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## Optimized Dispersion and Stability of Hybrid Fe<sub>3</sub>O<sub>4</sub>/Pd Catalysts in Water for Suzuki Coupling Reactions: Impact of Organic Capping Agents

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Pd nanoparticles were easily immobilized on Fe<sub>3</sub>O<sub>4</sub> microspheres without any treatment such as functionalization with organic groups. The Fe<sub>3</sub>O<sub>4</sub> microspheres were synthesized by using different capping agents, and the effect of the capping agents on the dispersion stability and catalytic activity of the Fe<sub>3</sub>O<sub>4</sub>/Pd composite for Suzuki coupling reactions in water

### Introduction

In recent years, a number of nanoparticles (NPs) have been prepared by using various capping agents,<sup>[1-3]</sup> because capping agents are essential to control shape, size, and crystal structure in nanomaterial synthesis. Furthermore, as the effective dispersion of NPs in various solvents is important for biological and pharmaceutical applications,<sup>[4,5]</sup> the use of hydrophilic or hydrophobic capping agents and surface modification of NPs have been attempted to control the dispersion stability in organic and nonorganic solvents.<sup>[6,7]</sup> Surface modification of magnetic NPs has received particular attention because of their utility in various state-of-the-art technological applications and the fundamental scientific interest in magnetic NPs, including their use as magnetic storage media,<sup>[8]</sup> in medical diagnosis and therapy,<sup>[9,10]</sup> and as contrast agents in magnetic resonance imaging.<sup>[11,12]</sup> Considerable effort has been made in the development of hybrid catalysts by using Fe<sub>3</sub>O<sub>4</sub> microspheres and transition-metal NPs.<sup>[13, 14]</sup> Hybrid magnetic catalysts offer the advantage of facile separation from the products by using an external magnet, and thus, lend themselves to effective recycling. To functionalize the surface of Fe<sub>3</sub>O<sub>4</sub> microspheres in the hybrid catalyst, Fe<sub>3</sub>O<sub>4</sub> microspheres have been coated with various materials such as SiO<sub>2</sub>, polymers, and carbon.<sup>[15-17]</sup> Functional groups such as 3-aminopropyl triethylsilane and hyperbranched polyglycerol have been coated onto the surface of Fe<sub>3</sub>O<sub>4</sub> microspheres to immobilize monodisperse transition-metal NPs.<sup>[18, 19]</sup> These functional groups conferred dramatic stabilization to the metal NPs; however, multiple steps are required to synthesize the catalysts. Therefore, a simple technique for the synthesis of stable hybrid magnetic

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were evaluated. The catalytic activity varied depending on the dispersion stability of  $Fe_3O_4/Pd$  catalysts in water. The Pd nanoparticles immobilized onto  $Fe_3O_4$  microspheres capped with trisodium citrate showed strong dispersion stability in water over the reaction duration of seven days (at pH 7), high catalytic activity, and recyclability under mild conditions.

catalysts without the requirement for the treatment of Fe<sub>3</sub>O<sub>4</sub> microspheres is desired. To fabricate a suitable hybrid magnetic catalyst, it is guite essential to develop techniques for controlling the dispersion of NPs in various solvents to apply them to functional materials. According to the classical Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, the stability of a particle dispersion is determined by the sum of repulsive electrostatic forces and attractive van der Waals forces.<sup>[20]</sup> Thus, several approaches have been made for surface modification of NPs or microspheres to facilitate dispersion in organic solvents, and many organic capping agents have been used for enhancing the dispersion stability.<sup>[21,22]</sup> Furthermore, a dispersion of NPs in physiological solutions for biological in vitro and in vivo studies has been reported.<sup>[23]</sup> A variety of surfactants have been utilized to promote the solubility of iron oxide NPs or microspheres in various solvents.<sup>[7, 16]</sup>

C–C coupling reactions such as the Mizoroki–Heck and Suzuki coupling reactions are important in many types of organic syntheses, as well as in the chemical, pharmaceutical, and agricultural industries.<sup>[24–26]</sup> Immobilization of Pd NPs on inorganic supports such as silica, alumina, or mesoporous materials, as well as carbon, has been known to produce active catalysts for C–C coupling reactions.<sup>[27–29]</sup> Many researchers have also reported hybrid magnetic catalysts exhibiting highly efficient catalytic activity and recyclability.<sup>[30,31]</sup> Nevertheless, improving the yield of Suzuki coupling reactions in water still remains a major challenge.

Until now, attempts to synthesize well-defined hybrid magnetic catalysts have mainly focused on the synergetic effect of the hybrid catalyst and recyclability, however, an adequate explanation of the surface modification effect by using various capping agents for the catalytic reaction has rarely been provided. In this paper, we present the design and synthesis of Pd NPs immobilized onto  $Fe_3O_4$  microspheres coated with different capping agents such as  $Na_3Cit$  (Cit = citrate), poly(ethylene glycol) (PEG), and poly(vinylpyrrolidone) (PVP), comparing

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#### **Dispersion-Dependent Catalytic Activity**



 $\label{eq:Scheme 1.Dispersion-dependent catalytic activity of Fe_3O_4/Pd catalysts in water for Suzuki coupling reactions.$ 

them with  $Fe_3O_4$  microspheres without any capping agents. Finally, the effect of catalyst dispersibility on the catalytic activity for the Suzuki coupling reaction in water is discussed (Scheme 1).

### **Results and Discussion**

### Characterization of Fe<sub>3</sub>O<sub>4</sub>/Pd catalysts

Fe<sub>3</sub>O<sub>4</sub> microspheres were synthesized by the solvothermal method.<sup>[16,32,33]</sup> This method involves the partial reduction of FeCl<sub>3</sub> with ethylene glycol (EG) as a solvent, the use of sodium acetate (NaAc) as a reducing agent, and Na<sub>3</sub>Cit, PEG, and PVP as electrostatic stabilizers at 200 °C. Additionally, some ethanol was added to improve the solubility of the solid reagents. SEM images of the resulting Fe<sub>3</sub>O<sub>4</sub> microspheres are shown in Figure 1. All the Fe<sub>3</sub>O<sub>4</sub> microspheres are spherical with a rough

surface. If Na<sub>3</sub>Cit, PEG, and PVP were used as capping agents, the respective average diameters of the Fe<sub>3</sub>O<sub>4</sub> microspheres were 142, 150, and 153 nm. However, the average diameter increased to 175 nm in the absence of capping agents (Figure 1 d). Each type of Fe<sub>3</sub>O<sub>4</sub> microspheres consisted of aggregates of small magnetite particles with a mean size of 3 nm, as observed by TEM (Figure 2).

The TEM images reveal that Pd NPs of approximately 4 nm were immobilized onto each Fe<sub>3</sub>O<sub>4</sub> microsphere by substituting the sodium cations with Pd ions in aqueous medium (Figure 2).<sup>[16]</sup> Size distribution graphs of each Pd NPs are shown in Figure 2, exhibiting





Figure 1. SEM images of a) Na\_3Cit–Fe\_3O\_4, b) PEG–Fe\_3O\_4, c) No–Fe\_3O\_4, and d) PVP–Fe\_3O\_4 microspheres.

that the sizes of Pd NPs were less than 5 nm. During the catalyst preparation, because the Pd NPs were immobilized onto  $Fe_3O_4$  microspheres in aqueous solution,  $Na_3Cit-Fe_3O_4$  and PEG-Fe<sub>3</sub>O<sub>4</sub> could be well dispersed in the aqueous solution owing to hydrophilic functional groups of the capping agents, resulting in high monodispersity of the Pd NPs on the  $Fe_3O_4$  microspheres (Figure 2a and b). The  $Fe_3O_4$  microspheres without capping agents also exhibited high dispersion in water because of the hydroxyl groups on magnetite, which resulted in strong immobilization of the Pd NPs (Figure 2c). The use of PVP as an organic capping agent interrupted the dispersion of



**Figure 2.** TEM images of immobilized Pd NPs onto a) Na<sub>3</sub>Cit–Fe<sub>3</sub>O<sub>4</sub>, b) PEG–Fe<sub>3</sub>O<sub>4</sub>, c) No-Fe<sub>3</sub>O<sub>4</sub>, and d) PVP–Fe<sub>3</sub>O<sub>4</sub> microspheres. Size distribution graphs of each Pd NPs are also shown.

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Figure 3. a) XRD pattern of each  $Fe_3O_4/Pd$  catalysts and b) SQUID data (b).

 $Fe_3O_4$  in aqueous solution because of its hydrophobic nature as compared to the other capping agents, making the immobilization of the Pd NPs difficult (Figure 2d).

XRD patterns (Figure 3a) were used to identify the crystal phase of the respective Fe<sub>3</sub>O<sub>4</sub>/Pd microspheres. Specifically, the peaks were assigned to the (220), (311), (400), (422), and (511) reflections of the cubic spinel structure of Fe<sub>3</sub>O<sub>4</sub> (JCPDS No. 19-0629) and the (111), (200), and (220) reflections of face-centered cubic Pd (JCPDS No. 46-1043). If the  $Fe_3O_4$  microspheres were capped with Na<sub>3</sub>Cit, the overall intensity of the XRD peaks of Na<sub>3</sub>Cit-Fe<sub>3</sub>O<sub>4</sub>/Pd decreased. The superconducting quantum interference device (SQUID) data (Figure 3b) are shown as the magnetization as a function of the applied field at 300 K. The saturation magnetization value of Na<sub>3</sub>Cit-Fe<sub>3</sub>O<sub>4</sub>/ Pd was 45.2 emu  $g^{-1}$ , which was similar to that of Na<sub>3</sub>Cit–Fe<sub>3</sub>O<sub>4</sub> (ca. 48.2  $emu g^{-1}$ ). The small decrease in the saturated magnetization value of the Na<sub>3</sub>Cit-Fe<sub>3</sub>O<sub>4</sub>/Pd microspheres compared to that of the Na<sub>3</sub>Cit-Fe<sub>3</sub>O<sub>4</sub> microspheres can be attributed to the slight increase in mass owing to the immobilized Pd NPs on the surface of the Fe<sub>3</sub>O<sub>4</sub> microspheres.<sup>[34]</sup> Moreover, the remanence (Mr) and coercivity (Hc) of the Fe<sub>3</sub>O<sub>4</sub> microspheres were both close to zero, indicating superparamagnetism. The elemental compositions of the respective Fe<sub>3</sub>O<sub>4</sub>/Pd catalysts were obtained using energy-dispersive X-ray spectroscopy (EDS) (see the Supporting Information, Figure S1).

#### Suzuki coupling reactions over Fe<sub>3</sub>O<sub>4</sub>/Pd catalysts

As mentioned above, the Suzuki coupling reactions between bromobenzene and phenylboronic acid were used to investigate the catalytic activity of the hybrid catalysts; the results are summarized in Table 1. These results suggest that the

| Table 1. Suzuki coupling reaction of bromobenzene with phenylboronic $\operatorname{acid}^{[a]}$                                |                           |                 |              |                                 |                            |                          |
|---|---------------------------|-----------------|--------------|---------------------------------|----------------------------|--------------------------|
|   | Br +                      | но<br>В-<br>НО́ |              | <b>,</b>                        | ►                          |                          |
| Entry   | Cat. [mol %]              | 7 [°C]          | <i>t</i> [h] | Base                            | Solvent                    | Yield <sup>[b]</sup> [%] |
| 1   | 1 (Na₃Cit)                | 80              | 5            | K <sub>2</sub> CO <sub>3</sub>  | DMF:H <sub>2</sub> O (4:1) | 91                       |
| 2   | 1 (Na₃Cit)                | 50              | 5            | K <sub>2</sub> CO <sub>3</sub>  | H₂O                        | 97                       |
| 3   | 0.1 (Na₃Cit)              | 50              | 5            | K <sub>2</sub> CO <sub>3</sub>  | H₂O                        | 65                       |
| 4   | 0.05 (Na₃Cit)             | 50              | 5            | Cs <sub>2</sub> CO <sub>3</sub> | H₂O                        | 89                       |
| 5   | 0.05 (Na₃Cit)             | 50              | 7            | Cs <sub>2</sub> CO <sub>3</sub> | H₂O                        | 98                       |
| 6   | 0.05 (Na₃Cit)             | 50              | 5            | CsOH                            | H₂O                        | 66                       |
| 7   | 0.05 (Na₃Cit)             | 40              | 12           | Cs <sub>2</sub> CO <sub>3</sub> | H₂O                        | 48                       |
| 8   | 0.05 (Na₃Cit)             | 40              | 24           | Cs <sub>2</sub> CO <sub>3</sub> | H₂O                        | 94                       |
| 9   | 0.1 (Na <sub>3</sub> Cit) | 40              | 12           | Cs <sub>2</sub> CO <sub>3</sub> | H₂O                        | 76                       |
| 10  | 0.05 (Na₃Cit)             | 100             | 1            | Cs <sub>2</sub> CO <sub>3</sub> | H₂O                        | 80                       |
| 11  | 0.05 (Na₃Cit)             | 100             | 1.5          | Cs <sub>2</sub> CO <sub>3</sub> | H₂O                        | 98                       |
| 12  | 0.05 (Na₃Cit)             | 25              | 24           | Cs <sub>2</sub> CO <sub>3</sub> | H₂O                        | 13                       |
| 13  | 0.05 (PEG)                | 50              | 7            | Cs <sub>2</sub> CO <sub>3</sub> | H₂O                        | 89                       |
| 14  | 0.05 (No)                 | 50              | 7            | Cs <sub>2</sub> CO <sub>3</sub> | H₂O                        | 57                       |
| 15  | 0.05 (PVP)                | 50              | 7            | Cs <sub>2</sub> CO <sub>3</sub> | H <sub>2</sub> O           | 37                       |
| [a] Reaction conditions: bromobenzene (0.5 mmol), phenylboronic acid (0.6 mmol), $H_2O$ (3.0 mL) [b] Determined by using GC–MS. |                           |                 |              |                                 |                            |                          |

bases, reaction time, and temperature utilized have dramatic effects on the yields of the cross-coupling product in this reaction. At 80  $^\circ\text{C}$ , 91 % conversion was obtained in the mixture of DMF:H<sub>2</sub>O (4:1) (entry 1). Interestingly, if the reaction temperature was decreased to 50 °C, using only H<sub>2</sub>O as a solvent, high catalytic activity was achieved with the Na<sub>3</sub>Cit-Fe<sub>3</sub>O<sub>4</sub>/Pd catalyst, because this catalyst, capped by Na<sub>3</sub>Cit, could be well dispersed in water (entry 2). Preliminary screening for determining the most suitable base system for the catalyst revealed that Cs<sub>2</sub>CO<sub>3</sub> could efficiently catalyze this reaction (entries 3, 4, and 6). The optimum reaction conditions were found to be as follows: catalyst: Na<sub>3</sub>Cit-Fe<sub>3</sub>O<sub>4</sub>/Pd (0.05 mol%); solvent: H<sub>2</sub>O (3.0 mL), temperature: 50 °C, reaction time: 7 h (entry 5). At 40°C, a reaction time of 24 h was necessary to obtain high yield (entries 7-9). As expected, 98% conversion was achieved within 1.5 h at high temperature (100°C, entries 10 and 11). The product yield decreased at room temperature, even though a reaction time of 24 h was used (entry 12). The Na<sub>3</sub>Cit-Fe<sub>3</sub>O<sub>4</sub>/Pd catalyst could be separated by using an external magnet and could be recycled five times under the same reaction conditions (entry 11, Table 1, see Figure 4). As shown in Figure S2, the structure of the Pd NPs on the  $Fe_3O_4$  microspheres remained almost unchanged after the reaction, demonstrating the catalyst recyclability.

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**Figure 4.** Conversion yields during five recycling runs. Reaction condition: Na<sub>3</sub>Cit-Fe<sub>3</sub>O<sub>4</sub>/Pd catalyst (Pd base: 0.05 mol%), bromobenzene (1.0 mmol), phenylboronic acid (1.2 mmol), Cs<sub>2</sub>CO<sub>3</sub> (2.0 mmol), H<sub>2</sub>O (5.0 mL) and 100 °C for 1.5 h.

Investigation of the dispersibility of nanomaterials in various solvents is crucial for environmentally friendly applications.<sup>[35]</sup> Changes in the surface charge of the nanostructure in liquid media may produce drastic effects on the reactivity of nanomaterials.<sup>[36–38]</sup> Thus, surface modification of catalysts is considered a highly promising method for increasing the dispersion stability for efficiently enhancing the catalytic activity without aggregation. Here, we established a practical method for dispersing Fe<sub>3</sub>O<sub>4</sub>/Pd catalysts in aqueous solution and confirmed the catalytic activity by considering the differences in dispersibility.

The stabilities of the  $Fe_3O_4/Pd$  catalysts coated with different capping agents of various hydrophilicities are shown in Figure 5. Each  $Fe_3O_4/Pd$  catalyst was dispersed in water with a concentration of 1 mg mL<sup>-1</sup>. The PVP– $Fe_3O_4/Pd$  microspheres began to form agglomerates in 30 min because of the hydrophobicity of the PVP capping agent (Figure 5 a). No– $Fe_3O_4/Pd$  was more stable in water than PVP– $Fe_3O_4/Pd$ , because the bare  $Fe_3O_4$  microspheres have OH<sup>-</sup> anions on the surface (Figure 5).



Figure 5. Dispersion stability of Fe<sub>3</sub>O<sub>4</sub>/Pd catalysts after a) 30 min, b) 22 h, c) 5 d, and d) 7 d. [a] PVP-Fe<sub>3</sub>O<sub>4</sub>/Pd, [b] No-Fe<sub>3</sub>O<sub>4</sub>/Pd, [c] PEG-Fe<sub>3</sub>O<sub>4</sub>/Pd, and [d] Na<sub>3</sub>Cit-Fe<sub>3</sub>O<sub>4</sub>/Pd.

ure 5 b). Na<sub>3</sub>Cit–Fe<sub>3</sub>O<sub>4</sub>/Pd microspheres exhibited higher dispersion stability than PEG–Fe<sub>3</sub>O<sub>4</sub>/Pd (Figure 5 c and d) because citrate and OH<sup>-</sup> anions on the Fe<sub>3</sub>O<sub>4</sub> surface<sup>[16]</sup> enhanced the dispersion stability in water. The effect of the different capping agents on the zeta potential at pH 7 is shown in Figure 6 to



**Figure 6.** Zeta potential and reaction conversion of Fe<sub>3</sub>O<sub>4</sub>/Pd microspheres capped by different capping agents at pH 7. Reaction conditions: Na<sub>3</sub>Cit–Fe<sub>3</sub>O<sub>4</sub>/Pd catalyst (Pd base: 0.05 mol%), bromobenzene (0.5 mmol), phenylboronic acid (0.6 mmol), Cs<sub>2</sub>CO<sub>3</sub> (1.0 mmol), H<sub>2</sub>O (3.0 mL), and 50 °C for 7 h.

confirm the dispersion stability in water. On the basis of the literature, it was concluded that if the zeta potential of the particles is higher than 30 mV or lower than -30 mV, the dispersion is stable.<sup>[23]</sup> As the zeta potential increased, the Suzuki coupling reaction yield also increased (Figure 6), which indicates that high dispersion stability of the catalysts in water without aggregation leads to higher catalytic activity because of the increase in the available catalytically active sites. The Na<sub>3</sub>Cit–Fe<sub>3</sub>O<sub>4</sub>/Pd catalyst had the highest zeta potential (38.3 mV) and gave rise to the highest product yield (98%, Figure 6). Because of the good dispersion stability of the developed Na<sub>3</sub>Cit–Fe<sub>3</sub>O<sub>4</sub>/Pd catalyst in water, this catalyst produced a higher product yield than previously reported Fe<sub>3</sub>O<sub>4</sub>-supported Pd nanocatalysts,<sup>[31,39,40]</sup> and has environmentally positive impact and good overall industrial applicability.

The optimized reaction conditions using the Na<sub>3</sub>Cit-Fe<sub>3</sub>O<sub>4</sub>/ Pd catalyst were applied to various substituents with good yields in the environmentally sound solvent, water (Table 2). Activating aryl chlorides is one of the main problems in Suzuki coupling reactions because of their generally low conversion yields under normal reaction conditions. Almost complete conversion of substrates with C-Br and C-Cl bonds was obtained; however, substrates with the C-OTf (Tf=trifluoromethanesulfonyl) bond gave low conversion (entries 1-3). The catalytic activity with the electron-withdrawing arylboronic acid was better than that with the electron-rich congener (entries 4 and 5). Electron-withdrawing substituents can produce a favorable effect in palladium-catalyzed reactions.[41] However, in this study, the reactions of various aryl bromides, including electron-withdrawing and electron-donating substrates, proceeded readily and were even completed in some cases (entries 6-10).

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## Conclusions

Fe<sub>3</sub>O<sub>4</sub> microspheres were synthesized with various capping agents, and Pd NPs were immobilized onto the Fe<sub>3</sub>O<sub>4</sub> microspheres in situ. The zeta potentials confirmed the differences in the dispersion stability in water (at pH 7) based on the different capping agents. Na<sub>3</sub>Cit–Fe<sub>3</sub>O<sub>4</sub>/Pd exhibited good stability (38.3 mV) in water, resulting in the highest catalytic activity among the evaluated Fe<sub>3</sub>O<sub>4</sub>/Pd catalysts for the Suzuki coupling reaction. Na<sub>3</sub>Cit–Fe<sub>3</sub>O<sub>4</sub>/Pd could be recycled for five cycles with high product yield after its successful extraction with an external magnet. The developed catalyst system has the distinct advantages of high dispersion stability in water, recyclability, and high catalytic activity. The dispersion stability in a range of solvents is prospectively advantageous for practical industrial application.

## **Experimental Section**

## Synthesis of Na<sub>3</sub>Cit–Fe<sub>3</sub>O<sub>4</sub> microspheres (Fe<sub>3</sub>O<sub>4</sub> microspheres surrounded by Na<sub>3</sub>Cit)

Magnetite particles were synthesized by using a solvothermal method.<sup>[16,17]</sup> The details were as follows: ferric chloride hexahydrate (FeCl<sub>3</sub>·6 H<sub>2</sub>O) (1.4 g, 5.2 mmol) and Na<sub>3</sub>Cit (0.29 g, 0.96 mmol) were dissolved in EG/ethanol (36 mL/4 mL) solution; then, NaAc (1.9 g, 23 mmol) was added under vigorous stirring for 5 min. The resulting mixture was then transferred to a Teflon-lined stainless-

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steel autoclave (with a capacity of 50 mL) for heating at 200  $^{\circ}$ C for 10 h. Then, the autoclave was carefully taken out and allowed to cool to RT. The as-made black products were thoroughly washed with ethanol three times, and they were then vacuum-dried.

# Synthesis of PEG-Fe<sub>3</sub>O<sub>4</sub> microspheres<sup>[33]</sup> (Fe<sub>3</sub>O<sub>4</sub> microspheres surrounded by PEG)

FeCl<sub>3</sub>·6H<sub>2</sub>O (1.4 g, 5 mmol) was dissolved in EG (40 mL) to form a clear solution, followed by the addition of NaAc (3.6 g) and PEG (1.0 g). The mixture was stirred vigorously for 30 min and then sealed in a Teflon-lined stainless-steel autoclave (50 mL capacity). The autoclave was heated to and maintained at 200 °C for 4 h, and allowed to cool to RT. The black products were washed several times with ethanol and dried at 60 °C for 6 h.

# Synthesis of PVP–Fe $_{3}O_{4}$ microspheres<sup>[33]</sup> (Fe $_{3}O_{4}$ microspheres surrounded by PVP)

In a typical hydrothermal method, PVP (1.0 g) was dissolved in 40 mL of EG, followed by the addition of 5 mmol of FeCl<sub>3</sub>·6H<sub>2</sub>O and 30 mmol of NaAc. The mixture was stirred vigorously for 15 min, and then was sealed in a Teflon-lined stainless-steel autoclave. The autoclave was heated to 200 °C and maintained at this temperature for 4 h, and then was cooled to RT. The resulting black product was washed with ethanol and deionized water several times, and was finally dried at 80 °C in an oven overnight.

# Synthesis of $Fe_3O_4$ microspheres<sup>[33]</sup> ( $Fe_3O_4$ microspheres without capping agents)

FeCl<sub>3</sub>·6H<sub>2</sub>O (1.4 g, 5 mmol) was dissolved in EG (40 mL) to form a clear solution, followed by the addition of NaAc (3.6 g). The mixture was stirred vigorously for 15 min, and then was sealed in a Teflon-lined stainless-steel autoclave. The autoclave was heated to 200 °C and maintained at this temperature for 5 h, and then was cooled to RT. The resulting black product was washed with ethanol and deionized water several times, and was finally dried.

### Immobilization of Pd NPs onto each Fe<sub>3</sub>O<sub>4</sub> microspheres

Pd NPs were immobilized onto  $Fe_3O_4$  microspheres according to the modified procedure by Yang et al.<sup>[16]</sup> The  $Fe_3O_4$  microspheres (100 mg) were incubated in 0.2 M NaOH aqueous solution to ionize the carboxyl groups. The residual NaOH was removed by washing with deionized water through centrifugation. Then, the ionized  $Fe_3O_4$  microspheres were dispersed in the solution (30 mL, 0.1 M) of PdCl<sub>2</sub> during 1 h under sonication. After this, the microspheres were harvested with the aid of a magnet and washed with deionized water three times. Then, the microspheres were redispersed in deionized water (20 mL), and 50 mm NaBH<sub>4</sub> aqueous solution (1 mL) was added dropwise in an ice water bath during 5 min with vigorous stirring. The final product was purified through washing with ethanol three times and dried under vacuum.

#### General procedure for the Suzuki coupling reactions

The catalyst (generally 0.05 or 0.1 mol% with respect to the Pd content), bromobenzene (0.05 mL, 0.5 mmol, 1.0 equiv), phenylboronic acid (0.073 g, 0.6 mmol, 1.2 equiv), cesium carbonate (0.33 g, 1.0 mmol, 2.0 equiv) and water (3.0 mL) were mixed in a 10 mL vial glass. The mixture was vigorously stirred at 50 °C. After the reaction, the catalyst was separated by an external magnet and the reaction mixture was filtered with diethylether. Drying with MgSO<sub>4</sub>, filtration and solvent evaporation of the filtrate yielded the reaction products.

#### **Catalyst characterization**

The morphology of each sample was characterized by TEM (FEI, Tecnai F30 Super-Twin, National Nanofab Center, South Korea) by placing a few drops of the corresponding colloidal solution on carbon-coated copper grids (200 mesh, F/C coated, Ted Pella Inc., Redding, CA, USA). The SEM images were taken using a SEM (VEGA3, TESCAN). Magnetization data were taken using a SQUID (MPMS-7, Quantum design). The coupling reaction products were analyzed by <sup>1</sup>H nuclear magnetic resonance (NMR) using Varian Mercury Plus (300 MHz). Chemical shift values were recorded as parts per million (ppm) relative to tetramethylsilane as an internal standard unless otherwise indicated, and coupling constants are in Hertz. Mass spectra were obtained on Shimadzu GC/MS QP-2010 SE (EI) (Pusan National University). The elemental compositions of the hybrid catalysts were obtained by using EDS (550i, IXRF Systems, Inc.), and the XRD patterns were recorded by a Rigaku GDX-11P3A diffractometer (Pusan National University). Zeta potential of the Fe<sub>3</sub>O<sub>4</sub>/Pd microspheres in aqueous phase was measured by using a Zeta Potential & Particle size Ananlyzer (ELS-Z2, Otsukael).

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## **FULL PAPERS**

**Lemon boost:** Immobilized Pd nanoparticles onto  $Fe_3O_4$  microspheres synthesized with different capping agents exhibit different catalytic activities for Suzuki coupling reactions depending on the dispersion stability in water. Capping by trisodium citrate leads to the highest yield and recyclability with strong and long-term dispersion stability in water. Cit = citrate, PEG = poly-(ethylene glycol), PVP = poly(vinylpyrrolidone).



 Dispersed and aggregated Fe<sub>3</sub>O<sub>4</sub>/Pd catalyst in water

 Disparsion
 Na<sub>5</sub>Cit-Fe<sub>3</sub>O<sub>4</sub>/Pd > PEG-Fe<sub>3</sub>O<sub>4</sub>/Pd > No-Fe<sub>3</sub>O<sub>4</sub>/Pd > PVP-Fe<sub>3</sub>O<sub>4</sub>/Pd

 Catalytic
 Na<sub>5</sub>Cit-Fe<sub>3</sub>O<sub>4</sub>/Pd > PEG-Fe<sub>3</sub>O<sub>4</sub>/Pd > No-Fe<sub>3</sub>O<sub>4</sub>/Pd > PVP-Fe<sub>3</sub>O<sub>4</sub>/Pd

 Activity
 Na<sub>5</sub>Cit-Fe<sub>3</sub>O<sub>4</sub>/Pd > PEG-Fe<sub>3</sub>O<sub>4</sub>/Pd > No-Fe<sub>3</sub>O<sub>4</sub>/Pd > PVP-Fe<sub>3</sub>O<sub>4</sub>/Pd

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Optimized Dispersion and Stability of Hybrid Fe<sub>3</sub>O<sub>4</sub>/Pd Catalysts in Water for Suzuki Coupling Reactions: Impact of Organic Capping Agents