

# A novel SiO<sub>2</sub> supported Pd metal catalyst for the Heck reaction

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A ligand-free heterogeneous metal catalyst system (represented as Pd/SiO<sub>2</sub> (O)) derived by calcination of Pd(acac)<sub>2</sub>/SiO<sub>2</sub> in air and its catalytic properties toward the Heck coupling of bromobenzene (PhBr) and styrene have been studied. X-ray photoelectron spectroscopy (XPS) and catalytic results demonstrate that most of Pd<sup>2+</sup> is reduced to Pd<sup>0</sup> on SiO<sub>2</sub> by *N,N*-dimethylacetamide (DMA) during the Heck reaction and that the resulting Pd<sup>0</sup>/SiO<sub>2</sub> is highly active for the Heck reaction, the remaining Pd<sup>2+</sup>/SiO<sub>2</sub> is not responsible for the high activity. Pd/SiO<sub>2</sub> (O) possesses incomparable advantages over a heterogeneous homolog (represented as Pd/SiO<sub>2</sub> (H)) prepared by reduction of Pd(acac)<sub>2</sub>/SiO<sub>2</sub> in H<sub>2</sub> as a pre-catalyst in both activity and catalyst recycling. The activity over Pd/SiO<sub>2</sub> (O) is comparable to that over a homogeneous Pd system. Transmission electron microscopy (TEM) analysis illustrates that the high activity over Pd/SiO<sub>2</sub> (O) consists in the small size of supported Pd particles generated *in-situ* with gentle reducing agents at a mild temperature.

**KEY WORDS:** SiO<sub>2</sub>-supported Pd; Heck reaction; ligand-free; recyclable; highly active.

## 1. Introduction

Among the various ways to synthesize arylated olefins, the construction of C(sp<sup>2</sup>)–C(sp<sup>2</sup>) single bonds through the Heck coupling is probably the most attractive [1–4]. Traditional Pd complex catalysts employ costly organic ligands such as phosphines. Since ligand-free Pd turned out to be feasible for the Heck reaction on aryl iodides [5], extensive studies of ligand-free Pd catalyzed Heck reactions on aryl halides have increasingly been appearing [2,6–10]. Due to the drawbacks with homogeneous catalysts, it has been desirable to develop heterogeneous Heck reaction catalysts for industrial applications and notable progress has been seen in this area [6,9,10]. Instead of organic ligands, ligand-free catalyst systems use inexpensive bases such as NaOAc, Na<sub>2</sub>CO<sub>3</sub>, NaHCO<sub>3</sub>, Ca(OH)<sub>2</sub>, K<sub>3</sub>PO<sub>3</sub>, and amines, etc. In homogeneous catalysis, the high activity and selectivity of catalysts can readily be achieved, but the problem of catalyst separation and the metal contamination of products cannot be avoided using such coupling reactions in the fine chemical industry. In heterogeneous catalysis, the circumstances are contrary. While the difficulties of catalyst separation and product purification can be overcome, the improvement of activity and selectivity would be realized by designing heterogeneous analogs of homogeneous catalysts.

SiO<sub>2</sub> is one of the most commonly used supports for preparing heterogeneous metal catalysts. Nevertheless, less attention has been drawn to the investigation of amorphous SiO<sub>2</sub>-supported metal catalysts toward the

Heck reaction. Only a few limited catalytic results have been published for the Heck reactions of halobenzene over amorphous SiO<sub>2</sub>-supported Pd metal catalysts [11–19]. These catalysts were conventionally prepared from Pd<sup>2+</sup>/SiO<sub>2</sub> using a pre-reduction method. Conventional Pd<sup>0</sup>/SiO<sub>2</sub> has been considered to have no potential competitiveness with homogeneous Pd catalysts because their activities are far from approaching those of homogeneous Pd catalysts. In this paper, we report on a highly active Pd/SiO<sub>2</sub> catalyst generated *in-situ* from Pd<sup>2+</sup>/SiO<sub>2</sub> for the Heck coupling of PhBr and styrene (figure 1). The advantages of this system are evident by comparison with the homogeneous analog and conventional Pd<sup>0</sup>/SiO<sub>2</sub>. The Pd valence in this system with relation to the Heck reaction is illustrated in terms of the catalytic behavior and the spectroscopic characterization. The explanation of the highly active catalyst for the Heck reaction is made in terms of the size effect of supported Pd particles.

## 2. Experimental

Silica gel (SiO<sub>2</sub>, Merck grade 10184) having a surface area of 300 m<sup>2</sup>/g, palladium acetylacetonate (Pd(acac)<sub>2</sub>, 99%), palladium acetate (Pd(OAc)<sub>2</sub>, 99.8%), PhBr (99%), styrene (> 99%), 1,4-benzoquinone (BQ, 98%), 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<sub>2</sub> and Ar had a purity of 99.999%.

SiO<sub>2</sub>-supported Pd pre-catalysts were prepared as follows: SiO<sub>2</sub> (1.0 g) was pre-dehydrated at 400 °C in

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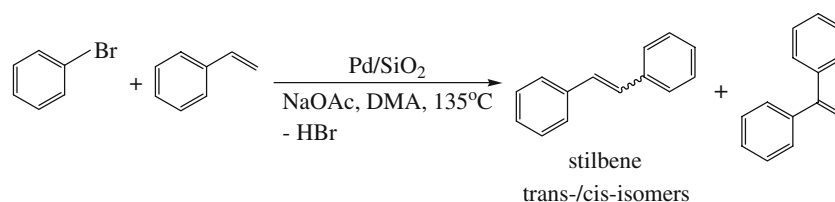


Figure 1. Heck coupling of PhBr and styrene.

flowing purified air for 8 h, and impregnated with a toluene (5 ml) solution of Pd(acac)<sub>2</sub> (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)<sub>2</sub>/SiO<sub>2</sub> with 1 % Pd loading. Pd/SiO<sub>2</sub> (H) and Pd/SiO<sub>2</sub> (O) were obtained from Pd(acac)<sub>2</sub>/SiO<sub>2</sub> by reduction in flowing H<sub>2</sub> at 400 °C for 2 h and by calcination in flowing purified air at 400 °C for 8 h, respectively. Before the treatments at 400 °C, Pd(acac)<sub>2</sub>/SiO<sub>2</sub> 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, 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/SiO<sub>2</sub> (H) or Pd/SiO<sub>2</sub> (O)) or an equivalent amount of homogeneous pre-catalyst (Pd(acac)<sub>2</sub> or Pd(OAc)<sub>2</sub>) under Ar. Then 10 ml of DMA was added as the solvent and the mixture was stirred at room temperature for 10 min under Ar. The flask was placed in a pre-heated oil bath with vigorous stirring. 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. The Pd contents in the samples and on the support were determined by inductively coupled plasma (ICP) on a Varian Vista-MPX CCD simultaneous ICP-OES spectrograph.

For the 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 next reaction cycle.

The oxidation state of supported Pd was examined by XPS using an ESCALAB 250 X-ray photoelectron spectrometer. The UV-visible spectra of reaction solutions were recorded on a Shimadzu UV-2550 spectrophotometer. The microscopic images of supported Pd particles were observed by means of TEM on a JEOL TecnaiG<sup>2</sup> microscope.

### 3. Results and discussion

Table 1 shows the comparative catalytic data of four different pre-catalysts for the Heck coupling of PhBr

and styrene at 135 °C. Trans-stilbene was formed as the dominant coupling product in all cases. Pd(acac)<sub>2</sub> in solution resulted in the highest activity with a conversion of 82% within 0.5 h, Pd/SiO<sub>2</sub> (H) displayed the lowest activity: The conversion was only 4% within 2 h and did not reach 58% until 59 h. The latter results are consistent with those reported for Pd<sup>0</sup>/SiO<sub>2</sub> handled under similar conditions [15]. Surprisingly, Pd/SiO<sub>2</sub> (O) 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. In fact, Pd/SiO<sub>2</sub> (O) gave rise to an activity intermediate between those of Pd(acac)<sub>2</sub> and Pd(OAc)<sub>2</sub> in solution. Note that Pd(acac)<sub>2</sub> and Pd(OAc)<sub>2</sub> utilized as catalyst precursors to make Pd/SiO<sub>2</sub> led to an equivalent activity in the cases of both Pd/SiO<sub>2</sub> (H) and Pd/SiO<sub>2</sub> (O).

Figure 2 presents the comparative kinetics of the Heck coupling of PhBr and styrene over the four pre-catalysts at 135 °C. It is worth indicating that Pd/SiO<sub>2</sub> (O) behaves comparably to a homogeneous catalyst system: Its activity surpasses that of the homogeneous Pd(OAc)<sub>2</sub> analog and approaches that of the homogeneous Pd(acac)<sub>2</sub> analog.

After certain period of the reaction, the Pd leaching into the liquid phase was determined using ICP. Small amounts of Pd were detected in the cases of both Pd/

Table 1  
SiO<sub>2</sub> Properties of Pd catalysts<sup>a</sup> in the Heck coupling of PhBr and styrene with 0.14 mol% Pd at 135 °C under Ar

Pre-catalyst	Reaction time (h)	Conversion (%) <sup>b</sup>	Yield of trans-stilbene(%)	TON <sup>c</sup>
Pd/SiO <sub>2</sub> (H)	1	3	3	21
	2	4	3	29
	20	18	16	128
	59	58	53	414
Pd/SiO <sub>2</sub> (O)	1	45	41	321
	2	76	69	543
	4	88	80	629
Pd(acac) <sub>2</sub>	0.5	82	73	586
Pd(OAc) <sub>2</sub>	0.5	55	50	393
	1	63	58	450
	2	67	61	479

<sup>a</sup>0.15 g of Pd/SiO<sub>2</sub> (H) or Pd/SiO<sub>2</sub> (O) with 1% Pd loading, 0.0043 g of Pd(acac)<sub>2</sub>, 0.0032 g of Pd(OAc)<sub>2</sub>.

<sup>b</sup>Total yield of coupling products.

<sup>c</sup>Turnover number for conversion (moles of coupling products formed/ moles of Pd).

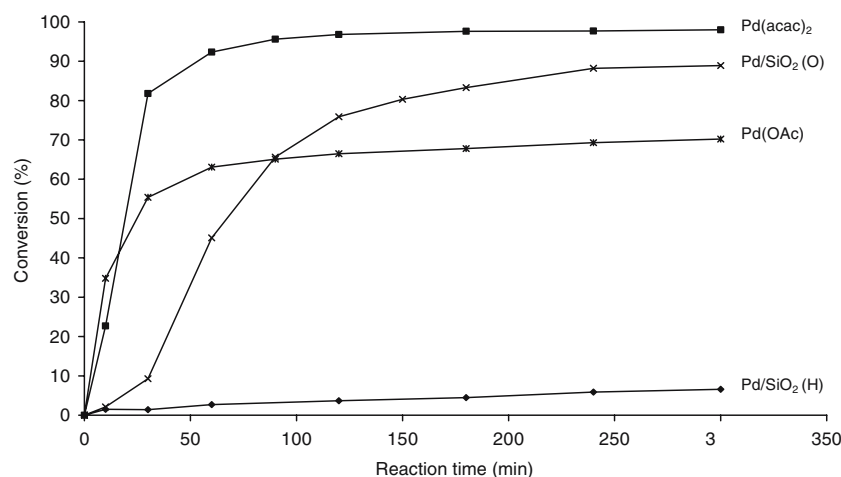


Figure 2. Heck reaction profiles of PhBr and styrene with different catalyst systems (0.14 mol% Pd) at 135 °C under Ar.

SiO<sub>2</sub> (H) and Pd/SiO<sub>2</sub> (O) with 0.14 mol% Pd: 2.5% and 4.7% of the initial Pd at 6 h and 17 h with Pd/SiO<sub>2</sub> (H), corresponding to 3.0 ppm and 5.7 ppm, 1.7% and 5.9% of the initial Pd at 7 h and 17 h with Pd/SiO<sub>2</sub> (O), corresponding to 2.1 ppm and 7.2 ppm. Therefore, the extent to which the Pd is leached into the liquid phase stays substantially small after a few hours of reactions. The actual levels of Pd in the reaction products are low, which conform to the standard of Pd allowed (< 20 ppm) in active pharmaceutical ingredients (APIs) [20]. This is of particular significance for a Heck reaction with Pd/SiO<sub>2</sub> (O), since a high and maximal yield of Heck coupling is already achieved when the reaction is ceased at 7 h.

Table 2 gives 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 Pd/SiO<sub>2</sub> (O), the used catalyst was able to be recycled at least twice with nice activity. Within 6 h, an optimal conversion could be reached in each cycle with merely a slight loss of catalytic activity one cycle after another: 90% in the first cycle, 85% in the second cycle and still 78% in the third cycle. In the case of Pd/SiO<sub>2</sub> (H), by contrast, the used catalyst presented continuously and seriously decreased activity when

recycled. At 20 h, the conversion was noted to decline considerably in the recycles with respect to that in the first cycle: 18% in the first cycle, 13% in the second cycle and only 4% in the third cycle. The results clearly account for the incomparable advantages of using Pd/SiO<sub>2</sub> (O) over using Pd/SiO<sub>2</sub> (H) as the pre-catalyst in both catalytic activity and catalyst recycling for the Heck reaction.

Figure 3 shows the XPS spectra in the Pd 3d binding energy region of Pd(acac)<sub>2</sub>-derived SiO<sub>2</sub>-supported samples. Following the calcination of Pd(acac)<sub>2</sub>/SiO<sub>2</sub> in air at 400 °C, typical Pd<sup>2+</sup> 3d<sub>3/2</sub> and 3d<sub>5/2</sub> peaks appeared at 341.7 and 336.4 eV [21], which confirms the formation of Pd oxides on the surface after treatment with air at an elevated temperature [22]. Following the reduction of Pd(acac)<sub>2</sub>/SiO<sub>2</sub> in H<sub>2</sub> at 400 °C, only characteristic Pd<sup>0</sup> 3d<sub>3/2</sub> and 3d<sub>5/2</sub> peaks were observed at 340.2 and 335.5 eV. There was no change in binding energy for the resulting Pd<sup>0</sup>/SiO<sub>2</sub> after the Heck reaction. This proves that Pd<sup>0</sup>/SiO<sub>2</sub> acts as an active site for the Heck reaction. During the Heck reaction in the presence of Pd/SiO<sub>2</sub> (O), however, an obvious color change occurred from brown to grey in the solid phase, which was indicative of the Pd valence change from +2 to 0. The XPS spectrum of Pd/SiO<sub>2</sub> (O) evolved. After the Heck reaction, it consisted of intense Pd<sup>0</sup> 3d peaks and small Pd<sup>2+</sup> 3d ones. A similar XPS result was obtained after the treatment of Pd/SiO<sub>2</sub> (O) with DMA alone at 135 °C. These demonstrate that most of Pd<sup>2+</sup>/SiO<sub>2</sub> was *in-situ* reduced to Pd<sup>0</sup>/SiO<sub>2</sub>. The reducing agents are likely to be CO and N(CH<sub>3</sub>)<sub>3</sub> released by decomposition of DMA during the Heck reaction, assuming that the decomposition of DMA follows a similar mechanism to that of *N,N*-dimethylformamide (DMF) [23].

In order to elucidate whether ligand-free Pd<sup>2+</sup> can be active for the present Heck reaction as well or not, we carried out a homogeneous reaction in the co-presence of Pd(OAc)<sub>2</sub> and BQ at a molar ratio of 1:7 with

Table 2

Results of catalyst recycling in the Heck coupling of PhBr and styrene with 0.14 mol% Pd at 135 °C<sup>a</sup> under Ar

Pre-catalyst	Cycle	Conversion (%)	Yield of trans-stilbene (%)	TON <sup>b</sup>
Pd/SiO <sub>2</sub> (O)	1	90	82	643
	2	85	77	607
	3	78	71	557
Pd/SiO <sub>2</sub> (H)	1	18	16	128
	2	13	12	93
	3	4	4	29

<sup>a</sup>Data collected at 6 h of reaction over Pd/SiO<sub>2</sub> (O) and 20 h of reaction over Pd/SiO<sub>2</sub> (H).

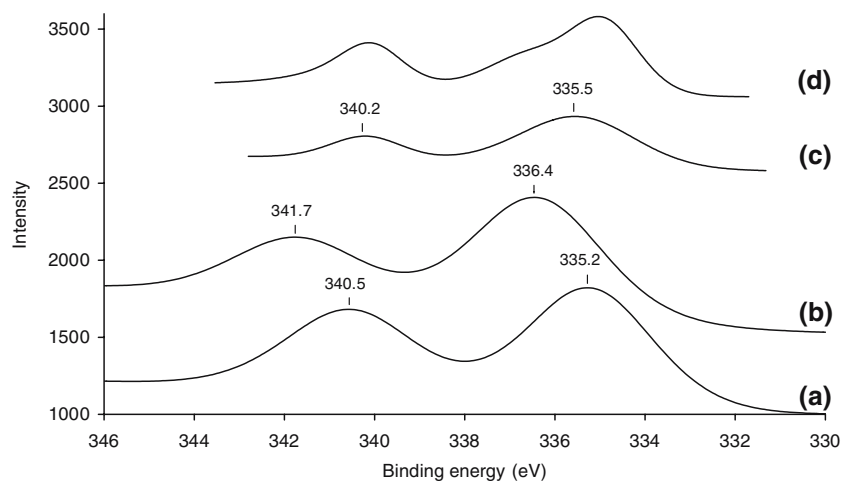


Figure 3. Pd 3d<sub>3/2</sub>, 3d<sub>5/2</sub> XPS spectra of (a) Pd(acac)<sub>2</sub>/SiO<sub>2</sub>, (b) Pd/SiO<sub>2</sub> (O), (c) Pd/SiO<sub>2</sub> (H), (d) Pd/SiO<sub>2</sub> (O) after the Heck reaction.

0.14 mol% Pd under the same operating conditions. BQ is said to be a more effective stoichiometric oxidant of Pd<sup>0</sup> than O<sub>2</sub> [24]. The addition of BQ was aimed at preventing Pd<sup>2+</sup> from being reduced to Pd<sup>0</sup> in DMA and thus at keeping Pd in the divalent state as much as possible under catalytic conditions. As a result, the shoulder peak near 352 nm for Pd(OAc)<sub>2</sub> in the UV-Vis spectrum remained substantially unchanged throughout the reaction as shown in figure 4, indicative of the successful stabilization of Pd(OAc)<sub>2</sub> in the presence of BQ. In spite of the co-presence of a large excess of DMA as a reducing source, the reduction of Pd(OAc)<sub>2</sub> can be inhibited through the oxidative process with BQ. This is probably because both CO and N(CH<sub>3</sub>)<sub>3</sub> out of DMA are weaker reducers. Meanwhile this system gave rather low conversions, which were fully incomparable to those obtained over a ligand-free homogeneous Pd(OAc)<sub>2</sub> system in the absence of BQ, as shown in figure 5. Note that BQ itself is innocent to the Pd<sup>0</sup>-catalyzed Heck

reaction according to our experiments. Pd(OAc)<sub>2</sub> itself is known as a typical Heck reaction catalyst precursor to give rise to soluble Pd<sup>0</sup> under homogeneously catalytic conditions, via which catalysis works [25]. The Pd(OAc)<sub>2</sub> homogeneous catalyst systems possess a high activity for the Heck reaction [25,26]. In our case where Pd(OAc)<sub>2</sub> was tested as a homogeneous catalyst precursor without BQ under similar catalytic conditions (coupling of PhBr and styrene in DMA at 135 °C), the high catalytic activity is reasonably attributed to soluble Pd<sup>0</sup> generated during the Heck reaction, which is the actual catalytic species. Once Pd(OAc)<sub>2</sub> is stabilized under catalytic conditions using BQ, the achieved low catalytic activity instead of a high one cannot be explained in terms of the formation of trace amounts of soluble Pd<sup>0</sup>. In fact, our supplementary catalytic data indicated that a conversion of 85% could be reached within 5 h even in the presence of 1 ppm of soluble Pd<sup>0</sup> under operating conditions. By contrast, only 20% of

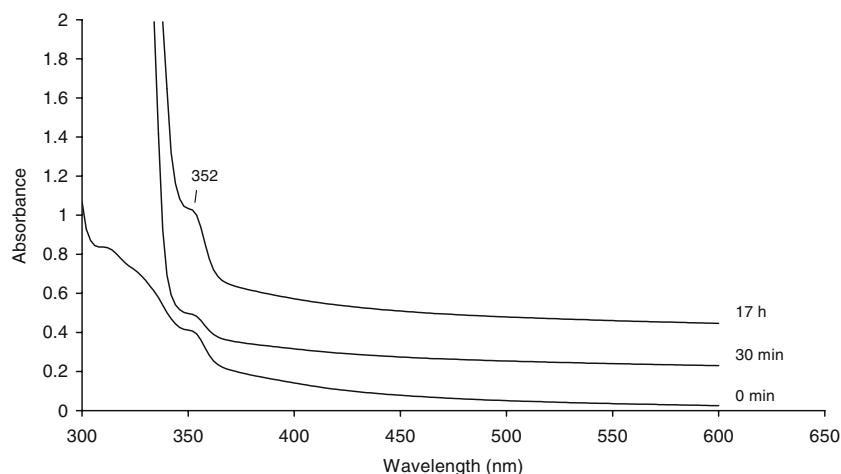


Figure 4. UV-Vis spectral evolution of the Heck reaction solution in the co-presence of Pd(OAc)<sub>2</sub> and BQ (1:7 molar ratio).

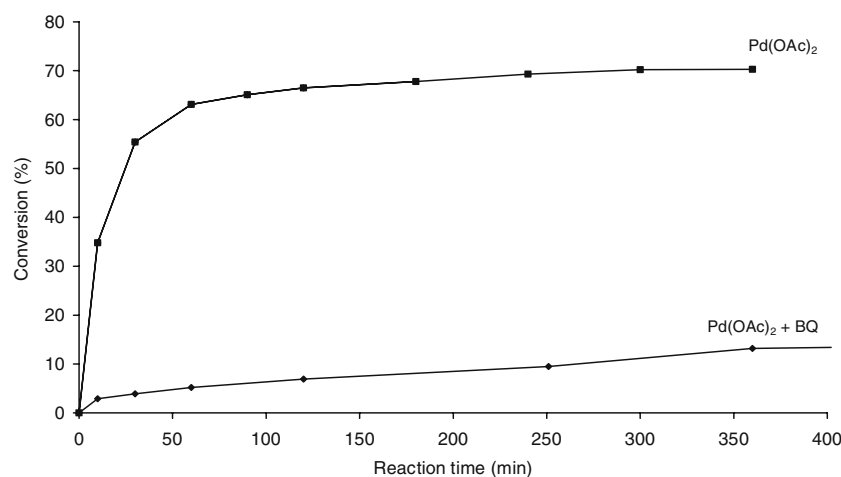


Figure 5. Heck reaction profiles of PhBr and styrene with different catalyst systems (0.14 mol% Pd) at 135 °C under Ar.

conversion can be obtained after 17 h of reaction in the system with the co-presence of Pd(OAc)<sub>2</sub> and BQ. This does not seem to reconcile the possibility that the reaction is catalyzed by a trace portion of soluble Pd<sup>0</sup> formed from Pd(OAc)<sub>2</sub>. Instead, it appears likely without further evidence that this low catalytic activity results from the catalysis of the (Pd(OAc)<sub>2</sub> + BQ) system via Pd<sup>2+</sup>/Pd<sup>4+</sup>. The Heck reaction mechanisms with palladacycles and other Pd<sup>2+</sup> compounds involving a Pd<sup>2+</sup>/Pd<sup>4+</sup> catalytic cycle have been advanced [26–33] and the formation of a transient palladacycle by the reaction of Pd(OAc)<sub>2</sub> with an olefin has been proposed [26]. In the present Heck reaction system with Pd/SiO<sub>2</sub> (O), most of Pd<sup>2+</sup>/SiO<sub>2</sub> is practically converted to Pd<sup>0</sup>/SiO<sub>2</sub> that coexists with the remaining Pd<sup>2+</sup>/SiO<sub>2</sub>. The resulting supported Pd comprising fine Pd particles as the dominant component and isolated Pd<sup>2+</sup> as the minor component shows an appreciable catalytic activity for the Heck reaction, consistent with the contributions of different groups to this aspect that the most active species is a Pd<sup>0</sup> component starting from a Pd<sup>2+</sup> compound [34]. Although the Pd<sup>2+</sup>/Pd<sup>4+</sup> mechanism cannot be ruled out when a small amount of Pd<sup>2+</sup> is detectable during a reaction period, it is strongly believed not to be responsible for the high catalytic activity as a side mechanism [34]. Therefore, we reckon that the catalytic role of ligand-free Pd<sup>2+</sup> is negligible in a sense, at least insignificant for the present Heck reaction.

In contrast to Pd/SiO<sub>2</sub> (H), Pd/SiO<sub>2</sub> (O) shows a considerably high catalytic activity in the present work. Moreover the latter used catalyst can be significantly recycled with satisfactory activity and stability. We presumably related such a difference in catalytic performance to the difference in the surface properties of supported Pd, especially the size of supported Pd particles. We thus performed TEM analyses on different Pd/SiO<sub>2</sub> samples. The observed images are shown in

figure 6. Apparently, the size of Pd particles on Pd/SiO<sub>2</sub> (H) grew from 12 to 15 nm roughly after 17 h of the Heck reaction. The size of Pd particles generated *in-situ* from Pd/SiO<sub>2</sub> (O) was found to be approximately 7 nm at 17 h of the Heck reaction. It is evident that the size of Pd particles resulting from Pd/SiO<sub>2</sub> (O) is much smaller than that of Pd/SiO<sub>2</sub> (H) at the same reaction time and that the size of Pd particles resulting from Pd/SiO<sub>2</sub> (O) is even smaller than that of Pd/SiO<sub>2</sub> (H) before the reaction. The size of supported Pd particles is most likely to dominate the catalytic activity in the Heck reaction. The smaller the Pd particle size, the more active the supported Pd. The smaller size of Pd particles produced *in-situ* from Pd/SiO<sub>2</sub> (O) arises actually from two factors. One is the lower *in-situ* reduction temperature (135 °C) and the other the weaker reducing agent. It is commonly assumed that the Pd<sup>2+</sup> species is reduced *in-situ* by a dipolar aprotic solvent like DMA or DMF or *N*-methylpyrrolidinone (NMP) [4]. Such a solvent is supposed to decompose readily under an acidic or basic condition and to give CO and an amine which act as reducing agents [23]. These weak reducing agents together with a temperature of 135 °C afford gentle reduction conditions to produce small Pd particles from Pd<sup>2+</sup> on SiO<sub>2</sub>.

#### 4. Conclusions

Under reaction conditions, most of Pd<sup>2+</sup>/SiO<sub>2</sub> is reduced to Pd<sup>0</sup>/SiO<sub>2</sub> by DMA (presumably by CO and N(CH<sub>3</sub>)<sub>3</sub> evolved by decomposition of DMA). The resulting Pd<sup>0</sup>/SiO<sub>2</sub> turns out to be a highly active catalyst. The remaining Pd<sup>2+</sup>/SiO<sub>2</sub> is unlikely to be significantly active for the Heck reaction. Pd/SiO<sub>2</sub> (O) is a highly active ligand-free pre-catalyst for the Heck coupling of PhBr and styrene. Within 1 h, the TON value for conversion over it attains to 15 times that over Pd/SiO<sub>2</sub> (H) with 0.14 mol% Pd. The activity over Pd/SiO<sub>2</sub> (O) is comparable to that over a homogeneous Pd

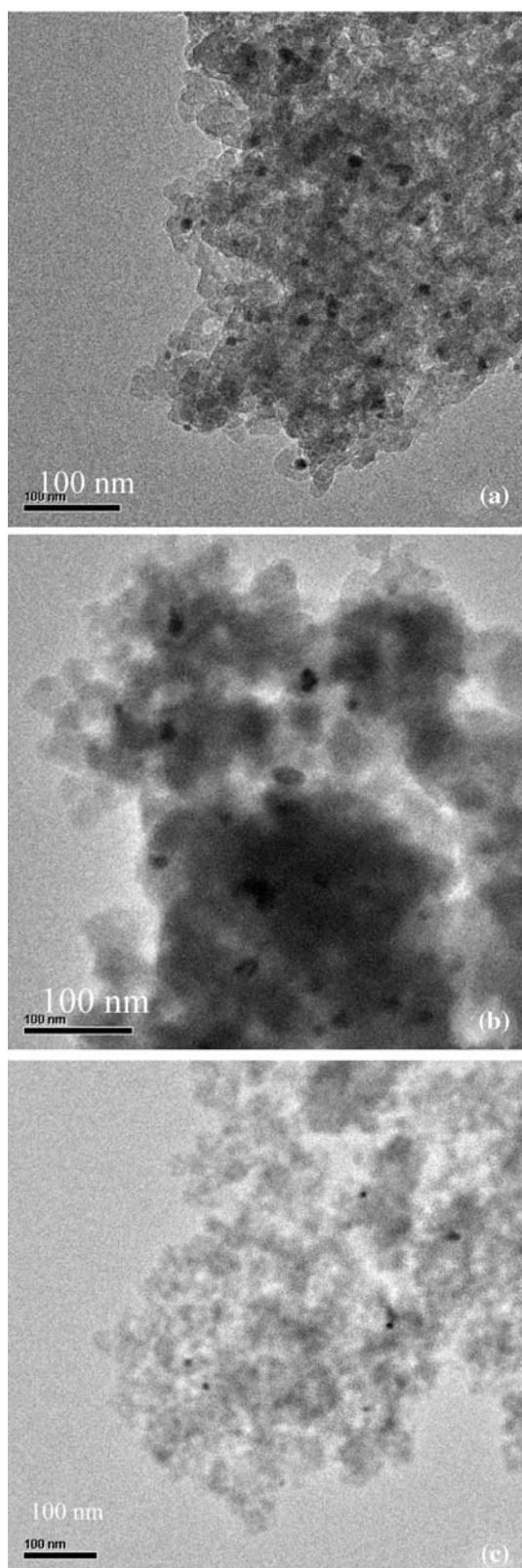


Figure 6. TEM micrographs of the surfaces of (a) Pd/SiO<sub>2</sub> (H) freshly prepared, (b) Pd/SiO<sub>2</sub> (H) after 17 h of the Heck reaction, (c) Pd/SiO<sub>2</sub> (O) after 17 h of the Heck reaction.

system. The used catalyst from Pd/SiO<sub>2</sub> (O) is recyclable with good activity and stability, which that from Pd/SiO<sub>2</sub> (H) is by no means. After the Heck reaction, lower Pd is found to be leached into the liquid phase from the support, which results in lower contamination of the coupling products. The high catalytic activity over Pd/SiO<sub>2</sub> (O) is apparently ascribed to the small size of supported Pd particles generated in-situ with gentle reducing agents (CO and N(CH<sub>3</sub>)<sub>3</sub>) at a mild temperature (135 °C).

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