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Magnetically Recyclable Pd/Fe_3O_4/g-C_3N_4 as Efficient Catalyst for the Reduction of nitrophenol and Suzuki-Miyaura Reaction at Room Temperature

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Herein, we present the design and synthesis of a novel magnetic stable and recyclable catalyst Pd/Fe_3O_4/g-C_3N_4 with approachable active palladium nanoparticles (Pd NPs) based on the platelet-like graphitic carbon nitrides (g-C_3N_4). The Pd NPs, g-C_3N_4 and magnetic particles (Fe_3O_4) are tightly connected through non-covalent interactions owing to the layered structure of g-C_3N_4 with abundant nitrogen atoms, facilitating the stability of Pd/Fe_3O_4/g-C_3N_4 and activating the Pd NPs at the same time. The Pd/Fe_3O_4/g-C_3N_4 catalyst with a narrow particle size distribution (2.55 nm) of Pd NPs displayed the maintenance of the planar structure of g-C_3N_4. The activity parameter of the catalyst turned out to be excellent (12.4 s^{-1} mM^{-1}) by fitting the curves derived from the reduction of nitrophenol. Meanwhile, the Suzuki-Miyaura coupling reaction at room temperature processed smoothly with the Pd/Fe_3O_4/g-C_3N_4 catalyst. It is meaningful to stress that 2-bromobenzonitrile and *p*-tolylboronic acid could afford the medical intermediate sartanbiphenyl at total conversion without side reactions in 25 min. Furthermore, the nanocatalyst owes the properties of easy recycle using a powerful magnet as well as high turnover frequency (at least 5 runs) with retention of high catalytic activity.

Keywords: Magnetic Pd nanocatalyst; Fe_3O_4; g-C_3N_4; nitrophenol; Suzuki-Miyaura Reaction

The Pd-catalyzed Suzuki-Miyaura reactions, considering its great applied potential that exists in the chemical transformations to prepare high-value products, has been attracting significant attention. The biaryl compounds are of the most crucial organic synthetic intermediates of liquid crystals, polymers, pesticide and medicine[1-3], which could be effectively prepared by the Suzuki coupling reaction. However, the Suzuki coupling reaction has traditionally processed smoothly using homogeneous soluble palladium catalysts with the aid of phosphine ligands under inert atmosphere[4]. In addition, there are still problems on the separation and recovery of the catalysts, which will cause contamination in the final product and in turn limit their industrial application[5, 6].

An alternative solution to solve the problem is the application of metal nanoparticles (NPs). Owing to the strong electrical and chemical properties of the metal NPs, especially the Pd NPs, great potentials in fuel cells[7], hydrogenation[8], dehydrogenation[9], and C–C coupling[10] have been exploited, resulting in excellent catalytic efficiency with high stability in the reaction process. Reetz et al. reported that the Pd NPs prepared by the electrochemical method could catalyze the Suzuki coupling reaction of the bromide and iodide substrate smoothly[11]. It is believed that the high dispersion in the catalysis system and the three-dimensional rotational freedom of the active Pd NPs mainly dominate the catalytic activity. Though thought to be the frontier between the homogeneous and heterogeneous catalysts[12], the metal NPs are beset by the difficulties in size control and recyclability. Smaller size of the Pd NPs, with high specific surface area, would result in high catalytic performance in terms of more active sites. However, the drawbacks of the easy aggregation between the smaller Pd NPs with higher surface energy and low efficiency level largely confined their practical applications[13-15]. Based on this, various supports for the dispersion and stabilization of the Pd NPs, such as silica materials , metal oxides (CeO_2, ZrO_2, MgO, Fe_3O_4 and etc.), carbon, inorganic porous materials, LDH and polymers[16], are of great potential in the balance of the size effect and the catalytic efficiency. Furthermore, the use of supports will benefit the recycle and reuse of the catalysts.

The inorganic porous materials, as an important branch of the supports, have recently been the topic research issue in the heterogeneous catalysis on account of their intrinsic structural advantages and superior catalytic efficiency in the catalytic applications. Among the various inorganic porous materials for the Pd NPs, the nano-lamellar graphitic carbon nitrides (g-C_3N_4) have attracted much attention in the area of catalysis due to the layered structure similar to graphite, nitrogen rich for the anchor of Pd NPs and surface defects for further chemical modifications. The g-C_3N_4 and the modified g-C_3N_4 activated Pd NPs have been successfully applied in the reduction of various substances like alkene, alkyne, quinoline, phenol and nitriles[17] with excellent conversions and selectivity.

Very recently, the Suzuki coupling reactions were studied in the presence of the g-C_3N_4 supported Pd NPs[18], though high yields were obtained with Pd/g-C_3N_4, the separation and reuse of the catalyst using the traditional methods of filtration and centrifugation remains not convenient for practical use. The introduction of magnetic particles (Fe_3O_4)[19] into the original Pd/g-C_3N_4 could be the most effective solution in view of the advantages of the easy combination and high stability of the Fe_3O_4 NPs with Pd/g-C_3N_4 through non-covalent interaction and the convenient separation of the used catalyst from the reaction system with a permanent magnet without obvious loss.

Additionally, 4-nitrophenol, known as hazardous substances due to their poisonousness, genotoxicity, and carcinogenicity, can be transformed into nontoxic substances through the catalytic reduction process which is efficient and green[20-22]. Therefore, the catalytic reaction of 4-NP by BH_4^- is always adopted to confirm the catalytic performance of the prepared catalyst[23].

In this paper, as the further extension of the research of our group[18], we improved the design and synthesis strategy of the Pd/g-C_3N_4 and combined the magnetic Fe_3O_4 with the as-prepared Pd/g-C_3N_4 to obtain the novel magnetic stable and recyclable catalyst Pd/Fe_3O_4/g-C_3N_4 for the purpose of developing a catalytic system where the catalyst could be recycled with a powerful magnet and the catalyst could catalyze the Suzuki-Miyaura reaction with excellent results. The Pd/Fe_3O_4/g-C_3N_4 catalyst was synthesized easily by depositing the Pd NPs on the g-C_3N_4 support through chemical reduction of the $Pd(OAc)_2$ solution containing the g-C_3N_4 and Fe_3O_4 by $NH_2NH_2 \cdot H_2O$. The Suzuki coupling reaction test of the phenyl iodides and bromobenzenes processed smoothly with high conversions and selectivity under ambient atmosphere and the catalytic efficiency turned out to be excellent in the reduction process of the 4-NP. More importantly, the used catalyst retrieved by a powerful magnet could be recycled for five runs with high catalytic performance.

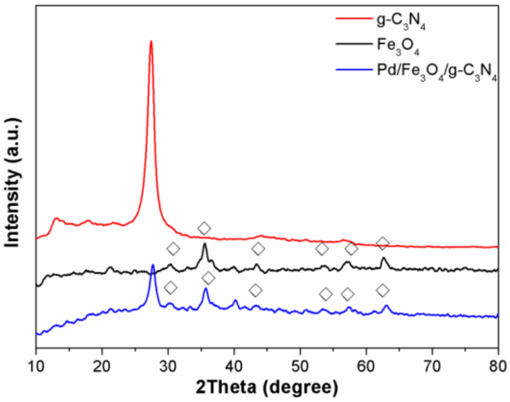

Fig. 1 Powder X-ray patterns of g-C_3N_4, Fe_3O_4 and Pd/Fe_3O_4/g-C_3N_4 catalyst.

To achieve the crystallinity and material component of g-C_3N_4, Fe_3O_4 and Pd/Fe_3O_4/g-C_3N_4, XRD measurements were conducted. The peak at 27.46° (Fig. 1) corresponds to the (002) interlayer stacking peak of g-C_3N_4[24]. The relative small (100) peak at 13.17° originates from the in-plane structural packing mechanism[25]. Pure Fe_3O_4 exhibits high similarity with the data reported in the literature (JCPDS-International center diffraction data, PDF card 79-0419[26]. Owing to the interaction of the Pd NPs and g-C_3N_4 in Pd/Fe_3O_4/g-C_3N_4, the intensity of the (002) peak of g-C_3N_4 weakened largely and the (100) peak vanished. The indexed (111) and (200) diffraction peaks at 39.66° and 46.46° are ascribed to the Pd NPs (card 46-1043), corresponding to the face centered cubic (fcc) Pd lattices[18]. The Fe_3O_4 peaks of the catalyst basically remain the same with the pure Fe_3O_4.

The information of chemical bonds are depicted in Fig. 2 by means of FT-IR spectra. The single peak at 3200 cm^{-1} of g-C_3N_4 are the stretching vibration of NH unit, featured to be extended widely. The multiple peaks in 1650-1000 cm^{-1} are designated to be the characteristic peaks of s-triazine unit for the emerge of C=N and C-N[27]. The spectrum of Fe_3O_4 exhibits two small but distinct peaks at570 cm^{-1} and 420 cm^{-1}, which is known as the vibrations of Fe^{2+}-O^{2-} and Fe^{3+}-O^{2-} respectively[28]. Interestingly, with introduction of Pd and Fe_3O_4, the peak shift and intensity of the spectrum in the Pd/Fe_3O_4/g-C_3N_4 is identical with that of g-C_3N_4, confirming the combination of Pd NPs, Fe_3O_4 and g-C_3N_4 through non-covalent interactions.

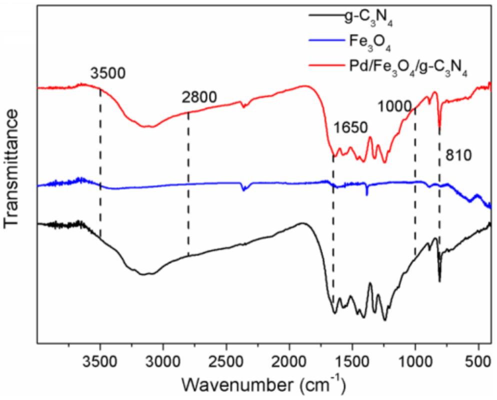

Fig. 2 The FT-IR spectra of g-C_3N_4, Fe_3O_4 and Pd/Fe_3O_4/g-C_3N_4.

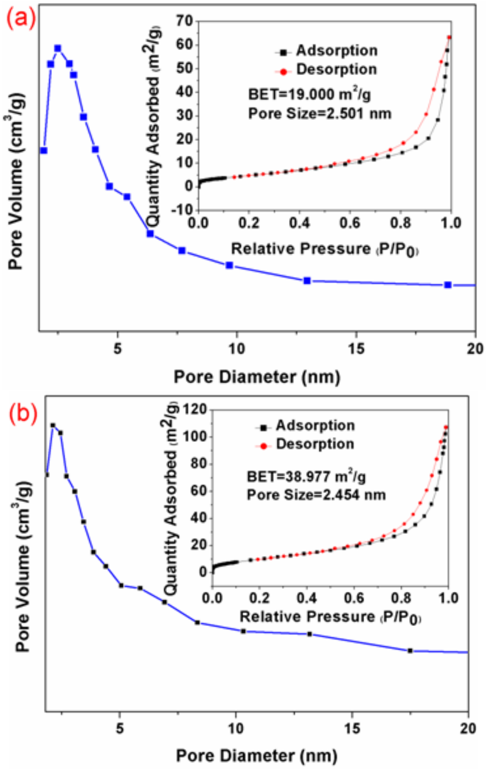

Fig. 3 Pore size distribution curves for (a) g-C_3N_4 support. (b) Pd/Fe_3O_4/g-C_3N_4 catalyst.

In order to obtain structural information of the prepared materials on a mesoscopic scale, the isotherms and the pore size distributions were measured by BET method. The g-C_3N_4 support possesses a surface area of 19.000 m^2/g and a typical mesoporous structure with a pore size of 2.501 nm (Fig. 3a inset), derived from the curve trend[29]. After the formation of Pd/Fe_3O_4/g-C_3N_4 with g-C_3N_4 as the support (Fig. 3b), the tendency of the hysteresis loops and pore diameter stayed unchanged and larger specific surface area are induced by the Fe_3O_4, suggesting the preservation of morphology of the g-C_3N_4. The Pd contents in the prepared catalyst were determined to be 0.71 % by means of ICP-AES.

TEM analysis was applied to characterize the microstructure of the g-C_3N_4, Fe_3O_4 and the Pd/Fe_3O_4/g-C_3N_4 catalyst and the results are shown in Fig. S4. The g-C_3N_4 support, based on Fig. S4a, has a typical platelet-like morphology with several layers. Contrary to the reported spherical structure, the Fe_3O_4 NPs (Fig. S4b) exhibited a parallelogram micropattern with the size ranging from 5 nm to 18 nm. After the loading of Pd NPs and Fe_3O_4 on the g-C_3N_4 (Fig. S4c), smaller sized Pd NPs with mean size of 2.55 nm were obtained by averaging 200 Pd NPs randomly chosen compared with Pd/g-C_3N_4[18], which may be the lift of catalysis efficiency due to small size effect (Fig. S4c inset). Interestingly, the distribution of Fe_3O_4 did not reflect regularity and they are more like surrounded on the edge of the g-C_3N_4. It is the strong electron donating properties of the nitrogen of g-C_3N_4 that largely stabilize the Pd/Fe_3O_4/g-C_3N_4.

The selective reduction of 4-nitrophenol (4-NP) was modeled in the presence of an excess amount of $NaBH_4$ to figure out the efficiency of the as-prepared Pd/Fe_3O_4/g-C_3N_4 catalyst. Owing to the strong absorption of the substrates, the transformation process could be easily monitored by UV-Vis absorption spectroscopy quantitatively and qualitatively. After the mixing of $NaBH_4$ into the 4-NP aqueous solution, 4-nitrophenolate was screened accompanied with the color changing from colorless to yellowish from bare eye. Furthermore, the absorption single peak at 317 nm characteristic for 4-NP redshifted to 400 nm with the outcome of 4-nitrophenolate ion for higher conjugation degree (Fig. S3a). The color faded from yellowish to colorless slowly after the addition of Pd/Fe_3O_4/g-C_3N_4 with the absorption peak at 400 nm gradually down to be vanished in 210 seconds and emerge of a new peak at 300 nm characteristic for 4-AP (Fig. S3b). As comparison, the same processes were conducted in the absence of the catalyst. With the aid of pure g-C_3N_4 or Fe_3O_4 even in 30 min, the peak at 400 nm kept unchanged, indicating that Pd NPs dominate the catalytic process. Interestingly, when merely $NaBH_4$ was put into the 4-NP solution, the reaction occurred slightly after 20 h with minor decrease of the peak at 400 nm.

We further tested the general applicability of the Pd/Fe_3O_4 /g-C_3N_4 by amplifying the reactions to 0.5 mmol with various nitroarenes in pure water at room temperature in the presence of $NaBH_4$ as the reducing agent (Table S2).

With high catalytic activity of the Pd/Fe_3O_4/g-C_3N_4 towards the reduction of nitroarenes by $NaBH_4$ at hand, we further tested the versatility of the catalyst for the Suzuki cross coupling reaction under ambient conditions on account of its the Mott-Schottky heterojunction that benefits the charge transportation[30]. As known, the Sartan drugs have been the most effective pharmacotherapy to resist hypertension after they were launched, which makes the sartanbiphenyl intermediate the pivotal role for the giant market[31]. The coupling system of *o*-bromobenzonitrile and *p*-tolylboronic acid with Pd/Fe_3O_4/g-C_3N_4 as the catalyst under ambient atmosphere was modeled to ascertain the optimum conditions. Effect of the reaction time durations, temperatures(Table S3), solvents(Table S4), substrates(Table S5) has been tested on the Suzuki-Miyaura reaction, 1H NMR and Mass of coupling products are shown in Fig S5 and Fig S6, which is can be seen in Supporting information.

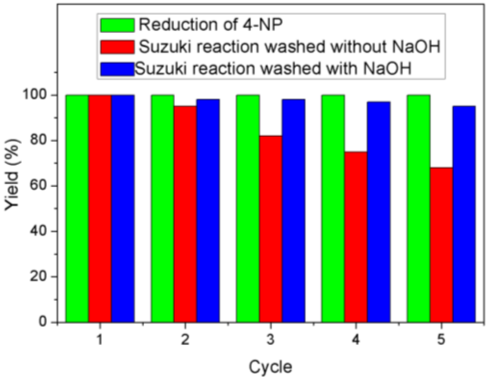

Fig. 4 The recycling of the Pd/Fe_3O_4/g-C_3N_4 catalyst for the catalytic transformation of 4-NP and Suzuki-Miyaura reaction.

The efficiency, stability, sustainability, and recyclability (ESSR) criteria[12] is concerned as a pivotal issue for evaluating a heterogeneous catalyst, especially the one containing magnetic. Here, the recyclability of the catalyst using the chemical reduction of 4-NP and the Suzuki-Miyaura reaction towards the synthesis of sartanbiphenyl were tested with 0.13 mol% Pd/Fe_3O_4/g-C_3N_4. After each cycle of the reaction for the 4-NP to 4-AP, the catalyst was recycled with external magnetic field. It is interesting to note that the reduction process of 4-NP proceeded smoothly with total conversion of the raw material to the desired product even after 5 runs. When the same process was applied to the Suzuki coupling reaction, however, gradually lowered conversions after 5 cycles were emerged. Notably, the catalyst recovered its catalytic efficiency once it was washed one more time with 1 M NaOH solution and the catalytic performance stayed almost unaltered after 5 runs with high yields. It is the NaOH solution that benefited the removal of the residue formed in the last turn, which in turn reactivated the catalytic activity. The catalyst can be recycled and reused for 5 runs without much loss of the catalytic efficiency. The excellent results owe to the stable and active Pd NPs on the support of Fe_3O_4/g-C_3N_4 where abundant amino groups as anchor sites locate in the planar g-C_3N_4.

In summary, the Pd/Fe_3O_4/g-C_3N_4 magnetic nanocatalyst with high stability and activity of the Pd NPs was successfully synthesized on the foundation of g-C_3N_4 powder and the Fe_3O_4 magnetic nanoparticles. The specific properties of the planar layers with electron conjugation with amino groups of g-C_3N_4 favor the anchor of Fe_3O_4 and Pd NPs, and stabilization of the Pd/Fe_3O_4/g-C_3N_4 catalyst. The prepared catalyst demonstrated considerable catalytic efficiency in the Suzuki-Miyaura reaction with high selectivity under eco-friendly conditions. Furthermore, the catalyst performed well in the recycling experiments and it could be recovered from the reaction solution with a powerful magnet. No obvious loss of catalytic activity was screened after 5 runs, proving the Pd/Fe_3O_4/g-C_3N_4 as a novel, effective and magnetic recyclable catalyst.

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