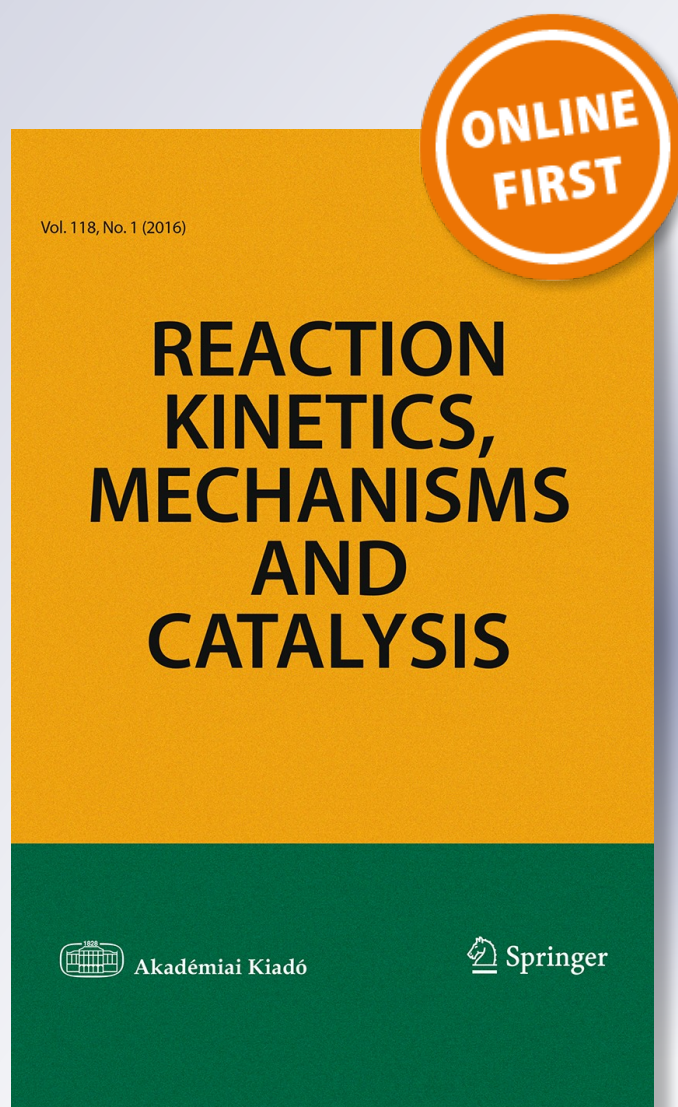# Heck arylation of alkenes with aryl bromides by using supported Pd catalysts: a comparative study

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Heck arylation of alkenes with aryl bromides by using supported Pd catalysts: a comparative study

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Gábor London[1]

Abstract Supported Pd catalysts were investigated in the Heck coupling reactions: Pd/C; $Pd/BaSO_4$; Pd EnCat. We optimized the experimental conditions of the Heck reaction of bromobenzene and styrene by using various bases in the presence of quaternary ammonium salts. It was found that the examined catalysts work as a reservoir of the catalytically active Pd species during the reaction. However, they have a different activity and recyclability under the investigated reaction conditions. Pd EnCat displayed the highest activity and selectivity in NMP with Na_2CO_3 as a base and Bu_4NCl as an additive. By using this catalytic system, the reactions of para-substituted aryl halides with styrene and methyl methacrylate afforded excellent conversions and selectivities.

Keywords Palladium on activated carbon · Palladium on barium sulfate · Pd EnCat · Tetrabutyl ammonium salts · Leaching

Introduction

The development of Pd catalyzed cross-coupling reactions opened up a chemical space of compounds useful in a large number of applications in materials science and pharmaceuticals [1, 2]. The Heck reaction (Fig. 1) is the most widely used method for the coupling of alkenes with aromatic halides or triflates [3, 4]. There are several catalytic systems that have been developed and optimized for such reactions including homogeneous and heterogeneous methodologies [5, 6].

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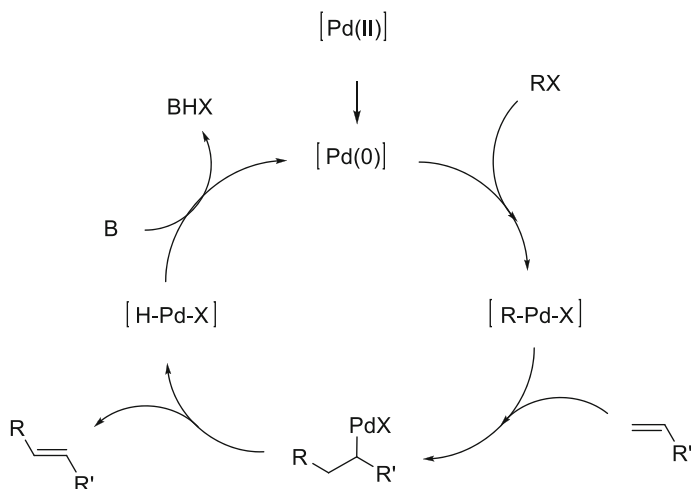2   Department of Organic Chemistry, University of Szeged, Dóm tér 8, 6720 Szeged, Hungary

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Fig. 1 The catalytic cycle of the Heck coupling reaction

In recent years, in line with environmental and economic concerns, research efforts in organic reaction method development have been increasingly focused on the use of easily available heterogeneous catalytic systems [7, 8]. Heterogeneous catalysts represent environmentally more favorable alternatives of many homogeneous systems as the former catalysts can be easily recovered and reused, which ultimately reduces the energy need and the amount of waste produced during chemical processes [9–11]. However, heterogeneous Heck reactions sometimes require extended reaction times (6–24 h or more) and high amounts of Pd catalysts (1–5 mol%) especially for the coupling reactions of less reactive aryl bromides and chlorides with non-activated alkenes [12]. Therefore, recent interest has been focused on highly active and selective catalyst systems that even provide opportunity to use the Heck reaction in tandem reactions [13, 14].

The solvent plays an important role in the Heck reaction. Polar aprotic solvents, used both in homogeneous and heterogeneous conditions, tend to increase the conversions, even at short reaction times. This may be due to their coordination ability resulting in the formation of Pd(0) complexes, thereby stabilizing nanoparticles or other Pd species. The Heck reaction has been frequently performed on heterogeneous Pd catalysts, but there are few publications on such catalysts working without leaching of Pd from the support materials. However, the latter catalysts usually show reduced activities, as the leached Pd species has been found to be the active catalyst of the reaction in a number of cases [15–17, 28, 29]. It seems that a suitable Pd support is more likely to produce a slow-release pre-catalyst (SRPC), which releases Pd slowly and continuously into the reaction media. Therefore, the best heterogeneous catalysts become less active after 6–8 catalytic cycles and sometimes even longer reaction times are needed. A large number of reports on the Heck reaction suggested that the reaction rate correlated with the leached and stabilized Pd particles in the reaction media [16–18]. The solvated Pd species must

be stabilized, otherwise aggregation of the active Pd nanoparticles occur, which results in the formation of inactive clusters, called palladium black.

Here we report on a comparative study of supported Pd catalysts in the Heck reaction. The catalysts used were as follows: Pd/C [17, 19–21] one of the most widely used heterogeneous Pd catalysts in Heck reactions; Pd/BaSO$_4$ [22–24], which has been shown to act as a catalyst reservoir in Stille and Suzuki–Miyaura couplings, but rarely used in Heck arylations, and Pd EnCat 30 [25–30], a commercial Pd(OAc)$_2$ catalyst, obtained by microencapsulation of palladium-acetate in polyurea matrix, formed by the condensation of multi-functional oligo-arylisocyanates [31–35]. The properties of Pd EnCat were reported by the manufacturer, where only low leaching of Pd was detected [36]. On the other hand, it was found that Pd EnCat became a nanoporous material when swollen in THF and the Heck reaction took place outside the support via soluble Pd species [37]. In other studies, it was reported that Pd EnCat acted as a reservoir of soluble Pd(0) nanoparticles and the application of polar aprotic solvents (e.g. DMF) resulted in an enhanced polymer swelling [27, 37, 38].

We examined the effect of the reaction conditions and additives on the catalytic activity and tested the reusability of the catalysts.

Experimental

The reagents, solvents and catalysts (Aldrich, Alfa Aesar, Fluka, VWR) were purchased as reagent-grade and used without further purification. The analyses were carried out by gas chromatography–mass spectrometry (GC–MS) performed on an Agilent 6890 N GC equipped with a DB-5 capillary column and an Agilent 5973 mass selective detector.

General procedure for the Heck reaction

A two-neck round-bottom flask equipped with a thermometer and a reflux condenser was loaded with aryl halide (4 mmol), alkene (4.8 mmol), base (5.8 mmol), ammonium salt additive (1 mmol) and catalyst (0.1 mol% Pd compared to the aryl halide; Pd/C-10 %; Pd/BaSO$_4$-5 %; Pd EnCat-4.3 % Pd content) in 5 ml of solvent. The reaction proceeded under stirring at 423 K for 3 h. Afterwards, the reaction mixture was diluted with diethyl ether and filtered on a pad of alumina. The clean filtrate was analyzed by GC–MS.

General procedure for catalyst recycling

After the reaction was completed, the reaction mixture was cooled down to ambient temperature and filtered on a Büchner funnel. The residual solid was washed with acetone, water and acetone again, in order to remove solid impurities and the catalyst was air dried. The subsequent reaction was carried out with the recycled catalyst under the original reaction conditions.

General procedure for the hot filtration test

Bromobenzene (4 mmol), styrene (4.8 mmol), Na_2CO_3 (5.8 mmol), Bu_4NCl (1 mmol) and catalyst (0.1 mol% Pd) together with 5 ml of solvent was placed in a round-bottom flask, which was then immersed in a pre-heated heating mantle and the mixture was stirred for 10 min. Then the reaction mixture was hot-filtered, a sample was taken, and the filtrate was stirred for 3 h at 423 K.

Results and discussion

The Heck coupling of bromobenzene with styrene was used as a model reaction (Fig. 2). The reaction leading to the formation of stilbene is of practical importance as the product and its derivatives have a wide range of applications in medicine, photochromic materials and laser dyes [39].

Initially, the reactions were performed in NMP and DMF in the presence of Na_2CO_3 as a base without any additive at 423 K for 3 h. In line with earlier reports [40, 41], we found that the presence of a small amount of water in DMF was beneficial for the reaction (Table 1). The addition of 5 % of water to the reaction mixture increased the conversion in the case of Pd EnCat and Pd/C. However, it had no effect on the reaction catalyzed by $Pd/BaSO_4$. This may be due to the enhanced solubility of the base in the reaction mixture. On the other hand, in the case of Pd EnCat, the added water may also help to dissolve Pd(II) species from the organic polymer matrix, which caused a pronounced improvement in the conversion (Table 1, Entry 9). The selectivity of the formation of the main product, *trans*-stilbene, was only decreased by the formation of minor amounts of *cis*-stilbene and 1,1-diphenylethylene. Most importantly, in contrast to previous reports, no dehalogenation and/or aryl–aryl coupling product was observed in any of the reactions [42].

As the reactions afforded moderate to good conversions in most cases, we tested the effects of other bases. The application of NaOAc was not beneficial as it was found to decrease the conversion (Table 2). A similar trend was observed for other bases including Cs_2CO_3, triethylamine (Et_3N) and benzyldiethylamine ($BnEt_2N$). When Cs_2CO_3 was applied, conversions up to 20 % were obtained, whereas in the presence of Et_3N, only traces of products were formed. Furthermore, our assumption that the application of $BnEt_2N$ would have a beneficial effect on the conversion via the formation of $BnEt_2NHBr$, a quaternary ammonium salt, was not justified by experimental results.
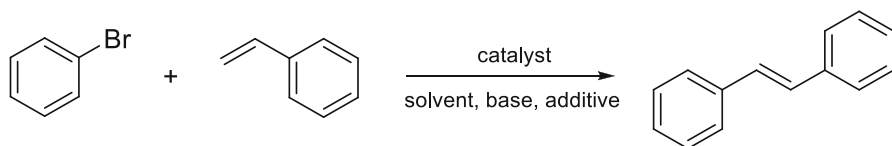

Fig. 2 Heck reaction of bromobenzene with styrene

Table 1 The effect of solvents on the Heck reaction of bromobenzene with styrene in the presence of Na_2CO_3

Entry	Catalyst	Solvent	Conversion (%)[a]	Selectivity (%)[a,b]
1	Pd/C	NMP	83	92
2	Pd/C	DMF	57	>90
3[c]	Pd/C	DMF/H_2O	66	91
4	Pd/$BaSO_4$	NMP	99	91
5	Pd/$BaSO_4$	DMF	65	>90
6[c]	Pd/$BaSO_4$	DMF/H_2O	65	89
7	Pd EnCat	NMP	66	89
8	Pd EnCat	DMF	65	>90
9[c]	Pd EnCat	DMF/H_2O	91	91

Reaction conditions: bromobenzene (4 mmol), styrene (4.8 mmol), Na_2CO_3 (5.8 mmol), catalyst (0.1 mol% Pd), solvent (5 ml) T = 423 K, t = 3 h

[a] Determined by GC-FID analysis

[b] Selectivity of *trans*-stilbene

[c] 5 V/V% water content

Table 2 Effect of solvents on the reaction of bromobenzene with styrene in the presence of NaOAc

Entry	Catalyst	Solvent	Conversion (%)[a]	Selectivity (%)[a,b]
1	Pd/C	NMP	75	90
2[c]	Pd/C	DMF/H_2O	54	91
3	Pd/$BaSO_4$	NMP	85	90
4[c]	Pd/$BaSO_4$	DMF/H_2O	57	89
5	Pd EnCat	NMP	61	90
6[c]	Pd EnCat	DMF/H_2O	69	89

Reaction conditions: bromobenzene (4 mmol), styrene (4.8 mmol), NaOAc (5.8 mmol), catalyst (0.1 mol% Pd), solvent (5 ml) T = 423 K, t = 3 h

[a] Determined by GC-FID analysis

[b] Selectivity of *trans*-stilbene

[c] 5 V/V% water content

Heck reaction in the presence of quaternary ammonium salts as additives

Quaternary ammonium salts usually have a beneficial effect on the Heck reaction in the presence of inorganic bases [43, 44]. They can be applied as phase transfer catalysts, and also as stabilizing agents, which ensure the formation of Pd(0) species in the reductive elimination step (Fig. 1) [45]. We applied tetrabutylammonium bromide (Bu$_4$NBr), tetrabutylammonium chloride (Bu$_4$NCl) and tetrabutylammonium acetate (Bu$_4$NOAc) as additives, in combination with each catalyst and solvent, in order to have an overview on the effect of the different counter ions on

the catalytic activity. The results are listed in Tables 3 and 4. In line with our expectations, the additives increased the conversions. However, their effect was found to vary with the experimental conditions.

When NMP was used as a solvent, Bu_4NOAc promoted the reaction less efficiently as the other additives, which gave excellent results both in terms of conversion and selectivity (Table 3). On the other hand, in DMF/H_2O, the effect of Bu_4NBr was less favorable than those of Bu_4NCl and Bu_4NOAc. The conversions in DMF/H_2O solvent system were somewhat lower than those in NMP.

It may be assumed that the counterion of the quaternary ammonium salt plays an important role in the stabilization of the Pd(II) complexes. The chloride anion of Bu_4NCl might substitute bromide or iodide anions in one of the Pd(II) complexes to form a less stable complex, which may undergo reductive elimination at the end of the catalytic cycle more rapidly. Moreover, Bu_4NCl may also promote the ionic mechanism of the Heck reaction by dismission of a less stable chloride anion instead of a neutral ligand.

As for the solvent effect, we observed that the conversions were higher in NMP than those in DMF or DMF/H_2O. For the different Pd species, NMP seems to be a more favorable neutral ligand than DMF, and therefore NMP may also promote the Pd leaching more efficiently.

As Pd EnCat was substantially different from Pd/C and $Pd/BaSO_4$, we tested the effect of the reaction temperature and time on its catalytic activity (Figs. 3 and 4). Pd leaching to the solution was expected to proceed faster and/or at lower temperatures from the polymer than from inorganic supports. However, the activity of Pd EnCat in the presence of Na_2CO_3 and Bu_4NCl was only slightly affected. It was found that even for this catalyst, a reaction temperature of 423 K and a reaction time of 3 h were required to afford good conversions.

Table 3 Effect of additives on the reaction of bromobenzene with styrene in NMP in the presence of Na_2CO_3

Entry	Catalyst	Additive	Conversion (%)[a]	Selectivity (%)[a,b]
1	Pd/C	Bu_4NBr	93	92
2	Pd/C	Bu_4NCl	99	91
3	Pd/C	Bu_4NOAc	92	91
4	$Pd/BaSO_4$	Bu_4NBr	98	92
5	$Pd/BaSO_4$	Bu_4NCl	97	95
6	$Pd/BaSO_4$	Bu_4NOAc	82	90
7	Pd EnCat	Bu_4NBr	95	94
8	Pd EnCat	Bu_4NCl	99	94
9	Pd EnCat	Bu_4NOAc	81	93

Reaction conditions: bromobenzene (4 mmol), styrene (4.8 mmol), Na_2CO_3 (5.8 mmol), additive (1 mmol), catalyst (0.1 mol% Pd), solvent (5 ml) T = 423 K, t = 3 h

[a] Determined by GC-FID analysis

[b] Selectivity of *trans*-stilbene

Table 4 Effect of additives on the reaction of bromobenzene with styrene in DMF/H_2O in the presence of Na_2CO_3

Entry	Catalyst	Additive	Conversion (%)[a]	Selectivity (%)[a,b]
1	Pd/C	Bu_4NBr	75	90
2	Pd/C	Bu_4NCl	97	90
3	Pd/C	Bu_4NOAc	90	86
4	$Pd/BaSO_4$	Bu_4NBr	54	90
5	$Pd/BaSO_4$	Bu_4NCl	87	90
6	$Pd/BaSO_4$	Bu_4NOAc	75	91
7	Pd EnCat	Bu_4NBr	82	88
8	Pd EnCat	Bu_4NCl	99	89
9	Pd EnCat	Bu_4NOAc	90	90

Reaction conditions: bromobenzene (4 mmol), styrene (4.8 mmol), Na_2CO_3 (5.8 mmol), additive (1 mmol), catalyst (0.1 mol% Pd), solvent (5 ml) T = 423 K, t = 3 h

[a] Determined by GC-FID analysis

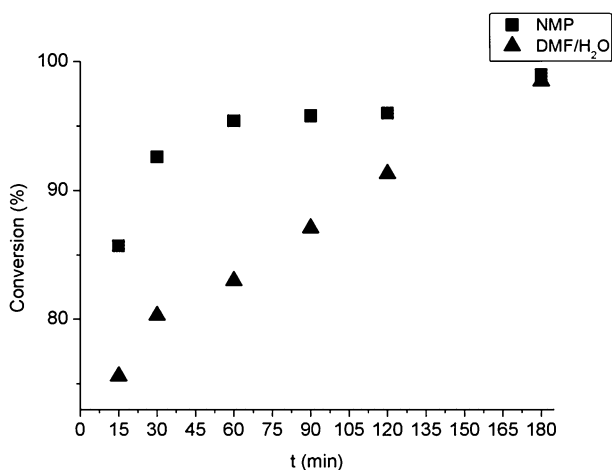[b] Selectivity of *trans*-stilbene

Fig. 3 Effect of reaction time on the Heck reaction of bromobenzene and styrene in the presence of Pd EnCat catalyst. Reaction conditions: bromobenzene (4 mmol), styrene (4.8 mmol), Na_2CO_3 (5.8 mmol), Bu_4NCl (1 mmol), Pd EnCat (0.1 mol% Pd), solvent (5 ml), T = 423 K

The combination of quaternary ammonium salts with NaOAc as a base resulted in improved conversions as compared to those obtained in the absence of additives. Nevertheless, the application of NaOAc resulted in lower conversions than those observed for the ammonium salt/Na_2CO_3 system (Tables 5 and 6). The solvent effect complied with the trend observed before, as the conversions in DMF/H_2O were somewhat lower than those in NMP. Bu_4NOAc was the least beneficial additive in combination with NaOAc in NMP.
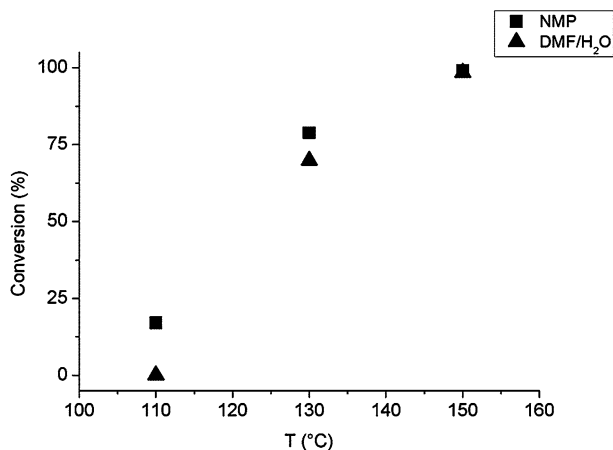
Fig. 4 Effect of the reaction temperature in different solvents on the Heck reaction of bromobenzene and styrene in the presence of Pd EnCat catalyst. Reaction conditions: bromobenzene (4 mmol), styrene (4.8 mmol), Na_2CO_3 (5.8 mmol), Bu_4NCl (1 mmol), Pd EnCat (0.1 mol% Pd), solvent (5 ml), t = 3 h

Table 5 Effect of additives on the reaction of bromobenzene with styrene in NMP in the presence of NaOAc

Entry	Catalyst	Additive	Conversion (%)[a]	Selectivity (%)[a,b]
1	Pd/C	Bu_4NBr	93	91
2	Pd/C	Bu_4NCl	87	91
3	Pd/C	Bu_4NOAc	80	90
4	$Pd/BaSO_4$	Bu_4NBr	95	90
5	$Pd/BaSO_4$	Bu_4NCl	93	88
6	$Pd/BaSO_4$	Bu_4NOAc	77	87
7	Pd EnCat	Bu_4NBr	98	92
8	Pd EnCat	Bu_4NCl	98	94
9	Pd EnCat	Bu_4NOAc	97	94

Reaction conditions: bromobenzene (4 mmol), styrene (4.8 mmol), NaOAc (5.8 mmol), additive (1 mmol), catalyst (0.1 mol% Pd), solvent (5 ml) T = 423 K, t = 3 h

[a] Determined by GC-FID analysis

[b] Selectivity of *trans*-stilbene

Our results confirmed that the catalytic performance of Pd EnCat, containing $Pd(OAc)_2$ as a precatalyst, exceeded those of Pd/C and $Pd/BaSO_4$ under most experimental conditions.

Catalyst recycling

We tested the activities of the catalysts upon recycling and found that the activities of the recycled catalysts strongly depended on the solvent. When NMP was used as

Table 6 Effect of additives on the reaction of bromobenzene with styrene in DMF/H_2O in the presence of NaOAc

Entry	Catalyst	Additive	Conversion (%)[a]	Selectivity (%)[a,b]
1	Pd/C	Bu$_4$NBr	68	90
2	Pd/C	Bu$_4$NCl	66	90
3	Pd/C	Bu$_4$NOAc	67	90
4	Pd/BaSO$_4$	Bu$_4$NBr	62	89
5	Pd/BaSO$_4$	Bu$_4$NCl	35	86
6	Pd/BaSO$_4$	Bu$_4$NOAc	55	89
7	Pd EnCat	Bu$_4$NBr	80	89
8	Pd EnCat	Bu$_4$NCl	71	88
9	Pd EnCat	Bu$_4$NOAc	66	87

Reaction conditions: bromobenzene (4 mmol), styrene (4.8 mmol), NaOAc (5.8 mmol), additive (1 mmol), catalyst (0.1 mol% Pd), solvent (5 ml) T = 423 K, t = 3 h

[a] Determined by GC-FID analysis

[b] Selectivity of *trans*-stilbene

a solvent, Pd/BaSO$_4$ was found to be the most active catalyst in the second catalytic cycle (Fig. 5), similarly to those observed for the Stille and Suzuki couplings [23, 24]. However, in the third cycle, its activity was strongly decreased (the conversion was 29 %). This decrease, however, was less pronounced than those for Pd EnCat and Pd/C, affording only 15 % of conversions.

In contrast to the above findings, the activity of Pd/BaSO$_4$ in DMF/H_2O diminished in the second cycle, whereas Pd EnCat and Pd/C remained reasonably active. Furthermore, Pd/C was found to preserve its activity for five cycles with only moderate decrease in conversion. It may be assumed that the extent of Pd leaching in NMP was higher than that in DMF/H_2O and also that Pd aggregation and deactivation occurred more readily in NMP. Therefore, we presume that Pd/C

Fig. 5 Recycling of the catalysts in NMP. Reaction conditions: bromobenzene (4 mmol), styrene (4.8 mmol), Na$_2$CO$_3$ (5.8 mmol), Bu$_4$NCl (1 mmol), catalyst (0.1 mol% Pd), solvent (5 ml), T = 423 K, t = 3 h (For further details on the recycling procedure, see "Experimental" section)

Fig. 6 Recycling of the catalysts in DMF/H$_2$O. Reaction conditions: bromobenzene (4 mmol), styrene (4.8 mmol), Na$_2$CO$_3$ (5.8 mmol), Bu$_4$NCl (1 mmol), catalyst (0.1 mol% Pd), solvent (5 ml), T = 423 K, t = 3 h (For further details on the recycling procedure, see "Experimental" section)
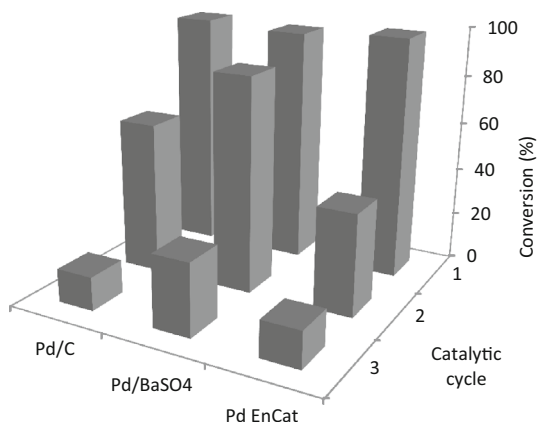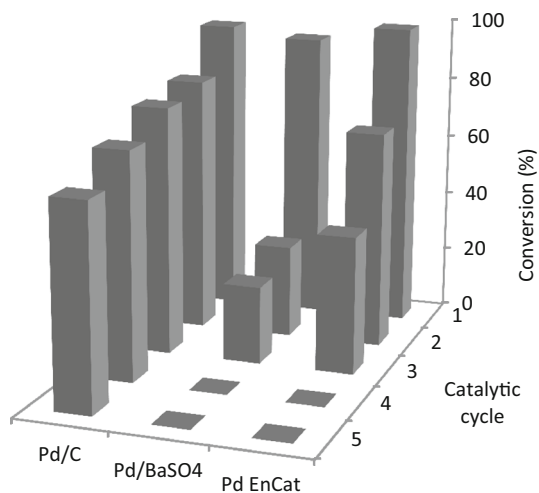

remained more active in DMF/H$_2$O, as related to a more monodispersed re-deposition of the leached Pd species on the surface of the support.

Hot filtration test

It is widely suspected that no truly heterogeneous catalyst system exists for the Heck reaction, and, therefore, leaching of Pd from the support is necessary for the catalytic reaction. The significant activity decrease in the catalyst recycling tests prompted us to investigate the extent of metal leaching (Table 7). We performed control experiments in which the reaction mixtures were filtered off after 10 min, the conversions were determined and the filtrates were heated for another 3 h. Our

Table 7 Results of the hot filtration test in NMP and DMF/H$_2$O

Entry	Solvent	Catalyst	Conversion (%)[a]	
			T = 10 min[b]	T = 3 h
1	NMP	Pd/C	8	27
2	NMP	Pd/BaSO$_4$	4	37
3	NMP	Pd EnCat	13	24
4	DMF/H$_2$O	Pd/C	13	30
5	DMF/H$_2$O	Pd/BaSO$_4$	8	17
6	DMF/H$_2$O	Pd EnCat	31	46

Reaction conditions: bromobenzene (4 mmol), styrene (4.8 mmol), Na$_2$CO$_3$ (5.8 mmol), Bu$_4$NCl (1 mmol), catalyst (0.1 mol% Pd), solvent (5 ml) T = 423 K

[a] Determined by GC-FID analysis

[b] Sample was taken after filtration

results were in line with the findings reported in the literature [15–17], as we experienced significant leaching in the induction period. In all cases, the conversions continued to increase after filtration, which confirmed the presence of catalytically active Pd species in the filtrates. Surprisingly, the highest conversion was observed for Pd EnCat in both NMP and DMF/H_2O at the time of filtration (Table 7, Entries 3 and 6). The reason may be that the polyurea support is capable of swelling, and hence the Pd(II) pre-catalyst could leave the support more easily. Furthermore, the reduction of Pd(II) leached from Pd EnCat to the active Pd(0) took place rapidly which is reflected in the conversion values measured after 10 min reaction. Only modest leaching was detected from Pd/$BaSO_4$ as is clear from the low initial conversions (Table 7, Entries 2 and 5). This could be explained by the lower surface area of the support that is influencing metal dispersion and thus the efficiency of metal leaching. On the contrary, Pd leaching from activated carbon was slightly elevated, but in view of the better recyclability of Pd/C (Fig. 6) it is plausible that after the coupling disperse re-deposition of the metal occurs onto the support due to its high surface area. In recent literature reports, the nature of the catalytically active Pd species during coupling reactions was investigated [46, 47]. The results pointed out that after an induction period, due to the increasing Pd(0) concentration in the solution, nanoparticles were formed, which resulted in a faster reaction. Considering our results, it is clear that the incubation period for the formation of the active catalyst is dependent on the Pd source. It is likely that a reaction time of 10 min was enough for the generation of active dissolved Pd(0) species in low concentrations, which afforded low initial conversions. However, the formation of Pd(0) nanoparticles, which is responsible for the faster stage of the reaction [46], was limited by the low Pd(0) concentration and prevented the completion of the reaction after the Pd source was filtered off.

Substrate scope

Considering that the Pd EnCat/Na_2CO_3/Bu_4NCl system gave the highest conversion and selectivity in NMP, we expanded the substrate scope of the reaction. An important difference between Pd EnCat and Pd/C is the nature of the support and its potential involvement in unwanted side-reactions. While Pd EnCat has standardized properties, carbon supports may possess various acidic or basic oxygen-containing functional groups on their surface depending on their origins, which may catalyze various side reactions [48]. Moreover, the preparation of Pd/C also affects its catalytic properties [17]. Para-substituted aryl halides in combination with styrene and methyl methacrylate were studied to investigate the synthetic applicability of this catalytic system. According to the data listed in Table 8, we observed excellent conversions with high selectivities. The only exception was 4-bromoanisole, due to the presence of an electron donating *para*-methoxy group, which slowed down the reaction (Table 8, Entries 4 and 11). Moreover, the reactions of 1-bromo-4-nitrobenzene and 4-bromobenzonitrile with methyl methacrylate resulted in complete conversions in 1 h (Table 8, Entries 8 and 9).

Table 8 Heck reaction of different substrates with the most efficient Pd EnCat/Na$_2$CO$_3$/Bu$_4$NCl catalytic system

Entry	R$_1$	X	R$_2$	R$_3$	Conversion (%)[a]
1	NO$_2$	Br	Ph	H	99
2	CN	Br	Ph	H	100
3	C(O)CH$_3$	Br	Ph	H	>99
4	OCH$_3$	Br	Ph	H	43
5	OCH$_3$	I	Ph	H	98
6	Cl	Br	Ph	H	99
7	H	Br	Ph	H	99
8[b]	NO$_2$	Br	CO$_2$Me	Me	>99
9[b]	CN	Br	CO$_2$Me	Me	100
10[b]	C(O)CH$_3$	Br	CO$_2$Me	Me	99
11	OCH$_3$	Br	CO$_2$Me	Me	76
12	OCH$_3$	I	CO$_2$Me	Me	95
13	Cl	Br	CO$_2$Me	Me	99
14	H	Br	CO$_2$Me	Me	99

Reaction conditions: aryl halide (4 mmol), alkene (4.8 mmol), Na$_2$CO$_3$ (5.8 mmol), Bu$_4$NCl (1 mmol), Pd EnCat (0.1 mol% Pd), NMP (5 ml) T = 423 K, t = 3 h

[a] Determined by GC-FID analysis

[b] The reaction was complete after 1 h

Conclusions

We optimized the reaction conditions for the Heck coupling reaction of bromobenzene and styrene by using supported Pd catalysts and various bases in the presence of quaternary ammonium salts as additives. Our catalytic systems displayed highly increased conversions in the presence of only 0.25 eq. of quaternary ammonium salts, unlike the *Jeffery systems*, for which 1 eq. of additive was typically used. We found that Pd EnCat showed the highest activity and selectivity by using NMP as a solvent, Na$_2$CO$_3$ as a base and Bu$_4$NCl as an additive. For this catalytic system, we also observed excellent conversions when para-substituted aryl halides and methyl methacrylate were used as substrates. It may be suggested that the investigated catalysts worked as a reservoir for the catalytically active Pd species during the reaction. However, the reusability of Pd EnCat was less good as that of Pd/C, which could be recycled five times in DMF/H$_2$O, with only a moderate loss of activity, as related to its high surface area that ensured Pd re-deposition. Pd/BaSO$_4$ showed a decreased efficiency as compared to Pd/C and Pd EnCat, furthermore leaching from the BaSO$_4$ support started less vigorously, however recyclability remained low. It may also be suggested that an efficient catalyst in the Heck reaction needs to be an SRPC, for which the support works as a reservoir of the active Pd species formed in the reaction media during leaching. The support was found to play a crucial role in the reaction by affecting re-deposition of the catalytically active Pd species, which is the key feature for a reusable SRPC.

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