Heck Chemistry - a Highly Active Ligand-Free Metal Catalyst System in Situ Generated from PdII Supported on SiO2

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Abstract A ligand-free Pd catalyst system derived from Pd(acac)2/SiO2 and its catalytic properties toward the Heck coupling of bromobenzene and styrene have been studied. Combined studies by X-ray photoelectron spectroscopy (XPS), ultraviolet and visible absorption spectroscopy (UV-vis), thermogravimetric analysis (TGA) and powder X-ray diffraction (XRD) indicate that calcination of Pd(acac)2/SiO2 in air at 400°C produces PdII/SiO2 that contains isolated Pd2+ ions coordinated to the lattice oxygen as the dominant component and PdO particles as the minor component. XPS and UV-vis observations together with catalytic results reveal that most of PdII is reduced to Pd0 on SiO2 by the reaction media during the Heck reaction and that the resulting catalyst system is highly active. Transmission electron microscopy measurements show that the in situ prepared Pd0/SiO2 has much finer Pd particles than conventional Pd0/SiO2. The rapid growth of the supported Pd particles during the highly efficient Heck reaction suggests that the catalysis occurs via an Ostwald ripening mechanism. Resulting in excellent catalytic properties, PdII/SiO2 possesses incomparable advantages over conventional Pd0/SiO2 as a precatalyst in catalytic activity, catalyst recycling and product contamination control.

Keywords Heck reaction, in situ generated, palladium, silica, supported

1. Introduction

Among the various ways to synthesize arylated olefins, the construction of C(sp2)-C(sp2) single Bonds through Heck coupling is probably the most attractive way.1-5 It constitutes a very selective approach of forming new C-C bonds in a single operational step by coupling aryl and vinyl halides/triflates with olefins, in order to obtain a variety of substituted olefins, dienes and other unsaturated compounds.2,3,5

Many of these compounds are useful as natural products, dyes, UV screens, raw materials for novel polymers, and intermediates for agrochemicals and pharmaceuticals.3,5 Significant benefits of developing Heck reactions lie in the tolerance of Heck reactions toward a large variety of functional groups on both reactants1,5 and a wide availability of aryl chlorides and bromides. Traditional Heck reactions are typically carried out with 1-5 mol % of a Pd catalyst in the presence of a phosphine ligand and moreover the maximum turnover number (TON) attains 20-100 only.6 This obviously restricts large-scale industrial application. A major challenge in this area has in the past years been the development of new catalysts with higher TON. Quite a few advances have been made, including the use of sterically bulky and electron-rich phosphines, phosphorus-, nitrogen- and sulfur-based palladacycles and nucleophilic carbenes.6 However, all of these catalyst systems still suffer from drawbacks such as high ligand cost, high ligand sensitivity toward air and moisture, toxicity and the use of various additives.

Ligand-free catalyst systems are viewed as promising for C-C coupling reactions from both operational and economic points of view.7-10 Since ligand-free Pd turned out to be feasible for Heck reactions on aryl iodides,11 extensive studies of ligand-free Pd catalyzed Heck reactions on aryl halides have increasingly been appearing.8,9,12-16 Due to the known drawbacks of homogeneous catalysts, it is desirable to develop heterogeneous Heck reaction catalysts for industrial applications and notable progress has been seen in this area.12-16 Instead of organic ligands, ligand-free Heck reaction catalyst systems usually employ a variety of inexpensive bases such as NaOAc, Na2CO3, NaHCO3, Ca(OH)2, Mg(OH)2, K2PO3, and amines.

Amorphous SiO2 is one of the most commonly used supports for preparing heterogeneous metal catalysts. This material possesses the advantage of good stability in mechanics and chemistry. Nevertheless, little attention has been paid to on amorphous SiO2-supported metal catalyst systems for Heck reactions. To our knowledge, only a few limited catalytic results have appeared concerning Heck reactions...
over amorphous SiO₂-supported Pd metal catalyst systems.17-26 Nearly all of these catalysts were conventionally prepared from Pd⁰/SiO₂ using a pre-reduction method. A conventional Pd⁰/SiO₂ system has been considered to have no potential competitiveness with homogeneous Pd catalysts because its activity is far from that of homogeneous Pd catalysts. The only example of Pd⁰/SiO₂ used as a precatalyst has emerged in a letter about Heck couplings of aryl iodides and alkyl acrylates in the presence of Pd(NH₃)₄Cl₂/SiO₂.23 This supported complex was prepared by an ion-exchange method and was not subjected to any further treatments prior to Heck reactions. The catalytic activity was similar to that over conventional Pd⁰/SiO₂ in an organic solvent, although it had a slight advantage in an ionic liquid.23

In recent years, we have focused our research on catalysis by the Pd/SiO₂ system for the Heck coupling of bromobenzene (PhBr) and styrene shown in Scheme 1. In the present article, we present extended studies concerning the performances of the catalyst system in situ generated from Pd⁰/SiO₂ for the Heck reaction. The chemistry of Pd⁰/SiO₂ with regards to the Heck reaction is elucidated in terms of detailed studies by several characterization techniques such as X-ray photoelectron spectroscopy (XPS), ultraviolet and visible absorption spectroscopy (UV-vis) and transmission electron microscopy (TEM). We also attempt to interpret the high activity of such a catalyst system in situ prepared for Heck reactions in virtue of the size of supported metal particles. Nevertheless, the effect of the supported metal particle size on Heck reactions is referred to homogeneous catalysis instead of heterogeneous catalysis.

2. Results and Discussion

2.1. Behavior of Various Pd Catalysts in Heck Reactions

Table 1 shows the comparative catalytic data of four different catalyst systems for the Heck coupling of PhBr and styrene at 135 °C. In the cases with 0.14 mol % Pd, Pd(acac)₂ in solution resulted in the highest activity with a conversion of 82 % within 0.5 h; conventional Pd⁰/SiO₂ displayed the lowest activity: The conversion was only 10 % within 2 h and did not reach a maximum of 59 % until after 45 h. The latter results are consistent with those reported for Pd⁰/SiO₂ handled under similar conditions.21 Consistent comparative results were observed with 0.023 mol % Pd: Pd(acac)₂ in solution was the most active system with a conversion of 82 % within 0.5 h; conventional Pd⁰/SiO₂ was the least active with a conversion of 18 % at 20 h. Pd(OAc)₂ in solution gave relevant results in accordance with those in the literature as well.6 Surprisingly, Pd⁰/SiO₂ brought about unusual activities: A conversion of 76 % was obtainable within 2 h and the reaction gave a maximal conversion of 88 % after 4 h with 0.14 mol % Pd; a conversion of 57 % was achievable within 1 h and the reaction presented a maximal conversion of 70 % with 0.023 mol % Pd. In fact, Pd⁰/SiO₂ gave rise to an activity intermediate between those of Pd(acac)₂ and Pd(OAc)₂ in solution. Our additional experimental data show that Pd(OAc)₂, when utilized as a catalyst precursor to make Pd/SiO₂, actually is not different from Pd(acac)₂ in the catalytic properties of both conventional Pd⁰/SiO₂ and Pd⁰/SiO₂ for this Heck reaction under the above working conditions.

| Precatalyst | Pd mol % | Reaction time (h) | Conversion (%) | Yield of trans-stilbene (%) | Turnover number |
|-------------|-----------|------------------|---------------|---------------------------|---------------|
| Pd⁰/SiO₂    | 0.14      | 1                | 8             | 7                         | 57            |
|             | 0.14      | 2                | 10            | 9                         | 71            |
|             | 0.14      | 20               | 46            | 43                        | 329           |
|             | 0.14      | 45               | 59            | 55                        | 421           |
|             | 0.023     | 1                | 1             | 1                         | 43            |
|             | 0.023     | 2                | 3             | 2                         | 130           |
|             | 0.023     | 20               | 18            | 16                        | 783           |
|             | 0.14      | 2                | 76            | 69                        | 543           |
|             | 0.14      | 4                | 88            | 80                        | 629           |
|             | 0.023     | 1                | 57            | 52                        | 2478          |
| Pd(acac)₂   | 0.14      | 0.5              | 82            | 73                        | 586           |
|             | 0.223     | 0.5              | 82            | 74                        | 3565          |
| Pd(OAc)₂    | 0.14      | 0.5              | 55            | 50                        | 393           |
|             | 0.14      | 1                | 63            | 58                        | 450           |
|             | 0.14      | 2                | 67            | 61                        | 479           |
|             | 0.023     | 0.5              | 28            | 23                        | 1217          |
|             | 0.023     | 1                | 31            | 28                        | 1348          |
|             | 0.023     | 2                | 34            | 31                        | 1478          |

* 0.15 g of Pd⁰/SiO₂ or Pd⁰/SiO₂ with 1 % Pd loading, 0.0043 g of Pd(acac)₂, 0.0032 g of Pd(OAc)₂.
* For 0.14 mol % Pd: 10 mmol of PhBr, 15 mmol of styrene, 10 mmol of NaOAc, 10 ml of DMA; for 0.023 mol % Pd: 60 mmol of PhBr, 90 mmol of styrene, 60 mmol of NaOAc, 30 ml of DMA.
* Total yield of coupling products.
* Turnover number for conversion (moles of coupling products formed/moles of Pd).
On the other hand, the effect of the NaOAc amount used on the catalytic activity shows that Pd\textsuperscript{II}/SiO\textsubscript{2} is such an active system that the base can easily be consumed stoichiometrically within a short reaction time. The relationship between the maximal conversion of PhBr and the NaOAc:PhBr molar ratio was established following a series of experiments over Pd\textsuperscript{II}/SiO\textsubscript{2} with 0.14 mol % Pd. In any experiment, a maximal conversion of PhBr at a certain NaOAc:PhBr molar ratio could be achieved after 5 h of reaction. As a consequence, such a catalytic conversion ascended linearly with the increase of the NaOAc amount added over the range of the NaOAc:PhBr molar ratio between 0 and 1, as seen in Figure 1. This implies that the catalytic reaction proceeds equally fast in the presence of a lesser amount of NaOAc and that the reaction rate over Pd\textsuperscript{II}/SiO\textsubscript{2} seems independent of the NaOAc:PhBr molar ratio.

Figures 2 and 3 present the comparative kinetics of the Heck coupling of PhBr and styrene over the four precatalysts at 135°C. It is worth indicating that the Pd\textsuperscript{II}/SiO\textsubscript{2} system behaves comparably to a homogeneous catalyst system: Its activity is higher than that of the homogeneous Pd(OAc)\textsubscript{2} system and close to that of the homogeneous Pd(acac)\textsubscript{2} system with 0.14 mol % Pd after 2 h; its activity reaches 2.1 times that of the homogeneous Pd(OAc)\textsubscript{2} system and 77 % of that of the homogeneous Pd(acac)\textsubscript{2} system with 0.023 mol % Pd at 2 h.

In Table 2 are compared the catalytic properties of the Pd/SiO\textsubscript{2} system in the present work and representative supported Pd systems reported to date for the Heck coupling of PhBr and styrene. There are only six cases of supported Pd II (Pd\textsuperscript{II}/C,\textsuperscript{31} Pd\textsuperscript{II}/HT,\textsuperscript{32} Pd\textsuperscript{II}/Beta,\textsuperscript{33} Pd\textsuperscript{II}/TiO\textsubscript{2},\textsuperscript{34} Pd\textsuperscript{II}/Al\textsubscript{2}O\textsubscript{3}\textsuperscript{14} and Pd\textsuperscript{II}/MCM-41\textsuperscript{15}) known as the precatalyst for this Heck reaction. Unlike in the case of Pd\textsuperscript{II}/SiO\textsubscript{2}, these supported Pd\textsuperscript{II} samples prepared by impregnation, coimpregnation and precipitation, except Pd\textsuperscript{II}/Beta, did not undergo any further treatments (e.g. calcination) before the Heck reaction. Apparently, Pd\textsuperscript{II}/support results in a much higher catalytic activity than Pd\textsuperscript{0}/support in every case in view of both turnover number (TON) and reaction time. The catalytic activity of our Pd\textsuperscript{II}/SiO\textsubscript{2} system is appreciably high among all the supported Pd systems listed in Table 2.
In Situ Generated from PdII Supported on SiO2

Figure 3. Heck reaction profiles of PhBr and styrene with different catalyst systems (0.023 mol % Pd) at 135 °C under Ar

Table 3. Results of catalyst recycling in the Heck coupling of PhBr and styrene with 0.14 mol % Pd at 135 °C under Ar.a

| Pre-catalyst | Cycle | Conversion (%) | Yield of trans-stilbene (%) | TONb | Soluble Pd amount (ppm)c |
|--------------|-------|----------------|----------------------------|------|--------------------------|
| PdII/SiO2    | 1     | 98             | 89                         | 700  | 2.8                      |
|              | 2     | 95             | 86                         | 678  | 3.4                      |
|              | 3     | 95             | 87                         | 678  | 2.5                      |
|              | 4     | 94             | 85                         | 671  | 4.2                      |
|              | 5     | 71             | 64                         | 507  | 3.8                      |
|              | 6     | 37             | 29                         | 264  | 2.7                      |
|              | 7     | 39             | 36                         | 279  | 7.6                      |
|              | 8     | 27             | 25                         | 193  | 8.8                      |
|              | 9     | 8              | 7                          | 57   | 8.4                      |

a Data collected after 4.5 h of reaction over PdII/SiO2 and after 17 h of reaction over Pd0/SiO2.
b Turnover number for conversion (moles of coupling products formed/moles of Pd).
c After 4.5 h of reaction over PdII/SiO2 and after 17 h of reaction over Pd0/SiO2.

Figure 4. Heck reaction profiles of PhBr and styrene with PdII/SiO2 (0.14 mol % Pd) at 135 °C under Ar.

Table 3 and Figure 4 give the results of catalyst recycling in the Heck coupling of PhBr and styrene with 0.14 mol % Pd at 135 °C. In the case of PdII/SiO2, the used catalyst could be recycled 3 times with good activity. Within 4.5 h, a nearly total conversion could be reached in each reaction cycle. After 4.5 h of reaction, the soluble Pd amount was found to range from 2.5 to 4.2 ppm in the reaction mixture, which meets government requirements of less than 5 ppm residual heavy metal in product streams in the pharmaceutical industry.38 In the case of conventional Pd0/SiO2, by contrast, the used catalyst presented continuously and seriously decreased activity when recycled. The conversion at 17 h declined considerably in the recycles with respect to that in the first cycle. After each reaction cycle, the soluble Pd amount surpassed 5 ppm, which showed a higher product contamination. The results clearly demonstrate the incomparable advantages of using PdII/SiO2 over using conventional Pd0/SiO2 as a precatalyst in catalytic activity, catalyst recycling and product contamination control for the Heck reaction.

Our detailed studies on conventional Pd0/SiO2 gave an insight in the nature of the true catalyst and showed that soluble leached Pd is likely fully responsible for catalysis in the Heck coupling of PhBr and styrene. With Pd/SiO2, such a Heck reaction likely occurs in solution following a “release and catch” mechanism.16 Catalytic Pd species are leached out of Pd/SiO2, then catalyze the coupling reaction in solution, and redeposit on Pd/SiO2 at the end of the catalytic cycle. Pd/SiO2 is viewed as merely a precatalyst or reservoir to liberate active Pd into solution.

2.2. Chemistry of PdII Supported on SiO2 with Regards to Heck Reactions

The chemical evolution of Pd(acac)2-derived SiO2-supported samples with regards to a Heck reaction was probed with the aid of a variety of analytical methods. To our knowledge, a systematic monitoring of the evolution of a supported Pd precatalyst before and after a C-C coupling reaction has not yet been reported.

Figure 5 presents the thermogravimetric analysis (TGA) profiles of Pd(acac)2 and Pd(acac)2/SiO2 having 1 % Pd loading under atmospheric air from room temperature to 400 °C at a heating rate of 10 °C/min. The weight loss of Pd(acac)2/SiO2 below 180 °C is attributed to the desorption of molecular water adsorbed on the SiO2 surface. From 180 °C, a second step of weight loss on Pd(acac)2/SiO2 consistently corresponds to the liberation of organic groups from Pd(acac)2, by comparison with the curve of weight loss of Pd(acac)2 alone. What is more, the overall TGA profile of Pd(acac)2/SiO2 clearly indicates that the thermal
decomposition of Pd(acac)₂ on SiO₂ is already quantitatively complete in air by 250 °C. The markedly lower temperature (213 °C) at which Pd(acac)₂/SiO₂ decomposes completely than that of Pd(acac)₂ (275 °C) alone implies that the interaction of Pd(acac)₂ with SiO₂ occurs significantly and speeds up the decomposition of Pd(acac)₂, or that the size of Pd(acac)₂ particles decreases upon deposition on SiO₂. Figures 6 and 7 show the XPS spectra in the Pd 3d binding energy region and the UV-vis diffuse reflectance (UV-vis DR) spectra in the 200-800 nm region of Pd(acac)₂ and Pd(acac)₂-derived SiO₂-supported samples, respectively. The XPS spectrum of Pd(acac)₂ exhibited only a pair of intense Pd 3d₃/₂ and 3d₅/₂ peaks at 341.7 and 336.4 eV by deconvolution, which indicated the occurrence of a pure Pd²⁺ state.

Following the calcination of Pd(acac)₂/SiO₂ in air at 400°C, the Pd 3d binding energy shifted back to the same positions centered at 341.7 and 336.4 eV that Pd(acac)₂ displayed. These two peaks are typical of Pd²⁺ 3d₃/₂ and 3d₅/₂ features, confirming the formation of Pd²⁺ cations coordinated to the surface oxygen sites. Actually, two similar absorption peaks have been discerned on Pd²⁺/5 Å and Pd²⁺/NaY obtained by calcination of zeolite-entrapped Pd(NH₃)₄Cl₂ under O₂ at 300 °C. The nature of the related Pd²⁺ species with these two peaks has been identified as the coordination of Pd²⁺ to the zeolite lattice oxygen. The presence of broad absorption features in the UV-vis DR spectra of calcined samples suggests the coexistence of PdO particles with isolated surface Pd²⁺. A quite weak and broad peak appeared at 33.9 ° in the powder X-ray diffraction (XRD) pattern of the calcined sample as shown in Figure 8, indicative of the formation of trace amounts of fine PdO particles on SiO₂. These results suggest that calcination of Pd(acac)₂/SiO₂ under air at 400 °C leads to the formation of Pd²⁺/SiO₂ that contains isolated Pd²⁺ coordinated to the lattice oxygen as the dominant Pd²⁺ component and PdO particles as the minor Pd⁴⁺ component.

Following 2 h of reduction of Pd(acac)₂/SiO₂ in H₂ at 400°C, only characteristic Pd⁰ 3d₃/₂ and 3d₅/₂ peaks were observed at 340.2 and 335.5 eV by deconvolution; no significant UV-vis peak was discerned. The results indicated that Pd(acac)₂/SiO₂ was indeed converted to pure Pd⁰/SiO₂ under the reductive conditions. During the Heck reaction in the presence of Pd⁰/SiO₂ calcined from Pd(acac)₂/SiO₂, an obvious color change occurred from brown to grey in the solid phase. It was indicative of the Pd valence change from +2 to 0. The spectra of Pd⁰/SiO₂ evolved after 2 h of Heck reaction: the XPS spectrum consisted of intense Pd⁰ 3d peaks and small Pd²⁺ 3d ones (Figure 6(e)); the UV-vis DR spectrum presented no longer the 474 nm peak and the broad
feature but only the 299 nm peak. The observation of the only 299 nm peak, attributable to Pd$^{2+}$ coordinated to the lattice oxygen is consistent with the presence of the remaining XPS Pd$^{2+}$ 3d peaks. These demonstrate that most of Pd$^{II}$/SiO$_2$ including isolated surface Pd$^{2+}$ and PdO particles was in situ reduced to Pd$^{0}$/SiO$_2$. The reducing agents are definitely the reaction media. The UV-vis DR results also suggest that Pd$^{II}$/SiO$_2$ contains two types of isolated Pd$^{2+}$ which are coordinated to two types of lattice oxygen sites and that one of them is hardly in situ reduced under the reaction conditions used here.

![TEM images and Pd particle size distributions of (a) Pd$^{0}$/SiO$_2$ prepared by H$_2$ reduction of Pd(acac)$_2$/SiO$_2$ at 400°C; (b) Pd$^{II}$/SiO$_2$ after 2 h of Heck reaction at 135°C and (c) Pd$^{II}$/SiO$_2$ after the second Heck reaction cycle at 135°C.](image)

Figure 9. TEM images and Pd particle size distributions of (a) Pd$^{0}$/SiO$_2$ prepared by H$_2$ reduction of Pd(acac)$_2$/SiO$_2$ at 400°C; (b) Pd$^{II}$/SiO$_2$ after 2 h of Heck reaction at 135°C and (c) Pd$^{II}$/SiO$_2$ after the second Heck reaction cycle at 135°C.

At the same time as the XPS and UV-vis studies, the TEM technique was used to measure the size of the supported Pd particles obtained by H$_2$ reduction of Pd(acac)$_2$/SiO$_2$ or in situ reduction of Pd$^{II}$/SiO$_2$. The TEM measurements can afford quantitative evidence in size for the distinct properties of different metal particle catalysts. Figure 9 illustrates the TEM micrographs and Pd particle size distributions of SiO$_2$-supported Pd particle catalysts. For Pd$^{0}$/SiO$_2$ freshly prepared by 2 h of H$_2$ reduction, the Pd particle size distribution was centered around 9 nm, covering over a wide range of 2-20 nm (Figure 9(a)). In contrast, for Pd$^{0}$/SiO$_2$ in situ generated from Pd$^{II}$/SiO$_2$ by 2 h of Heck reaction, the Pd particle size distribution showed a coverage in the range of 3-11 nm with a maximum at 6 nm. In light of the XPS information, most of Pd$^{II}$/SiO$_2$ has been in situ reduced to Pd$^{0}$/SiO$_2$ after 2h of Heck reaction. Comparison of the two distribution diagrams clearly shows that the supported Pd particles in situ generated have a much smaller mean size than those prepared by H$_2$ reduction. After the second reaction cycle, the Pd particle size distribution with Pd$^{II}$/SiO$_2$ shifted tremendously to greater sizes and the percentage of Pd particles below 12 nm fell heavily in favor of the emergence of greater Pd particles, as seen in Figure 9(c). This implies that the Pd particles grew obviously on the SiO$_2$ surface as the Heck reaction proceeded. The combined results from the Heck reaction over Pd$^{II}$/SiO$_2$ and the TEM...
analysis lead us to suggest that during the Heck reaction, the supported smaller Pd particles shrink rapidly via leaching of molecular Pd, the supported greater Pd particles grow fast via aggregation of molecular Pd, following an Ostwald ripening mechanism. In this process, leached molecular Pd takes part in the catalysis in solution. The smaller are supported Pd particles, the more easily they leach into solution and the higher is resulting catalytic activity. Although the catalysis with Pd\textsuperscript{0}/SiO\textsubscript{2} is homogeneous in nature, the higher activity is likely associated with the smaller supported Pd particles eventually.

3. Conclusions

By calcination in air at 400°C, Pd(acac)\textsubscript{2}/SiO\textsubscript{2} is transformed into Pd\textsuperscript{II}/SiO\textsubscript{2} consisting of isolated Pd\textsuperscript{2+} ions coordinated to lattice oxygen in majority and PdO particles in minority. Under the reaction conditions used here, most of the isolated surface Pd\textsuperscript{2+} ions and the PdO particles are reduced to the supported Pd particles by the reaction media. The resulting catalyst system turns out to be much more active for the Heck coupling of PhBr and styrene. The used catalyst can be recycled three times without significant loss of activity. The soluble Pd amount in the reaction mixture falls at an acceptable level (< 5 ppm) after each reaction cycle. Pd\textsuperscript{0}/SiO\textsubscript{2} in situ generated in the Heck reaction at 135°C has much finer Pd particles than Pd\textsuperscript{0}/SiO\textsubscript{2} conventionally prepared by H\textsubscript{2} reduction at 400°C. The rapid growth of the supported Pd particles during the Heck reaction suggests that the supported smaller Pd particles are susceptible to leach molecular Pd into solution that takes part in the catalysis, after which molecular Pd aggregates onto the supported greater Pd particles. The in situ generated catalyst system possesses incomparable advantages over the conventionally prepared one in catalytic activity, catalyst recycling and product contamination control.

4. Experimental

Silica gel (SiO\textsubscript{2}, Merck grade 10184) having a surface area of 300 m\textsuperscript{2}/g, palladium acetylacetonate (Pd(acac)\textsubscript{2}, 99 %), palladium acetate (Pd(OAc)\textsubscript{2}, 99.8 %), PhBr (99 %), styrene (> 99 %), anhydrous sodium acetate (NaOAc, ≥ 99 %), anhydrous N,N-dimethylacetamide (DMA, 99.8 %) and anhydrous toluene (99.8 %) were purchased from Sigma-Aldrich. Silica gel (SiO\textsubscript{2}, Merck grade 10184) having a surface area of 300 m\textsuperscript{2}/g, palladium acetylacetonate (Pd(acac)\textsubscript{2}, 99 %), palladium acetate (Pd(OAc)\textsubscript{2}, 99.8 %), PhBr (99 %), styrene (> 99 %), anhydrous sodium acetate (NaOAc, ≥ 99 %), anhydrous N,N-dimethylacetamide (DMA, 99.8 %) and anhydrous toluene (99.8 %) were purchased from Sigma-Aldrich. The gases H\textsubscript{2} and Ar had a purity of 99.999 %.

SiO\textsubscript{2}-supported Pd particle pre-catalysts were prepared as follows: SiO\textsubscript{2} (1.0 g) was pre-dehydrated at 400°C in flowing purified air for 8 h, and impregnated with a toluene (5 ml) solution of Pd(acac)\textsubscript{2} (0.029 g) under Ar. The impregnated system was stirred for 2 h under Ar followed by evacuation of the solvent to give dry Pd(acac)\textsubscript{2}/SiO\textsubscript{2} containing 1 % Pd. Pd\textsuperscript{II}/SiO\textsubscript{2} and conventional Pd\textsuperscript{0}/SiO\textsubscript{2} were obtained from Pd(acac)\textsubscript{2}/SiO\textsubscript{2} by calcination in flowing purified air at 400°C for 8 h and by reduction in flowing H\textsubscript{2} at 400°C for 2 h, respectively. Before the treatments at 400°C, Pd(acac)\textsubscript{2}/SiO\textsubscript{2} was heated from room temperature to 400°C in flowing gas at a heating rate of 10°C/min in both cases.

The catalytic reactions were conducted at 135°C in glass flasks under Ar. In a typical experiment with 0.14 mol % Pd with respect to PhBr, to a 50 ml three-neck flask equipped with a septum were introduced 10 mmol of PhBr, 15 mmol of styrene, a certain amount of NaOAc, 0.15 g of heterogeneous pre catalyst (Pd\textsuperscript{0}/SiO\textsubscript{2} or Pd\textsuperscript{0}/SiO\textsubscript{2}) or an equivalent amount of homogeneous pre catalyst (Pd(acac)\textsubscript{2} or Pd(OAc)\textsubscript{2}) under Ar. Then 10 ml of DMA was added as the solvent. After the mixture had been stirred at room temperature for 10 min under Ar, the flask was placed in a pre-heated oil bath with vigorous stirring (500 rpm). The reaction mixture was sampled at the reaction temperature and atmosphere through a 0.45 μm Whatman syringe filter. The reactants and products in the samples were analyzed by gas chromatography on a Perkin-Elmer Clarus 500 gas chromatograph with a J&W DB-1 capillary column (30 m x 0.320 mm x 1.00 μm) and a flame ionization detector. The Pd contents in the samples (leached Pd) were determined by the inductively coupled plasma (ICP) technique on a Varian Vista-MPX CCD simultaneous ICP-OES spectrophotograph.

For the determination of the content of leached Pd, a certain volume of hot filtrate collected from the reaction mixture was first subjected to evaporation of the organic components in a glass vessel by heating under vacuum. Then a certain volume of aqua regia was added to the obtained sample. After gentle boiling for 10 min, the solution was diluted to a certain volume with deionized water followed by filtration with a Whatman syringe filter. The clear solution was analyzed by ICP. Analysis of each sample was performed twice regularly.

For catalyst recycling, a solid sample containing a used supported catalyst was filtered off from the reaction mixture in air after a reaction cycle had ceased, and washed with DMA. Then it was directly transferred into a clean flask for the following reaction cycle.

The oxidation states of Pd in Pd(acac)\textsubscript{2} and Pd(acac)\textsubscript{2}-derived SiO\textsubscript{2}-supported samples were examined by XPS using an ESCALAB 250 X-ray photoelectron spectrometer with a non-monochromatic Al Kα radiation source at 1486.6 eV and 200 W. Each sample was mounted on a sample holder with the aid of double-sided conducting adhesive tape. The sample was vacuum treated for 4 h before XPS analysis under 2.0 x 10\textsuperscript{-8} mbar. The UV-vis DR spectra of solid samples were recorded on a Shimadzu UV-2550 spectrophotometer. The phase structures of solid samples were determined by XRD on a Siemens D5005 spectrometer. The thermal decomposition of Pd(acac)\textsubscript{2} and Pd(acac)\textsubscript{2}/SiO\textsubscript{2} was monitored by TGA using an SDT 2960 simultaneous DSC-TGA analyzer. The microscopic images of supported Pd particles were observed by means of TEM on a JEOL TennaG2 microscope. The Pd particle size distributions were determined by counting the sizes of 100~150 Pd particles on several images taken from different places.
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