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Betti base-modified magnetic nanoparticles as a novel basic nanocatalyst in Knoevenagel condensation and its related palladium nanocatalyst in Suzuki coupling reactions

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Betti base-modified Fe_3O_4 nanoparticles have been successfully designed and synthesized for the first time through the condensation of Fe_3O_4 magnetic nanoparticles coated by (3-aminopropyl)triethoxysilane with β-naphthol and benzaldehyde. Their application as a novel magnetic nanocatalyst in the Knoevenagel condensation and also application to immobilization of palladium nanoparticles for Suzuki coupling reactions have been investigated which opens a new field for application of Betti base derivatives in organic transformations. The synthesized inorganic–organic hybrid nanocatalyst has fully been characterized using Fourier transform infrared, X-ray diffraction, vibrating sample magnetometry, transmission and scanning electron microscopies, energy-dispersive X-ray, wavelength-dispersive X-ray and X-ray photoelectron spectroscopies and inductively coupled plasma techniques. The catalyst was easily separated with the assistance of an external magnet from the reaction mixture and reused for several consecutive runs with no significant loss of its catalytic efficiency. Copyright © 2016 John Wiley & Sons, Ltd.

Keywords: betti base; organocatalyst; magnetic; palladium; nanoparticles; Knoevenagel; Suzuki

Introduction

Nanoscale palladium particles make them attractive in catalysis due to their large surface area. Several palladium nanoparticles (NPs) as catalysts for carbon–carbon coupling reactions such as the Suzuki–Miyaura reaction have been reported.[1–3] Palladium-catalysed cross-coupling reactions of organo-halides with olefins (Heck) and organo-boronic acids (Suzuki) for carbon–carbon bond formation are extremely useful to the chemical industry and in research. Since their discovery they have evolved into a general technique in preparing biologically active functionalized biphenyls which are important intermediates or products in drug discovery, pharmaceuticals and agricultural compounds.[4,5] Historically, palladium complexes such as $[Pd(OAc)_2]$ and $[Pd(PPh_3)_2Cl_2]$ have been widely used as homogeneous catalyst systems in cross-coupling reactions.[4] Among various palladium catalysts for the Suzuki–Miyaura coupling reaction, homogeneous catalysts have been widely investigated, while less expensive heterogeneous catalysts have received scanter attention. Homogeneous palladium catalysts are not used in industrial application due to the difficulty in separating and recycling, low catalytic efficiency and the high leaching of metal species. In order to solve the problem, new strategies should be developed.[6–9]

In recent decades, as an important family of separation materials, magnetic Fe_3O_4 NPs have attracted considerable attention in chemistry and material sciences, due to their potential applications in catalysis and biomedicine.[10] The immobilization of homogeneous catalysts on solid supports opens up new avenues for design and engineering of new and stimulating catalysts. These structures are easily separable from a reaction mixture, allowing the recovery of the solid and eventually its reuse. The highest level of evolution in the surface immobilization strategy is the covalent attachment of an organic compound or ligand to the solid surface.[11]

Betti base (1-α-aminobenzyl-2-naphthol), easily prepared via modified Mannich reaction from 2-naphthol, benzaldehyde and ammonia, contains two potentially reactive functional groups (amino and hydroxyl) and two rigid rings (phenyl and naphthyl), which might manifest good activity in chemical transformation after functionalization with other groups. Betti base and its derivatives have been known since the beginning of the twentieth century[12]; however, further research into their applications has remained unreported for some time. Only in recent decades has there been an increasing focus on the application of Betti base in asymmetric reactions due to the functional groups and chiral centre. Many authors have already reported the use of Betti base derivatives as chiral catalysts in asymmetric addition of Et_2Zn to aldehydes[13] and the asymmetric allylic alkylation reaction.[14] Nevertheless, upon searching the literature, no example dealing with Betti base supported on magnetic NPs was found, which encouraged us to design and support Betti base on the surface of Fe_3O_4 NPs and to investigate their application as a novel magnetic base nanocatalyst and also their ability to immobilize palladium NPs as a magnetic palladium nanocatalyst in Suzuki coupling reactions.

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Experimental

Preparation of Magnetic Fe_3O_4 NPs

Naked Fe_3O_4 NPs were prepared by chemical co-precipitation of Fe^{3+} and Fe^{2+} ions with a molar ratio of 2:1. Typically, $FeCl_3{\cdot}6H_2O$ (5.838 g, 0.0216 mol) and $FeCl_2{\cdot}4H_2O$ (2.147 g, 0.0108 mol) were dissolved in 100 ml of deionized water at 85 °C under nitrogen atmosphere and vigorous mechanical stirring (500 rpm). Then, 10 ml of 25% NH_4OH was quickly injected into the reaction mixture in one portion. The addition of the base to the Fe^{2+}/Fe^{3+} salt solution resulted in the immediate formation of a black precipitate of magnetic NPs. The reaction continued for another 25 min and the mixture was cooled to room temperature. Subsequently, the resultant ultrafine magnetic particles were treated by magnetic separation and washed several times with deionized water.

Preparation of Fe_3O_4/Pr-NH_2

The obtained magnetic NP powder (500 mg) was dispersed in 50 ml of toluene solution by sonication for 20 min, and then 3-aminopropyltriethoxysilane (APTES; 5 mmol) was added to the mixture. The mixture was refluxed under argon atmosphere at 100 °C for 48 h. The product was separated by filtration, washed with ethanol and dried under vacuum for 24 h at 50 °C. The precipitated product (Fe_3O_4/Pr-NH_2) was dried at room temperature under vacuum.

Preparation of Fe_3O_4/Betti Base/Pd(0)

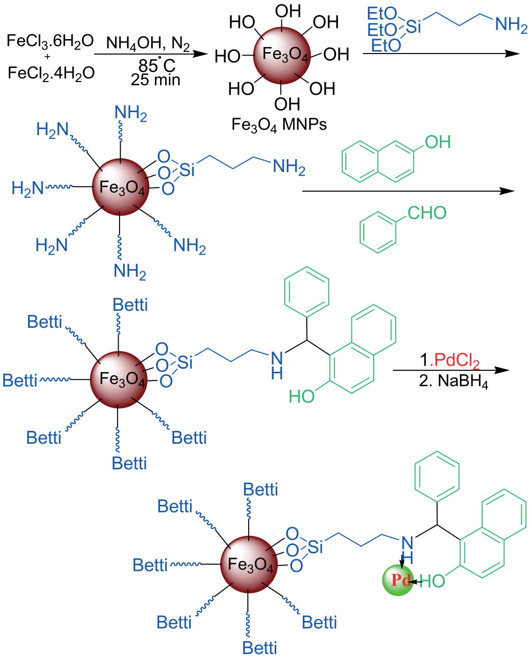
The obtained Fe_3O_4/Pr-NH_2 nanoparticles (500 mg) were dispersed in 70 ml of ethanol by sonication for 20 min, and then β-naphthol (1 mmol) and benzaldehyde (1 mmol) were added to the reaction mixture. The reaction mixture was stirred under nitrogen atmosphere at 80 °C for 24 h. Then, the reaction mixture was cooled to room temperature, and the resulting NPs were washed with ethanol several times and separated using magnetic decantation and dried at room temperature.

Then, the Fe_3O_4/Betti base (500 mg) was dispersed in CH_3CN (30 ml) in an ultrasonic bath for 30 min. Subsequently, a yellow solution of $PdCl_2$ (30 mg) in 30 ml of acetonitrile was added to the dispersion of Fe_3O_4/Betti base and the mixture was stirred for 10 h at 25 °C. Then, the Fe_3O_4/Betti base/Pd(II) was separated by magnetic decantation and washed with CH_3CN, water and acetone to remove the unattached substrates.

The reduction of Fe_3O_4/Betti base/Pd(II) by $NaBH_4$ was performed as follows: 500 mg of Fe_3O_4/Betti base/Pd(II) was dispersed in 20 ml of water, and then 1 mmol of $NaBH_4$ in 1 ml of water was added and the reaction was carried out at room temperature for 5 h. The final product, Fe_3O_4/Betti base/Pd(0), was washed with water and dried in vacuum at 40 °C. Scheme 1 depicts the synthetic procedure for Fe_3O_4/Betti base/Pd.

Knoevenagel Condensation Catalysed by Fe_3O_4/Betti Base

In a typical reaction, a mixture of Fe_3O_4/Betti base composite (0.05 g), benzaldehyde (1 mmol) and ethanol (5 ml) was placed in a round-bottom flask. The reaction vessel was sonicated for 5 min at room temperature to disperse the magnetic NPs in the solution. Then, malononitrile (1.1 mmol) was added to the mixture and stirred at room temperature for 60 min. The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was separated with a magnet and was washed with hot ethanol. Then, the solvent was evaporated. The products were identified using ^1H NMR, ^{13}C NMR and Fourier transform infrared (FT-IR) spectroscopies.



Scheme 1. Preparation of catalysts: Fe_3O_4/Betti base and Fe_3O_4/Betti base/Pd.

Suzuki–Miyaura Coupling Reaction

In a typical reaction, 7 mg of Fe_3O_4/Betti base/Pd (0.002 mmol Pd) was placed in a 25 ml Schlenk tube, and 1 mmol of aryl halide in 3 ml of water–ethanol (1:1), 0.134 g (1.1 mmol) of phenylboronic acid and 0.276 mg of K_2CO_3 (2 mmol) were added. The mixture was then stirred for the desired time at 40 °C. The reaction was monitored by TLC. After completion of the reaction, 5 ml of ethanol was added, and the catalyst was removed using an external magnet. Further purification was achieved by column chromatography (*n*-hexane–acetone; 4:1). The products were identified using ^1H NMR and ^{13}C NMR spectroscopies.

Results and Discussion

Fe_3O_4 particles were synthesized according to our previously works,[15] and subsequently were coated with APTES to achieve aminopropyl-functionalized magnetic NPs. Ultimately, the reaction of amino groups with β-naphthol and benzaldehyde gave the corresponding Betti base. Finally, the Betti base immobilized on Fe_3O_4 (Fe_3O_4/Betti) was coordinated with $PdCl_2$ and subsequently its reduction by $NaBH_4$ led to the corresponding palladium NPs supported on magnetic NPs. Finally, the mixture was collected using an external magnet, followed by drying in vacuum. The routes employed for the fabrication of the catalysts are shown in Scheme 1. The content of linked Betti base on Fe_3O_4 was measured through elemental analysis which revealed a loading of *ca* 0.28 mmol of Betti base per gram of Fe_3O_4. In addition, the palladium content of the catalyst as estimated using atomic absorption spectroscopy was 0.25 ± 0.001 mmol g^{-1}. This indicated that all of the anchored organic ligand moieties have approximately and efficiently coordinated with palladium ions providing catalytic active sites. The characterization of the catalyst was carried out using FT-IR spectroscopy, X-ray diffraction (XRD), CHN elemental analysis, field emission scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), wavelength-dispersive X-ray spectroscopy (WDX), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy, inductively coupled plasma (ICP) analysis and vibrating sample magnetometry (VSM). The as-synthesized catalyst can be well dispersed in various polar or nonpolar solvents, such as water, ethanol, acetone, dimethylformamide (DMF), ethyl acetate, cyclohexane, etc.

Figure 1 shows FT-IR spectra of Fe_3O_4 and Fe_3O_4/Betti base. The FT-IR spectrum of the magnetic NPs alone shows a stretching vibration at 3381 cm^{-1} which incorporates the contributions from both symmetric and asymmetric modes of the O–H bonds which are attached to the surface iron atoms.[16] The bands at low wavenumbers ($\leq$700 cm^{-1}) come from vibrations of Fe–O bonds of iron oxide, which for bulk Fe_3O_4 samples appear at 570 and 375 cm^{-1} but for Fe_3O_4 NPs at 624 and 572 cm^{-1} as a blue shift, due to the size reduction.[17–19] The presence of an adsorbed water layer is confirmed by a stretch for the vibrational mode of water found at 1622 cm^{-1}. The FT-IR spectra of Fe_3O_4/Betti base and Fe_3O_4 show Fe–O vibrations in the same vicinity. The introduction of Betti base groups to the surface of Fe_3O_4 is confirmed by the bands at 1022, 1642, 2927, 3028 and 1384 cm^{-1} assigned to the Fe–O–Si, C=C, alkyl C–H, aryl C–H stretches and amine C–N stretching, respectively. All of those bands reveal that the surface of Fe_3O_4 NPs is successfully modified with Betti base groups for the metal–ligand coordination.

The morphology and size of the catalyst were evaluated using SEM and TEM analysis (Figs 2 and 3). The SEM image of the final catalyst shows the formation of uniform and monodispersed NPs (Fig. 2).

TEM images of the Fe_3O_4/Betti base/Pd catalyst reveal that the palladium NPs with nearly spherical morphology are grafted on amidoxime-functionalized Fe_3O_4 NPs (Fig. 3). In the TEM images, iron oxide NPs of 15–20 nm in diameter and palladium nanoparticles of *ca* 3 nm entrapped in iron oxide are observed.

The elemental composition was determined using EDX analysis and the results, shown in Fig. 4, indicate Si, O, C, N, Fe and Pd signals that are provided by Fe_3O_4/Betti base/Pd. For further characterization of the sample, WDX-coupled quantified SEM mapping of the sample was also investigated (Fig. 5). WDX can provide qualitative information about the distribution of different chemical elements in the catalyst matrix. Looking at the compositional maps of Fe, Si, C, N and Pd, and mainly the combined composition image, the presence of palladium NPs with good dispersion is clearly distinguished in the composite.

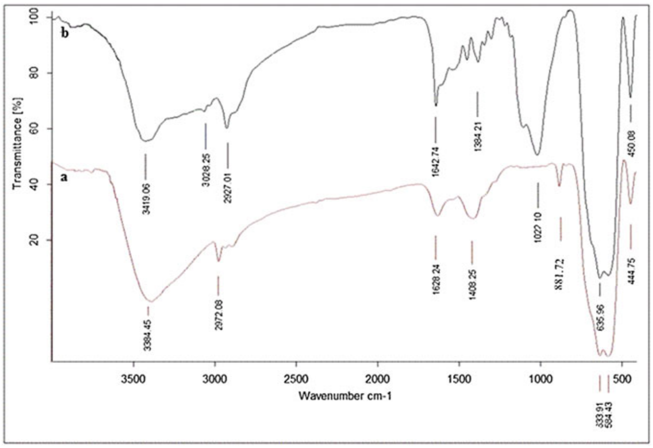


Figure 1. FT-IR spectra of (a) Fe_3O_4 and (b) Fe_3O_4/Betti base.

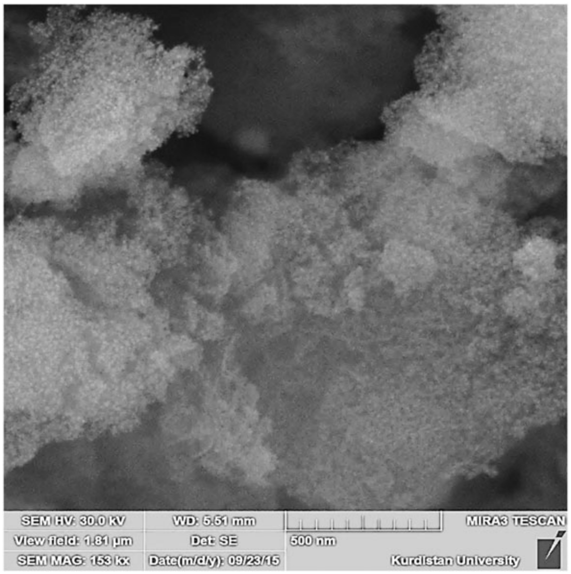


Figure 2. SEM image of Fe_3O_4/Betti base/Pd.

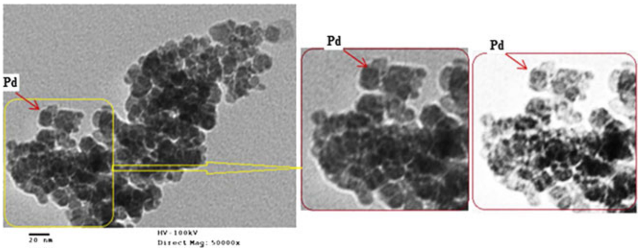


Figure 3. TEM images of Fe_3O_4/Betti base/Pd.

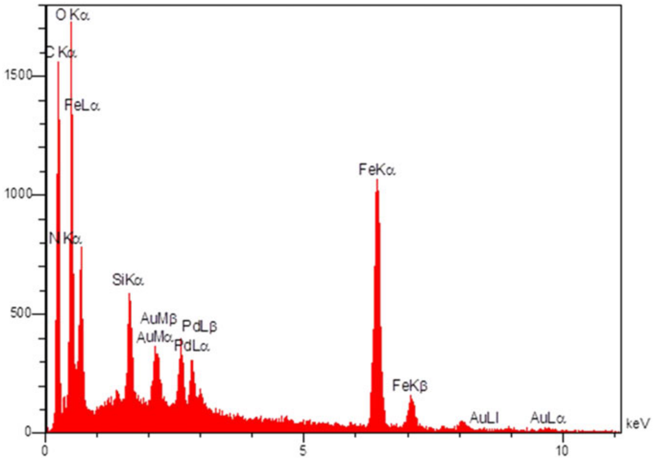


Figure 4. EDX spectrum of Fe_3O_4/Betti base/Pd.

The XRD pattern of Fe_3O_4/Betti base/Pd is presented in Fig. 6. The characteristic diffraction peaks at 2θ of 30.3°, 35.6°, 43.2°, 53.8°, 57.3° and 62.8° correspond to the diffraction of (220), (311), (400), (422),

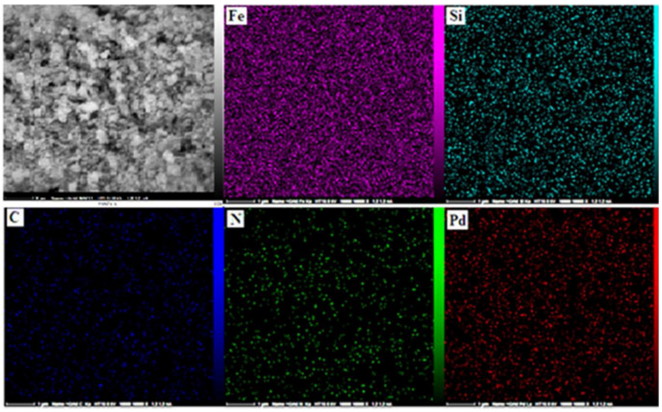


Figure 5. SEM image of Fe_3O_4/Betti base/Pd and elemental maps of Fe, Si, C, N and Pd atoms.

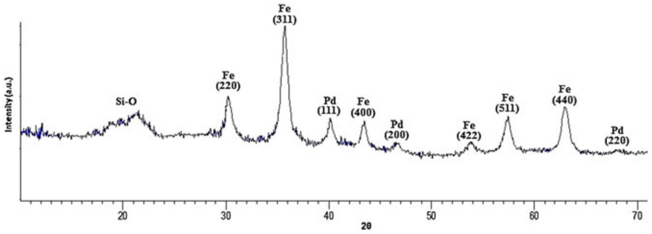


Figure 6. XRD pattern of Fe_3O_4/Betti base/Pd.

(511) and (440) of Fe_3O_4. The entire diffraction pattern matches with the magnetic cubic structure of Fe_3O_4 (JCPDS 65–3107).[20] Typical diffraction peaks of Pd(0) corresponding to (111), (200) and (220) are observed at 40.2°, 46.7° and 68.2° (JCPDS 87–0638) in the pattern. The results from XRD imply that the palladium NPs have been successfully immobilized onto the surface of the magnetic particles.

VSM measurements were carried out at room temperature. The magnetization curves measured for Fe_3O_4 and Fe_3O_4/Betti base/Pd are presented in Fig. 7. The magnetic saturation values of Fe_3O_4 and Fe_3O_4/Betti base/Pd are 61.8 and 55.2 emu g^{-1}, respectively. The decrease in the saturation magnetization is due to the presence of the Betti base and palladium NPs on the Fe_3O_4 surface. Moreover, the inset image in Fig. 7 shows the separation–redispersion process of the Fe_3O_4/Betti base/Pd catalyst. Therefore, the above mentioned results indicate an easy and efficient way to separate and recycle the prepared catalyst from the reaction solution using an external magnetic force.

Then, in order to evaluate the basic activity of Fe_3O_4/Betti base and metal-containing Fe_3O_4/Betti base/Pd as heterogeneous catalysts, the Knoevenagel condensation and Suzuki–Miyaura coupling reactions were chosen as probe reactions, respectively. The addition of malononitrile to various benzaldehydes using Fe_3O_4/Betti was performed under air (balloon). To optimize the reaction conditions, 4-chlorobenzaldehyde (1 mmol) and malononitrile (1.1 mmol) were used as model substrates. Conditions such as catalyst amount, solvent and time were investigated. The best result is obtained by carrying out the reaction with a 1:1 molar ratio of 4-chlorobenzaldehyde and malononitrile at 40 °C in 2 ml of EtOH for 1 h. The results are summarized in Table 1.

To study the effect of amount of catalyst, the Knoevenagel condensation was carried out with various amounts of catalyst (Table 1). When the amount of catalyst increases from 0.04 to 0.05 g, the product yield increases significantly from 82 to 96%, which is due to the availability of more basic sites. After that, the yield remains almost stable between 0.05 g and 0.06 g. Therefore, 0.05 g was chosen as the optimized amount of catalyst for further experiments.

It should be noted that the non-functionalized magnetic NPs (Fe_3O_4) are not active in the Knoevenagel condensation, with less than 10% conversion observed after 4 h (Table 1, entry 4). This indicates the need for the Betti base coating on the surface of the magnetic NPs to create basic sites.

With a reliable set of conditions in hand (Table 1, entry 6), we also probed the scope and generality of the developed protocol with a variety of aromatic, aliphatic and heteroaromatic aldehydes using magnetic Betti base and the results are summarized in Table 2. All the reactions are able to undergo the corresponding Knoevenagel condensation well. In addition, it is found that substituent groups of aromatic aldehydes have an effect on the Knoevenagel reaction: aldehyde with electron-withdrawing group is observed to be more reactive than that with electron-donating group (Table 2, entries 3 and 4). Moreover, heteroaromatic and aliphatic aldehydes are

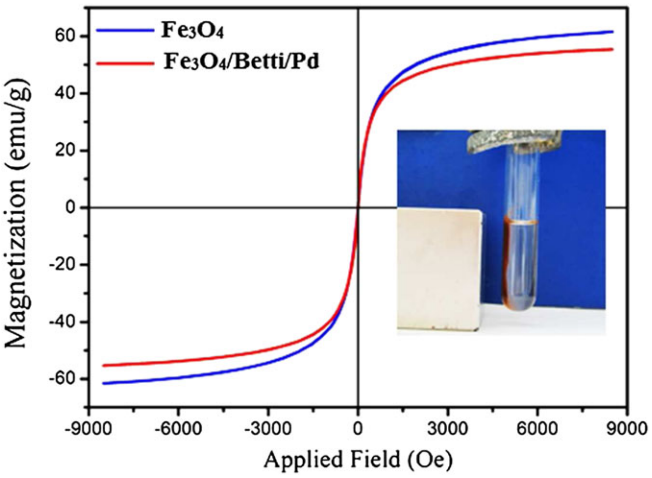
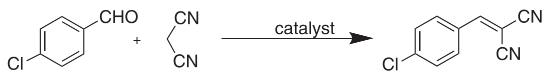


Figure 7. VSM curves of Fe_3O_4 and Fe_3O_4/Betti base/Pd.

Table 1. Optimization of Knoevenagel reaction conditions[a]



Entry	Catalyst (mg)	*T* (°C)	Solvent	Time (h)	Yield (%)[b]
1	—	40	—	10	0
2	—	40	MeCN	10	0
3	—	40	EtOH	10	0
4	Fe_3O_4 (40)	40	EtOH	4	10
5	Fe_3O_4/Betti (40)	40	EtOH	2	82
6	Fe_3O_4/Betti (50)	40	EtOH	1	96
7	Fe_3O_4/Betti (60)	40	EtOH	1	96
8	Fe_3O_4/Betti (50)	30	EtOH	2	90
9	Fe_3O_4/Betti (50)	25	EtOH	3	70
10	Fe_3O_4/Betti (50)	40	—	2	75
11	Fe_3O_4/Betti (50)	40	MeCN	2	85

[a] Reaction conditions: 4-chlorobenzaldehyde (1 mmol), malononitrile (1.1 mmol), Fe_3O_4/Betti base, solvent (5 ml).

[b] Isolated yield.

Table 2. Knoevenagel condensation with various substrates catalysed by Fe_3O_4/Betti base[a]

Entry	RCHO	Time (h)	Yield (%)[b]
1	C_6H_5	1.2	95
2	4-$CH_3C_6H_4$	1.5	90
3	4-ClC_6H_4	1	96
4	4-$NO_2C_6H_4$	0.5	96
5	4-OHC_6H_4	2	90
6	4-Pyridyl	1.5	92
7	2-Furyl	1.5	96
8	Cinamyl	4	70
9	Propyl	1	90

[a] Reactions were carried out under aerobic conditions in 5 ml of EtOH, 1.0 mmol of aldehyde and 1.1 mmol of malononitrile in the presence of catalyst (50 mg) at 25 °C.

[b] Isolated yield.

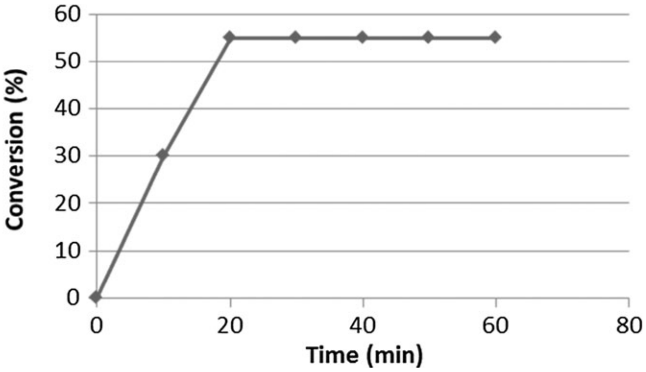
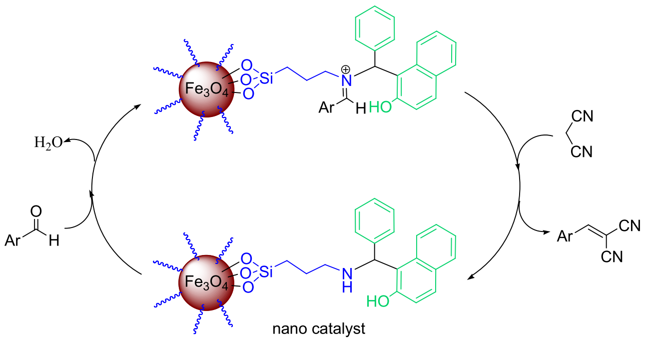


Figure 9. Heterogeneity test for Knoevenagel condensation of 4-chlorobenzaldehyde and malononitrile.



Scheme 2. Possible mechanism for the Knoevenagel condensation catalysed by Fe_3O_4/Betti base.

found to be more reactive (Table 2, entries 6, 7 and 9). Cinnamaldehyde is found to be much less reactive than other aldehydes in the Knoevenagel condensation with only approximately 70% conversions being observed (Table 2, entry 8).

Considering that one key feature of our catalyst was magnetic response, we investigated the reusability and the recycling of the catalyst, and found that the catalyst can be completely recovered using an external permanent magnet, giving GC yield still higher than 90% after five recycles during Knoevenagel condensation (Fig. 8).

In general, when using a supported catalyst, a crucial issue is the possibility that some active sites are lost from the solid support to the liquid phase, and these leached species are responsible for a significant loss of the catalytic activity. Therefore, in order to prove the heterogeneous nature of the catalyst, a heterogeneity test was performed, in which the catalyst was separated from the reaction mixture using a magnet at approximately 50% conversion of the starting material. The reaction progress in the filtrate was monitored (Fig. 9). No further reaction conversion is observed even at extended time, indicating that the nature of reaction process is heterogeneous and there is no reaction in the homogeneous phase.

A possible mechanism for the reaction using magnetic Fe_3O_4/Betti base as clean catalyst is shown in Scheme 2. According to the mechanism, magnetic Fe_3O_4/Betti base readily catalyses the formation of Knoevenagel product. The higher reactivity of the iminium ion compared to the carbonyl species facilitates Knoevenagel reaction between aryl aldehyde and malononitrile.

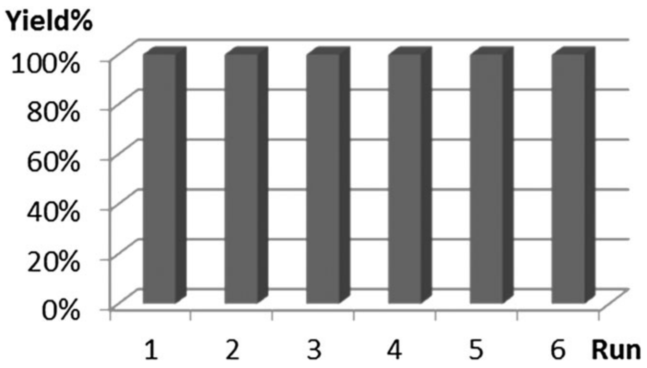


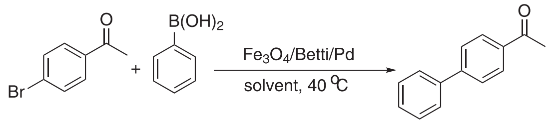
Figure 8. Separation and reuse of the magnetic Fe_3O_4/Betti base catalyst.

Continuing the work, the catalytic activity of Fe_3O_4/Betti base/Pd was evaluated in the Suzuki–Miyaura reaction. Initially, we optimized the conditions for the coupling reaction between bromoacetophenone and phenylboronic acid as a model reaction. The influence of reaction parameters such as the base (Et_3N, NaOAc and K_2CO_3), the solvent (nonpolar, protic and aprotic) and the amount of catalyst were investigated (Table 3). Among the bases evaluated, K_2CO_3 is found to be the most effective. Water–EtOH (1:1) is the best choice as solvent.

To investigate the generality of this cross-coupling, we studied the reaction of phenylboronic acid with a range of aryl halides under the optimized conditions (Table 4). Phenyl iodide, bromide and chloride all react efficiently with phenylboronic acid (Table 4, entries 1–14). Aryl halides with electron-withdrawing or electron-releasing groups react with phenylboronic acid to afford the corresponding products in high yields. It is found that the yield when using an *ortho*-substituted aryl iodide is lower (Table 4, entry 4) than when using a *para*- or *meta*-substituted aryl iodide (Table 4, entries 5 and 6). The coupling reaction of aryl chlorides with phenylboronic acid requires extended reaction time compared to aryl iodides and bromides, producing the desired products in moderate yield (Table 4, entries 13 and 14).

One of the main advantages of magnetite NP-supported catalysts is the easy separation and recycling of the catalyst. To study the recycling properties of this catalyst, the reaction of bromoacetophenone with phenylboronic acid under the optimized reaction conditions was selected. The results show that the catalyst

Table 3. Optimization of conditions for Suzuki–Miyaura reaction of bromoacetophenone with phenylboronic acid[a]



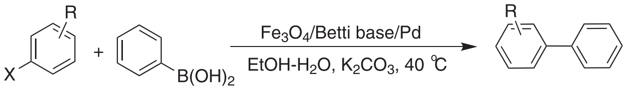
Entry	Solvent	Pd (mol%)	Base	Time (h)	Yield (%)[b]
1	DMF	0.02	K_2CO_3	1	88
2	Toluene	0.02	K_2CO_3	1	65
3	EtOH	0.02	K_2CO_3	1	75
4	H_2O	0.02	K_2CO_3	1	60
5	$EtOH–H_2O$[c]	0.02	K_2CO_3	0.5	96
6	$EtOH–H_2O$[c]	0.02	NaOAc	1	65
7	$EtOH–H_2O$[c]	0.02	Et_3N	1	80
8	$EtOH–H_2O$[c]	0.01	K_2CO_3	1	70

[a] Reaction conditions: bromoacetophenone (1 mmol), $PhB(OH)_2$ (1.1 mmol), Fe_3O_4/Betti base/Pd, solvent (3 ml).

[b] Isolated yield.

[c] $EtOH–H_2O$ = 1:1.

Table 4. Suzuki cross-coupling of aryl halides with phenylboronic acid catalysed by Fe_3O_4/Betti base/Pd[a]



Entry	RC_6H_4X	X	Time (h)	Yield (%)[b]
1	H	I	0.25	98
2	$4-CH_3$	I	0.50	96
3	$4-COCH_3$	I	0.30	98
4	$2-CH_3O$	I	0.50	85
5	$4-CH_3O$	I	0.50	96
6	$3-NO_2$	I	0.75	95
7	H	Br	1	96
8	$4-COCH_3$	Br	0.50	96
9	$4-CH_3O$	Br	2	92
10	$4-CH_3$	Br	1.5	90
11	4-Cl	Br	1	96
12	$3-NO_2$	Br	2	92
13	H	Cl	10	70
14	$4-CH_3$	Cl	12	65

[a] Reactions were carried out under aerobic conditions in 3 ml of $EtOH–H_2O$ (1:1), 1.0 mmol of aryl halide,1.1 mmol of phenylboronic acid and 2 mmol of K_2CO_3 in the presence of catalyst (7 mg, 0.02 mol% Pd) at 40 °C.

[b] Isolated yield.

is recyclable in seven consecutive runs just by decantation with a magnetic bar with no significant loss of catalytic activity (Fig. 10). In addition, one of the attractive features of this catalytic system is the rapid and efficient separation of the catalyst using an appropriate external magnet, which minimizes the loss of catalyst during separation.

The leaching of palladium into the reaction solution after five runs was determined using ICP analysis to be 1.35%, which indicates the stability of the catalyst during the reaction. In addition, SEM and TEM images (Fig. 11) of the catalyst after the five run show that the nanostructure of the catalyst is preserved. In addition the TEM image of the catalyst after being reused five times shows that the palladium NPs are still well dispersed and no obvious aggregation is observed. To investigate the heterogeneity of the catalyst, we conducted a hot filtration test for the Suzuki reaction between bromoacetophenone and phenylboronic acid using Fe_3O_4/Betti base/Pd under the same conditions. The reaction was allowed to proceed for 20 min (yield of 75%), and then the catalyst was separated. However, there is no increase in yield of the desired product when the reaction is continued for a further 1 h after the catalyst was magnetically separated, confirming the heterogeneous character of the catalyst.

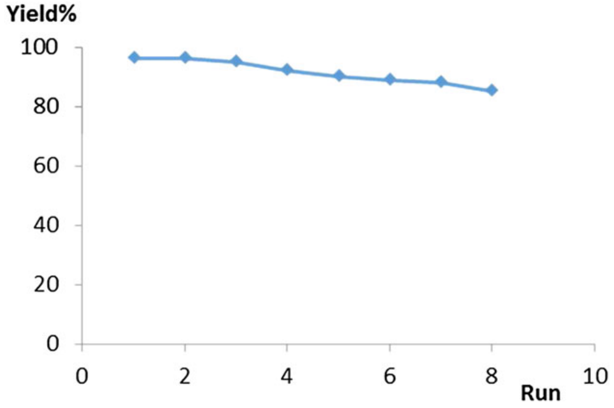


Figure 10. Recycling of Fe_3O_4/Betti base/Pd for Suzuki coupling reaction under similar conditions.

We also performed solid-phase poisoning tests using 3-mercaptopropyl-functionalized silica ($SH-SiO_2$) as an effective palladium scavenger which selectively coordinates and deactivates the leached out palladium.[21] Thereby, cessation of the reaction is expected if the coupling reaction is catalysed by palladium species leached from the solid support. The kinetic profiles of typical Suzuki reactions in the presence and absence of $SH-SiO_2$ are shown in Fig. 12. The results clearly indicate that the catalytic activity of Fe_3O_4/Betti base/Pd is not affected even in the presence of the poisoning agent.

(Reactions conditions: 2 ml of mixture of EtOH and H_2O (1:1), 1.0 mmol of bromoacetophenone, 1.1 mmol of phenylboronic acid and 2 mmol K_2CO_3 in the presence of catalyst (0.007 g, 0.02 mol% Pd) and 0.1 mmol of $SH-SiO_2$ at 40 °C. Conversion of reactant was determined using GC.)

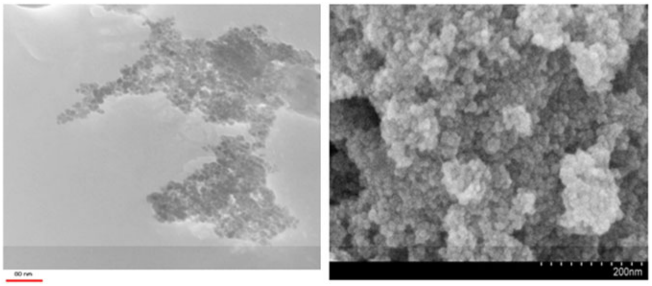


Figure 11. TEM and SEM images of reused catalyst after five runs.

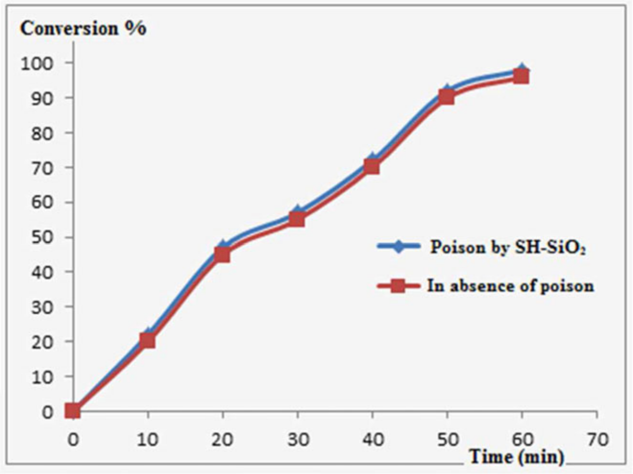


Figure 12. Kinetic profiles for Suzuki coupling reaction of bromoacetophenone with phenylboronic acid in the absence of SH-SiO_2 as solid poison and in the presence of SH-SiO_2.

Conclusions

In summary, the successful synthesis of two novel magnetically separable catalysts in which magnetic Fe_3O_4 was modified by Betti base groups as nanomagnetic base catalyst in the Knoevenagel condensation and also its application to immobilization of palladium NPs for Suzuki coupling reactions has been investigated. Studies of the structure of these materials suggest that they have stable structures with relevant organic components covalently attached to their surfaces. Moreover, the synthesized hybrid materials were found to be environmentally friendly catalysts with a high catalytic performance. The benefits of these catalysts are the cheap and uncomplicated synthetic pathways, and mild and efficient C–C coupling reactions in green media. Notably, the recyclability of the catalysts using an external magnet and no palladium leaching from Fe_3O_4/Betti/Pd are good characteristics.

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