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Steric and Electronic Effects of Phosphane Additives on the Catalytic Performance of Colloidal Palladium Nanoparticles in the Semi-Hydrogenation of Alkynes

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Abstract: We report on the influence of phosphanes on the catalytic activity and selectivity of colloidal, tetraoctylammonium bromide (TOAB) stabilized palladium nanoparticles (NPs) in the semihydrogenation of alkynes to olefins. Full characterization of the catalytic system (HRTEM, EDX, XPS, IR, NMR) confirmed the formation of spherical particles with a narrow size distribution (1.9 ± 0.5 nm). The catalytic performance of the Pd NPs in the semihydrogenation of 1-octyne, 2-octyne and phenyl acetylene to the respective olefins and the influences on the selectivity was investigated. The system shows high activities and selectivities at mild conditions (0 °C and 1.0 bar H₂ pressure). It was shown that generally, phosphanes lead to an increase of both the reaction rate and selectivity towards the olefin where both sterics and electronics of the ligand play a crucial role for the catalyst performance. A moderate steric demand of the ligand with a rather weak o-donoring ability turned out to give the highest catalytic performance.

Introduction

The selective semi-hydrogenation of alkynes to olefins is of high relevance for the production of polyolefins and fine chemicals.^[1] The undesired full hydrogenation to alkanes is thermodynamically favored, as the hydrogenation of the olefin is energetically preferred over desorption from the catalyst surface,^[2,3] and therefore, the isolation of the olefin is difficult. The best known concept to convert alkynes to olefins – particularly acetylene to ethylene, which is of high industrial interest^[1] – without (significant) over-hydrogenation is the doping of a catalytically active metal, e.g. palladium,^[4] as the most prominent example,

nickel^[5] with a second metal. The alloying results in a reduction of the adsorption energy of the olefin, leading to its desorption from the metal surface and hence to an increased reaction selectivity.^[6,7] In addition, the isolation of Pd atoms leads to an increased catalyst stability as undesired oligomerization (socalled 'green oil' formation) and carbon deposition side reactions causing catalyst deactivation are suppressed.^[8,9] The selective hydrogenation of alkynes to olefins with monometallic NPs would be an attractive alternative; however, it is, on the other hand, very difficult. For this, modifications on the catalyst surface have to be undertaken, usually by using surfactants.^[10] An elegant approach to study the effect of additives on the selectivity is to use colloidal, monometallic NPs.^[11,12] Studying the catalytic behavior of such model particles allows for a fundamental understanding of structure-performance relationships. The colloid surfactant molecules, particularly o-donor type stabilizing agents, exert spatial control of the accessibility and the electronic properties of the surface atoms of the colloids, and therefore influence the catalytic activity/selectivity as well.[10,13] The interaction of the additive with the particle surface can lead to a preferred alkyne adsorption instead of the competitive olefin coordination to the surface and therefore increase the selectivity towards the semihydrogenation product.^[14] A systematic study of the effect of additives on the chemoselectivity of colloidal metal NPs has, however, so far not been carried out for this reaction type. Dupont et al. reported on the formation of stable and highly monodispersed Pd NPs stabilized in a nitrile-functionalized ionic liquid (IL), which are highly active in the semi-hydrogenation of alkynes in a multiphase system.^[15] Phosphane-functionalized IL surfactants showed an enhanced catalyst performance.[16] Another study shows the effect of the nature of thiolate capping

FULL PAPER

agents and influence of the chemical and structural composition of the surface monolayers on the catalytic activity and selectivity of colloidal Pd^[17] and Pt^[18] NPs. Beller et al. reported on a change of stereoselectivity in the semi-hydrogenation of alkynes to the respective E- and Z alkenes upon addition of multidentate phosphane ligands using a monometallic Ni catalyst.^[19] Yang, Li et al. have studied the electronic influence of triphenylphosphane on the catalytic performance of Pd NPs in selective hydrogenations.^[20] A deeper investigation on a series of similar additives bearing subtle differences regarding spatial and electronic features could give rise to new insights of the underlying mechanisms responsible for catalyst activity and selectivity.

Therefore, in this study, we report on the influence of the addition of triorganylphosphanes PR₃ bearing different substituents R (alkyl, aryl) on the catalytic activity and selectivity of colloidal Pd NPs for the semi-hydrogenation of alkynes. We investigated the steric and electronic effects of the phosphanes in order to learn more on the crucial parameters for controlling the selectivity of the reaction. Furthermore, we have studied the influence of different phosphanes on the stability of the colloids in solution and the interactions of the ligands with the particle surface. For the synthesis of the Pd colloids, we chose a simple literature-known route via reduction of K₂[PdCl₄] with NaBH₄ in presence of the surfactant tetraoctylammonium bromide (TOAB),^[21] which can easily be substituted by stronger (σ -donor) stabilizing agents, such as phosphanes.

Results and Discussion

Synthesis and characterization of TOAB-stabilized Pd NPs

Highly monodispersed Pd NPs were prepared in toluene on the basis of a modified literature-known procedure.^[21] Reduction of K₂[PdCl₄] with an excess of aqueous NaBH₄ in toluene in the presence of an excess of TOAB (10 equiv.) as capping agent yielded colloidal Pd NPs as a black solution (Scheme 1). The NPs were analyzed by high-resolution transmission electron microscopy (HRTEM; Figure 1) and dynamic light scattering (DLS; see the SI, Figures S1 and S3) confirming NPs with a narrow size distribution (1.5 ± 0.9 nm). Noteworthy, variation of the literature-reported work-up procedure led to an undesired surface modification resulting in a color change of the colloidal solution from dark brown to amber and no catalytic activity. Therefore, the synthesis procedure was optimized in terms of avoiding acidic or basic treatment leading to a reproducible and simple synthesis protocol. The particles were stable for weeks at low temperatures (ca. 4 °C). Decreasing the amount of the capping agent TOAB to 5.0 equiv. with respect to palladium results in less stable particles, which agglomerate and precipitate in a shorter amount of time (i.e. after one week). Figure 1 shows representative HRTEM images of the spherical, well-defined Pd@TOAB NPs in toluene with lattice planes separated by 0.8 Å.







Figure 1. HRTEM images showing a small size distribution (above and bottom left) and the lattice planes of the Pd@TOAB NPs (bottom right).

No agglomerates were detected (SI, Figure S3). EDX spectra confirm the sample composition of Pd, N, C and Br (from TOAB). Chlorine residues from the Pd precursor were not detected. Elemental mapping shows that the capping agent is distributed homogeneously over the entire sample (SI, Figure S4). The crystallite size of the NPs is also confirmed by PXRD measurements, as the Pd reflections are very broadened (SI, Figure S7). The Fourier-transform-attenuated-total-reflectioninfrared spectrum (FT-ATR-IR; SI, Figure S2) of a sample of Pd@TOAB NPs exhibits bands which are in accordance with those of neat TOAB, namely characteristic v (C-H,sp³) absorption bands in a range from 2953 to 2850 cm⁻¹ as well as a very weak v (C-H,sp²) absorption band at 3004 cm⁻¹. Furthermore, symmetric and antisymmetric v (C-C/C-Me) vibrations are observed at 1466 and 1353 cm⁻¹, and at 753 and 720 cm⁻¹, respectively, which is in accordance to a previously reported IR spectrum of neat TOAB.^{[21] 1}H-NMR spectroscopy confirms an intact structure of the capping agent without any impurities, as the recorded spectrum matches with the recorded reference spectra of neat TOAB (SI, Figure S5). X-ray photoelectron spectroscopy (XPS) shows the main signal corresponding to metallic Pd(0) (SI, Figure S8).

Influence of temperature and H_2 pressure on the catalytic activity and selectivity of Pd@TOAB NPs

For a systematic investigation of the catalytic activity of Pd@TOAB NPs in the semi-hydrogenation reaction of alkynes, 1-octyne was used as model substrate (Scheme 2). Error calculations assuming an instrumental GC inaccuracy of 1 % showed that all calculated error bars on both conversion and selectivity are too small to be considered (detailed calculation in the SI, Table S1) and have no impact on the following interpretation of the catalytic results. We have investigated the effect of temperature and H₂ pressure on substrate conversion and product selectivity (Table 1 and SI, Figure S10).



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FULL PAPER

Table 1. Parameter optimization in the semi-hydrogenation of 1-octyne using 1 mol% Pd@TOAB NPs after 3 h reaction time.

Entry	Т [°С]	p(H ₂) [bar]	Conv. [%] ^[a]	Yield 1-octene [%] ^[b]	Yield <i>n</i> -octane [%]	Oligom. [%] ^[c]	TOF [h ⁻¹] ^[d]
1	25	0.5	100	15	54	31	460
2	0	0.5	45	84	11	5	210
3	0	1.0	80	80	8	12	325
4	0	2.0	100	11	65	24	340

[a] Conversion of 1-octyne. [b] Selectivity towards 1-octene.

[c] Oligomerization to higher hydrocarbons. [d] for details see SI, chapter 2.11.

Table 1 shows that a variation of either reaction temperature or hydrogen pressure significantly influences both activity and selectivity. Noteworthy, oligomerization of 1-octene to dimers and higher products has been detected in all experiments of this study by LIFDI-MS measurements (SI, Figures S16-S17 and Table S3). The oligomerization to dimers and trimers catalyzed by Group 10 metals is well-known since the early works of Wilke, Keim, Jolly and others.^[22] Regarding heterogeneous acetylene semihydrogenation catalysis, oligomerization of the product and subsequent carbon deposits on the catalyst surface was reported in literature earlier.^[3] In contrast, to the best of our knowledge, for this reaction oligomerization as side-reaction has not been reported so far for colloidal metal NPs. Low temperatures and a relatively low hydrogen partial pressure have a positive influence on the selectivity. Starting at room temperature and a H_2 pressure of 0.5 bar, expectedly, a highly active but unselective system was observed (Table 1, Entry 1).

Consequently, carrying out the reaction at lower temperature (0 °C) and 0.5 bar H₂ leads to an improved selectivity but decreased activity (Table 1, Entry 2). Increasing the H₂ pressure to 1.0 bar at 0 °C results in a high conversion of 80 % and an enhanced selectivity towards 1-octene of 80 % after 3 h (Table 1, Entry 3). Here, an oligomerization of 1 % and full-hydrogenation to n-octane of 8 % was observed with a TOF of 325 h⁻¹. Further increase of the hydrogen pressure at low temperatures does not result in increased activity, as a similar TOF value of 340 h⁻¹ is observed, but in decreased selectivity as olefin hydrogenation and oligomerization are observed (Table 1, Entry 4). Expectedly, at elevated temperatures and hydrogen pressure, alkane formation and oligomerization are increased. Noteworthy, no particle precipitation is observed independent on the applied catalytic conditions. A linear correlation of the catalyst amount and the reaction rate is monitored (SI, Figure S11), suggesting no influence of the catalyst concentration on its performance. Structural analysis of the catalyst after catalysis runs by DLS and HRTEM shows a slight particle agglomeration (SI, Figures S20 and S21), which is not uncommon for colloids stabilized by weak capping agents.^[13] Nevertheless, no precipitation of the catalyst is observed. These experiments show a highly active catalytic system at mild conditions (low temperature, low H₂ partial pressure). Yet, without any additives the selectivity towards 1-octene is rather low as hydrogenation of alkynes is not stopped at the olefin but reacts further to alkanes. Most likely, the favored olefin hydrogenation over olefin desorption is responsible for the observed overreduction.[2,3]



Figure 2. DLS (left) and HRTEM measurements (right) of Pd@TOAB exposed to PPh₃ under inert conditions with and without 1-octyne (DLS) and without 1-octyne (HRTEM).

Influence of phosphane additives on the catalytic performance of Pd@TOAB NPs

For further improvement of the catalytic performance of the Pd@TOAB colloids and a comprehensive understanding of th major factors influencing the catalytic system, we have adde phosphanes with different steric and electronic features in ca catalytic amounts. Upon addition of 1.0 equiv. PPh3 with respe to Pd to the colloidal solution, a shift in the ³¹P-NMR from -5.3 pp to -5.0 ppm with a signal broadening is observed, which points phosphane coordination to the Pd surface (SI, Figure S26). The coordination of PPh₃ results in particle agglomeration as show by DLS and HRTEM in Figure 2. Taking an equilibrium coordination and dissociation into account, the addition of or 1.0 equiv. PPh₃ might be to insufficient for long-term stab colloids. Conversely, this implements that TOAB can be considered as a stronger capping agent than PPh₃. Notabl particle agglomeration is not observed when 1-octyne is prese in the Pd@TOAB/PPh3 solution, indicating an addition stabilizing effect by alkyne coordination to the NPs surface. F catalysis experiments, variation of the phosphane amount fro 30 equiv. to 0.5 equiv. with respect to Pd showed that selective remains nearly constant, whereas the activity increased wi decreasing PPh₃ amount, with an optimum at 1.0 equiv, PP based on the amount of Pd (Table 2 and Figure 3). Here, at f conversion a 1-octene selectivity of 83 % is observed (6 oligomerization and 10 % n-octane) with a TOF of 840 h⁻¹, which compared to the catalysis without any additive is increased by factor of 2.5.

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Table 2. Additive approach in the semi-hydrogenation of 1-octyne using 1 mol% $Pd@TOAB$ after 2 h reaction time (0 °C, 1.0 bar H2).					
Equiv. PPh3 ^[a]	Conversion [%]	Selectivity [%]			
0.5	38	81			
1.0	99	83			
2.0	74	98			
5.0	62	100			
10	54	100			
20	23	100			

[a] Equivalents based on the amount of Pd.

FULL PAPER



Figure 3. Kinetic study of the additive approach using 1.0 equiv. PPh₃ based on the amount of Pd leading to an enhanced selectivity and conversion (1 mol% Pd@TOAB, 0 $^{\circ}$ C, 1.0 bar H₂).

Comparison of our system with literature-known monometallic Pd NPs for the semi-hydrogenation of 1-octyne show a rather high activity for the herein reported catalyst (see the SI, Table S9). Similar systems, such as Pd@PVP NPs provide a TOF of 1320 h⁻¹,^[22] while the TOF of Pd NPs stabilized by an ionic liquid was only estimated about 23 h⁻¹ for the semi-hydrogenation of 3-hexyne.^[11] Nevertheless, for both examples the catalysis was carried out at higher temperatures and the authors do not state whether their catalyst is colloidal or heterogeneous. A further decrease of the PPh₃ concentration to 0.5 equiv. leads to a decreased selectivity and activity including 1 % oligomerization and 6 % n-octane. Based on the (simplified) concept of the model of magic number clusters, for a perfect Pd NP with icosahedral structure and a diameter of ca. 1.5 nm, it can roughly be estimated that ca. 70-75 % of all Pd atoms are located at the surface of the NPs. Therefore, by adding 1.0 equiv. of phosphane, it can be deduced that the additive is always in small excess and that the catalyst surface can be fully coordinated with phosphane. The decrease in activity by increased PPh₃ amount from 1.0 to 30 equiv. might occur from a competitive coordination of the phosphane and the alkyne. Under catalytic conditions, a signal

splitting in the ³¹P-NMR spectra of the phosphane signal using 1.0 equiv. PPh₃ is observed. Here, an optimum of coordinated and non-coordinated phosphane is achieved. With higher amounts of PPh₃, only one broadened signal is detected (SI, Figure S27). In addition, using higher amounts of PPh₃ (5.0 to 30 equiv. phosphane), crystals of the complex [Pd(PPh₃)₄] were isolated and identified via ¹H-/³¹P-NMR and IR spectroscopy (SI, Figures S6, S23 and S32), which clearly point to a leaching of Pd atoms from the NPs by using an excess of phosphane. Control experiments using various amounts of [Pd(PPh₃)₄] as catalyst show no activity in the semi-hydrogenation of 1-octyne under the described reaction conditions (SI, Figure S13), also explaining why the activity is decreased with higher PPh₃ amounts. Therefore, the following catalysis studies were carried out at 0 °C using 1.0 bar H₂ and 1.0 equiv. phosphane per Pd (here, no Pd leaching was observed). In detail, addition of 1.0 equiv. PPh₃ results in almost full substrate conversion after 2 h with an increased selectivity of 83 % towards 1-octene. The particle size does not change during catalysis (SI, Figure S21). Substitution of a phenyl group with a methyl group in the phosphane, namely MePPh₂, shows even higher selectivity after 2 h reaction time (92% conv. and 92% sel.). Nevertheless, consecutive substitution of the phenyl groups by sterically less demanding methyl groups, namely Me₂PPh and Me₃P, leads to an increased selectivity but also strongly decreased catalytic activity (SI, Figures S14 and S15 and Table S2). The stronger interaction of these smaller phosphanes with the Pd NPs results in particle precipitation, as the stabilization effect of phosphanes is weaker than that of TOAB. In consequence, catalyst deactivation by particle agglomeration and precipitation is observed. By testing a series of sterically different demanding phosphanes, a relation between the cone angle^[24] and the catalytic activity was found with an optimum using PPh3 with a cone angle of 145° (Figure 4 and SI, Table S2). Phosphanes with a high steric demand, e.g. P(o-tolyl)₃, PⁱPr₃ and PCy₃, do not destabilize the particles but also show a decreased activity compared to PPh₃. The decreased activity can be explained by the steric inhibition of the phosphane of the particle surface impeding substrate coordination to the catalyst.



Figure 4. Substrate conversion after 2 h as a function of the phosphane cone angle (left) and the electronic properties (right). Catalysis tests were performed under standard catalytic conditions (1 mol% Pd@TOAB, 1.0 equiv. phosphane based on the amount of Pd, 0 °C, 1.0 bar H₂).

FULL PAPER

Table 3. Comparison of catalytic tests with 1-octyne as substrate using 1.0 equiv. phosphanes bearing the same cone angle of 145° under standard conditions (1 mol% Pd@TOAB NPs, 0 °C, 1.0 bar H₂).

Entry	Additive	Conversion after 2 h [%]	Sel. 1-octene at full conv. [%]	Full hydrogenation [%]	Oligomerization [%]
1	-	56	22 (5 h)	35 (5 h)	43(5 h)
2	PPh ₃	99	83 (2 h)	9 (2 h)	6(2 h)
3	P(p-tolyl) ₃	46	61 (5 h)	32 (5 h)	10(5 h)
4	P(p-F-phenyl) ₃	34	50 (6 h)	36 (6 h)	14(6 h)

In contrast to the arylphosphane P(o-tolyl)₃, which shows a similar selectivity at full conversion compared to PPh₃, the alkylphosphanes P'Pr₃ and PCy₃ show a decreased selectivity at full conversion. Hence, it can be concluded that the influence of the phosphane on the selectivity does not underly steric reasons but rather electronic ones, as an increased σ -donor ability seems to be undesirable for a high selectivity. Further investigation on the influence of the phosphane on the catalytic activity indicated not only steric reasons but also electronic differences as a comparison of PPh₃, $P(p-tolyl)_3$ and $P(p-fluorophenyl)_3$ shows (Figure 4, Table 3 and SI, Figures S14, S15 and Table S2). These phosphanes all exhibit a Tolman cone angle of 145° but show a drastic difference in catalytic activity. In detail, catalysis tests with both the electron donating $P(p-tolyl)_3$ (Table 3, Entry 2) and the more electron-withdrawing P(p-fluorophenyl)₃ (Table 3, Entry 4) result in a decreased activity. In addition, the best selectivity at full conversion is achieved using PPh₃ as additive (Table 3, Entry 2). This illustrates that both steric and electronic properties play a crucial role in influencing the colloidal catalyst system and that PPh₃ combines these requirements in an optimal way. Hydrogenation experiments using the olefin, namely 1-octene, as substrate under standard catalytic conditions (0 °C, 1.0 bar H₂ pressure) using Pd@TOAB NPs and 1.0 equiv. PPh₃ show that the formation of n-octane was suppressed efficiently, as after 5 h only 5 % of 1-octene was hydrogenated (SI, Table S6). In contrast, without PPh₃, full conversion of 1-octene was reached at 3 h. For a more comprehensive understanding of the increased selectivity, the hydrogenation of cis-2-octene was tested with and without PPh₃ as additive. By adding 1.0 equiv. PPh₃, olefin hydrogenation is not observed, while without PPh₃ already after 1 h cis-2-octene is hydrogenated to n-octane in 87 % conversion (SI, Table S7). This experiment gives evidence that the semi-hydrogenation of alkynes by addition of phosphanes can be extended to other substrates and not exclusively for 1-octyne. The catalysis tests using phenylacetylene and 2-octyne with PPh₃ and MePPh₂ as additives exhibit similar results with respect to conversion and selectivity compared to 1-octyne as substrate (Table 4 and SI, Tables S4 and S5). A comparison of the conversions of 1-octyne, 2-octyne and phenyl acetylene shows that without any additives, the TOF values of 2-octyne and phenylacetylene are higher than for 1-octyne, which was also reported in literature before.^[23] By the addition of PPh₃, the conversion of the terminal alkyne is slightly faster than that of the substrates with an internal C≡C bond (Table 4, Entry 1 vs. Entries 4 and 6). This can be explained by the influence of the PPh₃ coordination to favor the hydrogenation of terminal alkynes on the metal surfaces than that for internal ones or terminal alkyne with a higher steric demand, mainly due to coordination

constraints at the NP surface.^[25] The addition of PPh₃ further leads to an increase of the TOF value for all substrates.

Noteworthy, in the semi-hydrogenation of 2-octyne, phosphane addition leads not only to a suppressed alkane formation, but selectively to the *cis*-isomer which is typical for catalytic surface reactions pointing to a *syn*-hydrogen addition.^[26] Interestingly, MePPh₂ as additive solely enhances the conversion and selectivity using 1-octyne and phenylacetylene, whereas a deactivation is recorded with 2-octyne as substrate. This finding also strengthens the assumption that not only steric but also electronic considerations have to be considered.

For a deeper understanding of the positive influence of phosphane additives on the catalytic activity of the Pd NPs, mechanistic investigations were carried out by means of in-situ NMR, IR and HRTEM measurements. For this, colloidal Pd@TOAB/PPh3 NPs were selected as catalyst, since they exhibit an overall high activity, conversion and selectivity for all examined substrates. Furthermore, PPh₃ is generally stable towards oxidation under an oxygen containing environment. In the ³¹P-NMR spectrum (recorded in toluene-*d*₈), a resonance shift from -5.3 to -5.0 ppm and signal broadening indicate a Pd-PPh₃ coordination (SI, Figures S27 and S28) explaining the increased selectivity by changing the electronic properties of the metal surface. Nevertheless, surprisingly, the ³¹P-NMR spectrum also shows about 30 % phosphane oxidation directly after addition of 1.0 equiv. PPh₃ (referred to Pd) to a solution of 1-octvne and 1 mol% Pd@TOAB NPs, which is supported by IR measurements (Figure 11 and SI, Figure S20). Since the synthesis is being carried out under air, it is very likely that after formation of Pd metal atoms and subsequent Ostwald ripening, Pd surface atoms are oxidized by air oxygen.^[26] Decreasing the PPh₃ amount from 1.0 equiv. to 0.5 equiv. results in almost full phosphane oxidation and no phosphane coordination, illustrated in the ³¹P-NMR spectra by the presence of only one signal for PPh₃O at 24.9 ppm, and the absence of the signal for coordinated PPh₃ at -5.0 pm, respectively (SI, Figure S29). The absence of PPh₃ results, as already stated before, in a lower selectivity suggesting that phosphane coordination is crucial for an enhanced selectivity. To verify whether the phosphane or the phosphane oxide is responsible for the increased activity, catalytic experiments using 1.0 equiv. PPh₃O or MePPh₂O were performed. Almost the exact results as without additive were obtained, indicating that phosphane oxides do not bind to the Pd surface, and that they are not capable of reducing the surface Pd-O species (SI, Table S1 and Figure S14). Therefore, it can be assumed that the phosphane is responsible for (a) the reduction of Pd-O, (b) the coordination to the Pd(0) surface, and (c) the enhanced selectivity in semi-hydrogenation catalysis.

FULL PAPER

Table 4 Substrate variation using	1 mol% Pd@TOAB NPs and 1.0 equiv_PPha	(catalysis conditions: 0 °C 1 0 bar H	PPh ₂ amount is based on Pd
able 4. Substrate variation using			

Entry	Substrate	Additive	Conversion [%]	Selectivity with full conv. [%]	Oligomerization with full conv. [%]	TOF [h ⁻¹]
1	1-octyne	-	56 (5 h)	22 (5 h)	8 (5 h)	330
2	1-octyne	PPh ₃	99 (2 h)	83 (2 h)	4 (2 h)	840
3	2-octyne	-	59 (4 h)	66 (4 h)	4 (4 h)	480
4	2-octyne	PPh_3	72 (4 h)	92 (4 h)	0 (4 h)	520
5	phenylacetylene	-	66 (4 h)	41 (4 h)	9 (4 h)	760
6	phenylacetylene	PPh ₃	91 (4 h)	87 (4 h)	6 (4 h)	900

To answer the question whether the oxygen is originating from the palladium surface or is physically dissolved in the solvent, ³¹P-NMR in situ studies were performed both under air and under argon. These experiments show that phosphane oxidation is enhanced by using moist solvents but also is present under inert conditions (SI, Figures S29 and S30). In addition, experiments on catalyst deactivation were performed (SI, Figure S18 and S19). After full conversion of 1-octyne to 1-octene under standard conditions (T = 0 °C, $p(H_2)$ = 1 bar, 1 mol% Pd@TOAB NPs, 1.0 equiv. PPh₃, 2 h reaction time), solvent and (by)product(s) were removed in vacuo. Accordingly, fresh solvent and substrate were added, and a new catalysis run was carried out in order to investigate the principal recyclability and activity of the catalyst after product separation. Herein, it must be noted that due to particle agglomeration, a lower activity for the second catalytic test is expected. Using 1.0 equiv. PPh₃ as additive, comparable activity and selectivity was observed in the second catalysis test, suggesting that this amount of additive is sufficient for an enhanced performance (SI, Figures S18 and S19). Nevertheless, by adding additional 1.0 equiv. PPh₃ after the first catalytic test a higher activity was observed. The results lead to the assumption that both solvent and Pd surface contain a small amount of oxygen, which can react with the phosphane. The latter is confirmed by XPS as the Pd 3d core level spectrum of freshly synthesized Pd@TOAB NPs (SI, Figure S8) proves a small amount of oxidized Pd species (19 %) which was also previously reported in literature, where XPS spectra of freshly synthesized Pd@TOAB NPs clearly indicate a partial palladium oxidation on the particle surface.^[21]

When any possible oxygen source during particle synthesis is avoided, no particle stabilization is achieved, suggesting that a certain amount of surface oxygen is crucial for the formation of a stable colloidal system. This hypothesis is supported by the reactivity of the colloidal system under reductive conditions. Adding PPh₃ and hydrogen pressure to the system, without any alkyne, Pd(0) precipitation is observed accompanied by the formation of phosphane oxide confirmed by ³¹P-NMR, IR and HRTEM measurements (Figure 2 and SI, Figures S22-S25). The groups of Dupont and Dyson reported on Pd NPs stabilized by an ionic liquid, which exhibit oxidized surface Pd atoms, as shown by XPS experiments,^[11,27] assuming that a thin layer of metal oxide is beneficial for particle stabilization as the polarity of the oxygen atoms facilitates a better interaction with the ionic capping agent. In contrast, upon addition of 1-octyne to the system, no precipitation of Pd(0) is observed; ³¹P-NMR spectra confirm that PPh₃O formation is still present, suggesting that the alkyne has a stabilizing effect on the colloidal system under catalytic conditions (SI, Figures S28 and S31). It can be assumed that for an improvement of the catalytic system, a distinct amount of phosphane is required to remove oxygen species from the palladium surface, resulting in an increased amount of catalytic active sites. An additional phosphane coordination to the palladium surface leads to increased selectivity.

Conclusion

In this work, we demonstrate the enormous influence of ligands on (a) the catalytic performance of (weakly stabilized) colloidal metal nanoparticles in the semi-hydrogenation of alkynes, (b) the selectivity towards the olefin product, and (c) the stability of the colloids in solution. The addition of the optimal amount of phosphane ligands to the surface of Pd colloids is an effective site-blocking strategy for the semi-hydrogenation. Studies with a set of electron-donating and withdrawing phosphanes show that optimal catalytic performance requires a balance of electron density at the NP. The activity as well as selectivity is strongly influenced by the electron-donating or -withdrawing nature of the added phosphane. We found that both the more electrondonating P(p-tolyl)₃ as well as the more electron-withdrawing P(p-F-phenyl)₃ do not lead to an ideal performance compared to PPh₃. The catalytic activity of Pd NPs depends on the additive as follows: $PPh_3 > P(p-tolyl)_3 > P(p-F-phenyl)_3$, suggesting that strongly electron-withdrawing phosphanes decrease the activity of the surface catalyst atoms. On the other hand, stronger donors, such as P(p-tolyl)₃ bind more strongly to the catalyst surface, thus making it less accessible for substrate molecules, hence the decreased activity. Comparison of the selectivity at full conversion shows minor differences; in all cases, the selectivity was strongly increased compared to catalysis without any additive. Therefore, we conclude that the substitution of the phenyl groups does not lead to a change in selectivity and only influences the activity of our system. This points to the steric bulk of the additive as origin of selectivity, while the binding strength of the phosphane appears to influence the activity; the stronger the phosphane-Pd bond is, the lower the activity is. Studies with phosphanes having different cone angles showed that phosphanes with smaller cone angles lead to particle precipitation. Phosphanes with a high steric demand e.g. P(o-tolyl)₃, P'Pr₃ and PCy₃ stabilize the particles as colloids, but they lead to a decreased activity compared to PPh₃. This is most likely a consequence of the shielding of the surface by the additive, so that the substrate cannot access the catalyst. Therefore, PPh₃ seems to have a perfect balance between steric demand for stabilizing the particle in solution and to allow the

FULL PAPER

substrate to access the surface, and a certain lability of the bond to Pd.

Mechanistic investigations (in-situ NMR and HRTEM) during catalysis show the presence of both phosphane and phosphane oxide species on the metal surface, suggesting that oxygen plays a role in stabilizing the colloids in solution, but also for the selectivity. As a perspective, avoiding bromide-containing surfactants is likely to lead to an enhanced catalyst performance, since halides are known catalyst poisons. Gaining more knowledge on the interplay of the ligand and the catalyst surface will lead to extending our studies to less expensive, i.e. ignoble and more abundant metals for semi-hydrogenation catalysis, especially for industrially relevant substrates.

Experimental Section

Materials and analytical methods

All chemicals and solvents were purchased from different suppliers or presynthesized in the Fischer group (e.g. Sigma Aldrich, VWR). Catalysis experiments were performed under an atmosphere of purified argon using conventional Schlenk and glovebox techniques. Solvents were dried using an MBRAUN Solvent Purification System, final H₂O contents were checked by Karl Fischer titration and did not exceed 5 ppm.

NMR spectra (¹H, ¹³C, ³¹P) were measured in C_6D_6 and toluene- d_8 at 298 K using a Bruker Avance DPX-250, Bruker DRX 400, Bruker Avance 300 or a Bruker AV400 US spectrometer operating at the appropriate frequencies. Chemical shifts are given relative to TMS (¹H, ¹³C) or 85 % H₃PO₄ (³¹P), and spectra were referenced relative to the residual solvent signal.

FT-IR spectra were recorded on a Bruker Alpha FT-IR spectrometer with ATR (attenuated total reflexion) geometry, using a diamond ATR unit under argon atmosphere. Signal intensities are described with the following abbreviations: s = strong, m = medium, w = weak. The spectra were processed with OPUS (Version 7.5, Bruker Optik GmbH 2014).

LIFDI-MS measurements were conducted on a Thermo Scientific Exactive Plus instrument, equipped with an Orbitrap detector and a "LIFDI 700" ionization source, located at the University of Würzburg. All samples were prepared with dry toluene and filtered under argon atmosphere.

DLS measurements were performed on a Malvern Zetasizer Nano using quartz cuvettes in 173° backscattering mode. A general-purpose method was used to calculate the mean particle sizes and dispersities.

HRTEM samples were prepared by dropping a solution of Pd@TOAB in toluene on carbon-coated Cu400 TEM grids. Samples were imaged by HR-TEM "FEI TITAN Themis 60 300" equipped with X-FEG type emission gun operated at 300 kV, spherical aberration Cs image corrector improving resolution limit in TEM mode below 0.7 nm, high angle annular dark field detector (HAADF) for high atomic number (Z)-contrast in scanning transmission electron microscopy (STEM) and SUPER X energy dispersive X-ray (EDX) spectrometer with 4x30 mm2 windowless silicon drift detectors. Particle size determination was carried out using ImageJ (version 2019).

X-ray photoelectron spectra were recorded on a Leybold-Heraeus LHS 10 spectrometer using a non-monochromatised Al Kα source (1486.7 eV). Samples involved in catalytic reactions were dissolved in toluene and spincoated on a Si-wafer. Sample preparation and transfer into the XPS spectrometer were carried out under argon atmosphere. The analyser was operated at a constant pass energy of 100 eV leading to an energy resolution with a full width at half-maximum (fwhm) of ~1.1 eV. The energy scale of the spectra was corrected for sample charging by using the C 1s main signal (284.5 eV). All spectra were recorded in an ultra-high vacuum chamber at a pressure below 5×10⁻⁸ mbar. Core level spectra were deconvoluted by using Voigt functions and linear background subtraction. Due to the charging correction by an intrinsic signal of the sample, which might be erroneous comparison to reference samples with known oxidation states reveals the oxidation states of the new materials.

Powder X-ray diffraction measurements were performed on a Panalytical Empyrean instrument. The sample was put in a capillary under argon

atmosphere and placed on a silicon wafer cut. The detection was carried out with a Pixel3D detector. All measurements were performed with Cu-K α (λ = 1.54 Å) radiation and at 298 K.

Pd NP synthesis

The Pd NPs were obtained by reduction of K₂[PdCl₄] with NaBH₄ and subsequent stabilization with the capping agent tetraoctylammonium bromide (TOAB). The method is a variation of those proposed by the Coronado et al.20 In a typical synthesis, 5 mL of a 30 mM aqueous solution of K₂[PdCl₄] (37 mg, 0.11 mmol, 1.0 equiv.) was mixed with 20 mL of a 50 mM TOAB solution (602 mg, 1.1 mmol, 10 equiv.) in toluene. After 30 min, the transfer of the [PdCl₄]²⁻ from the aqueous solution to the organic phase was completed as revealed by the red color of the organic phase containing the [PdCl₄]²⁻/TOAB mixture. The aqueous phase was disposed. Then, 6 mL of a freshly prepared 0.1 M NaBH₄ (11 mg, 0.285 mmol, 2.5 equiv.) aqueous solution was added at 60 °C, keeping the mixture under vigorous stirring (1400 rpm). Consequently, the solution darkened immediately, indicating the formation of NPs. The mixture was stirred for 30 min at 25 °C and after removing the aqueous phase, the organic phase was washed with deionized water (3x50 mL) and finally dried over anhydrous Na₂SO₄. The samples were degassed under an atmosphere of purified argon.

 $^{1}\text{H-NMR}$ (400 MHz, C₆D₆): 3.5 (m, 2 H, NCH_2), 1.7 (dt, 2 H, NCH_2CH_2), 1.4 (m, 10 H, CH_2), 1.0 (t, 3 H, CH_3).

IR (ATR, neat, cm $^{-1}$): 720 (s), 753 (m), 1353 (m), 1466 (s), 2850 (s), 2871 (s), 2953 (m), 3004 (w).

Catalysis experiments

All catalysis experiments were carried out under inert atmosphere and ndodecane was chosen as internal standard. For semi-hydrogenation experiments, 0.9 mL of the NP solution (1 mol% catalyst in toluene), 0.1 mL substrate (1-octyne, 2-octyne, phenyl acetylene) and 0.1 mL dodecane were placed in a 90 mL Fischer Porter bottle and cooled to 0 °C. This solution was purged with 1.0 bar H₂ and continuously stirred for 5 h. For GC measurements, aliquots were taken under a continuous argon flow. After taking of aliquots, the Fischer Porter bottle was again purged with 1.0 bar H₂.

For recycling experiments, all liquids were removed in high vacuum and fresh solvent and substrate was added. For quantification of the oligomerization products, all low-boiling components were evaporated at reduced pressure and Pd@TOAB was removed by filtration of the residue over SiO₂ in hot toluene. LIFDI-MS measurements were carried out for an exact determination of the residue components.

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Keywords: colloidal nanoparticles • additive approach • semihydrogenation reaction • phosphane ligands • homogeneous catalysis

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FULL PAPER

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FULL PAPER

Entry for the Table of Contents



Colloidal Pd nanoparticles, stabilized by the ionic capping agent N(Octyl)₄Br were tested as quasi-homogeneous catalysts for the semihydrogenation of liquid alkynes. The addition of phosphanes to the catalyst surface leads to a boost of both activity and product selectivity, owing to the steric and electronic properties of the additives.