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Palladium nanoparticles immobilized on core-shell magnetic fibrous as highly efficient and recyclable heterogeneous catalyst for reduction of 4-nitrophenol and Suzuki coupling reactions

Xuanduong Le, Zhengping Dong,* Yansheng Liu, Zhicheng Jin, Thanh-Do Huy, Minhong Le and Jiantai Ma*

aGansu Provincial Engineering Laboratory for Chemical Catalysis, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, PR China.

bFaculty of Technical Physics and Chemistry, Le Quy Don Technical University, Hanoi, Vietnam.

*Corresponding author, E-mail addresses: dongzhp@lzu.edu.cn (Zhengping Dong), majiantai@lzu.edu.cn (Jiantai Ma).

Tel.: +86 931 891 2311; Fax: +86 931 891 2582.
Abstract

In this study, a novel core-shell magnetic fibrous nanocatalyst Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 with easy accessibility of active sites and convenient recovery by applying an external magnetic field was successfully developed. Fe$_3$O$_4$@SiO$_2$@KCC-1 was functionalized with amino groups acting as robust anchors so that the palladium nanoparticles (Pd NPs) with an average diameter of about 4 nm were well-dispersed on the fibers of the Fe$_3$O$_4$@SiO$_2$@KCC-1 without obvious aggregation. The synthesized Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst exhibited excellent catalytic activity in the reduction of 4-nitrophenol by sodium borohydride, and Suzuki cross coupling reactions of aryl chlorides with aryl boronic acids due to the easy accessibility of the active sites. Furthermore, the Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst was conveniently recovered by magnet and could be reused for at least five cycles without significant loss in activity; thus, confirming its good stability. Therefore, the above mentioned approach based on core-shell magnetic fibrous Fe$_3$O$_4$@SiO$_2$@KCC-1 provided a useful platform for the fabrication of Pd NPs based catalysts with easy accessibility, superior activity and convenient recovery.
1. Introduction

In the catalytic area, noble metal nanoparticles (NMNPs) based heterogeneous catalysts have attracted significant attention due to the high catalytic efficiency in numerous liquid-phase catalytic processes.\textsuperscript{1-3} In particular, palladium nanoparticles (Pd NPs) based catalysts have been extensively studied because of the superior catalytic performances toward diverse reactions such as Suzuki coupling,\textsuperscript{4,5} Heck C-C coupling,\textsuperscript{6} degradation of pollutants,\textsuperscript{7} hydrogenation,\textsuperscript{8} and fuel cells.\textsuperscript{9} The catalytic activity of Pd NPs is strongly dependent on the active atoms on the surface that are usually related to the surface properties.\textsuperscript{10} Therefore, smaller Pd NPs tends to show a superior catalytic activity as it has a higher surface-to-volume ratio.\textsuperscript{11,12} As the size of Pd NPs reduce, the surface energy of Pd NPs increase; thus, leading to a tendency of inter-particle aggregation. The aggregation of Pd NPs will reduce the catalytic efficiency of the catalysts.\textsuperscript{13} Therefore, stability of the Pd NPs is another crucial issue for their further application. One solution for Pd NPs stabilization involves the using of appropriate support materials. Various supports such as carbon,\textsuperscript{14,15} Al\textsubscript{2}O\textsubscript{3},\textsuperscript{16,17} mesoporous silica,\textsuperscript{18} and core-shell magnetic mesoporous\textsuperscript{19} have been used for the immobilization of Pd NPs owing to their excellent stability, high surface areas, and robust surface chemistry. All the above-mentioned materials have large specific surface areas which lead to the great dispersion of the NPs, thus prevent the aggregation of NPs and improve the activity of the catalyst system. However, for all the reported catalysts, poor accessibility to these active sites leads to reduction of the mass transfer effect. Silica supports with easily accessible high surface areas, not due
to the pores, therefore, are highly desirable. Vivek Polshettiwar reported the synthesis of fibrous silica nanospheres (KCC-1) by the microwave assisted hydrothermal technique and our laboratory research group reported synthesis of KCC-1 by the hydrothermal method.\textsuperscript{20-22} Furthermore, Liu et al. reported the fabrication of core-shell magnetic fibrous Fe$_3$O$_4$@SiO$_2$@KCC-1, which both have unique properties of KCC-1 and physical properties of magnetic materials.\textsuperscript{23} Therefore, the Fe$_3$O$_4$@SiO$_2$@KCC-1 is extremely useful in the design of supported catalysts because of the unique physical properties such as easily accessible of active sites, high surface area, reusability and superparamagnetism.

Recently, the transformation of harmful organic wastes into reusable compounds with low toxicity in aqueous solutions under mild conditions has become an extremely important area of study for chemists. As is well known, 4-nitrophenol (4-NP), a well-characterized industrial pollutant which has been listed on the “Priority Pollutant List” by the U.S. Environmental Protection Agency, is harmful to aquatic life and human health in terms of its toxicity, potential carcinogenicity, and mutagenicity.\textsuperscript{24-26} The use of catalytic reduction process for the disposal of 4-NP is expected to be the most efficient, green, and economical way.\textsuperscript{27, 28} Additionally, much recent work has been directed toward the Suzuki cross coupling reaction because it is the most powerful and widely used method for synthesis of biaryls which are important compounds in pharmaceutical, agrochemical, natural product, and advanced materials chemistry.\textsuperscript{29-31} Due to the inherent advantages, several heterogeneous catalysts for Suzuki cross coupling reaction have been developed. Particular attentions
are paid to the use of aryl chlorides as substrates because they are much cheaper and readily available than the usually used aryl bromides and iodides. Therefore, the catalytic activity of heterogeneous catalysts for Suzuki cross coupling of aryl chlorides is considerably challenged. So far, heterogeneous examples for the Suzuki cross coupling reaction of less reactive aryl chlorides are quite rare.\textsuperscript{32}

Based on the aforementioned considerations, herein, we report the synthesis of a novel core-shell magnetic fibrous Pd/Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@KCC-1 nanocatalyst system which has the following advantages (Scheme 1). First, the Pd/Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@KCC-1 nanocatalyst exhibits high accessibility and excellent catalytic activity for reduction of 4-NP and Suzuki cross coupling reactions of aryl chlorides with aryl boronic acids. Second, the catalyst could be easily recovered from the reaction mixture by a magnet because of the inner magnetic Fe\textsubscript{3}O\textsubscript{4} core. Third, the as-prepared catalyst is long-life, namely, it exhibits high reusability without visibly decrease in the catalytic performance after five cycles. Therefore, this study of Pd/Fe\textsubscript{3}O\textsubscript{4}@SiO\textsubscript{2}@KCC-1 nanocatalyst system provides a useful platform for exploring environmentally friendly Pd NPs based catalysts with superior activity, convenient recovery, and reusability.
2. Experimental section

2.1. Material

Tetraethoxysilane (TOES), 3-aminopropyltriethoxysilane (APTES), and Pd(II) acetate were purchased from Aladdin Chemical Co., Ltd. 4-NP, 1-pentanol, urea, and aryl halide were purchased from Lanzhou Aihua Chemical Company. Aryl boronic acids were obtained from Shanghai Chemical Reagent Co. Ltd. Organic solvents used were of analytical grade and did not require further purification.

2.2. Synthesis of Fe₃O₄ and Fe₃O₄@SiO₂ core-shell microspheres

The Fe₃O₄ NPs and Fe₃O₄@SiO₂ core-shell microspheres were synthesized according to the method reported.\(^3\) \(\text{FeCl}_3\) (2.6 g, 16 mmol), trisodium citrate (1.0 g, 3.4 mmol), and sodium acetate (NaAc) (4.0 g, 48.8 mmol) were dissolved in ethylene glycol (80 mL) with magnetic stirring. The obtained yellow solution was then transferred and sealed into a Teflon-lined stainless-steel autoclave. The autoclave was heated at 200°C for 12 h and then cooled to room temperature naturally. After treatment, the Fe₃O₄ NPs and Fe₃O₄@SiO₂ core-shell microspheres were collected by centrifugation and washed with ethanol twice.

Scheme 1 Preparation of the Pd/Fe₃O₄@SiO₂@KCC-1 nanocatalyst.
°C for 10 h, and then allowed to cool to room temperature. The black products were isolated by strong magnetic suction, washed with ethanol and deionized water several times.

The Fe$_3$O$_4$@SiO$_2$ nano-spheres were prepared through a versatile solution sol-gel method as follows. The Fe$_3$O$_4$ NPs (0.7 g) was dispersed to a three-neck round-bottom flask charged with absolute ethanol (140 mL), deionized water (40 mL), and ammonia solution (3 mL, 25%) by ultrasonication for 1 h. Then the mixture was mixed uniformity under mechanical stirring for 15 min at room temperature. Afterward, 2.0 mL TEOS was added dropwise and the mixture was allowed to proceed for 12 h under strong mechanical stirring. The resultant core-shell Fe$_3$O$_4$@SiO$_2$ nano-sphere product was separated by strong magnetic suction. Followed by washing with ethanol and deionized water several times.

2.3. Synthesis of Fe$_3$O$_4$@SiO$_2$@KCC-1 core-shell microspheres

The Fe$_3$O$_4$@SiO$_2$@KCC-1 core-shell microspheres were synthesized according to the literature method (scheme 1).

Fe$_3$O$_4$@SiO$_2$ (0.25 g) was dispersed in an aqueous solution (30 mL) containing urea (0.3 g) to from solution A under ultrasonication 1 h. CPB (0.5 g) was added to 0.75 mL of n-pentanol and 30 mL cyclohexane to from solution B. Solution A was added to solution B under stirring at room temperature. Then 1.25 g TEOS was added dropwise to the above solution. The resulting mixture was continually stirred for 1 h at room temperature and then placed into a 120 °C environment for 5 h, thus inciting a reaction. After the reaction was completed, the mixture was allowed to cool to room temperature, and the Fe$_3$O$_4$@SiO$_2$@KCC-1
core-shell microspheres was isolated by strong magnetic suction, washed with
deionized water and acetone, and dried overnight in a drying oven at 40 °C. This
material was then calcined at 550 °C for 5 h in air.

2.4. Preparation of the Pd/Fe₃O₄@SiO₂@KCC-1 nanocatalyst

The aminopropyl functionalized Fe₃O₄@SiO₂@KCC-1 nanocomposite
Fe₃O₄@SiO₂@KCC-1-NH₂ was synthesized by the following procedures (Scheme 1).
In a 100 mL round-bottom flask, Fe₃O₄@SiO₂@KCC-1 (0.6 g) and APTES (0.15 g)
were introduced into 50 mL toluene by ultrasonication for 1 h. The mixture was
refluxed for 12 h at nitrogen protection. After being cooled to room temperature, the
solution was isolated by strong magnetic suction, and the solid was washed several
times with ethanol to remove the remaining non-supported APTES. It was then dried
in a drying oven at 40 °C overnight, from which Fe₃O₄@SiO₂@KCC-1-NH₂
nanocomposites were obtained.
Pd/Fe₃O₄@SiO₂@KCC-1 nanocatalyst was synthesized by the following
procedures. A 100 mL round-bottom flask was charged with 0.5 g
Fe₃O₄@SiO₂@KCC-1-NH₂ nanocomposite, 0.1 g Pd(OAc)₂, 30 mL deionized water,
and 20 mL acetonitrile, after which it was ultrasonically dispersed for 30 min. The
obtained suspension was stirred at room temperature for 2 h. Subsequently, the fresh
NaBH₄ solution (0.2 M, 10 mL) was added into the above-mentioned suspension.
After 2 h of reduction, the product was isolated by strong magnetic suction, washed
repeatedly with deionized water and ethanol, and dried overnight in a vacuum at 30
°C.
2.5. General procedure for the reduction of 4-NP

The reduction of 4-NP by NaBH₄ was chosen as a model reaction for investigation of the catalytic performance of Pd/Fe₃O₄@SiO₂@KCC-1 nanocatalyst. In short, 2.8 mL of deionized water and 30 µL of 4-NP (0.01 M) were mixed with 0.2 mL of freshly prepared aqueous NaBH₄ solution (0.5 M), resulting in the formation of a deep yellow solution. Then, 5 µL Pd/Fe₃O₄@SiO₂@KCC-1 nanocatalyst (5 mgmL⁻¹) was added to this resulting solution, and the reaction was allowed to proceed until the solution became colorless. The reaction conversion was determined by the ultraviolet visible spectroscopy (UV-Vis).

Reduction reactions were amplified 40X to characterize the reusability of the Pd/Fe₃O₄@SiO₂@KCC-1 nanocatalyst. The catalyst was recovered using a powerful magnet, washed with water and ethanol and dried in a vacuum at room temperature before being used in the next catalytic run. The reduction of 4-NP catalytic process was carried out within 5 min for each cycle. This procedure was repeated five times.

2.6. General procedure for the Suzuki cross coupling reaction

After optimizing the reaction conditions (Table 2), Suzuki coupling reactions were performed by placing aryl halide (0.5 mmol), phenyl boronic acid (0.75 mmol), K₂CO₃ (1.0 mmol), EtOH (5.0 mL), and Pd/Fe₃O₄@SiO₂@KCC-1 nanocatalyst (0.2 mol% Pd) in a 10 mL round bottom flask. The mixture was stirred at 80 °C for required time under air. After the completion of the reaction, the mixture was cooled to room temperature and the Pd/Fe₃O₄@SiO₂@KCC-1 nanocatalyst was separated by powerful magnet. The reaction mixtures were analyzed by Gas chromatography (GC).
or GC–mass spectrometry (GC-MS).

The recovery and reuse of the Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst was described below. A mixture of 1-Iodo-4-nitrobenzene (0.5 mmol), Phenyl boronic acid (0.75 mmol), K$_2$CO$_3$ (1 mmol), EtOH (5.0 mL), and Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst (0.2 mol% Pd) was stirred at 80 °C under air. After being cooled to room temperature towards the end of the reaction, the Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst was separated by powerful magnet. The separated catalyst was washed with ethanol and water, respectively, dried under vacuum at room temperature, and reused. The reaction mixtures were analyzed by GC or GC-MS. This procedure was repeated five times.

2.7. Characterization

Powder X-ray diffraction (XRD) spectra were obtained by a Rigaku D/max-2400 diffractometer using Cu-K$_\alpha$ radiation in the 2θ range of 10–90°. Fourier transform infrared (FT-IR) spectra were collected on a Nicolet Nexus 670 FT-IR spectrometer equipped with a deuterated triglycine sulfate pyroelectric detector by using KBr pellets. Transmission electron microscopy (TEM) images were obtained on a Tecnai G2 F30, FEI, USA. The UV-Vis measurement was conducted with the UV2800PC UV-Vis spectrophotometer. Magnetic measurement of Fe$_3$O$_4$@SiO$_2$@KCC-1 and Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 was performed using a quantum design vibrating sample magnetometer (VSM) at room temperature in an applied magnetic field sweeping from −15 to 15 KOe. The reaction conversion was estimated using GC (P.E. Auto System XL) or GC–MS (Shimadzu QP2010S).
3. Results and discussion

3.1. Catalyst preparation and characterization

As can be seen in Scheme 1, Fe₃O₄@SiO₂@KCC-1 was first functionalized with APTES, then the aminopropyl groups can be acted as adsorption centers for Pd²⁺. When the NaBH₄ was added to the solution, the Pd²⁺ ions were reduced and immobilized on the fibres of Fe₃O₄@SiO₂@KCC-1.

Fig. 1a shows the FT-IR spectra of the Fe₃O₄@SiO₂@KCC-1 (black line) and Fe₃O₄@SiO₂@KCC-1-NH₂ (red line). The adsorption peaks at 1096 and 805 cm⁻¹ correspond to the antisymmetric and symmetric stretching vibration of Si–O–Si bond in oxygen-silica tetrahedron, respectively. The peaks at 467 and 563 cm⁻¹ correspond to Si–O, and Fe–O stretching, respectively. The strong peak at 3424 cm⁻¹ shows the large number of Si–OH groups which are proved to be advantageous for the modification of APTES on the Fe₃O₄@SiO₂@KCC-1 surface by hydrogen bonds.⁴ The adsorption peak at 2926 cm⁻¹ corresponds to -CH stretching. In the FT-IR spectrum of Fe₃O₄@SiO₂@KCC-1-NH₂, the peak around 3400 cm⁻¹ represents the adsorption of –OH and –NH₂ groups. The nitrogen, hydrogen, and carbon contents were 0.70%, 0.86%, and 3.20% measured by the elementary analysis, respectively. The FT-IR spectra and elementary analysis data revealed that the APTES was successfully grafted on the Fe₃O₄@SiO₂@KCC-1 surface, thus enabling them to act as robust anchors for metal NPs.

The XRD patterns of the Fe₃O₄@SiO₂@KCC-1 and Pd/Fe₃O₄@SiO₂@KCC-1 samples are shown in Fig. 1b. The broad peak between 20 and 30° corresponds to...
amorphous silica, indicating that the silica was successfully coated on the surface of Fe₃O₄ core. The XRD pattern of the Pd/Fe₃O₄@SiO₂@KCC-1 shows characteristic peaks of magnetite NPs. The sharp and strong peaks confirm that the products are well crystallized.

**Fig. 1** (a) FT-IR spectra of Fe₃O₄@SiO₂@KCC-1 and Fe₃O₄@SiO₂@KCC-1-NH₂, (b) The XRD of Fe₃O₄@SiO₂@KCC-1 and Pd/Fe₃O₄@SiO₂@KCC-1.

The Fe₃O₄ NPs show five characteristic diffraction peaks at 2 theta = 30.3°, 35.6°, 43.2°, 57.2°, and 63° corresponding to (220), (311), (400), (511) and (440), respectively. The characteristic diffraction peaks at 39.8° corresponding to Pd (111).

The XRD pattern of the Pd/Fe₃O₄@SiO₂@KCC-1 demonstrates that the Pd NPs were successfully immobilized on the Fe₃O₄@SiO₂@KCC-1 surface. The weight
percentage of Pd in the Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst, as determined by atomic absorption spectroscopic analysis, were 9.01 wt%.

The morphologies and structural features of the core-shell magnetic fibrous Fe$_3$O$_4$@SiO$_2$@KCC-1 and Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst were analyzed by TEM. The as-prepared core-shell magnetic fibrous Fe$_3$O$_4$@SiO$_2$@KCC-1 with fibrous structure were uniform and monodispersed (Fig. 2a). As is illustrated in Fig. 2a, the Fe$_3$O$_4$@SiO$_2$@KCC-1 possesses the core of Fe$_3$O$_4$ NPs and silica fibres. The average diameter of Fe$_3$O$_4$@SiO$_2$@KCC-1 and the Fe$_3$O$_4$ core were 350 nm and 100 nm, respectively. The TEM images shown in Fig. 2b further confirm that the distance between the two fibers is about 18 nm (Fig. 2b). The larger distance between the fibers leads to the easily loading the Pd NPs on Fe$_3$O$_4$@SiO$_2$@KCC-1, resulting in the significant increase in the accessibility of the active sites on Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst. TEM images of Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst were shown in Fig. 2c. The Pd NPs were remarkably dispersed on the surface of the core-shell magnetic fibrous Fe$_3$O$_4$@SiO$_2$@KCC-1. The Pd NPs have a narrow size distribution with a mean particle size of about 4 nm (Fig. 2c, inset). From the inset picture of Fig. 2c, it can be seen that the resolved lattice fringes of Pd (111) planes (d=0.225 nm) detected in the HRTEM image were attributed to Pd nanocrystals.
Fig. 2 (a) and (b) TEM images of Fe$_3$O$_4$@SiO$_2$@KCC-1, (c) TEM images of Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 (inset picture; size distribution histogram and HRTEM image of the Pd NPs crystal structure in detail on Fe$_3$O$_4$@SiO$_2$@KCC-1).

The elemental composition of the Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 samples was determined by EDX analysis and X-ray photoelectron spectroscopy (XPS) (Fig. 3). The EDX spectrum shown in Fig. 3a reveals that the as-prepared products contain Fe, Si, Pd, Cu, C, and O, respectively. Among these elements, Cu and C are generally influenced by the copper network support films and their degree of oxidation; Si, O, Fe and Pd signals result from the Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst.
Fig. 3 (a) EDS spectrum of Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1, (b) XPS spectrum of Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 (inset image: high resolution spectrum of Fe 2p and Pd 3d)

XPS was performed to investigate the chemical state of the surface of obtained Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst (Fig. 3b). The XPS elemental survey scan of the surface of Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst revealed the presence of Si, O, Fe, Pd, N, and C elements in the samples. As shown in Fig. 3b, inset, the peaks observed in the XPS spectra of Fe 2p at binding energies of 711 and 724.5 ev are characteristic of Fe$_3$O$_4$. Moreover, the Fig. 3b, inset, also shows the XPS spectrum of Pd 3d$\text{5}/2$ and Pd 3d$\text{3}/2$ at binding energies of 335 and 340.5 ev, respectively.
Fig. 4 Room temperature magnetization curves of Fe₃O₄@SiO₂@KCC-1 and Pd/Fe₃O₄@SiO₂@KCC-1 nanocatalyst (inset image: the separation-redispersion process of the Pd/Fe₃O₄@SiO₂@KCC-1 nanocatalyst by external magnetic field)

Magnetic measurements were carried out by VSM at room temperature. The magnetization curves measured for Fe₃O₄@SiO₂@KCC-1 and Pd/Fe₃O₄@SiO₂@KCC-1 are shown in Fig. 4. The magnetic saturation values of the Fe₃O₄@SiO₂@KCC-1 and Pd/Fe₃O₄@SiO₂@KCC-1 are 20.4 and 12 emu/g, respectively. The decrease in the saturation magnetization was due to the presence of the APTES and Pd nanoparticles on the Fe₃O₄@SiO₂@KCC-1 surface. Moreover, Fig. 4 (inset image) shows the separation-redispersion process of the Pd/Fe₃O₄@SiO₂@KCC-1 nanocatalyst demonstrating that the catalyst is drawn from the solution to the sidewall of the vial by applying an external magnetic field is removed. Therefore, the abovementioned results indicated an easy and efficient way to separate and recycle the Pd/Fe₃O₄@SiO₂@KCC-1 nanocatalyst from the solution by external magnetic field.

3.2. Catalytic reduction for 4-NP
The catalytic activity of the Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst was studied by reduction reactions of 4-NP to 4-AP in presence of NaBH$_4$. The reduction process was monitored by UV-Vis absorption spectroscopy. As shown in Fig. 5a, pure 4-NP solution exhibited a distinct absorption maximum at 317 nm, which shifts to 400 nm in the presence of alkali because of the formation of 4-nitrophenolate ions. The reduction of 4-NP to 4-AP can be obtained in the presence of NaBH$_4$ without any catalyst, but such required about 430 min. Furthermore, when the support Fe$_3$O$_4$@SiO$_2$@KCC-1 was added to the 4-NP and NaBH$_4$ solution, it was found that, the color of the reaction mixture did not change even after 120 min, suggesting the Fe$_3$O$_4$@SiO$_2$@KCC-1 support was almost inactive for the reduction reaction (Fig. S1). Because of this, Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst was added in order to significantly shorten the reaction time. When the Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst was added into the reaction mixture, the BH$_4^-$ ions were adsorbed on the surface of Pd NPs and transfer a surface-hydrogen species to the surface of the Pd NPs. Simultaneously, the 4-nitrophenolate were also adsorbed on the surface of the Pd NPs resulting in the rapid occurrence and completion of the reduction reactions.

The addition of Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst into the reaction mixture led to the decrease in the peak intensity of 4-nitrophenolate ion at 400 nm with the concomitant increase in the peaks corresponding to 4-AP at 300 nm (Fig. 5b) reflects decay of 4-NP and formation of 4-AP. Thus, the conversion of 4-NP to 4-AP can be monitored by tracking the changes in the absorbance peak of 4-nitrophenolate ions at 400 nm. When the absorbance peak value of 4-nitrophenolate ions at 400 nm
decreased to zero, indicated the successful conversion of 4-NP to 4-AP. Fig. 5b shows completely reduced 4-NP to 4-AP after 275 seconds. The concentration of NaBH$_4$ was very high compared with that of 4-NP, the reaction followed pseudo-first-order reaction kinetics.$^{22}$ Therefore, we used pseudo-first-order kinetics to evaluate the kinetic rate constant ($k_{\text{app}}$) of the current reaction[eqn(1)]. The reaction conversion was calculated from $C_t/C_0$ (Fig. 5c), which was measured using the relative intensity of UV-Vis absorbance ($A_t/A_0$) at 400nm. $C_t$ and $C_0$ are the concentrations of the 4-NP at reaction time $t$ and the initial stage, respectively.

$$\frac{dC_t}{dt} = -k_{\text{app}} t, \text{ or } \ln(C_t/C_0) = \ln(A_t/A_0) = -k_{\text{app}} t \quad (1)$$

As shown in Fig. 5c, the linear correlation between $\ln(C_t/C_0)$ and reaction time ($t$) was confirmed through pseudo-first-order kinetics. We calculated the reaction apparent kinetic rate constant $k_{\text{app}}$ to be $1.96 \times 10^{-2}$ for the Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 catalyzed reductions of 4-NP. Then, $k_{\text{app}}$ was normalized to the concentration of Pd, deriving $k_{\text{nor}}$ to reveal the intrinsic catalytic activity of the catalyst ($k_{\text{nor}} = k_{\text{app}}/c_0(Pd)$).$^{14}$ We compared the activity of the Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 with Pd catalysts loaded on different supports for the reduction of 4-NP (Table 1). In Table 1, the Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 shown excellent catalytic activity for the reduction of 4-NP by NaBH$_4$, with the highest $k_{\text{nor}}$(2.78 s$^{-1}$mM$^{-1}$) among the Pd catalysts loaded on different supports (SBA-15,$^{39}$ PEDOT (conducting polymer),$^{40}$ Microgel-PS (microgel coated polystyrene),$^{41}$ FG (functionalized graphene nanohybrids),$^{42}$PiHP (hyperbranched polymer)$^{43}$, and Al$_2$O$_3$. $^{44}$ It is also higher than the Pd nanoclusters$^{45}$ and Pd nanocrystals$^{46}$ based catalysts. The excellent catalytic activity of the
Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst owes to the ease of access of its active sites, and the low aggregation of the Pd NPs on the Fe$_3$O$_4$@SiO$_2$@KCC-1 support. In this situation, reactant can be easily adsorbed on the Pd NPs surface, which allows the reduction reactions to start quickly and finish rapidly.

Fig. 5 (a) UV-Vis spectra of 4-NP before and after adding NaBH$_4$ solution, (b) the successive reduction of 4-NP to 4-AP over the prepared Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst, (c) plot of $C_t/C_o$ and ln($C_t/C_o$) versus reaction time for the reduction of 4-NP over Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1.
Table 1
Comparison of apparent kinetic rate constant (k\text{app}) and normalized rate constants (k\text{nor}) of Pd catalysts loaded on different supports for the reduction of 4-NP

<table>
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<th>Samples</th>
<th>c\text{c,(4-NP)} (mM)\text{a}</th>
<th>c\text{c,(Pd)} (mM)\text{a}</th>
<th>k\text{app}(s\text{-1})\text{b}</th>
<th>k\text{nor}(s\text{-1} mM\text{-1})\text{c}</th>
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<tr>
<td>Pd/FG</td>
<td>5.8×10\text{-2}</td>
<td>4.72×10\text{-3}</td>
<td>2.35×10\text{-3}</td>
<td>0.498</td>
<td>42</td>
</tr>
<tr>
<td>Pd nanoclusters</td>
<td>2</td>
<td>1.6</td>
<td>7.89×10\text{-4}</td>
<td>0.005</td>
<td>45</td>
</tr>
<tr>
<td>Pd/PiHP</td>
<td>2.3</td>
<td>9×10\text{-2}</td>
<td>20×10\text{-3}</td>
<td>0.222</td>
<td>43</td>
</tr>
<tr>
<td>Pd nanocrystals</td>
<td>8×10\text{-2}</td>
<td>3.6×10\text{-2}</td>
<td>4.83×10\text{-3}</td>
<td>0.134</td>
<td>46</td>
</tr>
<tr>
<td>Pd/Al\text{2}O\text{3}</td>
<td>0.1</td>
<td>8.48×10\text{-3}</td>
<td>9.2×10\text{-3}</td>
<td>1.085</td>
<td>44</td>
</tr>
<tr>
<td>Pd/Fe\text{3}O\text{4}@SiO\text{2}@KCC-1</td>
<td>0.1</td>
<td>7.06×10\text{-3}</td>
<td>19.6×10\text{-3}</td>
<td>2.78</td>
<td>This work</td>
</tr>
</tbody>
</table>

\text{a}: concentration. \text{b}: apparent rate constant. \text{c}: rate constant normalized to the molar concentration of Pd. Data were given or calculated in the respective papers; some data were not obtained.

3.3. Catalyst testing for Suzuki cross coupling reaction.

The above results revealed that the Pd/Fe\text{3}O\text{4}@SiO\text{2}@KCC-1 nanocatalyst exhibited excellent for the reduction of 4-NP. We then further explored the catalytic activity of Pd/Fe\text{3}O\text{4}@SiO\text{2}@KCC-1 nanocatalyst for the Suzuki cross coupling reactions. To explore the optimal reaction conditions, a series of reactions was performed using several times, solvents, bases, and temperature to obtain the best possible combination. Initially, the experiment was performed using Suzuki cross-coupling reaction of 1-ido-4-nitrobenzene (0.5 mmol) with phenyl boronic acid (0.75 mmol) in presence of Pd/Fe\text{3}O\text{4}@SiO\text{2}@KCC-1 (0.2% Pd) and 5 mL ethanol in air at 80 °C for 1 h, 2 h, and 3h corresponding products were obtained in the following yields: 91.0%, 94.0%, and 97%, respectively (Table 2: entries 1-3). The reaction product was obtained the highest yield for 3 h, so the reaction time of 3 h was chosen. As it is known, solvent plays a crucial role in the rate of Suzuki coupling reactions. When the reactions were...
carried out in methyl alcohol, ethyl acetate, deionized water, and acetone under the same conditions, the products obtained in poor to moderate yields of 85.0%, 79.6%, 27.8%, and 30%, respectively (Table 2: entries 4-7). The reactions were carried out under similar conditions using different base such as K$_2$CO$_3$, CH$_3$COONa, NaOH, and (C$_2$H$_5$)$_3$N, the yields were 97%, 80.3%, 90.1%, and 80.9%, respectively (Table 2: entries 3, 8-10). For the reactions at room temperature, 40 °C, and 60 °C corresponding products were obtained in the following yields: 54%, 78.8%, and 90.8%, respectively (Table 2: entries 11-13). The best catalytic activity of the Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst was observed using ethanol as solvent, and K$_2$CO$_3$ as base at 80 °C (Table 2: entry 3).

After screening the reaction conditions, the catalyst system was studied for the Suzuki cross coupling reaction of various aryl halides and aryl boronic acids (Table 3). As listed in Table 3, when the coupling of aryl iodides with aryl boronic acids proceeded at 80 °C for 3 h, the corresponding products were obtained in high yields (Table 3: entries 1-8). The Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst was also revealed excellent catalytic activity for the coupling between aryl bromides and aryl boronic acids the reaction times approached 6 h (Table 3: entries 9-18). However, for the reactions of 1-bromo-2-nitrobenzene poor yields (Table 3, entries 13 and 18) were obtained, due to the electron-withdrawing –NO$_2$ group in the ortho position. It is worth noting that aryl iodides and aryl bromides containing electron-donating group, such as –CH$_3$, –OH, –NH$_2$ were found to be the more active than aryl iodides and aryl bromides containing electron-withdrawing, such as –NO$_2$ (Table 3).
Table 2
The effects of solvent, base and temperature on the Suzuki cross coupling of 1-Iodo-4-nitrobenzene with phenyl boronic acid using the Pd/Fe₃O₄@SiO₂@KCC-1 nanocatalyst.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Base</th>
<th>Temp (°C)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ethanol</td>
<td>K₂CO₃</td>
<td>80</td>
<td>1</td>
<td>91.0</td>
</tr>
<tr>
<td>2</td>
<td>Ethanol</td>
<td>K₂CO₃</td>
<td>80</td>
<td>2</td>
<td>94.0</td>
</tr>
<tr>
<td>3</td>
<td>Ethanol</td>
<td>K₂CO₃</td>
<td>80</td>
<td>3</td>
<td>97.0</td>
</tr>
<tr>
<td>4</td>
<td>Methyl alcohol</td>
<td>K₂CO₃</td>
<td>80</td>
<td>3</td>
<td>85.0</td>
</tr>
<tr>
<td>5</td>
<td>Ethyl acetate</td>
<td>K₂CO₃</td>
<td>80</td>
<td>3</td>
<td>79.6</td>
</tr>
<tr>
<td>6</td>
<td>Deionized water</td>
<td>K₂CO₃</td>
<td>80</td>
<td>3</td>
<td>27.8</td>
</tr>
<tr>
<td>7</td>
<td>Acetone</td>
<td>K₂CO₃</td>
<td>80</td>
<td>3</td>
<td>30.0</td>
</tr>
<tr>
<td>8</td>
<td>Ethanol</td>
<td>CH₃COONa</td>
<td>80</td>
<td>3</td>
<td>80.3</td>
</tr>
<tr>
<td>9</td>
<td>Ethanol</td>
<td>NaOH</td>
<td>80</td>
<td>3</td>
<td>90.1</td>
</tr>
<tr>
<td>10</td>
<td>Ethanol</td>
<td>(C₂H₅)₃N</td>
<td>80</td>
<td>3</td>
<td>80.9</td>
</tr>
<tr>
<td>11</td>
<td>Ethanol</td>
<td>K₂CO₃</td>
<td>25</td>
<td>3</td>
<td>54.0</td>
</tr>
<tr>
<td>12</td>
<td>Ethanol</td>
<td>K₂CO₃</td>
<td>40</td>
<td>3</td>
<td>78.8</td>
</tr>
<tr>
<td>13</td>
<td>Ethanol</td>
<td>K₂CO₃</td>
<td>60</td>
<td>3</td>
<td>90.8</td>
</tr>
</tbody>
</table>

Although the catalyst was active for aryl iodides and aryl bromides, our main objective was to design a nanocatalyst for the Suzuki coupling of challenging substrates, that is, the Suzuki coupling reactions of aryl chlorides with aryl boronic acids. In our initial attempts, we used the same optimized conditions for the aryl iodides and aryl bromides, but the products were obtained in low yields.
Table 3

Suzuki cross coupling reactions of aryl halides with aryl boronic acids using Pd/Fe@SiO₂@KCC-1 nanocatalyst.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aryl halide</th>
<th>Aryl boronic acid</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH₃-I</td>
<td>Cl-B(OH)₂</td>
<td>3</td>
<td>98.9</td>
</tr>
<tr>
<td>2</td>
<td>I-Cl</td>
<td>Cl-B(OH)₂</td>
<td>3</td>
<td>96.8</td>
</tr>
<tr>
<td>3</td>
<td>HO-I</td>
<td>Cl-B(OH)₂</td>
<td>3</td>
<td>99.0</td>
</tr>
<tr>
<td>4</td>
<td>O₂N-I</td>
<td>Cl-B(OH)₂</td>
<td>3</td>
<td>96.0</td>
</tr>
<tr>
<td>5</td>
<td>CH₃-I</td>
<td>Cl-B(OH)₂</td>
<td>3</td>
<td>99.0</td>
</tr>
<tr>
<td>6</td>
<td>I-Cl</td>
<td>Cl-B(OH)₂</td>
<td>3</td>
<td>97.8</td>
</tr>
<tr>
<td>7</td>
<td>HO-I</td>
<td>Cl-B(OH)₂</td>
<td>3</td>
<td>99.0</td>
</tr>
<tr>
<td>8</td>
<td>O₂N-I</td>
<td>Cl-B(OH)₂</td>
<td>3</td>
<td>97.0</td>
</tr>
<tr>
<td>9</td>
<td>Br-Cl</td>
<td>Cl-B(OH)₂</td>
<td>6</td>
<td>89.0</td>
</tr>
<tr>
<td>10</td>
<td>H₃C-Br</td>
<td>Cl-B(OH)₂</td>
<td>6</td>
<td>91.8</td>
</tr>
<tr>
<td>11</td>
<td>H₂N-Br</td>
<td>Cl-B(OH)₂</td>
<td>6</td>
<td>90.6</td>
</tr>
<tr>
<td>12</td>
<td>O₂N-Br</td>
<td>Cl-B(OH)₂</td>
<td>6</td>
<td>86.8</td>
</tr>
<tr>
<td>13</td>
<td>NO₂-Br</td>
<td>Cl-B(OH)₂</td>
<td>6</td>
<td>26.2</td>
</tr>
<tr>
<td>14</td>
<td>Br-Cl</td>
<td>Cl-B(OH)₂</td>
<td>6</td>
<td>90.8</td>
</tr>
<tr>
<td>15</td>
<td>H₃C-Br</td>
<td>Cl-B(OH)₂</td>
<td>6</td>
<td>93.2</td>
</tr>
<tr>
<td>16</td>
<td>H₂N-Br</td>
<td>Cl-B(OH)₂</td>
<td>6</td>
<td>91.8</td>
</tr>
<tr>
<td>17</td>
<td>O₂N-Br</td>
<td>Cl-B(OH)₂</td>
<td>6</td>
<td>87.3</td>
</tr>
<tr>
<td>18</td>
<td>NO₂-Br</td>
<td>Cl-B(OH)₂</td>
<td>6</td>
<td>28.1</td>
</tr>
</tbody>
</table>

Reaction condition: aryl halide (0.5 mmol), aryl boronic acid (0.75 mmol), K₂CO₃ (1.0 mmol), EtOH 5.0 mL, Pd/Fe@SiO₂@KCC-1 nanocatalyst (0.2 mol% of Pd), and 80 °C, in air.

Yield was determined by GC-MS or GC analysis.
Therefore, we optimized several reaction parameters, including the solvent, reaction temperature and referenced in literatures, and finally found that the use of tetra-n-butylammonium bromide (TBAB) and changed the solvent from ethanol to (n-methyl-2-pyrrolidone) NMP and raised the reaction temperature to 140 °C was necessary to achieved good yields. After optimizing the reaction conditions, the Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst was studied for Suzuki cross coupling reactions of several aryl chlorides with aryl boronic acids, which are summarized in Table 4.

Table 4
The Suzuki cross coupling reactions of aryliclorides with arylicboronic acids using Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aryl chlorides</th>
<th>Aryl boronic acid</th>
<th>Time (h)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cl</td>
<td>Cl</td>
<td>12</td>
<td>83.2</td>
</tr>
<tr>
<td>2</td>
<td>H$_3$C</td>
<td>Cl</td>
<td>12</td>
<td>86.0</td>
</tr>
<tr>
<td>3</td>
<td>HO</td>
<td>Cl</td>
<td>12</td>
<td>85.8</td>
</tr>
<tr>
<td>4</td>
<td>H$_3$C</td>
<td>Cl</td>
<td>12</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td>Cl</td>
<td>Cl</td>
<td>12</td>
<td>83.8</td>
</tr>
<tr>
<td>6</td>
<td>H$_3$C</td>
<td>Cl</td>
<td>12</td>
<td>87.8</td>
</tr>
<tr>
<td>7</td>
<td>HO</td>
<td>Cl</td>
<td>12</td>
<td>86.2</td>
</tr>
<tr>
<td>8</td>
<td>H$_3$C</td>
<td>Cl</td>
<td>12</td>
<td>79.8</td>
</tr>
</tbody>
</table>

Reaction condition: aryl chlorides (0.5 mmol), aryl boronic acid (0.75 mmol), K$_2$CO$_3$ (1.0 mmol) were added in 5 ml NMP at 140 °C for 12 h in the presence of TBAB (0.05 mmol) and Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 (2.5 mol% of Pd). Yield was determined by GC-MS or GC.
Interestingly, the Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst was also revealed excellent catalytic activity for the Suzuki coupling between aryl chlorides and aryl boronic acids. The highly dispersed smaller Pd NPs and easy accessibility of active sites, as few heterogeneous catalyst systems show good activity toward aryl chlorides, which are sustainable substrates for Suzuki cross coupling reactions, under ligand-free condition.  

3.4. Reusability of the Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst.

For practical application of heterogeneous systems, the recyclability of catalyst is an important factor. The stability and reusability of the Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst were performed by catalyzed the reduction of 4-NP and Suzuki coupling reaction of 1-Iodo-4-nitrobenzene with Phenyl boronic acid.

![Fig. 6](Image)

**Fig. 6** The reusability of Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst for the reduction of 4-NP by NaBH$_4$ and Suzuki cross coupling reaction of 1-iodo-4-nitrobenzene with phenyl boronic acid.

As shows in Fig. 6, the recovered Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst exhibited almost constant catalytic activity for at least five successive cycles in the reduction of
4-NP and Suzuki cross coupling reaction of 1-iodo-4-nitrobenzene with Phenyl boronic acid. Moreover, the catalyst was easily separated magnetically from the reaction mixture, washed with ethanol and deionized water, and finally dried for the next run. This result suggests that the Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst possesses robust stability.

4. Conclusion

In this study, a novel core-shell magnetic fibrous Fe$_3$O$_4$@SiO$_2$@KCC-1 based Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst with easy accessibility of the active sites was successfully synthesized. The catalyst could be easily recovered by applying an external magnetic field, and reused for next catalytic run. The Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst showed excellent catalytic activity for the reduction of 4-NP and Suzuki coupling reaction of a range of aryl bromides and iodides with aryl boronic acids. Notably, the catalyst was also displayed good catalytic activity for Suzuki coupling reaction of aryl chlorides with aryl boronic acids. Moreover, the catalyst was chemically stable and could be easily recycled for at least five times in the corresponding reaction without reduction in the catalytic activity. The Pd/Fe$_3$O$_4$@SiO$_2$@KCC-1 nanocatalyst acts as relatively green, superparasitism, eco-friendly nature and convenient recovery, and as a promising candidate for Pd NPs based catalytic applications in industrial synthesis.

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References
