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Pd-loaded superparamagnetic mesoporous NiFe$_2$O$_4$ as a highly active and magnetically separable catalyst for Suzuki and Heck reactions

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ABSTRACT

A superparamagnetic solid catalyst has been successfully synthesized by loading palladium nanoparticles into the pore network of a mesoporous NiFe$_2$O$_4$ support (Pd/NF300), which was used as a magnetically separable and highly active catalyst for Suzuki and Heck C–C coupling reactions. Various techniques were employed to characterize the synthesized NiFe$_2$O$_4$ supports and Pd-loaded catalysts. The Pd/NF300 catalyst showed high activity for both Suzuki and Heck reactions even under a very low Pd using amount (0.08 mol% Pd based on aryl halide). Moreover, the catalyst could be magnetically separated, recycled, and showed a very slight reduction in catalytic activity after five cycles. A synergetic catalytic effect between the well dispersed Pd^0 and the basic mesoporous structure of magnetic supports has been proposed to understand its greatly enhanced catalytic activities.

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1. Introduction

Suzuki and Heck coupling reactions catalyzed by palladium metal or palladium complexes have been well-established for the formation of C–C bonds due to their high tolerance against most solvents, high selectivity and moderate toxicity [1–6]. Much progress has been made by using various Pd complexes as homogeneous catalysts [7–9]. The catalytic properties of such Pd-based catalysts can be tuned by various ligands, such as phosphines [10], dibenzylideneacetone (dba) [11] and carbenes [12]. Carefully designed ligands would lead to catalysts with higher catalytic activities, prolonged lifetimes, and higher stability to the specific reactions. However, the relatively high costs of the palladium complexes, and the difficulties in removing the catalysts and separating the products continuously from the reaction systems, are the practical limitations to the industrial application of Pd-based homogeneous catalysts. Moreover, serious environmental and economic problems should also be addressed before their applications in industry [13]. In this regard, heterogeneous Pd-based catalysts will be a promising alternative to some of these problems, owing to their air-stability, recoverability, reusability and non-residual property [14]. Up to date, various solid supports, such as clays [15,16], carbon [17–19], zeo-

lites [20–22], mesoporous silica [23,24], and metal oxides [25,26], have been adopted for Pd-based heterogeneous catalysts, in which Pd complexes or nanoparticles are involved as active species. One fantastic design of monolith type material supports bearing both palladium nanoparticles and a hierarchical porosity that combines a macroporous structure (for good mass transport) with microporous domains (for large specific surface area) could be a significant improvement. Unfortunately, synthesis of these supports required multiple steps [27–30].

In recent years, magnetic materials have emerged as viable alternatives to conventional heterogeneous supports [31–36]. The magnetic separation technology offers many advantages over conventional filtration and other purification methods. For example, in the recycling process, the catalysts can be simply and efficiently recovered from reaction media with the external magnetic field. This can be considered as a green technology that avoids the consequences brought about by filtration steps. Magnetically separable Pd-based catalysts have been reported in recent years [37–40]. However, in most cases, specific functionalization procedures were inevitably needed to anchor the active Pd species onto the magnetic support surfaces. Due to the relatively low surface area of the magnetic supports ever reported [37–40], high Pd using amounts (about 1–10 mol% Pd based on aryl halide) were necessary to induce effective coupling when using these catalysts, which clearly made these particulate supports unattractive because of the high cost of Pd metal. In order to solve this problem, it is necessary to greatly

increase the active surface area of the catalyst. Mesoporous materials possess extraordinarily high surface areas, tunable pore sizes in nanoscale and well-defined pore size distributions, therefore they are the suitable supports to load noble metal nanoparticles of high active surface areas.

Recently, our group has developed a simple template-free strategy to prepare a high surface area superparamagnetic mesoporous spinel ferrite by controlled thermal decomposition of their metal oxalate precursors [41]. Herein, we report the successful loading of Pd^0 species onto this magnetic mesoporous material, which is used as a highly efficient, environmentally friendly, magnetically separable and reusable catalyst for Suzuki and Heck reactions. A synergistic catalytic reaction mechanism is discussed and proposed accounting for the extremely high catalytic activity.

2. Experimental details

2.1. Preparation of Pd^0/magnetic $NiFe_2O_4$

Mesoporous $NiFe_2O_4$-300 (NF300) and $NiFe_2O_4$-700 (NF700) were synthesized according to our earlier publication 41. A typical preparation procedure: 10 mmol $NiCl_2 \cdot 6H_2O$, 20 mmol $FeSO_4 \cdot 7H_2O$ and 5 mmol AOT were dissolved in 80 mL water at 80 °C in oil bath with stirring for at least 1 h; then 30 mL 1 M oxalic acid solution was slowly dropped into the former solution. Precipitates yielded during the process. The precipitated products were quickly cooled down by ice water, then separated by centrifugation, subsequently washed with deionized water and ethanol several times, and dried at 60 °C overnight. Mesoporous samples were obtained by calcining the precursor $NiFe_2(C_2O_4)_3 \cdot 6H_2O$ at 300 and 700 °C for 60 min, respectively. The heating rate during calcinations should be controlled to be as low as 1 °C min^{-1}.

Then 1 g of these materials were suspended in 100 mL of aqueous ammonium tetrachloropalladate (II) (0.07 g) solution and stirred at 25 °C for 12 h. The solid catalysts were collected by an external magnet, washed thoroughly with excess of deionized water and dried at 100 °C overnight. Then the catalysts (1 g) were reduced under flowing 5% H_2/Ar at 200 °C for 3 h to give air-stable black powder products. The temperature program: heating from room temperature to 200 °C at 1 °C min^{-1}, maintain the temperature for 3 h, then natural cooling to room temperature. The reducing gas was always on until the end.

2.2. Material characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max 2200PC diffractometer using Cu Kα radiation at 40 kV and 40 mA. The N_2 sorption measurements were performed using Micromeritics Tristar 3000 at 77 K for mesoporosity, and the mesoporous specific surface area and the pore size distribution were calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. Transmission electron microscopy (TEM) images were obtained on a JEOL-2010 electron microscope operated at 200 kV. A vibrating-sample magnetometer (PPMS Model 6000 Quantum Design, San Diego, USA) was used to study the magnetic properties. X-ray photoelectron spectroscopy (XPS) signals were collected on a VG Micro MK II instrument using monochromatic Mg Kα X-rays at 1253.6 eV operated at 200 W. The basicities of the supports were determined using the temperature-programmed desorption of carbon dioxide (CO_2-TPD) as follows. The supports (50 mg) were treated by heating at 450 °C under N_2 and then exposed to the probe gas stream at room temperature. Physically adsorbed CO_2 was removed by flushing N_2 at room temperature for 1 h. Then the TPD analysis was run under N_2 flow at a heating rate of 10 °C min^{-1} up to 500 °C and

the amount of CO_2 desorbed was detected by a gas chromatography.

2.3. Catalyzed Suzuki cross-coupling reactions

All reactants and solvents were used without further purification or drying. The reaction parameters (solvent, reaction time and base concentration) were investigated to find the optimal conditions, which were determined to be as follows. Typically, aryl halide (5 mmol), phenylboronic acid (7.5 mmol), potassium carbonate (5.5 mmol), 10 mL 1-methyl-2-pyrrolidinone (NMP), 4 mL H_2O and Pd-containing catalyst (0.004 mmol based on Pd, i.e., 0.08 mol% Pd based on aryl halide) were added to a 25 mL round-bottom flask equipped with a magnetic stirring bar. The reaction mixture was stirred at 80 °C for 1–12 h. After the reaction, the Pd-containing catalyst was separated with a magnet, washed with dichloromethane for removing the adsorbed organic substrates and dried at room temperature. The pure product was isolated and confirmed with gas chromatographic mass spectrometry (GC–MS) (Agilent, 6890N/5973N).

2.4. Catalyzed Heck coupling reactions

The optimal reaction parameters (solvent, reaction time and base concentration) for Heck reactions were also determined as follows. Typically, aryl halide (5 mmol), styrene (7.5 mmol), triethylamine (5.5 mmol), and Pd-containing catalyst (0.004 mmol Pd, i.e., 0.08 mol% Pd based on aryl halide) were added to a 25 mL round-bottom flask equipped with a magnetic stirring bar. 10 mL of N,N-dimethylformamide (DMF) were added and the reaction mixture was stirred at 80–140 °C. The separation and product isolation procedures were the same as that adopted for the Suzuki coupling reactions.

2.5. Recycling procedures

In the Suzuki recycling experiment, 4-bromoacetophenone (20 mmol), phenylboronic acid (30 mmol), potassium carbonate (22 mmol), 40 mL NMP, 16 mL H_2O and Pd catalyst (0.016 mmol) were added into the reactor and stirred at 80 °C. After 3 h, the reaction was completed. The catalyst was separated with a magnet and washed with dichloromethane several times. Then the catalyst was dried under vacuum and reused in the next run. For Heck recycling experiment, iodobenzene (20 mmol), styrene (30 mmol), triethylamine (22 mmol), 40 mL DMF and Pd catalyst (0.016 mmol) were added in the reactor and stirred at 80 °C for 4 h. Then the separation and following procedure were the same as those for Suzuki recycling reaction.

3. Results

3.1. Characterization of the supports and catalysts

Fig. 1 gives the CO_2-TPD spectra for NF300 and NF700 supports. Both of them show broadened desorption peaks at temperatures between 50 and 400 °C, which can be assigned to bicarbonates formed on Brønsted OH groups. The CO_2-TPD results suggest relatively weak basicity for both supports. Apparently, the desorption peak of NF300 is clearly located at a higher temperature (132 °C) than that (80 °C) of NF700, indicating that NF300 possesses relatively higher basic strength. On the other hand, the overall amount of CO_2 desorbed from NF300 is greatly larger than that of NF700, revealing its remarkably higher amount of basic sites/Brønsted OH groups per unit weight, which is due to its much higher surface area (301.6 m^2 g^{-1}) of NF300 than that (27.7 m^2 g^{-1}) of NF700.
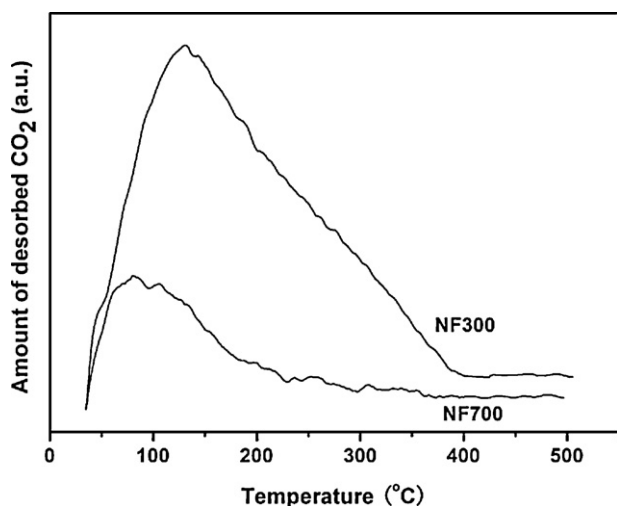
Fig. 1. Temperature-programmed desorption profiles of CO_2 on NF300 and NF700 samples by using the same amount (50 mg) of the samples.

Magnetic mesoporous NF300 sample was used as catalyst support in this study. As a contrast, the palladium particles were also loaded on NF700 as catalyst (Pd/NF700). As mentioned in Ref. [41], these two supports have the same composition. However, NF300 bears larger surface area, larger pore volume, smaller BJH pore size, lower crystallinity than NF700. Also, NF300 may have some residual organic groups, and higher amount of surface/lattice defects than NF700. Through wet impregnation with aqueous $(NH_4)_2PdCl_4$ solution and subsequent hydrogen reduction, both supports were successfully loaded with Pd^0, and the colors of two powders turned into black after Pd loading. The weight percentages of palladium loaded in NF300 and NF700 were found to be 2.1% and 1.0% by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis.

The TEM image of Pd/NF300 shown in Fig. 2a demonstrates that the Pd/NF300 material is still mesoporous after loading. No discrete large palladium particles can be found on support surface, and most of the palladium particles are believed to have been loaded within the pore channel due to the growth/agglomeration inhibition effect of the mesoporous frameworks of the support. Comparatively, we can find that part of palladium nanoparticles have agglomerated into bigger particles and dispersed onto the external surface of NF700 support (Fig. 2c). This may be resulted from lower surface area and pore volume of NF700, which cannot accommodate the large amount of palladium loading. After five repeated Heck reaction cycles (Fig. 2b and d), we did not observe significant change in the morphology of the catalysts, but some Pd particles might have aggregated onto the surfaces of the matrices. This may take place through the leaching/re-deposition processes during the catalytic reactions.
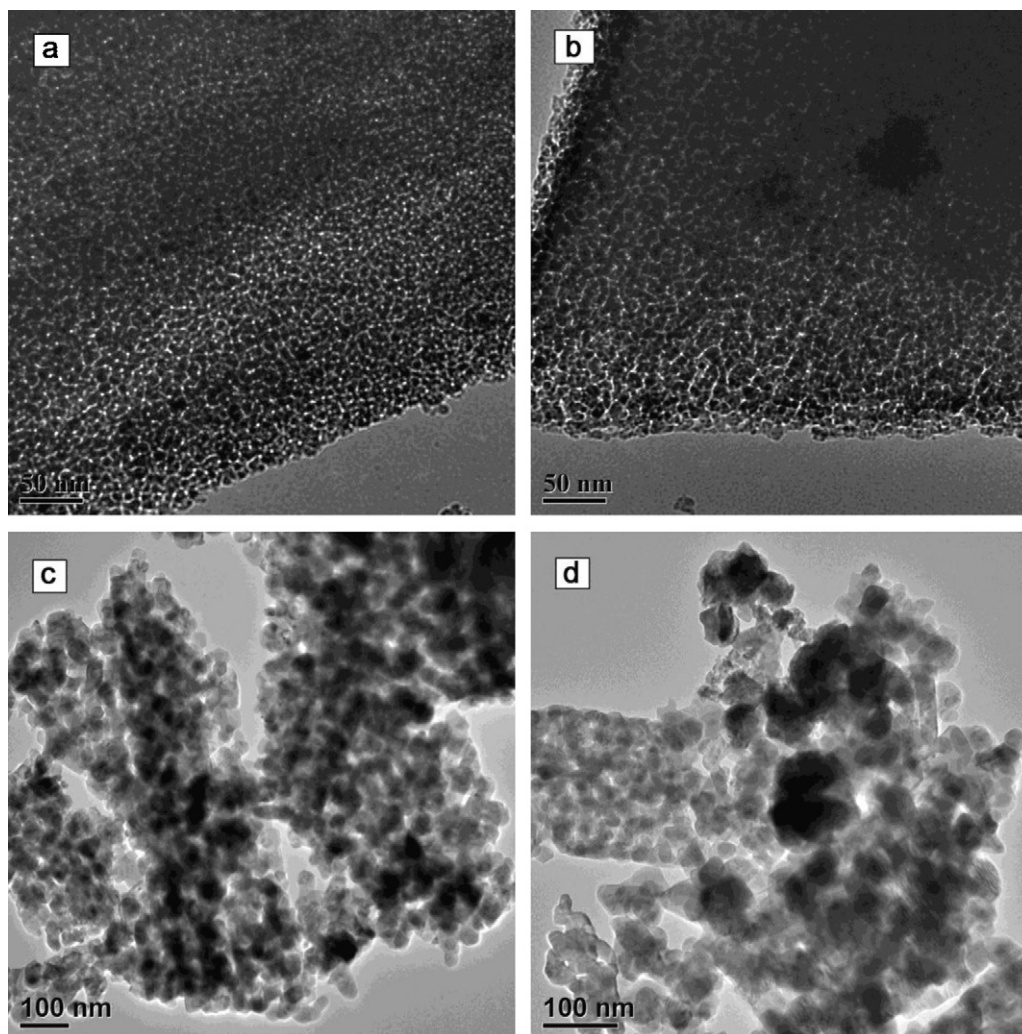

Fig. 2. TEM images of the Pd/NF300 (a and b) and Pd/NF700 (c and d) catalysts before reaction and after five cycles of Heck reactions.
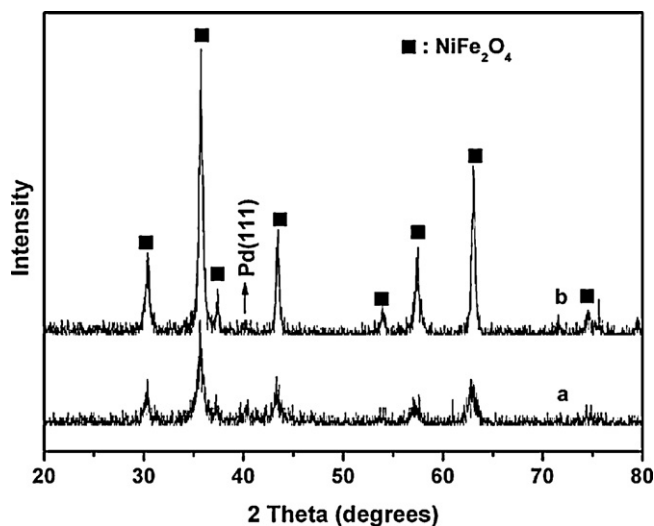
Fig. 3. XRD patterns of the catalysts Pd/NF300 (a), Pd/NF700 (b).

Fig. 5. Nitrogen adsorption–desorption isotherms and corresponding BJH desorption pore size distribution plots (inset) of the Pd/NF300 and Pd/NF700 catalysts.

The powder X-ray diffraction patterns of the Pd/NF300 and Pd/NF700 catalysts are shown in Fig. 3. The characteristic XRD peaks of the fcc crystal structure of metallic palladium ((2 0 0), (2 2 0) and (3 1 1)) cannot be clearly seen from the patterns because of the relatively low Pd content. But broadened (1 1 1) diffraction peaks still can be identified in both patterns. The diffraction peak at 39.86° indicates that Pd particles are in metallic state. Moreover, there were no Bragg reflections due to any crystalline PdO phase within the detection limit.

Furthermore, the materials were characterized by X-ray photoelectron spectroscopy to ascertain the oxidation state of Pd species. The XPS spectrum of the Pd/NF300 catalyst (see Fig. 4) show typical Pd^0 absorptions at 335.75 and 341.00 eV for $3d_{5/2}$ and $3d_{3/2}$, respectively, with a spin-orbit separation of 5.25 eV. No peaks for Pd^{2+} were observed. This absorption doublet typically seen in Pd^0 containing catalysts confirms that most of the Pd^{2+} ions have been reduced to Pd^0 by H_2, which are well dispersed in the pore network of the magnetic mesoporous support. The XPS spectrum of Pd/NF700 shows almost the same result.

After loading palladium particles, the Pd/NF300 catalyst still possesses mesoporous structure, as can be confirmed by the typical Langmuir IV type N_2 sorption isotherms (Fig. 5). However,
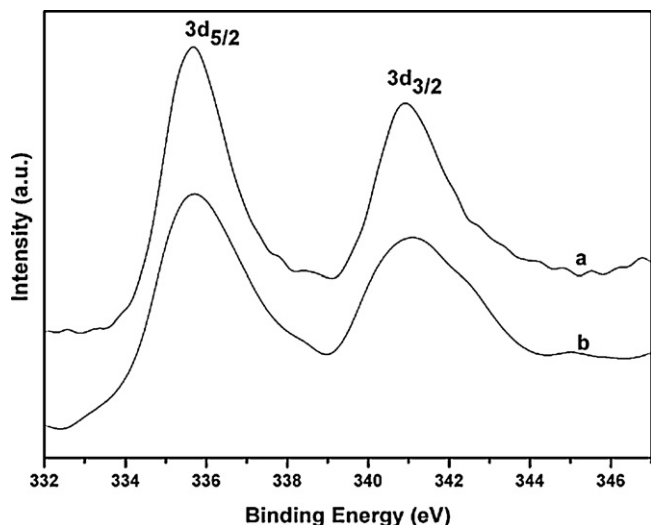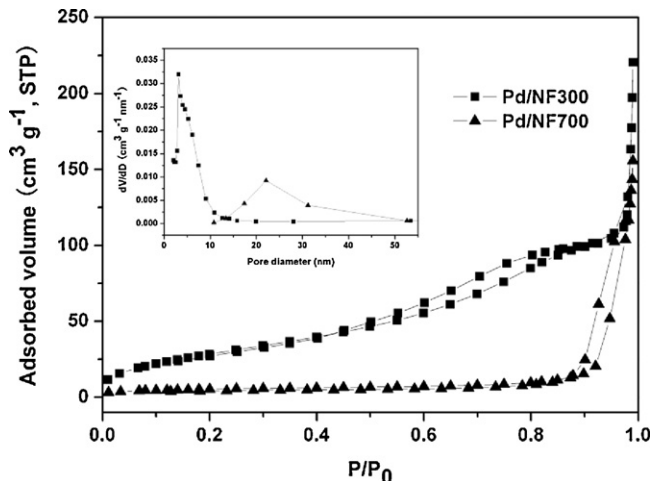
there is a significant decrease in the BET surface area of the material ($120.5\,m^2\,g^{-1}$) compared to the support without Pd loading ($301.6\,m^2\,g^{-1}$), due to the Pd deposition within the pore and/or on the surface, as expected. The Pd/NF300 catalyst has a sharp pore size distribution centered at 3.1 nm (Fig. 5 inset), which is a little larger than that of the support (centered at 2.5 nm). Such a larger average pore size might be caused by the filling of Pd nanoparticles in those mesopores which are smaller than, e.g., 2.5 nm. As far as known, it is the first report that Pd^0 was successfully loaded onto a single magnetic material which possesses mesoporous structure itself. When the Pd species were loaded on NF700, its surface area of Pd/NF700 decreased to $18.8\,m^2\,g^{-1}$ compared to that ($27.7\,m^2\,g^{-1}$) of the NF700 support. The Pd/NF700 sample shows a broadened pore size distribution centered at 22.1 nm.

The magnetization curves of the catalysts were measured at room temperature, as shown in Fig. 6. Neither of the curves reaches saturation point. The intensities of magnetization at 10 kOe for Pd/NF300 and Pd/NF700 are $3.92\,emu\,g^{-1}$ and $31.36\,emu\,g^{-1}$ respectively, which are a little lower than those of the corresponding supports ($4.00\,emu\,g^{-1}$ for NF300 and $32.08\,emu\,g^{-1}$ for NF700). This is mostly due to the Pd^0 loading on mesoporous $NiFe_2O_4$. For Pd/NF300, there is no apparent hysteresis detected, and the coercive force is as low as 25 Oe, suggesting a superparamagnetic feature of the catalyst. The magnetic properties of these
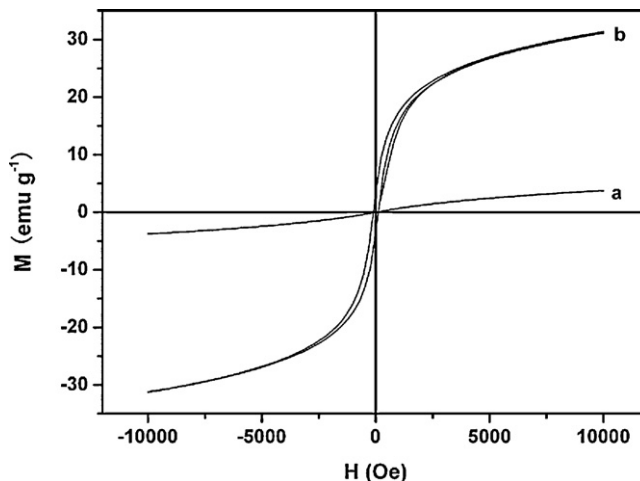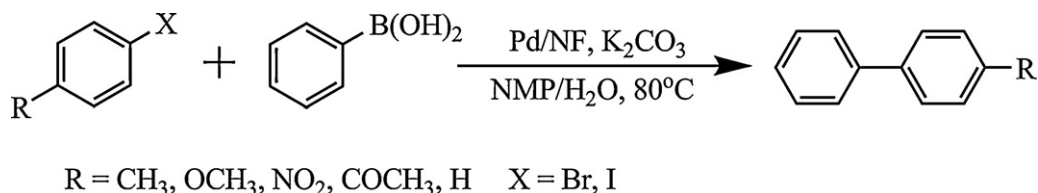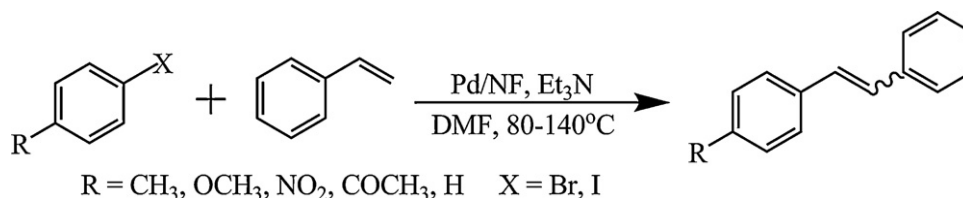

Fig. 4. XPS spectrums of the catalysts Pd/NF300 (a), Pd/NF700 (b).

Fig. 6. Magnetization curves of the Pd/NF300 (a), Pd/N700 (b) catalysts.

Scheme 1. Suzuki reaction of aryl halides and phenylboronic acid.

Scheme 2. Heck reaction of aryl halides and styrene.

catalysts are useful for their efficient recovery and recycling in liquid-phase reactions.

3.2. Catalytic activities

The catalytic activities of all the synthesized supports (NF300, NF700) and Pd-loaded catalysts (Pd/NF300, Pd/NF700) were tested for both Suzuki (Scheme 1) and Heck (Scheme 2) reactions. The results are summarized in Table 1. The reaction conditions, namely the use of various bases, additives, solvents and the ratio of the reacting components, were tested to make sure that the reactions were carried out under the optimized conditions (see Section 2). As a typical example for Suzuki reaction, bromobenzene was selected as a non-activated aryl halide. In general, non-activated aryl halides are less active than activated aryl halides. The reaction between iodobenzene and styrene was chosen as the typical Heck reaction. The influence of the solvent on catalytic activity was studied in the coupling of iodobenzene and styrene with catalyst Pd/NF300. The results are summarized in Table 2. Among all the solvents, DMF was the best solvent for this catalyst. NMP gave lower yields. The results obtained in the less polar solvents such as toluene, CH_3CN and THF, were not satisfactory.

The NF300 and NF700 supports themselves do not possess any catalytic activity for both Suzuki and Heck reactions as shown in Table 1. When Pd/NF700 was used as catalyst for the same two reactions, it shows lower catalytic activities. However, when Pd/NF300 was used as a catalyst, both Suzuki (bromobenzene with phenylboronic acid) and Heck (iodobenzene with styrene) reactions can

Table 1
Yield and reaction time of typical Suzuki and Heck reactions catalyzed by the mesoporous supports (NF300 and NF700) themselves and Pd-loaded catalysts (Pd/NF300 and Pd/NF700).

Entry	R	X	Catalyst	Yield (%)	Time (h)
1[a]	H	Br	NF300	0	12
2[a]	H	Br	NF700	0	12
3[a]	H	Br	Pd/NF300	97	12
4[a]	H	Br	Pd/NF700	13	12
5[b]	H	I	NF300	0	4
6[b]	H	I	NF700	0	4
7[b]	H	I	Pd/NF300	97	4
8[b]	H	I	Pd/NF700	9	4

[a] Suzuki reaction: bromobenzene = 5 mmol; phenylboronic acid = 7.5 mmol; K_2CO_3 = 10 mmol; NMP 10 mL, H_2O 4 mL; 0.08 mol% Pd; 80 °C. Yield = mol of product/mol of reactant converted.
[b] Heck reaction: iodobenzene = 5 mmol; styrene = 7.5 mmol; Et_3N = 5.5 mmol; DMF 10 mL; 0.08 mol% Pd; 80 °C. Yield = mol of product/mol of reactant converted.

Table 2
The influence of the solvent on catalytic activity for the coupling of iodobenzene and styrene with catalyst Pd/NF300.

Entry	Temp. (°C)	Solvent	Yield (%)
1	80	DMF	97
2	80	NMP	94
3	80	Toluene	21
4	80	CH_3CN	48
5	66	THF	0

Reaction conditions: iodobenzene = 5 mmol; styrene = 7.5 mmol; Et_3N = 5.5 mmol; solvent 10 mL; time = 4 h; 0.08 mol% Pd. Yield = mol of product/mol of reactant converted.

proceed at 80 °C with relatively high product yields under a low Pd using amount of 0.08 mol% based on aryl halide. These largely enhanced catalytic activities are believed to be resulted from the synergetic catalytic effect, which will be discussed later. So we choose Pd/NF300 as the appropriate catalyst for the other Suzuki and Heck reactions.

In further studies, Suzuki reactions of a wide range of other aryl halides with phenylboronic acid were conducted. The results are shown in Table 3. The Suzuki reaction of iodobenzene with phenylboronic acid could reach the complete conversion within 1 h. Various aryl bromides and chlorides were used in the reactions under the optimized conditions, and relatively high yields were obtained, though longer reaction periods were needed. Both electron-deficient and electron-rich substrates have coupled very efficiently under the catalysis.

The Pd/NF300 catalyst was also applied to catalyze Heck carbon–carbon coupling reactions of various aryl halides. The reactions were conveniently carried out in air at temperatures between 80 and 140 °C. Table 4 gives the catalytic reaction results. Aryl bromides and chlorides are difficult to be activated because of

Table 3
Suzuki reactions of various aryl halides with phenylboronic acid at 80 °C using Pd/NF300 as catalyst.

Entry	R	X	Yield (%)	Time (h)
1	CH_3	Br	95	12
2	OCH_3	Br	67	12
3	NO_2	Br	99	9
4	$COCH_3$	Br	100	3
5	H	I	100	1
6	H	Cl	19	24

Reaction conditions: aryl halide = 5 mmol; phenylboronic acid = 7.5 mmol; K_2CO_3 = 10 mmol; NMP 10 mL, H_2O 4 mL; 0.08 mol% Pd. Yield = mol of product/mol of reactant converted.

Table 4
Heck reactions of various aryl halides with styrene using Pd/NF300 as catalysts.

Entry	R	X	Yield (%)	Temp. (°C)	Time (h)
1	H	Br	41	140	24
2	CH_3	Br	30	140	24
3	OCH_3	Br	53	140	24
4	NO_2	Br	98	120	12
5	$COCH_3$	Br	96	120	12
6[a]	H	Cl	9	140	24

Reaction conditions: aryl halide = 5 mmol; styrene = 7.5 mmol; Et_3N = 5.5 mmol; DMF 10 mL; 0.08 mol% Pd. Yield = mol of product/mol of reactant converted.

[a] 0.4 mol% Pd was used, PPh_4Br was used as co-catalyst, the ratio of P/Pd is 10:1.

the relatively strong C–Br and C–Cl bonding. As a result, the coupling reactions of aryl bromides and chlorides with different olefins require higher reaction temperatures and prolonged reaction time.

The effect of electron-withdrawing substituents was observed in these two reactions. Aryl halides with electron-donating groups are less active than the ones with electron-withdrawing groups in the same para positions. The conversion rate of aryl bromide is dependent on the activation brought by the substitute in the para position, which is similar to homogeneous catalysts. Nevertheless, the Heck reactions of a variety of aryl bromides with styrene can still proceed to give the corresponding products in relatively high yields under the catalysis of Pd/NF300.

The catalytic activities of the heterogeneous magnetic catalysts reported in literature [37–40] and in this work, both for Suzuki reactions of bromobenzene with phenylboronic acid and Heck reactions of bromobenzene and iodobenzene with styrene, are compared. It is clear that the type of catalyst support plays an important role in determining the catalytic activity. Pd/NF300 reported in this work shows remarkably higher catalytic activity than the magnetic heterogeneous catalysts for Suzuki and Heck reactions ever reported.

3.3. Catalyst reusability

Another important issue concerning the application of a heterogeneous catalyst is its reusability and stability under reaction conditions. To gain insight into this issue, catalyst recycling experiments were carried out using a Suzuki reaction of 4-bromoacetophenone and phenylboronic acid, and a Heck reaction of iodobenzene and styrene. Before reuse, the magnetic catalyst can be easily and efficiently recovered from the reaction mixture with an external magnet, washed with dichloromethane and then dried. The results are shown in Table 5. The amounts of Pd leaching into solution for the Suzuki and Heck reactions were detected by checking the Pd loading amount before and after each reaction cycle through ICP. The loss of Pd amount for the Heck reaction were calculated to be: 1.5 wt.%, 1.1 wt.%, 2.0 wt.%, 0.9 wt.%, 1.3 wt.% of total Pd content for each run, respectively. Even though a small amount of Pd loss could be detected, the catalyst still showed relatively high

Table 5
Recycling performance of the Pd/NF300 catalyst.

Run	Suzuki reaction[a]			Heck reaction[b]		
	Yield	TON	TOF	Yield	TON	TOF
1st	100	1250	417	97	1212	303
2nd	99	1237	413	95	1204	301
3rd	100	1237	413	95	1204	301
4th	99	1225	408	93	1203	301
5th	99	1223	408	94	1202	300

[a] Reaction conditions: $4-BrPhCOCH_3$, $PhB(OH)_2$, K_2CO_3, NMP + H_2O, 0.08 mol% Pd, T = 80 °C and t = 3 h.
[b] Reaction conditions: PhI, styrene, Et_3N, DMF, 0.08 mol% Pd, T = 80 °C and t = 4 h.

reusability and stabilities for both the Suzuki and Heck reactions. Especially for the Suzuki reaction, almost no deactivation can be found even after five cycles.

4. Discussion

The postulated mechanisms for homogeneous Suzuki and Heck reactions catalyzed by Pd species have been well described in many organic chemistry textbooks. But for heterogeneous reactions, mechanisms are not yet fully understood and findings in this field are sometimes contradictory. Some authors insisted that the reactions take place at the surface of solid Pd as truly heterogeneous reactions [42,43]. On the other side, a variety of experimental results clearly demonstrated that the leached palladium from the solid support was the real active species serving as the homogeneous catalyst for Suzuki and Heck reactions [44]. In the present study, we have actually observed the presence of Pd leaching in our experiments. No matter which mechanism prove to be true, the initial oxidative addition step, which has been considered to be rate-determining [45], would always take place at the surface of solid Pd.

The enhanced catalytic activity of Pd/NF300 may be ascribed to a synergetic catalytic effect between the highly dispersed Pd nanoparticles and basic mesoporous $NiFe_2O_4$ support, as discussed in the following section.

The surface area of the catalyst will surely affect the catalytic activity. Homogeneous loading of Pd nanoparticles in the pore network is greatly helpful to achieve a high Pd^0 dispersion. As the activity of the catalysts mainly depends on the property and concentration of the active palladium species, the increased Pd^0 dispersivity would lead to the greatly increased concentration of active species in the reaction system, and consequently the enhanced catalytic activity. Therefore the catalyst activity was greatly enhanced with the Pd catalyst highly dispersed in/on high surface area mesoporous materials.

On the other hand, the CO_2-TPD result shows that the mesoporous $NiFe_2O_4$ supports possess a certain degree of basicity, especially for NF300 with higher specific surface area. This implies that there exists a considerable amount of Brønsted basic sites on the pore surface of mesoporous materials. Some authors proposed that for Heck and Suzuki reactions, palladium on basic supports may exhibit an increased activity compared to that of acidic supports, depending on the basicity of the supports [26,46]. The higher basicity of the support would lead to higher electronic density on the palladium surface, which, in turn, facilitates the oxidative addition. Therefore it is inferred that the basic supports in the present study should act as an electron donor for palladium, resulting in higher electronic density on the palladium surface and subsequently promoting the oxidative addition, as illustrated in Scheme 3, while acidic supports act as an electron acceptor [47]. In a homogeneous catalytic mechanism, the formation of the intermediates $ArPd^{II}X$ in the reaction solutions will promote the following reactions between the intermediates and phenylboronic acid for Suzuki reaction or styrene for Heck reaction, giving the final reaction products. As the oxidative addition step is the rate-determining step [45], therefore the basic support plays an important synergistic role in accelerating the catalytic reactions through promoting the formation of intermediate active species of $ArPd^{II}X$.

In a word, the basicity of the support surface, together with its large surface area, synergistically promote the oxidative addition of the aryl halide on palladium atoms, through the electron donating effect from the palladium surface with the assistance of the basic support, whichever mechanism, homogeneous catalysis or true heterogeneous catalysis, proved to be true.
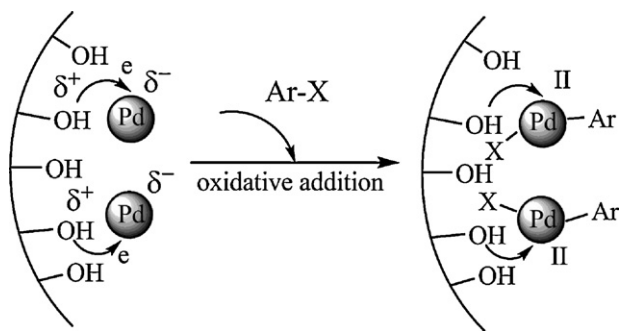
Scheme 3. Schematic drawings of the synergetic catalytic effect between the highly dispersed Pd^0 and surface basicity of the mesoporous support for the C–C coupling reactions: the oxidative addition step, which has been recognized as the rate-determining step [45], is promoted by the electron donating effect of basic support surface and the high dispersion of Pd^0 in the pore network of the mesoporous support.

5. Conclusions

In conclusion, magnetically separable palladium-loaded mesoporous NiFe$_2$O$_4$ catalysts (Pd/NF300 and Pd/NF700) have been successfully prepared. Compared to other magnetic Pd-loaded catalysts reported previously in literature, Pd/NF300 shows greatly enhanced catalytic activities for both Suzuki and Heck reactions in air using various aryl halides as reactants, under a very low Pd using amount of 0.08 mol% based on aryl halide. Superparamagnetic Mesoporous NF300 has been found to be a distinguished support possessing apparent basicity and well-defined mesoporous structure for high Pd dispersion, synergistically accelerating the catalytic reactions through promoting the oxidative addition step. All these properties lead to an excellent catalyst Pd/NF300 with high catalytic activity towards Suzuki and Heck reactions, excellent reusability and magnetic separability.

Acknowledgments

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