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Preparation of Water-dispersible Palladium Nanoparticles Stabilized by Carbon-Palladium Bonds and Its Application for Suzuki-Miyaura Coupling in Water

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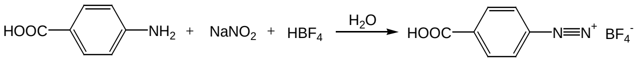
Water-dispersible palladium nanoparticle catalysts have been prepared using palladium-carbon covalent bonds. They worked as an excellent catalyst for Suzuki-Miyaura coupling reaction in water. Even though the particle size of Pd nanoparticles was much larger than the previously reported ones, they showed a very good catalytic activity for the coupling reaction.

Metal nanoparticles (NPs, diameter < 100 nm) and their applications have been intensively studied during the past decades according to the strong interest to their size-depending unique properties of NPs, being different from that of the bulk metal.[1-4] Spherical NPs and special structured NPs[5-7] including nanoporous ones[8-10] have been synthesized and applied so far. In particular, in the field of conductive pastes,[11] bio-sensing,[12] drug delivery,[13] metal NPs should be strong candidates as their key materials. Metal NPs have also become a very important class of catalysts owing to their inherently large relative surface area.[14-17] To date, various preparation procedures of dispersions of metal NPs have been developed and used as these materials. In most cases, such metal NPs are stabilized by several organic molecules, such as functional synthetic or bio polymers,[11,18] metal ligands,[19,20] surfactants,[21,22] dendrimers,[23] and inorganic solids,[24] in order to impede their aggregation due to van der Waals force during / after preparations. Some stabilizer free metal NPs were also prepared and used.[25] Polymer and ligand-stabilized metal NPs are highly stable and often can be re-dispersed into a disperse medium after purification and dry up. Their high stability in a disperse medium is highly useful to apply them as the materials for electronic wires, paints, as well as catalysts.

Organic reactions in aqueous media have been attracted much attention, firstly because use of water as a reaction solvent will reduce use of harmful organic solvents, and may lead to the development of environmentally friendly chemical processes. Water is the cheapest, safest and most nontoxic solvent in the world. However, water soluble thiol compounds are not often used as the stabilizers for NPs applied for catalysts because sulfur is often considered as a catalyst poison and there are only a few cases of thiol-stabilized NP catalysts owing to the lack of perfect thiol monolayer on small NPs.[26,27] In this study, palladium NPs were prepared with a water-soluble ligand which connected to palladium surface by palladium-carbon sigma bonds. They were used as highly effective green catalysts for Suzuki-Miyaura coupling reactions in aqueous media.

Palladium nitrate hydrate ($Pd(NO_3)_2 \cdot 2.4H_2O$, Pd content: 38.77 %) was purchased from Soekawa Chemicals (Japan) and used as the metal precursor without purification. Sodium borohydride was supplied from Wako (Japan). Water was purified by ion-exchange resins ($< 0.1\ \mu S\ cm^{-1}$).

As the stabilizing reagent, 4-carboxylbenzenediazonium fluoroborate (CBAzo) was selected. CBAzo was synthesized as described elsewhere (Scheme 1).[19] The product was confirmed using ^1H NMR, ^{13}C NMR, and IR measurements. Usually, diazonium compounds are not quite stable and they can be decomposed by oxidation or hydrolysis under ambient condition. However, CBAzo is enough stable and kept without decomposition at 5 °C under air for a month.



Scheme 1

Preparation of palladium NPs was carried out by a similar procedure reported as the preparation of silver NPs.[19] Palladium nitrate (0.4909 g, 1.79 mmol) was dissolved into water (110 cm^3) and nitrogen gas was bubbled for 15 min. Diazonium salt, CBAzo (0.423 g, 1.79 mmol) was dissolved into this solution. The mixed solution was then stirred under nitrogen atmosphere for 5 min, and aqueous $NaBH_4$ (0.0679 g, 1.79 mmol in 28 g of water) was introduced dropwise for 2 hrs at room temperature. If the aqueous $NaBH_4$ is added faster, nitrogen gas generated from CBAzo more rigorously and it forms. This gas bubbling often induces aggregation of Pd NPs. The solution was kept stirred for 2 hrs, and the color of the solution changed from brown to black which corresponding to the formation of Pd NPs. Pd NPs were then collected using centrifuge (10,500 rpm) and washed with water and organic solvents. TGA measurement (SII TG/DTA6200) was performed under air with a temperature increasing rate of 10 °C min^{-1} to confirm the contents of palladium and organic molecules. Measuring the weight loss during heating in TG-DTA measurement, we can obtain the palladium content. TEM Observation was carried out with a Hitachi H-9500 TEM with an acceleration voltage of 300 kV. Particle sizes were obtained by measuring in enlarged TEM images. XPS measurements were carried out with a JEOL JPS-9200 spectrometer.

The obtained palladium NPs were applied as a catalyst for Suzuki-Miyaura coupling reaction.[28] ^1H and ^{13}C NMR measurement of the confirmation of the products was carried out at room temperature with a Brucker AVANCE III Micro-bay (400 MHz). Tetramethylsilane (0.00 ppm) was used as an internal standard. The product yield was confirmed with a gas chromatography (Shimadzu GC-2010 Plus) equipped with a capillary column (TC-1, GL Sciences 15 m) and a FID detector.

Pd NPs were prepared by chemical reduction with $NaBH_4$. During the dropwise addition (2 h) of an aqueous solution of $NaBH_4$ into an aqueous solution of $Pd(NO_3)_2$, the color of the solution was immediately changed from brown to black. After the complete addition of $NaBH_4$, the mixed solution was kept stirred for 2 h. No significant precipitates were observed, which indicated that the stabilization by Pd-C bonding was successfully achieved as in the case of Ag.[19] An aliquot of the aqueous dispersion of palladium NPs was dropped onto a carbon-coated copper TEM grid and dried to obtain a TEM sample. The TEM image and the particle size distribution of the Pd NPs are shown in Fig. 1. Many particles show spherical forms but crystalline surfaces can also be observed in the image. Unfortunately, the particle size was not quite uniform and relatively larger. For example, the diameters of PVP-stabilized Pd NPs obtained by ethanol reduction,[15] surfactant-stabilized NPs obtained by photo reduction,[22] and of thiol-stabilized Pd NPs prepared by $NaBH_4$ reduction of Pd^{2+} are about 2 – 3 nm.[26,27] However, the average particle size of the obtained NPs is 26.6 nm and the standard deviation of the distribution is 12.2 nm from the measurement of 239 particles in the enlarged images. This is probably due to the slow formation rate of Pd-C bonds by this reduction procedure. The wide size distribution of the obtained Pd NPs can be ascribed to the instability of phenyl radicals, which are the intermediate compounds during the formation of Pd-C bonds. Some aggregated structures were observed in the TEM images, but they could be collected by centrifuge as a powder form and then they were well re-dispersed into water. No precipitate was observed after re-dispersion. The particles are not quite uniform and relatively larger than other Pd NPs prepared by chemical reduction. TG-DTA measurement revealed that the palladium content of Pd NPs was 86.5 wt%.

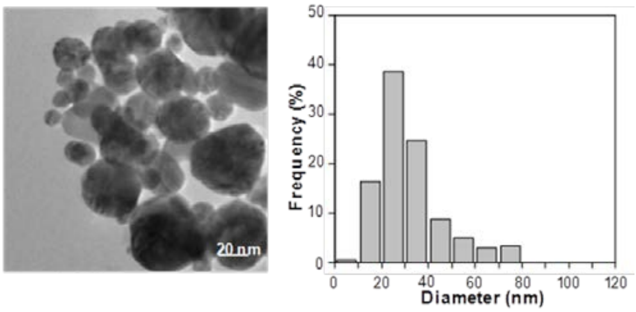
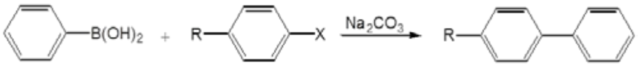


Figure 1. TEM image and size-distribution histograms of Pd-C bond-stabilized Pd NPs. The average size and the standard deviation of the particle size are 26.6 ± 12.2 nm.

XPS analysis of the obtained Pd NPs was also carried out with the dry powder. The C_{1s} peak was used as an energy reference and fixed at 285 eV. The O_{1s} peak was observed at *ca.* 531-532 eV, indicating the presence of carboxylic acid groups on the NP surface.[19,29] Peaks corresponding to Pd from the NPs were found at 340 eV ($3d_{3/2}$) and 334.6 eV ($3d_{5/2}$). These peaks can be explained by the fact that the surface Pd of the NPs was electron rich due to the direct attachment of π-electron rich aromatic rings to the NP surfaces.[30-32]

We have applied the obtained Pd NPs as a catalyst of Suzuki-Miyaura coupling reaction as shown in Scheme 2.



Scheme 2

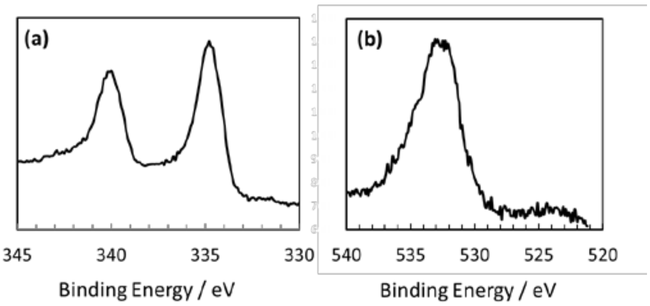


Figure 2. XPspectra obtained from Pd-C bond-stabilized Pd NPs: (a) Pd_{3d} and (b) O_{1s}. The peak shifts were observed in the spectrum (a) due to the electron-rich character on the Pd NPs. The C_{1s} peak was used as an energy reference at 285 eV.

Table 1. Suzuki-Miyaura coupling reaction of aryl halides and phenylboronic acids catalyzed by palladium NPs.[a]

Entry	R	X	Solvent	Base	Yield / %	
					3 h	**6 h**
1	H	Br	H_2O	Na_2CO_3	67	83
2	H	Br	$H_2O/EtOH^b$	Na_2CO_3	92	94
3	Me	I	$H_2O/EtOH^b$	Na_2CO_3	81	94
4	COOMe	Br	$H_2O/EtOH^b$	Na_2CO_3	87	86
5	H	Br	H_2O	Et_3N	43	51
6	H	Br	H_2O	K_2CO_3	95	96

[a]Reaction conditions: see scheme 2, phenylboroic acid (1.1 mmol), aryl halide (1 mmol), Pd NPs (0.03 mmol), solvent (10 cm^3). Reaction temperature: 90 – 95 °C. [b]Volume ratio H_2O : EtOH = 7 : 3.

In a first attempt, when Na_2CO_3 was selected as a base for this reaction, the coupling reaction proceeded in water at 90 – 95 °C. The yield of the desired biphenyl compound was as high as 67% at 3h and 83 % at 6 h (Entry **1**). This result clearly indicates that Suzuki-Miyaura coupling reaction can be proceeded even without organic solvents, that can be classified into a green reaction. Hydrophobic layers surrounding the NP surfaces shall play an important role for the high catalytic activity, because substrate compounds are not hydrophilic.[19] In order to increase the yield of the products, the reaction was performed in a water/ethanol (7/3 v/v) mixture (Entry **2**) and the yield raised up to 94 % after 6 h reaction. Methyl- and acetyl-substituted halogens (Entries **3** and **4**) also gave the target biphenyl compounds with high yields of 94 and 86 % for 6 h reaction, respectively. The best product yield of our catalyst for Suzuki-Miyaura coupling is ca. 95 % as Engries **2** and **6** shows no obvious increase of the product yield with the reaction time (6 h).

Our σ-bond (Pd-C) bond stabilized Pd NPs shows lower catalytic activities in water or in water/ethanol slightly lower than other Pd NPs when the same substrates as Entry **1** were used. Pd NPs (~ 3 nm, base K_2CO_3) stabilized by hydrophilic polymer,[33] hydrogel[34] and those (~ 6 nm, base Et_3N) stabilized by amphiphilic polymer[35] showed higher activity in water/ethanol than our NPs. Pd NPs supported by microporous polymers (base K_2CO_3) showed a similar catalytic activity.[36]

Therefore we have selected other bases such as trimethylamine and K_2CO_3 for this reaction (Entries **5** and **6**). Then, the product yield was increased up to 96 % when K_2CO_3 was used as a base. Even the activity was still lower than others but comparing the particle size of our Pd NPs (26.6 nm), it can be considered that the turn over frequency of our NPs is very high. These results strongly suggest that the hydrophobic layer generated by the ligand **1** on the particle surface strongly affect the catalytic activity of our Pd NPs.

In conclusion, for the first time we have easily and successfully prepared Pd NPs stabilized by aromatic ligand molecules with Pd-C bonds by $NaBH_4$ reduction of a Pd salt. The average particle size is ca. 27 nm which is much larger than the reported Pd NPs prepared by similar chemical reduction. But these Pd NPs can be re-dispersed in water. These Pd NPs showed a good performance as an effective catalyst for Suzuki-Miyaura coupling reaction in water even their sizes are relative large. These phenomena can be attributed to the hydrophobic layer on the particle surface, where the substrate can be concentrated.

Acknowledgement

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