# Investigation of Pd Leaching from Supported Pd Catalysts during the Heck Reaction

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*Received: May 13, 2005; In Final Form: July 19, 2005*

Palladium supported on amorphous silica, mercapto-functionalized silica, amine functionalized silica, and zeolite Y has been studied as a catalyst in the Heck reaction of iodobenzene with butyl acrylate in the presence of triethylamine base and dimethylformamide solvent. Trapping of soluble Pd with poly(4-vinylpyridine), hot filtration tests during the batchwise Heck reaction, and reaction tests of effluents from a fixed bed continuous reactor support the conclusion that leached Pd is the active phase in the Heck reaction for all of the catalysts tested. Two different paths of Pd leaching that depend on the chemical state of the Pd were elucidated in this study. Oxidative addition of aryl halide to reduced Pd caused leaching of samples containing metallic particles. However, for a zeolite Y sample containing unreduced cationic Pd, the presence of triethylamine base was required to leach Pd into solution. These two paths of Pd leaching are consistent with the generally accepted mechanism of the Heck reaction.

## Introduction

The Pd-catalyzed arylation or vinylation of olefins (i.e. the Heck reaction) is one of the most important C−C coupling reactions in organic synthesis. The Heck reaction is generally catalyzed by soluble Pd(II) or Pd(0) complexes in solution.[1−6] Homogeneous catalysts, however, suffer from the problems of separation, recycling, and deactivation via the aggregation of Pd nanoparticles formed in situ during the Heck reaction.[1,3] To overcome these problems, it is highly desirable to develop heterogeneous catalysts for industrial applications.

Conventional supported Pd catalysts with carbon, metal oxide, or zeolite as a support have been widely applied to the Heck reaction.[7,8] For example, Kohler et al. investigated a series of activated carbon supported Pd catalysts and found that the catalytic activity could be greatly improved by enhancing the Pd dispersion.[9] Palladium has also been supported on MgO, $Al_2O_3$, $TiO_2$, $ZrO_2$, and ZnO and tested as a catalyst in the Heck reaction.[10−13] The catalytic activity was influenced by the nature of the support and the dispersion of Pd.[13] Furthermore, Pd-zeolites are recognized as very active catalysts for the Heck reaction and enjoy easy separation and recovery.[14−18] Recently, Okumura et al.[19] investigated a series of zeolite Y supported Pd samples and found that the activity was related to the zeolite counterion and the charge state of Pd. Ion-exchanged zeolites containing $Pd^{2+}$ exhibited higher activity than reduced Pd in zeolite Y. These traditional supported Pd catalysts can leach Pd under reaction conditions and deactivate from the aggregation of Pd nanoparticles undergoing a Pd release/re-deposit process.

Recently, some advances in improving the catalytic activity and stability of heterogeneous catalysts have been reported in the literature. Mehnert et al. used chemical vapor deposition (CVD) to load Pd on MCM-41 and achieved high activity in Heck catalysis due to an ultrahigh dispersion of Pd.[20] Other novel synthesis approaches were used to prepare Pd Heck catalysts. Choudary et al. used hydrazine to reduce $PdCl_4^{2-}$ onto a layered double hydroxide support. Their supported catalyst exhibited higher activity and selectivity in the Heck reaction

than with a homogeneous $PdCl_2$ catalyst system.[21] Srivastava et al.[22] and Corain at al.[23] incorporated Pd nanoclusters into the pores of SAPO-31 and nanoporous resin, respectively. Okitsu and co-workers applied a sonochemical method to deposit Pd from $PdCl_2$ onto alumina support.[24] Other researchers dispersed colloidal Pd particles in block copolymer micelles, and these stabilized Pd colloids not only displayed similar activity to homogeneous Pd complexes classically used for the Heck reaction but also showed a much higher stability.[25,26]

In an effort to reduce leaching of Pd into solution, supports functionalized with P-, N-, or S-containing ligands have been used to anchor the Pd. Molnar et al.[27] investigated organically modified Pd-silica catalysts and found that Pd immobilized on silica modified with methyl or phenyl groups exhibited high activity and selectivity in the Heck coupling reaction and the choice of ligand for functionalization has an important influence on catalytic activity and stability. Mandal et al.[28] and Bedford et al.[29] investigated Pd nanoparticles immobilized on amine-functionalized zeolite and amine-functionalized mesoporous silica, respectively, and observed high activity and stability with both catalysts in the Heck reaction. Lagasi and Moggi reported that a Pd complex anchored on silica functionalized with chelating nitrogen ligands showed higher activity and better stability than a commercial Pd/C catalyst.[30] Paul and Clark[31] prepared a series of novel silica supported Pd catalyst exposing N−N, N−S, and N−O chelating ligands and compared the catalytic activity of various functionalized Pd complexes; their studies showed that the highest catalytic activity was obtained with N−N ligated Pd complex. Recently, Shimizu et al. reported that a Pd complex immobilized on mercapto-functionalized FSM-16 (mesoporous silica) also exhibited high activity and excellent recyclability.[32] Tsai et al.[33] and Gonzalez-Arellano et al.[34] investigated nanosized Pd bipyridyl complex and Pd(II)-Schiff base complex anchored onto MCM-41, respectively, and reported that the catalysts showed high reactivity and recyclability for the Heck reaction. A major complication in these studies is the possible leaching of active Pd species at very low levels. A recent report by Yu et al. demonstrated conclusively that both silica and polymer immobilized Pd-SCS pincer

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Investigation of Pd Leaching from Supported Pd Catalysts

*J. Phys. Chem. B, Vol. 109, No. 36, 2005* **17233**

complexes were only precursors of a leached solution phase Pd species, which functioned as the active species in the Heck reaction.[35]

An unresolved issue with solid Pd catalysts for the Heck reaction is whether the catalysis is truly heterogeneous. The reason that many researchers claim their catalysts to be recyclable and heterogeneous is a negligible loss in the catalytic activity or Pd loading after reuse. However, the Heck reaction can easily be catalyzed by only a ppm level of Pd in solution.[3] Thus, high activity can still be obtained after reuse of a solid Pd catalyst if the support contains a substantial amount of the unleached metal. The supported catalyst will continue to function as a reservoir of Pd that can be released at very low levels into solution. The general methods to test for the presence or absence of leached soluble Pd in the reaction solution are a hot filtration test or elemental analysis of Pd in the solution. However, in some cases, the leached soluble Pd can re-deposit back onto the support after completion of the reaction.[9,36,37]

In this study, we prepared four different supported Pd catalysts: amorphous silica supported Pd (Pd-SiO$_2$), zeolite Y ion-exchanged with [Pd(NH$_3$)$_4$]$^{2+}$ (Pd-Y), mercapto- and amine-functionalized amorphous silica with immobilized Pd (Pd-SH-SiO$_2$ and Pd-NH-SiO$_2$) and mercapto-functionalized SBA-15 with immobilized Pd (Pd-SH-SBA-15). A hot filtration test is used after 10−20% conversion of aryl iodide had been achieved to ensure that any leached soluble Pd in the filtrate would be sufficient to continue a homogeneous reaction after removing the solid catalyst. In addition, we explored the use of a Pd trap on the homogeneous reaction as well as the effect of solvent on the rate. To eliminate the transient nature of batch-wise experiments, we have also performed the reaction in a continuous flow reactor. Finally, we tested the effect of the individual Heck reagents on the leaching process.

## Experimental Section

**Catalyst Preparation.** *Pd−SiO$_2$*: Two types of amorphous SiO$_2$ were used as supports: Cab-O-Sil M-5 SiO$_2$ (particle size: 0.2−0.4 $\mu$m; BET surface area: 200 m$^2$/g) and Davisil silica gel 646 (particle size: 35−60 mesh; pore size: 150 Å; BET surface area: 300 m$^2$/g). Silica was first dried overnight at 373 K to remove water, then impregnated with an aqueous solution of tetraammine palladium nitrate (Sigma-Aldrich, 99.99%,). The impregnated support was dried in air at 373 K overnight before reduction. Finally, the sample was heated in flowing H$_2$ from 298 to 673 K with a temperature ramp of 1 K/min, then held at 673 K for 1 h. After cooling to room temperature in flowing H$_2$, the sample was flushed with a flow of pure N$_2$ for 15 min before exposure to air. To distinguish two different SiO$_2$ supported Pd catalysts, the Cab-O-Sil SiO$_2$ supported Pd is denoted as Pd−SiO$_2$(cab).

*Pd−Y*: Approximately 0.098 g of tetraamminepalladium chloride monohydrate (Sigma-Aldrich, 98%) was added into a suspension of 1 g of Na-Y zeolite (Union carbide, Y-54) in distilled deionized water (100 mL). The mixture was stirred for 24 h at room temperature, then filtered and washed with a distilled, deionized water until no chloride ions were detected in the filtrate by AgNO$_3$ test solution. The sample was finally dried overnight at room temperature before use.

*Pd on functionalized silica*: To prepare the mercapto-functionalized support, 12.5 g of Davisil Silica gel 646 or 2 g of mesoporous SBA-15 (pore size: 4.3 nm; BET surface area: 610 m$^2$/g) and 3-mercaptopropyl trimethoxysilane (4.9 g for Davisil silica gel 646 or 1 g for SBA-15) were added into 125 mL of dry toluene in a glovebox and stirred under refluxing

condition for 8 h. After the slurry was filtered, the solid sample was washed with toluene and then acetone and finally dried in air at room temperature. To prepare the amine-functionalized support, 6 g of Davisil Silica gel 646 and 12 g of 3-aminopropyl trimethoxysilane were added to 60 mL of dry toluene and the solution was stirred under refluxing conditions for 48 h. After the suspension was filtered, the solid sample was washed by Soxhlet extraction with dichloromethane. Finally, the solid sample was dried under a pressure of 0.01 Torr at 318 K for 2 h.

The functionalized silica supports were slurried with a solution of Pd acetate in acetone and stirred at 298 K for 24 h. After filtration, the powders were washed thoroughly with acetone until the washings were colorless, then dried overnight in air at 363 K, resulting in brown powders. The samples were then refluxed in toluene, ethanol, and finally acetonitrile. The conditioned samples were dried overnight in air at 363 K. The mercapto-functionalized SiO$_2$ with immobilized Pd having high and low Pd loadings were denoted as Pd-SH-SiO$_2$(I) and Pd-SH-SiO$_2$(II), respectively.

The catalyst samples were pressed, crushed, and sieved into a size range of 40−60 mesh prior to catalytic tests in the continuous reactor.

**Catalytic Tests.** *Batch reaction*: All reactants and solvents obtained from commercial sources (Aldrich/Fluka or Alfa/Aesar) were used as received without further purification. A mixed solution of iodobenzene (IDB) (10 mmol, 2.04 g), butylacrylate (BA) (15 mmol, 1.95 g), triethylamine (NEt$_3$) (12 mmol, 1.21 g), diethylene glycol dibutyl ether (DGDE) (1.00 g, as internal standard for GC analysis), solvent dimethylformamide (DMF) or toluene (10 mL), and 0.05−0.25 mol % of Pd (relative to iodobenzene) was added to a three-necked round-bottom flask equipped with a condenser and rubber septum. The reaction mixture was gently purged with Ar for 10 min, and then the reactor was immersed into a preheated oil bath at a reaction temperature of either 353 or 373 K under vigorous stirring. Samples were periodically withdrawn from the reaction mixture and diluted with 1.0 mL of ice-cooled tetrahydrofuran (THF) before GC-MS analysis (HP 6890 series). The IDB conversion was calculated from the peak area ratio of IDB relative to DGDE as obtained from GC-MS analysis. A hot filtration test during the batch reaction was performed after achieving 10−20% IDB conversion and then removing the solid catalyst using PTFE Millex filter with a 0.2 $\mu$m pore size while under hot conditions.

In some cases, insoluble poly(4-vinylpyridine) (2% cross-linked) (PVPy) was added to the reaction mixture as a trap for soluble Pd species. Addition of soluble pyridine was used as a control.

*Continuous reaction*: A stainless steel tube with a diameter of 0.4 cm and a length of 20 cm was used for the continuous Heck reaction. At the inlet, a zone of 8 cm was filled with glass beads, in which the reagents were uniformly mixed and heated to 373 K. Approximately 0.295 g of 40−60 mesh catalyst was loaded in the middle of the reactor and separated from glass beads by a glass wool plug. The feed consisted of 58.4 mmol of IDB, 99.2 mmol of BA, 65.6 mmol of NEt$_3$, 9.6 g of DGDE (internal standard for GC-MS analysis), and 54.6 mL of DMF, which was pumped across the catalyst bed at a flow rate of 1.8 mL/h. After Ar purging for 10 min, the reaction was performed at 373 K and the effluent solution was collected over time for GC analysis during the course of the reaction.

*Pd leaching test*: Each catalyst was pretreated at a certain temperature (353 or 373 K) in various solutions consisting of different reagents for a period of time, and the solid catalyst

**17234** *J. Phys. Chem. B, Vol. 109, No. 36, 2005*

Ji et al.

**TABLE 1: Comparison of IDB Conversion in the Pd Acetate and Pd-SiO$_2$(Cab) Catalyzed Heck Reaction at 373 K with and without Pyridine/PVPy$^a$**

| entry | catalyst | amount of added PVPy or pyridine (molar ratio) | reaction time (h) | IDB conv (%) |
|---|---|---|---|---|
| 1 | Pd acetate | without PVPy and pyridine | 1 | 85 |
| 2 | | without PVPy and pyridine | 2 | 92 |
| 3 | | PVPy/Pd = 700 | 1.5 | 6 |
| 4 | | PVPy/Pd = 700 | 2 | 10 |
| 5 | | pyridine/Pd = 700 | 1 | 96 |
| 6 | Pd-SiO$_2$(cab) | without PVPy and pyridine | 1 | 87 |
| 7 | | without PVPy and pyridine | 2 | 96 |
| 8 | | PVPy/Pd = 700 | 1 | 10 |
| 9 | | PVPy/Pd = 700 | 2 | 10 |
| 10 | | pyridine/Pd = 700 | 1 | 74 |

$^a$ Pd loading: 0.125 mol % (relative to iodobenzene).

was then removed using a 0.2 $\mu$m filter under the hot conditions. All of the missing reagents from a standard Heck reaction were added into the filtrate to test for activity. The presence or absence of any active soluble Pd species was reflected by the level of IDB conversion in the filtrate.

A leaching test during the continuous reaction was performed by collecting a fraction of the effluent from the reactor and allowing it to react further. Additional conversion of IDB in the effluent was used to determine the presence of leached soluble Pd formed in the continuous reaction.

*X-ray photoelectron spectroscopy*: The X-ray photoelectron spectra (XPS) were collected in a UHV chamber attached to a Physical Electronics 560 ESCA/SAM instrument. An Al K$\alpha$ source ($h\nu$ = 1486.8 eV) was used to excite the photoelectrons from the material. These electrons were energy selected by the cylindrical mirror analyzer (CMA) operated in constant pass energy mode, then counted by a channeltron at the rear of the CMA. The CMA was operated at a pass energy of 30 eV using large apertures, which provided a constant instrument energy resolution of 0.48 eV. The charge neutralizer, a source of low-energy electrons, was run during data acquisition to compensate for any positive charge buildup on the surface of the material. All data were acquired at ~2 × 10$^{-7}$ Torr. For energy calibration, the carbon 1s binding energy of adventitious carbon was assigned to be 284.8 eV.

## Results and Discussion

**Detection of Leached Soluble Pd.** Pyridines are known to bind strongly to Pd(II).[38] Thus, Yu et al.[35] successfully used insoluble poly(4-vinylpyridine) (2%cross-linked) (PVPy) as a Pd(II) trap to confirm the presence of leached, soluble Pd from an organometallic Pd complex anchored to silica. In the current work, we used both soluble pyridine and insoluble PVPy to differentiate between the solid Pd phase and leached, soluble Pd during the Heck reaction catalyzed by silica-supported Pd.

As a control, soluble Pd acetate was used as catalyst in the reaction. Pyridine or PVPy was added along with all the other reagents before starting the reaction. The results in Table 1 (entry 5) showed that pyridine addition with a mole ratio of 700 (pyridine to Pd) did not deactivate the catalyst since IDB conversion after 1 h was almost unchanged compared to the standard reaction (entries 1 and 2). These results are consistent with those reported by Klingelhofer et al., who studied the coupling of styrene with 4-bromoacetophenone.[26] In contrast, a reaction mixture containing the same mole ratio of PVPy to Pd (700:1) resulted in only a 6% IDB conversion after 1.5 h (entry 3) and remained at this low level even after 2 h (entry 4). Since addition of PVPy deactivated the homogeneous
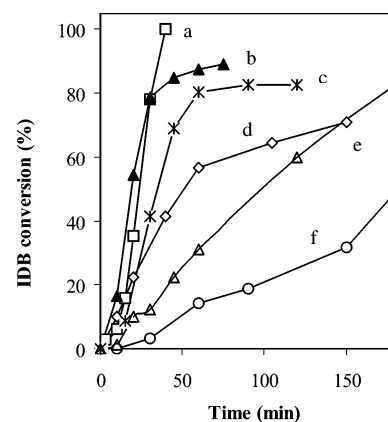


**Figure 1.** The kinetic plot of IDB conversion with time in the coupling reaction of iodobenzene with butylacrylate at 353 K using dimethylformamide as solvent, with a catalyst loading of 32 mg: (a) Pd-Y, (b) Pd-SH-SiO$_2$(I), (c) Pd-SH-SBA-15, (d) Pd-NH-SiO$_2$, (e) Pd-SH-SiO$_2$-(II), and (f) Pd-SiO$_2$.

catalyst, insoluble PVPy can be used as a trap for soluble Pd thus indicating the presence of a leached Pd species from a supported Pd catalyst during the Heck reaction.

Analogous experiments were performed with a silica-supported catalyst. Similar to the results with Pd acetate, addition of pyridine did not deactivate the catalyst (entry 10) whereas the addition of PVPy nearly quenched the reaction (entries 8 and 9) in the presence of Pd-SiO$_2$(cab), indicating that the catalytic activity of Pd−SiO$_2$(cab) was mainly from the soluble Pd leached from the solid catalyst.

To determine the degree of Pd leaching in the course of the reaction by 5 wt % Pd-SiO$_2$(cab) (catalyst loading: 210 mg, i.e. 1.0 mol % of Pd relative to IDB), approximately 2 mL of clear filtrate was removed after two different time intervals. The concentration of leached Pd in solution was found to be 12 and 4.5 ppm after 10 and 60 min, respectively. A decrease of Pd concentration in solution with time is consistent with the observation by Heidenreich et al.[39] Although the trace analysis of Pd in solution and the deactivation of Pd-SiO$_2$(cab) by PVPy suggests that Pd gets released from the support and that the soluble Pd might be responsible for most of the activity in Heck catalysis, we could not rule out the possibility that the polymer filled the pores of the solid catalyst and prevented accessibility of reactants to the active site. Therefore, additional experiments were needed to confirm the activity of soluble Pd leached from the solid catalyst.

**Comparison of Catalytic Activity.** Plots of IDB conversion with time at 353 K are shown in Figure 1 for a variety of solid Pd catalysts. Among these samples, Pd-Y revealed a high catalytic activity with a 100% IDB conversion in only 40 min. The least active catalyst was Pd-SiO$_2$. After an induction period of 10 min, the reaction reached only 48% IDB conversion obtained after 3 h. For supported Pd catalysts, the catalytic activity decreased in the following order: Pd-Y ~ Pd-SH-SiO$_2$-(I) > Pd-SH-SBA-15 > Pd-NH-SiO$_2$ > Pd-SH-SiO$_2$(II) > Pd-SiO$_2$. Pd-SH-SiO$_2$(II) had an induction period of 10 min, similar to Pd-SiO$_2$.

Table 2 lists the corresponding reaction rates and turnover frequencies at the initial period of reaction (in 30 min). Turnover frequency was based on total Pd loaded into the reactor. The trend in turnover frequency is the same as the trend in IDB conversion reported in Figure 1. The low turnover frequency of Pd-SiO$_2$ is likely caused by a lower dispersion of Pd on the support compared to the functionalized samples.

Investigation of Pd Leaching from Supported Pd Catalysts

*J. Phys. Chem. B, Vol. 109, No. 36, 2005* **17235**

**TABLE 2: Elemental Analysis and Reactivity of Supported Pd Catalysts in the Heck Reaction**

| sample | S or N (wt %) | Pd (wt %) | Pd/S (or N) molar ratio | IDB conv[a] (%) | reaction rate (mmol/h) | TOF (h$^{-1}$) |
|---|---|---|---|---|---|---|
| Pd-SiO$_2$ | | 3.50 | | 3.35 | 0.67 | 57 |
| Pd-SH-SiO$_2$(I) | 1.41 | 8.41 | 1.80 | 78.89 | 15.78 | 617 |
| Pd-SH-SiO$_2$(II) | 1.41 | 2.31 | 0.46 | 12.35 | 2.47 | 345 |
| Pd-SH-SBA-15 | 0.98 | 2.05 | 0.63 | 41.61 | 8.32 | 1361 |
| Pd-NH-SiO$_2$ | 0.95 | 6.69 | 0.93 | 32.00 | 6.40 | 328 |
| Pd-Y | | 3.88 | | 78.09 | 15.62 | 1337 |

[a] After 30 min regular Heck reaction at 353 K, Catalyst loading: 32 mg.

**TABLE 3: Comparison of IDB Conversion in Both Regular Reaction and Hot Filtration Test**

| | IDB conv (%) | | |
|---|---|---|---|
| catalyst | before filtration [reaction time][a] | hot filtration test [reaction time] | regular reaction [reaction time] |
| Pd-SiO$_2$ | 16 [60 min] | 28 [180 min] | 49 [180 min] |
| Pd-SH-SiO$_2$(I) | 14 [10 min] | 79 [60 min] | 88 [60 min] |
| Pd-SH-SiO$_2$(II) | 13 [30 min] | 30 [60 min] | 31 [60 min] |
| Pd-SH-SBA-15 | 10 [15 min] | 76 [60 min] | 80 [60 min] |
| Pd-NH-SiO$_2$ | 10 [15 min] | 52 [60 min] | 57 [60 min] |
| Pd-Y | 13 [15 min] | 90 [40 min] | 100 [40 min] |

[a] After a certain period of reaction, the whole solution was filtered to remove solid catalyst under the hot condition, and the reaction was further carried out with the filtrate at the same temperature as in the regular reaction (i.e. 353 K).

**TABLE 4: Influence of Solvent on Conversion of Iodobenzene[a]**

| catalyst | in DMF IDB conv (%) [reaction time] | in toluene IDB conv (%) [reaction time] |
|---|---|---|
| Pd-SiO$_2$ | 96 [120 min] | 6 [120 min] |
| Pd-SH-SiO$_2$(I) | 100 [30 min] | 23 [120 min] |
| Pd-Y | 100 [10 min] | 15 [120 min] |

[a] Reaction temperature: 373 K. Catalyst loading: 32 mg, 10 mL of toluene/DMF.

**Hot Filtration Test.** Since the results from PVPy addition are consistent with the presence of leached Pd, we performed a series of hot filtration tests to evaluate the activity of the soluble fraction. Previous works indicate that soluble Pd can redeposit onto supports at the completion of a Heck reaction. For example, Prockl et al.[40] observed that the concentration of Pd in solution correlated with the rate of Heck coupling of bromobenzene with styrene. Complete re-deposition of the Pd was observed at the end of the reaction. In our study, we found that the filtrate from a completed reaction with Pd-SH-SBA-15 showed no activity upon addition of fresh IDB and BA. It is likely that any soluble Pd that may have been present during reaction was captured by the support. Therefore, the rest of our hot filtration tests were conducted after running the normal reaction to 10−20% IDB conversion and then filtering the solid catalysts under hot conditions. The composition of the clear filtrate was monitored at the same temperature to evaluate the conversion of IDB in the absence of the solid-phase catalyst. The extent of Pd leaching is reflected by the rate of conversion of IDB in the filtrate. As shown in Table 3, all of the catalysts in this work showed activity after the hot filtration test. The reaction proceeded in the filtrate with high rates even without the solid catalysts. Comparing the levels of IDB conversion after hot filtration, Pd-Y leaches the most active Pd into solution. Similar levels of active Pd leaching were observed for Pd-SH-SiO$_2$(I) and Pd-SH-SBA-15. The Pd-SH-SiO$_2$(II) sample displayed less active Pd leaching than Pd-SH-SiO$_2$(I), presumably because of the lower Pd/S molar ratio of the former. For the Pd-Y sample, Pd was introduced into the zeolite-Y support via ion exchange. The

high dispersion of Pd in zeolite supercage might be the cause of serious Pd leaching from Pd-Y. Comparison of the rate of IDB conversion from both the hot filtration test and the regular reaction indicates that the activity in the regular reaction can be attributed to the Pd species in the solution. We did not find any evidence that solid Pd is the active species in the Heck reaction.

Since leached Pd was apparently the active catalytic phase, we attempted to discover the key features of the reaction medium responsible for Pd dissolution. First, a control experiment was performed to verify that weakly held Pd was not simply removed from the surface by washing in solvent. The catalysts were first pretreated in DMF at 353 K for a specified period of time. After filtering the hot solid catalyst, the clear filtrate was mixed with appropriate amounts of IDB, BA, base, and DGDE internal standard to run the Heck reaction at 353 K. As shown in Table 5, no IDB conversion was observed after 1 h in any case except for Pd-NH-SiO$_2$ (7% IDB conversion after 1 h). Thus, in nearly all cases, the Pd species were strongly bonded to the surface of the functionalized support. Therefore, the observed Pd leaching of supported catalysts was not due to removal of physisorbed Pd by DMF at reaction temperature but must instead be caused by the reagents during the reaction.

**Effect of Solvent on Catalytic Activity.** The nature of the solvent is known to have a dramatic effect on catalytic activity and the extent of Pd leaching.[1,9] An additional catalytic test with toluene as the solvent was performed in this study. The kinetic plots in Figure 2 indicate that Pd-SiO$_2$ had an induction period of as long as 1 h before IDB conversion was observed. In contrast, Pd-Y had a 10 min induction time, whereas no induction period was observed for Pd-SH-SiO$_2$(I). Nevertheless, Pd-Y and Pd-SH-SiO$_2$(I) exhibited a similar reaction rate during the initial period of the reaction. Table 4 directly compares the conversion of IDB in both toluene and DMF. The catalytic activity of the supported Pd catalysts in toluene was much lower than that in DMF. Although the influence of solvent on the catalytic activity and Pd leaching is still not completely understood, it has been known that Pd leaching from supported catalysts is more extensive in highly polar dimethyl acetamide and *N*-methylpyrrolidone than in nonpolar toluene.[15] We attempted to perform a hot filtration test during the reaction in toluene solvent, but the results were irreproducible. In some cases, activity of the filtrate was observed whereas in others there was no activity. Nevertheless, the very low reaction rate and irreproducible hot filtration tests suggest that leaching of Pd in toluene is lower than that in DMF.

**Heck Reaction in a Continuous Reactor.** Our results suggest that Pd is leached early in the reaction when carried out in a batchwise mode with DMF solvent. To check if Pd leaching is sustained during the reaction, a continuous fixed bed reactor system was constructed, and Pd-SiO$_2$ and Pd-SH-SiO$_2$(I) were tested as catalysts in the continuous Heck reaction. A plot of IDB conversion in the reactor effluent with time on-stream is shown in Figure 3. The Pd-SH-SiO$_2$(I) catalyst exhibited a

**17236** *J. Phys. Chem. B, Vol. 109, No. 36, 2005*

Ji et al.

**TABLE 5: Homogeneous Heck Reaction Catalyzed by Leached Soluble Pd Species[a]**

| pretreatment condition | IDB conv (%) | | | | | | |
|---|---|---|---|---|---|---|---|
| | Pd-SiO$_2$ | Pd-SH-SiO$_2$(I) | Pd-SH-SiO$_2$(II) | Pd-SH-SBA-15 | Pd-NH-SiO$_2$ | Pd-Y (ion-ex) | Pd-Y (reduced) |
| DMF alone | 0 [30] | 0 [15] | 0 [45] | 0 [45] | 7 [45] | 0 [15] | 0 [30] |
| DMF + base | 0 [30] | 0 [45] | 0 [45] | 0 [45] | 15 [45] | 12 [45] | 0 [30] |
| DMF + IDB | 100 [30] | 58 [45] | 6 [45] | 56 [45] | 82 [45] | 0 [15] | 6 [30] |
| DMF + IDB + base | 72 [30] | 36 [45] | | | | 34 [15] | |
| DMF + base + BA | 0 [30] | | | | | | |

[a] Removing the solid catalyst then adding all the missing reagents into the filtrate to run the homogeneous reaction for leached soluble Pd in the filtrate. All IDB conversions were obtained from the homogeneous reaction after 1 h. Pretreatment and reaction temperature was 373 K for Pd/SiO$_2$ and 353 K for all the other catalysts. The values in brackets are the pretreatment times [in minutes] of various catalysts in respective solutions.
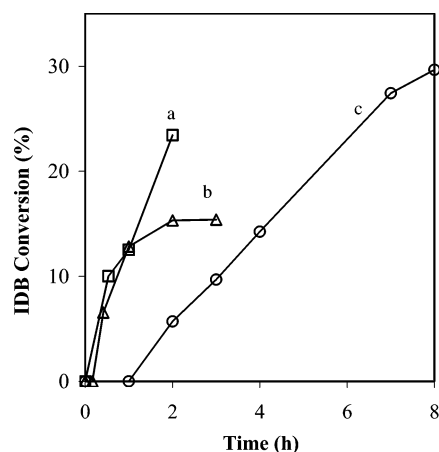


**Figure 2.** The kinetic plot of IDB conversion with time in regular reaction: (a) Pd-SH-SiO$_2$(I), (b) Pd-Y, and (c) Pd-SiO$_2$. Reaction conditions are similar to those in Figure 1 except for using toluene as solvent with a reaction temperature of 373 K instead of 353 K.
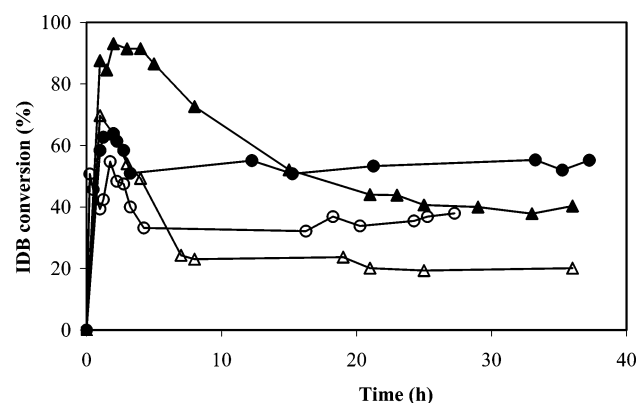


**Figure 3.** Plot of IDB conversion in the effluent of continuous reaction with time from the first and second runs at 373 K. The feed contains iodobenzene, butylacrylate, triethylamine, diethylene glycol dibutyl ether as internal standard, and dimethyl formamide as solvent, with a catalyst loading of ca. 295 mg. Pd-SiO$_2$: (●) 1st run, (○) 2nd run. Pd-SH-SiO$_2$(I): (▲) 1st run, (△) 2nd run.

maximum in IDB conversion (93%) during the initial period of the reaction and then the conversion gradually decreased with time to reach about 40% IDB conversion after almost 40 h on-stream. For Pd-SiO$_2$, the maximum in IDB conversion (ca. 64%) was achieved early in the test and then quickly dropped to about 50% after 3 h on-stream. This level of conversion was fairly constant for the following 30 h.

The effluent from the continuous reactor was collected over various time intervals and then was allowed to continue reacting in a batch reactor without any solid catalyst present. The additional conversion of IDB in the collected effluent samples is shown in Figure 4. In almost every case, the reaction continued to proceed in the effluent from the continuous reactor, which indicates the presence of soluble Pd during every stage
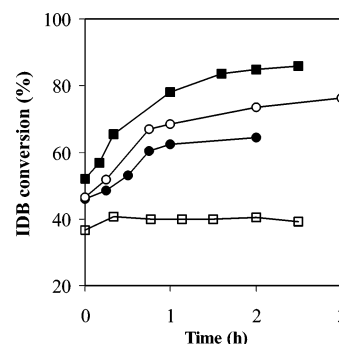


**Figure 4.** Activity of leached soluble Pd in the effluent of continuous reaction from the first run. Pd-SiO$_2$: (●) effluent from 3 to 11 h on-stream and (○) effluent from 21 to 33 h on-stream. Pd-SH-SiO$_2$(I): (■) effluent from 7 to 20 h on-stream and (□) effluent from 28 to 38 h on-stream. Reaction temperature of the batch reaction was 373 K.
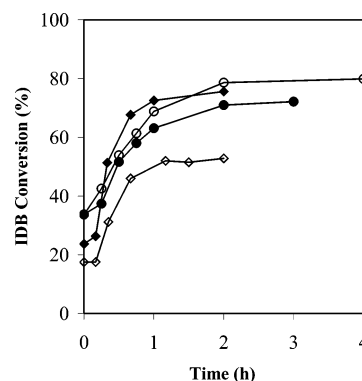


**Figure 5.** Activity of leached soluble Pd in the effluent of continuous reaction from the second run. Pd-SiO$_2$: (●) effluent from 4 to 16 h on-stream and (○) effluent from 27 to 41 h on-stream. Pd-SH-SiO$_2$(I): (◆) effluent from 7 to 21 h on-stream and (◇) effluent from 28 to 40 h on-stream. Reaction temperature of the batch reaction was 373 K.

of the continuous reaction. In the case involving Pd-SH-SiO$_2$-(I) (28−38 h) no additional reaction was observed, yet elemental analysis of the effluent revealed a Pd level of 4.9 ppm. Evidently, deactivation of leached Pd is possible during collection of the sample and exposure to air. This result clearly shows why a negative result from an activity test cannot prove the absence of Pd leaching during reaction.

A second test was also performed with the used Pd-SiO$_2$ and Pd-SH-SiO$_2$(I) catalysts. As shown in Figure 3, the plots of IDB conversion with time showed the maximum in conversion followed by a long steady period for both runs, but the steady-state conversion in the second run was lower than that for the first run. The reactivities of the effluents from the second runs were also evaluated and the results are summarized in Figure 5. In every case, the continued conversion of IDB in the effluent confirmed the presence of leached Pd. Combining the results from both the hot filtration test with the batch reactor and the effluent conversion test with the continuous reactor, we did not

Investigation of Pd Leaching from Supported Pd Catalysts

*J. Phys. Chem. B, Vol. 109, No. 36, 2005* **17237**

find any evidence for the contribution of the solid Pd in the catalytic reaction.

So far, the mechanism of Pd leaching is still not clear. Biffis et al. studied Pd leaching from supported metallic Pd particles.[41] Their research indicated that iodobenzene was the only reagent to cause Pd leaching, which corresponds to the oxidative addition of aryl halide to Pd.

To clarify the causes of Pd leaching, a detailed investigation of the conditions required for Pd solubilization was performed for the three different types of catalysts (i.e. Pd-SiO$_2$, Pd-Y, and Pd on functionalized silica). Each catalyst was pretreated in different solutions at 353 or 373 K for a specified time period and then removed by filtration under hot conditions. All the reagents for the Heck reaction were subsequently added to the filtrate to initiate the homogeneous reaction at the same temperature as the pretreatment. The presence of soluble Pd was determined by the conversion of IDB in the homogeneous reaction of the filtrate. A summary of the results of these tests is shown in Table 5. As mentioned above, treatment in DMF alone did not leach active Pd into solution from most of the samples; the small amount leached from Pd-NH-SiO$_2$ may be due to the trace amounts of physisorbed Pd from the acetate impregnation. Adding base into DMF apparently did not leach active Pd from Pd-SiO$_2$, Pd-SH-SiO$_2$, and Pd-SH-SBA-15. However, conversion of IDB in the filtrate from Pd-Y indicates base caused some leaching of Pd from the zeolite.

Pretreating catalysts in a mixture of DMF and IDB caused the filtrate from Pd-SiO$_2$, Pd-SH-SiO$_2$(I)/(II), and Pd-SH-SBA-15 to be active in the conversion of IDB. Evidently all four of these catalysts leached Pd in the presence of IDB. Although Pd-NH-SiO$_2$ had some weakly adsorbed Pd as demonstrated by the DMF test and the DMF/base test, the amount of active Pd leached by IDB was substantially higher according to the high activity of the filtrate for the Heck reaction. Interestingly, IDB treatment did not cause Pd leaching from Pd-Y. When Pd-Y was pretreated with DMF, base, and IDB, the conversion of the Heck reaction was greater than that of a treatment in DMF and base. The combination of base and IDB was more effective at leaching active Pd from the zeolite. An additional pretreatment test was to expose the Pd-SiO$_2$ catalyst to a solution of base and butylacrylate together with DMF for 30 min. No activity from the filtrate of this test indicates that BA does not cause Pd leaching from Pd-SiO$_2$.

From the results of these tests, two different paths of Pd leaching can be proposed: treatment with IDB caused Pd leaching from all of the Pd-SiO$_2$ catalysts, with or without functionalization, and treatment with base caused leaching from Pd-Y. Since Pd-Y contained cationic Pd in the supercages, we tested the effect of prereduction of Pd on the leaching path. No leaching of active Pd from a reduced Pd-Y sample (reduced in flowing H$_2$ at 673 K) was observed after treatment in the solution of base and DMF. However, a low level of IDB conversion (6%) was detected in the filtrate after pretreatment of the reduced Pd-Y in a solution of DMF along with IDB. These results are consistent with the idea that IDB leaches reduced Pd whereas base leaches cationic Pd. Biffis et al. demonstrated that significant Pd leaching was caused by arylhalides,[41] which is in complete agreement with our observations for Pd-SiO$_2$ catalysts. Interestingly, recent results reported by Sommer et al.[42] indicated that leaching of Pd from immobilized Pd(II) SCS pincer complexes is caused by reaction with base, which is also consistent with our results for cationic Pd in Pd-Y. Clearly, the path of Pd leaching is correlated to the chemical state of Pd on the surface of the catalysts.

**TABLE 6: XPS Pd Binding Energy of Different Catalysts$^a$**

| catalyst | Pd 3d$_{5/2}$ | Pd 3d$_{3/2}$ |
|---|---|---|
| Pd-SiO$_2$ | 335.8 | 340.5 |
| Pd-NH-SiO$_2$ | 335.6 | 340.5 |
| Pd-SH-SiO$_2$(I) | 336.4 | 341.6 |
| Pd-Y | 337.1 | 342.4 |

$^a$ Carbon 1s binding energy was assigned to be 284.8 eV.

Table 6 lists XPS Pd 3d binding energies of four catalysts. The Pd-Y sample exhibited the highest Pd 3d$_{5/2}$ and Pd 3d$_{3/2}$ binding energies of 337.1 and 342.4 eV, respectively, which is similar to the values for Pd(II) SCS pincer complex reported by Yu et al.[35,42] As expected, the Pd in Pd-Y was present as a Pd(II) complex. The binding energies for Pd-SiO$_2$ and Pd-NH-SiO$_2$ are consistent with metallic Pd. Although Pd-SH-SiO$_2$(I) had a slightly higher binding energy (~336.4 eV for Pd 3d$_{5/2}$) than Pd-NH-SiO$_2$, it was still lower than Pd-Y by 0.7 eV.

The generally accepted mechanism of the Heck reaction involves (1) oxidative addition of aryl halide to Pd(0), (2) addition of olefin to Pd complex, (3) $\beta$-hydride elimination of the product, and (4) regeneration of Pd catalyst via reduction with triethylamine. Correlating the chemical state of Pd to the Heck reaction mechanism, the leaching of metallic Pd is due to a direct oxidative addition of IDB to Pd. Gniewek et al.[43] studied Pd colloids stabilized with poly(vinylpyrrolidone) and showed that the Pd particle size decreased after treatment with aryl halide, which is consistent with the leaching results reported here. For our zeolite sample containing cationic Pd, the metal ions are probably first reduced in the presence of base, which causes some leaching, which is followed by oxidative addition of aryl halide and substantial leaching.

## Conclusions

The mercapto- and amine-functionalized SiO$_2$ or SBA-15 with immobilized Pd complexes displayed higher activity than a traditional supported Pd-SiO$_2$ sample in regular Heck reaction, presumably because the dispersion of Pd is higher on the functionalized supports. Results from Pd trapping with PVPy, hot filtration tests during batch reaction, and reactivity tests of effluents from continuous reaction indicate that Heck catalysis was achieved by the soluble fraction of Pd in all cases. The chemical state of the Pd identified by XPS correlated to the mechanism of Pd leaching. For cationic Pd in the supercages of zeolite Y, triethylamine base was needed to facilitate reduction and leaching of Pd. For all other samples that contained metallic Pd, oxidative addition of aryl halide was responsible for leaching of Pd. Neither functionalization of silica nor entrapment of Pd in zeolite Y prevented leaching during the Heck reaction in DMF.

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Ji et al.

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