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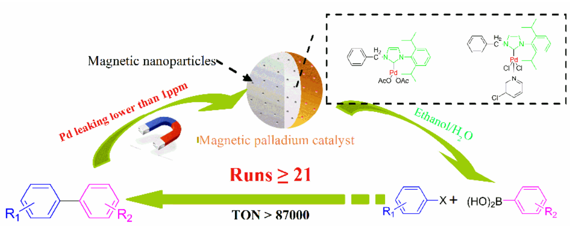
Graphical Abstract



The bulky NHC ligands were employed preparing magnetic palladium catalysts, which showed excellent activity, stability and reusability towards Suzuki-Miyaura reaction.

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ARTICLE

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Magnetically separable palladium catalyst containing a bulky N-heterocyclic carbene ligand for Suzuki-Miyaura reaction

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This work describes the preparation and characterization of a magnetic palladium catalyst with bulky N-heterocyclic carbene (NHC) ligand for Suzuki−Miyaura cross-coupling reaction. After the 1-(2,6-diisopropylphenyl)-1H-imidazole (1-Arylimidazole) was modified on the surface of magnetic polymer carriers, palladium diacetate was employed to synthesize the Pd-NHC complex, affording a palladium loading of 0.23 mmol/g. This magnetic catalyst showed a high catalytic activity towards Suzuki−Miyaura reaction of phenylboronic acids with aryl bromides in the ethanol/water solution (TON>87000). After 21 cycling runs, its catalytic activity decreased little and no leaking of palladium was found either in products or in reaction residue. When other sources of palladium ($PdCl_2$ and 3-Cl-pyridinyl) were employed to synthesize the palladium complex, the stability of the magnetic catalyst was greatly improved to perform the catalysis of Suzuki−Miyaura with aryl chlorides at 100 ℃.

Introduction

Palladium-catalyzed Suzuki–Miyaura cross-coupling reaction has been widely used in scientific research and industrial production during the past few decades. Although a large number of homogeneous catalysts showed excellent catalytic activity,[1-4] the homogeneous catalysis also suffers from the tedious separation of the expensive catalyst in order to low costs and avoid pollution.[5,6] Moreover, the utilization of recyclable catalysts is an inevitable trend with the development of green chemistry and engineering. Therefore, immobilization of palladium catalyst have attracted much attention and made great achievements.[7] However, most of those supported Pd catalysts have a lower activity in comparison with the similar homogeneous systems.

Series of carriers have been developed for immobilizing palladium catalyst, such as silica,[8-10] alumina,[11] microporous polymers,[12-16] carbon black,[17,18] dendrimers,[19,20] and polyoxometales.[21] It is known that the size of the carriers is one the most important factors which influence the catalytic activity of catalyst.[22] Large scale carriers benefit the separation and recycling processes, but catalytic efficiency was usually decreased due to its small special surface area in the heterogeneous reactions. However, nanoparticles, that make the catalyst much closer to the homogenous system resulting in high catalytic efficiency, are very difficult to be separated by conventional procedures like filtration or precipitation. Thus, some superparamagnetic nanoparticles were developed as the catalyst supports to bridge the gap between heterogeneous and homogeneous catalysis.[22] There are many benefits of these nano-magnetic carriers, for example, deposit-free, distribution in nanosized, easily magnetic separation, no metal leaking and non-toxicity, made it possible to integrate high catalytic activity and easy separation.[23-26] We have previously reported the preparation of some magnetic nano-spheres and micro-spheres and their applications in bioseperation and water purification.[27, 28] These magnetic carries exhibited high efficiency, strong specificity and easy recycling.

Since the palladium catalysts were used as the catalysts of Suzuki-Miyaura reaction, palladium complex and palladium nanoparticles have been widely researched and explored. Compared with palladium complex, the palladium nanoparticles become less stable and poorer selective due to its high activity, which just generated more byproducts in the reaction and easily became inactived in the process of storage and utilization. Thus, the tetrakis(triphenylphosphine)

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palladium(0) have been widely applied as the catalyst for Suzuki-Miyaura reaction in many fields. But this palladium complex is sensitive to air and moisture. Although much work has been carried to improve the stability of this ligand, the responding structure become more complicated and the synthetic process were tedious.[29-31] In contrast, the NHC ligands are more stable than the most electronrich phosphanes due to the stronger σ electron donation of its carbenes.[32] Therefore, NHC ligands have been applied in various catalytic reactions due to the nature of strong σ-donating ability and great steric effect.[33]

In recently years, Organ, Nolan and other researchers have done a great job on bulky nucleophilic carbine ligands.[32, 34-38] These studies suggest that some ligands including the structure of imidazol-2-ylidene with bulky substitutions showed much high stability and catalytic activity when they chelated with suitable palladium source to form responding palladium complex. However, few reports were found about the immobilization of these bulky NHCs. Thus, we were interested in the preparation of responding magnetic palladium catalyst to look at their catalytic activities.

In this contribution we showed the preparation procedures of the magnetic carriers with miniemulison polymerization and the synthesis of bulky NHC ligand of 1-(2,6-diisopropylphenyl)-1H-imidazole. Then, the NHC ligand was grafted on the surface of these magnetic carriers. Two diffident palladium sources were employed to coordinate the NHC ligand. Then, the catalytic properties of these magnetic catalysts for the Suzuki-Miyaura reaction were carefully investigated. The resulting magnetic catalysts are of prime interest due to its high catalytic activity, easy separation and good stability.

Expermental

Chemicals and Instruments

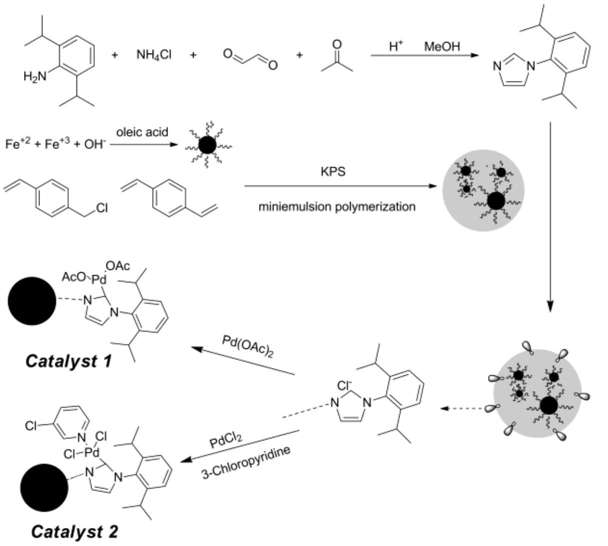
All the reagents and solvents were purchased from Sinopharm Chemical Reagent Co. Ltd and without any pretreatment. Reaction yields were analyzed by gas chromatography (GC, Agilent Tecnologies). The state of palladium was determined by X-ray diffractometer (XRD, Bruker). The size and morphology of magnetic nanoparticles were observed using transmission electron microscopy (TEM, HITACHI). Magnetic content of nanoparticles was analyzed by thermogravimetric analyser (TG, SHIMADZU). The magnetization measurements were performed at room temperature using a vibrating sample magnetometer (Mpms XL-7, Quantum Design). The ^{1}H NMR of the compounds were recorded on a 400MHz Bruker Avance spectrometer. Elementary analysis of dried samples was implemented by using vario EL III (elementar). Palladium amount on the carriers was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES, SHIMADZU). The BET analysis was performed on surface area analyzer (Quantachrome Instruments).

General Procedure for the preparation of magnetic palladium catalysts

Preparation of magnetic carriers: The modified magnetic nanoparticles were prepared to form a ferrofluid in cyclohexane with a magnetite content of 14 wt%.[39] A mixture of 14 mL ferrofluid and 0.3 g hexadecane was added into 24 g water containing 0.7 g sodium dodecyl sulphonate (SDS). After this mixture was stirred for 1 h, the sonication was performed for 10 min to form a ferrofluid miniemulsion. Another mixture of 2.4 g chloromethyl styrene, 0.6 g divinyl benzene and 0.12 g hexadecane was added into 12 g water containing 0.036 g SDS. Then, the monomer miniemulsion was prepared by sonication. After cyclohexane of the ferrofluid miniemulsion was carefully evaporated at 80 ℃, the monomer miniemulsion was added and co-sonicated for 10 minutes in an ice-cooled bath. Then, polymerization was proceeded at 80 ℃ for 24 h after adding potassium persulfate (KPS). The processes mentioned above were all performed with continuous stirring at 300 rpm.

Preparation of 1-Arylimidazole: 1-arylimidazolium was firstly prepared with 2,6-Diisopropylaniline (0.05 mmol) and 30% aq glyoxal in MeOH (20 mL). After a yellowish mixture appeared, NH$_4$Cl (5.35g, 0.1 mol) and 37% aq formaldehyde (8 mL, 0.1 mol) were added. The mixture was diluted with MeOH (200 mL) and the resulting mixture was refluxed for 1 h. Phosphoric acid (7 mL, 85%) was added over a period of 5 min. The resulting mixture was then stirred at reflux temperature for a further 8 h. Finally, the pure products were separated by careful chromatographic fractionation on silica gel (petroleum ether/EtOAc=3/1).[40]

Preparation of magnetic catalysts: To prepare the NHC-Pd complex, a mixture of achieved magnetic particles and 1-Arylimidazole (3 equiv) were stirred at 90 ℃ for 24 h in 100 mL toluene. After magnetic separation, the precipitate was washed by N,N-dimethylformamide (DMF) for several times and sufficiently dried. According to the nitrogen content from elementary analysis, the content of 1-(mesityl) imidazolium on the surface of these magnetic carriers reached 0.21 mmol/g. Then, these magnetic polymer carries and Pd(OAc)$_2$ (3equil) were stirred together in dimethyl sulfoxide (DMSO) at 50 ℃ for 12 h. The mixture was cooled to room temperature and magnetic separation was performed to obtain the magnetic palladium catalyst 1. The general preparation procedures of these magnetic palladium catalysts was showed in Scheme 1. To further stabilize the magnetic palladium catalysts, another palladium source (PdCl$_2$) was employed to prepare Catalyst 2. The magnetic supporter containing NHC ligand and PdCl$_2$ (3 equil) were added into 10 mL 3-chloropyridine. Then, this mixture was stirred at 100 ℃ for 12 h. After careful washing, the catalyst 2 was dried at 50 ℃ in vacuum oven for 24 h.



Scheme 1. The preparation procedures of magnetic palladium catalysts

General Procedure for the Suzuki-Miyaura reaction Catalyzed by the magnetic catalysts

The catalyst 1 was dispersed in 15 mL ethanol by sonication, then aryl bromides (2 mmol), phenylboronic acid (2.4 mmol) and K_2CO_3 (6 mmol) were added in. The reaction mixture stirred at 70 ℃ for 12 h. The catalyst was collected by magnetic separation and the products were extracted by chloroform. After the extract was completely dried, the samples were analyzed by GC and NMR.

The catalyst 2 and K_2CO_3 (3 mmol) were dispersed in DMF (10 mL) with the help of sonication. Then, aryl halide reagent (1 mmol) and arylboronic acid (2 mmol) were added in. After the mixture was subjected to sonication for 15min, it was stirred at 100 ℃ for 12 h. The catalyst was recovered by magnetic separation. After the solvent was removed, the products were dispersed in 15 mL chloroform and analyzed by GC as the same procedure above.

Result and discussion

Catalysts Preparation and Characterization

The miniemulison polymerization was employed to prepare magnetic carriers which was necessary for the sensitive magnetic response of the achieved polymer spheres. The size of the synthesized magnetic particles ranged from 42 to 125 nm with an average diameter of 97 nm based on TEM (Fig.1), and the catalyst particles were almost the same. The particle size distribution was so wide and some aggregations of magnetic spheres were observed due to the self-emulsifying behavior of chloromethyl styrene. It was also found that the magnetic response of these samples was so sensitive that one minute was enough to completely separate these magnetic particles by a handheld magnet. From the magnetization curve in Fig.2, the magnetic content of nanoparticles reached 38%. The saturation magnetization of magnetic nanopartilces reached as high as 19.3 emu/g. After the preparation of magnetic catalyst 1, its magnetic response was almost as same as the magnetic carriers. It meant that no leaking of magnetite particles occurred in the process of the immobilization of Pd-NHC complex. Furthermore, the catalyst could be easily and uniformly dispersed in solution again after the magnetic separation due to its superparamagnetism. It may act as a quasi homogeneous phase in the solvent, which greatly benefit to the catalytic activity of palladium complex.[41]

Depending on the functional group of chloromethyl of these magnetic carriers, 1-Arylimidazole could be easily modified on their surface. From the nitrogen content of these magnetic particles, which was measured by elementary analysis, about 0.21 mmol NHC ligand was grafted on each gram of magnetic carriers. After the palladium ion was been ligated on these NHC ligand, the content of palladium was determined to 0.23 mmol/g using ICP-AES, which was closed to the loading levels of 1-Arylimidazole on these magnetic carriers. Due to those two kinds of catalysts were synthesized with the same batch of modified magnetic nanoparticles, the palladium loading level of those two different catalysts was nearly the same (0.23 mmol/g, analyzed by ICP-AES). The related absorption isotherm was measured in Fig.2 and these data were much accord with the Langmuir equation. Thus, it meant that the monolayer of palladium ions was coordinated with these ligands on the surface of these magnetic carriers.

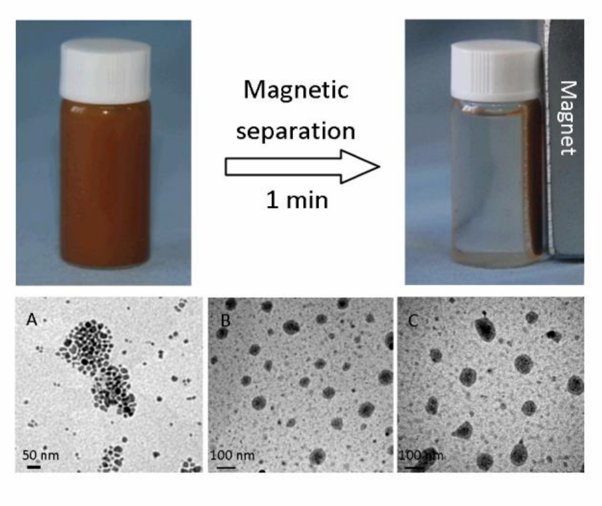


Fig. 1 The pictures of the magnetic separation and the TEM photos of magnetite nanoparticles (A) , the magnetic polymer carriers (B) and the catalyst 1(C).

In the process of the coordination between the immobilized NHC ligand and palladium ions, the formation of Pd nanoparticles was completely avoided, showed in Fig.3. It was found that the characteristic peaks of palladium nanoparticles were much evident when its content was only 0.02 mmol/g on the magnetic supporter. But, for palladium complex, there were no any characteristic peaks of palladium nanoparticles on its XRD pattern when its content reached 0.23 mmol/g. Therefore, the catalytic performances of these magnetic catalysts were mainly attributed to the palladium complex.

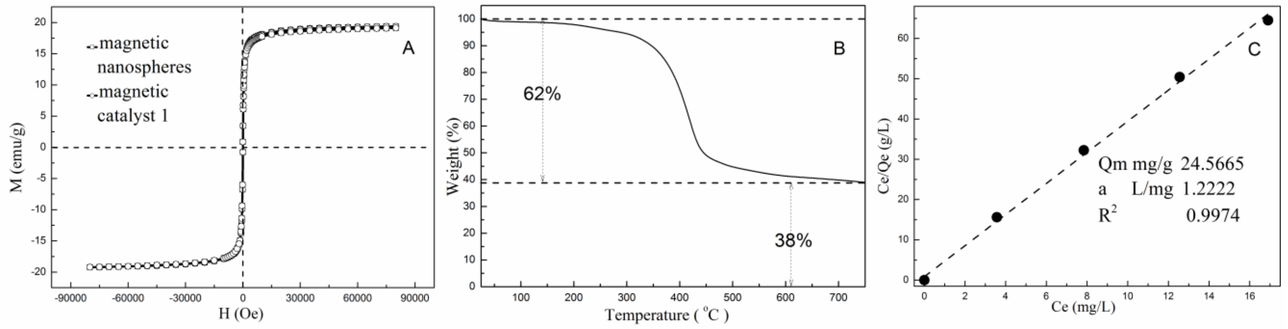


Fig.2 The VSM curves of magnetic particles and catalyst 1 (A); the TG curve of magnetic nanoparticles (B); and the adsorption isotherm of these magnetic carriers with palladium ions (C).

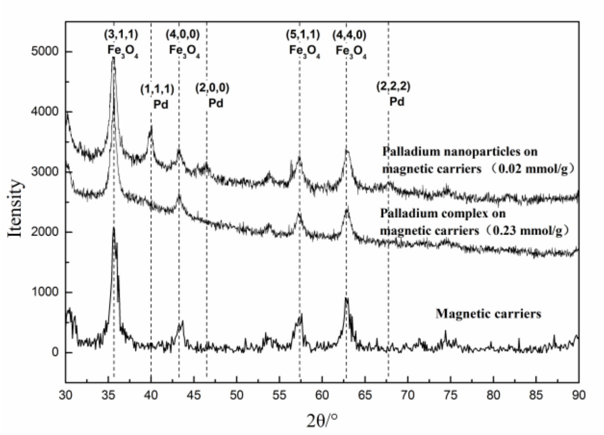
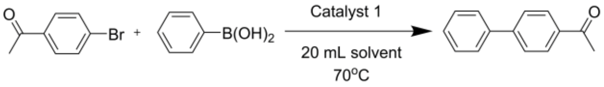


Fig.3 XRD patterns of the supported Pd nanopartilces and Pd complex.

Catalytic Properties of the magnetic palladium catalysts

High catalytic activity: The catalytic activity of catalyst 1 was firstly examined for its ability to catalyze the Suzuki-Miyaura reaction of phenylboronic acid with aryl bromides. In order to optimize the reaction conditions, different solvents and bases were used to confirm their effects in the Suzuki-Miyaura reaction of 4'-Bromoacetophenone (2 mmol) with phenylboroic acid (2.4 mmol). As shown in Table 1, a solution of ethanol /water (3:1) gave an excellent yield (99%) in the reaction at 70 ℃. Compared with this solvent, the aprotic solvents always resulted in lower yields. Different bases were investigated, as it shows in table 1.When K_2CO_3 was used as base, the catalyst can reach the highest yield (99%). However, the yields were slightly lower when stronger alkalis (NaOH or KOH) were used. The cesium carbonate and triethylamine were also employed, it was found that both of the yields were obviously low. It indicated that a suitable pH range was available to the catalysis of Suzuki-Miyaura reaction. Much high and very low alkalinity might decrease the catalytic efficiency of our magnetic catalysts. Therefore, based on the above experiments, the solution of Ethanol/water (3:1) and K_2CO_3 were usually employed in following experiments.

Table 1. Effect of solvent and bases on the Suzuki-Miyaura reaction

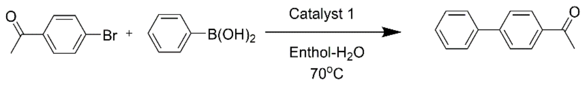


SOLVENT	Yield[a] Base: K_2CO_3	Base	Yield[b] Solvent:ethanol/H_2O =3:1
DMF/H_2O=1:1	50 %	K_2CO_3	99 %
DMF/H_2O=2:1	53 %	K_3PO_4	93 %
Dioxane/H_2O =1:1	81 %	KOH	92 %
THF/H_2O=1:1	76 %	NaOH	91 %
Toluene/H_2O =1:1	Trace	Na_2CO_3	97 %
Ethanol/H_2O =1:1	95 %	Cs_2CO_3	32 %
Ethanol/H_2O =3:1	99 %	Triethylamine	56 %

[a] aryl halide (2 mmol), phenylbonic acid (2.4 mmol), catalyst 1 (0.02 mol%) and K_2CO_3(3 mmol) were added into 20 mL solvent. The reaction temperature was set to 70 ℃, and the reaction time was 12 h. [b] aryl halide (2 mmol), phenylbonic acid (2.4 mmol), catalyst 1 (0.02 mol%) and base (3 mmol) were added into enthol/H_2O (3:1, 20 mL). the reaction temperature was set to 70 ℃, and the reaction time was also 12 h.
The mole fraction of palladium here means the moles of palladium atoms divided by the theoretical conversion moles of the reaction.

Although numerous researches have been carried out on Suzuki−Miyaura reaction with arylboronic acid reagents, high reaction temperature with a large amount (1−10 mol %) of catalyst were usually required.[42-45] Especially for some supported catalysts, the catalytic activity decreased greatly.[46-48] In table 2, it was found that the yield of the reaction reached 96 % with the presence of 0.02 mol% of palladium. Even 5 mol ppm (0.0005 mol% of Pd) palladium of catalyst 1 could also promote the catalysis(entry 3), which was unusual among the reported supported catalyst and even exceeded many homogeneous palladium catalyst.[49-51] Compared with the commercial heterogeneous palladium catalysts (EnCat TPP30 and NP30), in the presence of 0.15 mol% palladium, the yields were only 80% and 70%, respectively.[52] But, in Yamada's work, the responding TON values even reached 3570000 when a palladium atom was chelated with two polymeric imidazoles.[53, 54] This symmetrical structure might have great advantages on the catalytic activity of palladium complex. The similar work are still being carried out in our group.

Table 2. Comparison of the catalytic efficiencies for the magnetic catalyst 1

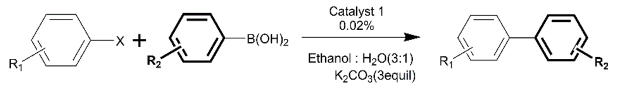


Entry	Pd (mol %)	Time (h)	Yield (%)	TON
1	2×10^{-2}	4	96	4800
2	1×10^{-3}	12	87	87000
3	5×10^{-4}	12	57	-

aryl halide (2 mmol), phenylbonic acid (2.4 mmol), catalyst 1 and K_2CO_3 (3 mmol) were added into enthol/H_2O (3:1, 20 mL). The reaction temperature was set to 70 ℃, and the reaction time was 12 h.

The adaptability of this magnetic catalyst was also investigated in table 3. Various aryl bromide with electron-donating or electron-withdrawing groups were employed. It was found that the electron-rich halides got lower yields compared with the electron-deficiency kinds although the oxidative addition is slower for aryl halides with electron-donating groups (entry 3-14).[55] Clearly, the Suzuki−Miyaura coupling of aryl bromides proceeded with high efficiently (yields >90%). However, the steric effect became more significant to hinder the reaction. When 2,6-Dimethylphenylboronic acid was used to react with bromobenzene, the yield decreased to 61% (entry 17).

Table 3. Comparison of the catalytic efficiencies for the magnetic catalyst 1 with various aryl bromides [a]



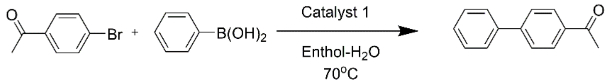
ENTRY	R_1	R_2	Yield (%)[b]	TON	Impurity content[c] (%)
1 [d]	p-$COCH_3$	H	91	4550	Trace
2 [e]	p-$COCH_3$	H	96	4800	Trace
3 [f]	p-$COCH_3$	H	99	4950	Trace
4	p-COH	H	95	4750	<0.1
5	p-OH	H	90	4500	0.3
6	p-OCH_3	H	97	4850	0.2
7	p-COOH	H	93	4650	0.3
8	H	p-CH_3	90	4500	-
9	H	Naph[g]	95	4750	-
10	p-CH_3	H	91	4550	0.2
11	p-CN	H	98	4900	0.3
12	o-CH_3	H	87	4350	0.3
13	p-NO_2	H	93	4650	<0.1
14	Naph[h]	H	95	4750	<0.1
15	H	2,6-Dimethyl	61	-	-

[a] aryl halide (2 mmol), phenylbonic acid (2.4 mmol), catalyst 1 (0.02 mol%) and K_2CO_3 (3 mmol) were added into enthol/H_2O (3:1, 20 mL). The reaction temperature was set to 70 ℃, and the reaction time was 12 h. [b] the reaction yield was determined by gc and hexadecane as internal standard [c] the purity was also determined by gc, which was calculated with the ratio of biphenyl/(biphenyl+product). [d] the temperature was 50 ℃ and reaction time was 4h. [e] the temperature was 70 ℃, and reaction time was 4h. [f] the reaction was performed under oxygen atmosphere. [g] the reaction substrate was 1-naphthaleneboronic acid. [h] the reaction substrate was 1-bromonaphthalene.

Byproduct was another important factor to evaluate the catalytic properties of the responding catalysts for Suzuki-Miyaura reaction because of the high requirements for its purity in the fields of pharmaceutical synthesis and functional materials. The homocoupling of phenylboronic acid have a strong impact on the purity of products because of the similar structure, which was difficult to be isolated. When some palladium nanoparticles were used as the catalyst, the yield of byproduct even exceeds 11%.[56] It was the reason why we prefer to use palladium complex rather than palladium nanoparticles as the catalytic center in our work. In table 3, it found that the yields of byproducts were no more than 0.3% when Suzuki-Miyaura reaction was catalyzed by this magnetic catalyst. This results are rather inspirational and the similar results were only found in Slaughter's work.[57]

Excellent Recyclability: The separation and reusability of noble metal catalyst is the trend of the catalysis industry along with the development of green chemistry not only for lowing the cost but also for avoiding the pollution. To gain insight into this issue, the recycling experiments were carried out. The results were shown in table 4 that the catalytic activity was nearly unchanged after 21 repeated runs. As we known, this result was relatively rare.[7] In each experiments, more than 99 wt% of this magnetic catalyst could be easily collected by a handhold NdFeB magnet (surface magnetization 0.3 T) after the reaction and washing. The magnetic separation is much easier, faster and cleaner compared with the conventional procedures just like filtration or precipitation.

Table 4. Recycling test of catalyst 1



Run	1	3	5	8	12	15	18	21
Yield(%)	96	97	99	99	93	98	96	97

aryl halide (2 mmol), phenylbonic acid (2.4 mmol), catalyst 1 (1 mol%) and K_2CO_3 (3 mmol) were added into enthol/H_2O (3:1, 20 mL). The reaction temperature was set to 70 ℃, and the reaction time was 12 h.

Another important advantage of this magnetic catalyst was that there was no Pd leaking. In Fig.4, the palladium concentration in the products was always lower than 0.1 ppm measured by ICP-AES (detection limit 5 ppb Pd). Even after 21 runs of the recycling, the palladium content of the catalyst changed little that more than 99.8% of palladium was still retained on the magnetic supporters (analyzed by ICP-AES). It meant, in this reaction, the palladium atom was completely immobilized by NHC ligand and the aryl bromides could not break the chelated structure of NHC ligand with palladium ions.

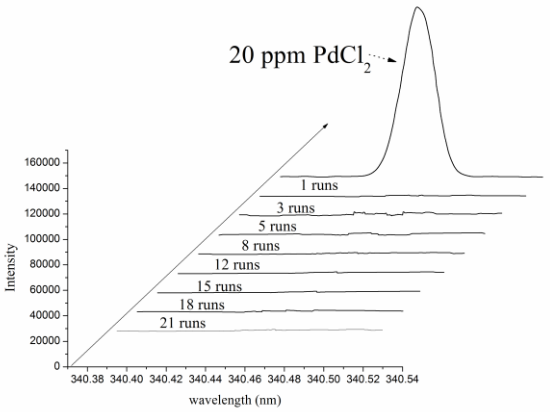


Fig.4 The Pd leaking of these magnetic catalyst 1 in process of its reusability.

The experiment of "hot filtration" was also carried out. After the coupling reaction of 1-bromo-4-methoxybenzene and phenylboronic acid proceeded for 1 h (with conversion at 73%), the magnetic catalysts was immediately separated under the hot conditions. Then, the reaction was continued for another 12 h. It was found that the finial conversion (73.8%) changed little. It meant that no palladium nanoparticles were leaked in the solution and the catalytic activity of the magnetic catalyst was mainly depended on the palladium complex. The reaction nature was the heterogeneous catalysis.

The palladium complex and palladium nanoparticles were easily converted into palladium black during the process of the catalysis resulting in the decrease of catalytic efficiency. Thus, the structure of magnetic catalyst was measured by XRD before and after use. The results were showed in Fig.5. It found that there were no any characteristic peaks of palladium particles, it is likely to prove that no palladium complex was reduced to palladium black during the reaction. This good stability might be attributable to the NHC-functionalized nanospheres, which could efficiently prevent the aggregation or agglomeration of palladium atoms through the spatial restrictions and electrostatic interactions with the NHC units on the magnetic spheres surface.

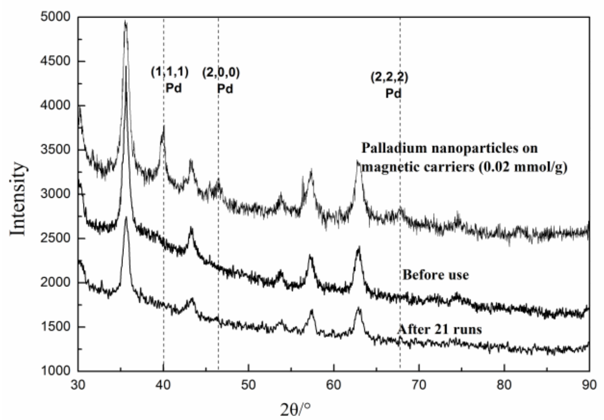


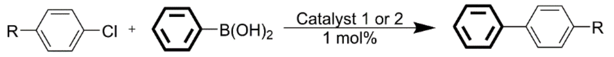
Fig.5 The XRD patterns of the magnetic catalyst before and after use

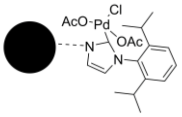
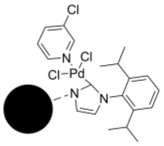
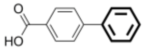
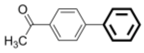
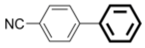
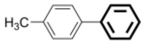
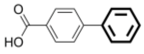
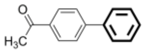
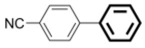
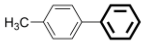
Because triphenyl phosphine palladium and palladium nanoparticles are usually sensitive to oxygen, the comparison of using oxygen and air as the reaction atmosphere was also performed. The result (entry 3 in table 3) indicated the catalytic activity of this magnetic catalyst had no evident difference in the different atmosphere. It meant that the palladium atom in this magnetic catalyst was not easily oxidized. It also found that the catalytic activity of this catalyst decreased little even after it was exposed to air for several days. In this aspect, the developed catalyst is stable enough for its application and storage.

The catalytic activity for Suzuki-Miyaura reaction of aryl chlorides and phenylboronic Acid

From a practical point of view, aryl chlorides become more attractive than aryl bromides as the substrates of Suzuki-Miyaura reaction because they are inexpensive and readily available.[25] But, the activation of C-Cl bond is more difficult compared with C-Br and C-I that harsher reaction conditions were usually required for the responding catalysis. It was found in table 3 that the activity of magnetic catalyst 1 decreased greatly when aryl chlorides were used. When the reaction temperature increased to 100 ℃, the reaction conversion was improved. However, the Pd leaking of catalyst 1 was drastically increased when aryl chlorides was introduced.

Table 5. Comparison of the catalytic efficiencies for the magnetic catalyst 1 and catalyst 2 with various aryl chlorides



		Catalyst 1		Catalyst 2	
					
ENTRY	Products	Yield	Pd leaking in product	Yield	Pd leaking in product
1^{A}		2 %	1 %	-	-
2^{A}		Trace	2.5 %	-	-
3^{A}		4 %	1.5 %	-	-
4^{A}		Trace	2 %	-	-
5^{B}		75 %	2.7 %	70 %	<1ppm
6^{B}		72 %	4 %	74 %	<1ppm
7^{B}		79 %	5 %	78 %	<1ppm
8^{B}		78 %	2 %	82 %	<1ppm

method a：1 mmol aryl chlorides and 1.2 mmol phenylboronic acid were selected as substrates, catalyst (1 mol%), solvent was 10 mL ethanol:H_2O (2:1), the base was K_2CO_3, reaction temperature was set to 70 ℃. method b: 1 mmol aryl chlorides and 2 mmol phenylboronic acid were selected as substrates, catalyst (1 mol%), solvent was 10 mL DMF, the base was K_2CO_3, reaction temperature was set to 100 ℃. ^{a}entry 1-4 used method a, others used method b, all of those reacted for 12 h.

In organ's work, they always used "throw-away" ligand to stabilize the responding homogeneous catalysts.[58] Therefore, a "throw-away" ligand (3-chloropyridine) was employed to stabilize the catalyst 1. The results were showed in table 5. It found that the palladium leaking of the magnetic catalyst 2 was completely avoided at 100 ℃. The conversion of this reaction could reach 82%.

From the results in table 5, it found that the aryl chlorides had a great impact on the stability of catalyst 1. At 70 ℃, the catalyst 1 could not activate the aryl chlorides resulting in the much lower reaction conversion. When the temperature was increased to 100 ℃, this catalyst could activate the C-Cl bond resulting in the enhancement of reaction conversion. However, the Pd leaking of catalyst 1 increased greatly when the reaction of aryl chlorides and phenylboronic acid was carried out at 100 ℃. According to the reaction mechanism of Suzuki-Miyaura reaction, it was believed that the aryl chlorides could coordinate with the palladium leading to the disintegration of chelated structure of NHC ligand with palladium in the step of oxidative addition. However, after the chelated structure of NHC ligand with palladium was further stabilized with 3-chloropyridine, the structure of catalyst 2 was stable enough to prevent the interference of aryl chlorides. Thus, no Pd leaking was found in the catalysis of catalyst 2.

Conclusions

In conclusion, we report and efficiently recoverable catalyst which combines the high catalytic activity of palladium complex for the Suzuki-Miyaura reaction with the sensitive magnetic separation of polymer magnetic carries. The high catalytic efficiency of this magnetic catalyst even exceeded some homogeneous catalysts. Furthermore, its excellent reusability brings great potential for this magnetic catalysts in some large scale applications. In particular, no palladium was leaked at the experimental conditions, which indicated the good stability of these magnetic catalysts.

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