

Magnetic Composite of γ -Fe₂O₃ Hollow Sphere and Palladium Doped Nitrogen-rich Mesoporous Carbon as a Recoverable Catalyst for C-C Coupling Reactions

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Abstract

In this article, Palladated-magnetic nitrogen doped porous carbon was prepared from nano magnetic γ - Fe_2O_3 hollow sphere (h- Fe_2O_3) with high specific surface area and pore volume. To the purpose, initially h- Fe_2O_3 was prepared and covered with glucose *via* hydrothermal treatment with subsequent polymerization of organic shell. The polymerization of melamine-resorcinol-formaldehyde (MRF) was achieved in the presence of Cl-functionalized glucose coated h- Fe_2O_3 (h- Fe_2O_3 @glu-MRF). Next, the prepared magnetic core-shell hollow sphere was palladated followed by carbonization to yield Pd@h- Fe_2O_3 @C introducing more pores in its structure. The resulted compound, Pd@h- Fe_2O_3 @C, was fully characterized, showing that carbonization process expressively increased the specific surface area. The resulted Pd@h- Fe_2O_3 @C was successfully used for promoting C-C coupling reactions under mild reaction conditions as a heterogeneous catalyst and its activity was compared with some prepared control catalysts. This novel catalyst was magnetically separated simply by a magnet bar and recycled and reused at least in five consecutive runs, without considerable loss of its activity. It is note mentioning that, high recyclability with low Pd leaching are another gains of this protocol.

Introduction

Nowadays, Nowadays, metal-catalyzed cross-coupling reactions are considered and well-established strategy in synthetic organic chemistry due to their remarkable applications in the preparation of various intermediates for the mass production of agrochemicals, pharmaceuticals, and natural products¹⁻⁴ as well as oligomers⁵⁻⁷ and conducting polymers⁸⁻¹⁰. The Pd-catalyzed cross-coupling, known as Stille, Buchwald, Sonogashira, Heck and Suzuki cross coupling reactions, has been documented as one of the most influential tools for the carbon-carbon bond formation. Palladium, especially in homogeneous catalysis is an unavoidable catalyst choice for such cross coupling reactions due several advantages such as selectivity, high synthetic yielding, and short reaction time¹¹⁻¹⁴. Nevertheless, the recovery of homogeneous Pd complexes for the sake of reusing them from the reaction mixture is often problematic and usually could not be reused for the second run of reaction. Whereas, separation and recovery of catalysts, when expensive noble metal catalysts are being used or the case is in environmental concerns is definitely highly desired. Henceforth, heterogenization of catalysts are actually the striking solution to these glitches. In this regard a wide range of inorganic and organic substances have already been designed and employed for supporting dissimilar metal catalysts to create heterogeneous catalysts. Among these solid supports, magnetic nano compounds and mesoporous materials have attracted much attention because to their exceptional properties such as relaxed recovery and high surface area¹⁵⁻¹⁹. In this regard, to enhance the specific surface area and decrease the content of active components, building a novel heterogeneous catalyst on a suitable metal support has been proposed. The hollow magnetic nanoparticles with exceptional merits for example low density, high specific surface area, great pore volume, and mechanical stability is an appropriate substrate for cumulative the selectivity and successful catalyst stability²⁰.

Alternatively, the action of carbon materials is powerfully dependent on their physico chemical properties for instance specific surface area, porosity and the existence of heteroatoms in the carbon structure. Literature survey has revealed²¹⁻²⁷, that doping of heteroatoms for example, nitrogen atoms in the carbon structure is able to improve the electric and chemical properties of carbon substances and extend their uses. The N-rich porous carbons (NPCs) shows great affinity for metal ions because of the amine functional groups on its structures. The N-rich porous carbons, as a novel porous material, have lately developed as multipurpose stages for the heterogeneous catalysis²⁸. The structure of N-rich porous carbons has a great number of enduring pores shaped by widespread chemical cross-linkage to deliver a great specific surface area. To obtain N-rich porous carbons the carbonization of substrates involving heteroatom has been proposed. Nevertheless, the control of the essential part of properties of the carbon substance via simple carbonization is perplexing, for example relating templates. Nevertheless, the great number of the templates are synthetic and their utilization is expensive and delays the synthetic course of carbon materials. In addition, these catalysts continuously achieved with a considerable reduction in activity due to the metal leaching. Furthermore, the metal agglomeration and supporting materials failure typically happened during the process of catalyst separation, recovery and reusing. This inadequacy could be better by applying suitable support which being able to have strong coordination and unbending structure. More outstandingly, the attendance of these groups emerge the option of modifications with more desirable properties or the synthesis of heterogeneous catalysts^{29,30}.

In the continuation of our interest in revealing the usefulness of nitrogen doped mesoporous carbons³¹⁻³⁴, in this investigation, we purpose to apply γ -Fe₂O₃ hollow sphere as a magnetic support for the synthesis of low density and tuning the textural aspects of N-doped carbons. In this work, melamine-based mesoporous polymer network as a carbon precursor was created in the presence of amine-functionalized γ -Fe₂O₃ hollow sphere covered with glucose-derived carbon. Consequently, the obtained nanomagnetic N-rich polymer was employed for the immobilization of Pd nanoparticles. To adapt the surface properties and presenting more porosity, N-rich polymer was next carbonized to give the desired palladated mesoporous carbon. The obtained catalyst, Pd@h-Fe₂O₃@C, showed outstanding catalytic activity, selectivity and reusability in two important reactions namely, the Suzuki and Sonogashira cross coupling reactions. Indeed by employing and comparing several control catalysts involving, Pd@h-Fe₂O₃, Pd@h-Fe₂O₃@MRF, Pd@h-Fe₂O₃@glu, Pd@h-Fe₂O₃@glu-RF, Pd@h-Fe₂O₃@glu-MRF, Pd@h-Fe₂O₃@MRF-C, Pd@h-Fe₂O₃@glu-RF-C of their Pd loading, leaching, specific surface area and catalytic activity with those of the catalyst, the key features and roles of carbonization the catalytic activity of polymer were examined.

Result And Discussion

Catalyst characterization

First, the morphology of the Pd@h-Fe₂O₃@C was studied using TEM technique. Clearly, from Fig. 1a, the hollow spherical morphology can be observed. Moreover, it is clearly that the spheres are surrounded with

gray coverage, confirming the successful incorporation of glucose and organic layer in the structure of the catalyst^{35,36}. In addition, tiny dark dots on the magnetic spheres that are indicative palladium NPs can be obvious. Notably, the palladium NPs were distributed on the porous carbon homogeneously. Using TEM technique the average size of palladium NPs was estimated and the size distribution curve of the nanoparticles is shown in Fig. 1b. The Gaussian-fitted curve shows the mean diameter (d) as 9.39 nm.

Next, FTIR spectroscopy was applied to verify the formation of Pd@h-Fe₂O₃@C and the compounds prepared in the course of synthesis of Pd@h-Fe₂O₃@C. The FTIR spectra of the Pd@h-Fe₂O₃@C (a), h-Fe₂O₃@glu-MFR (b) and pure glucose (c) are depicted in Supplementary, Fig. S1. This spectrum (a) clearly showed the characteristic bands of h-Fe₂O₃, i.e. the strong absorption bands at 470-590 cm⁻¹, which can be assigned to Fe-O stretching and the strong band at 3463 cm⁻¹, which can be attributed to -OH groups²⁰. The characteristic bands of glucose (c) can be listed as the bands at 3411, 2943 and 1461 cm⁻¹ that can be assigned to the -OH functionality and -CH₂ stretching. The FTIR spectrum of h-Fe₂O₃@glu-MFR (b) exhibited the characteristic bands at 1604, 2850, 2942 and 3406 cm⁻¹ can be due to the C=N, -CH₂ stretching and -OH functionality, which confirms the conjugation of organic layer. Moreover, the FTIR spectrum (b) showed the characteristic bands of magnetic core (h-Fe₂O₃), implying that the magnetic core preserved its structure upon functionalization processes. The FTIR spectrum (a) of Pd@h-Fe₂O₃@C is significantly distinguished from others and the intensity of the characteristic bands became very weak. This observation of some of characteristic bands is quite expectable and can be due to the high temperature thermal treatment and carbon generation.

The structure and formation of γ -Fe₂O₃ hollow sphere as well as palladium NPs was also studied by X-ray diffraction pattern of the catalyst (see Supplementary Fig. S2). As shown, the characteristic peaks of γ -Fe₂O₃ hollow sphere were appeared at $2\theta = 30.6^\circ$ {220}, 34.9° {311}, 43.5° {400}, 54.1° {422}, 57.5° {511}, 63.5° {440} and 74.2° {533} (labelled as F) can indicate the typical cubic structure hematite (JCPDS card No. 39-1346)²⁰. In the XRD pattern of Pd@h-Fe₂O₃@C, the peaks labelled as P are characteristic peaks of palladium NPs at $2\theta = 40.0^\circ$, 46.6° , 68.5° , 82.3° and 87.1° (JCPDS, No.46-1043) that can be assigned to the {111}, {200}, {220}, {311} and {222} planes³⁷. In the XRD pattern of Pd@h-Fe₂O₃@C, three bands was observed that can be assigned to the carbon material. Precisely, the bands at $2\theta = 25.3^\circ$, 45.0° and 81.7° that can be indexed to {002}, {100} and {110} crystal planes respectively³⁸, belonging to the hexagonal graphite (JCPDS card No. 41-1487)³⁹. It is worth mentioning that the characteristic bands at $2\theta = 81.7^\circ$ was overlapped with that of Palladium NPs. Furthermore, the average diameter size of Palladium NPs and γ -Fe₂O₃ were calculated by employing Debye-Scherrer equation, being about 10.2 and 19.5 nm.

Raman spectroscopy was also applied for the characterization of the catalyst (see Supplementary Fig. S3). The Raman spectrum of Pd@h-Fe₂O₃@C exhibited two bands at 1357 (D-band) and 1601 cm⁻¹ (G-band), related to graphitic carbon, can confirm the graphitic nature of the catalyst. In greater detail, the D-band is indicative of the sp³ configuration that can be attributed to presence of intrinsic defects and the

G-band can be attributed to the graphitic carbon⁴⁰⁻⁴². In this line, the I_D/I_G was calculated and measured to be 0.83, can confirm disordered graphitic structures or highly defective⁴³.

To elucidate whether decoration of the surface of h-Fe₂O₃ with carbon shell and palladium NPs can alter the magnetic property, Pd@h-Fe₂O₃@C was studied by room temperature vibrating sample magnetometer (VSM), and its magnetic features compared with that of h-Fe₂O₃ (see Supplementary Fig. S4). As obvious, the maximum saturation magnetization (M_s) values of h-Fe₂O₃ and Pd@h-Fe₂O₃@C were found to be 45.1 and 33.1 emu/g, respectively. Clearly, the M_s value of the hollow Fe₂O₃ nano sphere (45.1 emu/g) is higher than that of the catalyst which may be due to the incorporation of non-magnetic compounds and immobilization of palladium NPs on the surface of magnetic core. However, the hysteresis loops of the catalyst showed a paramagnetic behaviour without aggregation that can be easily separated from the reaction mixture using an external magnetic force.

In Supplementary Fig. S5, the thermal stability of the (a) h-Fe₂O₃@glu-MFR, (b) h-Fe₂O₃ and (c) Pd@h-Fe₂O₃@C were recorded using TG analysis and were compared. As shown, the h-Fe₂O₃ possessed high thermal stability and exhibited only the weight loss below 200 °C that is representative of loss of water. The comparison of h-Fe₂O₃@glu-MFR with that of h-Fe₂O₃ indicates that apart from the weight losses of magnetic core, a major weight loss at 450 °C can be detected that can be attributed to the degradation of organic layer. More detailed, the weight loss of about 19% can be due to the decomposition of MRF as an organic motif that indicates the successful formation of MRF in the structure of the catalyst. Considering the thermo gram of Pd@h-Fe₂O₃@C, it can be concluded that this sample exhibited significantly higher thermal stability compared to that of others, confirming the successful carbonization.

In the following, the effect of the carbonization of organic shell on the textural properties of the catalyst was studied. To this purpose, the N₂ adsorption-desorption isotherms of Pd@h-Fe₂O₃@C and h-Fe₂O₃ were recorded and depicted in Supplementary Fig. S6. As shown, the isotherms of two samples are distinguished. The shape of h-Fe₂O₃ exhibited type II isotherm, while Pd@h-Fe₂O₃@C showed type IV with H3 hysteresis loops³⁸. To further verify this issue, the specific surface area of two samples were calculated and compared. The specific surface area of the catalyst was calculated to be 426 m²g⁻¹ which was higher than that of h-Fe₂O₃ (53 m²g⁻¹). This can indicate the porous nature of Pd@h-Fe₂O₃@C. The total pore volume of two samples were also compared (see Supplementary Fig. S6). More precisely, this value for Pd@h-Fe₂O₃@C was much higher than that of h-Fe₂O₃, indicating the carbonization of organic layer resulted in the formation of pores. Moreover, the pore size distribution curves of the h-Fe₂O₃ and Pd@h-Fe₂O₃@C were obtained by the BJH method using the pore volumes in the measurement of N₂ desorption isotherms. As is evident from pore size distribution result of Pd@h-Fe₂O₃@C, two types of pores with mesoporous (2 nm) and micropores (8.9 and 11 nm) were clear. Nevertheless, compared to the Pd@h-Fe₂O₃@C, the microporous size uniformity has increased and appeared at 8.9 and 11 nm, presumably due to the carbonization of organic layer.

Finally, ICP-AES was exploited for measuring the content of palladium NPs in the catalyst. To prepare the sample for the analysis, a known quantity of Pd@h-Fe₂O₃@C was digested in a mixture of concentrated HCl and HNO₃ solution. Finally, the obtained extract was analysed and the results confirm that the content of palladium was 3.1 w/w%.

Investigation of the catalytic activity

To assess the catalytic activity of this heterogeneous system, the Pd@h-Fe₂O₃@C was utilized as a recyclable catalyst in Suzuki coupling reaction. Initially, the reaction of iodobenzene 1 and phenylboronic acid 2 was selected as a model substrate. The reaction was conducted in the presence of Na₂CO₃ and Pd@h-Fe₂O₃@C (0.5 mol%) at 75 °C in EtOH condition. After 1 h, the nature of the reaction mixture quickly changed to a dark viscous solid. After purification by column chromatography, the biphenyl 3a was afforded in 35% yield. The solvent was then screened in the reaction, such as water, EtOH, water/EtOH, DMF, CH₃CN, toluene and THF. As shown in Supplementary Table S1, the outcomes exposed that a mixture of water/EtOH can well support the reaction effectively. After using different solvent, a series of parameters including catalysis, reaction temperature and base were examined to find and secure the optimal reaction conditions. Ultimately, the experimental results established that the biphenyl could be achieved with 95% yield when the model reaction was carried out in the presence of Pd@h-Fe₂O₃@C (0.5 mol%) with Na₂CO₃ at 75 °C in water/EtOH.

Further, to determine its scope by applying various aryl halides, a range of reactions was carried out under the optimal reaction conditions. As shown in Table 1, a series of aryl halides with electron-donating and electron-withdrawing groups and phenylboronic acid were used in the reaction under optimized conditions. Eventually, the Pd@h-Fe₂O₃@C efficiently catalyzed the coupling reaction between aryl halides with phenylboronic acid and biphenyls were attained in high to excellent yields after purification. In detail, the electronic effect of the substituents was generally found to have no considerable influence since aryl iodides bearing donor- and acceptor substituents reacted with phenylboronic acid to afford the expected coupled products in excellent yields. Worthy to mention that, when iodobenzene was substituted by bromobenzene, the reactions needed longer reaction times for being completed. Notably, the scope of this methodology was found not to be operative to chlorobenzene.

Furthermore, the performance of Pd@h-Fe₂O₃@C catalyst was tested for the Sonogashira coupling reaction using iodobenzene 1 and phenylacetylene 4 as a model substrate. As shown in Supplementary Table S2, the optimization reaction conditions were investigated in different solvents, temperatures, bases, and in the presence of various amounts of the Pd@h-Fe₂O₃@C catalyst. Unlike the previous reaction and as the first parameter of this set, the role of Pd@h-Fe₂O₃@C as a catalyst was studied. Notably, in the absence of any catalyst and only in the presence of Na₂CO₃ (2 mmol) at 50 °C, the product was not formed (see Supplementary Table S2, entry 10), while, the use of a small amount (0.175 mol%) of catalyst provided the desired product in moderate to excellent yields (53-98%) (see

Supplementary Table S2, entries 1, 6 and 7). It was found that, when the model substrate was applied in the presence of Na_2CO_3 (2 mmol) at 50 °C using $\text{Pd@h-Fe}_2\text{O}_3\text{@C}$ (0.35 mol%) as catalyst, the yield of product could reach 95% after separation. Using the optimized reaction conditions, the scope and generality of this method were exemplified in the reaction of aryl halides 1 and phenyl/aliphatic acetylenes 4 using $\text{Pd@h-Fe}_2\text{O}_3\text{@C}$ catalyst, and the outcomes are presented in Table 2. The cross-couplings of phenyl/aliphatic acetylenes with aryl iodides bearing electron donating groups, -OMe, -Me and -COMe gave products in satisfactory yields. Moreover, aryl bromides and chlorides are efficiently reacted as substrates in this process, though, the reaction of aryl chlorides needed longer reaction times for being completed. Noticeably, propargylalcohol as an aliphatic acetylene was also fruitfully coupled to arylhalides with satisfactory yields. Nevertheless, the highest yields were obtained for aryl acetylene. Noteworthy, all compounds are known and some were identified by comparing physical properties through FTIR and melting point analyses.

Next, the catalyst structure-catalytic activity relationship was studied. Initially, the result of loading of Pd on the support was studied. In this regard, apart from the catalyst two more samples with different loading of Pd, i.e. $\text{Pd@h-Fe}_2\text{O}_3\text{@C}$ (Pd 2 and 3 wt%) were provided and their catalytic activities for catalyzing the model Sonogashira reaction was compared with that of the catalyst. The outcomes showed that the loading of Pd meaningfully influence the catalytic activity and use of lower content of Pd is more effective. Then, the influence of each component in the structure of the catalyst to the catalysis was studied. For this purpose, several control catalysts, including, $\text{Pd@h-Fe}_2\text{O}_3$, $\text{Pd@h-Fe}_2\text{O}_3\text{@glu}$, $\text{Pd@h-Fe}_2\text{O}_3\text{@glu-MRF}$, $\text{Pd@h-Fe}_2\text{O}_3\text{@glu-RF}$, $\text{Pd@h-Fe}_2\text{O}_3\text{@glu-RF-C}$ and $\text{Pd@h-Fe}_2\text{O}_3\text{@C}$ were prepared (see experimental section). To synthesis $\text{Pd@h-Fe}_2\text{O}_3$, Pd was easily coated on $\text{h-Fe}_2\text{O}_3$ and the prepared product was applied for catalyzing the model Sonogashira reaction (Table 3, entry 1). As shown, $\text{Pd@h-Fe}_2\text{O}_3$ is not an active catalyst and the product was obtained only 35%. Then, it was studied whether introducing of Glu shell is able to improve the catalytic activity. In this line, $\text{Pd@h-Fe}_2\text{O}_3\text{@glu}$ was provided and its catalytic activity was examined and the product was obtained with 50% yield (Table 3, entry 4). This results approved that Glu can somewhat improve the catalytic activity. For further revealing the key role of Glu in the catalysis, two control catalysts, $\text{Pd@h-Fe}_2\text{O}_3\text{@MRF}$ and $\text{Pd@h-Fe}_2\text{O}_3\text{@MRF-C}$ was prepared, in which the Glu was not present in the structure of the catalyst and the resorcinol-formaldehyde-melamine polymer was adjusted on the surface of $\text{h-Fe}_2\text{O}_3$ and subsequently palladated and carbonized (Table 3, entries 2 and 3). Based on the comparison of the results from catalytic activity of the catalyst and these samples the contribution of Glu was confirmed. In details, donor- and acceptor substituted it was found that Glu component not only influenced the catalytic activity, but also improved the separation and reusability of the catalyst. More exactly, the separation of the catalyst was simpler and more efficient than that of $\text{Pd@h-Fe}_2\text{O}_3\text{@MRF}$ and $\text{Pd@h-Fe}_2\text{O}_3\text{@MRF-C}$, while, the ICP examination of these samples approved the higher loading of Pd NPs in the catalyst.

Approving the role of melamine as a nitrogen source, the effect of N-precursor by creating another control samples, $\text{Pd@h-Fe}_2\text{O}_3\text{@glu-RF}$, $\text{Pd@h-Fe}_2\text{O}_3\text{@glu-RF-C}$ in which melamine was omitted in the structure of

polymer was clarified and compared with Pd@h-Fe₂O₃@glu-MRF and catalyst. As tabulated, melamine as an N-rich precursor has the ability to produce product with the highest catalytic activity (Table 3, entries 5-8). To elucidate the effect of polymer's type on the structure of the catalyst and Pd loading, the specific surface area of these samples were compared and showed that this value decreased in the following order: Pd@h-Fe₂O₃@C (426 m²g⁻¹) > Pd@h-Fe₂O₃@glu-RF-C (156 m²g⁻¹) > Pd@h-Fe₂O₃@glu-MRF (42 m²g⁻¹) > Pd@h-Fe₂O₃@glu-RF (33 m²g⁻¹). By these results the effect of the N-rich carbon precursor on the content and specific area of the carbon coated h-Fe₂O₃ was confirmed. Further, the effects of composite components on the loading and leaching of Pd NPs in catalyst as well as control samples were measured *via* ICP analysis and studied, Table 3. As tabulated, the order of loading and leaching of Pd increased in the following order: Pd@h-Fe₂O₃ > Pd@h-Fe₂O₃@MRF > Pd@h-Fe₂O₃@glu > Pd@h-Fe₂O₃@glu-RF > Pd@h-Fe₂O₃@glu-MRF > Pd@h-Fe₂O₃@MRF-C > Pd@h-Fe₂O₃@glu-RF-C > Pd@h-Fe₂O₃@C. The lowest loading of Pd was observed in Pd@h-Fe₂O₃ sample which can be due to the absence of strong chemical interaction between Pd NPs and h-Fe₂O₃ surface. It is worth mentioning that the low catalytic activity of this sample can be allocated to the low Pd loading. The loading of Pd in Pd@h-Fe₂O₃@MRF, Pd@h-Fe₂O₃@glu, Pd@h-Fe₂O₃@glu-RF and Pd@h-Fe₂O₃@glu-MRF samples compared to that of Pd@h-Fe₂O₃ can confirm that the presence of carbon shell could increase Pd immobilization. Nevertheless, the Pd leaching of this sample was relatively high. Pd@h-Fe₂O₃@MRF-C and Pd@h-Fe₂O₃@glu-RF-C that possessed carbon shell, the Pd anchoring were further enhanced compared to Pd@h-Fe₂O₃@MRF and Pd@h-Fe₂O₃@glu-RF, indicating the encouraging effect of carbonization of polymeric shell on immobilization of Pd NPs. Furthermore, the Pd leaching in samples were repressed compared to that of Pd@h-Fe₂O₃@glu-MRF and Pd@h-Fe₂O₃@glu-RF. In Pd@h-Fe₂O₃@C, the loading of Pd was increased compared to that of Pd@h-Fe₂O₃@glu-MRF, representing that Pd anchoring on carbonized sample was most better than un-carbonized one.

Catalyst recyclability

To explain whether Pd@h-Fe₂O₃@C can be considered as a reusable catalyst, the recycling of that catalyst was carried out for the Sonogashira model reaction and the results exhibited in Supplementary as Fig. S7. In detail, after the first run had been accomplished, the reaction mixture was cooled to ambient temperature, diluted by ethylacetate and the recovered catalyst was magnetically separated, washed with EtOH and dried and the recycled catalyst re-used for the subsequent run of Sonogashira model reaction under the same conditions. As shown, the Pd@h-Fe₂O₃@C catalyst was subjected to five successive runs and the catalytic activity of catalyst weakened gradually. Noteworthy, up to the fourth reaction run, only a reasonable decrease was detected, subsequently a more obvious loss of activity after the fifth run and the yield of product reached to 44%. To consider the effects of reusing on the morphology of the catalyst, FTIR spectra of the recycled catalyst was recorded and compared with that of the fresh catalyst, Fig 2. The FTIR spectrum of the recycled Pd@h-Fe₂O₃@C demonstrated the specific bands of the fresh Pd@h-Fe₂O₃@C. Nevertheless, some difference between two spectra were observed, that can be due to the

disposition of organic substances on the surface of the catalyst. Outstandingly, Pd leaching was insignificant after five reaction runs and can confirm that the catalyst was stable upon recycling and can be reused for the successive reaction runs.

The development and application of the reusable heterogeneous catalysts in the C-C coupling reactions have been the subject of various studies. Under convinced conditions, leaching of the supported Pd particles has also been observed. Information on the active Pd species in solution can be attained by the hot filtration test and it is classically accomplished by disturbing the reaction at a low conversion and then carrying it on after catalyst removal. If no additional conversion is identified in the catalyst-free solution phase, the leaching of Pd may be excluded. Herein, to establish the heterogeneous nature of the Pd@h-Fe₂O₃@C catalyst, the hot filtration test was investigated using iodobenzene and phenyl acetylene as the model substrates under the optimized reaction condition. After 1 h, the reaction was stopped and the catalyst was separated from the hot reaction mixture and the yield of product was analyzed with GCMS (45% conversion). The reaction was continued using the filtrate in the absence of the solid catalyst for more 3 h and no product was found, indicating that the leaching of Pd NPs during the catalytic cycle not observable. Furthermore, the ICP-AES analysis of the filtrate exhibited Pd content under detection level (i.e. <0.01 ppm) which more enumerates non-leaching of either Pd metal during the reactions, thereby confirming its heterogeneous stability and nature.

Methods

Synthesis of the catalyst

Synthesis of nanomagnetic Fe₂O₃ hollow sphere (a)

The palladated-encapsulated h-Fe₂O₃ was fabricated through *in situ* polymerization. The procedure included the preparation of magnetic core, synthesis of prepolymer solution, and the formation of palladated-magnetic carbon shell. Nanomagnetic Fe₂O₃ hollow sphere as a magnetic core, was prepared through solvothermal method²⁰. Initially, FeCl₃.6H₂O (5 mmol) was dissolved in 70 mL of ethylene glycol in a flask. Next, 30 mmol of sodium acetate trihydrate, 1.5 mmol of trisodium citrate dehydrate and urea (17 mmol) were added to the aforementioned solution. After stirring of the resultant mixture for 60 minutes, it was then transferred to the Teflon-lined stainless-steel autoclave (150 mL capacity) and kept at 220 °C overnight. Upon completion of the process, the reactor was cooled to ambient temperature and the brown product 1 was washed with EtOH/H₂O and dried at 80 °C for 24 h in oven.

Synthesis of h-Fe₂O₃@glu core-shell (b)

The resulting h-Fe₂O₃@glu core-shell was prepared by previous method with little modification, accordingly⁴⁴. Initially, h-Fe₂O₃ (1 g) well dispersed in deionized water (40 mL) by using ultrasonic irradiation (power 100 W) for 15 minutes. Afterward, glucose (6 g) was introduced in the prepared magnetic suspension and the resulting mixture was transferred into a Teflon-lined stainless steel autoclave (150 mL). Then, the container was closed and maintained at 200 °C for one day. At the end of the hydrothermal treatment, the reactor was cooled down to room temperature and the product 2 was collected by a magnet bar, rinsed with EtOH, centrifuged for five times and dried in oven at 80 °C.

Synthesis of h-Fe₂O₃@glu-Cl Core shell (c)

In the next step, the surface of h-Fe₂O₃@glu was functionalized with (3-Chloropropyl)trimethoxysilane (CPTES), according to previous literature⁴⁵, with a slight modification. For this, h-Fe₂O₃@glu (3g) was dispersed by sonication in 100 mL dry toluene for 1 h, and then CPTES (3 mL) was injected dropwisely into the h-Fe₂O₃@glu suspension in the presence of Et₃N (3 mL). The obtained mixture was heated and stirred continuously under reflux condition at 110 °C, for 24 h. The mixture was cooled to room temperature and h-Fe₂O₃@glu-Cl, 3, was magnetically collected and washed with toluene, and then dried under air for 12 h.

Synthesis of h-Fe₂O₃@glu-MFR (d)

The pre-polymer solution was prepared by mixing formaldehyde (10 mL) and melamine (2 g) in distilled water (10 mL), according to previous method⁴⁶. Next, the pH of the mixture was adjusted to 8.5–9.0 by adding TEA and stirred vigorously at 70 °C. When it became clearly transparent, another melamine (1 g) was added and stirred till it was dissolved completely. Similarly, water (10 mL) was added and stirred till the solution was transparent absolutely. On the other, h-Fe₂O₃@glu-Cl (0.5 g) well dispersed in water (20 mL) and stirred for half time. The magnetic suspension was adjusted to pH 4.5–5.0 with 15.0 wt.% acetic acid solution. The prepared solution was added into the magnetic suspension under stirring condition, dropwisely. After that, resorcinol was added to the prepared cross-linking with the M–F pre-polymer. After all of the pre-polymer was added, ammonium chloride (5 wt.%) as a nucleating agent was added into the solution, then it was stirred at 60 °C for 90 min. The pH of the mixture was adjusted to 9.0 with TEA solution, which completed the reaction. Then the resultant microcapsule 4 was magnetically collected, washed with EtOH until pH 7 was reached. The wet powders were dried in a vacuum oven at 100 °C overnight.

Immobilization of Palladium NPs on h-Fe₂O₃@glu-MFR (e)

Based on previous literature³³ with little modification, to immobilize Palladium NPs on the h-Fe₂O₃@glu-MFR, a solution of Pd(OAc)₂ (2 wt.%) in MeOH (10 mL) was added to the solution of suspended h-Fe₂O₃@glu-MFR (1 g) in toluene (50 mL) in a drop wise manner under stirring condition overnight. In the following, a solution of NaBH₄ in MeOH (12 mL, 0.1 N) was added under inert atmosphere to the above-mentioned suspension. Subsequently, the resulting mixture was stirred for 7 h. The obtained Pd@h-Fe₂O₃@glu-MFR, was magnetically separated, washed with toluene and MeOH and dried in an oven at 80 °C for 12 h.

Synthesis of Pd@h-Fe₂O₃@C (f)

The resulting Pd@h-Fe₂O₃@C was prepared by previous method³³. To this propose, Pd@h-Fe₂O₃@glu-MFR (5 g) was placed in a quartz container and heated up to 450 °C for 1 h under argon flow and heating rate of 30 °C min⁻¹. The sample was held at this temperature for 6 h. After cooling to room temperature, the product 5 (3 g) was washed and recovered as a black powder. The schematic processes of synthesis of the catalyst are depicted in Fig. 3.

Catalytic activity

Sonogashira reaction

In a round bottom flask, aryl halide (1.0 mmol), acetylene (1.2 mmol) and Na₂CO₃ (2.0 mmol) were mixed in the presence of Pd@h-Fe₂O₃@C (0.35 mol%) as a catalyst in H₂O (5.0 mL) and the resulting mixture was heated at 50 °C in an oil bath. The proceeding of the reaction was traced by TLC (n-hexane/ethyl acetate, 8:2). After finishing the reaction, Pd@h-Fe₂O₃@C was magnetically isolated, washed with EtOH repeatedly and dried in an oven at 60 °C for 6 h. Finally, the filtrate was extracted with diethyl ether for three times and then, the organic layer was washed with deionized water and dried over anhydrous Na₂SO₄ and purified using column chromatography over silica gel.

Suzuki reaction

A mixture of aryl halide (1.0 mmol), aryl boronic acid (1.2 mmol), K₂CO₃ (2.0 mmol) and Pd@h-Fe₂O₃@C (0.5 mol%) was prepared in the mixture of water/EtOH (1:1, 5 mL) and was heated at 85 °C in an oil bath, subsequently. The solvent for monitoring reaction process by TLC was n-hexane/ethyl acetate, 7:3. Then, the mixture was cooled to ambient temperature and the catalyst was separated by a magnetic field, washed with ethanol for three times and dried in oven at 60 °C for 6 h. After that, the solvent was removed and the product was extracted with 10 mL of n-hexane. To achieve corresponding biaryls, the product was purified by column chromatography over silica gel.

Characterizations of some products

1,2-diphenylethyne (5a): White solid, mp: 61-63 °C lit.⁴⁷; FT-IR (KBr): 3413, 3062, 2921, 1952, 1630, 1490, 1442, 1161, 916, 754.

1-methyl-4-(phenylethynyl)benzene (5b)⁴⁷: White solid, m.p: 71-73 °C lit.⁴⁷; FT-IR (KBr): 3552, 3474, 3414, 2958, 1626, 1500, 1261, 1098, 867, 751, 626.

1-methoxy-4-(phenylethynyl)benzene (5c)⁴⁷: White solid, m.p: 65-66 °C lit.⁴⁷; FT-IR (KBr): 3472, 3414, 2925, 1895, 1647, 1597, 1502, 1540, 1245, 1023, 821, 751, 685.

3-phenylprop-2-yn-1-ol (5e): FT-IR (KBr): 3300, 3065, 2922, 2859, 2237, 1959, 1888, 1745, 1597, 1488, 1441, 1363, 1259, 1027, 955, 800, 756, 690, 571, 520.

Conclusion

In summary, a novel magnetic *N*-doped mesoporous carbon with hollow morphology, Pd@h-Fe₂O₃@C, was prepared via coating of Glu carbon shell on h-Fe₂O₃, functionalization, and growth of MRF polymer, Pd immobilization followed by carbonization. The resulting core-shell established excellent catalytic activity for the C-C coupling reactions. The comparison of the catalytic activity of Pd@h-Fe₂O₃@C with that of some control samples including, Pd@h-Fe₂O₃, Pd@h-Fe₂O₃@MRF, Pd@h-Fe₂O₃@glu, Pd@h-Fe₂O₃@glu-RF, Pd@h-Fe₂O₃@glu-MRF, Pd@h-Fe₂O₃@MRF-C, Pd@h-Fe₂O₃@glu-RF-C, confirmed higher catalytic activity of the former. Notably, these comparisons and catalytic activity of their confirmed the importance of the carbonization as well as the presence of nitrogen groups in C could improve the Pd anchoring and suppress its leaching and introduction of more pores for achieving high catalytic activity through facilitating the mass transfer. It can be stated that the carbonization of MRF polymer can intensely increase the specific surface area and pore volume, the greater catalytic activity of Pd@h-Fe₂O₃@C. The recyclability test also confirmed high recyclability of Pd@h-Fe₂O₃@C with slight Pd leaching and no Pd aggregation. Furthermore, the hot filtration test showed the heterogeneous nature of the catalysis.

Declarations

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Author contributions

M.M.: Supervision, financial support, writing the manuscript, methodology. M.H.: Financial support, reviewing and editing the manuscript. Z.M.: Experimental work. K.K.: Experimental work.

Competing interests

The authors declare no competing interests.

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Tables

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Figures

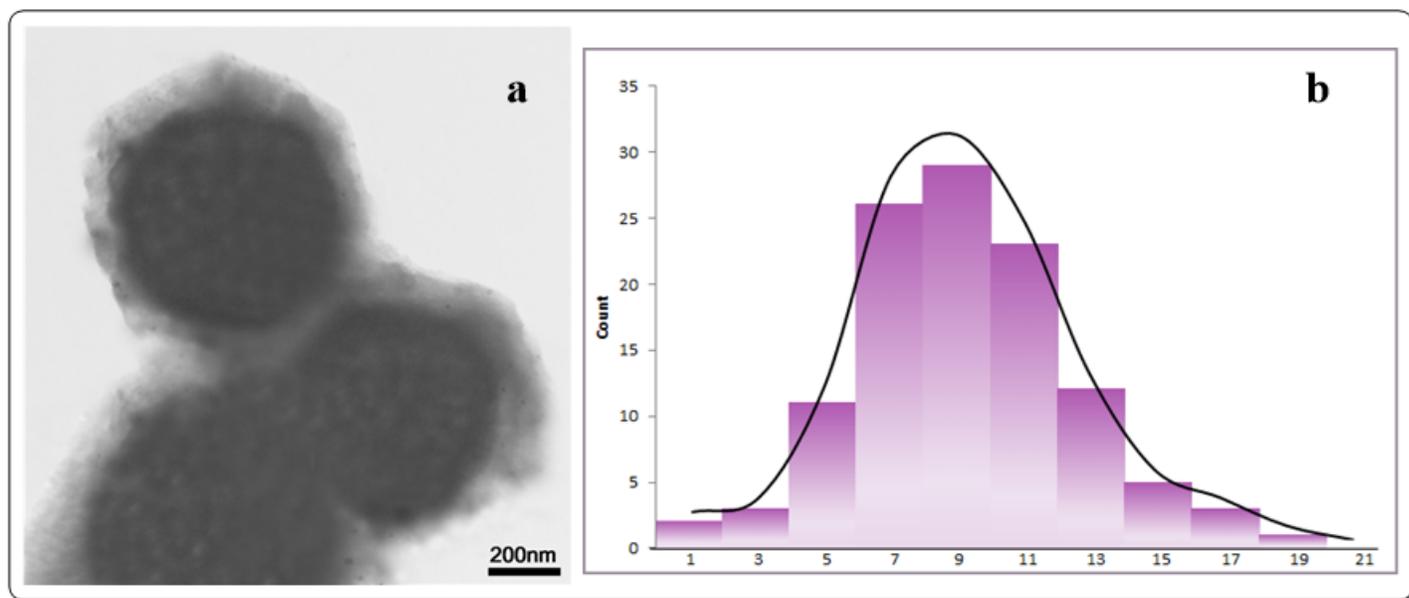


Figure 1

TEM images (a) of Pd@h-Fe₂O₃@C and size distribution histogram (b) of palladium NPs.

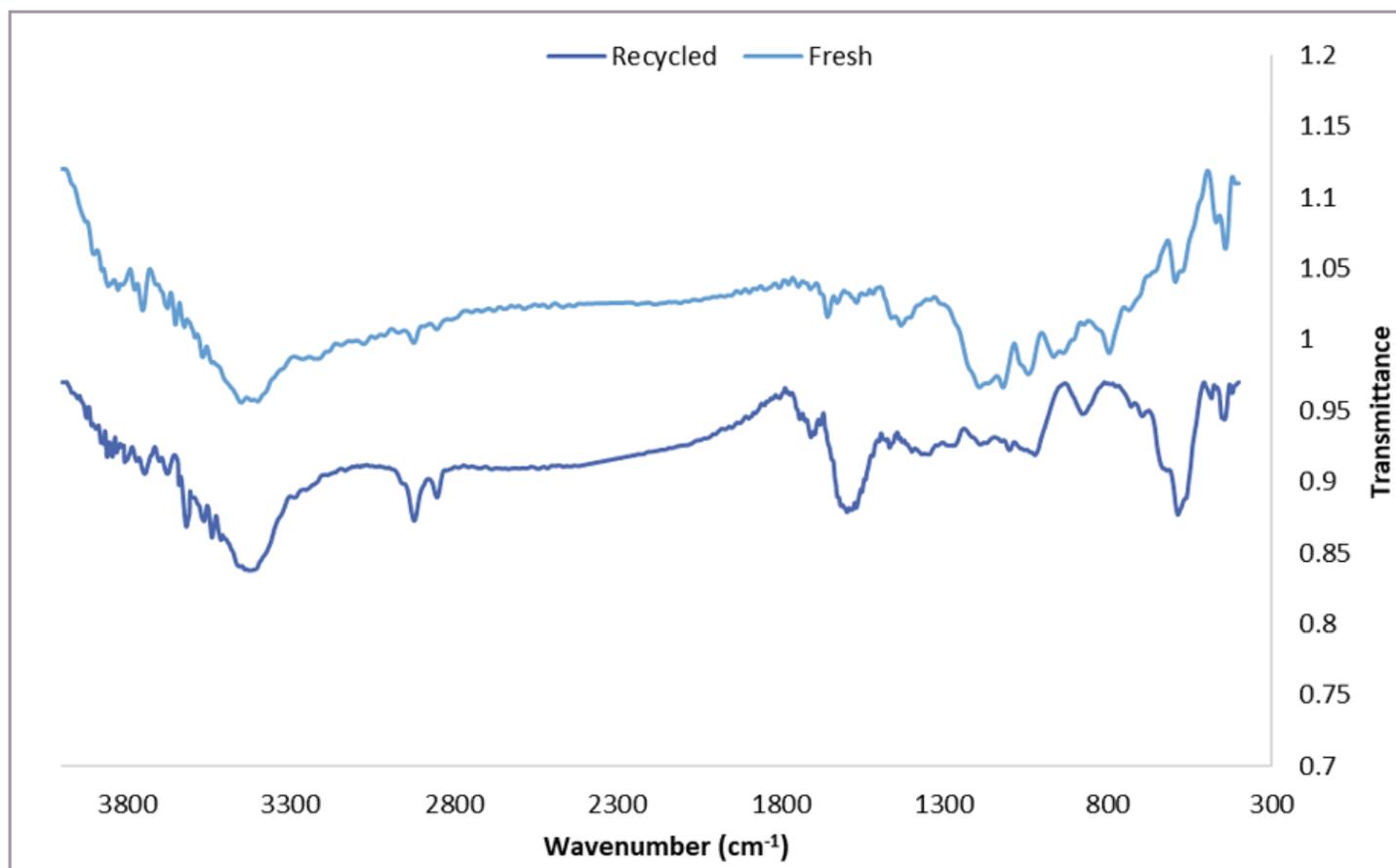


Figure 2

The FTIR spectra of fresh and recycle Pd@h-Fe₂O₃@C catalyst after five runs.

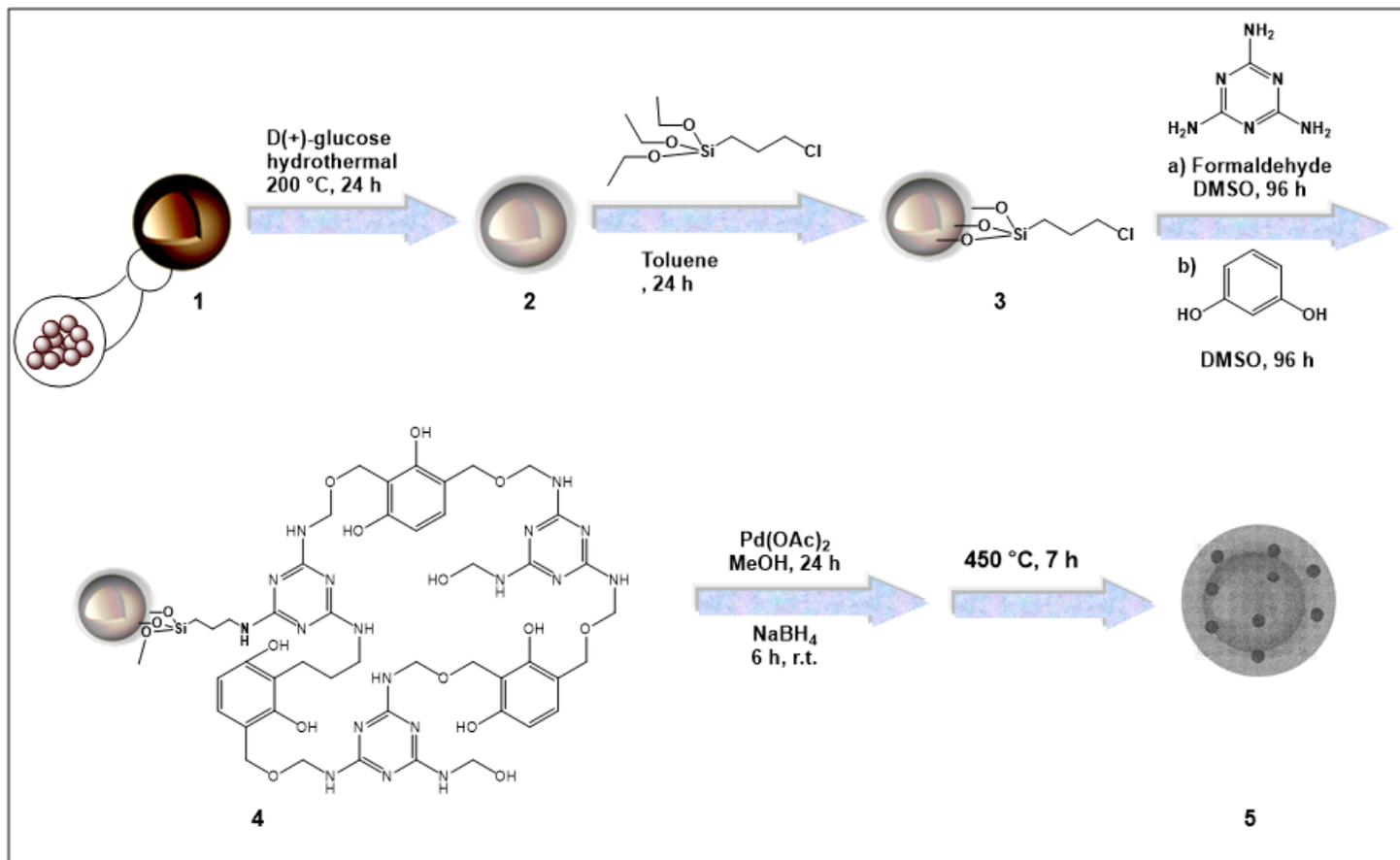


Figure 3

The possible formation process of Pd@h-Fe₂O₃@C catalyst.

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