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Support Engineering for the Stabilisation of Heterogeneous Pd_3P-Based Catalysts for Heck Coupling Reactions

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This work is dedicated to Prof. Dr. Evamarie Hey-Hawkins and her inspiring contributions in the field of phosphorus chemistry.

Herein we report the use of a supported Pd_3P catalyst for Heck coupling reactions. For the stabilisation of Pd_3P and Pd, as reference system, the silica support material was modified via phosphorus doping (0.5 and 1 wt% P). Through this so-called support engineering approach, the catalytic activity of Pd_3P was clearly enhanced. Whereas an iodobenzene conversion of 79% was witnessed for $Pd_3P@SiO_2$ in the coupling of styrene and iodobenzene in 1 h, 90% conversion could be achieved using $Pd_3P@1P\text{-}SiO_2$. This improved catalytic activity probably stems from an electronic modulation of the support surface via the introduction of phosphorus. Simultaneously, the recyclability was boosted and the $Pd_3P@1P\text{-}SiO_2$ catalyst has shown to maintain its catalytic activity over several recovery tests. Hereby, metal leaching could almost be suppressed completely to 3% by the use of a P-modified silica support.

Introduction

The use of phosphorus in catalysis has greatly been extended from the conventional application as phosphine ligands in homogeneous catalysis[1–3] and has now also found significant attention in the field of heterogeneous catalysis.[4–6] Hereby, transition metal phosphides have been investigated in detail in various catalytic reactions,[7] such as hydroformylation,[8–10] hydrogenation,[11–19] photocatalytic Suzuki coupling[20] and desulfurization reactions.[21–23] The high catalytic activity of transition metal phosphides can be traced back to the dilution of the transition metal using phosphorus, which leads to the formation of highly uniform and defined "frustrated" single metal sites.[4,9,10] This d-metal/p-block element combination strategy not only leads to the formation of highly active catalysts but can also be associated with a convenient catalyst synthesis, a low (noble) metal content and an improved catalyst stability.

On this basis, we recently have investigated the use of supported palladium phosphides as catalysts for the Wacker–Tsuji-oxidation of alkenes.[24] Through the incorporation of phosphorus into palladium and the subsequent formation of palladium phosphide, an enhanced selectivity and catalytic activity could be achieved in comparison with a purely Pd-based catalyst.[24] At the same time, the application of metal phosphides opens the perspective to reduce the noble metal content in comparison with pure Pd catalysts, which is important for a sustainable use of scarce metal resources. These outcomes paved the way for employing this system in further reactions, which are up-to-date majorly catalysed by pure palladium.

In this context, one very well-established application of Pd-based catalysts are Heck-coupling reactions, enabling the C–C bond formation starting from olefins and aryl or vinyl halides.[11,25–27] For this type of coupling reactions palladium-based complexes have extensively been investigated as homogenous catalysts showing moderate to excellent yields.[28–30] However, these reaction systems have the disadvantage of requiring complex techniques for the catalyst separation from the reaction mixture and therefore the catalyst reuse is largely limited.[31] Therefore, the application of solid state, heterogeneous catalysts, facilitating a facile catalyst separation, has gained considerable attention, not only in an academic but also in an industrial context.[25,31–36] A topic of debate is hereby the true heterogeneous nature of these catalysts, as there is literature evidence on leached Pd species, which could function as actual catalyst in the liquid phase.[25,34,37,38] This would make the use of a heterogeneous catalyst obsolete and also results in a tremendous metal loss (metal leaching) and consequently a hampered catalyst recovery and recycling.[33–35]

To overcome metal leaching and also to avoid the agglomeration of metal species during the reaction in heterogeneous catalysts, various strategies have been investigated,[39,40] whereby the main goal is an enhanced

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Part of a Special Collection on the p-block elements.

fixation of the catalytically active species on the support surface. For example, the support surface has been modified by different methods, such as by the use of various functional groups on the surface,[41] the introduction of defects into metal oxides[42] or the implementation of dopants (e.g. sulphur,[43,44] nitrogen[44–48] or oxygen[49,50]) into the support. The concept of doping, for example nitrogen doping, has found particularly attention for carbon-based supports,[51,52] and has demonstrated to be very successful in liquid phase reactions.[53] However, only very few examples include the use of phosphorus as dopant for support materials.[54–61] This seems counterintuitive since phosphine ligands have been shown extraordinary compounds for the coordination of transition metals in the field of homogeneous catalysis. Also, in the few studies reported, it was proven that phosphorus doping of support materials has the potential to result in an enhanced thermal stability and modified coordination environment of the catalytically active species, which finally influences the catalytic performance.[6,62,63]

The goal of this study is the investigation of heterogeneous Pd-based catalysts for Heck coupling reactions. The main focus was hereby a sustainable catalyst design, which requires a highly active catalyst with a low noble metal content, which can easily be recycled after the reaction without any substantial loss in catalytic activity. To achieve these goals, two approaches are pursed. Firstly, according to the d-metal/p-block element strategy, a Pd_3P-based catalyst with highly defined and uniformly distributed metal sites was synthesized. Secondly, the catalysts stability and consequently recyclability were enhanced via a so-called support engineering approach. Therefore, phosphorus, as dopant and anchoring point, was incorporated into silica as carrier material for Pd_3P. Pure Pd catalysts were considered as reference systems.

Results and Discussion

Support and catalyst synthesis and characterization

Phosphorus-modified silica supports were synthesized via impregnation of $NH_4H_2PO_4$ on silica. Earlier studies have achieved the synthesis of P-doped supports through the treatment of the corresponding support material with various P-precursors, such as H_3PO_4,[61] PPh_3[58,59] or $NH_4H_2PO_4$[55,57] followed by a calcination step. $NH_4H_2PO_4$ was selected as P-precursor in this study, due to its nontoxic and noncorrosive character, which simplifies the synthetic procedure. Depending on the phosphorus loading on the silica, the supports are labelled as 0.5P-SiO_2, 1P-SiO_2 and 5P-SiO_2, corresponding to 0.5 wt%, 1 wt% and 5 wt% P loading, respectively. Subsequently the impregnated silica samples were calcined under air. Throughout the thermal treatment the decomposition of $NH_4H_2PO_4$, forming NH_3 and H_3PO_4 is taking place,[64–66] whereby the in-situ formation of H_3PO_4 ultimately serves as phosphorus source for the silica modification. To find a suitable temperature for the thermal treatment, silica impregnated with $NH_4H_2PO_4$ was firstly analysed via TG-DTA (Thermogravimetric Analysis-Differential Thermal Analysis). The TG analysis was performed under air up to 650 °C with a temperature ramp of $10\,K\,min^{-1}$. The complete decomposition of $NH_4H_2PO_4$ was found to take place around 400 °C (Figure S18). Hence, a calcination temperature of 600 °C was selected for the preparation of P-modified supports to ensure the complete decomposition of $NH_4H_2PO_4$.

The modified supports were characterized using PXRD (Powder X-ray diffraction). However, even with a 5 wt% P loading no reflexes were visible, which indicates the amorphous nature of the formed phosphorus-containing species (Figure S1). It seems reasonable to assume the formation of phosphate species on the silica surface, since similar reaction conditions and subsequent observations were reported for the formation of silicon phosphates, such as $Si_3(PO_4)$ and $Si(HPO_4)_2\cdot H_2O$,[67] on silica.[68,69] Further a TG analysis (Figure S19) was performed for the 5P-SiO_2 support and a mass loss of 2.5% till approximately 350 °C could be observed, which indicates the loss of phosphorus species and adsorbed water from the support.

SEM analysis (Scanning Electron Microscopy) in conjunction with EDX (Energy-Dispersive X-ray Spectroscopy) measurements were carried out for the phosphorus-modified support materials. The EDX elemental mapping of phosphorus modified supports with 1 and 5 wt% phosphorus loading (1P-SiO_2 and 5P-SiO_2) indicated the presence of phosphorus on the silica support and showed a uniform distribution of P on the support (Figure 1, Figures S12 and S13). These observations confirmed the success of the described method for the phosphorus modification of silica. However, probing an element with composition of less than 1 wt% is indeed difficult with the capacity of SEM-EDX, and consequently elemental mapping results of the 0.5P-SiO_2 support material could not be obtained.

Inspired by the great catalytic performance of $Pd_3P@SiO_2$ in catalytic Wacker–Tsuji oxidation reactions of alkenes,[24] Pd_3P on silica and Pd on silica, as reference catalyst, were prepared for the application in Heck coupling reactions as part of this study. Therefore, either unmodified silica or the P-modified silica samples described before, were used as support materials. A

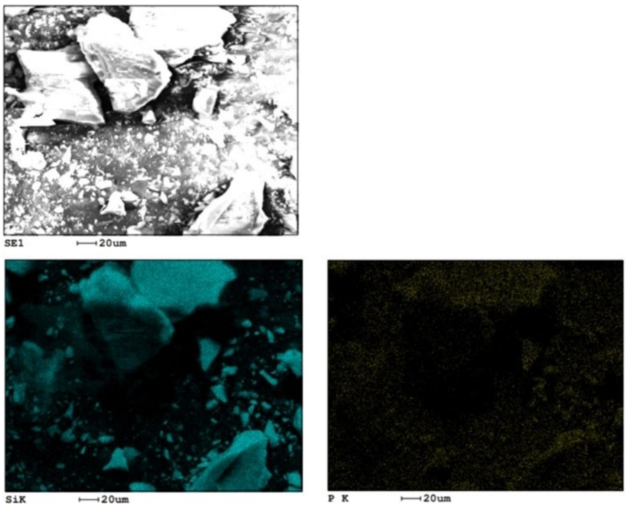

Figure 1. SEM image and EDX mapping of 1P-SiO_2, confirming the uniform P distribution on silica.

short overview of the catalysts, which are in the focus of this paper, is given in Table 1. For all catalyst syntheses, an impregnation loading of 10 wt% Pd on silica was selected, considering the facile phase identification of the materials via powder X-ray diffraction.

Supported Pd_3P on silica ($Pd_3P@SiO_2$) was synthesized according to a modified literature procedure.[8,24] Phosphoric acid (H_3PO_4) and palladium acetate ($Pd(OAc)_2$) were impregnated on silica with an exact Pd/P ratio of 3 and the sample was consequently reduced in pure hydrogen at 400 °C for 4 h. The PXRD analysis of the obtained product showed the formation of the Pd_3P phase. However, reflexes corresponding to metallic Pd at diffraction angles of 46.9° and 82.5° could also be observed in the diffractogram, indicating an incomplete phase formation (Figure 2a). Consequently, the duration of the thermal treatment was extended to 8 h, which resulted in the successful formation of phase pure Pd_3P ($Pd_3P@SiO_2$, Figure 2b). Broad reflexes, possibly due to small particle sizes, were observed for the synthesized palladium phosphide ($Pd_3P@SiO_2$) in comparison to the literature reported supported Pd_3P, which was synthesized using $NH_4H_2PO_4$ as phosphorus source.[70] However, $NH_4H_2PO_4$ was not used as phosphorus precursor in this study, since the Pd_3P formation on silica is only successfully using a large excess of $NH_4H_2PO_4$, which ultimately results in phosphorus-containing residues on the silica support.

Table 1. Overview of the prepared catalysts.

Catalyst	Description
$Pd@SiO_2$	Prepared with $Pd(OAc)_2$ on silica
$Pd@1P\text{-}SiO_2$	Prepared with $Pd(OAc)_2$ on 1 wt% P-modified silica
$Pd_3P@SiO_2$	Prepared with $Pd(OAc)_2$ and H_3PO_4 on silica
$Pd_3P@0.5P\text{-}SiO_2$	Prepared with $Pd(OAc)_2$ and H_3PO_4 on 0.5 wt% P-modified silica
$Pd_3P@1P\text{-}SiO_2$	Prepared with $Pd(OAc)_2$ and H_3PO_4 on 1 wt% P-modified silica
$Pd_3P@5P\text{-}SiO_2$	Prepared with $Pd(OAc)_2$ and H_3PO_4 on 5 wt% P-modified silica (prepared only for characterization purposes)

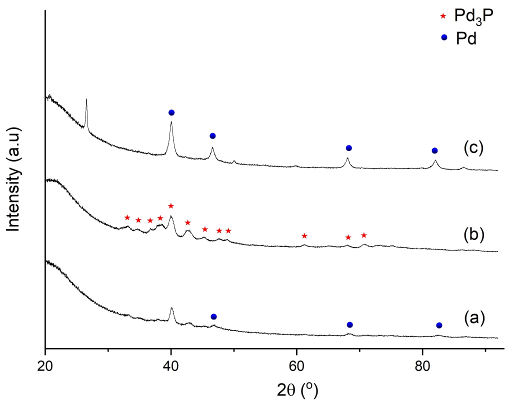

Figure 2. PXRD patterns of H_3PO_4 and $Pd(OAc)_2$ on silica treated thermally in various conditions: a) in H_2 atmosphere at 400 °C for 4 h, b) in H_2 atmosphere at 400 °C for 8 h, c) heating b to 600 °C for 6 h in Ar. *: Pd_3P [COD ID: 1539070] •: Pd [COD ID: 1011104].

In order to enhance the particle size through sintering and to obtain a clearer diffraction pattern, the synthesized $Pd_3P@SiO_2$ was heated to 600 °C for 6 h in argon. However, this only results in the loss of phosphorus and the formation of pure Pd (Figure 2c). These findings are in line with the reported formation mechanism of supported Pd_3P, starting with the formation of metallic Pd during the thermal treatment in H_2 followed by further incorporation of phosphorus forming palladium phosphide.[14,24] Applying an increased temperature only leads to the loss of P from the structure and ultimately results in the formation of metallic Pd.

For the synthesis of the purely Pd-based reference catalyst ($Pd@SiO_2$) similar conditions were applied as for the synthesis of $Pd_3P@SiO_2$. Again $Pd(OAc)_2$ was impregnated on silica, this time without the addition of phosphoric acid, and the sample was consequently treated for 8 h at 400 °C in pure hydrogen to obtain phase pure palladium on silica (Figure S3).

For the preparation of Pd_3P on support engineered SiO_2, $Pd(OAc)_2$ and H_3PO_4 with a Pd/P molar ratio of 3 were impregnated on the P-modified silica supports. Subsequently, the systems underwent thermal treatment in pure H_2 at 400 °C for 8 h. In all cases, PXRD analyses indicated the formation of the desired Pd_3P phase confirming the suitability of the applied synthesis method (Figure S2). Similarly, Pd on P-modified silica was synthesized and analysed via PXRD (Figure S3).

The prepared catalysts were further characterized with ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy) to quantify the Pd and P content within the samples. The Pd/P molar ratio of $Pd_3P@SiO_2$ was determined to be 2.31, with a Pd content of 8.60 wt%. Analysis of the Pd and P contents in $Pd@1P\text{-}SiO_2$ resulted in 9.30 wt% Pd and 0.72 wt% P and the deviation from the added 1 wt% can be due to a slight loss of phosphorus during the thermal treatment. Details of the ICP-AES results are provided in Table S5.

SEM analyses were performed for Pd and Pd_3P on silica catalysts ($Pd@SiO_2$, $Pd_3P@SiO_2$). In both cases, particles distributed on a porous structure, indicating Pd or Pd_3P particles on silica, can be observed (Figures S10 and S11). For all samples ($Pd@SiO_2$, $Pd_3P@SiO_2$, $Pd_3P@1P\text{-}SiO_2$ and $Pd_3P@5P\text{-}SiO_2$), EDX analyses were performed in conjunction with SEM measurements to quantify the Pd, P and Si contents and to map the elemental distribution within the materials. The EDX spectra and the elemental compositions obtained for the materials are provided in the Supporting Information (Figures S14–S17) and the mapping results show a uniform distribution of Pd and P on silica. The compositions determined are comparable to the values estimated from the precursor stoichiometry. Further, the distinct increase in phosphorus content can be observed from the EDX analysis of the samples on the P-modified supports. Exemplarily the SEM image and the EDX mapping of $Pd_3P@1P\text{-}SiO_2$ are shown in Figure 3.

Catalytic Heck coupling reactions

The catalytic performance of Pd_3P on silica and P-modified silica was evaluated in Heck coupling reactions using iodobenzene

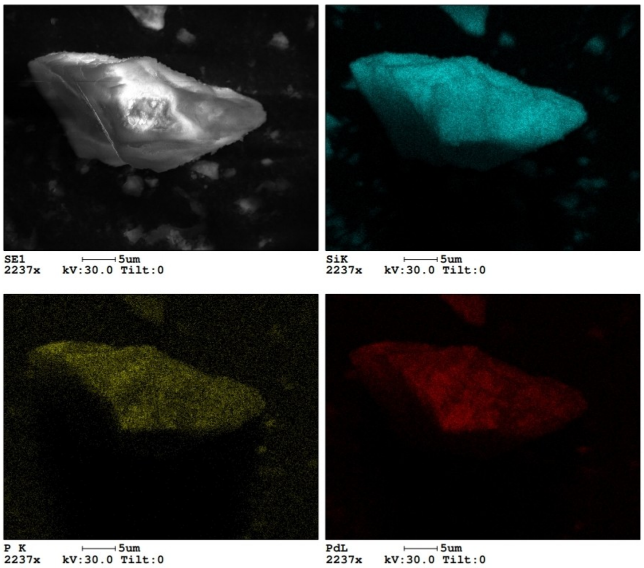

Figure 3. SEM image and EDX mapping of $Pd_3P@1P\text{-}SiO_2$, confirming the uniform P and Pd distribution on silica.

and styrene as test substrates. The investigation was further extended to the coupling reaction of styrene and methyl 4-iodobenzoate as well as iodobenzene and methyl acrylate. The reaction schemes are provided in the Supporting Information (Figure S21). Pure Pd on silica and Pd on P-modified silica were used as reference catalysts for this study and all conversions of the catalytic tests were determined via GC MS using *n*-decane as internal standard.

As a starting point for the investigation of the catalytic performance, tests using $Pd_3P@SiO_2$ as catalyst were performed in different solvents (DMF, NMP, DMSO) using various bases (K_2CO_3, K_3PO_4, Et_3N). The results are summarized in Table 2. The reaction systems utilising K_3PO_4-DMSO (Table 2, entry 6) and Et_3N-DMSO (Table 2, entry 5) were found to be the most promising, whereby conversions of 81% and 79% could be achieved in 1 h. Hence, further tests to assess the performance of the synthesized catalysts were conducted under these reaction conditions. Without the addition of base (Table 2, entry 7) a drop of the conversion to only 10% was observed, which is the result of insufficient catalyst regeneration at the end of the catalytic cycle in the absence of a base.

Table 2. Catalytic activity of $Pd_3P@SiO_2$ in various solvent - base systems.

Entry	Reaction time [min]	Solvent	Base	Conversion [%]
1	40	DMF	K_3PO_4	20
2	40	NMP	K_3PO_4	57
3	40	DMSO	K_3PO_4	75
4	40	DMSO	K_2CO_3	40
5	60	DMSO	Et_3N	79
6	60	DMSO	K_3PO_4	81
7	60	DMSO	–	10

Reaction conditions: styrene (1 mmol), iodobenzene (0.6 mmol), base (1 mmol), solvent (10 mL), $Pd_3P@SiO_2$ (10^{-3} mmol·mL^{-1}, Pd basis). Reactions were carried out at 140 °C. Conversions were calculated considering the concentration of iodobenzene.

Since superior performance of palladium phosphide catalysts in comparison to pure Pd has been reported in the literature in the context of hydrogenation,[71,72] hydrogen evolution,[73] and Wacker oxidation reactions,[24] catalytic tests using $Pd@SiO_2$ as reference catalyst were carried out. The comparison tests were performed using $Pd_3P@SiO_2$ and $Pd@SiO_2$ as catalysts (10^{-3} mmol·mL^{-1}, Pd basis) in DMSO at 140 °C for 60 min with K_3PO_4 as base. The conversion of iodobenzene was found to be 81% (Table 2, entry 6) using $Pd_3P@SiO_2$ as catalyst, while a comparable conversion of 86% was obtained for the reference catalyst $Pd@SiO_2$. In both cases a 100% selectivity towards stilbene was achieved. In order to verify the trend of the results at lower catalyst concentrations, the concentrations of the catalysts were reduced to 1/3rd of the pervious quantity ($3.3\cdot10^{-4}$ mmol·mL^{-1} instead of 10^{-3} mmol·mL^{-1} Pd in reaction system) and tests were performed at the conditions mentioned above (Figure S22). These results suggest that the incorporation of phosphorus into the metal structure and the subsequent Pd_3P phase formation does not diminishes its catalytic activity in comparison to the purely Pd-based catalyst (only 5% conversion difference using K_3PO_4 as base).

In a next step the influence of the support engineering, using phosphorus-modified silica as support material for Pd_3P and Pd, on the catalytic activity was investigated. Three catalysts, namely $Pd@1P\text{-}SiO_2$, $Pd_3P@1P\text{-}SiO_2$ and $Pd_3P@0.5P\text{-}SiO_2$ were tested as catalysts for the Heck coupling using Et_3N as base and the conversions of iodobenzene were determined after 60 min reaction time (Table 3). While no predominant variation of activity can be shown in the case of the purely Pd-

Table 3. Catalytic activity of Pd and Pd_3P on P-modified and unmodified silica supports.

Entry	Catalyst	Pd loading on SiO_2 [wt%]	Mol percentage of Pd [mol%]	Conversion [%]
1	$Pd@SiO_2$	10	1.6	92
2	$Pd@1P\text{-}SiO_2$	10	1.6	89
3	$Pd_3P@SiO_2$	10	1.6	79
4	$Pd_3P@0.5P\text{-}SiO_2$	10	1.6	90
5	$Pd_3P@1P\text{-}SiO_2$	10	1.6	90
6	$Pd_3P@1P\text{-}SiO_2$[a]	10	1.6	10
7	$Pd_3P@1P\text{-}SiO_2$	5	1.6	89
8	$Pd_3P@1P\text{-}SiO_2$	1	1.6	91
9	$Pd_3P@1P\text{-}SiO_2$	5	0.8	96
10	$Pd_3P@1P\text{-}SiO_2$	1	0.16	83

Reaction conditions: styrene (3 mmol), iodobenzene (1.8 mmol), base Et_3N (3 mmol), solvent DMSO (30 mL), catalyst (entry 1–8: 10^{-3} mmol·mL^{-1}, entry 9: $5\cdot10^{-4}$ mmol·mL^{-1}, entry 10: 10^{-4} mmol·mL^{-1}, Pd basis). Reactions were carried out at 140 °C for 60 min. Conversions and mol percentages were calculated considering the concentration of iodobenzene. [a]Reaction was carried out without any base.

based catalysts (entry 1 and 2), the Pd_3P catalysts on P-modified SiO_2 show an enhanced conversion of iodobenzene in contrast to Pd_3P on unmodified SiO_2. An increase of 11 % conversion was recorded for $Pd_3P@0.5P\text{-}SiO_2$ (entry 4) and $Pd_3P@1P\text{-}SiO_2$ (entry 5) in comparison to $Pd_3P@SiO_2$ (entry 3). This enhanced performance might be resulting from a modulation of the electronic environment via a charge transfer[74] from Pd to the P-modified support. At this point the catalytic performance of Pd_3P on the P-modified supports seems independent of the extent of phosphorus doping (0.5 versus 1 wt % P on silica). In all of these cases 100 % selectivity towards the stilbene product was observed.

Similar observations were made for Pt single atoms on phosphorus-modified CeO_2, where the tailoring of the Pt coordination environment via phosphorus led to a tremendous rise of the catalytic activity in hydrogenation reactions. The authors contributed this activity enhancement to a charge transfer from Pt to P, thus giving rise to a significantly higher valence state of Pt.[55]

To underline the potential of this catalytic system, the Pd quantity on the support material was further reduced to 5 wt % and 1 wt % and the overall Pd concentration in the reaction mixture was lowered (Table 3, entry 7 to 10). The PXRD patterns of the $Pd_3P@1P\text{-}SiO_2$ catalysts with various Pd loadings are provided in Figure S9. The catalytic test results show that independent of the Pd loading on the support and the molar Pd to iodobenzene ratio, high (consistent) conversions can be achieved using $Pd_3P@1P\text{-}SiO_2$. However, due to the unambiguous phase identification of the fresh and the recovered catalyst via PXRD, the $Pd_3P@1P\text{-}SiO_2$ catalysts for all further catalytic tests within this publication refer to catalysts with 10 wt % Pd loading on silica.

To further benchmark the catalytic performances of $Pd_3P@SiO_2$ and $Pd_3P@1P\text{-}SiO_2$ in comparison with other literature-reported heterogeneous Pd-based catalysts, the substrate scope was extended and Heck coupling reactions using iodobenzene and methyl acrylate were carried out. The test conditions were adapted from Nuri et al. using dimethyl amine (DMA) as solvent and Et_3N as base.[37] The reactions were conducted at 140 °C for 60 min and resulted in 100 % conversion of iodobenzene and 100 % selectivity towards methyl cinnamate (Figure S24). The results obtained using $Pd_3P@SiO_2$ and $Pd_3P@1P\text{-}SiO_2$ as catalysts are indeed very promising in comparison with other literature reported catalysts (Table S3).

Catalyst recovery tests

As mentioned before, the aim was not only to tune the catalytic performance through the use of metal phosphides and subsequent surface engineering but also to enhance the catalyst stability and reduce metal leaching. Therefore, the catalysts from the tests mentioned before were recovered by centrifugation, washed with acetone and dried for subsequent recovery tests.

Indeed, as shown in Figure 4, the recovered catalysts which underwent surface engineering via phosphorus modification show very promising recycling results. Whereas a drop in iodobenzene conversion of 21 % (from 92 % to 71 %, recovery test 1) was observed for the $Pd@SiO_2$ reference catalyst, only a 11 % drop in conversion was observed for the $Pd@1P\text{-}SiO_2$ catalyst.

Similar observations were made for the Pd_3P-based catalytic systems. Hereby, a drop in conversion of 12 % was observed after the first run using $Pd_3P@SiO_2$, followed by a further drop of 7 % in the third run. In contrast, the iodobenzene conversions using Pd_3P on P-modified silica are only reduced by 4 % for $Pd_3P@0.5P\text{-}SiO_2$ and 6 % using $Pd_3P@1P\text{-}SiO_2$. Even though after the first run, $Pd_3P@0.5P\text{-}SiO_2$ showed only a slight drop in conversion (4 %), an immense drop (24 %) can be noticed in the third run indicating a major loss of activity. In contrast, the catalytic activity of the twice recovered $Pd_3P@1P\text{-}SiO_2$ stays almost constant. This underlines that the extent of phosphorus loading (0.5 versus 1 wt % P) on the support does have a clear impact on the recycling behaviour.

Comparing all the recovery test results, a superior recycling performance can be observed for $Pd_3P@1P\text{-}SiO_2$ in comparison to other catalysts discussed. The catalysts recovered after each run were analysed with PXRD and the results are presented in the Supporting Information (Figures S4–S8). Except a decrease in reflex intensities contributed by reduced crystallinity after each run, there are no changes in the phase observed from the PXRD patterns.

Since such exceptional recovery results were observed for $Pd_3P@1P\text{-}SiO_2$, a base variation was investigated. Hence, recovery tests were performed in similar conditions using K_3PO_4 as the base (Figure 5). The major problem during these tests was the limited solubility of K_3PO_4 in DMSO, demanding multiple washings with solvents, such as water and acetone, in order to obtain the pure catalyst during recovery. Due to

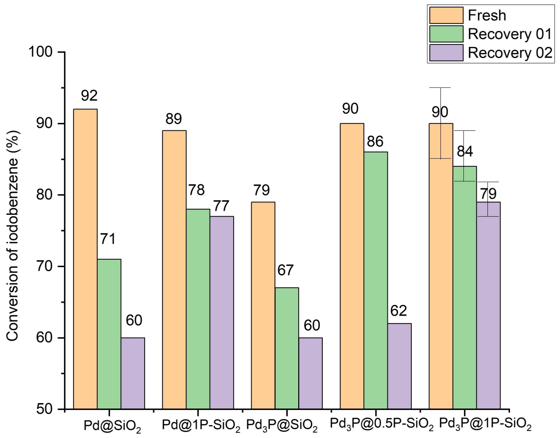

Figure 4. Results of recovery test conducted for the synthesized catalysts. Reaction conditions: styrene (0.1 $mmol \cdot mL^{-1}$), iodobenzene (0.06 $mmol \cdot mL^{-1}$), Et_3N (0.1 $mmol \cdot mL^{-1}$), solvent (DMSO), catalyst (10^{-3} $mmol \cdot mL^{-1}$, Pd basis). Reactions were carried out at 140 °C for 60 min. Conversions were calculated considering the concentration of iodobenzene. The error bars for the recovery experiment using $Pd_3P@1P\text{-}SiO_2$ were obtained from repetition experiments.

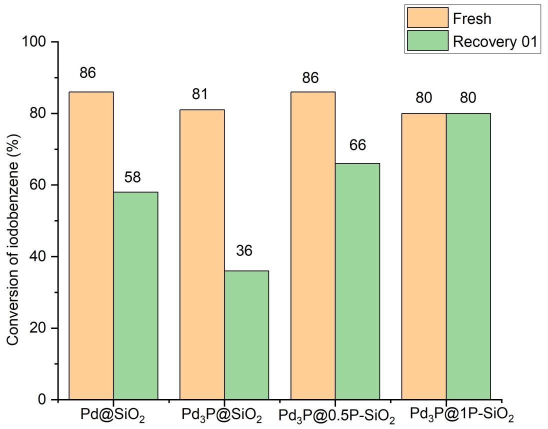

Figure 5. Results of recovery test conducted for the synthesized catalysts up to two runs. Reaction conditions: styrene (0.1 mmol·mL^{-1}), iodobenzene (0.06 mmol·mL^{-1}), K$_3$PO$_4$ (0.1 mmol·mL^{-1}), solvent (DMSO), catalyst (10^{-3} mmol·mL^{-1}, Pd basis). Reactions were carried out at 140 °C for 60 min. Conversions were calculated considering concentration of iodobenzene.

the difficulty in recovering process, only one recovery run was performed to obtain an indication about the catalyst performances.

A dominant drop in conversion is clearly visible after the first run conducted with Pd@SiO$_2$ and Pd$_3$P@SiO$_2$, whereas the conversion remained the constant using the support-engineered Pd$_3$P@1P-SiO$_2$ catalyst. Despite the fact, that the initial conversion using Pd$_3$P@0.5P-SiO$_2$ is about 6% higher than the activity observed for Pd$_3$P@1P-SiO$_2$, a 20% drop in conversion could be observed for Pd$_3$P@0.5P-SiO$_2$ after one round of recycling. This is still less activity loss compared to the unmodified supports, however, the finding confirms that the amount of phosphorus used for the surface engineering plays a critical role for the recycling behaviour. Overall, the superior recycling behaviour of Pd$_3$P@1P-SiO$_2$ in comparison to the other catalysts could be demonstrated again.

Another recovery test set has been performed using methyl 4-iodobenzoate and styrene in presence of Et$_3$N in DMSO. As shown before, in the case of the coupling reaction of iodobenzene and styrene, a slight increase in catalytic activity and an enhanced catalyst stability during the recycling tests were observed when Pd$_3$P on P-modified silica, instead of the unmodified support, was used. A clear stability enhancement was also witnessed for the pure Pd-based catalysts, Pd@1P-SiO$_2$, compared to Pd@SiO$_2$. These experiments confirmed the superior behaviour using P-modified supports (Figure S25).

Metal leaching investigation

From all the above results, the positive influence of the support engineering using phosphorus in the field of catalytic Heck coupling reactions using Pd and Pd$_3$P was noticed. Not only the catalytic activity could be enhanced in the case of Pd$_3$P (depending on the base and phosphorus-loading on the support), but also the recyclability was greatly improved. From the catalytic test and recycling data the 1 wt% phosphorus-modified support has shown to be the lead support candidate. This could be due to the fact that the phosphorus engineered supports may contribute to an enhanced support-metal interaction, which fixated the active metal species via phosphorus anchoring points.

To confirm this in greater detail, the metal leaching during the catalytic reaction was investigated by hot filtration tests and ICP-AES measurements of the fresh versus the recycled catalysts. This is very important since especially in heterogeneously catalysed Heck reactions high metal leaching rates of 17%,[37] 26%[38] and even 79%[75] have been reported in the literature. To investigate the influence of leached Pd species, hot filtration tests were conducted for the support modified and unmodified Pd and Pd$_3$P catalysts. In the case of the filtration of the hot reaction mixture, leached Pd species should in theory still be in solution and hopefully not be re-deposited on the surface yet.[76,77] Hereby, the mechanism of Pd species leaching from the solid material, catalysing the coupling reaction and redepositing to the surface is well discussed in literature.[37,78–80] Surprisingly, after the removal of the catalysts no substantial further conversion has been observed. The details of the test results are provided in the Supporting Information (Table S4). This hints towards the fact that no catalytically active species are leached from the metal catalysts. However, the hot filtration tests cannot proof that there is no metal leaching at all occurring, since also catalytically inactive metal species can be leached from the catalyst or metal species can become inactive during the leaching process.

Therefore, ICP-AES analyses of the solid catalysts before the first reaction and after one recovery were performed in addition to the hot filtration tests. Detailed mass percentages are given in the Supporting Information (Table S5). The amount of leaching and thus the impact of P-modification on the prevention of leaching is shown in Table 4. ICP-AES results indicate a strong susceptibility of Pd@SiO$_2$ and surprisingly Pd@1P-SiO$_2$ towards leaching. However, recovery catalytic tests confirm a superior behaviour of Pd@1P-SiO$_2$ compared to Pd@SiO$_2$. When Pd$_3$P is used instead of Pd, the leaching is tremendously reduced. This can be seen as a great advantage when metal phosphides are used instead of pure metals. The phosphorus within the phosphide structure already acts as

Table 4. Leaching of Pd after first recovery determined by ICP-AES of the fresh and recovered catalysts. Leaching was calculated according to the percentage of inert SiO$_2$ material. ICP-AES results are given in Table S5.

Catalyst	Pd leaching [%]
Pd@SiO$_2$	21
Pd@1P-SiO$_2$	25
Pd$_3$P@SiO$_2$	8
Pd$_3$P@1P-SiO$_2$	3

Reaction conditions: styrene (0.1 mmol·mL^{-1}), iodobenzene (0.06 mmol·mL^{-1}), Et$_3$N (0.1 mmol·mL^{-1}), solvent (DMSO, 30 mL), catalyst (10^{-3} mmol·mL^{-1}, Pd basis). Reaction carried out at 140 °C for 60 min.

inherent stabilisation agent. This effect can further be extended through the use of P-modified supports. When using Pd_3P@1P-SiO_2 for example only 3% leaching is observed, which is a remarkably low number in the field of heterogeneously catalysed Heck coupling reactions.

Conclusions

In this paper we investigated supported Pd_3P-based catalysts for Heck coupling reactions with the aim to find sustainable heterogeneous alternatives to conventional (typically homogeneous) palladium Heck coupling catalysts especially in terms of leaching prevention.

While the catalytic activity during the coupling reaction of iodobenzene and styrene with K_3PO_4 as base was comparable using Pd_3P@SiO_2 and the reference Pd@SiO_2 catalyst (81% versus 86% conversion in 1 h), a significantly enhanced catalyst stability could be observed when Pd_3P@SiO_2 in the presence of Et_3N as base was used. The catalytic activity of Pd_3P could be further improved via a so-called surface engineering approach, whereby silica was modified using phosphorus doping. Whereas in the coupling reaction of iodobenzene and styrene in the presence of Et_3N as base, a conversion of 79% was witnessed in 1 h using Pd_3P@SiO_2 as catalyst, 90% conversion was achieved through the use of Pd_3P on P-modified SiO_2 (Pd_3P@1P-SiO_2). This activity enhancement probably stems from charge transfer processes from the metal centre to the phosphorus species incorporated into the silica support. Moreover, through support engineering the catalyst stability could be even more increased and the lead candidate Pd_3P@1P-SiO_2 could be recycled reproducibly over 3 recovery tests without any substantial loss in catalytic activity. This finding was underlined by the remarkably low metal leaching of only 3% found for the Pd_3P@1P-SiO_2 system. The great catalyst stability is probably induced via a strong metal-support interaction through phosphorus-based anchoring points on the silica support. An enhanced catalyst stability, due to the P modification, was also demonstrated in the Heck coupling reaction of styrene and methyl 4-iodobenzoate with Et_3N. A drop of 22% in conversion was recorded for Pd_3P@SiO_2 after one round of catalyst recycling, whereas for the P-modified system (Pd_3P@1P-SiO_2) a decrease of only 10% was witnessed.

Based on these results, surface engineering is a promising approach to control and tune the metal's catalytic activity and to enhance the catalyst stability by the prevention of metal leaching. Future investigations will be focused on the extension of this concept towards other support materials.

Experimental Section

Starting materials

Palladium acetate ($Pd(OAc)_2$) with a purity of $\geq$99.9%, methyl acrylate (purity 99%), styrene (purity $\geq$99%) and potassium carbonate (purity $\geq$99%) were purchased from Sigma Aldrich, while iodobenzene (purity $\geq$99%) and methyl 4-iodobenzoate (purity $\geq$98%) were purchased from TCI. Silica (Cariact,Q 20 C) was purchased from Fuji Silysia Chemical Ltd and was used as the support material for the catalyst. The solvents DMSO (purity $\geq$99.9%) and acetone (HPLC grade) along with ortho-phosphoric acid (85%) were purchased from Fischer Scientific GmbH. NMP (purity $\geq$99.5%), HCl (37%) and DMF (purity $\geq$99.8%) were obtained from Acros and *n*-decane (purity 99%), which was used as an internal standard for GC measurements, as well as triethylamine (Et_3N) with a purity of 99% were bought from abcr GmbH. DMA with a purity 99% was purchased from Alfa Aesar and potassium phosphate trihydrate (purity $\geq$99%) was purchased from Carl Roth. Hydrogen gas (purity 99.999%) was purchased from Air Liquide. All chemicals were used without further purification.

Instruments

PXRD measurements were performed on a Stoe STADI-MP diffractometer operating with a Ge-monochromatized Cu source ($\lambda = 1.54178$ Å) in transmission mode. For the measurements about 3–5 mg of grinded sample were placed between thin films, which were then transferred to the sample holder. The measurements were performed from 2° to 92° (2θ) with a step size of 3° and a total measurement time of 80 min. TG-DTA measurements were conducted in Al_2O_3 crucibles with a simultaneous thermal analysis STA 409 coupled to a TASC 414/2 controller and a PU 1.851.01 power unit from Netzsch. Analyses were carried out from 30 °C to 650 °C with a ramp of $10\,^{\circ}C \cdot min^{-1}$ and an empty Al_2O_3 crucible as reference. SEM measurements were performed using a Zeiss Supra 40 VP microscope (Zeiss, Germany), equipped with a Schottky field emitter (2.0 nm resolution) at typically 15 keV. The powdered samples for the SEM analyses were dispersed in water, further dripped on a silicon wafer, attached to the sample holder and dried to obtain a thin layer of particles. EDX measurements were carried out with the help of a Supra40VP from Zeiss using a Sapphire Si(Li) detector from the company EDAX Genesis. Therefore, samples were either prepared as thin powder layer or through drop casting a water suspension on carbon tape. Due to the choice of the support, charging effects of certain samples were observed during the SEM and EDX measurements. ATR-IR spectra were recorded in the region of 4000–400 cm^{-1} using a Bruker Tensor 37 FTIR spectrometer equipped with a room temperature DLaTGS detector, a diamond ATR (attenuated total reflection) unit and a nitrogen-flushed measurement chamber. ICP-AES measurement were performed in an iCap 6500 device from ThermoFisher Scientific. The samples were therefore dissolved in nitric acid, hydrofluoric acid and hydrochloric acid at 130 °C for 12 h using a digestion system. $Pd(OAc)_2$ as well as all synthesized catalysts were stored in an Argon-filled glovebox (MBraun) prior to use to avoid undesired surface oxidation. The reactants and products from the catalytic testing were analysed qualitatively and quantitatively using an Agilent GC MS model 8860 GC and 5977B MSD with *n*-decane as internal standard. In a standard GC MS analysis, 20 μL sample (taken from the reaction mixture and filtered through a 0.2 μm syringe filter) were added to 1 mL acetone. 1 μL of this mixture was then automatically injected into the GC MS system with a plunger speed of 1000 $\mu L\,min^{-1}$, a split ratio of 100:1 and an injection temperature of 250 °C. For the measurements a fused silica capillary column (ID: 0.25 mm, film thickness: 0.25 μm, and length: 30 m) was used along with the following program: 2.25 min at 50 °C and then ramped at 40 °C·min^{-1} up to 240 °C for 1 min with helium as a carrier gas. In order to confirm the product spectrum, all catalysts were tested for higher conversions and longer GC analyses were performed with the following temperature program: injection temperature 290 °C, 2.25 min at 50 °C and then ramped at 10 °C·min^{-1} up to 280 °C for 1 min with helium as carrier gas. The conversions were estimated based on the area ratios of the substrate and the internal standard using the Agilent Mass Hunter software.

Preparation of phosphorus-modified silica

For a 1 wt% phosphorus modification (1P-SiO_2), 1.00 g of silica is impregnated with a solution of 37.1 mg (0.32 mmol) of $NH_4H_2PO_4$ in 0.9 mL of water. The mixture is subsequently dried at 60 °C for 12 h. The support then underwent thermal treatment in air at 600 °C for 6 h with a temperature ramp of 15 K/min. The procedure was repeated with half the amount of $NH_4H_2PO_4$, yet equal volume of water to obtain 0.5 wt% phosphorus modified silica. These samples were denoted by the amount of phosphorus present on the support: 0.5P-SiO_2 and 1P-SiO_2. For the purpose of support characterization, 5 wt% phosphorus modified silica (5P-SiO_2) was also prepared as described above using 185.5 mg $NH_4H_2PO_4$.

Preparation of Pd@SiO_2

100 mg (0.45 mmol) of $Pd(OAc)_2$ was dissolved upon sonication in 2 mL of concentrated hydrochloric acid and added via five 0.4 mL portions to 0.45 g of silica support. Between the consecutive impregnations the material was dried at 60 °C for 30 min to ensure a homogenous distribution of the metal species. Afterwards the substance was further dried at 60 °C for 12 h before being reduced in stagnant H_2 at 400 °C for 8 h with a heating ramp of 50 °C·min^{-1}. For the thermal treatment in H_2 atmosphere, the dried impregnated precursors were introduced into a quartz glass Schlenk tube, equipped with a pressure relief valve and two stopcocks, which were connected to a Schlenk line and the hydrogen gas bottle, respectively. The entire apparatus underwent evacuation before the introduction of hydrogen. Subsequently, the Schlenk tube was positioned into a box furnace, with which the thermal treatment was carried out. To maintain a consistent hydrogen atmosphere throughout the thermal treatment process, intermittent dosing of hydrogen was employed. To prevent surface oxidation, the sample was then stored in an argon-filled glovebox prior to use.

Preparation of Pd@1P-SiO_2

The Pd catalyst on phosphorus-modified silica was synthesized using the same procedure as mentioned above, but with change in support (1P-SiO_2).

Preparation of Pd_3P@SiO_2

The Pd_3P catalyst on unmodified silica was synthesized using the same procedure as mentioned above, except after dissolving the $Pd(OAc)_2$ in concentrated hydrochloric acid, an additional 10 μL of H_3PO_4 was added to the solution.

Preparation of Pd_3P@0.5P-SiO_2 and Pd_3P@1P-SiO_2

The same procedure as mentioned above was used to synthesize the Pd_3P catalyst on phosphorus-modified silica by adding 10 μL of H_3PO_4 into the $Pd(OAc)_2$ solution and impregnating this to either 0.5P-SiO_2 or 1P-SiO_2 instead of the pure silica.

Catalytic testing

For a standard Heck reaction, 10 mL of DMSO were given into a 25 mL round-bottom flask. To this flask 111 μL (101 mg, 0.97 mmol, 1.5 equiv.) of styrene, 72 μL (132 mg, 0.65 mmol, 1.0 equiv.) of iodobenzene and either 256 mg (0.97 mmol, 1.5 equiv.) of K_3PO_4 or 133 μL (98 mg, 0.97 mmol, 1.5 equiv.) of Et_3N were added. Finally, 10 mg (10 wt% Pd on silica, unless noted otherwise) of catalyst were added to the reaction mixture after which the system was heated to the desired temperature for the specific time while continuously stirring at 700 rpm. Subsequently the catalyst was separated from the reaction medium by either filtration or by letting it cool down completely and centrifuging the mixture to recover the catalyst for further use. The quantities discussed above are up scaled or downscaled depending on the nature of the test. The outcome of the catalytic tests was determined via GC MS using *n*-decane as internal standard. To verify the experimental results of the catalytic testing, blank reactions (reactions without the presence of any Pd-containing catalyst) and repetition experiments were conducted on a regular basis.

Hot filtration tests

The contribution of any leached species to the catalytic activities were assessed by conducting hot filtration tests. Therefore, catalytic tests were carried out as described before and the reaction mixtures were heated to 140 °C. The reactions were stopped before reaching higher conversions by removal of the heat source (oil bath). Subsequently the catalysts were separated from the reaction mixture via filtration of the hot reaction solution through a 0.2 μm syringe filter. A small fraction of filtrate (20 μL) was then analysed via GC MS, whereas the rest of the filtrate was allowed to react further at 140 °C. After the completion of the reaction time, the mixtures were analysed by GC MS to assess any additional conversion after the catalyst removal.

Catalyst recovery test

In order to perform the recovery tests, the catalyst was removed from the reaction mixture after the test through centrifugation. Afterwards the catalyst was washed with acetone and dried in oven at 60 °C overnight. The recovered catalyst was further quantified and used in the recovery test. Parallel tests were performed in order to obtain sufficient quantity of catalysts for the recycling experiments.

Supporting Information

The authors have cited additional references within the Supporting Information.[81–83] Information and experimental data concerning the support and catalyst synthesis and characterization, the catalytic Heck coupling reactions and the metal leaching investigation are provided in the Supporting Information.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Heck coupling · heterogeneous catalysis · metal leaching · palladium phosphide · support engineering

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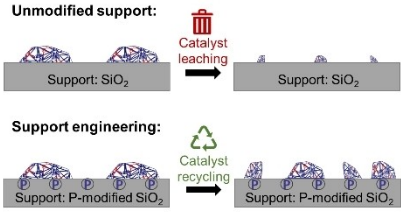
RESEARCH ARTICLE

The concept of support engineering using phosphorus-modified silica is used to modulate catalyst-support interactions and to stabilize catalytically active species on the support. Following this approach, an enhanced catalytic performance and catalyst stability as well as a reduction of metal leaching can be achieved for Pd_3P.



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Support Engineering for the Stabilisation of Heterogeneous Pd_3P-Based Catalysts for Heck Coupling Reactions