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Suzuki- and Heck-Type Cross-Coupling with Palladium Nanoparticles Immobilized on Spherical Polyelectrolyte Brushes

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Abstract: We report on a systematic study of the use of palladium nanoparticles immobilized on spherical polyelectrolyte brushes – Pd@SPB – for Heck- and Suzuki-type coupling reactions. The spherical polyelectrolyte brush particles serving as carriers for the palladium nanoparticles consist of a solid polystyrene core with a radius of 46 nm onto which long chains of cationic polyelectrolytes are grafted. The palladium nanoparticles have directly been generated within this brush layer and the stabilization of the nanoparticles is effected by the colloidal carriers, no further surface stabilization is necessary. We demonstrate that these composite particles present robust catalysts for the Heck- and Suzuki-type coupling reactions. This was shown by carrying out the Suzuki- and Heck-type coupling reactions at relatively low temperatures (Suzuki reaction: 50 °C, Heck reaction: 70 °C). We demonstrate that the catalytic composite particles are not changed by these reaction conditions and retain their full activity for at least four runs. The yields obtained for both reactions are good to excellent. The mild operation conditions of the palladium nanoparticles are traced back to the absence of surface stabilization. Further mechanistic implications are discussed.

Keywords: catalysis; Heck-type cross-coupling; palladium nanoparticles; spherical polyelectrolyte brush; Suzuki-type cross-coupling

Introduction

Metal nanoparticles show different properties in comparison to their bulk materials and to isolated atoms.[1,2] In principle, the high surface area per volume renders metal nanoparticles ideal candidates for catalysis.[3] The palladium-catalyzed Heck[4] and Suzuki[5] reaction (cobalt nanospheres are also able to catalyze these reactions[6]) between aryl halides and alkenes or boronic acids, respectively, are well-established tools for C–C bond formation in organic synthesis. Thus, a convenient route for cross-coupling reactions involves reusable palladium nanoparticles that promote these reactions in organic solvents or in water.[7–9] The handling of the nanoparticles, however, may impose problems during work-up unless the particles are immobilized on suitable carriers. Such a carrier system should allow separation, for instance, *via* filtration, have a long-term stability, should be easy to handle, and should prevent the metallic nanoparticles from coagulating. For a re-use of the catalyst nanoparticles the support should be inert towards the reaction conditions applied. Moreover, no stabilizing agent should be induced that may alter or block the surface of the nanoparticles. Such molecules could also be removed during the work-up procedure. The carrier systems should also be sufficiently stable during the recycling of the catalyst. In efforts to develop a heterogeneous catalyst system for different applications, a variety of solids, particularly, active carbon,[10] mesoporous silica,[11] inorganic oxides,[12] molecular sieves,[13] polymers,[14] capsules[15] and basic metal phosphates (apatites)[16] have been used as carrier systems.

In particular, recent work has demonstrated that Pd nanoparticles may lead to excellent yields in a variety of catalytic reactions.[17–21] An issue of great importance is the leaching of Pd during the catalytic cycle,[22–24] especially since recent work has given evidence that metal ions are the catalytically active species in the Heck reaction at elevated temperatures (see the discussion of this problem in Refs.[20,22–25]).

Recently, we showed that well-defined gold, platinum and palladium nanoparticles can be generated in

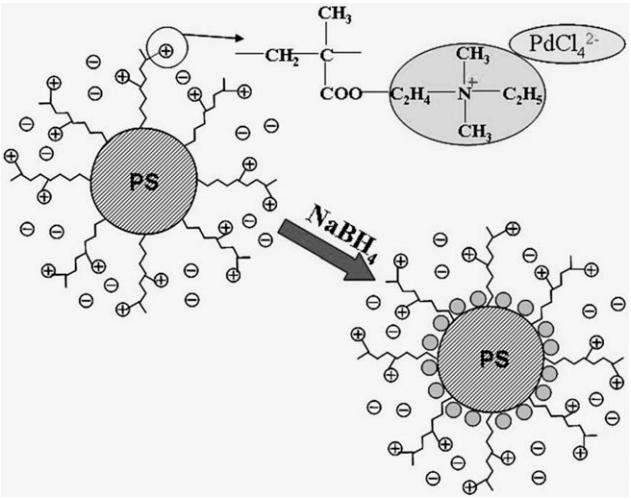


Figure 1. Scheme of the spherical polyelectrolytes used as carrier particles and the composite particles Pd@SPB. Long chains of poly[(2-methylpropenyloxyethyl)trimethylammonium chloride] are grafted to polystyrene cores of *ca.* 100 nm diameter. $PdCl_4^{2-}$ ions are introduced as counterions and subsequent reduction by $NaBH_4$ in aqueous solution leads to Pd nanoparticles of 2.6 ± 0.5 nm immobilized on the surface of the carrier particles.

spherical polyelectrolyte brushes (SPB)[26] and used as catalysts.[27–31]

Figure 1 shows the structure of the spherical polyelectrolyte brushes (SPB) in a schematic manner: Long polyelectrolyte chains with quaternary amino groups are chemically grafted to colloidal polymer particles of *ca.* 100 nm in diameter. The layer of polyelectrolyte chains attached to the surface of the carrier particles is very dense, that is, the contour length L_c of the chains is much higher than their average distance on the surface of the carrier particle. In this way a polyelectrolyte "brush" results in a system of strongly interacting polymer chains inserted densely to a curved surface.[26,32] Since the polyelectrolyte chains are grafted to the surface of the core particles by covalent bonding, a very stable support system results. The counterions neutralizing the charge of the polyelectrolyte chains are nearly fully confined in the brush layer.[26] Metal ions such as, for example, $PdCl_4^{2-}$ can be immobilized in this way and reduced to well-defined metal nanoparticles.[27–29,31] Work done by cryogenic transmission electron microscopy (cryo-TEM) has demonstrated that these metal nanoparticles are located near the surface of the core particles (see Figure 1 and Refs.[28,31]). It has been demonstrated that platinum nanoparticles immobilized on SPB can be re-used many times for catalytic hydrogenation reactions without any detectable loss of catalytic activity.[29] It should be noted that the metal nanoparticles generated in this way are not stabilized by any surface group or other stabilizing agents (beside water). Colloidal stability is brought about mainly by the special microenvironment provided by the organic carrier particles.

Here we show that Pd nanoparticles immobilized in spherical polyelectrolyte brushes (SPB) present a composite system that can be used as an efficient catalyst for the Heck and Suzuki reactions. We shall demonstrate that both reactions can be carried out under mild conditions and low temperatures (Suzuki reaction: 50 °C; Heck reaction: 70 °C). Special emphasis is laid on a possible degradation of the particles during these reactions and their catalytic activity after several runs.

Results and Discussion

Synthesis and Characterization of the Pd@SPB Composite Particles

The synthesis of the carrier particles has been done by photo-emulsion polymerization[33] as described recently.[27,28] Table 1 summarizes the pertinent parameters of the composite particles. Figure 2 displays a mi-

Table 1. Characterization of the Pd@SPB composite particle used in this study.[a]

R [nm]	L_c [nm]	M_w [g mol^{-1}]	σ [nm^{-2}]	D [nm]	L_c/R	d [nm]
46	182	150800	0.019	8.2	3.96	2.6 ± 0.5

[a] L_c: contour length of grafted chains determined from M_w; σ: graft density on surface of core particles; D: the average distance between two neighbouring points onto which the polyelectrolyte chains are grafted to; d: average size of the Pd nanoparticles.

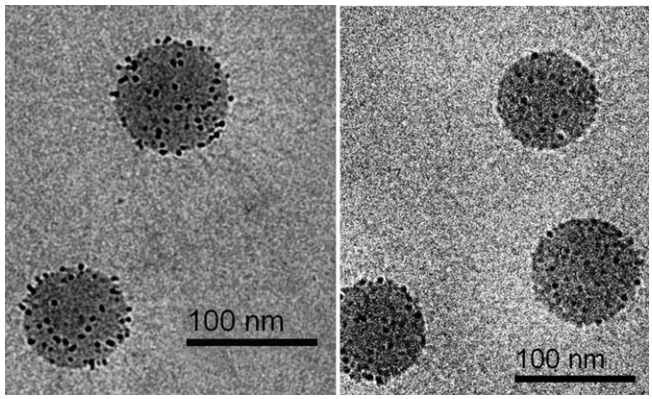
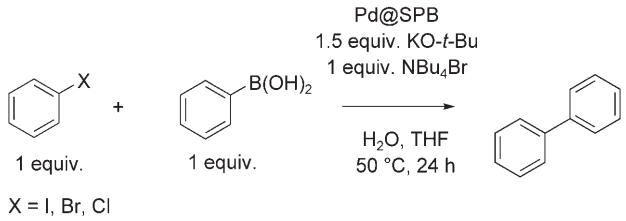


Figure 2. Cryo-TEM images of Pd@SPB composite particles before (*left*) and after (*right*) catalytic application in the Suzuki coupling. No noticeable change was observed after catalysis, the palladium nanoparticles were embedded firmly on the surface of SPB particles.

crograph of the particles obtained by cryo-TEM. It should be noted that the contrast of the polyelectrolyte chains in this system is not high enough so that they cannot be visualized in these micrographs.[26,29,31,34]

Suzuki-Type Cross-Coupling of Aryl Halides using Pd@SPB as Catalyst

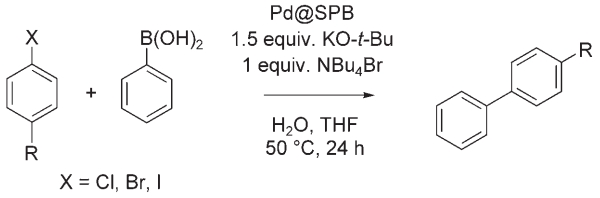
The Suzuki-type cross-coupling reaction between iodo-, bromo-, chlorobenzene and phenylboronic acid in water in the presence of Pd@SPB (see Scheme 1) was studied to investigate if the described catalyst system is suitable for all three halides. All catalytic experiments (see Table 2 and Figure 3) were carried out in sealable pressure tubes with Teflon stoppers in air (Suzuki: 50 °C, Heck: 70 °C) for 24 h. Pd loadings of 0.09 mol% (Suzuki) and 0.029 mol% (Heck) were used. In order to address the problem of homocoupling, runs were carried out in which we only added either the aryl halide or the boronic acid. It was observed that the boronic acid gave rise to homocoupling products in 14% yield under the above-mentioned mild reaction conditions. Heterocoupling was observed for bromides (conversions of 80–90%, Figure 3) and iodides (around 70%). Chlorides gave only low yields (*ca.* 6%). Substituents in the *ortho*- and *meta*-positions resulted in lower yields (due to steric hindrance) than *para*-substituted arenes. Selected results are listed in Table 2.



Scheme 1. Test reaction for Suzuki-type cross-coupling using palladium nanoparticles stabilized in SPB particles as catalyst.

Bromobenzene and phenylboronic acid were used to determine reproducibility of palladium-SPB composite catalyst. The flask filled with defined amounts of palladium-SPB composite catalyst, reactants, PTC (phase-transfer catalyst: tetrabutylammonium bro-

Table 2. Suzuki-type cross-coupling using palladium nanoparticles stabilized in SPB particles as catalyst, yields were determined by GC, hcp = homocoupling product (biphenyl).



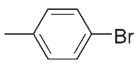
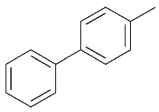
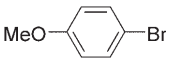
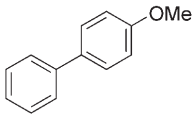
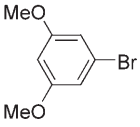
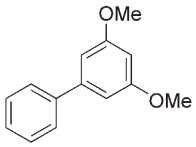
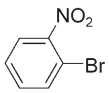
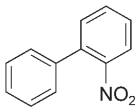
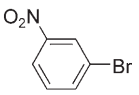
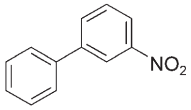
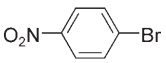
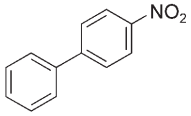
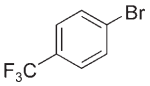
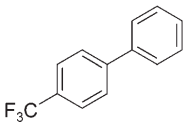
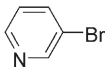
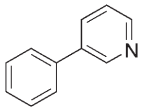
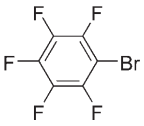
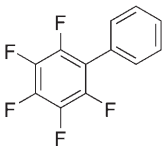
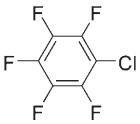
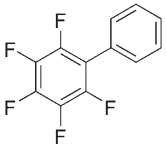
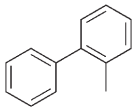
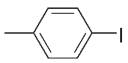
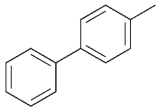
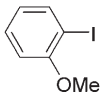
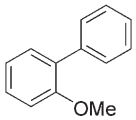
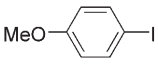
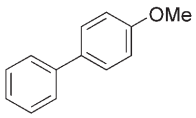
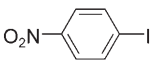
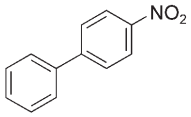
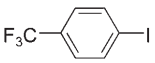
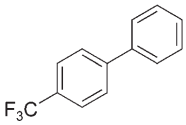
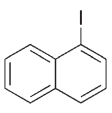
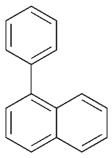
Halide	Product	GC conversion	Homocoupling
		83%	4%
		79%	5%
		15%	6%
		22%	1%
		50%	1%

Table 2. (Continued)

Halide	Product	GC conversion	Homocoupling
		94%	1%
		89%	1%
		19%	17%
		6%	2%
		1%	1%
		74%	2%
		78%	1%
		69%	2%
		83%	2%
		87%	0%
		80%	0%
		71%	0%

mide; without PTC the conversion of the reaction of iodobenzene and phenylboronic acid drops to 15% compared to 70%) and base was stirred at 50 °C for 24 h. After the reaction time the products were removed by ether and new educts and THF were added, this process was repeated four times. The con-

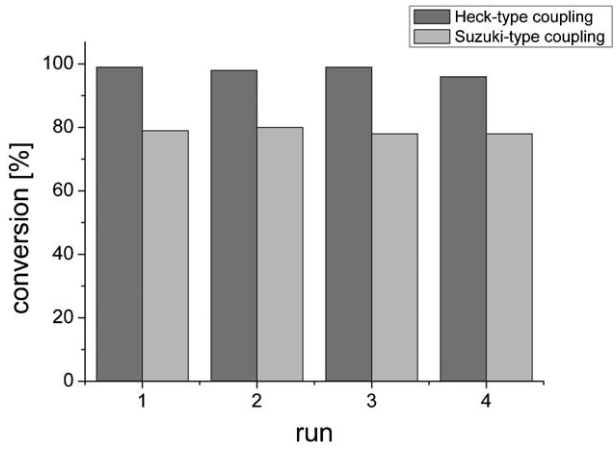


Figure 3. Reproducibility of the cross-coupling catalyzed by Pd@SPB.

version of each run was checked by GC using dodecane as an internal standard. Palladium-SPB composite particles after catalytic application were purified and separated by an ultrafiltration appliance with cellulose membrane (100 nm pore size supplied by Schleicher & Schuell). The results are shown in Figure 3. There is no noticeable change in conversion, which indicates the catalytic activity of the palladium nanoparticles remained stable at least within the four accomplished runs. Similarly, no noticeable difference was found in cryo-TEM images before and after catalytic reaction (see Figure 2). Palladium nanoparticles were still embedded firmly on the surface of the SPB particles. Also, the filtrate of a freshly prepared Pd@SPB solution was used as a catalyst in the Suzuki-type coupling between phenylboronic acid and bromobenzene (and Heck-type coupling involving styrene and iodobenzene), in both cases no cross-coupling reaction could be observed.

Hence, the present catalyst system could be easily recycled and re-used (Figure 3). The good reproducibility can be understood by the robustness of the catalyst system during catalysis and work-up (see the discussion of Figure 2). No change of the Pd nanoparticles or the entire composite system can be found. A check of the content of Pd in the crude product resulting from the cross-coupling of phenylboronic acid with bromobenzene demonstrated that the content of Pd was less than 6 ppm (*cf.* Refs.[16,35,36]).

Analysis of the Yields: Hammett Plots

A catalytic reaction expanded to different substrates can be regarded as a system of parallel reactions.[37] Hence, the ratios of the rate constants of the parallel reactions are equal to the ratios of the yields in good approximation. Therefore the Hammett equation – $\ln(k/k_H) = \sigma \cdot \rho$ – can be applied and a Hammett plot can be used to discuss the different reactivity arising from different substituents in the same position of the benzene ring. To avoid complications by steric effects, Hammett plots are done best for reactivities obtained with different substituents in the *para*-position. The Hammett analysis of the effect of *para*-substitution in the Suzuki reaction catalyzed by Pd@SPB has been compared to $Pd(OAc)_2$ as a catalyst (Figure 4 and Table 3).

The generally accepted mechanism[38] of the Suzuki as well as the Heck reaction involves an oxidative ad-

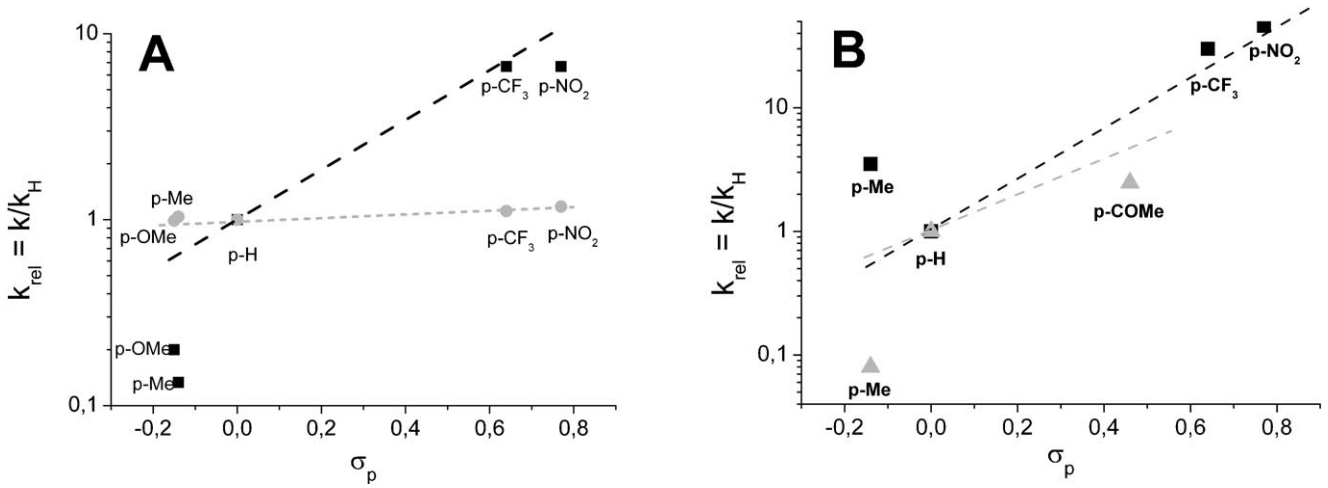
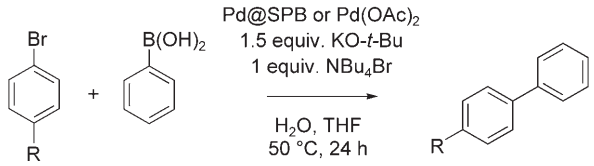


Figure 4. A: Hammett-plots of the Suzuki-type cross-coupling under the same reaction conditions (1 mmol aryl bromide, 1 mmol phenylboronic acid, 1.5 mmol KO-*t*-Bu, 1 mmol NBu_4Br as PTC, 2 mL H_2O, 2 mL THF, 0.09 mol% Pd) using two different catalyst systems; grey circles: Pd@SPB; black squares: $Pd(OAc)_2$. **B:** Hammett plots of the Heck-type cross-coupling compiled from the literature. Black squares: PS-3.3, Pd (Pd immobilized on polystyrene-β-poly-4-vinylpyridine block copolymer);[9] grey triangles: $Pd(OAc)_2$.[24] The figures show the relative rate constants plotted *vs.* σ_p (measure of total polar effect exerted by substituent X relative to H as substituent in the *para*-position to the reaction centre).

Table 3. Hammett analysis of the Suzuki-type cross-coupling.



R	σ_p	$Pd(OAc)_2$	Pd@SPB
OMe	−0.15	3%	79%
Me	−0.14	2%	83%
H	0	15%	80%
CF_3	0.64	>99%	89%
NO_2	0.77	>99%	94%

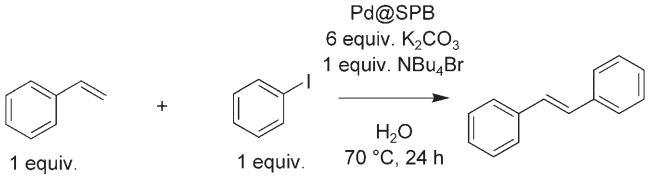
dition of a palladium species into the carbon-halide bond. Therefore the substitution should have a profound impact on the conversions.

The conversions for both the Suzuki and the Heck reactions are analyzed in Figure 4. A marked dependence of the rate on the substituent can be observed for the Heck-type coupling at elevated temperatures. Thus, for the data of Klingelhofer et al. (Pd immobilized on a polystyrene-β-poly-4-vinylpyridine block copolymer as catalyst)[9] the Hammett plot shows a slope of $\rho = 5 \pm 1$ and the data of Köhler et al. [$Pd(OAc)_2$ as catalyst][24] gives $\rho = 3 \pm 1$. Also, in case of the Suzuki-type cross-coupling, e.g., Pd@Smopex-111[36] yields for the coupling of activated *p*-bromoacetophenone a conversion of 97% using 2.5 wt% Pd in 2.5 h, while *p*-methoxybenzene (deactivated) needs for the same conversion 5 wt% Pd and 3 h. In this investigation we find a strong dependency on the *para*-substitution only if $Pd(OAc)_2$ is used as a catalyst ($\rho = 3 \pm 1$). In contrast to this, the heterogeneous system Pd@SPB gives $\rho = 0.18 \pm 0.03$ (see Figure 4). Such a value is far below the values obtained from ionic reactions in solution.[38] Certainly more work needs to be done to further elucidate the mechanism of the coupling catalyzed by Pd@SPB.

Heck-Type Cross-Coupling

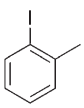
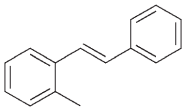
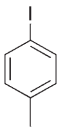
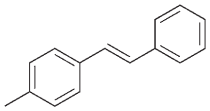
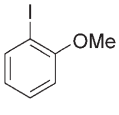
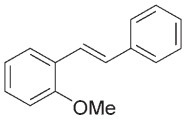
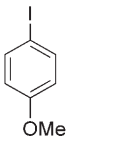
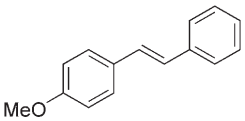
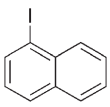
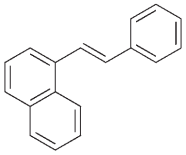
The Heck-type reaction (see Scheme 2 and Table 4) using palladium nanoparticles as catalyst was investigated using 8 different aryl halides. With a catalyst loading of 0.029 mol% Pd a variety of aryl iodides show almost complete conversion, aryl bromides do not react under the conditions employed. Under such mild conditions in water it is not possible to expand the scope of the Heck reaction to bromides or chlorides.

As already shown above for the Suzuki-type cross-coupling, the reproducibility of palladium nanoparti-



Scheme 2. Heck-type cross-coupling using palladium nanoparticles stabilized in SPB as catalyst.

Table 4. Heck reaction promoted by Pd@SPB in aqueous media.[a]

Iodide	Product	GC Conversion
		97%
		98%
		96%
		98%
		96%

[a] 1 mL of catalyst solution leads to a loading of 0.029 mol % Pd; The catalytic reactions were carried out at 70 °C for 24 h.

cles as catalyst of Heck-type reactions was also found to be very good. In four runs the products were removed by ether and new starting materials were added to the water phase.[18] Again, we found that Pd@SPB could be used repeatedly without loss of activity (Figure 3). After these four cycles the nanoparticles were filtered off and investigated by TEM in order to detect possible changes of the number and morphology of the nanoparticles. We found that the nanoparticles are still embedded in the SPB support.

Conclusions

In conclusion, we present a novel type of composite particles that can be used as a filterable and robust catalyst for cross-coupling reactions. The conditions

for both the Suzuki as well as for the Heck coupling are mild and environmentally benign. Neither moisture nor air has to be avoided. The catalyst works under mild conditions and can be recycled with no significant loss of activity. The carrier particles seem to ensure colloidal stability. We were not able to reproduce ultrahigh TONs (turnover number) for the Heck reaction of bromides using drastic conditions (elevated temperatures, organic solvents and Pd salts), but we found almost no dependency of the reaction rate on the *para*-substitution.

Experimental Section

Aryl halides (ACROS, except bromobenzene [Alfa Aesar]), phenylboronic acid (ACROS), styrene (ACROS), NBu_4Br tetrabutylammonium bromide (Fluka), potassium *tert*-butoxide (ACROS) and potassium carbonate (Merck) were used as received. Styrene (BASF) was destabilized on an Al_2O_3 column and stored in the refrigerator. Sodium tetrachloropalladate (Na_2PdCl_4; Aldrich) and reducing agent sodium borohydride ($NaBH_4$; Aldrich) were used as commercially available. Solvents were used without further purification. Water was purified using reverse osmosis (MilliRO; Millipore) and ion exchange (MilliQ; Millipore).

The synthesis of the SPB and the Pd@SPB system has been presented recently.[28–30] Table 1 summarizes the characterization of the carrier particles. Immobilization of palladium nanoparticles was described recently.[28,30] At first, Na_2PdCl_4 was added to the spherical polyelectrolyte brush, then $NaBH_4$ was used to reduce $PdCl_4^{2-}$ anions which were confined in the polyelectrolyte brush layer. Nearly monodisperse palladium nanoparticles were generated on the surface of the brush particles, and color of the mixture became dark gray. The SPB-palladium composite particles after synthesis were cleaned by ultrafiltration for further catalytic application. According to TEM measurements palladium nanoparticles have a size of 2.6 ± 0.5 nm.

Heck-Type Cross-Coupling

All Heck-type catalytic experiments were carried out in pressure tubes sealed by a Teflon stopper at 70 °C for 24 h. First, distilled water (2 mL) was filled in the tube. Second, substrates were added: styrene (104 mg) and an aryl halide, for example, iodobenzene (204 mg). Third, K_2CO_3 (829 mg) was added. Fourth, the catalyst was added: 1 mL of Pd catalyst solution (solid content 0.125%, 2.4% Pd@SPB), and finally NBu_4Br (322 mg) was added and used as phase-transfer reagent. The tube was sealed and the mixture stirred for 24 h. The organic products were extracted with 6 mL of ether. The conversion was checked by GC with dodecane (85 mg) as internal standard. Gas chromatography was carried out on an Agilent 6890N with FID equipped with Agilent 19091 J-413, HP-5 column.

Reproducibility experiments were carried out using 200-mL flasks equipped with a reflux condenser at 70 °C for 24 h. At first, distilled water (100 mL) was filled into the flask. To this mixture the substrates were added: styrene (1040 mg), iodobenzene (2040 mg), and K_2CO_3 (8290 mg). After that the catalyst was added: 10 mL of Pd catalyst solution (solid content 0.125%, 2.4% Pd@SPB) and NBu_4Br (3220 mg) was used as phase-transfer reagent. The mixture was stirred for 24 h. The organic products were extracted with 60 mL of ether. The conversion was checked by GC with dodecane (850 mg) as internal standard. After the extraction of the products the water phase containing the catalyst and base was reused for catalysis for three times (altogether four runs). After four cycles the particles were filtered off *via* ultrafiltration and investigated by cryo-TEM. Since iodides tend to be light-sensitive (UV light induced radical reactions), all catalytic reactions involving iodides were carried out with the exclusion of light.

Suzuki-Type Cross-Coupling

All Suzuki-type catalytic experiments were carried out in pressure tubes sealable with a Teflon stopper at 50 °C for 24 h. At first, distilled water (2 mL) and THF (2 mL) were filled in the tubes. To this solution the following substrates were added: phenylboronic acid (122 mg), an aryl halide, for example, bromobenzene (157 mg), and KO-*t*-Bu (168 mg). Third, the catalyst and the phase-transfer reagent were added: 1 mL of Pd@SPB composite (solid content 0.66%, 1.5% Pd@SPB) and NBu_4Br (322 mg). The tube was sealed and the mixture stirred for 24 h. The organic products were extracted with 6 mL of ether. The conversion was checked by GC with dodecane (85 mg) as internal standard. Since iodides tend to be light-sensitive (UV light induced radical reactions), any catalytic reactions involving iodides were carried out with the exclusion of light.

Experiments for the Hammett-plot using $Pd(OAc)_2$ as catalyst were carried out in the same way as using Pd@SPB, only that 0.1 mL of a 0.9 M $Pd(OAc)_2$ solution in THF was used. By adding the catalyst palladium black precipitated immediately. Results are summarized in Table 3; no homocoupling was observed.

Reproducibility experiments were carried out using 100-mL flasks equipped with a reflux condenser at 50 °C and 24 h. First, distilled water (20 mL) and THF (20 mL) were filled into the flasks. To this solution the following substrates were added: phenylboronic acid (1220 mg), bromobenzene (1570 mg) and KO-*t*-Bu (1680 mg). Third, the catalyst was added: 10 mL of Pd catalyst solution (solid content 0.66%, 1.5% Pd@SPB). Last, NBu_4Br (322 mg) was added and used as phase-transfer reagent. The mixture was stirred for 24 h. The organic products were extracted with 60 mL of ether. The conversion was checked by GC with dodecane (850 mg) as internal standard. After the extraction of the products the water phase containing the catalyst and base was reused for catalysis for three times (altogether four runs), after four accomplished cycles the particles were filtered off via ultrafiltration and investigated by cryo-TEM.

The analysis of the Pd content in the product of a Suzuki coupling was done by inductively coupled plasma mass spectrometer (ICP-MS; Fa. Agilent Technologies, HP 7500; sensitivity range 0.1–10 ppm, error of margin 0.2 ppm). 1 g of the sample was digested at first with 10 mL of 1.84 $g\,L^{-1}$ H_2SO_4 at 360 °C and then with 8 mL of a mixture of 1.41 $g\,L^{-1}$ HNO_3/1.84 $g\,L^{-1}$ H_2SO_4/1.67 $g\,L^{-1}$ $HClO_4$ = 2:1:1 vol% at 160 °C.

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References

[1] L. N. Lewis, *Chem. Rev.* **1993**, *93*, 2693.
[2] A. P. Alivisatos, *Science* **1996**, *271*, 933.
[3] M. Haruta, T. Kobayashi, H. Sano, N. Yamada, *Chem. Lett.* **1987**, 405.
[4] a) T. Mizoroki, K. Mori, A. Ozaki, *Bull. Chem. Soc. Jpn.* **1971**, *44*, 581; b) R. F. Heck, J. P. Nolley, *J. Org. Chem.* **1972**, *37*, 2320; c) R. F. Heck, *Acc. Chem. Res.* **1979**, *12*, 146.
[5] a) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457; b) A. Suzuki, in: *Metal-Catalyzed Cross coupling Reactions*, (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, Weinheim **1998**, p 49; c) I. P. Beletskaya, A. V. Cheprakov, *Chem. Rev.* **2000**, *100*, 3009.
[6] P. Zhou, Y. Li. P. Sun, J. Zhou, J. Bao, *Chem. Commun.* **2007**, 1418.
[7] M. T. Reetz, R. Breinbauer, K. Wanninger, *Tetrahedron* **1996**, *37*, 4499.
[8] M. Beller, H. Fischer, K. Kühnlein, C. P. Reisinger, W. A. Hermann, *J. Organomet. Chem.* **1996**, *520*, 257.
[9] S. Klingelhofer, W. Heitz, A. Greiner, S. Oestreich, S. Förster, M. Antonietti, *J. Am. Chem. Soc.* **1997**, *119*, 10116.
[10] A. Biffis, M. Zecca, M. Basato, *J. Mol. Catal. A* **2001**, *173*, 249.
[11] V. Poleshettiwae, A. Molnar, *Tetrahedron* **2007**, *63*, 6949.
[12] S.S Pröckl, W. Kleist, M. A. Gruber, K. Köhler, *Angew. Chem. Int. Ed.* **2004**, *43*, 1881.
[13] C. P. Mehnert, D. W. Weaver, J. Y. Ying, *J. Am. Chem. Soc.* **1998**, *120*, 12289.
[14] K. Esumi, R. Isono, T. Yoshimura, *Langmuir* **2004**, *20*, 237.
[15] S. V. Ley, C. Ramarao, R. S. Gordon, A. B. Holmes, A. J. Morrison, I. F. McConvey, I. M. Shirley, S. C. Smith, M. D. Smith, *Chem. Commun.* **2002**, 1134.
[16] M. Lakshmi Kantam, K. B. Shiva Kumar, P. Srinivas, B. Sreedhar, *Adv. Synth. Catal.* **2007**, *349*, 1141.
[17] V. Calò, A. Nacci, A. Monopoli, F. Montingelli, *J. Org. Chem.* **2005**, 70, 6040.
[18] Z. Zhang, Z. Zha, C. Gan, C. Pan, Y. Zhou, Z. Wang, M. Zhou, *J. Org. Chem.* **2006**, *71*, 4339.
[19] Z. Zhang, Z. Wang, *J. Org. Chem.* **2006**, 71, 7485.
[20] D. Astruc, *Inorg. Chem.* **2007**, *46*, 1884.
[21] Y. Tsuji, T. Fujihara, *Inorg. Chem.* **2007**, *46*, 1895.
[22] M. B. Thathagar, J. E. ten Elshof, G. Rothenberg, *Angew. Chem.* **2006**, *118*, 2952.
[23] J. G. de Vries, *Dalton Trans.* **2006**, 421.
[24] K. Köhler, W. Kleist, S. S. Pröckl, *Inorg. Chem.* **2007**, *46*, 1876.
[25] N. T. S. Phan, M. van der Sluys, C. W. Jones, *Adv. Synth. Cat.* **2006**, *348*, 609.
[26] M. Ballauff, *Progr. Polym. Sci.* **2007**, *32*, 1135.
[27] G. Sharma, M. Ballauff, *Macromol. Rapid Commun.* **2004**, *25*, 547.
[28] Y. Mei, G. Sharma, Y. Lu, M. Ballauff, M. Drechsler, T. Irrgang, R. Kempe, *Langmuir* **2005**, *21,* 12229.
[29] G. Sharma, Y. Mei, Y. Lu, M. Ballauff, T. Irrgang, S. Proch, R. Kempe, *J. Catal.* **2006**, *246*, 10.
[30] Y. Mei, Y. Lu, F. Polzer, M. Ballauff, *Chem. Mater.* **2007**, *19*, 1062.
[31] M. Schrinner, F. Polzer, Y. Mei, Y. Lu, B. Haupt, M. Ballauff, A. Göldel, M. Drechsler, J. Preussner, U. Glatzel, *Macromol. Chem. Phys.* **2007**, *208*, 1542.
[32] R. C. Advincula, W. J. Brittain, K. C. Caster, J. Rühe, (Eds.), *Polymer Brushes* Wiley-VCH, Weinheim, **2004**.
[33] X. Guo, A. Weiss, M. Ballauff, *Macromolecules* **1999**, 32, 6043.
[34] A. Wittemann, M. Drechsler, Y. Talmon, M. Ballauff, *J. Am. Chem. Soc.* **2005**, *127*, 9688.
[35] N. Nikbin, M. Ladlow, S. V. Ley, *Organic Process Research & Development* **2007**, *11*, 458.
[36] J. X. Kiang, J. Sclafani, K. Prasad, O. Repic, T. J. Blacklock, *Organic Process Research & Development* **2007**, *11*, 769.
[37] K. Kahlert, W. Pritzkow, G. Zimmermann, *J. prakt. Chem.* **1976**, *318*, 627.
[38] A. F. Littke, C. G. Fu, *Angew. Chem. Int. Ed.* **2002**, *41*, 4176.

