A Supported Palladium Phosphide Catalyst for the Wacker-Tsuji-Oxidation of Styrene

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The substitution of pure metal particles by metal phosphides in catalysis represents a promising opportunity to lower the required metal quantity in the context of a sustainable use of metal resources. Herein we show the synthesis of palladium phosphide, Pd_3P, supported on silica, which is tested as catalyst for the Wacker-Tsuji-oxidation of styrene to acetophenone. The synthesized catalyst is characterized by PXRD, SEM-EDX, FTIR, ICP-AES and XPS measurements. Four different reaction systems are investigated in this study including different co-catalysts and reaction media. Conversions of styrene up to 95% with a selectivity of 73% towards acetophenone are observed using Pd_3P/SiO_2 as catalyst, $CuCl_2$ as co-catalyst and O_2 as oxidant. An enhanced selectivity up to 100% towards acetophenone is obtained in other reaction systems. The use of Pd_3P/SiO_2 leads to an optimized selectivity and conversion in the oxidation reaction in comparison with the purely Pd-based system Pd/ SiO_2. These results give an insight on how the incorporation of phosphorus has a great effect on the performance of heterogeneous catalysts.

Introduction

The tremendous importance of phosphorus-based compounds in catalysis is widely known from the application of phosphine ligands in homogeneous catalysis.[1–3] However, in the last years, research also focused on the utilization of phosphorus compounds in heterogeneous catalysis, especially with respect to a more sustainable catalyst design.[4,5] To achieve this goal, one approach is focused on the reduction of the metal quantity within the catalytic system. The metal utilization efficiency can, for example, be optimized by a reduction in metal particle size, which results in a higher percentage of catalytically-active surface atoms.[6,7] An alternative tool, receiving more and more attention recently, is the introduction of a non-metal species, such as phosphorus, to decrease the required metal content. In this context metal phosphides of the form P_nM_m attracted a great deal of attention.[8,9]

In 1974 Muetterties et al.[8] established a method for the controlled synthesis of supported metal phosphides via the deposition of metal species on a support material, which was then phosphided by PH_3 under reducing conditions. Starting from this synthesis protocol, various other approaches for the preparation of supported metal phosphides have been published, in which phosphorus containing compounds such as phosphates,[10,11] phosphines[8,12–14] or elemental phosphorus[15–17] were used as phosphorus source. The reported mechanism for the formation of metal phosphides involves at first the decomposition of the metal precursor yielding pure metal particles. It is most probable that those metal particles are able to catalytically cleave the hydrogen during the thermal treatment, initiating the formation of PH_3 from the phosphorus source which, in a next step, facilitates the migration of phosphorus into the metallic particles at high temperatures.[10,11,17]

Concerning Pd-containing phosphides, polyphosphides (nP > mPd; PdP_2, PdP_3) and metal-rich phosphides (nP < mPd; $Pd_{15}P_2$, Pd_6P, $Pd_{4.8}P$, Pd_3P, Pd_5P_2, Pd_7P_3) have been reported in the literature.[5] Hereby, metal-rich phosphides combine a partly metallic character, due to the presence of metal-metal bonds, with an enhanced interatomic spacing of the metal species directed by the incorporated phosphorus atoms, both of which make palladium phosphides interesting candidates for catalysis.[5,8,10,18] Also, an analogy to isolated surface atoms can be drawn, which is supported by the fact that in palladium phosphides the oxidation state of palladium is found to be mostly zero.[19,20] It is widely known that the presence of isolated metal atoms, as found in homogeneous and single atoms catalysts, results in optimized catalyst performance, especially in terms of selectivity.[6,7,21] Palladium phosphides have been reported as catalysts for hydrogenation,[12,15,16,19,22–25] hydrodesulfurizations[10,11,26] and C—C coupling reactions,[20] as well as for catalytic water splitting.[27] In all of these cases, the authors have reported the positive effect of phosphorus incorporation into palladium with respect to the catalytic performance.[12] To the best of our knowledge no studies focused on the use of palladium phosphides in the field of the heterogeneously-catalyzed Wacker-Tsuji-oxidation up to now.

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Since Smidt discovered the Pd-catalyzed conversion of olefins yielding carbonyl-compounds in 1974 (Scheme 1),[28] research conducted in this field gained great attention, due to the industrial production of acetaldehyde and promising approaches regarding the conversion of olefins yielding ketones.[29,30]

The initial homogeneous Pd-based catalyst system required the addition of copper chloride with the purpose of reoxidizing Pd(0) to the catalytically active Pd(II) species. However, this involves the formation of undesired chlorinated byproducts and corrosion within the reaction vessel.[31] Since homogeneous systems often inherit a challenging catalyst recovery, the search for heterogeneous counterparts is seen as a promising path into the future of olefin-oxidation. The developments in this area mainly include palladium and copper co-exchanged zeolites,[32–35] heteropolyanion systems based on vanadium and molybdenum,[32,36–38] supported Pd-nanoparticles on ZrO_2,[39] titania[40] or carbon,[41,42] and the anchoring of palladium complexes on Janus-type particles.[43]

In this work, we therefore highlight the use of palladium phosphides as heterogeneous catalysts for the Wacker-Tsuji-oxidation of alkenes. The purpose of this study is to assess the catalytic activity of supported palladium phosphide in comparison with a purely Pd-based catalyst. The use of a heterogeneous catalyst will enable a facile catalyst separation and recovery. Both points are crucial for the development of sustainable catalysts in the field of olefin oxidation and other key organic transformations on a large industrial scale.

Results and Discussion

Synthesis of supported Pd_3P

Inspired by the great success of palladium phosphides in the field of catalysis,[16,17,25] Pd_3P supported on silica was synthesized with the aim to develop a sustainable catalyst for the Wacker-Tsuji-oxidation of styrene. Silica was selected as support material due to its good chemical stability, defined porosity, industrial relevance and its high surface area.[44] We herein chose the phase Pd_3P since the aim was to reduce the amount of required metal in comparison with pure Pd systems but also, we wanted to somehow maintain the metallic character of the system. Pd_3P crystallizes in the orthorhombic Cementite (Fe_3C, Figure 1) structure.[45] Palladium therein occupies two different lattice sites Pd(1) and Pd(2) with shortest Pd–Pd distances of 2.77 Å between two Pd(1) atoms, 2.83 Å between Pd(1) and Pd(2) and 3.22 Å between two Pd(2) atoms. The shortest Pd–P distance was found to be 2.30 Å (Pd–P).[11,46,47]

The impregnation of palladium precursors with $NH_4H_2PO_4$ or $NH_4H_2PO_2$ as phosphorus source on support materials, followed

Figure 1. Crystal structure of Pd_3P, which crystallizes in the Cementite structure.

by the thermal treatment in H_2 or H_2/N_2 gas mixtures is a facile method for the preparation of supported palladium phosphide catalysts.[19,48] To monitor the phosphide phase formation more closely as part of this study, $Pd(OAc)_2$ and $NH_4H_2PO_4$ (Pd/P = 0.5) were impregnated on silica and consequently reduced in pure hydrogen atmosphere at different temperatures (200 °C, 300 °C and 400 °C). A Pd to P molar ratio of 0.5 was used, since an excess of phosphorus is essential for the synthesis of palladium phosphides.[23,48] An impregnation loading of 10 wt.% Pd on silica was selected for this temperature study considering the ease of characterization, especially enabling a clear phase identification via PXRD. A similar synthetic procedure was reported by Yang et al., however, an Ar atmosphere was used for the thermal treatment.[20] The PXRD diffractograms of the impregnated precursors on silica and the samples reduced at various temperatures are provided in Figure 2.

The evolution of the Pd_3P phase from the precursors with increasing reduction temperature can be clearly seen from the diffractograms. Whereas the reduction of the precursors at 200 °C leads to the formation of Pd only, a further increase in temperature facilitates the formation of the Pd_3P phase.
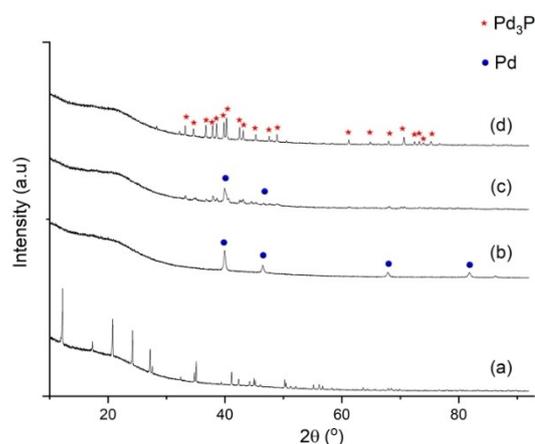
Figure 2. PXRD patterns showing the evolution of the Pd_3P phase from the precursors under reduction in pure H_2 at various temperatures: (a) impregnated precursors, (b) reduced at 200 °C, (c) 300 °C, (d) 400 °C. *: Pd_3P [COD ID: 1539070],[46] ●: Pd [COD ID: 1011104].

Scheme 1. Initial Wacker-Tsuji-oxidation of ethylene forming acetaldehyde.

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Reflexes corresponding to Pd₃P are clearly visible at a reduction temperature of 300 °C, however the reflex at a diffraction angle of 46° indicates the presence of the Pd phase and the material thus obtained is a mixture of Pd and Pd₃P phases (Figure 2). Reflexes corresponding to Pd₃P are distinctly visible after the thermal treatment at 400 °C and the reflex at 46° disappeared, which confirms the formation of phase pure Pd₃P on SiO₂.

These observations also support the formation mechanism of the Pd₃P phase. Whereas the precursors decomposed forming elemental Pd at lower temperatures, the phosphorus from the P-source is incorporated into Pd forming Pd₃P at higher temperatures.

In order to obtain further information concerning the gas atmosphere, in which the thermal treatment was carried out, the same precursors (Pd(OAc)₂ and NH₄H₂PO₄, Pd/P=0.5), impregnated on silica (10 wt.% Pd) were heated in Ar atmosphere at 500 °C for 4 hours. This experiment resulted in the formation of Pd₆P, which represent the next Pd rich phase in the Pd–P system (Figure S2). Subsequently, the thermal treatment of the impregnated precursors was repeated at 700 °C for 4 hours in Ar to examine the influence of temperature and the same resulted in the formation of a pure Pd phase (Figure S2). Therefore, these experiments clearly demonstrate that the choice of gas atmosphere as well as of the temperature for the thermal treatment are crucial points to consider for the metal phosphide phase formation.

To ensure the complete decomposition of the impregnated precursors (Pd/P=0.5), a TG-DTA analysis of the sample prior to reduction was performed in N₂ atmosphere. This is extremely important, since palladium precursors, such as Pd(OAc)₂ and PdCl₂, are known for their excellent activity in the homogeneously-catalyzed Wacker-Tsuji-oxidation of alkenes.[28,49] During the measurement an endothermic spike following a mass loss of roughly 15% was observed close to 290 °C (Figure S4) corresponding to the decomposition of the precursors. No further DTA spikes were observed until 900 °C. These observations confirmed the complete decomposition of the precursors at 290 °C and hence the presence of residual precursors in the final catalyst material can be largely ruled out.

SEM images were recorded and SEM-EDX measurements were performed to analyze the morphology of the particles, the P/Pd ratio and the distribution of P and Pd on silica. The SEM images mostly showed porous silica, in which we were able to observe particles with spherical morphology distributed at certain locations (Figure S5). The distribution of P and Pd on silica was imaged with the elemental mapping (Figure S7), which indicated an overall non-uniform distribution. The Pd rich areas in the images are assumed to be the Pd₃P particles and the excess P, which is not incorporated into Pd particles, is distributed over the silica particles. The P enriched areas are somehow expected, since the phosphorus precursor was added in excess during the impregnation step. An EDX measurement of the catalyst performed at various locations in the sample provided an average P to Pd ratio of 2.27, which is 13.5% higher than the P/Pd calculated from the precursors added. Similar observations were made by Wu,[48] who observed the presence of phosphates beside the metal phosphide on a silica surface using XPS analysis. The impact of the phosphorus modification of the solid support on the catalytic performance is in the focus of ongoing studies. From SEM-EDX measurements, the presence of Cl, which could stem from dissolving Pd(OAc)₂ in HCl for the impregnation of the support material, was ruled out.

A more precise quantification of the elemental composition of the Pd₃P/SiO₂ catalyst was carried out using ICP-AES analysis. The obtained results confirmed 9.28 wt.% of Pd and 5.23 wt.% of P in the sample. This corresponds to a P/Pd molar ratio of 2.0, which agrees with the precursor ratio used. Hence, it can be assumed that the variation of 13.5% observed in the EDX analysis is due to a non-uniform distribution of the metal phosphide.

To gain further insights into the surface properties of the Pd₃P/SiO₂ catalyst, XPS analysis was performed on a freshly prepared sample (Figure S10 and Table S1). The signals at binding energies of 340.9 and 335.6 eV correspond to 3d₃/₂ and 3d₅/₂ signals of palladium in a zero oxidation state.[48] Further, two phosphorus 2p signals at 134.0 and 134.9 eV were observed, which correspond PO₄³⁻ groups.[48] As mentioned before, the presence of phosphate species at the surface can be explained by the excess of the phosphorus precursor (NH₄H₂PO₄) used for the synthesis.[10,48] Other phosphorus signals could not be observed, which is probably due to the low concentration of P⁰ or Pδ⁻[19,48] in comparison with the carrier material and the phosphate species. Similar observations were also reported by Wu et al.[48]

Application of the supported Pd₃P catalyst in the Wacker-Tsuji-oxidation of styrene

The silica supported Pd₃P (10 wt.% Pd) material was tested as catalyst for the Wacker-Tsuji-oxidation of styrene to acetophenone. As part of our research, various reaction systems were investigated including the use of copper(I) or copper(II) chloride as co-catalysts for reoxidizing Pd(0) to Pd(II), as well as chloride-free alternatives using hydrogen peroxide (Scheme 2). The reaction conditions were adapted from Donck,[42] Xia,[49] Roussel and Vafaeezadeh.[43,50]

Donck et al.[42] established the CuCl system (Scheme 2, system A), in which palladium supported nanoparticles on carbon nanotubes were used as catalyst. We further substituted Cu(I)Cl by Cu(II)Cl₂ (Scheme 2, system B) to gain a deeper knowledge about the influence of the copper species on the catalytic performance. For the copper chloride-based systems, a 1:10 molar ratio of catalyst to co-catalyst was selected. Since the presence of copper chloride species and oxygen results in corrosive conditions and may lead to the formation of chlorinated byproducts, other approaches were also examined as part of this study, in which the application of chlorides could be avoided by applying hydrogen peroxide as sole oxidant. Therefore, a H₂O₂/sulfuric acid containing system (Scheme 2, system C) was compared to the use of a H₂O₂/acetic acid mixture (Scheme 2, system D).

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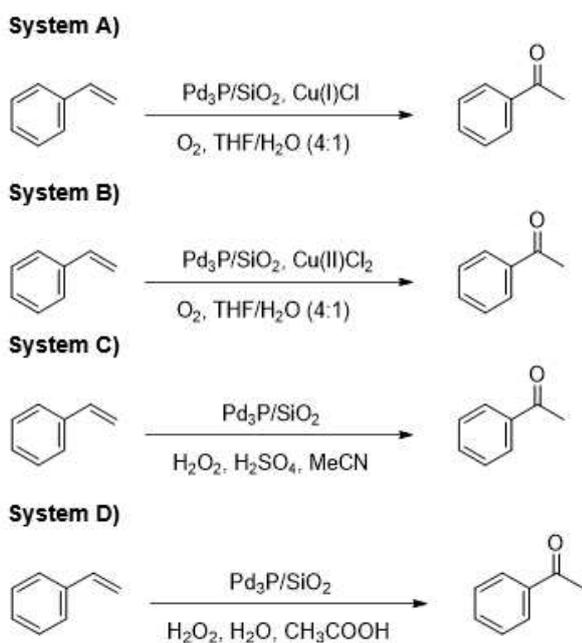
Scheme 2. Various reaction systems for the heterogeneously-catalyzed Wacker-Tsuji-oxidation using a Pd₃P-based catalyst.

In all cases, the Markovnikov product acetophenone was obtained as major product and, in certain cases, phenyl-acetaldehyde (anti-Markovnikov) and benzaldehyde were observed as minor products (Scheme 3). The formation of benzaldehyde is described elsewhere in the literature either using oxygen[51] or hydrogen peroxide[52] as oxidants and involves a peroxide intermediate, which subsequently decomposes.

The use of the copper(I) (system A) and copper(II) (system B) chloride-based systems at 50 °C for 6 hours did not show a complete conversion (entry 1 and 4). Therefore, the reaction time was increased to 16 hours. This adjustment did not show any impact on the CuCl system (entry 2). This can maybe be attributed to a disproportionation of Cu(I) towards Cu(II) and
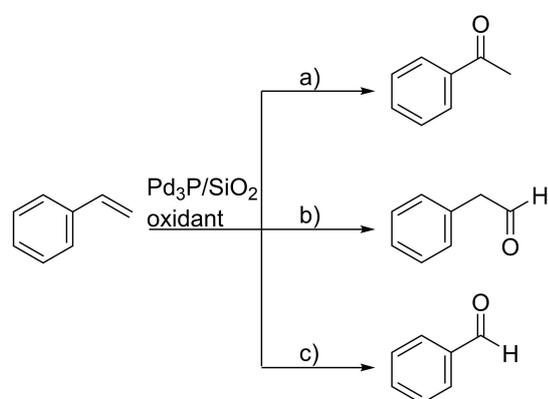
catalytically-inactive Cu(0). Consequently, the palladium(II)-recovery cannot be entailed in the required extent.[40] In contrast, the reaction time extension clearly influences the catalytic conversion using the CuCl₂ system. Whereas at 50 °C and 6 hours reaction time a conversion of 51 % was observed (entry 4), a conversion of 95 % could be achieved when the reaction time was extended to 16 hours (entry 5). However, despite the increase in conversion, a drop in selectivity towards acetophenone from 90 % to 73 % was witnessed. No conversion was observed for the blank tests (no Pd catalyst present) for system A and B (entry 3 and 6).

These results are superior to other literature-reported Pd-based systems. For instance, Byun et al. have investigated similar reaction systems with Pd–Fe₃O₄ heterodimer nano-crystals as catalyst for the oxidation of styrene. Hereby they have used CuCl₂ as the co-catalyst, similar to our reaction system B.[29] With a reaction temperature of 70 °C and a reaction time of 18 hours, a 20 % selectivity towards acetophenone is reported, whereas with our Pd₃P/SiO₂ system a selectivity of 73 % (entry 5) with excellent conversion could be achieved even at lower reaction temperature and time. However, in the Pd–Fe₃O₄ based investigation, the authors have used only 1 mol% catalyst in the reaction system compared to 2 mol% in our case. In contrast to our work, CuCl as co-catalyst exhibited superior performance in terms of conversion and selectivity compared to CuCl₂ in the Pd–Fe₃O₄ based system. A similar reaction system with dimethylamine and water as solvents is reported by Mitsudome et al. with Pd montmorillonite as catalyst.[53] A conversion of 86 % with an acetophenone selectivity of 82 % is achieved at 80 °C with 0.4 mol% catalyst and a catalyst to co-catalyst ratio of 1:4.

The catalytic testing of system C provided unexpected results since after 6 hours reaction time (entry 7) no solid catalyst material was found in the reactor. A deeper look into previous studies showed that this might be due to the total decomposition of the catalyst including the catalyst support by piranha solution (H₂SO₄ + H₂O₂).[54] Thus, no further reactions were conducted using system C.

A blank study of the acetic acid-based system D resulted in 70 % conversion of styrene, which was transformed into a wide range of products, mainly consisting of benzaldehyde and 1-phenyl-1,2-enthanediol (entry 14). Through the application of the Pd₃P/SiO₂ system, the product formation was strongly directed towards the formation of acetophenone. As expected, a higher mol% of the Pd₃P/SiO₂ catalyst resulted in a higher conversion of styrene within the same reaction time and temperature (entry 9 and 10). However, since the metal quantity should ideally be as low as possible, the metal content was reduced to 2 mol% catalyst and higher temperatures were applied (entry 11 and 12). With increasing temperatures higher conversions could be achieved. However, simultaneously a drop in selectivity towards acetophenone can be observed, as reported in similar reactions.[55] To counteract the loss in selectivity, the reaction temperature was therefore again reduced to 50 °C and the reaction time was extended to 16 hours (entry 13), which resulted in slightly lower conversions, but in a selectivity growth towards 86 %.

Scheme 3. Oxidation of styrene: a) Markovnikov product acetophenone, b) anti-Markovnikov product phenyl acetaldehyde and c) formation of benzaldehyde via a peroxide intermediate.

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A comparison of the different systems showed that the highest conversions could be achieved using system B, while the best selectivity towards acetophenone was observed with system D. We assume, that in the copper(II)-based system (system B) the reaction step concerning the regeneration of the active site is faster than in the hydrogen peroxide-based system (system D). However, this must be clarified in further studies.

The significance of substituting pure palladium particles by palladium phosphides was investigated in a trial using a pure palladium catalyst (entry 15) under the same reaction conditions as in system B (entry 5). The catalyst was prepared in a similar manner as the phosphide-based one, but without the presence of a P-source. We hereby were able to prove that the phosphide catalyst shows higher conversion and – even more interesting – an optimized selectivity towards the Markovnikov product acetophenone. The pure Pd catalyst provided acetophenone as the major product. However, the formation of phenyl acetaldehyde (anti-Markovnikov) and benzaldehyde were observed in higher concentrations than with Pd_3P/SiO_2. This result can probably be traced back to the more defined active sites of Pd_3P in comparison to Pd particles through the incorporation of phosphorus and the formation of a highly ordered metal phosphide phase.

Proposed mechanism for the heterogeneously-catalyzed Wacker-Tsuji-oxidation

On the basis of earlier described literature studies[41,43,49,50,56,57] and our experimental findings, a mechanism for the heterogeneously-catalyzed Wacker-Tsuji-oxidation using Pd_3P/SiO_2 can be proposed. As it is widely known, palladium(0) is catalytically inactive in oxidation reactions, while palladium(II) efficiently catalyzes these reactions.[56] XPS analyses of the Pd_3P/SiO_2 catalysts have shown Pd to be present in the zero oxidation state. The presence of oxidants – either copper chloride or hydrogen peroxide – in every system implies the oxidation to the Pd(II) state, which further enables the catalysis to occur. The major difference between the systems A and B (Figure 3) with systems C and D (Figure 4) is the oxidation/reduction site. Regarding the copper chloride system, the palladium itself is oxidized and subsequently reduced through electron transfer between copper and palladium.[56,57]
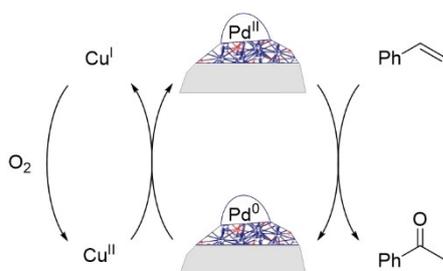
Figure 3. Simplified proposed mechanism for heterogeneously-catalyzed Wacker-Tsuji-oxidation catalyzed by Pd_3P/SiO_2 using a copper chloride co-catalyst.
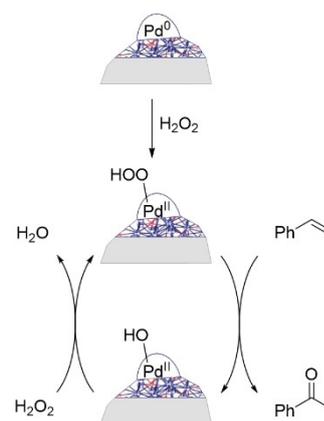
Figure 4. Simplified proposed mechanism for heterogeneously-catalyzed Wacker-Tsuji-oxidation catalyzed by Pd_3P/SiO_2 using a hydrogen peroxide co-catalyst.

Contrary, for the hydrogen peroxide-containing homogeneous analogues, it was reported that the hydrogen peroxide coordinatively binds to the metal center forming the Pd(II) state.[41,43,49,50] In the next step the substrate coordinates to the activated site. However, the palladium center was maintained in its +2 state during the whole cycle and the "OOH-ligand" itself underwent the reduction followed by reoxidation to the starting species.

Recovery tests

Since the separation of the pure Pd_3P catalyst from the co-catalyst in the copper chloride systems A and B was challenging, the catalyst recovery was tested for the acetic acid system D. After completion of the catalytic test (entry 13), the Pd_3P/SiO_2 catalyst was successfully recovered and a PXRD was recorded. Since only phase pure Pd_3P was observed in the diffractogram (Figure S3), it can be concluded that the catalyst is intact and can be recycled for further experiments.

The recovered catalyst was further used for the styrene oxidation reaction using reactions conditions as shown in Table 1, entry 13. A conversion of 50% was obtained, which is 20% less conversion in comparison to the freshly prepared catalyst. However, the selectivity towards acetophenone remained the same (86%). Further, a second catalytic test using the recovered catalyst was performed and resulted in 40% conversion and a consistent selectivity.

To investigate the loss in catalytic activity during the recycling experiments, ICP-AES analysis of the recovered catalysts were performed. Hereby, a large loss in Pd of the recovered catalysts was observed ranging from 44 to 75% (Table S2). Hence, the drop in activity may be accounted to the leaching of metal from the catalyst, leading to depletion of active species in the recovered catalyst. It is important to note at this point, that in system D acetic acid is used as solvent, which can cause leaching to occur.[58,59]

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Table 1. Comparison of various procedures and co-catalyst-systems in the Wacker-Tsuji-oxidation in terms of conversion (conv.) and selectivity (select.) towards acetophenone (Ap.).

Entry	System	Catalyst	Temp. [°C]	Time [h]	Conv. [%]	Ap. Select. [%][g]
1	A[a]	Pd$_3$P/SiO$_2$ (2 mol%)	50	6	20	100
2	A[a]	Pd$_3$P/SiO$_2$ (2 mol%)	50	16	20	100
3	A[a]	–	50	16	nil.	nil.
4	B[b]	Pd$_3$P/SiO$_2$ (2 mol%)	50	6	51	90
5	B[b]	Pd$_3$P/SiO$_2$ (2 mol%)	50	16	95	73
6	B[b]	–	50	16	nil.	nil.
7	C[c]	Pd$_3$P/SiO$_2$ (2 mol%)	50	6	44	100
8	C[c]	–	50	6	nil.	nil.
9	D[d]	Pd$_3$P/SiO$_2$ (4 mol%)	50	6	71	100
10	D[d]	Pd$_3$P/SiO$_2$ (2 mol%)	50	6	60	100
11	D[d]	Pd$_3$P/SiO$_2$ (2 mol%)	80	6	77	60
12	D[d]	Pd$_3$P/SiO$_2$ (2 mol%)	80	14	80	44
13	D[d]	Pd$_3$P/SiO$_2$ (2 mol%)	50	16	70	86
14	D[d]	–		80	6	70	nil.
15	B[e]	Pd/SiO$_2$ (2 mol%)	50	16	80	63

[a] Reaction conditions system A: styrene (1 mmol), CuCl (20 mol%), THF (2 mL), H$_2$O (0.5 mL), p(O$_2$) = 1.4 bar. [b] Reaction conditions system B: styrene (1 mmol), CuCl$_2$ (20 mol%), THF (2 mL), H$_2$O (0.5 mL), p(O$_2$) = 1.4 bar. [c] Reaction conditions system C: styrene (1 mmol), 30% H$_2$O$_2$ (3 mmol), 70% H$_2$SO$_4$ (0.013 mL), MeCN (2.5 mL). [d] Reaction conditions system D: styrene (1 mmol), 30% H$_2$O$_2$ (3 mmol), acetic acid (1.4 mL), H$_2$O (0.6 mL). [e] This reaction was conducted with Pd/SiO$_2$ instead of Pd$_3$P/SiO$_2$, other conditions were the same as mentioned under [b]. [f] nil. = lat. *nihil*, meaning no conversion detectable. [g] The selectivity is calculated according to Ap. Select. = n[acetophenone$_{formed}$]/n[styrene$_{converted}$]

To assess the influence of the leached Pd on the catalytic activity a filtration test was performed for the acetic acid-based system D (test conditions similar to Table 1, entry 13). The reaction mixture along with the catalyst was allowed to react for 6 hours and the reaction mixture was analyzed via GC-MS. A conversion of 60% was recorded with 100% selectivity to acetophenone. Afterwards, the catalyst was removed from the reaction mixture by filtration and the solution without catalyst was allowed to react further for another 14 hours without the addition of any new reagent. The products were subsequently analyzed, and an additional 9% conversion was witnessed with a 10% drop in selectivity due to the formation of benzaldehyde. Hence, only a very small contribution of the leached Pd species on the catalytic performance was observed.

Conclusion

In this paper we have demonstrated the synthesis of supported palladium phosphide, Pd$_3$P/SiO$_2$, and its application in the catalytic Wacker-Tsuji-oxidation of styrene. The Pd$_3$P/SiO$_2$ catalyst showed superior performance in terms of conversion and selectivity towards acetophenone in comparison with a pure Pd-based catalyst without the presence of any phosphorus species. The optimized results can be traced back to a higher uniformity of the active Pd sites within Pd$_3$P, achieved through phosphorus incorporation, in comparison to pure Pd nanoparticles, in which several Pd species are present. Moreover, for an equal quantity of catalysts, approximately 9% reduction in

mass of Pd metal can be achieved using Pd$_3$P in comparison with a pure Pd catalyst. Due to the heterogeneous nature of the catalyst, the separation of the products and the catalysts recovery are facilitated. Therefore, this new type of catalyst for the Wacker-Tsuji-oxidation shows a promising pathway for a more sustainable catalyst design, which might be suitable for large scale industrial applications. As part of future studies, we are currently investigating other palladium phosphide phases with even lower Pd content as well as alternative support materials.

Experimental Section

Materials, methods and instruments

Palladium acetate (Pd(OAc)$_2$), ammonium dihydrogen phosphate (NH$_4$H$_2$PO$_4$), cuprous chloride (CuCl), cupric chloride (CuCl$_2$) and styrene were purchased from Sigma Aldrich. Silica (Cariact, Q 20 C) was purchased from Fuji Silysia Chemical Ltd and was used as the support material for the catalyst. The internal standard for the GC measurements, *n*-decane, was purchased from abcr GmbH. Acetic acid (99–100%), H$_2$O$_2$ (30%) and H$_2$SO$_4$ (70% conc.) were purchased from VWR International and tetrahydrofuran (THF) and acetonitrile (MeCN, HPLC grade) from Fischer Scientific GmbH. Acetone (HPLC grade) was purchased from Carl Roth. All chemicals were used without further purification. PXRD measurements were performed using a Stoe STADI-MP diffractometer operating with Ge-mono-chromatized Cu–Kα-radiation (λ = 1.54178 Å) in transmission mode. A Netzsch STA 449 F3 (Netzsch, Germany) was used for the TG-DTA measurements with α-Al$_2$O$_3$ as reference material. SEM measurements were performed using a Zeiss Supra 40 VP microscope (Zeiss, Germany), equipped with a Schottky field emitter (2.0 nm resolution) and the EDX measurement was carried out with a Supra 40VP from Zeiss using a Sapphire Si(Li) detector from the company EDAX Genesis. 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. XPS measurements were performed using an EnviroESCA model instrument from Specs with Al–Kα source (1486.71 eV). The instrument was operated at 15 kV, 43 W (3 mA emission) and 30 eV pass energy for high resolution spectra. Spectra were recorded at 7 mbar nitrogen atmosphere in the analysis chamber to compensate for charging effects.[60] CasaXPS version 2.3.24PR1.0 was used for the evaluation with Shirley type background and 70% Gaussian and 30% Lorentzian profile. ICP-AES measurement were performed in an iCap 6500 device from Thermo Fisher Scientific. The samples were therefore dissolved in nitric acid, hydrofluoric acid and hydrochloric acid at 130°C for 12 hours using a digestion system. The catalytic tests were carried out in the micro-batch reactor model 2500 supplied by Parr Instruments. The reactants and products from the catalytic testing were analysed qualitatively and quantitatively using an Agilent GC MS model 8860 GC and 5977B MSD.

Synthesis of the supported Pd$_3$P catalyst

The silica supported Pd$_3$P catalyst was synthesized by a modified impregnation method adapted from the literature.[19,48] Palladium acetate (Pd(OAc)$_2$) dissolved in hydrochloric acid (HCl) and ammonium dihydrogen phosphate (NH$_4$H$_2$PO$_4$) dissolved in water were mixed in a round bottom flask with a Pd/P molar ratio of 0.5. The calculated quantity of silica, providing a metal impregnation

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loading (Pd/Silica) of 10 wt.%, was added to the solution and the mixture was stirred overnight. Consequently, the solvent was removed from the mixture under vacuum and the material was dried overnight at 50 °C. The dried precursors were then reduced in stagnant pure H_2 at 400 °C for 4 hours with a heating rate of 5 K/min. The PXRD analysis and IR spectroscopy of the product confirmed the formation of phase pure Pd_3P (Figure S1 and S9). The catalyst was stored in an Argon-filled glovebox (MBraun) prior to use to avoid undesired surface oxidation.

The Pd/SiO$_2$ catalyst (10 wt.%) was synthesized following the procedure mentioned above, without the addition of a P precursor. The PXRD result of the material indicated the formation of phase pure Pd (Figure S1).

Procedures for catalytic Wacker-Tsuji-oxidation

System A and B: A procedure for the copper chloride containing Wacker-Tsuji-oxidation was adapted from Donck et al.[42] In order to carry out the catalytic testing for the catalyst-co-catalyst system (Scheme 2), styrene (0.11 mL) was added to the solvent mixture containing THF and H_2O in the ratio 4:1. Further, catalysts and co-catalyst (CuCl or $CuCl_2$) were added and the autoclave was filled with oxygen at the required pressure. The reaction mixture was heated to the desired temperature with continuous stirring. After the assigned reaction time, the autoclave was allowed to cool down to room temperature and the catalyst was separated by filtration.

System C: Adapting the procedure reported by Xia et al.,[41] the catalytic testing of the oxidation of styrene with H_2O_2 in the presence of H_2SO_4 was carried out. In a typical test, styrene (0.11 mL), 30% H_2O_2 (0.31 mL), 70% H_2SO_4 (0.013 mL) and MeCN (2.5 mL) were added to an autoclave. To this mixture, the catalyst was added and the autoclave was heated to the desired temperature with continuous stirring. After the assigned reaction time, the autoclave was allowed to cool down to room temperature and the catalyst was separated by filtration.

System D: The procedure for the oxidation of styrene using hydrogen peroxide as oxidant and acetic acid and water mixture as solvent was adapted from Roussel and Vafaeezadeh et al.[43] In a typical test, styrene (0.11 mL), acetic acid (1.4 mL), water (0.6 mL) and 30% hydrogen peroxide (0.31 mL) were added to an autoclave. To this mixture, the catalyst was added and the autoclave was heated to the desired temperature with continuous stirring. After the assigned reaction time, the autoclave was allowed to cool down to room temperature and the catalyst was separated by filtration.

Blank test: For each system a blank experiment was conducted in which no Pd_3P/SiO_2 catalyst was added.

Filtration test: All components of the reaction system D including the catalyst were taken in the autoclave and heated to the desired temperature with stirring. After the desired time, the mixture was filtered to separate solid catalyst species. The filtrate alone was added to another autoclave and the reaction was allowed to continue without catalyst at the same temperature while stirring.

GC-MS analysis

The products after the catalytic testing were analysed qualitatively and quantitatively by GC-MS in acetone with *n*-decane as internal standard.

Conflict of Interest

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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