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Sonogashira coupling: silica supported aqueous phase palladium catalysts *versus* their homogeneous analogs

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Two palladium catalysts, $Pd(OAc)_2/n$ TPPTS, $n = 2, 5$ [TPPTS = $P(m\text{-}C_6H_4SO_3Na)_3$], immobilised in an aqueous film supported on a mesoporous silica were tested for the coupling of phenylacetylene with phenyliodide, in presence of a catalytic amount of CuI and of a base. The two solids show very different activities, which are both strongly dependent on their initial water content. Their stability toward palladium leaching is such that their recycling cannot be considered on a reasonable scale. The fact that in most cases the leached palladium is very active for the same coupling reaction suggests that these Pd-*n*P-SAP solids behave essentially as a reservoir of a highly soluble species, which forms during the successive catalytic cycles. A careful study of the related analogous homogeneous catalytic systems shows that most of the phosphine introduced with $Pd(OAc)_2$ stays free: the reactants inhibit considerably the reduction of Pd(II) to Pd(0) by the phosphine. The data when taken all together suggest that $Pd(CCPh)_2(PR_3)_n$, a lipophilic catalytic intermediate, may be the leaching entity.

Introduction

Among the various reactions which lead to C–C bond formation (hydroformylation, oligomerization, ···), the coupling reactions between Csp^3–Csp^2, Csp^2–Csp^2, Csp^2–Csp are the only ones which allow for a one pot significant hydrocarbon chain lengthening.[1] Most of the reported catalytic systems are based on palladium, either Pd(0) or Pd(II), stabilized and/or reduced by phosphines.[2–6] Although most of these catalysts are highly selective, they show only moderate activities under the conditions compatible with most organic reactions. Therefore, any method which will allow for their recycling or their use in a continuous flow reactor would considerably help in opening the field to industrial applications. We have recently shown the potential of the heterogeneous catalyst, generated *in situ* from $Pd(OAc)_2$/5 TPPTS, [TPPTS = $P(m\text{-}C_6H_4SO_3Na)_3$] and immobilised on a silica in a thin film of water.[7] This catalyst is both more active and more selective for the allylic substitution of (*E*)-cinnamyl ethyl carbonate by various nucleophiles than the same palladium system working in a biphasic water–organic solvent medium. The immobilised catalyst is also more stable; thus, it could be easily recycled.[8] We decided therefore to attempt to extend the field of applications of these Pd-Supported Aqueous Phase (Pd-SAP) catalysts to other related reactions; we present here our data for the coupling of an alkyne with an halogenated aromatic compound (eqn. 1).

$$\underset{\mathbf{1}}{\text{Ph–C≡C–H}} + \underset{\mathbf{2}}{\text{Ph–I}} \longrightarrow \underset{\mathbf{3}}{\text{Ph–C≡C–Ph}} + \text{HI} \qquad (1)$$

Results

It is well known that the homogeneous catalytic system which is efficient for the Trost–Tsuji reaction needs the addition of a co-catalyst, CuI, and of a base, in order to become active for reaction (1).[4] We have confirmed this observation here for the related heterogenised SAP type catalyst. From a preliminary screening of the reaction conditions, we could show that CuI and NEt_3 have to be used in the following amounts: CuI/Pd = 2 and $[NEt_3]/[PhI] = 4$; these values correspond to the best compromise between high efficiency of the solid and low palladium leaching.

Two catalysts, $Pd(OAc)_2/n$ TPPTS/H_2O/silica ($n = 2, 5$) were synthesised, in accordance on one hand with literature data which recommend a low ratio P/Pd, generally close to two.[9–13] On the other hand, a value of 5 of this ratio allows for the complete reduction of Pd(II) to Pd(0). The method of synthesis is that for the Trost–Tsuji type catalysts:[7] the solids are identified as Pd-2P-SAP and Pd-5P-SAP, respectively. The solids are characterized by a palladium content close to 0.7–0.8 wt% and a residual water content close to 2–3 wt%. CuI and NEt_3 are added at the same time as the reactants (see Experimental).

Catalytic properties of Pd-5P-SAP

We started with the study of the catalytic properties of Pd-5P-SAP for which we had already identified the palladium species present on silica as being mainly $Pd(TPPTS)_3$.[7]

Influence of the water content. The water content is one of the most important parameters for supported aqueous phase catalysts,[14–20] whatever the nature of the active entity (Rh, Ru, Pd complexes) and/or the type of reaction *i.e.* hydroformylation of heavy and functionalized olefins,[14,15] hydrogenation of α,β-unsaturated aldehydes,[16] Wacker oxidation,[17] enantioselective hydrogenation[18] and more recently C–C coupling reactions such as Trost–Tsuji allylic substitutions[7] or Heck reactions.[19] As we had observed it for the Trost–Tsuji reaction, the solid Pd-5P-SAP shows a significant activity for reaction (1) only when its water content lies above 20 wt% (Fig. 1A). For water contents comprised between 20 and 50 wt%, no important variation of the activity is noticed. Both reactants, **1** and **2**, are fully converted within *ca.* 1 h 30 min, with a selectivity for **3** close to 90%. The dimer PhCC–CCPh, the homocoupling product of phenylacetylene, is the only secondary reaction product. When the solid has a water content above 50 wt%, which corresponds roughly to the wetting volume of the silica

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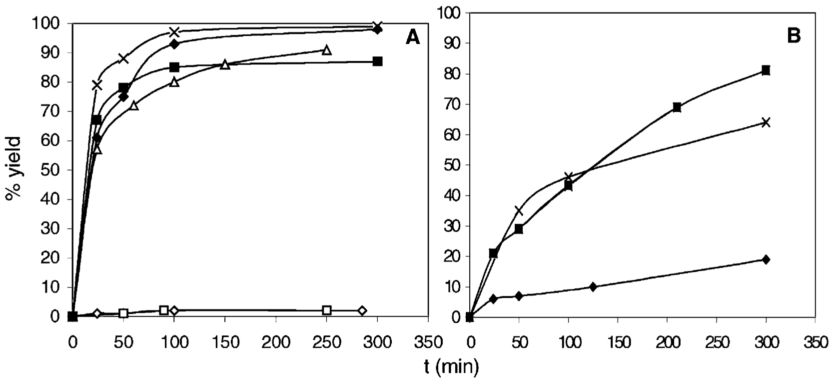

Fig. 1 Influence of the water content on the catalytic properties (% yield PhCCPh) of the solid Pd-5P-SAP (**A**) and Pd-2P-SAP (**B**). Exp. cond.: solvent: PhCN, $T = 50$ °C; [PhCCH] : [PhI] : [NEt_3] : [CuI] : [Pd] = 25 : 25 : 100 : 2 : 1; [PhCCH] = 54 mmol L^{-1}. (**A**) wt% H_2O: ◇, 2; □, 10; Δ, 20; ×, 30; ■, 40; ◆, 50. (**B**) wt% H_2O: Δ, 20; ×, 30; ■, 36; ◆, 50.

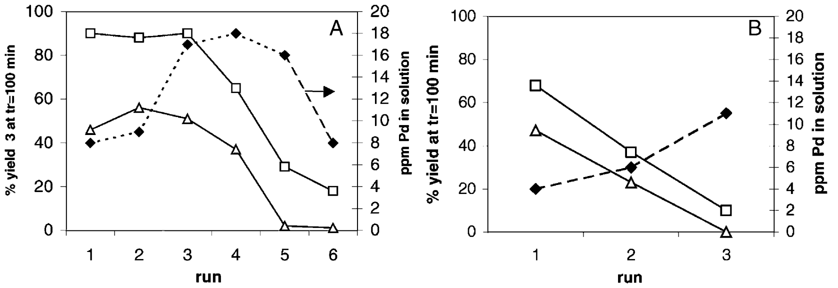

Fig. 2 Recycling tests for Pd-5P-SAP (40% H_2O) (**A**) and Pd-2P-SAP (30% H_2O) (**B**): % yield **3** (□) in presence of the solid; (Δ) with the related supernatant solution; (◆) ppm palladium in related solutions. Exp. cond. as for Fig. 1, except for solvent: water-saturated PhCN.

support, it does not disperse properly in benzonitrile; the reaction is dominated by mass diffusion problems and the tests are non reproducible. The water-dependence of the catalytic properties of Pd-5P-SAP is not strongly influenced by the amine concentration, at least in the tested range of concentrations (1.2 to 4 equiv. per PhI). It seems nevertheless that an excess of amine favors the achievement of higher conversions and higher yields. Simultaneously, the leaching of palladium does not increase with the concentration of the base; this suggests that the amine does not significantly extract palladium.

Recycling tests. These tests were performed with the solid Pd-5P-SAP (40% H_2O), one of the most active solids. We used water-saturated benzonitrile (1% H_2O) as the solvent to restrict the passage of water from the solid into the solvent. It was indeed clearly established that water leaching was the major source of the activity decrease of the same solid working under Trost–Tsuji conditions.[7,8] Under Sonogashira conditions, the stability of Pd-5P-SAP (40% H_2O) is excellent during the first three tests: both the activity (expressed as % yield of **3**) and the selectivity remain quasi-constant (Fig. 2A). Yet, the palladium leaching reaches an overall value of 15%. The successive supernatant solutions, once the solid is filtered off, are active towards a fresh dose of the reactants (Fig. 2A) and selective (85% **3**). At the fourth test and all consecutive tests, the activities of the solid and of the supernatant solution both drop sharply. In the case of the solid, this may be related to the important overall palladium loss (40% at the end of the sixth run). Simultaneously, the selectivity of the solid drops to 65%. Surprisingly, the successive supernatant solutions show similar palladium contents: this suggests then at least two palladium species leach in benzonitrile, but that only one of them is highly active. The recycling test always lasted 5 hours; this means that as the activity of the solid decreases, the percentage of conversion drops from 100% to 30% at the time the tests ended. This would suggest that the active species is formed during the catalytic cycle: its concentration would thus be too low in the solutions stemming from the 5th and 6th runs.

Catalytic properties of Pd-2P-SAP

Influence of the water content. The effect of the water content on the catalytic activity of Pd-2P-SAP is shown in Fig. 1B. Below a water content of 20 wt%, the solid is inactive for reaction (1). Above this value, its activity increases monotonically, and not abruptly as is the case with Pd-5P-SAP. With 50 wt% H_2O, the solid achieves quasi-full conversion of the reactants within *ca.* 5 h. The selectivity for the target coupling product never exceeds 80%; a small amount of the dimer PhCCCCPh is formed, and the formation of oligomers is strongly suspected. This latter reaction is indeed easy: it takes place even on pure silica (40% H_2O). In conclusion, under the same experimental conditions of catalysis, the solid Pd-2P-SAP is less active and less selective than the solid Pd-5P-SAP, whatever its water content.

Recycling tests. The recycling tests were done with Pd-2P-SAP (30 wt%H_2O). They were performed in water-saturated benzonitrile (*vide supra*). Under these latter conditions, the solid is slightly more active and the palladium leaching less severe than with anhydrous benzonitrile as the solvent. This suggests that water indeed leaches into the solvent. The deactivation of this sample of Pd-2P-SAP is very fast: after two recycles, more than 80% of the initial activity is lost (Fig. 2B). This deactivation is concomitant with palladium leaching, but overall the fraction of leached palladium is lower than in the case of Pd-5P-SAP (40 wt% H_2O). The solid also becomes significantly less selective (60%). The solutions, filtered off the solid after 5 h of reaction, are active towards a fresh dose of reactants; the more active the solid, the more active the resultant solution. The first two solutions are still selective for **3** (84%). The activity of the soluble palladium decreases showing that the most easily extracted species is formed under the conditions of catalysis.

Catalytic properties of the related homogenous systems

General comments. The different behaviour of the two solids

Pd-5P-SAP and Pd-2P-SAP under Sonogashira conditions is likely related to the nature and concentration of the palladium species present on the surface of the solids. In the case of Pd-5P-SAP, we could deduce from ^{31}P NMR studies of the impregnation solutions and of the resulting solids that $Pd(TPPTS)_3$ is the main phosphinated palladium complex.[7] From the stoichiometry of the reaction of reduction of Pd(II) to Pd(0) by TPPTS and the absence of free phosphine, we have assumed that most Pd(II) is indeed reduced.

In the case of $Pd(OAc)_2/2$ TPPTS, the reaction of palladium acetate with 2 TPPTS is fast: an equilibrium is reached after less than 2 h, a time delay which must be compared to the 24 h necessary with $Pd(OAc)_2$ and 5 TPPTS at room temperature. Oxidised phosphine (OTPPTS) (δ_1: 34.6 ppm), $Pd(TPPTS)_3$ (δ_2 = 23.1 ppm) and a species characterised by a peak at δ_3: 24.2 ppm (small peak) are the only phosphorus containing detectable species.[21,22] Given the stoichiometry of the reaction of formation of $Pd(TPPTS)_3$, no more than 40% of $Pd(OAc)_2$ can be reduced by the phosphine. Therefore, a large amount of $Pd(OAc)_2$ remains on the surface of silica in the case of Pd-2P-SAP.

Given that $Pd(OAc)_2$ is soluble both in water and in benzonitrile, it may indeed be among one of the species which leaches from the solid into the organic solution under the catalytic conditions. We have therefore tested its catalytic properties for the Sonogashira coupling reaction (eqn. 1) under a variety of conditions.

Catalytic properties of palladium acetate/*n* PPh_3 (*n* = 0, 2, 5). The catalytic properties of $Pd(OAc)_2$ were determined in benzonitrile under conditions where the reactants concentration and their ratio to palladium are close to those used for the experiments with the related SAP catalysts. Yet, it is clear that the value of the latter parameter is far from that effective in the supernatant solutions (25 *versus* 250). The amount of CuI added is such that the ratio Cu/Pd is close to 2. The experiments were conducted as follows: the time which corresponds to $t = 0$ is when the solution of the reactants is poured on the solids $Pd(OAc)_2$ and PPh_3 (see Experimental section for the full description). These conditions are classically used for homogeneous or biphasic catalytic tests.[23]

Palladium acetate is a poor catalyst for reaction (1): it transforms 50% of **1** within 1 h, but with a yield for **3** close to 20% only (Fig.3a). Polymerisation of phenylacetylene takes place, a well known reaction in presence of various palladium complexes.[10,24,25] $Pd(OAc)_2$ is thus not the highly active and selective leached catalyst.

Given that water is slightly soluble in benzonitrile (1% v/v), some phosphine may have leached together with palladium from Pd-nP-SAP. The addition of triphenylphosphine increases sharply the activity and the selectivity of $Pd(OAc)_2$ (Fig. 3a). Its activity depends on the amount of phosphine; it increases as follows:

$$Pd(OAc)_2 \ll Pd(OAc)_2/5\ PPh_3 < Pd(OAc)_2/2\ PPh_3 \approx Pd(PPh_3)_4$$

These results are in agreement with the literature data[9–13] which recommend a ratio of PPh_3/Pd close to 2, but interestingly $Pd(PPh_3)_4$ shows very similar catalytic properties under our conditions. The analysis by chromatography of the free phosphine present in the solution during catalysis indicates that with the complex $Pd(PPh_3)_4$ an average of 3.4 mols PPh_3 per Pd remain coordinated, while with $[Pd(OAc)_2/2\ PPh_3]$ only an average of 0.5 mols PPh_3 are coordinated and with $[Pd(OAc)_2/5\ PPh_3]$ only 1 mol PPh_3 is (Fig. 3d). The reduction of Pd(II) by PPh_3 is thus severely restricted by the reactants. In the absence of the reactants, the coordination of the phosphine is close to completion in both cases (Fig. 3e)[26] and the complex $Pd(PPh_3)_4$ stable (no phosphine liberated). Thus, if one admits that the active palladium species is a Pd(0) complex, then a second type of reduction may take place which involves phenylacetylene and is catalyzed by CuI.[4,27]

$Pd(OAc)_2$/*n* TPPTS in acetonitrile and water–acetonitrile. The hydrosoluble TPPTS reduces Pd(II) to Pd(0) in CH_3CN/H_2O faster than PPh_3 does it in DMF: the rate is one order of magnitude larger.[10] We have therefore studied the catalytic properties of $Pd(OAc)_2$/*n* TPPTS in CH_3CN/H_2O (v/v = 6/1) and compared them with those of $Pd(OAc)_2$/*n* PPh_3 in CH_3CN to separate the contribution of the solvent from the effect of the substitution of PPh_3 by TPPTS and/or that of water (Fig. 3c).

In CH_3CN, the activities of both $Pd(OAc)_2$ and $Pd(OAc)_2/5\ PPh_3$ are smaller than in PhCN while that of $Pd(PPh_3)_4$ is slightly larger (Fig. 3a, b). $Pd(OAc)_2$ catalyzes only the reaction of oligomerization of phenylacetylene; with all other systems, the selectivity for **3** is superior to 90%. The analysis of the free phosphine during these catalytic tests (Fig. 3f) reveals only one significant difference induced by the solvent: $Pd(PPh_3)_4$ loses an average of 2 mols PPh_3/Pd in CH_3CN. In CH_3CN/H_2O (v/v = 6/1), a monophasic system under the reaction conditions, both systems $[Pd(OAc)_2/n$ TPPTS] (n = 2, 5) are now highly efficient: the influence of the ratio TPPTS/Pd on the activity is weak, but slightly more significant on the selectivity; the best results are with 2 TPPTS/Pd. Overall, the yields of **3** are similar with both catalysts precursors. Interestingly, 73% Pd in the case of 2 TPPTS/Pd and only 10% Pd in the case of 5 TPPTS/Pd can be extracted by CH_2Cl_2 once full conversion of the reactants is achieved. This compares well with the observed heavy leaching of palladium with the related Pd-nP-SAP catalysts.

Finally, in order to get in solution a system whose composition would be closer to that on the surface of silica, we performed an experiment where $Pd(OAc)_2$ and 5 equivalents PPh_3 were reacted at 50 °C (15 min) in PhCN before the introduction of the reactants. Interestingly, this system is significantly less active than that obtained when no preliminary interaction is performed (Fig. 4a). During the interaction, about 2.5 mols PPh_3 are consumed (Fig. 4b); this suggests that some reduction of Pd(II) to Pd(0) by the phosphine may have occurred. Interestingly, after 15 min in the presence of the reactants, some phosphine is released so that 3.8 mol PPh_3/Pd are now free; this amount is close to that found when $Pd(OAc)_2$ and PPh_3 are not allowed to interact prior to the reaction.

Discussion

Both solids Pd-2P-SAP and Pd-5P-SAP are efficient catalysts for the coupling reaction of phenylacetylene with phenyliodide, in presence of copper(I) iodide and triethylamine. But they differ significantly in the importance of their activity and, less significantly, selectivity. The solid Pd-5P-SAP is under all conditions tested more active than the solid Pd-2P-SAP. They share in common some general features, such as:

—an activity for the coupling reaction which increases with the initial water content.

—a good selectivity for the coupling product PhCCPh, *i.e.* superior to 80%.

—a significant palladium leaching from the solid to the organic solvent, which decreases with increasing initial water content of the solids. This leaching is more important with the solid Pd-2P-SAP.

—a poor behavior towards recycling: the activity of the solid decreases with the number of recycles, but there is no simple relation between the activity decrease and the palladium loss.

The influence of the water amount on the activity seems to be different with Pd-2P-SAP and Pd-5P-SAP solids; indeed, the curves representing the percentage **3** as a function of the water concentration on the solid, expressed as the percentage by weight on the solid, show different shapes (Fig. 5a). Apparently an optimum amount of water around 30 wt% exists for

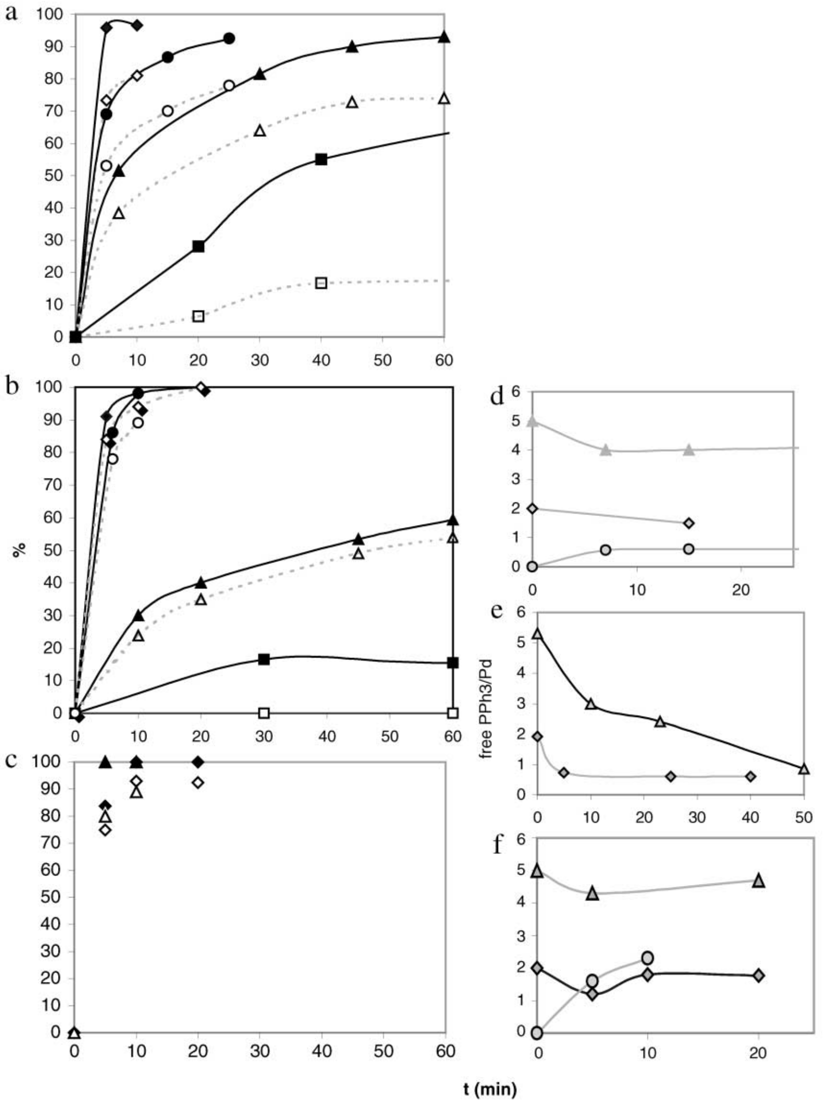

Fig. 3 Catalytic properties of: (□) Pd(OAc)$_2$; (◇) Pd(OAc)$_2$/2 PPh$_3$; (Δ) Pd(OAc)$_2$/5 PPh$_3$; (○) Pd(PPh$_3$)$_4$. Exp. cond.: see Fig. 1. Black symbols: % conv. PhCCH; white symbols: % yield PhCCPh. Solvent (a) PhCN, (b) CH$_3$CN, (c) CH$_3$CN/H$_2$O, (d) and (f): free PPh$_3$ in the related solutions during the catalytic tests, (e): free PPh$_3$ in PhCN solutions maintained at 50 °C, without reactants.

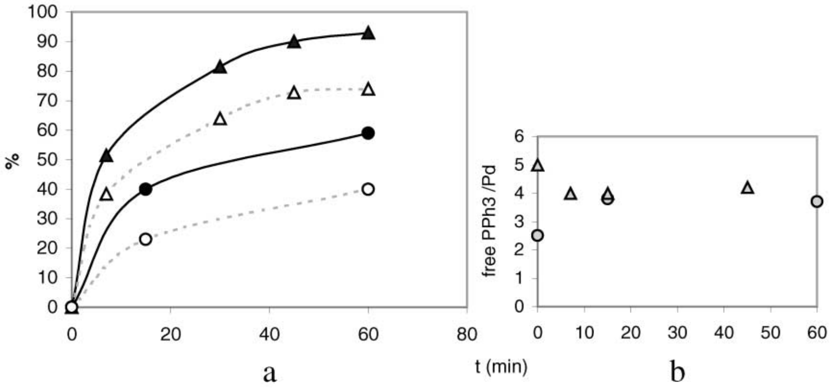

Fig. 4 (a) Catalytic properties of Pd(OAc)$_2$/5 PPh$_3$ in PhCN under the conditions described in the caption to Fig. 1. (Δ) no interaction; (○) interaction, reacted at 50 °C for 15 min prior to addition of the reactants. Black symbols: % conv. **1**; white symbols: % yield **3**. (b) free PPh$_3$ under the conditions of (a).

Pd-5P-SAP but none in the case of Pd-2P-SAP. This representation has no physical and/or chemical meaning, as no hypothesis is made on the process of water adsorption on these solids. In Fig. 5b and 5c, we try to relate the amount of water introduced to the specific surface of silica and to the pore volume, respectively; the differences in the behavior of the two solids are still difficult to rationalise. As the phosphine TPPTS is known to be very hydrophilic, we finally considered that water does not adsorb layer by layer on the whole surface of silica, but that it clusters essentially around these molecules and therefore around the complex Pd(TPPTS)$_3$. This hypothesis leads to a similar behaviour in terms of activity as a function of water amount for the two solids (Fig. 5d).

Although the palladium leaching is too severe with both solids under the tested conditions, the high activity of the solutions once the solid is filtered off is intriguing. From

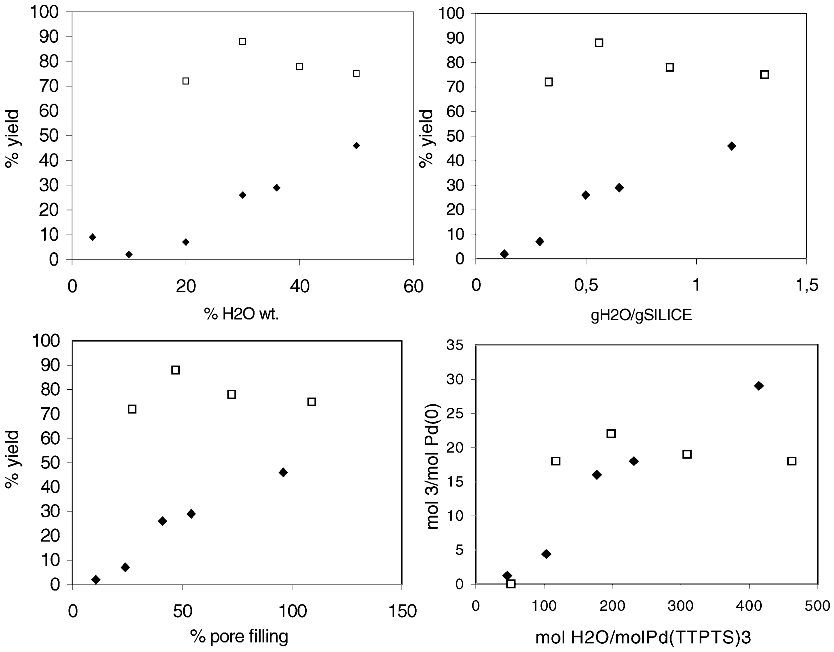

Fig. 5 Influence of the water content on the catalytic properties of Pd-2P-SAP (◆) and Pd-5P-SAP (□) under the conditions given in the caption to Fig. 1. $t_R = 50$ min.

the studies of the connected homogeneous catalytic systems, we can deduce that neither $Pd(OAc)_2$ nor $Pd(TPPTS)_3$ are the highly active entity which leaches into the organic phase. Nevertheless palladium acetate is certainly among these leached species, especially with Pd-2P-SAP where it cannot be fully reduced by the phosphine. It is most certainly a complex with a more lipophilic character which accumulates during catalysis. A complex such as $Pd(CCPh)_2$ is a reasonable candidate, on the basis of the mechanism proposed by Sonogashira;[4] it may be stabilised by phosphines.

During the course of these studies, we could also show the sharp influence of the reactants, PhCCH and PhI, on the process of reduction of Pd(II) to Pd(0) by the phosphines, PPh_3 or TPPTS. Thus according to a quantitative analysis of the free phosphine, only a small fraction of Pd(II) is reduced to $Pd(PR_3)_n$, although the reduction is achieved up to total consumption of the phosphine in the absence of the reactants.

This study shows clearly some of the limits of the SAP method for the immobilization of water soluble molecular catalysts. The complexity of the catalytic system, a multi component system, is certainly at the origin of some of the problems encountered here. We are currently investigating more deeply the working mode of the supported aqueous phase catalyst, so as to be able to adapt this methodology more efficiently to homogeneous catalysts in the future.

Experimental

Palladium acetate (99%), benzonitrile (anhydrous, 99%), copper(I) iodide and triethylamine (99.5%) were used as received from Aldrich. Silica (200 MP) was a generous gift from Grace: it is characterized by a specific surface area of 185 $m^2 g^{-1}$ as determined by N_2 adsorption at 77 K and a narrow pore size distribution centered at 24 nm diameter. All the experiments were performed under an inert atmosphere (nitrogen or argon) using standard Schlenk tube techniques. The ^{31}P NMR spectra were recorded on a Bruker AC 200 spectrometer (81 MHz) calibrated with H_3PO_4 as the external standard.

Synthesis of the catalysts

The solid Pd-2P-SAP was synthesized as follows: typically, 42.4 mg (0.188 mmol) $Pd(OAc)_2$ and 234 mg (0.376 mmol) TPPTS•3 H_2O were dissolved in 4.6 mL of degassed water in a Schlenk tube and the solution was stirred for 30 min. Silica (2 g), evacuated at 250 °C (10^{-4} Torr, 5 h) was then poured into the solution and the mixture stirred for 1h 30 min at room temperature. The solid was then evacuated to dryness (typically 1 h, 10^{-1} Torr, 4 h 10^{-4} Torr). The blood-red solid Pd-2P-SAP is characterized by a palladium content of 0.86 wt% and a residual water content close to 2 wt% The synthesis of Pd-5P-SAP differed from that of Pd-2P-SAP only by the amount of TPPTS which was taken equal to 587.8 mg (0.944 mmol): the yellow solid is then characterized by a palladium content of 0.76 wt% and a water content close to 3 wt%

Catalytic testing of the solids

All the catalytic tests were performed in a round-bottomed flask fitted with a reflux condenser and a septum to allow for the withdrawal of small samples at regular time intervals. Typically, the catalyst (here Pd-2P-SAP) (0.200 g, 0.016 mmol Pd) was introduced in the flask and the desired amount of water was added with a syringe (typically 120 µL for a 20 wt% H_2O solid). The wet solid was stirred for 30 min at room temperature. Simultaneously, a solution in benzonitrile (7.5 mL) containing PhCCH (44 µL, 0.4 mmol, 25 equiv.) PhI (45 µL, 0.4 mmol, 25 equiv.) and NEt_3 (225 µL, 1.6 mmol, 4 equiv./PhI) was prepared in a Schlenk tube. This solution was thoroughly stirred and then introduced with CuI (6.1 mg, 0.032 mmol, 2 equiv.) in the flask, which was immersed in an oil bath maintained at 50 °C. We have checked that the temperature is stabilized within less than 5 min. Analytical samples (0.1 mL) were injected after filtration in the chromatograph.

Catalytic properties of the supernatant solutions

At the end of each catalytic test performed with the solid catalysts, Pd-2P-SAP or Pd-5P-SAP, the reaction mixture was decanted for a few minutes at 50 °C and the supernatant solution was taken off through a filter with a syringe to a round-bottomed flask, equipped as described above for the catalytic tests, then immersed in an oil bath at 50 °C. A dose of reactants: PhI, PhCCH and one half NEt_3, calculated so as to have the same reactant concentration (54 mmol L^{-1}) as for the test in the presence of the solid, is added. No CuI was added with the reactants given that analysis of the copper content has shown that most of it is indeed in the supernatant solution.

Recycling of the solid

A typical experiment was as follows: the solid Pd-2P-SAP (461 mg, 0.037 mmol Pd) was reacted as described above with a solution in water-saturated benzonitrile (16 mL, 1 wt% H_2O) containing PhCCH (100 μL, 0.925 mmol, 25 equiv.), PhI (100 μL, 0.925 mmol, 25 equiv.) and NEt_3 (500 μL, 307 mmol, 100 equiv.) Then CuI was added (14.1 mg, 0.074 mmol, 2 equiv.) and the flask was immersed in an oil bath maintained at 50 °C. After completion of the reaction, the supernatant solution was removed with a syringe and its properties tested as described above. The solid was washed twice with water-saturated benzonitrile (5 mL) before being contacted with a fresh solution of the reactants and CuI as used in the first run.

Catalytic tests under homogeneous conditions

$Pd(OAc)_2$ (3 mg, 0.0133 mmol), PPh_3 (7 mg, 0.0266 mmol) and CuI (5 mg, 0.0266 mmol) were introduced under Ar in a round-bottomed flask equipped with a condenser. A solution of PhCCH (36.6 μL, 0.33 mmol) and PhI (37.4 mg, 0.33 mmol) in PhCN (6 mL), prepared in a Schlenk tube, was then added. Time $t = 0$ was when the flask was immersed in an oil bath preheated at 50 °C. The thermal equilibrium was reached within less than 5 min.

Data analysis

The catalyzed reaction was followed as a function of time by analysis of a small sample (typically 0.1 mL) with a chromatograph (HP 5890) equipped with an ionization detector (T_{inj} = 230 °C, T_{detector} = 240 °C) and a capillary column (HP5). The conditions were: 60 °C (5 min) −220 °C, 8 °C min^{-1}. These conditions allowed for the quantitative analysis of the reactants and the coupling product, and of the free phosphine PPh_3. In all cases, the calibration was performed using authentic samples.

Analysis of the palladium and copper contents of the solid (after attack with HF, followed by HCl) and of the solutions (after evaporation of the solvent to dryness, calcination of the residue and dissolution in aqueous HCl) was performed by ICP, coupled with MS when necessary (CNRS-Solaize).

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