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Heterogeneous Catalysis

Facile Light-Mediated Preparation of Small Polymer-Coated Palladium-Nanoparticles and Their Application as Catalysts for Alkyne Semi-Hydrogenation

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Abstract: A facile light-mediated preparation of small palladium nanoparticles (PdNPs) with a diameter of 1.3 nm and low dispersity by using low-priced and readily prepared photoactive polymers is presented. These polymers act as reagents for the photochemical reduction of Pd ions and they are also stabilizers for the PdNPs generated in situ. The PdNP–polymer hybrid materials prepared by this reliable approach are efficient hydrogenation catalysts that show high activity and *Z*-selectivity in the semi-hydrogenation of alkynes. These PdNP–catalyst hybrid materials can be readily recycled and reused up to five times.

Introduction

Metal nanoparticles have found wide applications in catalysis since they show high activity and high chemoselectivity in various reactions.[1] Moreover, their ready recyclability allows for the development of environmentally friendly processes.[1] For instance, Pd, Fe, Ni, or Au nanocatalysts have been successfully applied to the selective semi-hydrogenation of terminal and internal alkynes, using for example H_2, ammonium formate, or amine–borane complexes as reductants.[2] Different inorganic (for example, CeO_2, TiO_2, Cu_2O, SiO_2) or organic materials (ionic liquids, polymers, surfactants) have been used as supports for these transition-metal nanocatalysts.[2] Importantly, these novel hybrids may replace the well-established Lindlar catalyst in future. It is well known that the Lindlar catalyst suffers from a number of drawbacks: first, toxic $Pb(OAc)_2$ and large amounts of quinoline are required as catalyst poison to suppress over-hydrogenation of the targeted alkenes to the corresponding alkanes. Second, reactions run with the Lindlar catalyst often show problems with respect to *Z*/*E*-isomerization, over-hydrogenation, irreproducibility, and a limited substrate scope.[2i,j,3] Pd nanocatalysts, as compared to Fe-, Ni-, or Au-based materials, generally reveal higher activity in the semi-hydrogenation of alkynes under very mild reaction conditions (low catalyst loading, low temperature, low H_2 pressure, excellent selectivity). However, in many cases a complex multistep preparation of the PdNPs including the use of non-commercial chemicals and harsh reaction conditions is required, which may hamper their future industrial applications.[4] In contrast, Lipshutz et al. recently reported a simple PdNP/nanomicelle system for semi-hydrogenation of alkynes to *Z*-alkenes in water.[2j] The PdNP/nanomicelle catalyst charged with H_2 was elegantly prepared in situ by addition of $NaBH_4$ and $Pd(OAc)_2$ to an aqueous solution of nanomicelles made from the commercially available surfactant TPGS-750-M. The Lipshutz catalyst provided high yields of *Z*-alkenes and could be successfully recycled several times. However, two equivalents of the additive LiCl are necessary to obtain good *Z*-selectivities.[2j]

The use of light is a powerful tool to drive organic reactions, because light is readily available, cheap, and easy to apply in industrial processes.[5] In a series of papers, Scaiano et al. disclosed the potential of the Norrish Type I photoreaction for nanoparticle preparation by using the commercially available photoinitiator Irgacure-2959.[6] Along these lines, we recently introduced a method to prepare polymer coated AuNPs by using photoactive homo- and copolymers for radical-mediated photochemical AuNP synthesis.[7] These well-defined photoactive styrene type homo- and copolymers bear photocleavable α-hydroxyalkyl ketone (HAK) substituents that can be selectively cleaved by the Norrish Type I photoreaction under irradiation with UV light. Highly reductive ketyl radicals are generated in the photoreaction that are able to reduce gold salts to Au^0.[7] However, the photoactive styrene type homo- and copolymers were prepared by using controlled radical polymerization, and the monomers used in these initial studies had to be laboriously prepared in several steps.[7] Both the rather expensive controlled polymerization techniques and the multistep preparation of styrene monomers increase the price of the photoactive polymers, which may prevent the application of this method for preparation of polymer-coated NPs in industry.

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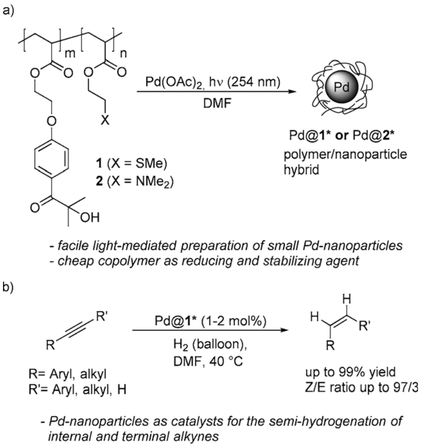
Therefore, we decided to focus on new low-cost processes for the preparation of polymer-coated metal nanoparticles and on their application in catalysis. Herein we present the ready preparation of an acrylate copolymer bearing photoactive HAK-groups as ester substituents and its successful application in photochemical preparation of remarkably small PdNPs (1.3 nm) (Scheme 1). The low-cost polymer plays a dual role in NP formation: It first acts as an electron source for the photoreduction of Pd ions and then as a stabilizer for the PdNPs generated in situ. We will show that these polymer-coated PdNPs are efficient and *Z*-selective alkyne semi-hydrogenation catalysts.



Scheme 1. a) Novel copolymers for the light-mediated preparation of small PdNPs; b) application of PdNPs as catalysts for the alkyne semi-hydrogenation.

Results and Discussion

Synthesis and characterization of Pd nanoparticles

We decided to prepare the statistical acrylate copolymer **1** bearing photoactive HAK entities and thioether units, because thioethers are known to interact with the surface of PdNPs, thereby stabilizing them towards aggregation.[8] Moreover, the thioether moiety may act as a Pd catalyst poison, leading to modulation of its reactivity.[8] The acrylate monomers 2-(4-(2-hydroxy-2-methylpropanoyl)phenoxy)ethyl acrylate (HMPA) and 2-(methylthio)ethyl acrylate (MTEA) were readily obtained in one step by esterification of acrylic acid or acryloyl chloride with two different commercially available alcohols.[9] The photoactive 2-hydroxy-1-(4-(2-hydroxyethoxy)-phenyl)-2-methylpropan-1-one (I-2959) is a cheap and well-established commercial photoinitiator and 2-(methylthio)ethan-1-ol can be also purchased at low cost. AIBN-initiated copolymerization of a 1:2 HMPA/MTEA mixture at 60 °C for 6 h in THF gave the statistical copolymer poly[2-(4-(2-hydroxy-2-methylpropanoyl)phenoxy)ethyl acrylate-*co*-2-(methylthio)ethyl acrylate] (poly(HMPA-*co*-MTEA), **1**) in 81 % yield of isolated product (HMPA/MTEA ratio in the copolymer = 1:2; $M_n = 16\,300\ \mathrm{g\,mol^{-1}}$; PDI = 2.0). Along with **1**, the copolymer poly[2-(4-(2-hydroxy-2-methylpropanoyl)phenoxy)ethyl acrylate-*co*-2-(dimethylamino)ethyl acrylate] (poly(HMPA-*co*-DAEA), **2**) (HMPA/DAEA-ratio in the copolymer ca. 1:2; $M_n = 4\,900\ \mathrm{g\,mol^{-1}}$; PDI = 2.1) where the thioether entity is replaced by a dimethylamino functionality and the homopolymer poly(HMPA), **3** ($M_n = 8\,800\ \mathrm{g\,mol^{-1}}$; PDI = 2.0) were prepared for comparison.

We next investigated the photomediated PdNP synthesis using copolymer **1** under an argon atmosphere in DMF, and irradiation was performed at $\lambda = 254$ nm in a photoreactor (see the Supporting Information). Irradiation of a mixture of **1** in the presence of $Pd(OAc)_2$ (ratio of photoactive entities (HMPA)/$Pd(OAc)_2 = 10{:}1$) for 10 min at room temperature led to the formation of a dark-brown solution indicating the successful synthesis of PdNPs. TEM measurements revealed the formation of small and monodisperse PdNPs (Pd@**1***) with a diameter of 1.3 ± 0.2 nm. Figure 1 a shows the TEM image obtained for the well-dispersed PdNPs.

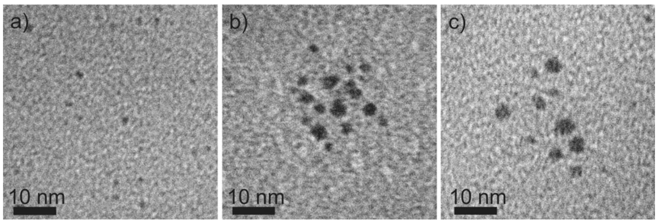
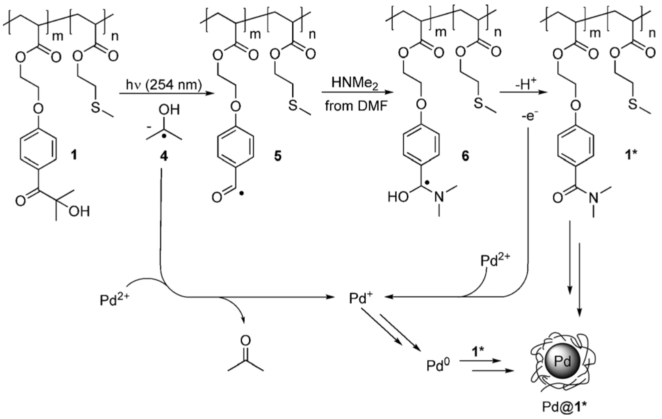


Figure 1. TEM-images of a) Pd@**1***, b) Pd@**3***, and c) Pd@**1*** catalyst after 6 cycles.

DLS measurements of the Pd–polymer hybrid (8.4 ± 2.3 nm) indicate that the PdNPs are covered by a thin circa 3.6 nm thick polymer layer (see the Supporting Information). The oxidation state of the PdNPs was investigated by XPS. Only the two signals with characteristic binding energies for Pd^0 were detected showing full photochemical reduction of the Pd salt to Pd^0 (see the Supporting Information).[10] PdNPs were readily isolated by simple evaporation of the solvent under vacuum and were stored under argon atmosphere at room temperature without aggregation or decomposition. The brown PdNP powder obtained after solvent evaporation was also subjected to thermogravimetric analysis revealing a Pd loading of 20 wt % in the Pd–polymer hybrid material (see the Supporting Information). ^{1}H NMR analysis of the Pd–polymer hybrids showed that about 50 % of the HAK groups were photochemically converted within 10 min of UV irradiation. The ketone was converted into a dimethylamide moiety by photochemical C–C bond cleavage and subsequent amidation with $HNMe_2$ derived from DMF (Scheme 2).[7,11] Upon increasing the irradiation time to 30 min, the HAK entities were fully converted into the corresponding carboxylic amides to afford the fully modified copolymer **1***. The PdNP diameter did not change upon prolonging the irradiation time (see the Supporting Information); however, DLS analysis indicated a slightly decrease of the PdNP hybrid diameter (5.7 ± 1.9 nm). The PdNPs derived from the copolymer **2** (Pd@**2***, 1.6 ± 0.3 nm) and from homopolymer poly(HMPA) **3** (Pd@**3***, 2.5 ± 0.6 nm; Figure 1 b) were prepared in analogy to Pd@**1*** (see the Supporting Information).



Scheme 2. Proposed mechanism for the photochemical generation of Pd-nanoparticles Pd@**1*** using copolymer **1** and light in DMF.

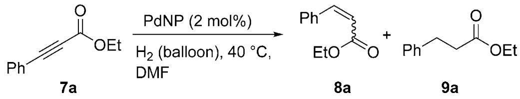
The following mechanism for PdNP formation is suggested. During UV irradiation, the photoactive HAK-groups in **1** undergo Norrish Type I C–C bond homolysis to generate reductive ketyl radicals **4** along with polybenzoyl radicals **5**.[12] The ketyl radicals **4** reduce Pd ions under formation of acetone as a by-product.[7] The concomitantly generated polybenzoyl radicals **5** are trapped by dimethylamine,[13] which is derived from DMF. The dimethylamine acyl radical adduct **6** also acts as a one-electron reductant to give the dimethylamide functionality upon oxidation.[14] The photochemically modified copolymer **1*** eventually stabilizes the PdNPs generated in situ (Pd@**1***). Importantly, isolated Pd@**1*** showed high solubility and stability in various organic solvents with different polarity, such as acetone, $CHCl_3$, DCM, DMF, DMSO, EtOAc, and THF, providing flexibility for applications in catalysis.

Catalytic semi-hydrogenation of internal and terminal alkynes

As a first test reaction, we studied the semi-hydrogenation of ethyl 3-phenylpropiolate (**7a**) to give *Z*/*E*-alkenes **8a** with Pd@**1*** as a catalyst at 40 °C under an H_2 atmosphere (1 atm) in different solvents (Table 1). In DCM, ethyl 3-phenylacrylate **8a** was formed in 68% yield with high *Z*-selectivity (*Z*/*E* = 95:5) after 5 h (Table 1, entry 1). Reaction was faster in THF. Quantitative conversion was achieved in 3 h and **8a** was formed in 97% yield with high Z-selectivity (96:4) (Table 1, entry 2). However, we identified 2% of the over-hydrogenation product **9a**.

Result was improved upon switching to DMF (Table 1, entry 3). Alkene **8a** was formed in excellent yield (99%) and *Z*-selectivity (97:3) in 2.5 h. The over-hydrogenated **9a** was only observed in traces. Extending the reaction time to 4 h did not alter the *Z*/*E* ratio, showing that product isomerization does not occur under the applied conditions, and that the 97:3 ratio is the kinetic product selectivity (Table 1, entry 5). However, we started to observe **9a** in 2% yield. Notably, Pd@**1*** prepared under 10 min or 30 min irradiation provided the same result in the semi-hydrogenation of **7a** (Table 1, compare entries 3 and 4). Increasing the amount of thioether moieties in copolymer **1** (ratio of HMPA/MTEA = 1:5; M_n = 27 700 g mol^{-1}; PDI = 2.0) reduced the activity of the resulting Pd@**1*** catalyst (Table 1, entry 6); however, the *Z*/*E* selectivity remained unaltered. This observation can be explained by a reduced diffusion rate of the substrate **7a** through the larger protecting polymer layer to the active PdNP site of the catalyst. The amino-functionalized hybrid catalyst Pd@**2*** was more active than Pd@**1*** and complete conversion was achieved within 1.5 h (Table 1, entry 7). However, over-hydrogenation product **9a** was formed in 17% yield along with the targeted alkene **8a** (67%), and semi-hydrogenation occurred in lower selectivity (91:9). A similar result was achieved with homopolymer-derived nanoparticles (Pd@**3***) (Table 1, entry 8), clearly revealing the importance of the thioether moieties in these polymer coated PdNPs for modulating their activity and selectivity.

Table 1. Reaction optimization and catalyst recycling.



Entry	PdNP	Cycle	*t* [h]	Conv. **7a** [%][a]	**8a** [%][a] (*Z*/*E*)[a]	**9a** [%][a]
1[b]	Pd@**1***	–	5	69	68 (95:5)	< 1
2[c]	Pd@**1***	–	3	> 99	97 (96:4)	2
3	Pd@**1***	–	2.5	> 99	99 (97:3)	< 1
4[d]	Pd@**1***	–	2.5	> 99	99 (97:3)	< 1
5	Pd@**1***	–	4	> 99	97 (97:3)	2
6[e]	Pd@**1***	–	4.5	> 99	99 (97:3)	< 1
7	Pd@**2***	–	1.5	> 99	67 (91:9)	17
8	Pd@**3***	–	1.5	> 99	63 (91:9)	25
9	Pd@**1***	2	2.5	> 96	96 (97:3)	< 1
10	Pd@**1***	3	2.5	> 99	98 (97:3)	1
11	Pd@**1***	4	2.5	> 99	96 (93:7)	3
12	Pd@**1***	5	2.5	> 99	98 (97:3)	1
13	Pd@**1***	6	5	84	83 (97:3)	< 1

[a] Determined by GC-FID using an internal standard; signals identified by GC-MS. [b] Reaction in DCM. [c] Reaction in THF. [d] Pd@**1*** prepared by 30 min irradiation. [e] HMPA/MTEA-ratio in the copolymer = 1:5; M_n = 27 700 g mol^{-1}; PDI = 2.0.

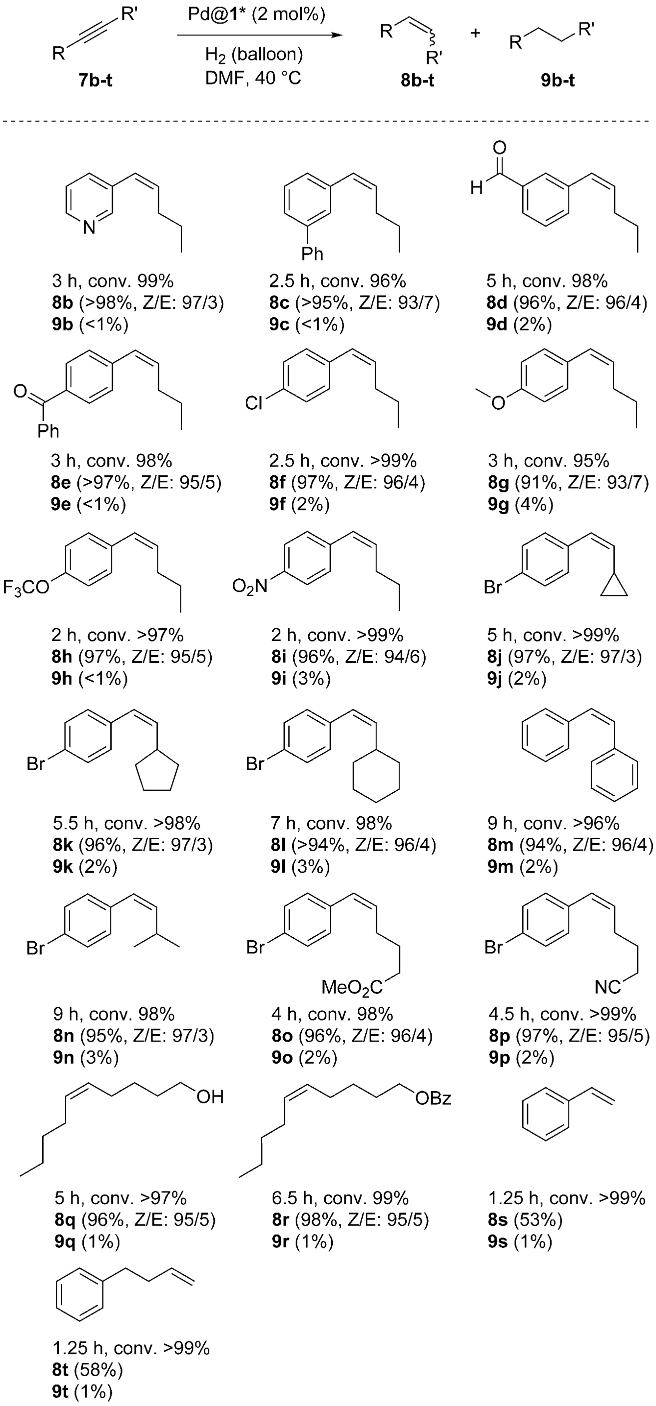
Under optimized conditions, recycling experiments using the Pd@**1*** catalyst were performed. The PdNP hybrid material was readily recovered after each run by the following procedure: DMF and the reduction products were separated by simple distillation from the catalyst. The Pd@**1*** catalyst remained in the reaction vessel as a brown solid which was then applied in the next cycle by simply charging the vessel with alkyne **7a**, DMF, and H_2. Using this procedure, the catalyst was recycled five times to give the *Z*-alkene **8a** in good to excellent yields (Table 1, entries 9–13). However, in the sixth run the activity of the catalyst decreased significantly (Table 1, entry 13). We analyzed the catalyst after 6 cycles by TEM (3.5 ± 1.0 nm) and DLS (10.7 ± 7.7 nm), revealing a significant increase of the Pd diameter from 1.3 to 3.5 nm (Figure 1 a,c). The ripening of Pd@**1*** to larger nanoparticles may have an influence on the decrease of its catalytic activity after the fifth cycle.[15]

Pd@**1*** catalyst recovery can also be achieved by simple precipitation by treatment of the reaction mixture with pentane while the organic products stay in the liquid phase (see the Supporting Information). Using this catalyst recycling procedure, Pd@**1*** was successfully reused over four cycles, providing the desired alkene **8a** in excellent yields (96–99%) and *Z*-selectivity (97:3; 2.5–4 h reaction time; see the Supporting Information). However, in the fifth run the catalytic activity significantly decreased and reaction time had to be increased to obtain complete conversion. Alkene **8a** was obtained in 95% yield with high *Z*-selectivity (96:4) after 9 h. To study possible reasons for catalyst ripening and for the decreased catalytic activity after the fourth run, the hybrid system was studied with respect to Pd leaching. To this end, the solution obtained after catalyst precipitation was analyzed regarding the amount of leached Pd by total reflection X-ray fluorescence (TXRF).[16] In the first three catalytic cycles, the amount of leached Pd was found to be below the detection limit of 8 ppm. To determine the catalytic active species in our Pd@**1*** catalyst system we also conducted a poisoning experiment. The addition of Hg^0 to the reaction mixture led to complete inhibition of the semi-hydrogenation of alkyne **7a**, indicating that a heterogeneous Pd species is responsible for the semi-hydrogenation of alkyne **7a** to alkene **8a.**[17] The reaction solution obtained after Pd@**1*** catalyst precipitation, which according to the TXRF analysis contains less than 8 ppm Pd, was found to be inactive in the semi-hydrogenation of alkyne **7a**. This result indicates that the Pd@**1*** hybrid is the active catalyst and that leached Pd is inactive in this reaction.

Next, the substrate scope was investigated with alkynes **7b–t** (Scheme 3). Reactions were monitored by GC, and hydrogenation time was adapted according to the reactivity of the given alkyne. All substrates **7b–t** were smoothly converted into the corresponding alkenes **8b–t** in high conversions in 1 to 9 h. Arylalkyl alkynes turned out to be good substrates, and for the arylpropyl alkynes the aryl group was systematically varied. The 3-pyridyl congener **7b** reacted in excellent yield (>98%) and Z-selectivity (97:3) to give **8b**. The biphenyl derivative **7c** was also tolerated to give the corresponding alkene **8c** in good yield (>95%) and *Z*-selectivity (93:7). For aryl alkynes bearing an electron withdrawing substituent such as the formyl, benzoyl, chloro, methoxy, trifluoromethoxy, and nitro group at the aryl moiety, yields (91% up to >97%) and *Z*-selectivities (93:7 up to 96:4) were high (see **8d–i**). However, small amounts (<1% up to 4%) of the over-hydrogenation products **9d–i** were identified. Notably, the formyl, benzoyl, and also the nitro functionality, which are readily converted using Pd on charcoal as a catalyst, remained untouched.

An influence of steric shielding on the semi-hydrogenation of internal alkynes **7j–7n** was studied. All alkynes turned out to be good substrates as documented by the semi-hydrogenation of arylcyclopropyl alkyne **7j**, and its cyclopentyl, cylohexyl, phenyl, and isopropyl congeners **7k–n**. The *Z/E*-selectivity remained high (96:4 or 97:3), but reaction time had to be increased up to 9 h for sterically more hindered systems in order to get a quantitative conversion.

Also, functional groups on the alkyl substituents like methyl ester or nitrile **7o,p** are tolerated to give the alkenes **8o,p** in good yields (96%, 97%) and Z-selectivities (96:4, 95:5). Furthermore, the selective reduction of the bisalkyl substituted alkynes was studied. The semi-hydrogenation of alkynes **7q** and **7r** gave the alkenes **8q,r** in excellent yields (96%, 98%) with good *Z/E*-ratios (both 95/5). Over-hydrogenation products were only identified in traces.



Scheme 3. Semi-hydrogenation of alkynes **7b-t**. Conversion of **7b-t**, yield and *Z/E*-ratio of **8b-t** and yield of **9b-t** determined by GC-FID using an internal standard; signals identified by GC-MS. Semi-hydrogenation of terminal alkynes performed with 1 mol% Pd@**1***.

Finally, we investigated the semi-hydrogenation of the terminal alkynes **7s** and **7t**. As expected for steric reasons, these substrates were found to be more reactive, and the catalyst loading was decreased to 1 mol%. Although over-hydrogenation products **9s,t** were only identified in 1% by GC analysis, the products **8s** (53%) and **8t** (58%) were obtained in significantly lower yields. Side products were not detected. We assume that the product alkenes strongly adsorb to the nanoparticle material or polymerize, leading to a decrease of the yield. Indeed, the ^{1}H NMR spectrum of the used Pd@**1*** catalyst after semi-hydrogenation of **7s** shows a significant increase of aromatic signals in comparison to the freshly prepared Pd@**1*** catalyst, supporting this hypothesis.

Conclusion

We introduced a low-cost photoactive copolymer that can be used as a reductant and stabilizer for PdNP preparation. UV irradiation of a DMF solution of copolymer **1** and $Pd(OAc)_2$ provides polymer-protected PdNPs. As compared to other methods for NP preparation an external reducing reagent is not necessary and also the addition of a NP-stabilizing additive is not required. The method is experimentally very easy to conduct and reliably provides small PdNPs (1.3 ± 0.2 nm) in short time (10 min). The polymer-coated PdNPs are stable over weeks, are readily isolated by simple evaporation of the solvent without aggregation or decomposition and are soluble in various organic solvents with different polarity. Moreover, the photochemically prepared PdNPs show high activity and selectivity as catalysts in the semi-hydrogenation of internal alkynes to the corresponding *Z*-alkenes. Various substituents and functional groups are tolerated, and the hybrid catalyst was successfully recycled five times to give the targeted *Z*-alkene in good to excellent yields.

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Keywords: heterogeneous catalysis · palladium nanoparticles · photoactive polymers · radicals · semi-hydrogenation

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FULL PAPER

Heterogeneous Catalysis

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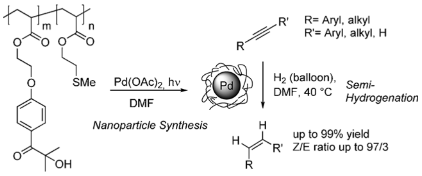
Facile Light-Mediated Preparation of Small Polymer-Coated Palladium-Nanoparticles and Their Application as Catalysts for Alkyne Semi-Hydrogenation



A facile light-mediated preparation of small palladium nanoparticles (PdNPs) with a diameter of 1.3 nm was achieved by using low-priced and readily prepared photoactive polymers. The PdNP–polymer hybrid materials are efficient hydrogenation catalysts that show high activity and *Z*-selectivity in the semi-hydrogenation of alkynes.