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Pd/MO$_x$ Materials Synthesized by Sol-Gel Coprecipitation as Catalysts for Carbon–Carbon Coupling Reactions of Aryl Bromides and Chlorides

Wolfgang Kleist,[a][‡] Jae-Kyu Lee,[a] and Klaus Köhler*[a]

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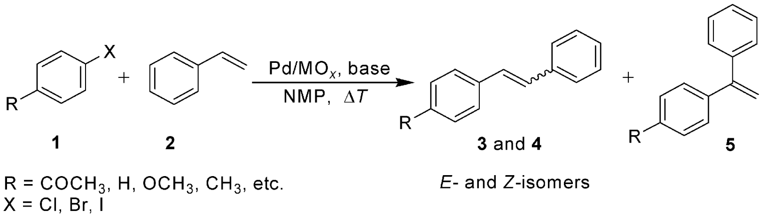
In order to control the interaction of palladium species with oxide supports, a sol-gel coprecipitation synthesis has been developed for Pd/MO$_x$. The resulting Pd/MO$_x$ catalysts are characterized by a rather strong interaction between the highly dispersed Pd^{2+} species and the alumina and silica lattices. During coupling reactions of the Heck type the catalytically active species is generated by partial dissolution of Pd from the support surface. Due to the strong bonding of Pd to the support this dissolution occurs to significant extent only at comparatively high temperatures (≥160 °C). These temperatures are exactly necessary for the activation of less-reactive substrates like bromobenzene and aryl chlorides. In this way we are able to synthesize supported catalysts that facilitate a controlled release of soluble Pd species under reaction conditions that are required for the activation of aryl bromides and chlorides. The Pd/MO$_x$ catalysts show excellent activity in the Heck reaction of bromobenzene (TON up to 10000; TOF up to 5000 h^{-1}) and 4-chloroacetophenone (TON up to 9300; TOF up to 1550 h^{-1}).

Introduction

A large number of detailed investigations on Heck-type coupling reactions (Scheme 1) in the presence of supported catalysts within the last years led to an eminent improvement of the mechanistic understanding in this area.[1–5] It could be shown independently by different groups that the reaction is catalyzed by soluble Pd species that are temporarily dissolved from the surface of the support.[6–12] In the original catalyst Pd has to be provided as an effective precursor species from which the active form can be generated in situ. Optimized procedures for the synthesis of such highly active Pd catalysts have been reported in the literature.[13,14] In general, these materials contain Pd^{2+} species in a high dispersion which facilitates an efficient in-situ reduction (Pd^0 is required for the oxidative addition of the aryl halide as the first step of the catalytic cycle) and dissolution under typical reaction conditions.[15] Beside an optimized synthetic procedure for the catalyst material, especially the right choice of reaction conditions during the catalytic reaction was found to be essential.

It emerged to be crucial that the dissolution and re-precipitation equilibriums are controlled effectively at any time during the catalytic reaction. Here it is important that the right amount of dissolved (= active) Pd species is provided in the reaction solution. While a too low Pd concentration might be not sufficient to achieve high reaction rates, agglomeration (and consequently deactivation) processes might occur if too much Pd is leached from the catalyst support simultaneously.



Scheme 1. Heck reaction of aryl halides and styrene.

One of the most important parameters that influences these dissolution/re-precipitation processes is the reaction temperature. Higher reaction temperatures can increase the total amount of dissolved Pd species, but they also acceler-

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[a] Department of Chemistry, Technische Universität München,
Lichtenbergstr. 4, 85747 Garching, Germany
Fax: +49-89-289-13183
E-mail: klaus.koehler@ch.tum.de
[‡] Present Address: Department of Chemistry and Applied Biosciences, Institute for Chemical and Bioengineering, ETH Zurich,
Wolfgang-Pauli-Str. 10, 8093 Zurich, Switzerland

ate deactivation of active species by Pd black formation. Higher reaction temperatures might be needed, however, for the activation of certain substrates. While aryl iodides and activated aryl bromides can be activated easily by a great variety of different Pd catalysts at reaction temperatures below 100 °C (due to their lower C–X binding energies),[16,17] the activation of less reactive aryl bromides and especially chlorides requires in general harsher reaction conditions and higher temperatures.[18] Consequently, an efficient catalyst for the activation of such less-reactive substrates should facilitate a controlled release of the supported Pd into the reaction solution at these higher reaction temperatures avoiding agglomeration and deactivation of Pd in solution. The development of such materials being more robust and applicable for a broader range of experimental conditions in particular for higher temperatures would be of particular interest for practical application of supported palladium catalysts.

In this work we present a new strategy to cope with this challenge. A sol-gel coprecipitation synthesis procedure has been developed for metal oxide supported Pd catalysts. It results in a stronger Pd-support interaction (compared to conventionally prepared supported catalysts) and leaching of Pd species into reaction solution starts at 160 °C only. Such high temperatures have to be applied for an efficient conversion of less-reactive substrates like bromobenzene and aryl chlorides.[19] Since leaching and stabilization of dissolved Pd species against Pd black formation may be influenced by ammonium halides, a variety of these salts have been tested as additives/promoters in the catalytic reaction too.

Results and Discussion

To achieve a strong Pd/support interaction, the Pd catalysts were prepared by combined sol-gel (metal alkoxides) and coprecipitation (palladium salt) procedures. $Al(O^iPr)_3$, which was used as the precursor for Pd/Al_2O_3 catalysts, was dissolved in 2-propanol at elevated temperature (65 °C). Precipitation of the metal oxide was induced by controlled addition of water and finally a solution of $PdCl_2$ in hydrochloric acid. After a reaction time of one and three days, respectively (see Exp. Sect.), two different Pd/Al_2O_3 materials (denoted as "Pd/Al-1" and "Pd/Al-3") were obtained. In the case of Pd/SiO_2 catalysts a different procedure had to be applied. A preformed gel, which was obtained by addition of water to a solution of $Si(OEt)_4$ in ethanol, was dissolved again in 1-butanol. Coprecipitation of Pd/SiO_2 ("Pd-Si") was then achieved by addition of a solution of $PdCl_2$ in hydrochloric acid. Note that these different procedures had to be applied in order to obtain an incorporation of the Pd into the outermost layers of the MO_x lattice for both types of materials. The raw materials were divided in two portions each which were calcined at 100 ("Pd/Al-1-100", etc.) or 450 °C ("Pd/Al-1-450", etc.). Each of these two fractions was split again and one part was treated at 200 °C for 2 hours in H_2 stream to reduce Pd^{2+} to Pd^0 ("Pd/Al-1-100-red" and "Pd-Al-1-450-red", etc.), the other was used without further treatment. Detailed information on the thermal treatment of the catalyst series can be found in Table 1.

Table 1. Nomenclature used and thermal treatments of the various palladium-metal oxide catalysts prepared by combined sol-gel coprecipitation. Samples denoted as "100" were dried in air atmosphere at a temperature of 100 °C for 2 h, those denoted as "450" at a temperature of 450 °C for 6 h. All of these catalysts were divided again into two portions: one was used without further treatment; the other was treated in a H_2 stream at 200 °C for 2 h (denoted as "red").

Catalyst	Thermal treatment	Reduction (H_2 stream)
Pd/Al-1-100	100 °C, 2 h	–
Pd/Al-1-100-red	100 °C, 2 h	200 °C, 2 h
Pd/Al-1-450	450 °C, 6 h	–
Pd/Al-1-450-red	450 °C, 6 h	200 °C, 2 h
Pd/Al-3-100	100 °C, 2 h	–
Pd/Al-3-100-red	100 °C, 2 h	200 °C, 2 h
Pd/Al-3-450	450 °C, 6 h	–
Pd/Al-3-450-red	450 °C, 6 h	200 °C, 2 h
Pd/Si-100	100 °C, 2 h	–
Pd/Si-100-red	100 °C, 2 h	200 °C, 2 h
Pd/Si-450	450 °C, 6 h	–
Pd/Si-450-red	450 °C, 6 h	200 °C, 2 h

The influence of these different reaction parameters (see Table 1) on the activity of the resulting catalysts was studied by comparing the catalytic activity of the different systems in the Heck reaction of bromobenzene and styrene. First, the influence of the pre-treatment (atmosphere) and calcination temperature was investigated in order to get information on the role of the oxidation state of Pd (0 or +2). For this purpose the four catalysts of the Pd/Al-1 series were tested in the Heck coupling of bromobenzene and styrene (Pd amount: 0.01 mol-% based on bromobenzene). After 2 hours at 160 °C the reaction was stopped and the mixtures were analyzed by GLC and GC/MS (Figure 1). The best results were achieved with the unreduced catalyst calcined at 450 °C (Pd/Al-1-450; 99% conversion, 90% yield of *E*-stilbene **3**). The unreduced catalyst calcined at 100 °C (Pd/Al-1-100; 65% conversion, 60% yield) and the reduced catalyst calcined at 450 °C (Pd/Al-1-450-red; 61% conversion, 56% yield) provided similar results. Only the reduced catalyst calcined at 100 °C (Pd/Al-1-100-red; 6% conversion and yield) showed low activity.

Although Pd^0 is the catalytically active species, Pd^{2+} on the catalyst surface exhibits a higher activity compared to Pd^0. This is explained by the fact that Pd species can be dissolved easier when a single (pre-reduced) Pd^0 surface atom is bound to a palladium oxide or hydroxide surface compared to metallic Pd^0. Dissolution is then induced by an oxidative addition of an aryl halide molecule.[4,15] Another conclusion that can be drawn from this comparison is that higher calcination temperatures also lead to higher catalytic performance. Calcination at high temperatures causes a stronger interaction between Pd and the catalyst support. As a consequence, Pd dissolution is hampered and occurs only at higher temperatures. In the case of Pd/Al-1-450 a controlled Pd leaching is possible, whereas the weaker

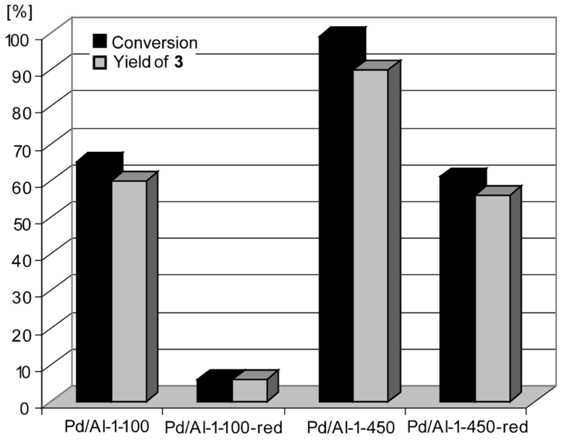

Figure 1. Influence of thermal treatment on the activity of the Pd-metal oxide catalysts; reaction conditions: 10 mmol bromobenzene, 15 mmol styrene, 12 mmol NaOAc, 10 mL NMP, 0.01 mol-% Pd, 160 °C, 2 h, argon atmosphere.

Pd-support interaction in Pd/Al-1-100 leads to a higher Pd leaching. Therefore in the latter case agglomeration of Pd particles and loss in activity are observed. Synergy of high temperature calcination and presence of Pd^{2+} leads to extremely active catalysts, while the combination of the undesired properties (weakly bound Pd^0) causes a dramatic decrease in activity.

In Figure 2 two modified preparation routes for Pd/Al_2O_3 catalysts are compared and the influence of the oxidic support (Al_2O_3 vs. SiO_2) is investigated. All catalysts were tested in the same reaction and under the same conditions mentioned above. First, the differences between the Pd/Al-1 and the Pd/Al-3 series are discussed. Both catalyst series were prepared using different conditions during the coprecipitation process: While coprecipitation of Pd/Al-1 catalysts was performed at room temp. for 1 day, Pd/Al-3 catalysts were stirred at 65 °C for 3 days. The latter procedure causes, again, a stronger interaction between Pd and the support (or even partial incorporation of Pd into the Al_2O_3 lattice). This is demonstrated by the fact that Pd can be removed completely from the Al-1 surface by washing with acetonitrile at room temp., whereas no dissolution from Al-3 catalysts is observed. The Pd/Al-3 series shows qualitatively the same influence of thermal treatment as the Pd/Al-1 catalysts discussed above. However, catalysts of the Al-3 series exhibit higher activity. Complete conversion of bromobenzene is observed for both unreduced Al-3 and the reduced Al-3-450-red catalysts. Even Al-3-100-red which contains comparably weakly bound Pd^0 (an undesired combination) reaches 84% conversion (compared to 6% for Al-1-100-red).

Pd/SiO_2 catalysts show similar tendencies concerning thermal treatment. Only small differences in activity are observed for the first three catalysts (100, 100-red and 450) of the Pd/Al-1 and the Pd/Si series. This means that the influence of the support is negligible and the differences can be explained by small variations in Pd dispersion. Pd/Al_2O_3 catalysts do not show XRD signals from metallic or oxidized Pd. Therefore a very high Pd dispersion (and stronger Pd-support interaction) is postulated in these catalysts. In contrast, the presence of larger crystalline Pd species can be observed by X-ray powder diffraction investigations for the catalysts of the Pd/SiO_2 series. The high catalytic activity of Pd/Si-450 is explained by the presence of crystalline PdO particles, whereas a lower activity was observed for the other three catalysts that exhibit signals from metallic Pd^0.

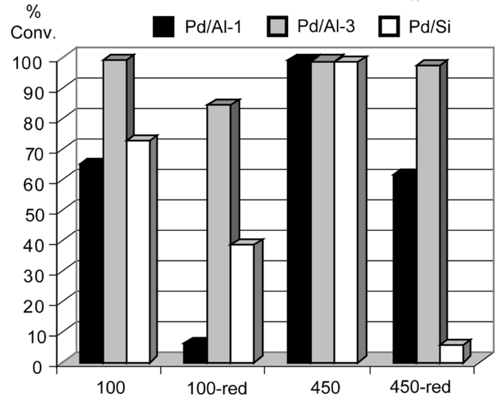

Figure 2. Comparison of the different Pd-metal oxide (SiO_2, Al_2O_3) catalyst series; reaction conditions: 10 mmol bromobenzene, 15 mmol styrene, 12 mmol NaOAc, 10 mL NMP, 0.01 mol-% Pd, 160 °C, 2 h, argon atmosphere.

Investigations on the influence of the reaction temperature on the catalyst activity were performed using several of the catalysts. The results for the coupling of bromobenzene and styrene with Pd/Al-3-100-red as catalyst at different temperatures are shown in Table 2. While only 31% conversion are reached after 2 hours at 140 °C catalyst performance increases significantly at 160 °C (84% conversion). For almost complete conversion in the same time a temperature of 180 °C is needed. This temperature dependence is consistent with the concept of a strong Pd-support interaction. Therefore high temperatures are necessary to release Pd from the surface and generate catalytically active species in solution.

Table 2. Influence of the reaction temperature on the catalytic activity and selectivity in the Heck reaction of bromobenzene with styrene; reaction conditions: 10 mmol bromobenzene, 15 mmol styrene, 12 mmol NaOAc, 10 mL NMP, 0.01 mol-% Pd (Pd/Al-3-100-red), 2 h, argon atmosphere.

Temperature [°C]	% Conversion	% Yield of **3**
140	31	31
160	84	83
180	92	91

Kinetic investigations were performed to study the correlation of the progress of the reaction and the content of leached Pd in solution. In Figure 3 the results for the reaction of bromobenzene and styrene in presence of 0.025 mol-% Pd/Al-3-450 are shown. The reaction was performed simultaneously in 14 pressure tubes; after the respective reaction time each reaction was stopped and one sample was taken to determine the conversion via GLC and another to quantify the Pd content in solution via AAS. A slightly elevated catalyst concentration of 0.025 mol-% was used to minimize fluctuations of Pd concentrations in the different tubes.

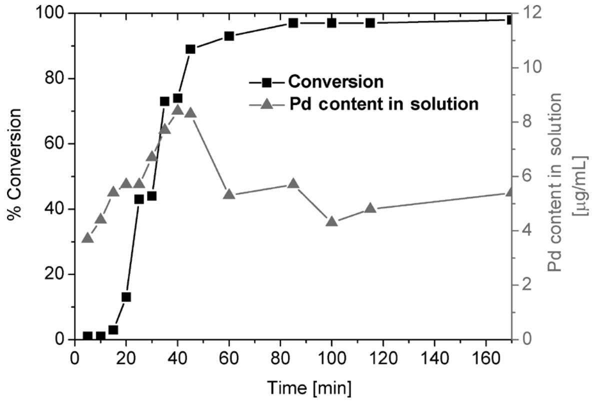

Figure 3. Correlation of the progress of the Heck reaction with Pd leaching (during the reaction): 10 mmol bromobenzene, 15 mmol styrene, 12 mmol NaOAc, 10 mL NMP, 0.025 mol-% Pd/Al-3-450, 160 °C, argon atmosphere.

Figure 3 shows a conversion curve that is typical for heterogeneously catalyzed Heck reactions. During an induction period (first 15 minutes) no conversion is observed and Pd dissolution is initiated. After a critical Pd concentration in solution is reached the reaction proceeds very fast. Nearly complete conversion of bromobenzene is achieved in the next 30 minutes. The concentration of leached Pd increases and reaches a maximum in the same timeframe. At the end of the reaction most of the dissolved Pd is re-deposited onto the support and only a small amount remains in solution. Figure 3 shows a clear correlation between the reaction progress and Pd leaching. The same qualitative behavior has also been observed for corresponding reactions in the presence of "conventionally" prepared supported Pd catalysts. However, the applied reaction temperatures for the successful coupling of bromobenzene and styrene are different. While in the presence of a "normal" Pd/TiO_2 catalyst 140 °C were sufficient,[11] an elevated reaction temperature of 160 °C had to be applied in this work using the sol-gel catalysts. Note that in both cases a maximum of ca. 35% of the total Pd amount was found in solution in the period between 20 and 40 minutes, which is exactly the timeframe in which complete conversion of the substrates is achieved. When we compare the results from Figure 3 with kinetic studies of the reaction of 4-chloroacetophenone and styrene,[12] one can clearly see that in this case exactly the same reaction temperature of 160 °C is necessary to generate a sufficient Pd concentration in solution. All these observations confirm the "quasi-homogeneous" reaction mechanism that has been proven in various similar studies of several groups.[6–12,15]

Investigations on the recovery and reuse of the catalysts show that Pd/MO_x can be easily filtered off and used for further experiments after washing with dichloromethane. In these experiments a higher Pd concentration of 0.1 mol-% was used to minimize losses of Pd during catalyst separation and washing. While complete conversion in the reaction of bromobenzene with styrene is achieved in the first run, in the second run a slight decrease to 95% conversion is observed. This marginal loss in activity of the catalyst can be attributed to a partial reduction of Pd^{2+} to Pd^0 and to a lowered Pd dispersion after the re-deposition of the dissolved Pd species at the end of the first run. However, the catalysts retain a high activity in recycling experiments.

In the first part of the investigations we showed that a high content and dispersion of Pd^{2+} at the surface of the support is crucial for the generation of highly active catalysts. As a second main condition the presence of a strong Pd-support interaction was found to be necessary for the generation of dissolved Pd species in the right concentration at the right reaction temperature. The Pd/Al-3-450 catalyst exhibits an extremely high activity (TON up to 10000; TOF up to 5000 h^{-1}) in the reaction of bromobenzene with styrene due to a combination of these positive properties. The required reaction temperature of 160 °C was quite high for reactions of aryl bromides; however, the catalyst released the optimum amount of Pd at these elevated temperatures. For the reaction of industrially important aryl chlorides, in general, harsher conditions are necessary. Due to an increased C–X bond energy quite high temperatures are required to insert Pd into the aryl–X bond in the oxidative addition step. Therefore Pd/Al-3-450 was chosen as the catalyst in the reaction of 4-chloroacetophenone with styrene.

Reactions of 4-chloroacetophenone were performed using 0.01 mol-% Pd and the same reaction conditions as described for reactions of bromobenzene with the only difference of 6 hours reaction time (compared to 2 hours for bromobenzene). In spite of this extended reaction time, only poor conversion (14%; Table 3, entry 1) was obtained. It is widely accepted that addition of salts like tetra-n-butylammonium bromide $N(C_4H_9)_4Br$ exhibits a promoting effect in Heck reactions.[2,15,20,21] The influence of different tetra-*n*-alkylammonium halides was studied and the results obtained are presented in Table 3. A comparison of the four different tetra-*n*-butylammonium halides (entries 2–5) showed that the bromide salt had the strongest promoting effect (although in this case only 1 mmol was applied, compared to 10 mmol of the fluoride, chloride and iodide). By addition of 1 mmol $N(C_4H_9)_4Br$ the conversion of 4-chloroacetophenone could be raised to 93%. Addition of the corresponding chloride and iodide yielded a comparable low conversion of 26%. Note that this conversion is still twice as high as without additional salt. The exceptionally high conversion obtained by using the fluoride salt (51%) may be explained by the fact that in this case a trihydrate salt was applied. The promoting effect of water in the reaction mixture is also a well known fact.[13,14] A comparison of differently substituted tetra-*n*-alkylammonium bromides showed only marginal influence of the length of the alkyl chains (Table 3, entries 4, 6–9). In all different cases conversions of 88 to 94% could be obtained. There are only a few heterogeneous catalysts known up to now that exhibit such high TON (8600–9300) and TOF (1450–1550 h^{-1}) in the reaction of an aryl chloride.[11,12,22–25] In the reaction of nonactivated aryl chlorides like chlorobenzene only conversions lower than 10% were observed. A further optimization of the variety of reactions parameters like base or solvent is necessary for improvements in this complex reaction system.

Table 3. Substituted ammonium halides as promoters in the Heck reaction of 4-chloroacetophenone with styrene; reaction conditions: 10 mmol 4-chloroacetophenone, 15 mmol styrene, 12 mmol NaOAc, 1 mmol NR_4X, 10 mL NMP, 0.01 mol-% Pd (Pd/Al-3-450), 6 h, 160 °C, argon atmosphere.

NR_4X	% Conversion	% Yield of **3**	TON	TOF [h^{-1}]
None	14	11	1370	230
$N(C_4H_9)_4F{\cdot}3H_2O$[a]	51	37	5180	860
$N(C_4H_9)_4Cl$[a]	26	24	2420	400
$N(C_4H_9)_4Br$	93	81	8900	1480
$N(C_4H_9)_4I$[a]	26	10	2430	410
$N(C_6H_{13})_4Br$	88	71	8680	1450
$N(C_7H_{15})_4Br$	93	85	9180	1530
$N(C_8H_{17})_4Br$	94	81	9310	1550
$N(C_{12}H_{25})_4Br$	91	85	9010	1500

[a] 10 mmol NR_4X.

Conclusions

In this work the synthesis of heterogeneous Pd/MO_x catalysts via combined sol-gel coprecipitation routes has been presented. Since it is known that in heterogeneously catalyzed Heck reactions the active Pd species are generated by dissolution of Pd from the catalyst surface, the control of this leaching process is essential. Coprecipitation of Pd and the metal oxide leads to a comparably strong Pd-support interaction and as a consequence quite high temperatures are necessary to dissolve Pd and generate the catalytically active species. However, the same high reaction temperatures are, in general, necessary to activate non-activated aryl bromides and aryl chlorides. Pd/MO_x catalysts prepared by optimized sol-gel methods exhibit a high dispersion of Pd^{2+} and they release exactly the right amount of Pd into the reaction mixture at these elevated temperatures. Therefore they were found to be highly active in Heck reactions of bromobenzene (TON up to 10000; TOF up to 5000 h^{-1}) and 4-chloroacetophenone (TON up to 9300; TOF up to 1550 h^{-1}). Kinetic investigations confirm the postulated "quasi-homogeneous" reaction mechanism by showing a clear correlation of the reaction rate and the Pd content in solution.

Experimental Section

Preparation of Catalysts: Pd/Al_2O_3 catalysts are prepared from $Al(O\textit{i}Pr)_3$ and $PdCl_2$. $Al(O\textit{i}Pr)_3$ (10 g, 49.0 mmol) is suspended in 2-propanol (300 mL) and heated to 65 °C. Water (15 mL) and, subsequently, a solution of $PdCl_2$ (42.5 mg, 0.24 mmol) in hydrochloric acid (30 mL) are added dropwise under vigorous stirring. The mixture is stirred for 24 h at room temp. and afterwards the solvent is evaporated. From the resulting raw material four different catalysts (Pd/Al-1 series) are prepared by thermal treatment (see Table 1).

A second charge of Pd/Al_2O_3 catalysts (Pd/Al-3 series) is prepared the same way, but the mixture is stirred for 3 days at 65 °C after the addition of the $PdCl_2$ solution. After evaporation of the solvent four different catalysts are prepared by thermal treatment (see Table 1).

Pd/SiO_2 catalysts are prepared from $Si(OEt)_4$ and $PdCl_2$. $Si(OEt)_4$ (22.2 mL, 100.0 mmol) is dissolved in ethanol (250 mL) and heated to 80 °C. Water (30 mL) is added dropwise under vigorous stirring and the reaction mixture is stirred for 3 h at 80 °C and another 10 h at room temp. Afterwards the solvent is evaporated and the resulting colorless gel is dissolved in 1-butanol (60 mL) and heated to 80 °C. A solution of $PdCl_2$ (102.0 mg, 0.58 mmol) in hydrochloric acid (60 mL) is added dropwise under vigorous stirring and the mixture is stirred for 2.5 h at 80 °C and another 24 h at room temp. After evaporation of the solvent four different catalysts (Pd/Si series) are prepared from the raw material (see Table 1).

Typical Procedure for Heck Reactions: Catalytic reactions are performed in sealed pressure tubes after 5 minutes of purging with argon. Reactants and solvents are used without additional drying.

Aryl halide (10 mmol), styrene (15 mmol), sodium acetate (12 mmol), NR_4X (1 mmol, only for reactions of 4-chloroacetophenone), and Pd catalyst (0.01 mol-% Pd based on aryl halide) are dissolved/suspended in 1-methyl-2-pyrrolidone (NMP, 10 mL) and heated to 160 °C for 2 h (bromobenzene) or 6 h (4-chloroacetophenone).

Filtered samples are extracted with water/CH_2Cl_2 and dried with $MgSO_4$. Products are identified by GC/MS. Conversion and yields are quantified by GLC using diethylene glycol dibutyl ether as internal standard ($\Delta_{rel} = \pm 5\%$).

The Pd content in solution during the reaction was determined as follows: After the desired reaction time, the pressure tube was removed from the oil bath. 5 mL of the reaction mixture were sampled and immediately filtered into a 10 mL flask. Subsequently, all liquid components were carefully evaporated by thermal treatment in a heating block. After cooling, the solid residue was treated with H_2SO_4 (98%, 2 mL) and heated to reflux for 1 h. HNO_3 (65%, 0.5 mL) was added and the resulting mixture was refluxed for 24 h. Subsequently, again HNO_3 (65%, 0.5 mL) was added and the mixture is refluxed for 24 h and cooled down to room temp. Afterwards, HCl (37%, 5 mL) and an aqueous solution of $LaCl_3$ (10%, 5 mL) were added. The mixture was diluted with bidestilled water to a total volume of 50 mL. The palladium content was determined by using a flame atomic absorption spectrometer Varian SpectrAA 400.

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