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Support Engineering for the Stabilisation of Heterogeneous Pd₃P-Based Catalysts for Heck Coupling Reactions

Arjun Neyyathala, Franziska Flecken, Fabian Rang, Christina Papke, and Schirin Hanf

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

Introduction

The use of phosphorus in catalysis has greatly been extended from the conventional application as phosphine ligands in homogeneous catalysis and has now also found significant attention in the field of heterogeneous catalysis. Hereby, transition metal phosphides have been investigated in detail in various catalytic reactions such as hydroformylation, hydrogenation, photocatalytic Suzuki coupling and desulfurization reactions. 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. 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-Tsui-oxidation of alkenes. 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. 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. For this type of coupling reactions palladium-based complexes have extensively been investigated as homogeneous catalysts showing moderate to excellent yields. 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. 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. 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. 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.

To overcome metal leaching and also to avoid the agglomeration of metal species during the reaction in heterogeneous catalysts, various strategies have been investigated whereby the main goal is an enhanced...
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,\(^6\) the introduction of defects into metal oxides,\(^{42}\) or the implementation of dopants (e.g. sulphur,\(^{43,44}\) nitrogen\(^{44-46}\) or oxygen\(^{46,50}\)) 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.\(^3\) However, only very few examples include the use of phosphorus as dopant for support materials.\(^{34-41}\) 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.\(^{39,42,63}\)

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 pursued. Firstly, according to the d-metal/p-block element strategy, a Pd/P-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/P. 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\(_4\)H\(_2\)PO\(_4\) 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\(_3\)PO\(_4\),\(^{31}\) PPH\(_3\),\(^{38,39}\) or NH\(_4\)H\(_2\)PO\(_4\),\(^{53,57}\) followed by a calcination step. NH\(_4\)H\(_2\)PO\(_4\) 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 up to 650 °C with a temperature ramp of 10 K min\(^{-1}\). The complete decomposition of NH\(_4\)H\(_2\)PO\(_4\) 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\(_4\)H\(_2\)PO\(_4\).

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\(_2\)(PO\(_4\))\(_3\) and Si\(_3\)(HPO\(_4\))\(_2\)H\(_2\)O.\(^{67}\) 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-Disperisive 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/P@SiO\(_2\) in catalytic Wacker–Tsuji oxidation reactions of alkenes,\(^{24}\) Pd/P 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.](image-url)
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,P on silica (Pd,P@SiO₂) was synthesized according to a modified literature procedure.¹²,²⁴ Phosphoric acid (H₃PO₄) 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,P 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 pure Pd,P (Pd,P@SiO₂, Figure 2b). Broad reflexes, possibly due to small particle sizes, were observed for the synthesized palladium phosphide (Pd,P@SiO₂) in comparison to the literature reported supported Pd,P which was synthesized using NH₄H₂PO₄ as phosphorus source.²⁹ However, NH₄H₂PO₄ was not used as phosphorus precursor in this study, since the Pd,P formation on silica is only successfully using a large excess of NH₄H₂PO₄ which ultimately results in phosphorus-containing residues on the silica support.

In order to enhance the particle size through sintering and to obtain a clearer diffraction pattern, the synthesized Pd,P@SiO₂ 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,P, starting with the formation of metallic Pd during the thermal treatment in H₂ followed by further incorporation of phosphorus forming palladium phosphide.¹¹,²⁴ 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@SiO₂) similar conditions were applied as for the synthesis of Pd,P@SiO₂. 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 pure palladium on silica (Figure S3).

For the preparation of Pd,P on support engineered SiO₂, Pd(OAc)₂ and H₃PO₄ with a Pd/P molar ratio of 3 were impregnated on the P-modified silica supports. Subsequently, the systems underwent thermal treatment in pure H₂ at 400 °C for 8 h. In all cases, PXRD analyses indicated the formation of the desired Pd,P 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,P@SiO₂ was determined to be 2.31, with a Pd content of 8.60 wt%. Analysis of the Pd and P contents in Pd,P@SiO₂ 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,P on silica catalysts (Pd@SiO₂, Pd,P@SiO₂). In both cases, particles distributed on a porous support, indicating Pd or Pd,P particles on silica, can be observed (Figures S10 and S11). For all samples (Pd@SiO₂, Pd,P@SiO₂, Pd,P@1P-SiO₂ and Pd,P@5P-SiO₂), 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,P@1P-SiO₂ are shown in Figure 3.

Table 1. Overview of the prepared catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd@SiO₂</td>
<td>Prepared with Pd(OAc)₂ on silica</td>
</tr>
<tr>
<td>Pd@1P-SiO₂</td>
<td>Prepared with Pd(OAc)₂ on 1 wt% P-modified silica</td>
</tr>
<tr>
<td>Pd,P@SiO₂</td>
<td>Prepared with Pd(OAc)₂ and H₃PO₄ on silica</td>
</tr>
<tr>
<td>Pd,<a href="mailto:P@0.5P-SiO">P@0.5P-SiO</a>₂</td>
<td>Prepared with Pd(OAc)₂ and H₃PO₄ on 0.5 wt%</td>
</tr>
<tr>
<td>Pd,P@1P-SiO₂</td>
<td>Prepared with Pd(OAc)₂ and H₃PO₄ on 1 wt% P-modified silica</td>
</tr>
<tr>
<td>Pd,P@5P-SiO₂</td>
<td>Prepared with Pd(OAc)₂ and H₃PO₄ on 5 wt% P-modified silica (prepared only for characterization purposes)</td>
</tr>
</tbody>
</table>

Figure 2. PXRD patterns of H₃PO₄ and Pd(OAc)₂ on silica treated thermally in various conditions: a) in H₂ atmosphere at 400 °C for 4 h, b) in H₂ atmosphere at 400 °C for 8 h, c) heating b) to 600 °C for 6 h in Ar. *: Pd,P [COD ID: 1539070] #: Pd [COD ID: 1011104].

Catalytic Heck coupling reactions

The catalytic performance of Pd,P on silica and P-modified silica was evaluated in Heck coupling reactions using iodosbenzene...
and styrene as test substrates. The investigation was further extended to the coupling reaction of styrene 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(P@SiO₂) as catalyst were performed in different solvents (DMF, NMP, DMSO) using various bases (K₂CO₃, K₂PO₃, Et₃N). The results are summarized in Table 2. The reaction systems utilising K₂PO₃-DMSO (Table 2, entry 6) and Et₃N-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.

Since superior performance of palladium phosphate catalysts in comparison to pure Pd has been reported in the literature in the context of hydrogenation, hydrogen evolution, and Wacker oxidation reactions, catalytic tests using Pd(P@SiO₂) as reference catalyst were carried out. The comparison tests were performed using Pd(P@SiO₂) and Pd@SiO₂ as catalysts (10⁻³ mmol·mL⁻¹, Pd basis) in DMSO at 140 °C for 60 min with K₂PO₃ as base. The conversion of iodobenzene was found to be 81 % (Table 2, entry 6) using Pd(P@SiO₂) as catalyst, while a comparable conversion of 86 % was obtained for the reference catalyst Pd@SiO₂. 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 1/3 of the pervious quantity (3.3 · 10⁻⁴ 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, phase formation does not diminishes its catalytic activity in comparison to the purely Pd-based catalyst (only 5 % conversion difference using K₂PO₃ as base).

In a next step the influence of the support engineering, using phosphorus-modified silica as support material for Pd, Pd, and Pd, on the catalytic activity was investigated. Three catalysts, namely Pd(P@1P-SiO₂), Pd(P@1P-SiO₂), and Pd(P@0.5P-SiO₂) were tested as catalysts for the Heck coupling using Et₃N 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>
<thead>
<tr>
<th>Entry</th>
<th>Reaction time [min]</th>
<th>Solvent</th>
<th>Base</th>
<th>Conversion [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40</td>
<td>DMF</td>
<td>K₂PO₃</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>NMP</td>
<td>K₂PO₃</td>
<td>57</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>DMSO</td>
<td>K₂PO₃</td>
<td>75</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>DMSO</td>
<td>K₂CO₃</td>
<td>75</td>
</tr>
<tr>
<td>5</td>
<td>60</td>
<td>DMSO</td>
<td>Et₃N</td>
<td>79</td>
</tr>
<tr>
<td>6</td>
<td>60</td>
<td>DMSO</td>
<td>K₂PO₃</td>
<td>81</td>
</tr>
<tr>
<td>7</td>
<td>60</td>
<td>DMSO</td>
<td>–</td>
<td>10</td>
</tr>
</tbody>
</table>

Reaction conditions: styrene (1 mmol), iodobenzene (0.6 mmol), base (1 mmol), solvent (10 mL), Pd(P@SiO₂) (10⁻³ mmol·mL⁻¹, Pd basis). Reactions were carried out at 140 °C. Conversions were calculated considering the concentration of iodobenzene.
based catalysts (entry 1 and 2), the Pd₃P catalysts on P-modified SiO₂ show an enhanced conversion of iodobenzene in contrast to Pd₃P on unmodified SiO₂. An increase of 11% conversion was recorded for Pd₃P@0.5P-SiO₂ (entry 4) and Pd₃P@1P-SiO₂ (entry 5) in comparison to Pd₃P@SiO₂ (entry 3). This enhanced performance might be resulting from a modulation of the electronic environment via a charge transfer[24] from Pd to the P-modified support. At this point the catalytic performance of Pd₃P 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 CeO₂, 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.[35]

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 Pd₃P@1P-SiO₂ 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 Pd₃P@1P-SiO₂. However, due to the unambiguous phase identification of the fresh and the recovered catalyst via PXRD, the Pd₃P@1P-SiO₂ 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 Pd₃P@SiO₂ and Pd₃P@1P-SiO₂ 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 Et₃N as base.[35] The reactions were conducted at 140 °C for 60 min and resulted in 100% conversion of iodobenzene and 100% selectivity towards methyl cinamate (Figure S24). The results obtained using Pd₃P@SiO₂ and Pd₃P@1P-SiO₂ 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 Pd₃P@SiO₂ reference catalyst, only a 11% drop in conversion was observed for the Pd₃P@1P-SiO₂ catalyst.

Similar observations were made for the Pd₃P@1P-SiO₂ catalytic systems. Hereby, a drop in conversion of 12% was observed after the first run using Pd₃P@1P-SiO₂, followed by a further drop of 7% in the third run. In contrast, the iodobenzene conversions using Pd₃P@1P-SiO₂ are only reduced by 4% for Pd₃P@0.5P-SiO₂ and 6% using Pd₃P@1P-SiO₂. Even though after the first run, Pd₃P@0.5P-SiO₂ 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 Pd₃P@1P-SiO₂ 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 Pd₃P@1P-SiO₂ 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 Pd₃P@1P-SiO₂, a base variation was investigated. Hence, recovery tests were performed in similar conditions using K₃PO₄ as the base (Figure 5). The major problem during these tests was the limited solubility of K₃PO₄ in DMSO, demanding multiple washings with solvents, such as water and acetone, in order to obtain the pure catalyst during recovery. Due to
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% [29] 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. [29, 37, 40] 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. [29, 37, 40] 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 prove 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

![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$_2$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.](https://chemistry-europe.onlinelibrary.wiley.com/doi/10.1002/chem.202302825)
inherent stabilisation agent. This effect can further be extended through the use of P-modified supports. When using Pd$_3$P@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$_3$P-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$_2$PO$_4$ as base was comparable using Pd$_3$P@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$_3$P@SiO$_2$ in the presence of Et$_3$N as base was used. The catalytic activity of Pd$_3$P 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$_3$N as base, a conversion of 79% was witnessed in 1 h using Pd$_3$P@SiO$_2$ as catalyst, 90% conversion was achieved through the use of Pd$_3$P on P-modified SiO$_2$ (Pd$_3$P@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$_3$P@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$_3$P@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$_3$N. A drop of 22% in conversion was recorded for Pd$_3$P@SiO$_2$ after one round of catalyst recycling, whereas for the P-modified system (Pd$_3$P@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 ≥ 99.9%, methyl acrylate (purity 99%), styrene (purity ≥ 99%) and potassium carbonate (purity ≥ 99%) were purchased from Sigma Aldrich, while iodobenzene (purity ≥ 99%) and methyl 4-iodobenzoate (purity ≥ 98%) were purchased from TCI. Silica (CariaQ,20 C) was purchased from Fuji Silysia Chemical Ltd and was used as the support material for the catalyst. The solvents DMSO (purity ≥ 99.9%) and acetonitrile (HPLC grade) along with orthophosphoric acid (85%) were purchased from Fischer Scientific GmbH. NMP (purity ≥ 99.5%), HCl (37%) and DMF (purity ≥ 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$_3$N) with a purity of 99% were bought from abcr GmbH. DMA with a purity 99.999% was purchased from Alfa Aesar and potassium phosphate trihydrate (purity ≥ 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 (λ = 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 0.3° and a total measurement time of 80 min. TG-DTA measurements were conducted in Al$_2$O$_3$ 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°C min$^{-1}$ and an empty Al$_2$O$_3$ crucible as reference. SEM measurements were performed using a Zeiss Supra 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 measurements 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 (M Braun) 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 M 5 model 8860 GC and 5977B MSD with n-decane as internal standard. In a standard GC M 5 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 M 5 system with a plunger speed of 1000 µL 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-SiO₂), 1.00 g of silica is impregnated with a solution of 37.1 mg (0.32 mmol) of NH₄H₂PO₄ 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 NH₄H₂PO₄, 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-SiO₂ and 1P-SiO₂. For the purpose of support characterization, 5 wt% phosphorus modified silica (5P-SiO₂) was also prepared as described above using 185.5 mg NH₄H₂PO₄.

Preparation of Pd@SiO₂

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 H₂ at 400 °C for 8 h with a heating ramp of 50 °C·min⁻¹. For the thermal treatment in H₂ 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-SiO₂

The Pd catalyst on phosphorus-modified silica was synthesized using the same procedure as mentioned above, but with change in support (1P-SiO₂).

Preparation of Pd₃P@5P-SiO₂

The Pd₃P 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 H₃PO₄ was added to the solution.

Preparation of Pd₃P@0.5P-SiO₂ and Pd₃P@1P-SiO₂

The same procedure as mentioned above was used to synthesize the Pd₃P catalyst on phosphorus-modified silica by adding 10 μL of H₃PO₄ into the Pd(OAc)₂ solution and impregnating this to either 0.5P-SiO₂ or 1P-SiO₂ 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, 0.37 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 K₂PO₃ or 133 μL (98 mg, 0.97 mmol, 1.5 equiv.) of Et₃N 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. 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.

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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 Pd₃P.

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Support Engineering for the Stabilisation of Heterogeneous Pd₃P-Based Catalysts for Heck Coupling Reactions