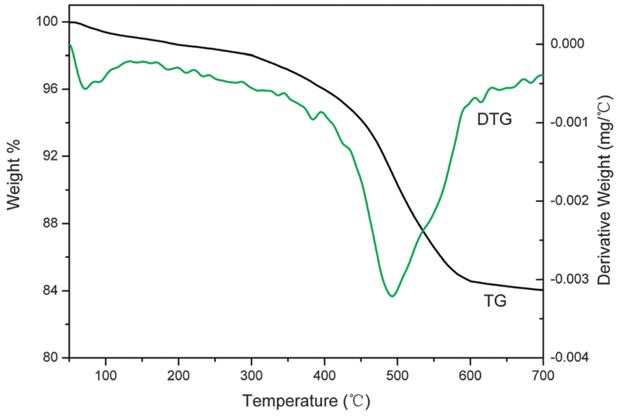


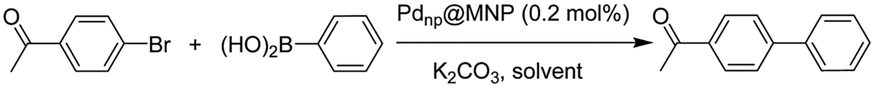
Fig. 5 TG-DTG analysis for $Pd_{np}@MNP$.

(JCPDS file No. 19-0629, Fig. 2). The broad peak from $2\theta = 20^\circ$ to 30° is consistent with an amorphous silica layer. No characteristic peaks for Pd nanoparticles are observed which proves the excellent dispersion of the Pd sites on the magnetic nanoparticles.[16] In addition, the average crystal size of the Fe_3O_4 cores, calculated using the Scherrer formula, is about 10.5 nm.

As both magnetite Fe_3O_4 and maghemite γ-Fe_2O_3 have good magnetic properties and similar XRD patterns,[25a] Raman spectroscopy was used to distinguish the different structural phases of iron oxides. The Raman spectrum of the as-synthesized magnetic catalyst shows the main feature at 667 cm^{-1} (A_{1g}) characteristic of magnetite (Fig. 3).[25]

The TEM images of the support $SiO_2@Fe_3O_4$ and the catalyst $Pd_{np}@MNP$ **6** are shown in Fig. 4. The dark nano-Fe_3O_4 cores are surrounded by a grey silica shell of about 3–5 nm thick and the average size of the Fe_3O_4 cores is about 8–12 nm (Fig. 4a), which is consistent with that determined using the Scherrer equation in the XRD pattern. After anchoring of Pd, the Pd nanoparticles are distinguishable with the difference in their contrast, as indicated by the arrows in Fig. 4b and c. Some Pd particles (about 4 nm) are attached to the support particles (about 25 nm).

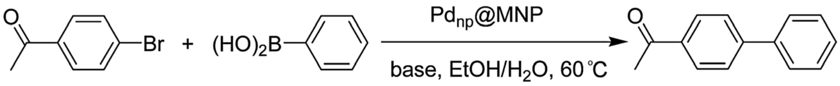
Table 1 Effect of the solvent on Suzuki–Miyaura reaction[a]



Entry	Solvent	Time (h)	Yield[b] (%)
1	MeOH	3	54
2	EtOH	3	65
3	^{i}PrOH	6	81[c]
4	H_2O	6	37[c]
5	95% EtOH	3	78
6	95% EtOH	6	96[c]
7	MeOH/H_2O (1 : 1, v/v)	3	94
8	^{i}PrOH/H_2O (1 : 1, v/v)	3	89
9	EtOH/H_2O (1 : 1, v/v)	3	97
10	EtOH/H_2O (2 : 1, v/v)	3	92
11	EtOH/H_2O (1 : 2, v/v)	3	75

[a] Reaction conditions: 4-bromoacetophenone (1.0 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (2.0 mmol), catalyst (0.2 mol% Pd) in 6.0 mL of solvent at 60 °C under air. [b] Isolated yield. [c] At 80 °C.

Table 2 Effect of the base and amounts of catalyst on Suzuki–Miyaura reaction[a]



Entry	Base	Time (h)	Yield[b] (%)
1	K_3PO_4	3	95
2	K_2CO_3	3	97
3	Cs_2CO_3	3	94
4	Na_2CO_3	3	89
5	Na_3PO_4	3	87
6	$NaHCO_3$	3	46
7	NEt_3	3	31
8	K_2CO_3	3	99[c]
9	K_2CO_3	3	83[d]

[a] Reaction conditions: 4-bromoacetophenone (1.0 mmol), phenylboronic acid (1.2 mmol), base (2.0 mmol), catalyst (0.2 mol% Pd) in 6.0 mL of EtOH/H_2O (1 : 1, v/v) at 60 °C under air. [b] Isolated yield. [c] Catalyst (1.0 mol% Pd) was used. [d] Catalyst (0.1 mol% Pd) was used.

The stability of the catalyst Pd$_{np}$@MNP was also investigated by the thermogravimetric (TG) analysis (Fig. 5). The TG curve indicates an initial weight loss of 1.8% up to 150 °C, which is owing to the adsorbed water on the support. Thermal degradation of the catalyst occurred after 250 °C, which revealed the excellent stability. Meanwhile, the DTG curve shows that the decomposition of the organic structure mainly occurred in one step from 370 to 560 °C, which is related to a main weight loss of 13.2%. Therefore, Pd$_{np}$@MNP was very stable and could be used within a broad temperature scale.

The activity of this novel catalyst was initially tested in Suzuki–Miyaura coupling. The coupling of 4-bromoacetophenone and phenylboronic acid was chosen as the model reaction. Due to environmental concerns, only alcohol or water chosen as solvent were examined, and a significant effect was observed (Table 1). While the model reaction was carried out in pure alcohol or water, moderate yield could be obtained (Table 1, entries 1–4). Interestingly, when we adopted the aqueous alcohol as the solvent, satisfactory results were obtained (Table 1, entries 5–9). The advantage of the co-solvent is attributed to the good solubility of the organic reactants and the inorganic base. The influence of different volume ratios of EtOH/H_2O was then tested, and the best one is 1 : 1 (Table 1, entry 9).

Next, a series of bases were taken into consideration for the model reaction in EtOH/H_2O (1 : 1, v/v). With regard to other

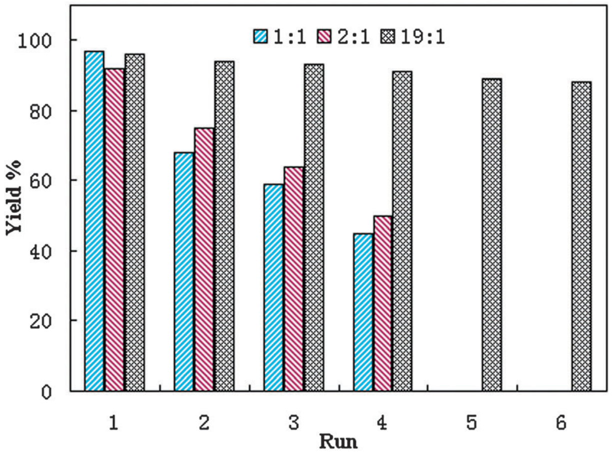


Fig. 6 Recycling experiment of the MNP-supported Pd catalyst.

bases, K_2CO_3 was found to act as an excellent base (Table 2, entry 2). K_3PO_4, Cs_2CO_3, Na_2CO_3, and Na_3PO_4 were also effective (Table 2, entries 1 and 3–5). The organic base NEt_3 was also studied, which afforded an unsatisfactory yield (Table 2, entry 7). Different amounts of catalyst between 0.1 and 1.0 mol% were further investigated for this reaction, and 0.2 mol% loading of Pd was found to be optimal. For the higher amounts of catalyst, the desired product was obtained in a nearly quantitative yield (Table 2, entry 8). However, the yield of the reaction was lower in 0.1 mol% Pd dosage (Table 2, entry 9).

The recovery and reuse of catalyst becomes an important factor due to stringent economical and ecological demands for sustainability. Therefore, the recyclability of this MNP-supported catalyst was immediately investigated by using the above model reaction in three different volume ratios of EtOH/H_2O (1 : 1, 2 : 1, and 19 : 1, respectively). After the completion of the reaction, the magnetic catalyst could be simply and efficiently recovered from the reaction mixture with an external magnet, washed with water and ethanol, dried under vacuum and reused in a subsequent reaction. More than 99% of the catalyst could be recovered from each run. As can be seen from Fig. 6, the catalyst reusability was obviously influenced by the amount of water in the reaction system. Although, some water could make the Suzuki reaction proceed well under milder conditions, the catalyst lost its activity gradually. A little corrosion on the silica layer of the supported catalyst in aqueous basic reaction medium caused leaching and aggregation of the Pd nanoparticles, which might be the main reason.[13e] Interestingly, it was found that the catalyst activity could be retained for a few more cycles when a less amount of water was used as the reaction solvent. However, a higher temperature and a longer time were necessary. It is worth noting that the catalyst could be reused without a significant loss of its activity in a test of six cycles, when the reaction was performed in 95% EtOH at 80 °C for 6 h.

Pd leaching of the catalyst was further determined. ICP analysis of the clear filtrate showed that the Pd content was less than 0.16 ppm, which revealed that the MNP-supported Pd catalyst was very stable and could endure this coupling condition. Meanwhile, the iron leaching was also determined and analysis of the reaction solution indicated that the Fe content was less than 0.23 ppm in the solution, which also demonstrated that nearly no corrosion on the silica layer of the $SiO_2@Fe_3O_4$ supported Pd catalyst occurred in the 95% EtOH reaction medium. Moreover, the filtered solution exhibited no reactivity to a fresh model reaction. The TEM analysis of the recovered catalyst indicated that the size and morphology of the catalyst after the sixth run had no apparent change and agglomeration (Fig. 4c).

With these good results in hand, several representative coupling reactions of a variety of aryl halides with arylboronic acids were then explored under two kinds of optimal conditions, in order to survey the versatility of this MNP-supported Pd catalyst. As shown in Table 3, the coupling between aryl bromides and phenylboronic acid, which contained electron-donating as well as electron-withdrawing groups, proceeded effectively to afford the corresponding products in good to excellent yields (Table 3, entries 1–8). And a wide range of functional groups, such as nitryl, cyano, fluoro, methoxy and aldehyde, could be well tolerated in the reaction. The *ortho*-substituted aryl bromide generated the corresponding product in lower yield for a longer time because of steric effects (Table 3, entry 9). Some substituted arylboronic acids were also tested, and they all reacted smoothly with aryl bromides and afforded the desired products in high yields (Table 3, entries 13–19). Strangely, all attempts to carry out the reaction of 4-bromoaniline and 4-bromophenol were unsuccessful, only about 20% yield of the corresponding products were obtained. When 4-iodoaniline and 4-iodophenol were chosen as the alternative substrates, the desired products could be obtained in good yields (Table 3, entries 10–12). Additionally, 4-chloroacetophenone and 4-chloronitrobenzene were chosen as the challenging substrates, however, the catalytic system was less effective even when using higher Pd loading and prolonged reaction time (Table 3, entries 20 and 21).

Experimental

General

Melting points were determined using a WRS-1B apparatus and were uncorrected. The IR spectra were recorded on a Nicolet spectrometer (KBr). ^{1}H NMR spectra were recorded on a Bruker DRX500 (500 MHz) and ^{13}C NMR spectra on a Bruker DRX500 (125 MHz) spectrometer. Elemental analysis was performed on an Elementar Vario EL β recorder. Palladium content of the catalyst was measured by inductively coupled plasma (ICP) on an L-PAD analyzer (Prodigy). X-ray diffraction (XRD) images were obtained from a Bruker XRD D8 Advance instrument with Cu Kα radiation (λ = 0.15418 nm). Transmission electron microscopy (TEM) images were obtained using a JEM-2100 instrument. The Raman spectra were obtained using a Renishaw inVia Raman Microscope. The 514 nm argon ion laser line was used for excitation and the laser power was kept below 0.1 mW, to avoid sample degradation.

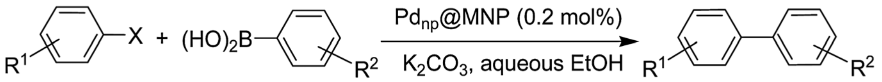
Synthesis of imino-pyridine ligand (1)

Pyridine-2-carbaldehyde (5.35 g, 50.0 mmol) and *p*-aminophenol (5.46 g, 50.0 mmol) were added into 25 mL of methanol and the resulting mixture was stirred under reflux for 3 h. The mixture was slowly cooled to room temperature and the pure solid product **1** (6.44 g, 32.5 mmol) was obtained by filtration immediately (yield: 65%). Yellow crystals, mp: 186–187 °C; ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.64 (s, 1H), 8.63 (s, 1H), 8.67–8.58 (m, 1H), 8.50 (s, 1H), 8.09 (d, J = 8.0 Hz, 1H), 7.92–7.88 (m, 1H), 7.48–7.45 (m, 1H), 7.30–7.26 (m, 2H), 6.82–6.79 (m, 2H).

Synthesis of compound 2

A round-bottom flask was charged with compound **1** (2.97 g, 15.0 mmol), K_2CO_3 (4.14 g, 30.0 mmol), propargyl bromide (1.79 g, 15.2 mmol) and acetone (50 mL). The resulting mixture was stirred at 50 °C under a nitrogen atmosphere for 18 h, and then cooled and filtered. The solvent was removed by rotary

Table 3 Suzuki–Miyaura coupling reaction of aryl halide with arylboronic acid



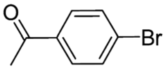
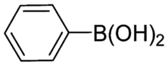
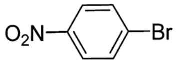
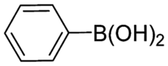
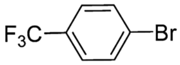
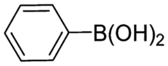
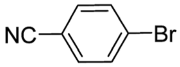
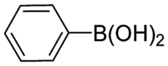
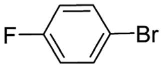
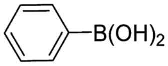
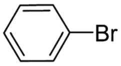
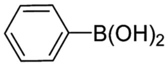
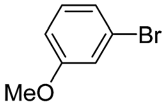
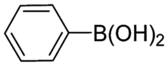
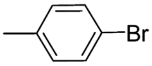
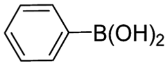
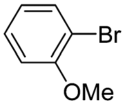
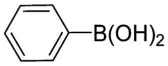
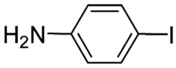
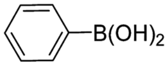
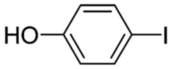
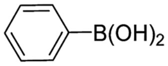
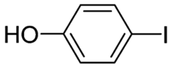
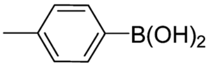
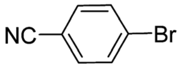
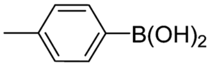
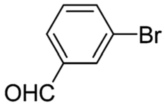
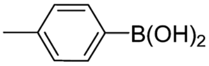
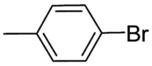
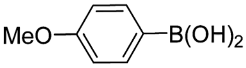
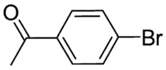
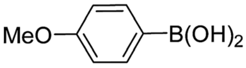
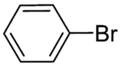
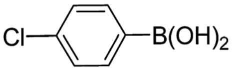
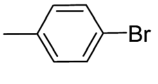
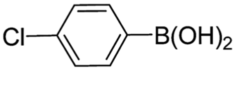
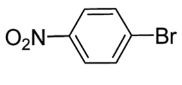
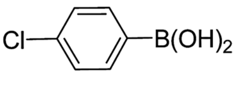
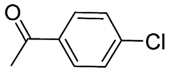
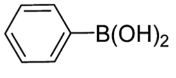
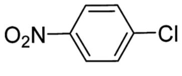
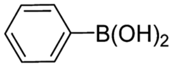
				Conditions A[a]		Conditions B[b]	
Entry	1	2	3	*t* (h)	Yield[c] (%)	*t* (h)	Yield[c] (%)
1			**3a**	3	97	6	96
2			**3b**	3	99	6	97
3			**3c**	3	95	6	90
4			**3d**	3	96	6	92
5			**3e**	4	92	6	88
6			**3f**	4	97	6	90
7			**3g**	4	93	8	91
8			**3h**	4	90	8	84
9			**3i**	8	80	12	72
10			**3j**	7	86	10	80
11			**3k**	5	91	8	89
12			**3l**	5	90	8	87
13			**3m**	3	94	6	92
14			**3n**	3	93	6	89
15			**3o**	4	86	6	85
16			**3p**	3	95	6	96
17			**3q**	4	91	6	82

Table 3 (*continued*)

Entry	1	2	3	Conditions A[a]		Conditions B[b]	
				t (h)	Yield[c] (%)	t (h)	Yield[c] (%)
18			**3r**	6	89	8	83
19			**3s**	3	97	6	94
20[d]			**3p**	12	<5	24	<5
21[d]			**3s**	12	12	24	17

[a] Reaction conditions A: aryl halide (1.0 mmol), arylboronic acid (1.2 mmol), K_2CO_3 (2.0 mmol), catalyst (0.2 mol% Pd) in 6.0 mL of EtOH/H_2O (1 : 1, v/v) at 60 °C under air. [b] Reaction conditions B: aryl halide (1.0 mmol), arylboronic acid (1.2 mmol), K_2CO_3 (2.0 mmol), catalyst (0.2 mol% Pd) in 6.0 mL of 95% EtOH at 80 °C under air. [c] Isolated yield. [d] Catalyst (1.0 mol% Pd) was used.

evaporation under reduced pressure, and product **2** was obtained as a brown solid (3.47 g, 98%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.72 (d, J = 4.2 Hz, 1H), 8.64 (s, 1H), 8.21 (d, J = 7.9 Hz, 1H), 7.82 (td, J = 7.6, 1.3 Hz, 1H), 7.46–7.31 (m, 3H), 7.10–7.00 (m, 2H), 4.74 (d, J = 2.4 Hz, 2H), 2.56 (t, J = 2.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.80, 156.81, 154.81, 149.66, 144.60, 136.62, 124.89, 122.59, 121.70, 115.56, 78.45, 75.66, 56.09.

Synthesis of 3-azidopropyltriethoxysilane (3)[21]

3-Chloropropyltriethoxysilane (4.82 g, 20.0 mmol) was added to a solution of sodium azide (1.95 g, 30.0 mmol) and tetrabutylammonium bromide (TBAB, 1.29 g, 4.0 mmol) in dry acetonitrile (75 mL) under a nitrogen atmosphere. And the reaction mixture was stirred under reflux for 48 h. After the reaction, the solvent was removed under reduced pressure. The crude mixture was then diluted in Et_2O (30 mL) and the suspension was filtered and washed with Et_2O (2 × 10 mL). The combined solvent was removed and product **3** was obtained as a pure and colorless liquid (4.06 g, 82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.82 (q, J = 7.0 Hz, 6H), 3.26 (t, J = 7.0 Hz, 2H), 1.74–1.68 (m, 2H), 1.22 (t, J = 7.0 Hz, 9H), 0.69–0.65 (m, 2H); FT-IR (KBr, cm^{-1}): 2979, 2886, 2099, 1443, 1394, 1242, 1072, 952, 776.

Synthesis of silica-coated Fe_3O_4 nanoparticles (SiO_2@Fe_3O_4)[22b]

Magnetite (Fe_3O_4) nanoparticles were prepared in a chemical co-precipitation step of ferric and ferrous ions in an alkaline solution. $FeCl_3\cdot 6H_2O$ (11.0 g) and $FeCl_2\cdot 4H_2O$ (4.0 g) were dissolved in 250 mL deionized water under nitrogen with vigorous stirring at 85 °C. The pH value of the solution was adjusted to 9 by conc. $NH_3\cdot H_2O$. After continuously stirring for 4 h, the magnetite precipitates were washed by amounts of deionized water to reach pH = 7. A black precipitate (Fe_3O_4) was collected with a permanent magnet under the reaction flask. Coating of a layer of silica on the surface of the nano-Fe_3O_4 was achieved by pre-mixing (ultrasonic) a dispersion of the above black precipitate (2.0 g) with ethanol (400 mL) for 30 min at room temperature. And conc. $NH_3\cdot H_2O$ (12 mL) and TEOS (4.0 mL) were added successively. After stirring for 24 h, the black precipitate (SiO_2@Fe_3O_4) was collected using a permanent magnet, followed by washing with ethanol three times and drying in a vacuum. FT-IR (KBr, cm^{-1}): 3445, 1638, 1097, 580.

Synthesis of azide-functionalized MNP (4)

1.5 g of SiO_2-coated Fe_3O_4 nanoparticles were dispersed in dry toluene (75 mL) by sonication for 1 h. 3-Azidopropyltriethoxysilane (0.5 g, 2.02 mmol) was then added, and the reaction mixture was refluxed for 24 h under nitrogen. After being cooled to ambient temperature, the azide-functionalized MNP **4** was collected by a permanent magnet and washed thoroughly with toluene and acetone, and then dried under vacuum overnight. The loading of the azide group was determined to be 0.40 mmol g^{-1} by elemental analysis. According to FT-IR spectra, the absorption band at 2104 cm^{-1} clearly indicates the successful attachment of the azide group onto the surface of SiO_2@Fe_3O_4. FT-IR (KBr, cm^{-1}): 3438, 2941, 2872, 2104, 1638, 1085, 801, 580.

Preparation of imino-pyridine ligand-functionalized MNP *via* click reaction (5)

Compound **2** (0.5 g, 2.12 mmol) and azide-functionalized MNP **4** (1 g) were mixed with CuI (17 mg, 0.09 mmol) in DMF/THF (1 : 1, 10 mL) under nitrogen, to this was injected DIPEA (2 mL), and the reaction mixture was stirred at room temperature for 3 d. Then the reaction mixture was subjected to magnetic separation, and the MNP **5** was washed sequentially with Et_2O (3 × 20 mL), H_2O (3 × 20 mL), then acetone (3 × 20 mL), and finally dried under vacuum. The loading of an imino-pyridine ligand was determined to be 0.34 mmol g^{-1}

by elemental analysis. Notably, the absorption band at 2104 cm^{-1} disappeared which implied that the "click" process was completed and the imino-pyridine ligand has anchored onto the MNP. FT-IR (KBr, cm^{-1}): 3445, 2941, 2872, 1638, 1594, 1506, 1085, 807, 580.

Preparation of Pd_{np}@MNP (6)

A 5 mL round-bottom flask was charged with $PdCl_2$ (17.0 mg, 96 μmol) and NaCl (6.6 mg, 113 μmol). MeOH (1 mL) was added and the mixture was left stirring at room temperature for 24 h, the mixture was then filtered through a plug of glass wool and the filtrate diluted with additional 9 mL of MeOH. The MNP **5** (0.5 g) was added to the flask, and the resulting mixture was heated to 60 °C for 24 h. At the end of this period, NaOAc (56.0 mg, 0.68 mmol) was added, the mixture was stirred at room temperature for 1 h. Finally, the catalyst Pd_{np}@MNP **6** was collected by a permanent magnet, and washed successively with MeOH, water and acetone, and then dried under vacuum overnight. The content of Pd was 1.18% as determined by ICP-AES.

General procedure for Suzuki–Miyaura coupling reaction

Under an air atmosphere, a round-bottom flask was charged with aryl halide (1.0 mmol), arylboronic acid (1.2 mmol), Pd catalyst (18.0 mg, 0.2 mol%), K_2CO_3 (2.0 mmol) and 6 mL of aqueous EtOH. The reaction mixture was stirred at 60 °C (conditions A, EtOH/H_2O, 1 : 1) or 80 °C (conditions B, EtOH/H_2O, 19 : 1) for a certain period of time as monitored by GC. After completion of the reaction, the catalyst was separated by a permanent magnet, and washed with water and EtOH, and dried under vacuum for the next run. The aqueous phase was extracted with ether (2 × 10 mL) and the combined organic layers were dried over Na_2SO_4, filtered, concentrated, and the residue was purified by recrystallization or flash chromatography on silica gel to afford the corresponding products.

Analytical data for the Suzuki–Miyaura coupling products

1-(Biphenyl-4-yl)ethanone (**3a**). White solid, mp: 120–121 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 8.06 (d, J = 8.0 Hz, 2H), 7.71 (d, J = 8.0 Hz, 2H), 7.65 (d, J = 7.5 Hz, 2H), 7.50 (t, J = 7.5 Hz, 2H), 7.43 (t, J = 7.5 Hz, 1H), 2.67 (s, 3H).

4-Nitrobiphenyl (**3b**). Pale yellow solid, mp: 114–115 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 8.33 (d, J = 8.5 Hz, 2H), 7.77 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 7.5 Hz, 2H), 7.53 (t, J = 7.5 Hz, 2H), 7.48 (t, J = 7.5 Hz, 1H).

4-(Trifluoromethyl)biphenyl (**3c**). White solid, mp: 69–70 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 7.69 (s, 4H), 7.60 (d, J = 7.5 Hz, 2H), 7.48 (t, J = 7.5 Hz, 2H), 7.41 (t, J = 7.5 Hz, 1H).

1,1′-Biphenyl-4-carbonitrile (**3d**). White solid, mp: 85–86 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 7.74–7.68 (m, 4H), 7.59 (d, J = 7.0 Hz, 2H), 7.50–7.43 (m, 3H).

4-Fluorobiphenyl (**3e**). White solid, mp: 73–74 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 7.72–7.69 (m, 4H), 7.59 (s, 2H), 7.49–7.43 (m, 3H).

1,1′-Biphenyl (**3f**). White solid, mp: 70–71 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, J = 7.5 Hz, 4H), 7.44 (t, J = 7.5 Hz, 4H), 7.35 (t, J = 7.5 Hz, 2H).

3-Methoxybiphenyl (**3g**). Colorless oil; ^1H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, J = 7.0 Hz, 2H), 7.47 (t, J = 7.5 Hz, 2H), 7.41–7.37 (m, 2H), 7.22 (d, J = 8.0 Hz, 1H), 7.17 (t, J = 7.0 Hz, 1H), 6.94 (dd, J = 8.0, 2.5 Hz, 1H), 3.89 (s, 3H).

4-Methylbiphenyl (**3h**). White solid, mp: 47–48 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 7.57 (d, J = 7.5 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 7.5 Hz, 2H), 7.32 (t, J = 7.5 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H).

2-Methoxybiphenyl (**3i**). Colorless oil; ^1H NMR (500 MHz, $CDCl_3$): δ 7.59 (d, J = 8.0 Hz, 2H), 7.47 (t, J = 7.5 Hz, 2H), 7.39–7.36 (m, 3H), 7.09 (t, J = 7.5 Hz, 1H), 7.04 (d, J = 8.5 Hz, 1H), 3.86 (s, 3H).

4-Aminobiphenyl (**3j**). White solid, mp: 52–53 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 7.54–7.52 (m, 2H), 7.43–7.37 (m, 4H), 7.28–7.25 (m, 2H), 6.77–6.74 (m, 2H), 3.69 (brs, 2H).

4-Hydroxybiphenyl (**3k**). White solid, mp: 163–164 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 7.55 (d, J = 7.0 Hz, 2H), 7.49 (d, J = 9.0 Hz, 2H), 7.43 (t, J = 7.5 Hz, 2H), 7.31 (t, J = 7.5 Hz, 1H), 6.92 (d, J = 7.5 Hz, 2H), 4.90 (s, 1H).

4-Hydroxy-4′-methylbiphenyl (**3l**). White solid, mp: 150–152; ^1H NMR (500 MHz, $CDCl_3$): δ 7.48–7.43 (m, 4H), 7.23 (d, J = 8.0 Hz, 2H), 6.92–6.88 (m, 2H), 4.91 (s, 1H), 2.39 (s, 3H).

4-Cyano-4′-methylbiphenyl (**3m**). White solid, mp: 109–110; ^1H NMR (500 MHz, $CDCl_3$): δ 7.73–7.66 (m, 4H), 7.51–7.49 (m, 2H), 7.30 (d, J = 8.0 Hz, 2H), 2.42 (s, 3H).

4′-Methyl-3-biphenylcarboxaldehyde (**3n**). White solid; ^1H NMR (500 MHz, $CDCl_3$): δ 10.09 (s, 1H), 8.35 (s, 1H), 8.08 (d, J = 7.5 Hz, 1H), 7.84 (d, J = 7.5 Hz, 1H), 7.61–7.53 (m, 3H), 7.29 (d, J = 7.5 Hz, 2H), 2.42 (s, 3H).

4-Methoxy-4′-methylbiphenyl (**3o**). White solid, mp: 109–110 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 7.53 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.5 Hz, 2H), 3.87 (s, 3H), 2.41 (s, 3H).

1-(4′-Methoxybiphenyl-4-yl)ethanone (**3p**). White solid, mp: 154–155 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 8.01 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 8.5 Hz, 2H), 7.60 (d, J = 8.5 Hz, 2H), 7.02 (d, J = 8.5 Hz, 2H), 3.87 (s, 3H), 2.64 (s, 3H).

4-Chlorobiphenyl (**3q**). White solid, mp: 76–77 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, J = 7.5 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H), 7.46–7.40 (m, 4H), 7.36 (t, J = 7.5 Hz, 1H).

4-Chloro-4′-methylbiphenyl (**3r**). White solid, mp: 126–127 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 7.52–7.50 (m, 2H), 7.47–7.45 (m, 2H), 7.41–7.38 (m, 2H), 7.26 (d, J = 7.5 Hz, 2H), 2.40 (s, 3H).

4-Chloro-4′-nitrobiphenyl (**3s**). Pale yellow solid, mp: 144–145 °C; ^1H NMR (500 MHz, $CDCl_3$): δ 8.31 (d, J = 7.5 Hz, 2H), 7.71 (d, J = 7.5 Hz, 2H), 7.57 (d, J = 7.5 Hz, 2H), 7.48 (d, J = 7.5 Hz, 2H).

Conclusions

In conclusion, we have successfully prepared a novel MNP-supported nano-Pd catalyst *via* a "click" route. The obtained solid catalyst exhibits high activity towards the Suzuki–Miyaura coupling reactions without any added phosphine ligand under aerobic conditions. Furthermore, the catalyst could be simply recovered from the reaction system by magnetic separation and reused several times without a significant loss in activity.

The excellent catalytic performance and easy separation make this catalyst a promising alternative to other supported Pd catalysts.

Acknowledgements

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