Heck coupling by Pd deposited onto organic–inorganic hybrid supports

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Abstract

Organic–inorganic hybrid silica materials were prepared by modification through reaction with various chloroorganohydrosilanes. The resulting precursors bearing surface methyl or phenyl groups were further reacted with $PdCl_2$ solution to deposit Pd through reduction with surface Si–H functions. The Pd-on-silica catalysts thus prepared were characterized by physical methods (BET, H_2 chemisorption, TEM, MAS NMR). The catalysts are active and highly selective in the Heck coupling with aromatic iodo and activated bromo compounds. Surface functional groups were found to affect catalyst activity. Leaching of Pd was detected, however, Pd species in solution do not appear to promote the reaction under the conditions applied. The performance of these new catalysts in recycling studies are found to be comparable to that of commercial Pd-on-carbon, which is considered to be one of the best heterogeneous catalyst.
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1. Introduction

Coupling reactions to form carbon–carbon bonds play a key role in organic synthesis. An important family of these transformations, which include the Heck, Suzuki, Sonogashira and Stille couplings, has the common feature of the use of palladium as catalyst. The most important of these, the Heck reaction, allows the arylation, alkylation or vinylation of various alkenes through their reaction with aryl, vinyl, benzyl, allyl halides, acetates or triflates in the presence of palladium and a suitable base in a single step under mild conditions [1–6]. Attractive features are the versatile application possibilities and the tolerance of the reaction for a wide range of functional groups. There are examples for the realization of the method on an industrial scale in fine chemical synthesis [7–9].

In line with the original discovery, early studies focused almost exclusively on the use of soluble Pd complexes with P ligands, but recent developments demonstrated the effective-ness of other metal complexes, such as Ni and Co [10–12] and Ru [13]. In addition, there are a few examples of ligand-free simple Pd catalyst systems, such as $Pd(OAc)_2$ and $PdCl_2$ [14–20]. These exhibit excellent activities but may suffer from the drawback of the precipitation of inactive Pd(0).

In recent years, however, most studies have focused on the use of soluble Pd complexes with various types of P ligands [5,6] with the aim of increasing the effectiveness of the catalysts. The driving force of these efforts is to develop Pd complexes with new ligands of high activity and find appropriate reaction conditions for the conversion of non-activated bromoarenes and the more readily available but least reactive chloroarenes [5,10,21–34]. It was also shown that ionic liquids greatly advance the Heck reaction and allow the recycling and reuse of the catalysts [15,16,35–37].

However, problems associated with the need and handling of sensitive ligands, and the difficulty of catalyst separation, recovery and recycling of the expensive Pd have led to the development of immobilized homogeneous catalyst systems. Successful methods include to support Pd complexes on polymers [38–41], the anchoring of Pd complexes to various solids such as modified silicas [42–44] or layered double

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hydroxide [45], and ion-exchange of Pd^{2+} into suitable solid materials [46–51]. Furthermore, there has been a search for suitable supported heterogeneous Pd catalysts. In fact, heterogeneous Pd catalyst systems were found to be highly effective. In addition, to stabilized colloidal palladium and palladium nanoparticles [52–60] numerous reports have shown the utility of various supported palladium catalysts [56,61]. Commercial Pd-on-active carbon was studied most [62–67] along with Pd supported on mesoporous MCM-41 [68,69], molecular sieves [47,48,70–73], oxides [71,74], layered double hydroxide [75] and $Pd(OH)_2/C$ [76]. The application of heterogeneous Ni, Cu and Co [77], and Ru [13] catalysts was also reported. An interesting new approach is the use of bifunctional heterogeneous systems composed of both Pd and basic sites such as basic zeolites [50] and alkali-exchanged sepolites [51].

Efforts have also been made to extend the scope of the heterogeneous Heck reaction for the least reactive chloroarenes. In fact, recent results show, that the Heck coupling of chloroarenes can be induced by Pd-on-carbon [67], Pd nanoparticles deposited on layered double hydroxide [75] or solid Pd catalysts having highly dispersed Pd^{2+} species [78] to give the corresponding vinylarenes in high yields under appropriate reaction conditions. An additional particular driving force of these studies is to address the problem of leaching of Pd, which was thoroughly studied with Pd-on-carbon [63–66].

Two very recent papers have disclosed results of particular interest with respect to the use of ligand-free palladium [20,79]. It was shown that $Pd(OAc)_2$ can be used as highly active catalyst in the Heck reaction provided the catalyst amount is kept below 0.1 mol%. Under such conditions even non-activated aryl bromides undergo smooth coupling reaction. The process appears to involve palladium nanoparticles and low palladium concentration prevents their aggregation and cluster formation [20,79].

In a recent communication, [80] we have presented preliminary results of our study on the preparation, characterization and application in the Heck coupling of a series of new type of Pd-on-silica catalysts prepared by applying organic–inorganic hybrid supports. In the present paper, we disclose additional results about the unique properties of these catalyst materials. Furthermore, detailed observations with respect to Pd leaching a major issue in the application of heterogeneous Pd catalysts in the Heck coupling are also presented.

2. Experimental

2.1. Materials

The silanes used for the modification of silica surface were purchased from Aldrich [tricholosilane (99%), dichloromethylsilane (99%), chlorodimethylsilane (98%)] and Fluka [dichlorophenylsilane (97%), chlorodiphenylsilane (<95%)]. Davisil silica gel (35–60 mesh) and 10% Pd/C used for comparative studies were Aldrich products.

Iodobenzene (98%), iodoanisole (98%), 4-bromoacetophenone (98%), methyl acrylate (99%), styrene (98%), 1-butene-3-one (99%), butyl vinyl ether (98%), palladium chloride (>99.9%) and palladium acetate (98%), all from Aldrich, were used as received, whereas bromobenzene, 4-bromonitrobenzene and 4-chloronitrobenzene (Reanal products) were purified by distillation or crystallization. *N*-methyl-2-pyrrolidone (NMP, 99.5%, Aldrich) was used as solvent, sodium acetate (Reanal) or triethylamine (Spectrum 3D, 99%) was applied as the base, decane (>99%, Aldrich) or biphenyl (Reanal, purified by crystallization from methanol) served as internal standard.

2.2. Catalysts preparation

2.2.1. Modifying the silica surface

In a three-necked flask equipped whit a reflux condenser, septum and an argon inlet dried silica (15 g, dried at 500 °C for 2 h) was suspended in dichloromethane (40 mL) under argon atmosphere. To this suspension chlorohydrosilane (55 mmol) was added by a syringe and the reaction mixture was stirred at room temperature for 30 min. The mixture was chilled by immersing into an ice-bath then methanol (15 mL) was added to transform the unreacted chlorine moieties to methoxy groups. After 30 min of stirring the reaction mixture was filtered, washed with methanol and dried (140 °C, 2 Torr, 2 h). Five silica supports were prepared using tricholosilane, dichloromethylsilane, chlorodimethylsilane, dichlorophenylsilane or chlorodiphenylsilane, and denoted SiO_2, SiO_2Me, SiO_2Me_2, SiO_2Ph and SiO_2Ph_2, respectively.

2.2.2. Loading palladium onto silica

Modified silica samples (1.994 g) were reacted with a 1.25×10^{-3} M $PdCl_2$ solution (10 mg $PdCl_2$ in 45 mL methanol) under magnetic stirring at room temperature for 30 min. The solid material, which turned from white to black was filtered, washed with methanol and dried in vacuo. The resulting five Pd-on-silica catalysts have an equal Pd loading of 0.3 wt.%.

2.3. General reaction procedure

Reactions were carried out in a 5 mL glass pressure tube without any special precaution to exclude air or moisture. Equimolar amounts (0.89 mmol) of the haloarane, alkene and base (sodium acetate or triethylamine), and the catalyst (68 mg, corresponding to 0.3 mol% Pd with respect to the reagents) were added to the solvent (NMP, 1.5 mL) and the mixture was stirred magnetically at 150 °C (±1 °C) for an appropriate time (5 h for styrene and 2 h for all other alkenes).

2.4. Study of Pd leaching

Pd leaching was studied in the reaction of iodobenzene and styrene in NMP or toluene as solvents using the general reaction procedure described above. In separate experiments, the reaction was stopped after 15, 30, 60 and 90 min (NMP as solvent) or after 6, 12, 18 and 24 h (toluene as solvent) and the Pd content of the reaction mixture separated from the catalyst after hot centrifugation was determined by ICP analysis. The activity of dissolved Pd in solution was studied by running reactions with the filtrates recovered after 15 min or 6 h, respectively, and conversions were measured.

2.5. Recycling of catalysts

After running the reaction of iodobenzene and styrene according to the general reaction procedure (NMP as solvent, triethylamine as base, 2 h reaction), the catalyst was removed by centrifugation, washed with acetone, air-dried (IR lamp, 1 h) and then re-used in Heck coupling. When recycling and leaching studies were combined, the reaction was stopped after 15 min; the catalyst was treated as above and re-used in new reactions.

2.6. Methods

Samples were analyzed by gas chromatography (HP 5890 equipment, HP-1 column, flame ionization detector). Product identification was based on GC, GC–MS (HP 5890 GC + HP 5970 mass selective detector) and liquid NMR of the isolated products.

Concentration of the leached Pd in the reaction mixture was measured by ICP-AAS (Jobin-Yvon 24 equipment).

The specific surface area of the modified silica and the supported catalysts was measured using N_2 adsorption–desorption at 77 K by a QUANTACHROME NOVA 2000 apparatus (pretreatment: 150 °C, 1 h, 10^{-2} Torr). Te Pd dispersion was determined by H_2 chemisorption at room temperature (sample pretreatment: 150 °C, 1 h, 10^{-2} Torr). Morphological characterization of the Pd nanoparticles was carried out by transmission electron microscopy (TEM, Philips CM 10 equipment). Pd particle sizes were determined from TEM as the average diameter of about 100 particles.

The silica samples modified by reaction with chlorohydrosilanes were also characterized by solid-state NMR spectroscopy. Spectra were recorded at room temperature using a Bruker Avance spectrometer operating at 11.7 T magnetic field (^{13}C: 125.7 MHz, ^{29}Si: 99.3 MHz). Samples were packed in 4 mm diameter ZrO_2 rotors and were spun at 5 kHz speed. ^{29}Si and ^{13}C CP-MAS spectra were referenced to external DSS sample. ^{29}Si CP-MAS experiments were acquired with the following parameter sets: ^1H 90° pulse was 4.0 μs; cross polarization contact time was 5 ms; ^1H decoupling 62.5 kHz, 5 s repetition delay was applied and a 403 ppm

spectral region was recorded with a carrier frequency placed at 0 ppm, the ^1H frequency was positioned to 4.7 ppm. 1 K tranzients were recorded in 4 K complex data-points resulting in 51.3 ms acquisition time. Lorentzian window function (with 50 Hz broadening factor) was applied prior to Fourier transformation. ^{13}C CP-MAS experiments were acquired with the following parameter sets: ^1H 90° pulse was 4.0 μs; cross polarization contact time was 2 ms; ^1H decoupling 62.5 kHz, 2 s repetition delay was applied and a 300 ppm spectral region was recorded with a carrier frequency placed at 110 ppm, the ^1H frequency was positioned to 4.7 ppm. 1 K tranzients were recorded in 2 K complex data-points resulting in 27.3 ms acquisition time. Lorentzian window function (with 50 Hz broadening factor) was applied prior to Fourier transformation. The spectra were referenced to tetramethylsilane.

3. Results and discussion

3.1. Catalyst characterization

A novel method for the controlled deposition of metals onto surfaces was disclosed by Fry in the early 1990s [81,82]. It was shown that the treatment of silica with trichlorosilane allows the immobilization of the Si–H function. This surface hydrosilane function is capable of reducing metal ions resulting in the deposition of a thin metal layer onto the silica surface. A silica-supported Pd catalyst thus prepared, after modification with Hg^{2+}, was found to exhibit excellent catalytic properties in the chemo- and regioselective partial hydrogenation of alkynes [81].

We prepared a set of Pd-on-silica catalysts with an important modification of the original synthesis protocol. First, silica was treated with various chlorohydrosilanes (trichlorosilane, dichloromethyl- and chlorodimethyl-silane, dichlorophenyl- and chlorodiphenyl-silane) to prepare silica materials with various organic functionalities, namely methyl or phenyl group(s), on the surface. The modified silicas were then reacted with a dilute $PdCl_2$ solution to prepare five Pd-on-silica catalysts with identical Pd loading of 0.3 wt.%. Both the silane-treated silica precursors and the samples loaded with Pd were characterized by physical and chemical methods.

Treatment of silica with chlorohydrosilanes results in some decrease in the BET surface area of the parent silica material (455 $m^2 g^{-1}$) (Table 1). In contrast, the increase in surface areas was observed on loading Pd onto the silane-treated silica precursors. TEM images show quite uniform particle sizes. The TEM image shown in Fig. 1, is characteristic of catalysts with 0.3% loading. Data derived from both TEM images (Table 1) and determined by H_2 chemisorption, which gave Pd dispersion values about 0.04–0.05, indicate that the Pd catalysts prepared are of low metal dispersion.

Table 1
Characterization of silica precursors and Pd-on-silica catalysts

Silica precursors		0.3% Pd-on-silica catalysts		
Silanes[a]	BET ($m^2 \, g^{-1}$)		BET ($m^2 \, g^{-1}$)	Particle size[b] (nm)
Cl_3SiH	390	Pd/SiO_2	419	9–11
Cl_2MeSiH	416	Pd/SiO_2Me	430	12–15
$ClMe_2SiH$	398	Pd/SiO_2Me_2	451	21–24
Cl_2PhSiH	417	Pd/SiO_2Ph	371	12–15
$ClPh_2SiH$	379	Pd/SiO_2Ph_2	430	9–13

[a] Silanes used in treatment of silica.
[b] Average diameter of about 100 particles determined from TEM.

3.2. Solid-state MAS NMR characterization

As a result of the applied treatment of the silica surface with different silanes, the cross polarized ^{29}Si-MAS spectra displayed different signal patterns [83,84]. When the silica was treated with SiHCl$_3$ the obtained precursor held mainly –SiH(OMe)$_2$ functionalities after the MeOH treatment and the ^{29}Si CP-MAS spectrum (Fig. 2a) yielded four characteristic signals. Of these the resonances at −111.7 and −102.9 ppm can be assigned to Q$_4$ and Q$_3$ sites (SiO$_4$ units), respectively. Compared to the spectrum of the original silica gel (not shown), Q$_2$ sites disappeared and the high intensity of the Q$_3$ signal diminished. The signals at −88.4 and −77.1 ppm belong to T^3 and T^2 sites, respectively (SiO$_3$ units possessing three or two siloxane bridges). The substitution of one chlorine to a methyl group in the silane provided –SiHMe(OMe) functionalities on the surface (Fig. 2b) and a ^{29}Si signal appeared at −35.3 ppm as a result of the Si–Me connection. Furthermore, Q$_3$ lost intensity relative to Q$_4$ resonances. One more methyl substitution (Fig. 2c) in the reagent silane provided –SiHMe$_2$ groups on the surface and the signal originating from the polarization transfer of methyl protons shifted to a higher chemical shift (−2.2 ppm), moreover, an increased Q$_3$/Q$_4$ intensity ratio was observed in the spectrum. Surface treatment with phenylsilanes resulted in similar changes. The –SiHPh(OMe) functionalities on the surface induced a high intensity signal corresponding to a polarization transfer from the aromatic protons appearing at
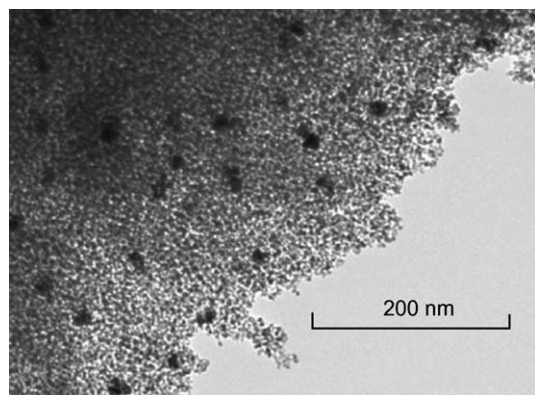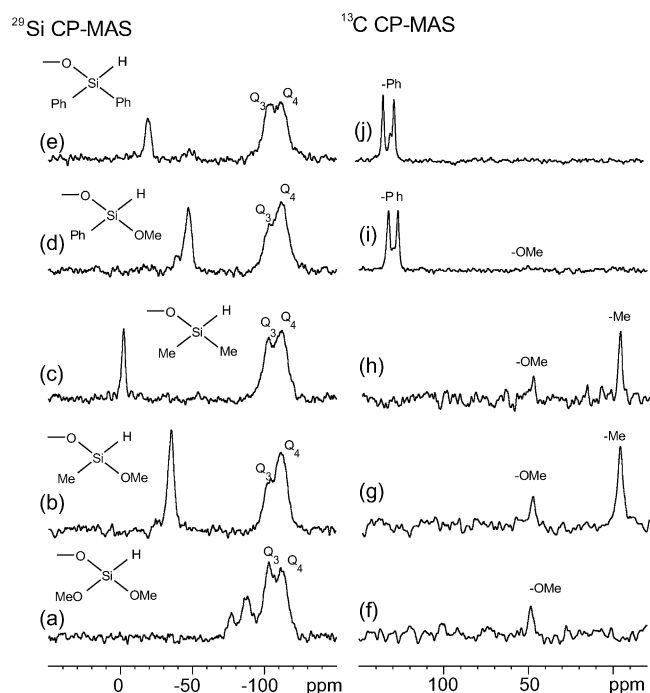

Fig. 2. ^{29}Si CP-MAS and ^{13}C CP-MAS NMR spectra of silica gel treated with trichlorosilane (spectra a and f), dichloromethylsilane (b and g), chlorodimethylsilane (c and h), dichlorophenylsilane (d and i) and chlorodiphenylsilane (e and j).

−47.1 ppm (Fig. 2d) as the Q$_3$ signals became smaller than Q$_4$. The introduction of one more phenyl group to the surface as –SiHPh$_2$ resulted in a 27.9 ppm chemical shift increase to −18.7 ppm with equal Q$_3$ and Q$_4$ signal intensities (Fig. 2e).

In order to identify organic functionalities attached to the surface, ^{13}C CP-MAS experiments were performed. The solid-state cross-polarized ^{13}C spectrum of the sample with –SiH(OMe)$_2$ groups on the surface shows a signal at 48.3 ppm (Fig. 2f) and can be assigned to methoxy groups attached to silicon atoms on the surface. The replacement of one –OMe group to a methyl functionality afforded a signal at −2.1 ppm (Fig. 2g). One more replacement to a methyl group did not cause significant chemical shift change of the methyl resonance (Fig. 2h), however, the methoxy signal is still present in the spectrum. The attached substrate with one phenyl group provided aromatic ^{13}C-signals at 127.1, 129.7 and 132.5 ppm. The methoxy signal has also appeared at 50.3 ppm with small intensity (Fig. 2i). The introduction of the second phenyl group did not cause any significant change in the ^{13}C-spectrum besides the disappearance of the methoxy signal (Fig. 2j).

3.3. Catalytic results

The five Pd-on-silica catalysts prepared and characterized as described above were applied in the reaction of iodo- and bromo-arenes with styrene and aliphatic vinylic compounds (Scheme 1). Catalyst quantities were chosen to have

Fig. 1. Transmission electron micrograph of a 0.3% Pd/SiO$_2$Ph catalyst.
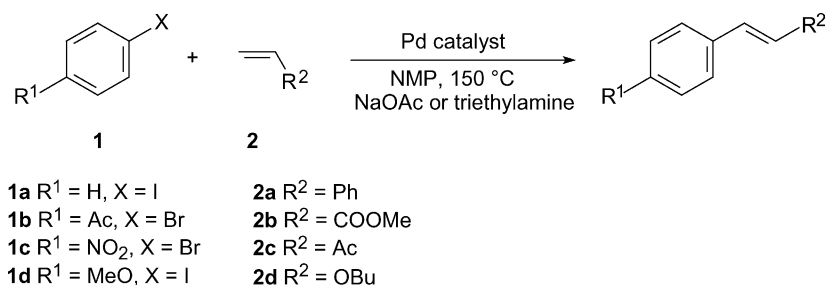
Scheme 1. Heck coupling of haloarenes and vinylic compounds.

Table 2
Catalytic performance of 0.3% Pd–silica catalysts in the Heck coupling[a]

Catalyst	1a + 2a		1a + 2b		1b + 2b		1c + 2b	
	Conv.	Sel.	Conv.	Sel.	Conv.	Sel.	Conv.	Sel.
Pd/SiO$_2$	54	86	81	99	47	99	64	99
Pd/SiO$_2$Me	58	86	84	99	67	99	100	99
Pd/SiO$_2$Me$_2$	35	85	54	99	19	99	68	99
Pd/SiO$_2$Ph	80	83	97	99	75	99	100	99
Pd/SiO$_2$Ph$_2$	57	86	51	99	58	99	66	99

[a] Reaction conditions: 0.89 mmol of haloarane, alkene and NaOAc, 68 mg of catalyst; 150 °C, reaction time: 5 h for styrene, 2 h for methyl acrylate.

0.3 mol% Pd in the reaction mixture with respect to the reactants.

As summarized in Table 2, all catalysts proved to be active in the Heck coupling. Conversion values change between 19 and 100%, whereas selectivities are found in the range 83–99%. It is significant that even less reactive activated bromoarenes (*p*-bromoacetophenone **1b** and *p*-bromonitrobenzene **1c**) react satisfactorily with methyl acrylate (**2b**). Bromobenzene and chlorobenzene, in turn, do not react. Furthermore, the highly selective formation of the corresponding *E* isomers is characteristic in all cases.

In addition to these features, it is of particular importance to note the effect of the organic functionalities on the silica surface on catalytic activities (Table 2). As seen, one surface methyl (0.3% Pd/SiO$_2$Me) or phenyl group (0.3% Pd/SiO$_2$Ph) bound to the silica surface results in a significant increase in catalytic activity as compared to the parent sample with a surface containing only methoxy moieties (0.3% Pd/SiO$_2$). In contrast, a sharp drop in catalytic activities is brought about by the introduction of a second organic group (Pd/SiO$_2$Me$_2$ and Pd/SiO$_2$Ph$_2$).

Silica-bound surface organic functions may affect both Pd deposition (reduction of Pd^{2+} to metallic Pd) and the actual reaction of organic molecules.

(i) The effect on Pd deposition is probably a simple electrostatic interaction. Since catalyst characterization techniques applied in the present study did not show any significant differences of the five catalyst samples, catalyst formation does not appear to be affected.
(ii) On the other hand, both steric hindrance and polar interactions may play a role in the chemical transformation. The presence of surface MeO groups and one additional hydrocarbon group appears to create a surface environment for favorable polar interactions without significant steric hindrance. Dimethyl- and diphenyl-modified catalysts, in turn, exhibit decreased activity as a results of decreasing polarity of the surface due to the replacement of MeO functions and increasing surface constraints, which may hinder the accessibility of Pd particles to reacting molecules.

Table 3 gives the summary of experimental data found over 0.3% Pd/SiO$_2$Ph, which proved to be the most active catalyst. It also includes data for other substrate combinations, namely iodoanisole (**1d**) and vinylic compounds but-1-ene-3-one (**2c**) and butyl vinyl ether (**2d**). These data indicate that styrene (**2a**) and methyl acrylate (**2b**) give the best results with all aromatic halides studied. The other alkenes (**2c** and **2d**), in turn, although react satisfactorily, exhibit much lower selectivities. In addition, to the corresponding aryl-substituted *E*-alkenes, the regular Heck coupling products, a range of other compounds are also formed. These include aryl self-coupling, α-substitution of the double bond

Table 3
Catalytic performance of 0.3% Pd/SiO$_2$Ph catalyst[a]

Haloarane	Alkene			
	2a	2b	2c	2d
Iodobenzene (**1a**)	94[b] (85)[c]	97[b] (100)[c]	87[b] (21)[c]	75[b] (31)[c]
Iodoanisole (**1d**)	93 (81)	82 (100)	93 (70)	80 (9)
p-Bromoacetophenone (**1b**)	66 (94)	75 (100)	83 (94)	31 (38)
p-Bromonitrobenzene (**1c**)	92 (100)	100 (100)	100 (100)	64 (46)

[a] Reaction conditions: 0.89 mmol of haloarane, alkene and triethylamine; 68 mg of catalyst; 150 °C, reaction time: 2 h for alkenes **2a**, **2c** and **2d**, 1 h for **2b**.
[b] Conversion (%).
[c] Selectivity of aryl-substituted *E*-alkene (%).

Table 4
Selectivities in the reaction of but-1-ene-3-one (**2c**) and butyl vinyl ether (**2d**)[a]

Haloarene	Alkene	
	2c	**2d**
1a	79% 3-hydroxy-2-phenylbutene	9% biphenyl
		42% 1-phenyl-1-butoxyethene
		20% unidentified
1d	30% 4-(*p*-metoxyphenyl)-2-butanone	70% 1-(*p*-methoxyphenyl)-ethanone
		21% 4-(*p*-methoxyphenyl)-2-butanone
1b	6% 2-(*p*-acetylphenyl)-1-butene-3-one	47% 1-(*p*-acetylphenyl)-1-butoxyethene
		15% unidentified
1c	–	54% 1-(*p*-nitrophenyl)-1-butoxyethene

[a] 0.3% Pd/SiO₂Ph catalyst, for reaction conditions, see Table 3.

and Heck coupling products with the carbonyl group or the double bond hydrogenated (Table 4). This is, however, not unexpected, since these vinylic compounds are known to yield such unusual products in Heck reaction [85–88].

3.4. Catalyst recycling

The best catalyst sample (0.3% Pd/SiO₂Ph) was chosen to test the possibility of catalyst recycling and the results obtained were compared to those found for Pd/C, which is considered to be one of the best heterogeneous catalyst in the Heck reaction [66]. The data presented in Fig. 3 indicate that the performance of the new 0.3% Pd/SiO₂Ph is very similar to that of commercial 10% Pd/C applied in this study: both can be re-used about four times with a small decrease in catalytic activity then a sudden drop in activity occurs.
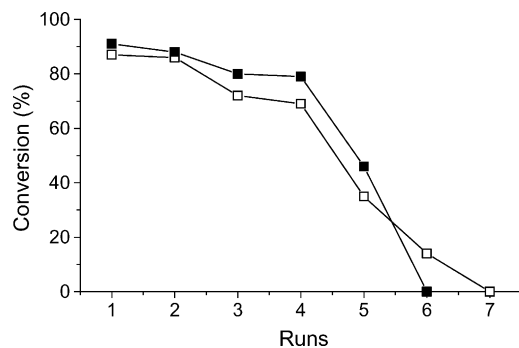

Fig. 3. Catalyst recycling in the Heck coupling of iodobenzene and styrene in the presence of 0.3% Pd/SiO₂Ph (■f) and 10% Pd/C (□). Reaction conditions: base: triethylamine, solvent: NMP, reaction time: 2 h.

3.5. Pd leaching

Development of heterogeneous that is reusable, catalysts for industrial applications remains an important goal for economic reasons. This is a particular challenge for the Heck coupling since leaching of Pd from heterogeneous catalyst systems is known to occur under certain reaction conditions [19,55,62–65,89]. The leaching phenomenon has been utilized by Köhler and co-workers to show that specially prepared solid Pd catalysts having highly dispersed Pd²⁺ species are able to catalyze the Heck coupling of chloroarenes [78]. A high amount (about 35%) of Pd was shown to be dissolved at about 45 min reaction time and redeposited by the end of reaction. A clear correlation was demonstrated between dissolution of Pd and reaction rate.

It has been demonstrated that dissolved Pd species can readsorb onto the support after completing the reaction. The leaching phenomenon, therefore, was studied following the guidelines suggested [47,62,90] that is the reaction was interrupted at low conversion and the filtrate was collected from the hot reaction mixture. This method, the so-called split technique can give reliable information of active Pd species in solution.

Data were collected by using 0.3% Pd/SiO₂Ph catalyst and running the reaction of iodobenzene with styrene in NMP or toluene as solvents. As seen from the results presented in Figs. 4 and 5, there is only a small increase in conversion in the initial period in the new reactions using the original reaction mixture after separating the catalyst. This indicates that the reaction mixture after the removal of the catalyst still contains some active species, either dissolved or as heterogeneous particles. These, however, quickly lose activity. Indeed, dissolution of Pd was confirmed by ICP measurements. However, the amount of Pd in solution is only about 1–2 ppm, which is much smaller then concentrations detected in earlier studies [62,64,89,90]. The only exception are the findings of Jacobs and co-workers who detected Pd concentrations in the range 0.01–0.65 ppm [48]. Furthermore, the change in Pd concentration as a function of time is also different. The
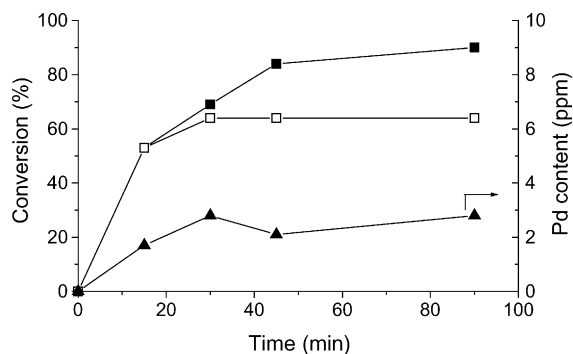

Fig. 4. Changes in conversions and quantity of leached Pd as a function of time in the Heck coupling of iodobenzene and styrene. (■f): Continuous reaction, (□): reaction of filtrate after catalyst removal (split time: 15 min), (▲): Pd in solution. Reaction conditions: base: triethylamine, solvent: NMP.
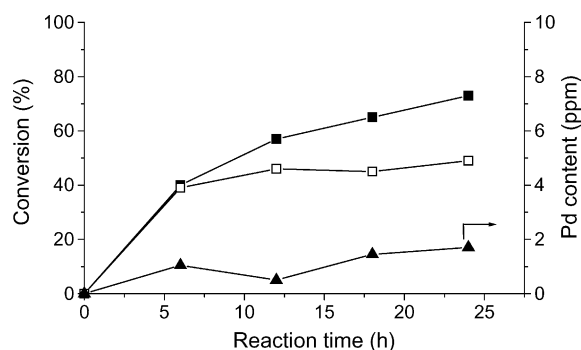
Fig. 5. Changes in conversions and quantity of leached Pd as a function of time in the Heck coupling of iodobenzene and styrene. (■f): Continuous reaction, (□): reaction of filtrate after catalyst removal (split time: 6 h), (▲): Pd in solution. Reaction conditions: base: triethylamine, solvent: toluene.
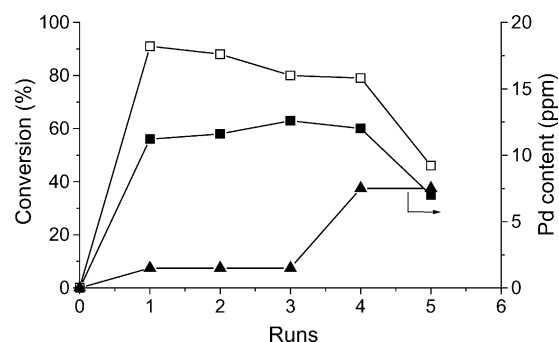

Fig. 6. Changes in conversion and quantity of leached Pd as a function of recycling in the Heck coupling of iodobenzene and styrene. (■f): Conversions after 15 min, (□): conversions after 120 min, (▲): Pd in solution after 15 min. Reaction conditions: base: triethylamine, solvent: NMP.

characteristic patterns observed earlier are either high initial concentration of dissolved Pd followed by a steady decrease [64,78] or the concentration of dissolved Pd slowly increases with reaction time [62]. In our case, random changes have been observed.

To gain further insight into the characteristics of these new catalysts leaching and recycling studies were combined. After determining the amount of dissolved Pd stopping the reaction after 15 min, a new reaction was started with the recovered catalyst and it was continued for the usual reaction time (2 h). The catalyst was recovered, washed with acetone and a second experiment was started repeating the same protocol. In the first four uses the catalyst exhibits high and very similar activities (Fig. 6) and the concentration of dissolved Pd is similar to those found in normal leaching studies. As expected on the basis of recycling studies, the activity drops in the 5th run. Moreover, there is a sudden increase in Pd concentration in solution.

To test the viability of soluble Pd species in Heck coupling under the reaction conditions used reactions without ligand assistance were also performed. Iodobenzene and styrene were reacted in the presence of Pd chloride or Pd acetate (Table 5). We observed the well-known fact that Pd acetate ex-

hibits much higher activity under identical reaction conditions (Table 5, entries 1, 2 and 3, 4). The activity of Pd acetate and that of 0.3% Pd/SiO₂Ph is comparable (Table 5, entries 3, 4 and 7). Note, that Pd content in the homogeneous reaction mixture was 0.3 mol%, which is identical with the quantity of Pd of the heterogeneous catalysts. Furthermore, when the quantity of Pd acetate is decreased to 10%, which is still one order of magnitude higher than those found in leaching experiments, the activity remained high in accordance with recent observations [20,79]. This was interpreted by supposing the involvement of acetate ions in stabilizing nanoparticles and participating in shifting the equilibrium between "higher order" and monomeric Pd species [14,19,20,79].

It is also known that colloidal Pd particles may be involved in homogeneous reactions. These species may precipitate and when deposited onto an inert support such as silica the resulting solid can be re-used as a heterogeneous catalyst [91]. We could also observe this phenomenon with Pd acetate (Table 5). The precipitate showed a decreased, although still quite high activity in the second use (Table 5, entry 3). When the reaction with Pd acetate was carried out in the presence of silica the recovered solid showed similar activity (Table 5, entry 4). It is somewhat surprising that the

Table 5
Reactivity of Pd ions in non-coordinating surroundings[a]

Entry	Catalyst[b]	Additive	Conversion %	Observation
1	PdCl₂	None	0	
2	PdCl₂	Silica (68 mg)	7 (1)[c]	Pale yellow coloration on silica
3	Pd(OAc)₂	None	92 (65)	Pd residue
4	Pd(OAc)₂	Silica (68 mg)	90 (69)	Gray coloration on silica
5	Pd(OAc)₂[d]	None	79 (3)	
6	Pd(OAc)₂[d]	Silica (68 mg)	93 (0)	Pale yellow coloration on silica
7	0.3% Pd/SiO₂Ph[e]	10 μL methanol	90 (87)	

[a] Reaction conditions: 0.89 mmol of iodobenzene, styrene and triethylamine; 0.19 M methanolic solution of PdCl₂ or Pd(OAc)₂ (10 μL); solvent: NMP; reaction time: 2 h.

[b] Quantities of Pd in the reaction mixture: entries 1–4 and 7 = 0.3 mol%, entries 5 and 6 = 0.03 mol%.

[c] Values in parentheses were found in the second run with recovered Pd material.

[d] Reaction in the presence of a decreased amount of Pd(OAc)₂ (1 μL).

[e] 68 mg.

deposited Pd could be re-used without any further treatment (entries 3, 4 and 7), which was found to be necessary in a previous study using celite as the carrier [19]. In contrast, considerable decreases in the activity in the second run occur in reactions with a decreased amount of catalyst (Table 5, entries 5 and 6). This appears to be a significant drawback with respect to the reuse of low amounts of Pd acetate [19,79].

Previous studies have shown the importance of reaction conditions in affecting the heterogeneity of the Heck coupling [56,66,91,92]. The above data, in line with literature observations, clearly indicate that the acetate ion plays an important role in the Heck reaction under homogeneous conditions. In the light of the above results it was an obvious step to carry out leaching experiments with these new catalysts in the presence of NaOAc as the base. Data are summarized in Fig. 7 and compared to the results found in the presence of triethylamine under otherwise identical conditions.

It is seen that the overall reactivity versus reaction time relationships of the two systems are very similar, although the initial rate with NaOAc is somewhat smaller (Fig. 7A). In contrast, the difference between the quantities of dissolved Pd species are quite substantial: the concentration of Pd in solution is much higher when NaOAc is used. Similarly, the results of split experiments with the two bases differ significantly. As discussed, only a very small activity is observed in the reaction mixture after catalyst removal in the presence of triethylamine (Fig. 7B). In sharp contrast, the reaction in a similar experiment with NaOAc as base continued almost as if uninterrupted. It is also very significant, that a reaction, which was started with triethylamine and continued after split with added NaOAc showed a conversion profile very similar to that of the run with NaOAc: the conversion level found in this experiment after 2 h was as high as those of the uninterrupted and split experiments. This is a clear indication that acetate ions are certainly involved in the formation of the active Pd species. The results also show that Pd species in concentrations of 1–2 ppm are able to induce high reaction rates under appropriate reaction conditions. The turnover number for this last experiment was calculated to be as high as 140.

4. Conclusion

Palladium was deposited onto silica modified with various organohydrosilanes. The Pd-on-silica catalysts thus prepared were found to exhibit high activity and selectivity in the Heck coupling with aromatic iodo and activated bromo compounds. Although chloro and non-activated bromo compounds do not react, the performance of these new catalysts in recycling studies are found to be comparable to that of commercial Pd-on-carbon, which is considered to be one of the best heterogeneous catalyst.

The modifying methyl and phenyl groups covalently attached to the surface affect catalyst activity. The sample with one phenyl group on the surface exhibits the best performance. Decreasing polarity of the surface due to the replacement of MeO functions and increasing surface constraints are the probable reasons for decreased activity of dimethyl- and diphenyl-modified catalysts.

Low amounts of Pd were detected to leach into solution, however, Pd species in solution do not appear to promote the reaction under the conditions applied.
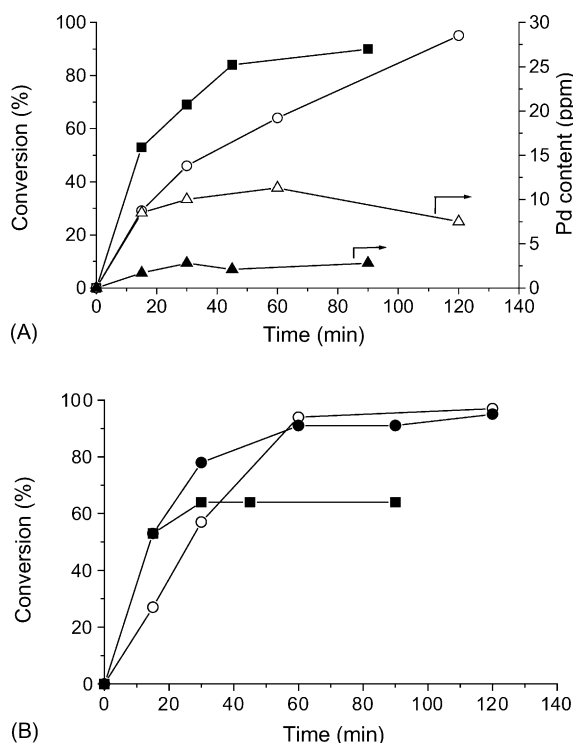
Fig. 7. Changes in conversions and quantity of leached Pd as a function of time in the Heck coupling of iodobenzene and styrene in the presence of 0.3% Pd/SiO$_2$Ph. Reaction conditions: solvent: NMP, split time: 15 min. (A) (■): Reaction using triethylamine as base, (○): in the presence of NaOAc as base, (▲,△): Pd in solution of the corresponding reactions. (B) (■): Reaction of filtrate after catalyst removal (split time: 15 min, triethylamine), (○): reaction of filtrate after catalyst removal (split time: 15 min, NaOAc), (●): reaction with triethylamine was interrupted after 15 min, the catalyst was removed and the reaction was continued with added NaOAc (10 mg, 122 mmol).

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