Size-Dependent Catalytic Activity and Fate of Palladium Nanoparticles in Suzuki–Miyaura Coupling Reactions

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Supporting Information

ABSTRACT: Stable, catalytically active palladium nanoparticles of various average diameters (1.9−7.4 nm) have been synthesized and characterized by X-ray diffraction, spectroscopy, and microscopy techniques to demonstrate remarkable size-dependent and renewed catalytic activity toward the Suzuki–Miyaura coupling reaction in green protocol. The catalytic activity is found to depend on the amount of the reducing agent, stabilizer−precursor ratio, solvent composition, and aryl halides used. The product obtained by this reaction is characterized by 1H NMR, 13C NMR, and IR spectroscopy analyses. A newly developed kinetic equation illustrates that while the catalyst particles of the lowest dimension are gradually exposed to the reactants and hence activated due to partial removal of capping polymer from the catalyst surface, others are deactivated due to agglomeration during the progress of the reaction, as conformed by the microscopic profiles of the used and unused catalysts.

INTRODUCTION

Nanoparticles play tremendous roles in various fields because of their large surface-to-volume ratio, more energized surface molecules, electron confining ability, capability of tuning the properties of material, providing bridge between bulk material and single molecules, etc.1−4 On the other hand, transition metals are used as catalysts in a large number of organic reactions, including the carbon−carbon (C−C) coupling reaction using metals like Cu, Cr, Co, Pd, Ni, etc.5−7 Among these, Pd is special and found to be the metal of the most comprehensive use.

Among different C−C coupling reactions, Suzuki−Miyaura is an efficient one8−18 because handling and removal of reagents and products are easy compared to those of the corresponding compounds in organometallic reactions.19−22 Moreover, the reaction is not affected by the number of functional groups present in aryl halides or arylboronic acids. Pd-catalyzed C−C and carbon−heteroatom coupling reactions are performed mostly by expensive, toxic, and air-sensitive P- and/or N-donating ligands like tetrakis(triphenylphosphine)-palladium(0), tris(dibenzylideneacetone)dipalladium(0) in organic solvents, and poly(2-oxazoline) palladium carbine complex in water, and poly(2-oxazoline) palladium carbine in aerated solutions.30−35 In fact, despite routine use of nonaqueous solvents in many organic syntheses, the most abundant, versatile, nontoxic solvent water is now regaining importance for economic, environmental, and safety concerns.36−42

The last 2 decades have witnessed extensive use of homogeneous Pd catalysts because of their higher activity and selectivity.43−46 But considering the contamination of ligand and Pd metal in the products, as well as tedious separation and recycling involved in homogeneous catalysis in large scale and industrial syntheses, microheterogeneous catalysis especially by nanoparticles is now favored.19−30 In previous studies,31,32 we observed that strong ligands provide small but catalytically less active nanoparticles, since these ligands cover the nanoparticle surface almost entirely preventing any reactant molecules to approach. Conversely, linear polymers like poly(vinyl alcohol) (PVA), poly(vinylpyrrolidone), sodium polyacrylate, etc. can control the shapes and sizes of the nanoparticles, without affecting their inherent catalytic activity.53,54 Reportedly, PVA is mainly a steric stabilizer of nanoparticles, although it weakly interacts with metal nanoparticles by its functional group and covers the surface of nanoparticles like ligands. Moreover, polymer-stabilized lyophilic metal nanoparticles can be uniformly dispersed with reactants and products in solvents resembling a homogeneous catalytic system.55

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Our aim here is to study the Suzuki−Miyaura coupling reaction by using a very low content of synthesized palladium nanoparticles of various diameters under green protocol and also to determine the size-dependent catalytic activity and change of the PVA-protected synthesized nanocatalysts during the progress of the reaction.\(^{56}\)

**RESULTS AND DISCUSSION**

**X-ray Powder Diffraction (PXRD) Analysis.** The X-ray powder diffraction (PXRD) pattern of Pd nanoparticles of catalyst-A is shown in Figure 1. Only two characteristic peaks of carbon-loaded palladium are marked at the \(2\theta\) values of 40.01 and 68.06\(^\circ\) corresponding to (111) and (220) planes of face-centered cubic (FCC) crystal of Pd (JCPDS FN: PDF#870637). Moreover, two characteristics peaks of graphite carbon are marked at 36.59 and 44.52\(^\circ\) corresponding to (020) and (101) planes of orthorhombic primitive and hexagonal primitive lattices (JCPDS FN: PDF#898491, 898487).

**UV−Visible Absorption Spectra Analysis.** The UV−visible spectra of all five sets of nanoparticles show typical characteristic spectra of nanoparticles of Pd metals (Figure 2), with obvious absence of surface plasmon peak.\(^{51,57}\) Each profile shows continuous increase in absorbance at lower wavelength (higher frequency), indicating the formation of nanoparticle with higher band gap. The absorbance values particularly at the UV region, of different sets of global nanoparticles synthesized, vary as \(A > B > C > D > E\), according to the reverse order of average diameter, as presented in Scheme 1.

**Transmission Electron Microscopy (TEM) Characterization of Pd/PVA Catalysts.** The transmission electron microscopy (TEM) images (a−e) and the corresponding histograms (i−v) of almost globular synthesized Pd nanoparticles marked as A−E, respectively, are presented in Figure 3. The histograms are drawn on the basis of single or multiple micrographs of the same catalyst particles and presented on the right-hand side of the corresponding micrographs. The corresponding average diameter of the particles decreases with increase of the amount of reducing agent and stabilizer used, as expected.\(^{57−59}\) The high-resolution TEM images of catalysts A, C, and E (Figure 4) reveal that \(d\) spacing is around 0.232 nm, which corresponds to (111) planes of FCC Pd nanoparticles (PDF#011312).

**Salient Features of the Suzuki−Miyaura Coupling Reaction.** Palladium nanoparticles of smaller diameters are more effective catalysts compared to larger ones, as evidenced from Figure S1 and Tables S1−S5 presented in the Supporting Information. These also act excellently in green solvents compared to hazardous aprotic organic solvents like CH\(_3\)CN, where the catalytic efficiency of the Pd nanoparticles is decreased plausibly due to agglomeration. Table 1 shows the effect of medium and the leaving group of the aryl halides in the Suzuki−Miyaura reaction. Initially, three pure solvents C\(_2\)H\(_5\)OH, H\(_2\)O, and CH\(_3\)CN are studied, and it is found that protic organic solvent, ethanol, is the best, as revealed from the percent yield of biphenyl, turn over number (TON), and turn over frequency (TOF). The presence or generation of heterogeneity in the reaction mixture due to less solubility of any component of the reaction mixture or less dispersion of the catalyst seems to be the cause of decreased kinetics in highly polar protic solvent H\(_2\)O and dipolar aprotic CH\(_3\)CN. Notably, base K\(_2\)CO\(_3\) and product biphenyl are less soluble in CH\(_3\)CN and water, respectively. Since the relative stability of the transition state with respect to that of the reactants is required for better kinetics,\(^{50}\) the reaction has also been studied in 1:1 and 1:3 v/v ratios of aqueous ethanol. It is found that the latter provides much better kinetics than that obtained from pure H\(_2\)O and C\(_2\)H\(_5\)OH. It is found that the TON and TOF values can be improved significantly by reducing the content of the catalyst in the reaction mixture and increasing the time of reaction, as evident in Table 1. Reaction conducted at room temperature (30 °C) shows 63% yield of biphenyl in 4.5 h (Table 2). The percentage of yield and apparent TON are gradually increased with time for each catalyst, indicating the ability of the catalyst to regenerate and continue the reaction (Tables S1−S5). The TOF value decreases with increase of time, indicating decrease in the concentration of the reactants with time (Tables S1−S5). The rate is found to be independent of the concentration of phenylboronic acid, as can be revealed in Table S6. The coupling product obtained from column chromatography of reaction is identified by \(^1\)H NMR, \(^13\)C NMR, and IR spectroscopy techniques (Figures S2−S4, SD1). Since the rate-determining step of the reaction is the oxidative addition of Pd to ArX with the formation of Ar−Pd−X as intermediate,\(^{61,62}\) the reaction is of first order with respect

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**Figure 1.** X-ray powder diffraction pattern of Pd(0) nanoparticles of catalyst-A (in the presence of graphite powder).

**Figure 2.** UV−visible spectra of 10 times diluted solution of catalyst (A−E).
to ArX, where X = Cl, Br, I, etc., and the C–X bond energy (presented in parenthesis in kJ mol⁻¹) is in the order C–Cl (338) > C–Br (276) > C–I (238), the yield and TON values are greater for catalyst-A in the reverse order of aryl halides. The percentage of yield for biphenyl on catalyst concentration, "a" is the initial concentration of the product that increases the rate of change of the activation of the catalyst (dCat/ dt) are obtained from the intercepts and slopes of the plots of 1/ln[a/(a-x)]versus time (t) (Figure S6). The values of k₁ and b for different catalysts are presented in Table 4.

Table 4 shows that the rate constant (k₂) of the Suzuki–Miyaura reaction increases ∼65.7/12.5 times, whereas the average particle diameter (Table 3) decreases and the increment in total surface area is ca. 4 times (7.4/1.9) for changing the catalyst from A to E. This indicates that greater catalytic activity of catalyst A is not only due to increased surface area but also due to the presence of more active surface molecules in A compared to other catalysts, B–E during the progress of the reaction. The positive sign of b in catalyst A indicates more activation of the catalyst, whereas the negative sign might be stated as effective deactivation for catalysts, B–E. The activation found for catalyst-A might be due to the removal of PVA from the part of surface of the nanoparticles and associated disintegration causing decrease in the diameter of the particles during reaction at the time of removal of PVA. From B to D, the deactivation increases plausibly because of immediate growth of particles. For catalyst E, the effective deactivation was not large seemingly because the average diameter of particles was initially very large. The values reveal that the second-order rate constants gradually increase with decrease in the diameter of the particles, indicating greater binding ability of the particles with ArX. The activation parameter b reveals that it decreases with increase in diameter. The set of nanoparticles with greater average diameter has relatively less number of active sites in the reaction. So, the progress of the reaction cannot make their fate much worse in terms of the number of active sites.

By comparing the value of rate constant of the Suzuki–Miyaura coupling reaction with iodobenzene and phenylboronic acid using 0.2 mol % Pd nanoparticles (catalyst-A) at two different temperatures (30 and 60 °C) (Tables 2 and S1), the activation energy of the reaction was found to be 60.6 kJ mol⁻¹. The result

Recyclability of the Catalyst. To study the level of reusability for practical applications, the best- and worst-performing catalysts A and E were selected for the recycling in the Suzuki–Miyaura reaction (Table 5). The result
shows that the % yield in 1.5 h increases slightly in the third cycle in comparison to that in the first cycle for catalyst-A, whereas it decreases gradually for catalyst-E with increase of the cycle number. This indicates that catalyst-A can be used for a greater number of times in recycling of catalyst than catalyst-E.

The scanning electron microscopy (SEM) images of catalyst-A before and after single run (use) are depicted in Figure 3. Transmission electron microscopy (TEM) images (a−e) and the corresponding histograms (i−v) of almost globular synthesized Pd nanoparticles marked as A−E.

Figure 5a,b, respectively. In Figure 5a, it is evident that the globular nanoparticles with average diameter of 20.1 nm are mostly present in PVA matrix, whereas the particles are mostly distinct and uniformly distributed in the absence of such matrix, as evident in Figure 5b. The average diameter of the particles of used catalyst-A is 8.3 nm, less than that obtained before use of the catalyst. This type of removal of PVA from the surface of the catalyst with an effect of increased rate of reaction (current density) in cyclic voltammetric experiment was observed in our previous study.60 For catalyst-E, the average diameter of the Pd nanoparticles is 27.4 nm before use of the catalyst (Figure 5c). It is decreased to 15.2 nm after the first run due to the removal of PVA during reaction (Figure 5d). Pd nanoparticles are initially stabilized (wrapped) by PVA for both catalysts A and E, but for catalyst A to a greater extent than catalyst E because of the higher surface energy of the former. Due to approach of reactant molecules toward Pd nanoparticle surface for undergoing reaction, PVA is removed from certain relevant portion of the surface of nanoparticle and covers the other nearby part of the nanoparticle to a greater extent, facilitating disintegration of nanoparticles. Thus, the particle size is reduced in both cases at the initial state of the reaction. However, the particles with greater size, containing less stabilizing layer initially, would agglomerate first with the progress of the reaction. Thus, the particles of catalyst-E quickly agglomerate to a sufficient extent to form several flakes reducing the number of active sites during reaction, as evident from Figure 5d.

■ CONCLUSIONS
Sets of PVA-encapsulated Pd nanoparticles of average diameter 1.9−7.4 nm have been synthesized and used in size-dependent catalysis of the Suzuki−Miyaura reaction. The catalyst shows a high efficiency in 75% (v/v) ethanol−water, which seems to be the best medium of optimum composition in ethanol−water binary solvent system. Besides evaluation of the effect of the leaving group and catalytic parameters, a new kinetic equation is proposed to study the catalyst activation and deactivation during the progress of reaction. It is understood from the new analysis strategy that the effective catalyst concentration is changed with the progress of the reaction. For catalyst with the least average diameter (1.9 nm), PVA encapsulated is partly removed during the reaction, causing disintegration, so effective catalyst concentration is increased, whereas for other catalysts synthesized and studied, it is decreased due to agglomeration in the absence of a sufficient stabilizing layer. Microscopic studies of the catalysts before and after use conform to the findings.

■ EXPERIMENTAL SECTION

General Information. The UV−visible spectra of the as-synthesized particles were recorded using a UV-1800 Shimadzu UV spectrophotometer. NMR spectra of the product of the Suzuki−Miyaura coupling reaction were obtained using a Bruker Advance 300 MHz spectrometer equipped with a high-resolution multinuclear probe in CDCl3. X-ray powder diffraction (PXRD) patterns of carbon powder-adsorbed Pd catalytic were recorded on a Bruker AXS D8-Advance instrument with Ni-filtered Cu Kα radiation (λ = 1.5418 Å) at 40 kV and 40 mA, employing a scanning rate of 0.2 s per step. SEM measurements were performed under vacuum by INSPECT F 50, using 20.00 kV. Transmission
electron microscopy (TEM) images were recorded with an H7600 TEM, HITACHI instrument. IR spectra were recorded using NICOLET MAGNA IR 750.

**Materials.** PdCl2 with a purity of 99% was purchased from Arora-Matthey Ltd; water from Synergy of Millipore; NaBH4, phenylboronic acid, iodobenzene, bromobenzene, and chlorobenzene from Spectrochem Pvt. Ltd; and PVA (number-average molecular weight: 125 000) from Lab Rasayan Co. The solvent and other reagents were of AR/GR grade from Merck, India.

**Size Control Syntheses of Palladium Nanoparticles.** The typical preparation of catalyst-A is described as follows: 0.5 mL of 0.05636 (M) K2PdCl4 aqueous solution was taken in a 100 mL beaker along with 24.5 mL of 1 mass % (mass/volume) PVA solution. The whole solution was continuously stirred with addition of 3.19 mg (8.454 × 10⁻⁵ mol) of NaBH4 for 10 min. The yellow color of Pd(II) solution changed to dark brown at room temperature (30 °C), indicating the formation of palladium nanoparticles. For the size control syntheses of Pd/PVA catalysts designated as A, B, and C, NaBH4 was varied in the ratio of 6:3:2 keeping fixed concentration of K2PdCl4 and PVA, as presented in Scheme 1. In the preparation of catalyst samples A, D, and E, the PVA solution was varied in the ratio of 24.5:5:1 keeping a fixed concentration of NaBH4 and K2PdCl4 at the start of the reaction.68 These particles were then characterized by using various techniques.

**Table 1. Results of the Suzuki–Miyaura Coupling Reaction of Aryl Halide with Phenylboronic Acid at 60 °C by Using Catalyst-A in Different Solvents**

| entry | aryl halide | solvent | time (min) | Pd (mol %) | yieldb (%) | TON | TOF (min⁻¹) |
|-------|-------------|---------|------------|-------------|------------|-----|-------------|
| 1     | iodobenzene | C₂H₅OH  | 30         | 0.2         | 44         | 220 | 7.3         |
| 2     | iodobenzene | H₂O     | 30         | 0.2         | 28         | 140 | 4.7         |
| 3     | iodobenzene | CH₃CN   | 30         | 0.2         | 10         | 50  | 1.7         |
| 4     | iodobenzene | C₂H₅OH/H₂O  | 30         | 0.2         | 36         | 180 | 6.0         |
| 5     | iodobenzene | C₂H₅OH/H₂O  | 30         | 0.2         | 52         | 260 | 8.7         |
| 6     | iodobenzene | C₂H₅OH/H₂O  | 90         | 0.01        | 50         | 5000| 55.6        |
| 7     | iodobenzene | C₂H₅OH/H₂O  | 150        | 0.01        | 79         | 7900| 52.7        |
| 8     | iodobenzene | C₂H₅OH/H₂O  | 60         | 0.2         | 78         | 390 | 6.5         |
| 9     | iodobenzene | C₂H₅OH/H₂O  | 60         | 0.2         | 47         | 235 | 3.9         |
| 10    | chlorobenzene | C₂H₅OH/H₂O  | 60         | 0.2         | 32         | 160 | 2.7         |

aReaction conditions: 1.0 mmol aryl halide, 1.3 mmol phenylboronic acid, 2.0 mmol anhydrous K₂CO₃, 5 mL of solvent, and temperature 60 °C.  
bIsolated yield.  
cC₂H₅OH/H₂O (1:1) (v/v).  
dC₂H₅OH/H₂O (3:1) (v/v).

**Table 2. Results of the Suzuki–Miyaura Coupling Reaction of Iodobenzene with Phenylboronic Acid at Room Temperature (30 °C) in 75% EtOH–H₂O by (0.2 mol %) Pd(0) Nanoparticles (Catalyst-A)**

| entry | time (h) | yielda (%) | TON | TOF (min⁻¹) |
|-------|----------|------------|-----|-------------|
| 1     | 1.0      | 19         | 095 | 1.6         |
| 2     | 1.5      | 27         | 135 | 1.5         |
| 3     | 2.5      | 42         | 210 | 1.4         |
| 4     | 4.5      | 63         | 315 | 1.2         |

aIsolated yields.

**Table 3. Kinetic Parameters Exhibiting Different Catalytic Activities of the Sets of Pd Nanoparticles Synthesized, Designated by A–E in the Suzuki–Miyaura Coupling Reaction of Iodobenzene with Phenylboronic Acid**

| catalysts | diameter of Pd nanoparticles (nm) | yieldb (%) | rate constant (k₁) (min⁻¹⁻¹) |
|-----------|----------------------------------|------------|-------------------------------|
| A         | 1.9                              | 95         | 0.0348                        |
| B         | 3.4                              | 49         | 0.0059                        |
| C         | 4.2                              | 38         | 0.0036                        |
| D         | 6.4                              | 33         | 0.0034                        |
| E         | 7.4                              | 26         | 0.0025                        |

aReaction conditions: iodobenzene (1 mmol), phenylboronic acid (1.3 mmol), anhydrous K₂CO₃ (2 mmol), Pd catalyst (0.2 mol %), C₂H₅OH/H₂O (5 mL) (3:1) (v/v), reaction time 1.5 h, and temperature 60 °C.  
bIsolated yield.

Figure 4. High-resolution TEM images of palladium nanoparticles of (a) catalyst-A, (b) catalyst-C, and (c) catalyst-E.
Palladium Nanoparticles-Catalyzed Suzuki−Miyaura Coupling Reaction. The Suzuki−Miyaura coupling reaction (Scheme S1 in Supporting Information) was carried out in a closed 25 mL round-bottom flask by taking 1×10⁻³ mol aryl halide, 1.3×10⁻³ mol phenylboronic acid, 2×10⁻³ mol anhydrous K₂CO₃, and nanocatalyst containing 2×10⁻⁶ mol of Pd atom at room temperature (30°C) and 60°C at different intervals for a definite period of time. Afterward, biphenyl was separated by extraction with diethyl ether (thrice with 15 mL of diethyl ether) dried by addition of anhydrous sodium sulfate and analyzed by column chromatography. In column chromatography, a slurry of silica gel in petroleum ether (60−80°C) was taken as stationary phase and 5% ethyl acetate−petroleum ether as mobile phase at a rate of flow of 0.1 mL min⁻¹, during the separation and purification. The product (biphenyl) was identified by determination of melting point and ¹H NMR spectroscopy analysis at every stage. During the course of reaction at 60°C, it was observed that the whole reaction mixture becomes pale brownish throughout the solution. After a definite time, 15 mL of ice-cold brine solution was added and the whole solution becomes white, with some white shining crystal deposits at the bottom of the flask. The kinetic analyses of catalysts A−E were done by estimating the amounts of biphenyl product at different time intervals through column chromatography.

The recycling process was performed with catalysts A and E, at 60°C by separation of biphenyl from the reaction mixture and by extraction with diethyl ether (three times) without addition of brine solution. Then, the catalyst was separated by centrifuge, dried, redispersed, and used in the next cycle.

Table 4. Intercept and Slope of the Plots of (1/t) ln(a/(a − x)) versus t Following Equation 3 and the Corresponding Rate Constant and Rate of Activation/Deactivation of Catalyst

| parameters                          | catalysts |
|-------------------------------------|-----------|
| intercept (CΔk₂) × 10³              | A         | B         | C         | D         | E         |
| slope (Δ[a/2]) × 10⁴                | 1.51      | −0.11     | −0.09     | −0.11     | −0.04     |
| second-order rate constant (k₂) × 10³| 65.7      | 29.6      | 20.2      | 18.0      | 12.5      |
| rate of activation of catalyst (b) × 10³ | 4.60      | −0.72     | −0.86     | −1.19     | −0.70     |
| Adj. R²                             | 0.97      | 0.98      | 0.98      | 0.96      | 0.96      |

*aInitial concentration of the catalyst in the solution (C₀) is 0.296 mM.

Table 5. Recyclabilities of Catalysts A and E in the Suzuki−Miyaura Coupling Reaction of Iodobenzene and Phenylboronic Acid at 60°C by Using by 0.2 mol % Pd(0) Nanoparticles

| catalysts | no. of recycle with yieldb (%) |
|-----------|--------------------------------|
|           | 1st   | 2nd   | 3rd   |
| A         | 95    | 96    | 96    |
| E         | 26    | 22    | 15    |

*bReaction conditions: iodobenzene (1 mmol), phenylboronic acid (1.3 mmol), anhydrous K₂CO₃ (2 mmol), Pd catalyst (0.2 mol %), C₂H₅OH/H₂O (5 mL) (3:1) (v/v), reaction time 1.5 h, and temperature 60°C. bIsolated yield.

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Figure 5. SEM images of palladium nanoparticles of catalyst A and E before use (a, c) and after single run (1.5 h) (b, d). The histograms are presented on the right-hand side of the corresponding images.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01598.
Conversion efficiency of the Suzuki–Miyaura coupling reaction; kinetic parameters toward the Suzuki–Miyaura cross-coupling reaction; profile to prove that the rate of reaction is independent of the concentration of phenylboronic acid; $^1$H NMR, $^{13}$C NMR, and IR spectra of bipheny1; characterization data of bipheny1; $\ln(a/(a-x))$ versus time and $(1/t)\ln(a/(a-x))$ versus time t diagrams of the Suzuki–Miyaura cross-coupling reaction by using catalysts A–E; derivation of the kinetic equation; Suzuki–Miyaura coupling reaction (PDF)

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Notes

The authors declare no competing financial interest.

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