

Magnetic Core–Shell to Yolk–Shell Structures in Palladium-Catalyzed Suzuki–Miyaura Reactions: Heterogeneous versus Homogeneous Nature

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This study describes a comparative investigation on the heterogeneous versus homogeneous nature of the Pd-catalyzed Suzuki–Miyaura cross-coupling reaction mechanism with specific magnetic hierarchical core–shell and yolk–shell structures. The hierarchical core–shell Fe₃O₄@SiO₂-Pd@mCeO₂ (m=mesoporous) catalyst contains a core of nonporous silica-sheltered magnetite (Fe₃O₄) nanoparticles (NPs), a transition layer of active palladium (Pd) NPs, and an outer shell of porous ceria (CeO₂). The magnetic yolk–shell Fe₃O₄@h-Pd@mCeO₂ (h= hollow) catalyst was prepared by selectively etching the nonporous silica interlayers. Notably, the results of the hot-filtration heterogeneity test, the effect of Pd concentration, and

solid-phase poisoning, indicate that the two kinds of catalysts function in Pd-catalyzed Suzuki–Miyaura cross-coupling reactions through different catalytic mechanisms. Moreover, both catalysts demonstrated better catalytic activity than the $Fe_3O_4@SiO_2-Pd$ catalyst. This finding can be ascribed to the outermost CeO₂ shell having a high concentration of trivalent cerium and oxygen vacancies, which gives rise to the increased electron density of Pd NPs, and a faster rate-determining step in the oxidative addition reaction for the Suzuki reaction. In addition, we propose a feasible mechanism elucidating the synergistic effect between the supporting CeO₂ and active species.

Introduction

The Pd-catalyzed Suzuki-Miyaura cross-coupling reaction is one of the most useful tools for the formation of carboncarbon (C–C) bonds in organic synthesis.^[1] This reaction has become a main branch in modern organic synthetic chemistry for the synthesis of bioactive compounds,^[2] polymers,^[3] pharmaceutical intermediates,^[4] and functional materials.^[5] Generally, the homogeneous metal Pd complexes are known to display better catalytic activities than the heterogeneous Pd catalyst systems. However, when it comes to large-scale application in liquid-phase reactions, more difficulties arise, such as the barriers of recycling of the catalyst, obstacles in further purification of the final product, and difficulties in preventing the Pd catalyst from aggregating. Meanwhile, the removal of Pd complexes from reaction systems needs further improvement, considering their high cost and potential toxicity. Therefore, much attention has been directed towards the development

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of heterogeneous Pd catalyst systems with the metal Pd NPs loaded on inorganic or organic supports. $^{\rm [6]}$

In recent years, a broad array of highly effective heterogeneous Pd catalysts has been developed for Suzuki reactions.^[7,8] These Pd catalysts can be used repeatedly and consequently offer an efficient and economical way to carry out Suzuki reactions. Moreover, they do not require phosphine ligands, are not susceptible to moisture or air, and provide products in high yields with short reaction times. As such, heterogeneous Pd catalysts are considered to be promising alternatives to homogeneous metal Pd complexes. However, an inherent problem with heterogeneous Pd-catalyzed Suzuki reactions is their mechanistic nature.^[6,9–14] Viewpoints about this in the literature differ as to whether heterogeneous Pd-catalyzed cross-coupling reactions result from the leaching of active Pd NPs or the supporting Pd NPs themselves.^[9, 10, 15-24] A direct comparison of the results of each case proves futile, since the reaction conditions, the nature of the employed Pd NPs and their stabilizers vary from experiment to experiment. Therefore, the design of strategies to avoid the variety of factors for comprehensive mechanistic study is a considerable challenge.

Generally, nano-sized noble-metal catalysts have more exposed surface area that enhances catalytic activity.^[25] However, owing to their high surface energies, naked noble metal NPs tend to leach and sinter during catalytic reactions and lead to a sharp drop in catalytic activity and selectivity in reactions. Another considerable factor underlying the utilization of Pd NPs is the capacity to extract them from an intricate heterogeneous system.^[26-28] Therefore, the design of structures for so-

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phisticated mechanistic study should also avoid these factors. More recently, novel hierarchical core-shell structures composed of an inner protected Fe₃O₄ core-shell nanostructure, a porous outer shell, and noble-metal NPs active species clamped by the inside and outside shell, which can stabilize the active metal NPs to a higher degree and reduce the amount of leaching.^[29-35] The magnetic yolk-shell structures, which have a characteristic hollow component, an extraordinary configuration of a movable magnetic interior core, void space, and a penetrable outer shell renders them viable candidates.^[36-42] As such, they have also been a hot spot of scientific research of late motivating application research in areas like photocatalysis,^[43] nanoscale reactors,^[44] and drug carriers.^[45] Zhao et al. synthesized multicomponent and multifunctional Fe₃O₄@SiO₂-Au@mSiO₂ hierarchical core-shell structures for the reduction of 4-nitrophenol and styrene epoxidation.^[46] Our team also synthesized a similar hierarchical Fe₃O₄@C-Pd@mCeO2 catalyst for the Suzuki-Miyaura cross-coupling reactions and the reduction of 4-nitrophenol.^[47] However, with the Fe₃O₄@C-Pd@mCeO₂ catalyst it is difficult to form the yolkshell structures. Most of the CeO₂ layers crack after high-temperature-calcination removal of the carbon shell.

In this study, we report the design and fabrication of a welldefined magnetic hierarchical Fe₃O₄@SiO₂-Pd@mCeO₂ catalyst and the corresponding magnetic yolk-shell Fe₃O₄@h-Pd@mCeO₂ catalyst. The mesoporous CeO₂ shell had a Ce^{3+}/Ce^{4+} redox cycle. In tandem with the active noble-metal NPs, the mesoporous shell enhanced catalytic and electrochemical performances because of the synergetic effects between CeO₂ NPs and noble-metal NPs.^[48] Both the hierarchical Fe₃O₄@SiO₂-Pd@mCeO₂ core-shell and Fe₃O₄@h-Pd@mCeO₂ yolk-shell structures were highly mesoporous for the permeation of reactants and products, and magnetic for reusability, and had good dispersibility in water and ethanol. The catalytic activity was systematically evaluated by assessing each structure's application in the Suzuki-Miyaura cross-coupling reactions. These specific core-shell and yolk-shell structures provided a platform from which we studied the aforementioned "mechanistic nature" issue witnessed in Pd-catalyzed cross-coupling reactions. We also propose a feasible mechanism explaining the electron-donating effect between the CeO₂ support and the Pd NP active species and describe the catalytic reaction mechanism with the characterization of catalyst and the experimental results.

Results and Discussion

The procedure for the synthesis of the magnetic hierarchical core–shell and yolk–shell catalysts is shown in Scheme 1. First, the Fe₃O₄ NPs were modified by trisodium citrate (Na₃Cit) through a solvothermal reaction.^[46] The modified Fe₃O₄ NPs exhibited remarkable dispersibility in the polar solvents (water and ethanol). Second, we coated a uniform SiO₂ shell on the surface of Fe₃O₄ NPs by using a sol–gel process consisting of hydrolysis and condensation of tetraethyl orthosilicate (TEOS) in an ethanol/ammonia mixture. Thus we created a Fe₃O₄@SiO₂ core–shell structure. To deposit Pd NPs efficiently, Fe₃O₄@SiO₂

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Scheme 1. Synthesis of $Fe_3O_4@SiO_2\mbox{-}Pd@mCeO_2$ and $Fe_3O_4@h\mbox{-}Pd@mCeO_2$ NPs.

modified with (3-aminopropyl)triethoxysilane NPs were (APTES). This process imbued the surface with amino groups, which increased the coordination bond interaction of Pd. Next, Pd NPs were introduced to the surface of the Fe₃O₄@SiO₂ NPs by using a PdCl₂ precursor with NaBH₄ reductant. The prepared Pd-immobilized Fe₃O₄@SiO₂ NPs are denoted Fe₃O₄@SiO₂-Pd. Finally, using Ce(NO₃)₃·6H₂O as the cerium source and hexamethylene tetramine (HMT) to incrementally produce OH-, we created a homogeneous CeO₂ coating around the Fe₃O₄@SiO₂-Pd NPs by means of a sol-gel process.^[49] Subsequently, we eliminated HMT with a calcination process, creating Fe₃O₄@SiO₂-Pd@mCeO₂ NPs with sandwich-like structures. Finally, we selectively etched the nonporous silica interlayers using an alkaline (NaOH, 10 wt%) solution, giving rise to the formation of a magnetic yolk-shell Fe₃O₄@h-Pd@mCeO₂ catalyst.

The morphology and structure of the obtained composites were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), high-resolution (HR)-TEM, high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM), and energy-dispersive X-ray spectroscopy (EDS) mapping. Figure 1a, b shows the SEM images of the Fe₃O₄ NPs and Fe₃O₄@SiO₂ NPs. Clearly, the Fe₃O₄ NPs are 200–250 nm and spherical, while the later-obtained Fe₃O₄@SiO₂ NPs (Figure 1b) are a larger 270–320 nm.



Figure 1. SEM images of (a) Fe_3O_4 , (b) $Fe_3O_4@SiO_2$ (inset is the corresponding TEM image), (c) $Fe_3O_4@SiO_2-Pd@mCeO_2$, (d) $Fe_3O_4@h-Pd@mCeO_2$.



The uniform SiO₂ shell, about 35 nm thick, formed on individual Fe₃O₄ NPs seeds (inset in Figure 1b), creating a core-shell Fe₃O₄@SiO₂ structure. The SEM images in Figure 1c illustrate that the Fe₃O₄@SiO₂-Pd@mCeO₂ catalyst retains a clean spherical shape after loading onto the CeO₂ shell. However, the yellow coil in Figure 1d indicates that parts of the spherical Fe₃O₄@h-Pd@mCeO₂ catalyst were broken down in the etching process. Figures S1a and b in the Supporting Information show the EDS spectra of Fe₃O₄@SiO₂-Pd@mCeO₂ and Fe₃O₄@h-Pd@mCeO₂ catalysts. We estimated the loading amounts of Pd to be 2.51 and 2.83 wt%, respectively.

The TEM image of $Fe_3O_4@SiO_2-Pd$ (Figure 2a) indicates the numerous Pd NPs deposited uniformly on the SiO_2 shell. After further deposition of CeO_2 , a CeO_2 shell on $Fe_3O_4@SiO_2-Pd@mCeO_2$ with a thickness of 25 nm was obtained (Figure 2c). The HR-TEM images (Figure 2b, d) elucidate that the Pd NPs and the CeO_2 nanocrystallites had sizes of approximately 5–10 and 5 nm, respectively. The lattice fringes are visible, with *d*



Figure 2. TEM and HR-TEM images of (a) $Fe_3O_4@SiO_2-Pd$, (b) Pd, (c) $Fe_3O_4@SiO_2-Pd@mCeO_2$, (d) CeO_2 , (e,f) $Fe_3O_4@h-Pd@mCeO_2$.

spacings of 0.23 and 0.32 nm corresponding to the lattice spacing of the Pd NPs (111) lattice planes and the cubic uorite phase CeO₂ (111) lattice planes.^[50] Figure 2e, f show TEM images of Fe₃O₄@*h*-Pd@*m*CeO₂ with yolk–shell structures after the SiO₂ shell etching reaction. These consist of Fe₃O₄ cores, an apparent chamber, and the outer CeO₂ layers. Unfortunately, the rupture of outer CeO₂ layers resulted in the formation of individual Fe₃O₄ balls and dispersive CeO₂ NPs (the arrows in Figure 2f).

It was difficult to identify the interface effect between Pd NPs and CeO₂ because of the concentrated electron density of polycrystalline CeO₂ and the specific core–shell architecture.^[51] Therefore, the encapsulated Pd NPs could not be explicitly recognized from the TEM images of the Fe₃O₄@SiO₂-Pd@mCeO₂ and Fe₃O₄@h-Pd@mCeO₂ structures. HADDF-STEM and EDS ele-

mental mapping depicted the elemental distribution of these novel structures. The HADDF-STEM image in Figure 3 shows the "shell-in-shell" structure of the Fe₃O₄@SiO₂-Pd@mCeO₂ catalyst. The corresponding EDS mapping images indicate that Fe, Si, Pd, Ce, and O were dispersed evenly with differently sized spherical shapes. The HADDF-SETM image of the Fe₃O₄@*h*-Pd@mCeO₂ catalyst (Figure S1c in the Supporting Information) and the corresponding EDS mapping images also affirmed the differently sized spherical shape and the distribution of elements Fe, Pd, Ce, and O but without element Si.



Figure 3. HADDF-STEM images of $Fe_3O_4@SiO_2-Pd@mCeO_2$ and the corresponding EDS mapping images.

To detail the surface chemical composition and further confirm the formation of the Pd NPs and the CeO₂ shell, X-ray photoelectron spectroscopy (XPS) was conducted (Figure 4 and Figure S2 in the Supporting Information). As noticeable in Figure 4d, it is hard to detect the peak for Fe from the wide scan survey of Fe₃O₄@SiO₂-Pd (Figure S2a). This suggests that the majority of the Fe₃O₄ was in fact coated by a silica layer



Figure 4. XPS spectra of (a) Ce 3d of $Fe_3O_4@SiO_2-Pd@mCeO_{2r}$ (b) Ce 3d of $Fe_3O_4@h-Pd@mCeO_{2r}$ (c) Pd 3d, (d) Fe 2p.



and formed a core-shell structure.^[52] The high-resolution XPS spectrum of Pd (Figure 4c) depicts its binding energies: 341.2 and 335.8 eV, associated with the Pd $3d_{3/2}$ and Pd $3d_{5/2}$ of Pd⁰, respectively.^[53] These values confirm the formation of metallic Pd on the surface of Fe₃O₄@ SiO₂ NPs. The XPS spectra of Figure S2d, Figure S2b and c indicate that C, O, and Ce existed on the surface of Fe₃O₄@SiO₂@mCeO₂, Fe₃O₄@SiO₂-Pd@mCeO₂, and Fe₃O₄@h-Pd@mCeO₂. With regard to the XPS signals of the Ce 3d spectra (Figure S2e, Figure 4a and b): the five characteristic peaks of Ce $3d_{\scriptscriptstyle 3/2}$, situated at 916.2, 907.2, 903.9, 900.7, and 899.3 eV correspond to $u^{\prime\prime\prime},~u^\prime,~u^\prime,~u,~and~u_0~units,^{\scriptscriptstyle [54,55]}$ whereas the other five characteristic peaks of Ce 3d_{5/2}, situated at 898.6, 888.6, 884.4, 882.2, and 880.6 eV match well with components v''', v'', v, and v₀ units.^[54,55] The signals v₀, v', u₀, and u' were characteristic peaks of Ce^{3+} , and the other peaks corresponded to the characteristic peaks of Ce⁴⁺. The presence of Ce^{3+} strongly suggests the synergistic effect between CeO_2 and Pd NPs. The concentration of Ce³⁺ in CeO₂ can be determined with the equations in the Supporting Information. The Ce³⁺ to Ce⁴⁺ ratio in the Fe₃O₄@SiO₂@mCeO₂, Fe₃O₄@SiO₂-Pd@mCeO₂, and Fe₃O₄@h-Pd@mCeO₂ catalysts was calculated to be 16.8, 18.5, and 23.3%, respectively.

The phase and composition of the as-synthesized samples were thoroughly examined using X-ray diffraction (XRD). All the peaks at 29.9, 35.2, 43.0, 56.8, and 62.5° are in agreement with the Fe₃O₄ face-centered cubic structure in Figure 5a–f.^[47] From Figure 5b it can be seen that there is no distinct change in the XRD pattern of Fe₃O₄@SiO₂ NPs relative to the XRD pattern of Fe₃O₄ NPs. In the XRD pattern of Fe₃O₄@GiO₂-Pd in Figure 5c, except for the peaks of the Fe₃O₄ core, another peak located at 40.0° is associated with face-centered Pd (111) peaks (JCPDS no. 05-0681).^[50] Figure 5d–f show the XRD patterns of Fe₃O₄@SiO₂@mCeO₂, Fe₃O₄@SiO₂-Pd@mCeO₂, and Fe₃O₄@h-Pd@mCeO₂ NPs, respectively. These figures index the peaks at 28.7, 33.1, 47.8, and 56.2°, corresponding to the (111), (200), (220), and (311) Bragg diffraction planes of CeO₂ (JCPDS No.34-0394).^[56] There were no diffraction peaks characteristic of Pd



Figure 5. XRD patterns of (a) $Fe_3O_4 NPs$, (b) $Fe_3O_4@SiO_2 NPs$, (c) $Fe_3O_4@SiO_2^-Pd NPs$, (d) $Fe_3O_4@SiO_2@mCeO_2 NPs$, (e) $Fe_3O_4@SiO_2^-Pd@mCeO_2 NPs$, (f) $Fe_3O_4@h-Pd@mCeO_2 NPs$.

NPs in Figure 5e, which is a testament to their low content loading and their high dispersity. $^{\left[56\right] }$

The Fourier transform infrared spectroscopy (FTIR) spectra of Fe₃O₄, Fe₃O₄@SiO₂, Fe₃O₄@SiO₂-NH₂, Fe₃O₄@SiO₂-Pd, Fe₃O₄@SiO₂-Pd@mCeO₂, and Fe₃O₄@h-Pd@mCeO₂ NPs are shown in Figure S3 in the Supporting Information. As depicted in Figure S3a, the bands at 580 and 1650 cm⁻¹ were assigned to the stretching vibration of Fe–O and the C=O of Na₃Cit.^[57] The broad peak around 3400 cm⁻¹ is attributed to the vibration of OH. Figure S3b displays the absorption band at 1088 cm⁻¹ and corresponds to an antisymmetric stretching vibration of the Si-O-Si bond at the oxygen-silica tetrahedron. This indicates that the surfaces of Fe₃O₄ NPs were successfully coated by the silica shells. After functionalization with APTES, an obvious band appears at 2926 cm^{-1} (Figure S3c) and is a factor of the C-H stretching vibrations of APTES. From the FTIR spectra of Figure S3d and e, we note that the absorption peaks of Fe₃O₄@SiO₂-Pd and Fe₃O₄@SiO₂-Pd@mCeO₂ are similar to those of the Fe₃O₄@SiO₂-NH₂ NPs. However, the absorption peak of Si–O–Si at 1088 cm⁻¹ evidently disappears in the spectrum of yolk-shell Fe₃O₄@h-Pd@mCeO₂ (Figure S3f), which indicates that the middle SiO₂ shell was thoroughly etched.

Magnetic hysteresis loops of the samples were measured using a superconducting quantum interference device (SQUID) magnetometer at room temperature from $-20\,000$ to 20000 Oe. Figure S4 depicts the magnetization curves of Fe₃O₄ NPs (black), Fe₃O₄@SiO₂ NPs (red), Fe₃O₄@SiO₂-Pd NPs (blue), Fe₃O₄@SiO₂-Pd@mCeO₂ NPs (gray), and Fe₃O₄@h-Pd@mCeO₂ NPs, respectively. At room temperature, the saturation magnetization value is 79.5, 22.8, 22.1, 18.2, and 38.5 emu g⁻¹, respectively.

Brunauer-Emmett-Teller (BET) measurements were carried out to further analyze the pore-size distribution and surface area. Figure S5 (Supporting Information) shows the N₂ adsorption-desorption isotherms of the Fe₃O₄@SiO₂-Pd@mCeO₂ and Fe₃O₄@h-Pd@mCeO₂ NPs, which exhibit characteristic type-IV curves. The BET surface area was calculated to be 95 and 90 m²q⁻¹, respectively. As mentioned above, a fraction of the CeO₂ layers was broken down in the etching process. The fragmented CeO₂ nanoparticles and Fe₃O₄ nanospheres can reunite to form a stabilized group, or they may attach themselves to an independent Fe₃O₄@h-Pd@mCeO₂ nanosphere. From the SEM images of Fe₃O₄@SiO₂-Pd@mCeO₂ and Fe₃O₄@h-Pd@mCeO₂, we also found that the reunion phenomenon of the Fe₃O₄@h-Pd@mCeO₂ catalyst is more obvious, which may be the reason for the diminished BET surface areas of the yolkshell Fe₃O₄@h-Pd@mCeO₂ catalyst. The pore-size distribution of the Fe₃O₄@SiO₂-Pd@mCeO₂ and Fe₃O₄@h-Pd@mCeO₂ NPs (inset in Figures S5a and b) indicates that the pore sizes range primarily from 2.0 to 6.0 nm, with a characteristic peak appearing at around 4.2 and 4.8 nm, respectively; this indicates a mesoporous CeO₂ shell. This result is consistent with the literature.^[49]

The successful preparation of the $Fe_3O_4@SiO_2-Pd@mCeO_2$ and $Fe_3O_4@h-Pd@mCeO_2$ catalysts could be ascribed to the following essentials. Firstly, the Fe_3O_4 NPs were decorated with citrate groups by a solvothermal method, which makes them more soluble in water and ethanol for the further coating by



other oxides or polymers. Thus, a uniform SiO₂ layer can be lightly coated on the surface of Fe₃O₄ NPs by a sol–gel process. To deposit Pd NPs efficiently, Fe₃O₄@SiO₂ was modified with APTES to provide plentiful amino groups on the surface of SiO₂, which boosted the interaction with Pd through the coordination bonds. Since the obtained Fe₃O₄@SiO₂-Pd was hydrophilic and highly soluble in ethanol and water, the succeeding coating of CeO₂ was accomplished in the presence of HMT. The as-prepared catalyst was able to be readily dispersed in water, ethanol, dimethylformamide (DMF), and tetrahydrofuran (THF) and formed a steady dispersion owing to the electrostatic repulsion effect, and could be rapidly isolated from the water dispersion by an external magnetic field. Thus, the Fe₃O₄ core–shell and yolk–shell catalyst could be recycled from the reaction system by an external magnetic field.

After detailed characterization of the synthesized material, we selected the reaction of 4-iodoanisole and phenylboronic acid as a benchmark reaction to evaluate the catalytic efficiency of our catalysts for the Suzuki reaction. We chose water and ethanol as the green solvent to carry out this reaction without any external agents like phosphine ligands or biphasic media. As depicted in Table S1 in the Supporting Information, the reaction did not proceed at all in water (Table S1, entry 1). A lowlevel yield of the desired product was acquired by Fe₃O₄@SiO₂@mCeO₂ without Pd NPs, with ethanol as solvent (Table S1, entry 2). No obvious enhancement in yield was observed by prolonging the reaction time (Table S1, entry 3) or by using a mixed solvent of water and ethanol (Table S1, entry 4). This illustrates that CeO₂ has catalytic activity, but not as the primary catalytic active site required for the Suzuki-Miyaura reaction.^[58] Next, we conducted the reaction using ${\sf Fe_3O_4@SiO_2-Pd}$ catalyst with the same solvent, and obtained the desired result, with excellent yield, within three hours (Table S1, entry 5-7). Based on these results, it is clear that the cross-coupling reaction was primarily catalyzed by Pd NPs. When Fe₃O₄@SiO₂-Pd@mCeO₂ and Fe₃O₄@h-Pd@mCeO₂ were used as catalysts (Table S1, entry 8-13) the yield improved relative to the corresponding Fe₃O₄@SiO₂-Pd catalyst. Interestingly, it could be found that the Fe₃O₄@h-Pd@mCeO₂ catalyst had a better catalytic activity than the Fe₃O₄@SiO₂-Pd@mCeO₂ catalyst from the yields.

To compare catalytic activity, the reaction kinetics of the template reaction was studied with the reaction rate as the measurement criteria with 0.5 mmol% Pd loading. The kinetic profiles (Figure 6a) clearly show the hierarchy of catalytic Fe₃O₄@*h*-Pd@*m*CeO₂ > Fe₃O₄@SiO₂-Pd@*m*CeO₂ > activity: Fe₃O₄@SiO₂-Pd. The initial reaction rates were calculated to be 1.8, 1.2, and 1.0 mmol mL⁻¹ min⁻¹ for the catalysts $Fe_3O_4@h$ -Pd@mCeO₂, Fe₃O₄@SiO₂-Pd@mCeO₂, and Fe₃O₄@SiO₂-Pd, respectively. After that, the effect of the solvent was investigated (Table S2 in the Supporting Information). The use of isopropyl alcohol (IPA), THF, DMF, 1,4-dioxane, dimethyl sulfoxide (DMSO), dimethylacetamide (DMA), toluene, or dimethylbenzene in combination with potassium carbonate as the base each give high coupling yields. Significantly, addition of 10% H₂O to a particular selected solvent could effectively raise the yield of the product (Table S2, entries 1-16). We further com-

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Figure 6. Plots of Suzuki–Miyaura coupling reactions; reaction conditions are given in Table 1: (a) conversion; (b) catalyst removed after 30 min; (c) varying Pd concentrations for Fe₃O₄@SiO₂-Pd; (d) varying Pd concentrations for Fe₃O₄@SiO₂-Pd@mCeO₂; (e) varying Pd concentrations for Fe₃O₄@h-Pd@mCeO₂. (f) PVPy added as a poison at start of reaction; GC conversion, conversion were averages of two independent runs.

pared the catalytic performance of different magnetic Pdbased catalysts by studying the coupling reaction of iodobenzene and phenylboronic acids. The results are summarized in Table S3 in the Supporting Information. For the sake of comparing the performances of magnetic core-shell immobilized Pd nanocatalyst systems for Suzuki reactions, we have collected some typical results from the literature, as shown in the Table S4. All these catalytic systems with low mol% Pd gave rise to excellent coupling product yields with at least two to ten stable reaction cycles. Some of them, including Fe₃O₄@SiO₂-Pd@mCeO₂, were reported to leach trace amounts of Pd after stable reaction cycles. Accordingly, Fe₃O₄@SiO₂-Pd@mCeO₂ represents one of the good-performance magnetic core-shell immobilized Pd nanocatalyst systems for Suzuki reactions to date. Nevertheless, even though some of them acquired high yields, toxic solvents (such as THF, CH₂Cl₂, or DMF) were used or the reaction was given a long time to occur. The better catalytic activity can be attributed to the high dispersion of the catalyst in the solvent, the outer CeO₂ shell effectively prevent the leaching and agglomeration of Pd NPs during the reactions, and the synergistic effect between the supporting CeO₂ and active Pd NPs species.

Although various metal oxides were used to elevate the catalytic activity and stability of the Pd NPs', the interfacial effect between those oxides and the active Pd NPs was ambiguous



due to multiple factors (such as morphology, surface area, and accessible active sites).^[59] The selective CeO₂ shell, which had a Ce⁴⁺/Ce³⁺ redox cycle, is a promising carrier owing to its high oxygen mobility, high oxygen storage capability, and low cost.^[60] CeO₂ has a fluorite structure, in which the center of the Ce^{4+} cation is encircled by each O^{2-} anion in a tetrahedron arrangement. The non-stoichiometric oxides $CeO_{2-x'}$ which were achieved through wet-chemical synthesis, had a high density of oxygen vacancies because of the partial O atom elimination from O²⁻ of the CeO₂ structure.^[61] Therefore, the surplus electrons, after the elimination process, were either delocalized in the conductor band, distributed to Ce³⁺ cations, or localized in the center Ce^{4+} to form Ce^{3+} . Simultaneously, the adsorption and dissociation of water occurring on the O vacancy of CeO_{2-x} produced the reactive $\mathsf{OH}^{\delta-}$ groups.^{[62]} Both Ce^{3+} species and $OH^{\delta-}$ groups were active reactive δ^{-} sites, and they imbued the Pd NPs with electrons.^[62] The Ce³⁺ cations and O vacancy therefore impart a synergistic effect that enhances the catalytic activity.

A proposed mechanism for this synergistic effect is illustrated in Scheme 2. During the synthesis of CeO_2 , Ce^{3+} cations (the presence of which was confirmed by X-ray photoelectron



Scheme 2. The proposed mechanism for the synergistic effect between the CeO_2 and Pd NPs.

spectroscopy (XPS) as shown in Figure 4) and the O vacancy formed. The active $OH^{\delta-}$ groups were produced by means of the adsorption and dissociation of H₂O on the O-vacancy sites. Afterwards, the electron pair of the Ce³⁺ cations and $OH^{\delta-}$ groups were transferred to the Pd NPs as a result of the electron-donating effect. This increased the electron density of the Pd NPs; this had the effect of accelerating the oxidative addition reaction, which was regarded as the rate-determining step in the C–C coupling reactions,^[1] to form Ar–Pd^{II}–X. Our kinetic investigations using Fe₃O₄@SiO₂-Pd@mCeO₂ as catalyst showed a strong positive influence between the concentration of the aryl halide and the initial rates, whereas no influence of the phenylboronic acid (Figure S6a–d in the Supporting Information) was detected. These observations demonstrate that the

oxidative addition reaction is the rate-determining step in our catalytic system.^[14]

By using the optimized reaction conditions, cross-coupling reactions of several aryl iodides, aryl bromides, and aryl chlorides with arylboronic acid were used with a Pd loading of 0.5 mmol% (Table 1). Aryl iodides and aryl bromides could be

Table 1. Results for cross-coupling of aryl halides with arylboronic acid. ^[a] Catalyst R_1 R_2 R_1 R_2 R_1 R_2						
Entry	R ₁	Х	R ₂	Yield ^[b]	Yield ^[c]	
1	OCH₃	Ι	Н	94	>99	
2	OCF ₃	I	Н	96	>99	
3	NH_2	1	Н	90	93	
4	2-CH₃	I	Н	78	84	
5	COCH₃	1	Н	93	>99	
6	OCH₃	Br	Н	85	92	
7	COCH₃	Br	Н	87	93	
8	OCH₃	CI ^[d]	Н	68	72	
9	COCH₃	CI ^[d]	Н	88	92	
10	Н	1	2-CH₃	75	82	
11	Н	I	4-CH₃	95	97	
12	Н	I	4-OCH ₃	96	>99	
13	Н	I.	4-F	90	96	
14 ^[e]	Н	I	H	>99	>99	

[a] Reaction conditions: aryl halide (1.0 mmol), arylboronic acid (1.2 mmol), potassium carbonate (2.5 mmol), 5 mL ethanol/water (9:1), catalyst (0.5 mmol % Pd), at 80 °C for 3 h. [b] GC yield: 20.62 mg with Fe₃O₄@SiO₂-Pd@mCeO₂ as catalyst. [c] GC yield: 17.4 mg with Fe₃O₄@*h*-Pd@mCeO₂ as catalyst. [c] GC yield: 17.4 mg with Fe₃O₄@*h*-Pd@mCeO₂ as catalyst. [d] DMF/H₂O 9:1, 100 °C. [e] Catalyst (0.1 mmol % Pd), 1 h, TOF = 990 mol product mol⁻¹ Pd h⁻¹.

coupled efficiently with phenylboronic acid. The system attained high conversion to the cross-coupled products within three hours, regardless of the electron-withdrawing substituent (–COCH₃), electron-donating group (–OCH₃), or coordinating group (–NH₂) (entries 1–3 and 5–7). *ortho*-Methyl aryl iodide gave inferior yields of the 2-arylation product (entry 4) due to steric hindrance. Aryl chlorides could also be coupled with phenylboronic acid using the mixed solvent of DMF and water under a higher temperature (entries 8 and 9). Aryl chlorides containing electron-withdrawing substituents gave an excellent yield within three hours (entry 9). Aryl chlorides with electron-donating substituents gave inferior product yields (entry 8).

Furthermore, various substituted arylboronic acid substrates underwent the cross-coupling reaction with iodobenzene in our catalytic system (entries 10–13). *ortho*-Methyl phenylboronic acid gave inferior yields of the 2-arylation product (entry 10) due to steric hindrance. Neither the electron-donating group (4-OCH₃) nor electron-withdrawing substituent (4-F) had this inhibition effect under the same conditions (entries 12 and 13). The reaction of iodobenzene and phenylboronic acid reached full conversion in just one hour with a 0.1 mmol% Pd loading (entry 14), and the TOF was 990 mol product mol⁻¹Pdh⁻¹. The results in Table 1 illustrate that our catalysts have excellent catalytic activities and substrate compatibility with the same reac-



tion conditions, thus, the factors of reaction conditions and reactants for studying the reaction mechanism can be eliminated.

In addition to prominent catalytic activity, isolation and recyclability of a catalyst are considerable requirements for any practical catalytic reaction. In our systems, the catalysts were readily recovered from their dispersion using an external magnet. To test the recyclability of the catalyst, a benchmark reaction was chosen as a comparison. As illustrated in Figure S7a, the Fe₃O₄@SiO₂-Pd@mCeO₂ catalyst could be recycled by using selective magnetic separation up to ten times without a notable decrease in yield. However, as revealed by Figures S7b and c, the recycling test for Fe₃O₄@h-Pd@mCeO₂ and Fe₃O₄@SiO₂-Pd indicated a decrease in catalytic efficacy after the reaction was repeated five and three times, respectively.

Assessing the leaching of active Pd NPs into the reaction mixture is another key factor in testing the stability of the Pd catalyst. To verify the possibility of leaching, the three kinds of catalyst were detected by inductively coupled plasma atomic emission spectrometry (ICP-AES) after ten cycles, five cycles, and three cycles. The results are listed in Table S5 in the Supporting Information. The benchmark reaction shows a determinable Pd loss for the Fe₃O₄@SiO₂-Pd@mCeO₂ catalyst. This result might, to some extent, explain the slight yield decreases following increased recycling. Figures S8a and S9b show the SEM and TEM images of the Fe₃O₄@SiO₂-Pd@mCeO₂ catalyst for the Suzuki reactions after ten runs of recycling. These images indicate that the catalyst retained its spherical shape after recycling. For Fe₃O₄@h-Pd@mCeO₂ and Fe₃O₄@SiO₂-Pd catalysts, the leaching of Pd NPs is notable (Table S5). The SEM image of the Fe₃O₄@SiO₂-Pd catalyst (Figure S9a), compared with the TEM image (Figure 2a), reveals that most of the Pd NPs leached into the solvent. The SEM image (Figure S8b) and TEM images (Figures S9c and d) of the Fe₃O₄@h-Pd@mCeO₂ catalyst display that most of the outer CeO₂ shell was damaged, while only parts of the catalyst maintained a yolk-shell structure. Prominently, the recyclability of the Fe₃O₄@SiO₂-Pd@mCeO₂ catalyst was the best among the three. One could easily ratiocinate that the hierarchical core-shell structures effectively hinder the aggregation and leaching of Pd NPs owing to the robust protection provided by porous CeO₂ shells. The easy isolation and good reusability of the catalyst illustrate that our catalysts have high separability and stability for studying a reaction mechanism.

Another important aspect of a catalyst is the nature of active noble-metal species (homogeneous or heterogeneous) in cross-coupling reactions. The literature differs as to whether the Pd-catalyzed Suzuki–Miyaura reactions result from leaching Pd NPs or the heterogeneous Pd NPs themselves. This has been a topic of intense debate and is far from being rid of controversy. Thus, we carried out a hot-filtration test, solid-phase poisoning, and assessed Pd concentrations to validate whether the Pd active sites were encapsulated by the CeO₂ shell, or the homogeneous Pd species leached from the CeO₂ shell during the reaction process were true catalysts. The results imply that $Fe_3O_4@SiO_2-Pd@mCeO_2$ completes the reaction in a true heterogeneous manner, but not $Fe_3O_4@h-Pd@mCeO_2$

or ${\sf Fe}_3{\sf O}_4@{\sf SiO}_2\text{-Pd}.$ This assertion is based on the following observations.

During the experiment, we removed the catalyst with a magnet, and permitted the reaction to continue. The yield stopped increasing immediately for the Fe₃O₄@SiO₂-Pd@mCeO₂ catalyst but not for the Fe₃O₄@h-Pd@mCeO₂ or Fe₃O₄@SiO₂-Pd catalysts (see Figure 6b). If a trace amount of soluble leaching Pd species was the active species, the catalytic yield would have increased, even after the removal of catalyst. The hot-filtration tests indicated that the catalysis is from the leached Pd over Fe₃O₄@h-Pd@mCeO₂ and over Fe₃O₄@SiO₂-Pd, and unclear over Fe₃O₄@SiO₂-Pd@mCeO₂. A positive hot-filtration test means the occurrence of homogeneous catalysis, whereas a negative hot-filtration test does not necessarily imply the emergence of heterogeneous catalysis for a number of reasons (e.g., fast deactivation or redeposition of soluble active species). Consequently, the distinction between heterogeneous and homogeneous catalytic activity cannot be declared solely based on the results of our hot-filtration test.^[63]

The inverse relationship between the active Pd concentration and the conversion rate is associated with the homogeneous mechanism.^[64] The inverse relationship refers to the relationship between the active Pd concentration and turnover number (TON) or turnover frequency (TOF). If the TON or TOF increases with decreasing active Pd concentration, it means that the homogeneous rather than heterogeneous catalysis works for the Suzuki reaction.^[65] To investigate this inverse relationship, we assessed the effect of Pd concentration on catalytic activity. Figure 6c-e depicts the reaction profiles of the catalyst with a Pd concentration of 0.1, 0.5, 1, and 5 mmol%. The TON and TOF for the different Pd concentrations are shown in Table S6. It is also clear from Table S6 that the TOF increases on going from 5 to 0.1 mmol% over Fe₃O₄@h-Pd@mCeO₂ and over Fe₃O₄@SiO₂-Pd, and is inconspicuous over Fe₃O₄@SiO₂-Pd@mCeO₂. This can be explained by the equilibrium between the Pd present in the clusters, which formed from the soluble leaching of Pd, and the Pd NPs involved in the catalytic cycle.^[66] At lower Pd concentrations, this equilibrium can shift away from the inactive clusters, resulting in a higher percentage of active Pd catalyst. The Fe₃O₄@SiO₂-Pd@mCeO₂ catalyst (Figure 6d) displayed an increased conversion rate when the Pd concentration increased. Interestingly, the Fe₃O₄@h- $Pd@mCeO_2$ and $Fe_3O_4@SiO_2-Pd$ catalysts did not show the same reactivity trend when varying the Pd concentration. As illustrated in Figure 6c, e, both the reactions with a Pd concentration of 1 mmol% were faster than those with higher Pd concentrations (5 mmol%). This deactivation of Pd catalyst, the socalled "homeopathic" mechanism, happened as a result of the soluble leaching Pd nucleating to form Pd clusters that continued to grow.^[9] As the Pd concentration increased, greater leaching occurred, and the quenching of the active Pd catalyst in solution became more efficient.

The benchmark reaction was also conducted in the presence of poly(4-vinylpyridine) (PVPy), which is a well-known solid poison that restricts homogeneous Pd species in the liquid phase through chelation.^[14] A comparison of conversion clearly illustrates that the catalytic efficacy of the $Fe_3O_4@SiO_2^-$ Pd@mCeO₂ catalyst was not affected by the addition of PVPy, whereas the catalytic efficiency of $Fe_3O_4@h-Pd@mCeO_2$ and $Fe_3O_4@SiO_2-Pd$ was notably reduced (see Figure 6a, f). To obtain more accurate and meaningful results on this issue, we also carried out a mercury poisoning test, which can form an amalgam with leaching Pd nanoparticles.^[67] Of note is that, as pointed by Whitesides,^[68] the mercury poisoning test can account for a homogeneous nature but not a heterogeneous one. After Hg (300 equiv) addition, an inhibition of catalytic activity was observed for $Fe_3O_4@h-Pd@mCeO_2$ and $Fe_3O_4@SiO_2-Pd@mCeO_2$ (Figure S10 in the Supporting Information).

Based on these heterogeneity tests, we ascribe different catalytic mechanisms for the hierarchical core-shell structures and the yolk-shell structures (Scheme 3). The active Pd of the $Fe_3O_4@SiO_2-Pd@mCeO_2$ catalyst was supposed to be a heterogeneous mechanism for the Suzuki reaction. In this case, both aryl halide and arylboronic acid come into contact by colliding directly on the Pd NPs surface rather than through the leaching of Pd NPs within the solution.

Conclusion

In this study, we successfully prepared a hierarchical core-shell $Fe_3O_4@SiO_2-Pd@mCeO_2$ catalyst and yolk-shell $Fe_3O_4@h-Pd@mCeO_2$ catalyst by integrating the hydrothermal method, in situ interfacial deposition, and the sol-gel process. Both the $Fe_3O_4@SiO_2-Pd@mCeO_2$ and $Fe_3O_4@h-Pd@mCeO_2$ catalysts exhibited high levels of magnetism, accessible mesoporous CeO_2 , and large dispersibility in the solvent. Greater catalytic performance was demonstrated in the Suzuki-Miyaura cross-coupling reaction than when using the $Fe_3O_4@SiO_2-Pd$ catalyst without an outer CeO_2 shell. We proposed a feasible mechanism underlying the synergistic effect between the supporting

CeO₂ and the active Pd NPs species, which resulted in the enhanced catalytic activity of our catalysts relative to some of the published literature. The excellent stability of the Fe₃O₄@SiO₂-Pd@mCeO₂ catalyst meant it could be recycled ten times without any obvious decrease of yield.

Fundamentally, the hot-filtration heterogeneity test and Pd concentration and solid-phase poisoning test in this study were conducted to assess the heterogeneous or homogeneous nature of the Pd catalyst. Our results demonstrate that the active Pd in the Fe₃O₄@SiO₂-Pd@mCeO₂ catalyst operates by a heterogeneous mechanism, whereas the active Pd in Fe₃O₄@h-Pd@mCeO₂ and Fe₃O₄@SiO₂-Pd catalysts abide by a homogeneous mechanism. Our comparative study demonstrates that understanding of the leaching processes is vital in designing heterogeneous catalysts for cross-coupling, because the definitions of heterogeneous/homogeneous are too broad for diverse reaction systems.

Our methodology provides a general way to design and assemble core-shell or yolk-shell nanostructures with mutable morphologies and controllable component performances. It raises the overall application potential of this type of nanocomposite. Moreover, it provides strong evidence validating the "mechanistic nature" issue in Pd-catalyzed Suzuki-Miyaura cross-coupling reactions.

Experimental Section

Synthesis of core–shell $Fe_3O_4@SiO_2$ and APTES-modified $Fe_3O_4@SiO_2$

The dispersible magnetic Fe₃O₄ modified by Na₃Cit was synthesized according to the study reported by Zhao.^[46] We synthesized Fe₃O₄@SiO₂ by using a universal solution sol-gel method as follows: an aqueous dispersion of Fe₃O₄ (35 mL, 0.02 g mL⁻¹) was added to a reaction vessel that contained absolute ethanol



Scheme 3. The proposed mechanism for Fe₃O₄@SiO₂-Pd@mCeO₂ and Fe₃O₄@h-Pd@mCeO₂.



(140 mL) and NH₃·H₂O (2.5 mL, 28 wt%), and was then mechanically stirred for 15 min at room temperature. Next, TEOS (2.0 mL) was added drop-by-drop for one minute; the ensuing reaction was maintained for eight hours. The resulting core-shell Fe₃O₄@SiO₂ were extracted with a magnet and washed with water and ethanol six times. The obtained products were dispersed in absolute IPA with a content of about 1 wt% for next uses.

For surface modifications, we further diluted the previously obtained IPA dispersion (20 mL) with IPA (50 mL) containing APTES (1 mL) by means of ultrasonication. The ensuing solution was bubbled with N₂ for thirty minutes, and then mechanically stirred at 70 °C for six hours. Finally, we collected the APTES-modified Fe₃O₄@SiO₂ with a magnet, and repeatedly washed them with deionized water and ethanol.

Synthesis of core-shell Fe₃O₄@SiO₂-Pd

We added APTES-modified Fe₃O₄@SiO₂ (1.0 g) to toluene (40 mL) containing PdCl₂ (0.2 g). After mechanically stirring the solution for five hours at room temperature, the resulting solid sample was extracted with a magnet and washed with toluene. Then, NaBH₄ (50 mg) was employed to reduce the PdCl₂ in a solvent of toluene and ethanol (v/v 20:1). This suspension was isolated by a magnet, washed with toluene and ethanol several times, and dried in vacuum, which yielded the sample denoted Fe₃O₄@SiO₂-Pd. To determine the content of Pd (10.05 wt%), the product was decomposed in concentrated nitric acid and analyzed with ICP-AES.

Synthesis of core-shell Fe₃O₄@SiO₂-Pd@mCeO₂

 $Fe_3O_4@SiO_2-Pd$ (150 mg) was dispersed in ethanol (120 mL) and sonicated for thirty minutes. We then added $Ce(NO_3)_{3'}6H_2O$ (200 mg) to that solution and subjected it to an ultrasound treatment process for fifteen minutes. Subsequently, deionized water (100 mL) containing HMT (1.0 g) was added to the solution, and was subjected to ultrasound for another ten minutes. We mechanically stirred the solution for two hours at 70 °C. The resulting samples were obtained with a magnet, and washed with water six times to remove any possible ionic remnants. We vacuum-dried the products at 40 °C for two hours to gain $Fe_3O_4@SiO_2-Pd@mCeO_2$ nanoparticles. The product was decomposed in concentrated nitric acid for the ICP-AES analysis to determine the content of Pd (2.85 wt%).

The synthesis of $Fe_3O_4@SiO_2@mCeO_2$ was the same as that of $Fe_3O_4@SiO_2\text{-Pd}@mCeO_2$ without Pd.

Synthesis of yolk-shell Fe₃O₄@h-Pd@mCeO₂

The annealed Fe₃O₄@SiO₂-Pd@mCeO₂ (0.2 g) was added to 10 wt% NaOH solution (15 mL), which was stirred for four hours at 50 °C to remove the SiO₂ shell. The products were washed with deionized water until they attained neutral pH levels, and were then dried under vacuum at 60 °C. The Pd content was 3.05 wt% from the analysis with ICP-AES.

Suzuki-Miyaura cross-coupling reactions

The catalysts with Pd content (0.5 mmol%) (20.60 mg for $Fe_3O_4@SiO_2-Pd@mCeO_2$, 17.40 mg for $Fe_3O_4@h-Pd@mCeO_2$, 5.30 mg for $Fe_3O_4@SiO_2-Pd$), potassium carbonate (2 mmol), aryl halide (1.0 mmol), and arylboronic acid (1.2 mmol) were added to

a Schlenk tube containing a magnetic stir bar. Solvent (5 mL) was added. The mixture was stirred at 80 °C in air. We monitored the reaction process by GC at fixed time intervals. After completion of the reaction, the catalyst was separated from the mixture with a magnet, washed several times with water and ethanol, and then dried under vacuum at 60 °C overnight. The resulting solution was extracted by EtOAc three times for GC-MS analysis. Our recycling experiment followed the same procedure.

Hot-filtration test

The hot-filtration test—a benchmark Suzuki–Miyaura reaction was conducted according to a typical procedure. First, the reaction was allowed to proceed for about thirty minutes. The solid catalyst was then separated from the mixture with a magnet while the mother liquor stayed and reacted for an extended duration under identical conditions. The conversion was monitored by GC at different times.

The effect of Pd concentrations

This part of the experiment followed the previously mentioned procedure, with Pd concentrations of 0.1, 0.5, 1, and 5 mmol%, respectively.

Solid-phase poisoning test

The solid-phase poisoning test as a benchmark Suzuki–Miyaura reaction was performed in the presence of poly(4-vinylpyridine) (2% cross-linked) (PVPy) or mercury (1.5 mmol, 300 mg) using 300 equivalents to total palladium content. The reaction and analysis conditions were as mentioned above.

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Keywords: cross-coupling · heterogeneous catalysis · kinetics · palladium · reaction mechanisms

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