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A highly controllable, effective, and recyclable magnetic-nanoparticle-supported palladium catalyst for the Suzuki–Miyaura cross-coupling reaction

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ABSTRACT

In this work, a highly efficient palladium catalyst was facilely immobilized on the surfaces of magnetic nanoparticles with the coordination of *N*-heterocyclic carbene. The prepared Pd–NHC@NCPs were characterized by transmission electron microscopy, Fourier transform infrared spectroscopy, energy dispersive spectroscopy, X-ray photoelectron spectroscopy, and inductively coupled plasma atomic emission spectrometry. With suitably designed emulsion polymerization and immobilization, the final palladium loading could reach 0.78 mmol/g. The catalyst showed outstanding catalytic performance in the Suzuki-Miyaura cross-coupling reaction among various substrates, with little catalyst usage (0.03 mol.%), short reaction time, and mild reaction conditions. In addition, the catalyst could be separated conveniently from the reacting system with an external magnet and show good catalytic performance even after being reused five times or more, indicating good recyclability.

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1. Introduction

Among different kinds of organic synthesis, the Suzuki–Miyaura cross-coupling reaction has received considerable attention due to its universality in industrial production and huge potential for synthesizing hundreds of intermediates and compounds [1–3]. To realize high operability and efficiency of the reaction, many transition metal catalysts and their complexes have been utilized in various systems [4]. N-heterocyclic carbene (NHC)–Pd complexes have become the most prospective choice, which exhibit a perfect combination of the catalytic activity of the noble metal and the low toxicity, strong σ -donation, high dissociation energy, and environmental stability of the *N*-heterocyclic carbine [5,6].

However, considering the price of and foreseeable pollution by the noble metal palladium, recycling the catalysts has become a significant issue [7]. The traditional homogeneous systems could hardly break through this limitation even by exploitation of complicated separation methods. As a result, numerous efforts have recently been put into the improvement of heterogeneous catalyst systems, including introducing various kinds of carriers, such as polyethylene glycol, polystyrene, MOFs, Al₂O₃, and SiO₂ [8–13]. However, there exists a contradiction between the size and

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separability of the carriers. Due to the larger specific surface, application of nanomaterial could result in larger anchoring site and lower steric hindrance than with bulky carriers. Nevertheless, nanodimension also brings about difficulties in separation. To handle such problems, magnetic nanoparticles, especially Fe_3O_4 , may provide a solution to fill the gap between homogeneity and heterogeneity [14–18]. This kind of nanoparticle is easy to separate with an external magnetic field due to its superparamagnetism, which is quite economical and time-saving compared with traditional separation methods such as centrifugation and filtration.

Recently, several works have focused on the preparation of NHC-Pd complexes immobilized on magnetic nanoparticles (Pd-NHC@NCPs) [19-25]. Laska [26] grafted the catalysis moiety onto the surface of the Fe₃O₄ nanoparticles directly. However, in this case, the agglomeration of magnetic nanoparticles happened easily, which resulted in poor stability and a decrease in catalyst activity after several cycles. Considering the instability of pure Fe₃O₄ nanoparticles, especially under oxidizing and acidic conditions [14], surface functionalization or encapsulation was paid attention as a way to realize reliable immobilization of NHC-Pd onto the surface of Fe₃O₄. In the existing literature, ways of functionalization can generally be summarized into two kinds. In one kind, magnetic nanoparticles were functionalized with silane group agents. Deng [25] successfully immobilized acenaphthoimidazolyildene palladacycle onto the surface of magnetic nanoparticles, with a long-chain triethoxysilyl tail. The palladium loading





JOURNAL OF CATALYSIS

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was around 0.01 mmol/g and the usage of catalyst in the reaction was around 0.5 mol.%. Wilczewska [22] utilized magnetic nanoparticles with aminosilane shells as carriers; NHC ligand precursor and palladium acetate were subsequently introduced onto the surface of the carrier. The palladium loading ratio reached 6 wt%. Nevertheless, in this research, complicated organic synthesis steps were common and the huge steric hindrance brought about by the functional group limited the regulation of palladium loading on each carrier, which led to a large dosage of the catalyst. In another kind of functionalization, magnetic nanoparticles were encapsulated with polymer shell. Liao [27] fabricated a networked metal-organic gel on the basis of PEG-modified magnetic nanoparticles, in which palladium was buried in the gel with organic ligands through self-assembly. In Suzuki-Miyaura cross-coupling, the catalyst amount was 1 mol.% Pd and the catalyst could be reused up to four times. However, the performance of the catalyst was hindered to some extent by the buried catalytic active sites. Yang and co-workers [28] immobilized palladium on magnetic nanoparticles that were coated with poly(undecylenic acid-co-N-i sopropylacrylamide-co-potassium 4-acryloxyoylpyridine-2,6-dicar boxylate). The yield of the following Suzuki reaction could reach 97% with 0.1 mol.% catalyst addition, but the reaction conditions and rate were not satisfactory. The same situation could also be found in Wang's work [23], where bulky NHC ligands were grafted to the surface of poly(DVB-co-VBC)@ Fe₃O₄. Although the catalysts were at the nanoscale, it still took 12 h to reach a high yield. A more effective way to prepare Pd-NHC@NCPs with controllable composition, structure, and catalytic efficiency at the same time is lacking.

In our previous work [29], our research group successfully developed an efficient and flexible method to get waterdispersed Fe₃O₄ nanoclusters with co-precipitation and micromixing, which was available to produce well-dispersed and wellmodified clusters of sizes ranging from 30 to 200 nm with decreased demand for surfactants. Screening the reaction conditions in a controlled and expanded window associated with these nanoclusters, in this work, we successfully prepared a protective polymer shell with evenly distributed functional sites via emulsion copolymerization for each nanocluster. Through the full and careful utilization of the nanoparticle surface, the capacity of the palladium was controllably improved and the catalyst addition in the following cross-coupling reaction was greatly decreased due to the controllable dispersion of the catalytic sites. With the prepared Pd-NHC@NCPs, the Suzuki-Miyaura reaction could be conducted with higher reactivity, milder conditions, and shorter reaction time. Moreover, thanks to the reliable chemical bonding, the inhibition of palladium leaching and excellent recovery of catalysts were as expected.

2. Experimental

2.1. Materials

Fe₃O₄ magnetic nanoparticles were prepared and dispersed following the procedure introduced in our previous work [29]. Polysorbate-80 (Tween 80, 98%), styrene (St, C₈H₈, >99%, stabilized with *p-tert*-butylcatechol), sodium hydroxide (NaOH, >96%), methyl alcohol (CH₃OH, 99.9%), and 4-nitrobromobenzene (C₆H₄-BrNO₂, 99%) were purchased from Sinopharm, China. Tetrahydrofuran (THF, C₄H₈O, >99.9%) was purchased from Fisher Chemical, USA. Divinylbenzene (DVB, C₁₀H₁₀, containing ethylvinylbenzene and diethylbenzene, stabilized with *p-tert*-butylcatechol), 2,2'-azo bis(2-methylpropionitrile) (AIBN, C₈H₁₂N₄, >99%), sodium dodecyl sulfate (SDS, C₁₂H₂₅SO₄Na, 99%), *N*-methylpyrolidone (C₅H₉NO, 99%), 1-methylimidazole (C₄H₆N₂, 99%), sodium carbonate (Na₂-CO₃, 99.5%), *N*, *N*-dimethylformamide (DMF, C₃H₇NO, 99.9%), potassium carbonate (K₂CO₃, 99%), isopropyl alcohol (*i*-PrOH, $C_{3}H_{8}O$, 99.9%), and dimethyl phthalate ($C_{10}H_{10}O_{4}$, 99%) were purchased from J&K Scientific, China. Ethanol (C₂H₆O, >99.8%) and 1-octane (C₈H₁₈, >99%) were purchased from Aladdin, China. 4-(Chloromethyl)styrene (VBC, C₉H₉Cl, 90%, stabilized with *p*-tertbutylcatechol), 4-bromotoluene (C7H7Br, 99%), 4-bromoanisole (C₇H₇BrO, 97%), *p*-bromoacetophenones (C₈H₈Br₂O, 98%). 4-nitrobromobenzene (C₆H₄BrNO₂, >99%), phenylboronic acid (C₆H₇BO₂, 99%), and bromobenzene (C₆H₅Br, 99%) were purchased from TCI, China. Hydrochloric acid (HCl, 37%) and concentrated nitric acid (HNO₃, 68%) were purchased from Tongguang Fine Chemicals Company, China. Palladium (II) acetate (Pd(OAc)₂, 99%) was purchased from 3A Chemical, China. 4-Methoxyphenylboronic acid (C₇H₉BO₃, 98%) and 4-tolylboronic acid (C₇H₉BO₂, 99.5%) were purchased from Amethyst Chemicals, China. Among all the reagents, St, DVB, and VBC were washed with 5% NaOH solution and deionized water three times, respectively, following by reduced pressure distillation. AIBN was recrystallized with ethanol twice. Water used throughout the experiment was prepared by an ultrapure water system (Center 120FV-S).

2.2. Characterization

The morphology of the immobilized NCP was observed with a transmission electron microscope (TEM, JEM2010, JEOL), with an energy-dispersive spectroscopy (EDS, HORIBA X-man^N) attachment to analyze elemental distribution. The composition of the particles was analyzed with Fourier transform infrared spectroscopy (FT-IR, Nexus670, Nicolet) with wavelengths ranging from 4000 cm^{-1} to 400 cm^{-1} ; samples were pressed to tablets with KBr before the measurement. The surface chemical properties were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250 Xi, Thermo Fisher Scientific Inc., USA), where AlKa radiation (72 W, 12 kV) at a pressure of 10^{-9} Torr was applied. The diameter of the analyzed area was 400 um. Inductively coupled plasma-atomic emission spectrometry (ICP-AES, iCAP6300, Thermo Fisher Scientific) was applied to measure the amount of immobilized palladium. The specific surface area of the sample was measured with a chemisorption analyzer in liquid nitrogen and calculated with the BET equation. X-ray powder diffraction (XRD) patterns were collected on an X-ray powder diffractometer (D8-Advance, Bruker) operating at 40 kV and 40 mA using CuK α radiation at a scanning rate of 5 min⁻¹. The yield of the Suzuki–Miyaura cross-coupling reaction was measured by gas chromatography (GC, Agilent Technologies, 8860) with an HP-5MS capillary column (5% phenyl, 95% methylpolysiloxane; 30 m \times 0.25 mm i.d. \times 0.25 μ m film thickness). The parameters of the gas chromatography were as follows: oven temperature was programmed to be maintained at 100 °C for 0.5 min, heated at a rate of 15 °C/min, and maintained at 250 °C for 10 min; inlet temperature, 280 °C; detector temperature, 280 °C; carrier gas, nitrogen, 1 mL/min; injection volume, 0.2 µL; split ratio: 100:1. An isopropanol solution of dibutyl phthalate (3.7 wt%) was used as an internal standard. Turnover number (TON) and turnover frequency (TOF) calculated through the results of GC were applied to evaluate the performance of the catalyst:

TON = mole number of the product/mole number of the catalyst (2.1)

$$TOF = TON/reaction time (h).$$
 (2-2)

2.3. Chloromethylation of magnetic polymer nanocomposite particles

As introduced in our previous work, the prepared modified Fe₃O₄ magnetic nanoparticles (100 mg) were dispersed in THF (10 mL) with Tween 80 (10 mg) and mixed with ultrapure water (40 mL) to prepare magnetic nanoclusters [29]. Then the dispersion was shifted into a three-necked flask with supplemental Tween 80 to reach a total amount of 40 mg of the surfactant. Another surfactant, SDS (2.2 mg), was added to the system to reach a mixing mole ratio of 4 to 1 between Tween 80 and SDS. Three kinds of monomers, St (250 µL), DVB (200 µL), and VBC (50 µL), were mixed with initiator AIBN (15 mg) to obtain a homogeneous oil phase. Then the mixture was added slowly into the solution containing nanoclusters, with stirring at a speed of 700 rpm. The mixture was stirred for 1 h to get a stable dispersion. Finally, the flask was put into a 60 °C water bath to initiate polymerization with stirring (400 rpm). This reaction was maintained for 5 h to obtain magnetic polymer nanocomposite particles. The product could easily be separated with an external magnetic field. After being washed three times each with water and ethanol, the product was dried for 12 h in a vacuum oven at 40 °C.

2.4. Preparation of 1-methylimidazole-mobilized nanocomposite particles-Cl (NHC@NCPs)

To realize successful immobilization, the above-prepared NCPs-Cl (150 mg) were mixed with 1-methylimidazole (0.45 mL) and *N*methyl pyrolidone (25 mL). The mixture was dispersed uniformly with ultrasonic and shifted into an 80 °C water bath with stirring (100 rpm) for 12 h. After the reaction, the product was washed three times with *N*-methylpyrolidone (20 mL), 0.1 M HCl solution (20 mL), and methyl alcohol (20 mL) in turn and finally dried for 12 h in a vacuum oven at 40 °C.

2.5. Preparation of palladium-mobilized NHC@NCPs (Pd-NHC@NCPs)

With ultrasound, the dried NHC@NCPs (100 mg) and Pd(OAc)₂ (22.5 mg) were uniformly dispersed into 2 mL DMF. Then Na₂CO₃ solution (2 mL, 53 mg/mL) was added into the system. The mixture was put under ultrasound at 0 °C for 30 min and shifted to a shaking bed with a temperature of 50 °C for another 2 h. The product was separated from the system with an external magnetic field. After being washed five times each with water (20 mL) and methyl alcohol (20 mL), the product was dried for 12 h in a vacuum oven at 40 °C. The general synthesis method for the Pd–NHC@NCPs is shown in Scheme 1.

2.6. General procedure for Suzuki–Miyaura cross-coupling reaction catalyzed by Pd–NHC@NCPs

A certain amount of prepared Pd–NHC@NCPs was mixed with 1 mmol aryl bromides, 1.2 mmol arylboronic acid, 2 mmol K_2CO_3 , and 4 mL solvent. The mixture was sealed in a 10-mL round-bottomed flask and put into a shaking bed to react at a constant temperature. After the reaction, the flask was shifted to an ice-water bath at 0 °C to terminate the reaction. The product was extracted with n-hexane, followed by weighing and analysis. To recycle the catalyst and avoid the loss of catalyst that remained on the oil–water interface, the hexane phase was first evaporated by nitrogen blowing. In this way, the catalyst could return to the water phase and be separated quickly with an external magnetic field. Then the separated catalyst was washed alternately with ethanol and ultrapure water five times each and put in a 40 °C vacuum oven for 12 h for recycling.



Scheme 1. Preparation of Pd-NHC complex immobilized magnetic polymer nanocomposite particles.

3. Results and discussion

3.1. Analysis of Pd-NHC@NCPs

During the chloromethylation, the functional monomer VBC, containing a chloromethyl group, was added into the emulsion polymerization system. After 5 h of co-polymerization, a brown latex was obtained, which could be separated completely from the reaction medium. Also, due to the precise addition of the surfactant, no pure polymer microspheres could be found in the clear water. As can be seen from Fig. 1a, the product NCPs possessed uniform morphology with a size around 60 nm and Fe₃O₄ nanoclusters were embedded in the center. XPS analysis confirm the existence of the elements of Cl, C, and O on the surface of the prepared NCPs-Cl, as shown in Fig. 2. FT-IR was utilized to analyze the production of each step during preparation of Pd-NHC@NCPs. From Fig. 3, with the comparison between 3a and 3b, the characteristic peak at 1265 cm⁻¹ in 3b also indicated the existence of the chloromethyl unit in the polymer by adding VBC. The chloromethyl unit was assumed to connect with NHC precursors through alkalization with *N*-imidazole, especially 1-methylimidazole in this work, which is the simplest and most universal *N*-imidazole. As shown in Fig. 3c, the peak at 1635 $\rm cm^{-1}$ was attributed to C=N in 1methylimidazole [30,31]. This proved that the NHC precursor had been successfully grafted onto the surface of the nanocomposite.

After the reaction between NHC@NCPs and Pd(OAc)₂, it could be seen from Fig. 1b that the final particles were almost the same size as NCPs-Cl, indicating that the immobilization did not make any difference in the morphology. Besides, in Fig. 3d, the characteristic peak assigned to C=N at 1635 cm^{-1} disappeared and the peak at 1685 cm⁻¹ might indicate the successful immobilization of palladium onto the surface of NHC@NCPs particles, which caused the shift. Similar evidence could also be found in the energy spectrum in Fig. 4, where an obvious peak of Pd could be found in Fig. 4b. Also, with the EDS elemental dot-mapping of the catalyst, it was clear that the distributions of Fe, O, and Pd were quite consistent and the outline of each distribution was similar to the morphology of the nanocomposite, which indicated the uniform distribution of Pd on the particle surface (see Fig. 5). Through the measurement of ICP-AES of the final catalyst, palladium loading was up to 0.78 mmol/g in Pd-NHC@NCPs, proving excellent loading efficiency of palladium on the nanoparticle. The loading efficiency was much higher than for catalysts using polystyrene resin as carrier [32,33]. Also, it offered conditions for flexible adjustment in palladium loading with different feed ratios. The adjustable loading was owing to the considerable specific surface area of the nanoscale carrier, which was analyzed to be 74.6 m^2/g with BET. Through the aforementioned characterization, by the method of emulsion polymerization and solid-phase synthesis, Pd-NHC@NCPs were successfully prepared with a high loading



Fig. 1. TEM images of (a) NCPs-Cl and (b) Pd-NHC@NCPs.



Fig. 2. XPS spectra of NCPs-Cl (a) full-spectrum scanning and (b) high solution scanning of chlorine.



Fig. 3. FT-IR spectra of the prepared (a) NCPs; (b) NCPs-Cl; (c) NHC@NCPs; (d) Pd-NHC@NCPs.

efficiency. For the traditional bulk resin carrier, the functional sites were always trapped in the network of the polymer, which brought huge challenges for the mass transfer of palladium ions and limited the loading ratio as a result. However, in this work, palladium was immobilized efficiently due to the finely designed and distributed functional sites on the surface.

3.2. Optimization of the reaction conditions

To optimize the solvents and bases in applying the prepared Pd-NHC@NCPs in Suzuki-Miyaura cross-coupling reaction, the most typical cross-coupling of bromobenzene and phenylboronic acid was utilized. As shown in Table 1, when *i*-PrOH or DMF was applied as the solvent, the yield of target product biphenyl could only reach 16% or 15% with 0.5 mol.% (mole ratio of the immobilized palladium to bromobenzene in the substrate) of the aforementioned catalyst, even when reacting under 70 °C for 12 h. However, when pure water was utilized as the solvent, rapid phase separation happened between the solvent and the other components, along with sedimentation of catalysts and substrates in the bottom. Due to the low polarity of bromobenzene, effective contact with the other reactants could not be guaranteed unless a polar organic solvent was introduced, whereas for the base K₂CO₃, only in water could it accelerate the reaction. Based on the above, mixed water and organic solvent would be the best choice of solvent. In entry 3, mixed solvents, DMF, and water were prepared with equal volume. Under this condition, with 0.5 mol.% catalyst, the yield of biphenyl could reach 99% after 6 h reaction under 70 °C. The yield decreased with decreasing temperature and reaction time, as shown in entry 4. In comparison, as shown in entries 5, 6, and 7, when ethanol and water were mixed with equal volume, the reaction was speeded up obviously. Even when the concentration of catalyst was cut down to 0.03 mol.%, the yield



Fig. 4. EDS energy spectra of (a) NCPs-Cl and (b) Pd-NHC@NCPs.



Fig. 5. TEM image of Pd-NHC@NCPs and its EDS elemental mappings.

of the product could still reach 93% in 5 min and 100% in 10 min, while without catalyst, the reaction could hardly proceed. In brief, equal volumes of ethanol and water were most appropriate for the prepared catalyst in our work. Under this condition, the cross-coupling reaction could be completed with little catalyst, mild reaction conditions, and an extremely short time.

3.3. Application of Pd-NHC@NCPs in different derivatives

Inspired by the outstanding catalytic activity of Pd–NHC@NCPs in cross-coupling reaction between bromobenzene and phenylboronic acid, Suzuki–Miyaura reactions among their derivatives were conducted under similar conditions. As shown in Table 2, the yield of all the reactions could exceed 92% within 30 min. When a strong electron-withdrawing group such as acetyl was connected to aryl bromide, the reaction could be accomplished swiftly in 10 min, with TOF of 2.000×10^4 (entry 14). Also, thanks to the nitro group in 4-nitrobromobenzene, which is a strong electron-withdrawing group, the yield could reach 94% in 10 min (entry 13). However, due to the low solubility of 4-nitrobromobenzene in the EtOH–H₂O mixture, the DMF–H₂O mixture was chosen as the solvent instead in order to attain sufficient interaction between the substrates in this entry. In contrast, when the electron-donating group was connected to aryl bromide, methyl or methoxy for instance (in entry 9 or 10), the reaction rate was relatively low due to the low activity of the substrates.

Table 1

Suzuki-Miyaura cross-coupling reaction of bromobenzene and phenylboronic acid under different reaction conditions:



Entry	Solvent	Temperature/°C	Time	Pd/mol.%ª	Yield/% ^b
1	<i>i</i> -PrOH	70	12 h	0.50	16
2	DMF	70	12 h	0.50	15
3	DMF/H ₂ O (1:1)	70	6 h	0.50	99
4	DMF/H ₂ O (1:1)	50	5 h	0.50	84
5	EtOH/H ₂ O (1:1)	50	2 min	0.03	52
6	EtOH/H ₂ O (1:1)	50	5 min	0.03	93
7	EtOH/H ₂ O (1:1)	50	10 min	0.03	100
8	EtOH/H ₂ O (1:1)	50	5 h	0	0

Note: Reaction conditions: bromobenzene (1 mmol), phenylboronic acid (1.2 mmol), K₂CO₃ base (2 mmol), solvent (4 mL).

^a The concentration of the catalyst was the mole ratio of the immobilized palladium to bromobenzene in the substrate.

^b The yield was calculated from gas chromatography.

Table 2

Suzuki-Miyaura cross-coupling reaction of derivatives of aryl bromides and arylboronic acid:

R_1 Br + $(HO)_2B$ R_2 R_1 R_2								
Entry	R ₁	R ₂	Time/min	Yield/%	TON	TOF		
7	Н	Н	10	100	3333	2.000×10^4		
9	4-CH ₃	Н	30	93	3100	6200		
10	4-OCH ₃	Н	30	98	3267	6534		
11	Н	4-CH ₃	30	95	3167	6334		
12	Н	4-OCH ₃	30	100	3333	6666		
13 ^a	4-NO ₂	Н	10	94	3133	1.880×10^4		
14	4-COCH ₃	Н	10	100	3333	2.000×10^4		

Notes: Reaction conditions: aryl bromide (1 mmol), arylboronic acids (1.2 mmol), K_2CO_3 base (2 mmol), solvent: EtOH:H₂O = 1:1 (volume) (4 mL) (except entry 13), temperature 50 °C. Concentration of the catalyst: 0.03 mol.% (mole ratio of catalyst to aryl bromide).

^a Solvent: DMF: $H_2O = 1:1$ (volume) (4 mL).

Nevertheless, a satisfactory yield could still be obtained when the reaction time was extended to 30 min. In conclusion, with the prepared Pd–NHC@NCPs as catalysts, Suzuki–Miyaura cross-coupling reactions of various derivatives of aryl bromides and arylboronic acids could be realized with high reaction rates and mild reaction conditions.

3.4. Recyclability of Pd-NHC@NCPs

Owing to the magnetic separability of Pd-NHC@NCPs, the catalysts could be separated from the reacting system with an external magnet after each reaction; reusing the catalysts became possible. To measure the recyclability of the aforementioned Pd-NHC@NCPs in this work, recycling experiments of cross-coupling reaction between bromobenzene and phenylboronic acid were conducted. As shown in Fig. 6, in the fifth cycle, the yield of biphenyl could still reach 92% within 10 min under 70 °C. However, a decline in the initial reaction rate could be found in each cycle. It seemed that with different cycles, it took longer to activate the reaction, although high yield could still be obtained within 10 min. Through ICP-AES measurement, it was observed that 83.2% of the palladium remained in the system. On one hand, due to the small catalyst usage, the trace loss during washing and separating might have a great influence. On the other hand, it could be found from the TEM that after recycling, a small quantity of palladium nanoparticles (4 nm in size) could be found in the view, as shown in Fig. 7b and 7c. The formation of palladium nanoparticles was further proved by X-ray diffraction and HRTEM. As shown in Fig. 8, the characteristic peak at $2 = 39.4^{\circ}$ of the XRD pattern and the lattice fringes with *d* spacing of 0.23 nm observed by HRTEM both corresponded to the (111) crystal plane of palladium nanoparticle. It has already been proved in Fig. 5 that palladium was distributed evenly on the surface of the nanocomposite in the form of complexes instead of nanoparticles. As for the difference in Fig. 7 before and after the recycling, it could be speculated that the partial palladium complex transformed into palladium nanoparticles during



Fig. 6. The yield and initial reaction rate of recycling the Suzuki–Miyaura crosscoupling reaction of bromobenzene and phenylboronic acid with prepared Pd– NHC@NCPs. Reaction conditions: aryl bromide (1 mmol), arylboronic acids (1.2 mmol), K_2CO_3 base (2 mmol), solvent: EtOH:H₂O = 1:1 (volume) (4 mL) (except entry 15), temperature 70 °C. Concentration of the catalyst: 0.03 mol.% (mole ratio of catalyst to aryl bromide)).



Fig. 7. TEM images of Pd-NHC@NCPs (a) before and (b, c) after five times recycling.



Fig. 8. (a) XRD spectra and (b) HRTEM image of Pd-NHC@NCPs after five times recycling.

recycling, which might weaken the catalytic activity to some extent. The *N*-imidazole, 1-methylimidazole in this work, despite its simplicity, could only provide limited steric hindrance and electronic effect, which could not maintain excellent catalytic activity in the long term. Such problems are expected to be solved by changing the NHC ligands into ones possessing large steric hindrance in our future research to combine stabilization with our advantages of controllable immobilization.

3.5. Comparison of the catalytic effect of Pd-NHC@NCPs

For the evaluation of the catalytic performance of the prepared Pd–NHC@NCPs catalyst in our work, a comparison among palladium catalysts in the Suzuki–Miyaura cross-coupling reaction between bromobenzene and phenylboronic acid in different works was carried out. From Table 3, it could be seen that the catalyst used in this work had excellent catalytic activity, whether compared with polymer or silane-based palladium catalysts. High yield could be obtained within minutes with a very small amount of catalyst even under mild reaction conditions. The outstanding performance could be attributed to the nanoparticle carriers, which possessed large specific surface area, uniform size distribution, and controllable functional sites on their surfaces, leading to controllable palladium immobilization. What is more, the surfactant Tween 80 was applied during the polymerization, which was usually supposed to provide more effective interaction among oilsoluble aryl halides, water-soluble arylboronic acids, and base, promoting the reaction to some extent.

Table 3

Comparison among palladium catalysts in the Suzuki-Miyaura cross-coupling reaction between bromobenzene and phenylboronic acid.

Catalyst	[Cat.] mol.%	Solvent	Temperature/°C	Time/h	Yield/%	TON	TOF	Ref.
Pd@PS-Met ^c	0.1	H ₂ O	80	4	96	960	240	[33]
NO ₂ -NHC-Pd@Fe ₃ O ₄ ^c	0.15	EtOH/H ₂ O (1:1)	50	1	95	633	633	[24]
NHC-Pd@ p-(DVB-co-VBC)Fe ₃ O ₄ ^a	0.02	EtOH/H ₂ O (3:1)	70	12	99	4950	412.5	[23]
NHC-Pd@silane-y-Fe ₂ O ₃ ^b	7.3	DMF	50	12	93	12.7	1.10	[19]
Pd@ IPr-Fe ₃ O ₄ ^c	0.16	i-PrOH	80	2	90	562.5	281.2	[21]
Pd@gel-Fe ₃ O ₄ ^c	1	MeOH	60	5	89	89	18	[27]
Pd–PUNP@Fe ₃ O ₄ ^c	0.1	H ₂ O	90	1	95	950	950	[28]
GO–NH ₂ –Pd ^c	1	EtOH/H ₂ O (2:1)	60	4	73	73	18	[34]
Pd–NHC@NCPs ^c	0.03	EtOH/H ₂ O (1:1)	50	10 min	100	3333	2.000×10^4	Present work

^a Suzuki-Miyaura cross-coupling reaction between 4'-bromoacetophenone and phenylboronic acid.

^b Suzuki-Miyaura cross-coupling reaction between 1-bromo-2-methylbenzene and phenylboronic acid.

^c Suzuki-Miyaura cross-coupling reaction between chlorobenzene and phenylboronic acid.

4. Conclusions

A kind of effective Pd-NHC@NCPs was successfully synthesized and was proved to possess outstanding performance in the Suzuki-Miyaura cross-coupling reaction. The methods were facile, including co-polymerization of the magnetic nanocomposite with the functional group chloromethyl on the surface, preparation of covalent compounds NHC@NCPs, and solid-phase coordination of palladium. Through characterization by TEM, FT-IR, XPS, EDS, and ICP-AES, it was proved that the Pd–NHC complex was covalently grafted to the surface of the nanoparticles, which had a surface area of 74.6 m²/g. The palladium loading could reach 0.78 mmol/ g with high loading efficiency, which was much higher than ever reported. Also, in the series of Suzuki-Miyaura cross-coupling reactions, the prepared catalysts showed excellent catalytic performance. Especially in the reaction between bromobenzene and phenylboronic acid, complete cross-coupling could happen only within 10 min, with 0.03 mol% Pd-NHC@NCPs and under 50 °C. After five times recycling, the catalytic activity remained high. All the phenomena proved the effective and controllable immobilization of palladium on the carrier, which gave high catalytic activity rivaling that of conventional homogeneous palladium catalysts and outstanding recyclability at the same time. In such circumstances, the consumption of the expensive palladium was avoided to the greatest extent, which will be promising in industrial production.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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