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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We report on the influence of phosphanes on the catalytic activity and selectivity of colloidal, tetraoctylammonium bromide (TOAB) stabilised palladium nanoparticles (NPs) in the semi-hydrogenation of alkynes to olefins. Full characterisation 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 semi-hydrogenation of 1-octyne, 2-octyne and phenylacetylene 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 steric and electronic effects of the ligand play a crucial role for the catalyst performance. A moderate steric demand of the ligand with a rather weak σ-donating 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 favoured, 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,[4] without (significant) over-hydrogenation, is the doping of a catalytically active metal, e.g. palladium,[5] as the most prominent example, nickel[6] 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 oligomerisation (so-called „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 behaviour of such model particles allows for a fundamental understanding of structure-performance relationships. The colloid surfactant molecules, particularly σ-donor type stabilising 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 semi-hydrogenation 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 stabilised by a nitrile-functionalised ionic liquid (IL), which are highly active in the semi-hydrogenation of alkynes in a multiphase system.[15] Phosphane-functionalised IL surfactants showed an enhanced catalyst performance.[16] Another study shows the effect of the nature of thiolate capping 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...
phosphine ligands using a monometallic Ni catalyst. Yang, Li et al. have studied the electronic influence of triphenylphosphine on the catalytic performance of Pd NPs in selective hydrogenations. 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 triorganylphosphinates R₃P, bearing different substituents R (alkyl, aryl) on the catalytic activity and selectivity of colloidal Pd NPs for the semi-hydrogenation of alkenes. We investigated the steric and electronic effects of the phosphinates in order to learn more on the crucial parameters for controlling the selectivity of the reaction. Furthermore, we have studied the influence of different phosphinates 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 tetracetylammonium bromide (TOAB), which can easily be substituted by stronger (α-donor) stabilising agents, such as phosphines.

Results and Discussion

Synthesis and characterisation of TOAB-stabilised Pd NPs

Highly monodispersed Pd NPs were prepared in toluene on the basis of a modified literature-known procedure. Reduction of K₂[PdCl₄] with an excess of aqueous NaBH₄ in toluene in the presence of an excess of TOAB (10 equiv.) yielded colloidal Pd NPs as a black solution (Scheme 1). The NPs were analysed 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 colour change of the colloidal solution from dark brown to amber and no catalytic activity. Therefore, the synthesis procedure was optimised 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.

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 crystal size of the NPs is also confirmed by PXRD measurements, as the Pd reflections are very broad (SI, Figure S7). The Fourier-transform-attenuated-total-reflection-infrared 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 ν(C–H, sp²) absorption bands in a range from 2953 to 2850 cm⁻¹ as well as a very weak ν(C–H,sp³) absorption band at 3004 cm⁻¹. Furthermore, symmetric and antisymmetric ν(C₂=C/C-Me) vibrations are observed at 1466 and 1353 cm⁻¹, and at 793 and 720 cm⁻¹, respectively, which is in accordance to a previously reported IR spectrum of neat TOAB. 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 H₂ 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 alkenes, 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).

Table 1 shows that a variation of either reaction temperature or hydrogen pressure significantly influences both activity and selectivity. Noteworthy, oligomerisation 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 oligomerisation to dimers and trimers catalysed by Group 10 metals is well-known since the early works of Wilke, Keim, Jolly and others. Regarding heterogeneous acetylene semi-hydrogenation...
The coordination of PPh$_3$ points to phosphane coordination to the Pd surface (SI, Figure S26). Consequently, carrying out the reaction at lower temperature (0°C) and 0.5 bar H$_2$ leads to an improved selectivity but decreased activity (Table 1, Entry 2). Increasing the H$_2$ 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 oligomerisation 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 oligomerisation are observed (Table 1, Entry 4). Expectedly, at elevated temperatures and hydrogen pressure, alkane formation and oligomerisation 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 and dissociation into account, the addition of only 1.0 equiv. PPh$_3$ might be to insufficient for long-term stable colloids. Conversely, this implies that TOAB can be considered as a stronger capping agent than PPh$_3$. Notably, particle agglomeration is not observed when 1-octyne is present in the Pd@TOAB/PPh$_3$ solution, indicating an additional stabilising effect by alkylne coordination to the NPs surface. For catalysis experiments, variation of the phosphane amount from 30 equiv. to 0.5 equiv. with respect to Pd showed that selectivity remains nearly constant, while the activity increased with decreasing PPh$_3$ amount, with an optimum at 1.0 equiv. PPh$_3$ based on the amount of Pd (Table 2 and Figure 3).

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

| Entry | T [°C] | p(H$_2$) [bar] | Conv. [%]$^a$ | Yield 1-octene [%]$^b$ | Yield n-octane [%]$^b$ | Oligom. [%]$^c$ | TOF [h$^{-1}$]$^d$ |
|-------|-------|--------------|----------------|-----------------------|----------------------|----------------|----------------|
| 1     | 25    | 0.5          | 100            | 15                    | 54                   | 31             | 460            |
| 2     | 0     | 0.5          | 45             | 84                    | 11                   | 9              | 210            |
| 3     | 1.0   | 0.5          | 80             | 80                    | 8                    | 12             | 325            |
| 4     | 2.0   | 0.5          | 100            | 11                    | 65                   | 24             | 340            |

$^a$ Conversion of 1-octyne. $^b$ Selectivity towards 1-octene. $^c$ Oligomerisation to higher hydrocarbons. $^d$ For details see SI, chapter 2.11.

### 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 H$_2$).

| Equiv. PPh$_3$$^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.

### 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 the major factors influencing the catalytic system, we have added phosphanes with different steric and electronic features in co-catalytic amounts. Upon addition of 1.0 equiv. PPh$_3$ with respect to Pd to the colloidal solution, a shift in the $^{31}$P-NMR spectrum from $-5.3$ ppm to $-5.0$ ppm with a signal broadening is observed, which points to phosphane coordination to the Pd surface (SI, Figure S26). The coordination of PPh$_3$ results in particle agglomeration as shown by DLS and HRTEM in Figure 2. Taking an equilibrium of coordination and dissociation into account, the addition of only 1.0 equiv. PPh$_3$ might be to insufficient for long-term stable colloids. Conversely, this implies that TOAB can be considered as a stronger capping agent than PPh$_3$. Notably, particle agglomeration is not observed when 1-octyne is present in the Pd@TOAB/PPh$_3$ solution, indicating an additional stabilising effect by alkylne coordination to the NPs surface. For catalysis experiments, variation of the phosphane amount from 30 equiv. to 0.5 equiv. with respect to Pd showed that selectivity remains nearly constant, while the activity increased with decreasing PPh$_3$ amount, with an optimum at 1.0 equiv. PPh$_3$ based on the amount of Pd (Table 2 and Figure 3).
Here, at full conversion a 1-octene selectivity of 83% is observed (6% oligomerisation and 10% n-octane) with a TOF of 840 h⁻¹, which is increased by a factor of 2.5 in comparison to the catalysis without any additive.

Comparison of our system with literature-known monometallic Pd NPs for the semi-hydrogenation of 1-octyne show a rather high activity for the catalyst reported in this work (see the SI, Table S9). Similar systems, such as Pd@PVP NPs provide a TOF of 1320 h⁻¹[2] while the TOF of Pd NPs stabilised 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% oligomerisation and 6% n-octane. Based on the (simplified) concept of the model of magic number clusters, for a perfect Pd NP withicosahedral 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 present in small excess and that the catalyst surface can be fully covered with phosphane. The decrease in activity by increasing the PPh₃ amount from 1.0 to 30 equiv. might occur from a competitive coordination of the phosphane and the alkyn. Under catalytic conditions, a signal splitting in the ³¹P-NMR spectrum 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)₂C₆H₄(η²-C₆H₄-3,4-Me₂)] were isolated and identified via ¹H-/³¹P-NMR and IR spectroscopy (SI, Figures S56, S23 and S32), which clearly points to a leaching of Pd atoms from the NPs by using an excess of phosphane. Control experiments using various amounts of [Pd(PPh₃)₃] as catalyst show no activity in the semi-hydrogenation of 1-octyne under the described reaction conditions (SI, Figure S13), which also explains 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 MePPh₃, 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 Me₃PPh 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 stabilisation 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[23] 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), PPr₃ and PCy₃ do not destabilise the particles, but they lead to a decreased activity compared to PPh₃. This can be explained by the steric inhibition of the phosphane of the particle surface impeding substrate coordination to the catalyst. In contrast to the arylphosphane P(o-tolyl)₂, which shows a similar selectivity at full conversion compared to PPh₃, the alkylphosphanes PPr₃ and PCy₃ lead to 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 Ï–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(o-tolyl)₂ and P(Ph-fluorophenyl)₃ shows (Figure 4, Table 3 and SI, Figures S14, S15 and S10). These phosphanes all exhibit a cone angle of 145° but show a drastic difference in catalytic activity. In detail, catalysis tests with both the electron donating P(η²-tolyl), (Table 3, Entry 2) and the more electron-withdrawing P(η²-fluorophenyl), (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 of 1-octene as substrate under standard catalytic conditions (0 °C, 1.0 bar H₂ pressure) using Pd@TOAB NPs and 1.0 equiv. PPh₃ shows 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 to n-octane 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 a competitive reaction to the hydrogenation of 1-octene to 2-octene.

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).
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 alkenes 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 MePPh₃ 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 phenylacetylene 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.²⁶,²⁷ By the addition of PPh₃, the conversion of the terminal alkyne is slightly faster than that of the substrate 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 the hydrogenation of terminal alkenes 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-hydrogenation addition.²⁶ Interestingly, MePPh₃ as additive solely enhances the conversion and selectivity using 1-octyne and phenylacetylene, while a deactivation is observed for 2-octyne as substrate. This finding also strengthens the assumption that not only steric but also electronic influences have to be considered.

For a deeper understanding of the positive influence of phosphane additives on the catalytic activity and selectivity of the Pd NPs, mechanistic investigations were carried out by means of in situ NMR, IR and HRTEM measurements. For this, colloidal Pd@TOAB/PPPh₃ NPs were selected as catalyst, since they exhibit an overall high activity, conversion and selectivity for all examined substrates. Furthermore, PdPPh₃ is generally stable towards oxidation under an oxygen containing environment. In the ³¹P-NMR spectrum (recorded in toluene-d₈), 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-octyne and 1 mol% Pd@TOAB NPs, which is supported by IR measurements (SI, Figures S22 and S28). 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 oxidised by air oxygen.²⁸ 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 spectrum 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 ppm, 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 MePPh₃O 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(O) surface, and (c) the enhanced selectivity in semi-hydrogenation catalysis.

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, pH₃ = 1 bar, 1 mol% Pd@TOAB NPs, 1.0 equiv. PPh₃, 2 h reaction time), solvent and byproduct(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

### 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 [%] | Oligomerisation [%] |
|-------|----------|--------------------------|-------------------------------|----------------------|-------------------|
| 1     | –        | 56                       | 22 (5 h)                      | 35 (5 h)             | 43(5 h)           |
| 2     | PPh₃     | 99                       | 83 (2 h)                      | 9 (2 h)              | 6(2 h)            |
| 3     | P(2-toly)₃ | 46                       | 61 (5 h)                      | 32 (5 h)             | 10(5 h)           |
| 4     | P(2-F-phenyl)₃ | 34 | 50 (6 h) | 36 (6 h) | 14(6 h) |

### Table 4. Substrate variation using 1 mol% Pd@TOAB NPs and 1.0 equiv. PPh₃ (catalysis conditions: 0°C, 1.0 bar H₂). PPh₃ amount is based on Pd.

| Entry | Substrate | Additive | Conversion [%] | Selectivity with full conv. [%] | Oligomerisation with full conv. [%] | TOF (h⁻¹) |
|-------|-----------|----------|----------------|-------------------------------|-----------------------------------|-----------|
| 1     | 1-octyne  | –        | 56 (5 h)       | 22 (5 h)                      | 8 (5 h)                           | 330       |
| 2     | 1-octyne  | PPh₃     | 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  | PPh₃     | 72 (4 h)       | 92 (4 h)                      | 0 (4 h)                           | 520       |
| 5     | phenylacetylene | – | 66 (4 h) | 41 (4 h) | 9 (4 h) | 760 |
| 6     | phenylacetylene | PPh₃ | 91 (4 h) | 87 (4 h) | 6 (4 h) | 900 |
when any possible oxygen source during particle synthesis is avoided, no particle stabilisation 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 alkyn, Pd(0) precipitation is observed accompanied by the formation of phosphate oxide, as 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 stabilised by an ionic liquid, which exhibit oxidised surface Pd atoms, as shown by XPS experiments, suggesting that a thin layer of metal oxide is beneficial for particle stabilisation 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 alkyn has a stabilising 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 phosphate is required to remove oxygen species from the palladium surface, resulting in an increased amount of catalytic active sites. An additional phosphate coordination to the palladium surface leads to increased selectivity.

Conclusions

In this work, we demonstrate the enormous influence of ligands on the (a) the catalytic performance of (weakly stabilised) 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 phosphate 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 phosphines show that optimal catalytic performance requires a balance of electron density at the NP. The activity as well as selectivity are strongly influenced by the electron-donating or -withdrawing nature of the added phosphine. We found that both the more electron-donating P(µ-tolyl)₃ as well as the more electron-withdrawing P(µ-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: PPh₃ > P(µ-tolyl)₃ > P(µ-F-phenyl)₃, suggesting that strongly electron-withdrawing phosphines decrease the activity of the surface catalyst atoms. On the other hand, better donors, such as P(µ-tolyl), bind stronger 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 phosphine appears to influence the activity; the stronger the phosphane-Pd bond is, the lower the activity is. Studies with phosphines having different steric demands showed that those with smaller cone angles lead to particle precipitation. Phosphines with a high steric demand e.g. P(o-tolyl)₃, PPh₃ and PCy₃ stabilise 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 stabilising the particle in solution and to allow the 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 phosphate and phosphate oxide species on the metal surface, suggesting that oxygen plays a role in stabilising the colloids in solution, but that it also influences 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 (e.g. Sigma Aldrich, VWR) or synthesised. 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 CD₂Cl₂ and toluene-d₈, at 298 K using a Bruker Avance DPX-250, Bruker DRX 400, Bruker Avance 300 or a Bruker AV400 US spectrometer operating at the corresponding 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” ionisation 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.
The authors declare no conflict of interest.

**Keywords:** colloidal nanoparticles · additive approach · semi-hydrogenation reaction · phosphane ligands · homogeneous catalysis

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We refer to previous works in the area of semiconductor nanomaterials for further information.

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