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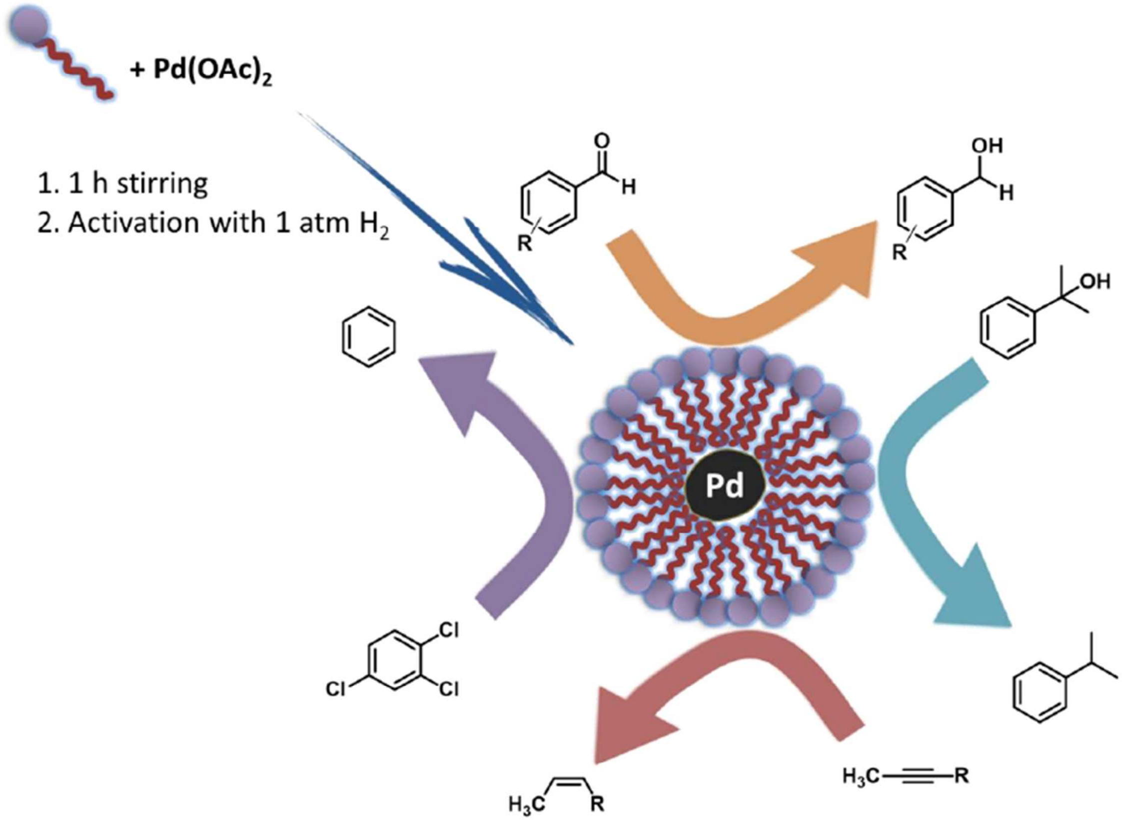
Selective Hydrogenations and Dechlorinations in Water Mediated by Anionic Surfactant Stabilized Pd Nanoparticles

Giorgio La Sorella, Laura Sperni, Patrizia Canton, Lisa Coletti, Fabrizio Fabris, Giorgio Strukul, Alessandro Scarso[*]

Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia, via Torino 155, Mestre Venezia (ITALY). Tel:+39-041-2348569; Fax: +39-041-2340517; alesca@unive.it



We report a facile, inexpensive and green method for the preparation of Pd nanoparticles in aqueous medium stabilized by anionic sulfonated surfactants sodium 1-dodecanesulfonate **1a**, sodium dodecylbenzenesulfonate **1b**, dioctyl sulfosuccinate sodium salt **1c** and poly(ethylene glycol) 4-nonylphenyl-3-sulfopropyl ether potassium salt **1d** simply obtained by stirring aqueous solutions of $Pd(OAc)_2$ with the commercial anionic surfactants further treated under hydrogen atmosphere for variable times. The aqueous Pd nanoparticles solutions were tested in the selective hydrogenation reactions of aryl-alcohols, -aldehydes and –ketones leading to complete conversion to the deoxygenated products even in the absence of strong Brønsted acids in the reduction of aromatic aldehydes and ketones, in the controlled semi-hydrogenation of alkynes leading to alkenes and in the efficient hydro-dechlorination of aromatic substrates. In all cases the micellar media were crucial to stabilize the metal nanoparticles, to dissolve substrates, to steer product selectivity and to enable recycling. What is interesting is also that a benchmark catalyst like Pd/C can be often surpassed in activity and/or selectivity in the reactions tested by simply switching to the appropriate commercially available surfactant, thereby providing an easy to use, flexible and practical catalytic system capable of efficiently addressing a variety of synthetically significant hydrogenation reactions.

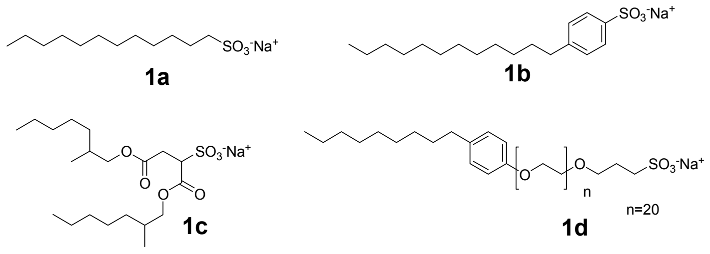
Introduction

Thanks to their peculiar properties, metal nanoparticles (NP) are attracting much interest in the field of catalysis as witnessed by the numerous reviews on this subject.[1] Usually metal NP in the catalysis field are prepared in proper solvents from a metal salt precursor and a reducing agent in the presence of a stabilizer in order to avoid aggregation. Examples of suitable stabilizers are numerous, ranging from classical solid supports such as carbon,[2] metal oxides[3] and zeolites,[4] as common practice in heterogeneous catalysis, as well as organic supports like polymers,[5] dendrimers[6] and many others. In this general framework the stabilization of metal NP in water is likely to gain a central role aiming at the development of new catalytic systems able to work in environmentally friendly solvents such as water.

In this respect however, one has to face two opposite features, on the one hand the use of water as the solvent allows in principle an easier product separation and catalyst recycling, but on the other hand, most organic substrates are insoluble in this solvent causing lower reaction rates. While hydrogenation reactions in water for rather soluble substrates have been reported using different Pd based supported heterogeneous catalysts displaying good selectivities and activities,[7] more hydrophobic substrates require often the use of polar co-solvents thus decreasing the advantages in terms of better environmental impact due to the use of water as solvent.

A possible solution to the problem is the use of surfactants that self-aggregate into micelles or larger assemblies generating apolar environments able to provide a separate phase for organics as well as naked metal NP stabilization in water through a "ligand" effect. The capping of metal NP with suitable self-aggregating agents produces a sort of supramolecular catalytic environment capable of driving the selectivity of these catalytic systems in a way that often outperforms traditional heterogeneous catalysts.[8] Examples of this approach have been applied to different metal species. Stabilization of Co NP based on the formation of water/isooctane or hexane microemulsions in the presence of sodium di(ethylhexyl) sulfosuccinate with sodium tetraborohydride was described leading to nanoparticles in the size range of 2–5 nm.[9] In other cases, the role of the surfactant employed was twofold. This is the case of the non ionic copolymers poly(ethylene oxide) – poly(propylene oxide) – poly(ethylene oxide) (PEO*x*–PPO*y*–PEO*x*) that acted both as a reductant and as stabilizer for the growth of Au NP,[10] or the employment of polyaniline for the formation of Pd-NP[11]or the use of cucurbit[6]uril leading to active and recyclable Pd-NP.[12] Alternatively commercial or specifically synthesized cationic and zwitterionic surfactants were employed for this purpose and have been applied to a wide range of chemical transformations.[13] Lipshutz and co-workers disclosed the micellar promoted semi-hydrogenation of alkenes mediated by Pd-NP stabilized by the neutral designer surfactant TPGS-750-M in water with $NaBH_4$ as reducing agent.[14]

Herein we present a facile, inexpensive and green method to synthesize Pd nanoparticles in water stabilized by commercial anionic sulfonated surfactants like sodium 1-dodecanesulfonate **1a**,[15] sodium dodecylbenzenesulfonate **1b**, dioctyl sulfosuccinate sodium salt **1c** and poly(ethylene glycol) 4-nonylphenyl-3-sulfopropyl ether potassium salt **1d** (Scheme 1) characterized by a range of particle size and stability and catalytic activity. We tested these Pd systems in water in the hydrogenation reactions of aromatic aldehydes, ketones and aryl-alcohols, in the hydrodechlorination reaction of aromatic substrates and in the chemoselective semi-hydrogenation reactions of alkynes to the corresponding alkenes observing a modulation in catalytic activity, of the product selectivity and recyclability by simply changing the surfactant.



Scheme 1. Sulfonated anionic surfactants employed for the stabilization of Pd-NP in water.

Results and discussion

Preparation and characterization of the Pd-NP in the presence of surfactants

The preparation of the solutions containing the Pd-NP was carried out consisting in the simple dissolution of $Pd(OAc)_2$ in water in the presence of a given surfactant subsequently left under hydrogen atmosphere for a variable time observing the change of the solution color from orange to grey-black as an evidence of the presence of Pd-NP. The time required for this operation varied from two minutes, as in the case of **1d**, up to ten minutes for **1b**. The concentration of surfactant employed was in all cases at least one order of magnitude higher than the corresponding c.m.c. and it was optimized in order to grant the system the highest stability using the lowest possible amount of surfactant.

Table 1: Pd-NP average size determined by TEM analysis.

Surfactant	**Pd particle size (nm)**
1a	4.4
1b	5.0
1c	5.1
1d	6.1

The solutions of Pd-NP obtained with the different series of anionic surfactants **1a-d** were characterized by means of transmission electron microscopy (TEM) analysis.[16] In all samples the technique revealed the presence of pseudo-spherical nanoparticles with an average diameter of about 4-6 nm (Table 1) and a relatively narrow distribution between 2 and 9 nm. High Resolution Electron Microscopy (HREM) evidenced that in most cases the nanoparticles were pure Pd single crystals. What was markedly different from one surfactant to another was the degree of dispersion of the NP, as is clearly evident from Figure 1.

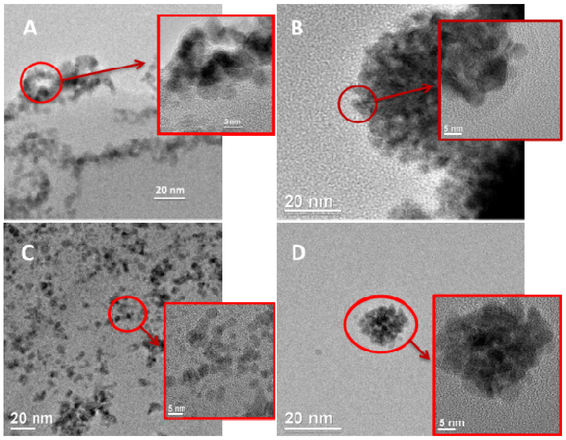


Figure 1. TEM images of the Pd-NP stabilized by sulfonated anionic surfactant obtained stirring for 1 h and treating with hydrogen a solution of 3 mL of water with $Pd(OAc)_2$ 2.4 mM and A) **1a** 80 mM; B) **1b** 100mM; C) **1c** 90mM; D) **1d** 80mM.

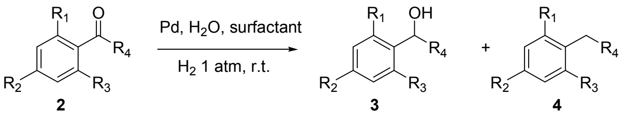
In the presence of surfactant **1c** we obtained well-dispersed and rather small-sized nanoparticles, while with surfactant **1a** and **1b** similarly-sized Pd-NP were observed but either confined at the external edge of a large organic area or present in large aggregates. In the sample with surfactant **1d** slightly larger NP were still visible but highly aggregated into clusters that assumed a diameter of about 25 nm.

The observed differences are likely to be due to the different interaction between the surfactant and Pd. In all cases the presence of the sulfonated group allowed an attractive interaction with the $Pd(OAc)_2$ precursor favoring the formation of similarly sized primary Pd-NP upon reduction. A role on the subsequent aggregation seems to be played by the nature of the hydrophobic tail of the surfactant. Where no donor heteroatoms are present, as in **1a** and **1b**, Pd-NP are forced to remain in close contact with the hydrophilic heads on the external surface of the aggregates. With surfactant **1c** bearing two hydrophobic tails the formation of vesicles is likely to occur and this could be related to the lower aggregation phenomena observed for the Pd NPs. Surfactants bearing extra oxygen atoms in the hydrophilic portion, as **1d**, may interact with Pd favoring the dissolution of the metal more deeply in the micellar aggregate and the subsequent aggregation of the NP in clusters stabilized by the long polyethylene glycol chains. Furthermore, as will be clear afterwards, the catalytic behavior of the different systems is often hardly ascribable to the large differences observed in the extent of aggregation, which raises the question whether these differences apply also to the operating catalyst.

The different aqueous NP solutions were tested in a series of hydrogenation reactions. In particular, the reactions that attracted our interest were i) the reduction of aromatic ketones and aldehydes to alcohols and of aryl-alcohol to toluene derivatives, ii) the chemoselective semi-hydrogenation reaction of alkynes to alkenes and iii) the hydrodehalogenation of aromatic chlorinated substrates.

Catalytic hydrogenation of aromatic carbonyl compounds and benzyl alcohols

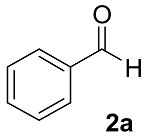
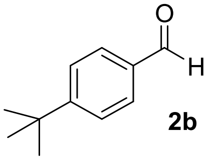
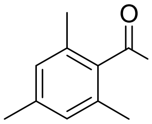
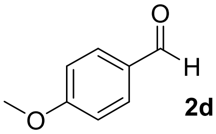
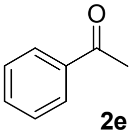
As far as the hydrogenation of aromatic carbonyl compounds like ketones and aldehydes is concerned, the reaction can be carried out with hydrogen donors such as e.g. polymethylhydrosiloxane (PMHS)[17] or with molecular hydrogen. The reaction proceeds stepwise leading initially to the corresponding benzyl alcohol that can be further reduced to the corresponding alkyl substituted aryl derivative (Scheme 2). In this step, the presence of a source of acidity, provided by a heterogeneous support[18] or by an acid co-catalysts,[19] is generally necessary in order to obtain the complete substrate de-oxygenation when the reaction is carried out with molecular hydrogen. Preliminary experiments showed that catalysts made of Pd-NP in the presence of **1a**, **1c** and **1d** were active in the hydrogenation of benzaldehyde derivatives and their catalytic activity was compared with that of commercial 10% Pd/C in methanol (Table 2) taken as a benchmark for this reaction. Under the same experimental conditions, formation of Pd black was observed during the hydrogenation reaction with benzaldehyde using surfactant **1b**, therefore this surfactant was excluded in the further catalytic aldehyde reduction studies.



Scheme 2. Hydrogenation of aromatic aldehydes **2** and ketones catalyzed by Pd-NP in water.

As is evident from data reported in Table 2, the catalytic behavior of Pd-NP systems is only dependent on the surfactant present in solution. In our experimental conditions we did not add any external source of acidity, nevertheless we observed, in some cases, complete hydrogenation to the alkylbenzene derivative. In fact, the hydrogenation of benzaldehyde **2a** turned out to be possible with all Pd@surfactant systems developed, observing always the initial formation of the benzyl alcohol derivative **3a** that more slowly converted to the corresponding alkylbenzene derivative **4a** over time. In all cases the Pd@surfactant systems showed a generally lower catalytic activity with respect to Pd/C in methanol probably also because of the well known lower solubility of hydrogen in water rather than in methanol.[20] However the reduced catalytic activity enabled a better chemoselectivity of the hydrogenation reaction leading to a better control on the hydrogenation of individual benzaldehydes **2** selectively forming the corresponding benzyl alcohols **3** or alternatively leading to full de-oxygenation by simply changing the surfactant and the reaction time.

Table 2. Hydrogenation reaction of aromatic aldehydes **2a-d** and ketones **2e** with different Pd/surfactant **1a,c,d** in water and with Pd/C in MeOH.

ɨ	Substrate		Pd@1a[a]		Pd@1c[b]		Pd@1d[a]		Pd/C	
1	 **2a**	Time (min)	50	350	60	500	60	350	10	50
		Conv. (%)	97	>99	97	>99	99	>99	94	>99
		3a (%)	88	1	92	1	96	80	73	-
		4a (%)	9	99	5	99	3	20	21	>99
2	 **2b**	Time (min)	40	120	60	120	70	500	10	60
		Conv. (%)	95	>99	97	>99	99	>99	81	>99
		3b (%)	62	-	76	-	96	3	68	-
		4b (%)	33	>99	21	>99	3	97	13	>99
3	 **2c**	Time (min)	50	350	60	500	500		10	50
		Conv. (%)	98	>99	98	>99	98		97	>99
		3c (%)	84	-	94	1	96		70	-
		4c (%)	15	>99	4	99	2		27	>99
4	 **2d**	Time (min)	40	150	60	250	120	500	10	30
		Conv. (%)	92	99	96	99	92	>99	97	>99
		3d (%)	77	2	78	4	74	2	55	-
		4d (%)	15	98	18	95	18	98	42	>99
5	 **2e**	Time (min)	60	1440	1440		1440		60	1440
		Conv. (%)	94	99	90		45		97	98
		3e (%)	90	1	20		39		93	18
		4e (%)	4	98	70		7		4	80

Experimental conditions: Pd/C 7.6 mg (0.0072 mmol Pd), substrate 0.72 mmol, H_2 1 atm, MeOH 3 mL, T 25°C. $Pd(OAc)_2$ 0.0072 mmol, substrate 0.72 mmol, H_2 1 atm, water 3 mL, T 25°C. a) [surfactant **1a** and **1d**] = 80 mM; b) [surfactant **1c**] = 100 mM.

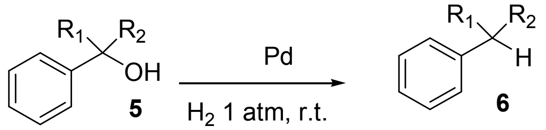
Overall, **1a** provided a catalytic system characterized by slightly higher activity with respect to **1c**, although Pd with surfactant **1a** showed the presence of more aggregated Pd-NP. This may result by the coordination of the oxygen atoms of **1c** to the metal centers that provide stability to the Pd-NP but at the same time tend to reduce their activity. At variance, surfactant **1a** binds less strongly the Pd-NP and this turns out into a slightly more active catalytic system despite the higher aggregation observed.

Observing the results obtained in the hydrogenation reactions catalyzed by Pd/C, a different reactivity of the aldehydes investigated can be noticed. The presence of a methoxy group in the *para*- position in the aromatic structure of **2d** makes this substrate more active compared to benzaldehyde **2a** in the hydrogenation and in the de-oxygenation reactions. **2a** and **2c** showed a comparable reactivity, despite the higher steric hindrance of the latter, while the hydrogenation reaction of **2b** turned out to be slightly slower. Conversely, the results obtained in the reactions catalyzed by Pd@**1a** and Pd@**1c** showed that the order of reactivity was inverted. The more reactive substrate became **2b** that showed the lowest activity with Pd/C. The higher lipophilicity deriving from the presence of the tert-butyl group in the para- position in the molecular structure of **2b** can favor its migration inside the micelles and could explain this effect.

The results obtained with Pd@**1d** deserve a separate discussion since a complete reversal of the activity order was observed. **2a** became the most reactive substrate followed by **2b**. The hydrogenation reaction of **2d** proceeded at a lower rate, while **2c** returned to be the least reactive substrate. The cause of this particular reactivity might probably be found in the PEG oxygen donors present in surfactant **1d** that stabilize the catalytic system lowering its activity, a recurring effect with these systems (*vide infra*).

Systems Pd@**1a** and Pd@**1c** seemed quite active also in the subsequent de-oxygenation reaction. We decided to stress this property performing the hydrogenation reaction using acetophenone **2e** as an intrinsically less reactive substrate. With **2e** the differences in catalytic behavior for the Pd@surfactant NP with respect to Pd/C were more evident. In fact, Pd@**1d** proved to be the least active catalyst, while Pd@**1a** and Pd@**1c** gave results comparable with those obtained with Pd/C. More specifically, comparing the results obtained in the reactions catalyzed by Pd@**1a** and Pd/C, it seemed that Pd@**1a** in water had a higher catalytic activity in the de-oxygenation reaction than Pd/C in methanol despite the higher solubility of hydrogen in the latter medium.

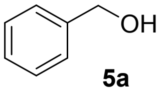
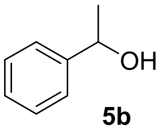
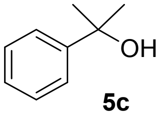
In order to investigate better this aspect, we decided to compare the Pd@surfactant and Pd/C systems directly in the de-oxygenation reaction of primary, secondary and tertiary benzyl alcohols using the conditions of the hydrogenation reaction of carbonyl groups (Scheme 3).



Scheme 3. De-oxygenation reaction of benzyl alcohols **5** to the corresponding alkylbenzene derivatives **6**.

The results (Table 3) showed that it is possible to reach a catalytic activity greater than that observed with Pd/C in methanol using the appropriate Pd/surfactant in water. When we performed the de-oxygenation reaction of **5a, 5b** and **5c** with Pd/C, the difference in activity for the three substrates was evident. In fact **5a** reacted rather quickly (>99% conversion in 1.5 h), the reaction of **5b** did not provide a high conversion (70%) even after 24 hours, while the same time allowed to obtain only 40% conversion of **5c** even increasing up to 5 times the amount of Pd/C. With the Pd@surfactant systems, the order of substrates reactivity was confirmed, but Pd@**1a** and Pd@**1c** systems proved to be very active also in the de-oxygenation of secondary and tertiary benzyl alcohols. With these substrates we observed that Pd@**1a** was the best catalyst. Pd@**1c** showed slightly lower catalytic activity but both catalysts in water gave a quantitative conversion of the substrates under the same mild conditions of Pd/C in methanol. The comparatively poor reactivity observed with Pd@**1d** could be easily ascribed to the aggregation phenomena that causes the formation of large metal cluster.

Table 3. De-oxygenation reaction of benzyl alcohols **5a-c** with Pd@surfactant **1a-d** in water and Pd/C in THF.

#	Substrate	Catalyst	Time (h)	Conversion (%)
1	 **5a**	Pd@**1a**	6	>99
		Pd@**1c**	10	>99
		Pd@**1d**	24	50
		Pd/C	1.5	>99
2	 **5b**	Pd@**1a**	20	>99
		Pd@**1c**	24	>99
		Pd@**1d**	24	10
		Pd/C	24	70
3[a]	 **5c**	Pd@**1a**	24	>99
		Pd@**1c**	24	>99
		Pd@**1d**	24	8
		Pd/C	24	40

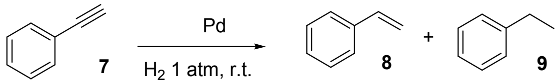
Experimental conditions: Pd/C 7.6 mg (0.0072 mmol Pd), substrate 0.72 mmol, H_2 1 atm, MeOH 3 mL, T 25°C. $Pd(OAc)_2$ 0.0072 mmol, substrate 0.72 mmol, H_2 1 atm, water 3 mL, T 25°C, [surfactant **1a** and **1d**] 80 mM, [surfactant **1c**] 90 mM. a) Pd/C 38 mg (0.036 mmol Pd).

In no case was the addition of acid co-catalyst necessary to promote the reaction. Commercial activated carbons are generally obtained by an oxidation treatment that introduces in the structure acidic groups that favor metal adsorption and stability.[21] In the micellar aggregates, the negatively charged surface sulfonate groups present in the surfactant can polarize water causing the development of an acidic layer on the micellar surface that may well co-catalyze the de-oxygenation reaction of the substrate.

Catalytic semi-hydrogenation of alkynes to alkenes

The semi-hydrogenation reaction of alkynes to the corresponding alkenes is an extremely important chemical transformation[22] since the production of *Z*-alkenes starting from internal alkynes allows to obtain important molecular building blocks for the synthesis of several fine chemicals.[23] Apart from the traditional Lindlar catalyst[24] that makes use of toxic Pb salts, alternative heterogeneous approaches are based on metal catalysts like Pd supported on a surface that impart pre-orientation of the substrates thus selectively leading to the *Z* products,[25] even though sometimes possible isomerization to the *E* isomer was observed. In the past years, most of the homogeneous catalytic systems developed for this reaction were mainly based on transition metal complexes (Rh, Pd, Pt, etc.) in most cases operating in organic solvents.[22] However, the most common strategy is the use of heterogeneous catalysts with selective poisoning in order to maximize the selectivity to alkenes and to limit the possible *Z-E* isomerization.[23]

We selected phenylacetylene **7** (Scheme 4) as a model substrate to optimize the reaction conditions for the Pd@surfactant catalytic systems. Initially the reaction was carried out in tetrahydrofuran with a commercial 10% Pd/C catalyst. In order to maximize the selective conversion to styrene **8**, the reaction was repeated with different amounts of catalyst observing that an interesting level of both activity and selectivity was achieved working with 0.04 mol% of Pd compared to **7** in THF.



Scheme 4. Hydrogenation reaction of phenylacetylene **7** leading to styrene **8** and eventually to ethylbenzene **9**.

The reaction was then extended to the Pd@surfactant systems under the same conditions. Unfortunately Pd@**1c** and Pd@**1d** proved unsuitable for this selective reaction. In fact when the conversion of **7** reached values in a range of 80-90%, the hydrogenation reaction of styrene became very fast and high yields of ethylbenzene **9** were obtained (see e.g. Table 4, entry 6). Differently, the use of **1a** and **1b** gave Pd-NP micellar systems with both high catalytic activity and high alkene chemoselectivity.

Table 4. Semi-hydrogenation reaction of phenylacetylene **7** with Pd/surfactant **1a-c** in water and with 10% Pd/C in THF.

#	Catalyst	[Surfactant] (mM)	Cat/Subs (mol%)	Solvent	Time (min)	Conversion (%)	Selectivity to styrene (%)
1	Pd/C	-	1	THF	10	94	93
2	Pd/C	-	0.1	THF	50	88	97
3	Pd/C[a]	-	0.04	THF	90	96	95
4	Pd@**1a**[b]	80	1	H_2O	50	94	97
5	Pd@**1b**[b]	100	1	H_2O	25	86	98
6	Pd@**1c**[b]	80	1	H_2O	80	84	62
7	Pd@**1b**[c]	100	0.5	H_2O	27	99	98
8	Pd@**1b**[d]	100	0.33	H_2O	120	96	97
9	Pd@**1b**[c]	120	0.5	H_2O	75	85	98

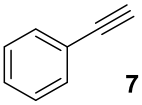
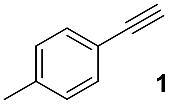
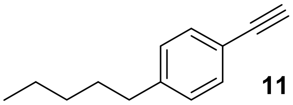
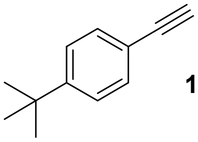
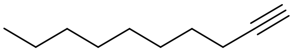
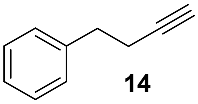
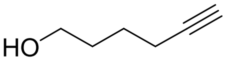
Experimental conditions: phenylacetylene (1.5 mmol), reaction volume 3 mL, H_2 1 atm, T 25°C. a) phenylacetylene (3.5 mmol). b) phenylacetylene (0.7 mmol). c) phenylacetylene (1.4 mmol). d) phenylacetylene (2.1 mmol).

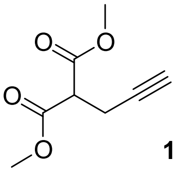
The results reported in Table 4 show that the selectivity to **8** obtained using Pd@**1a** and Pd@**1b** in the aqueous solvent in the presence of surfactants appeared to be even slightly higher than that in THF with Pd/C under the same catalyst to substrate ratio, even if the productivity was lower because of the lower substrate concentrations used. In this reaction, Pd@**1b** seemed to be the best option in terms of both activity and selectivity observed. As a consequence we focused on this catalytic system for the subsequent tests. Additional catalytic tests were carried out to optimize the amounts of surfactant **1b** and Pd. It was observed that the best results were obtained when the amount of Pd was lowered down to 0.5 mol% and the concentration of **1b** was 100 mM (Table 4, entries 7-9) obtaining a very high selectivity (98%) and high conversion (99%, Table 4, entry 7). A larger amount of surfactant or a further decrease in the Pd amount led to an increase of the reaction time without any beneficial effect for the selectivity of the reaction. With the best catalytic system at hand, we applied the latter experimental conditions to a series of different alkynes, testing the Pd@**1b** selectivity and comparing the results observed with the traditional Pd/C catalyst.

The results are reported in Table 5 where reaction times and conversions, as well as catalyst amounts and substrate concentrations were chosen in order to maximize selectivities to the intermediate alkenes in the consecutive reaction that are almost always in the ≥ 95% range with some minor exceptions (entries 5, 10). In order to have comparable performance in terms of conversion, the amount of Pd necessary with Pd@**1b** was about 5 times higher than that with Pd/C. This compensates in part for the much lower solubility of hydrogen in water with respect to

THF. Under these conditions the measured turnover frequencies (TOF) for Pd@**1b** are not dramatically lower than for Pd/C.

Table 5. Semi-hydrogenation of phenyl acetylene derivatives **7-13** and other alkynes **14-18** with Pd@**1b** in water and with Pd/C in THF.

#	Substrate	Catalyst	Time (min)	Conversion (%)	TOF (h^{-1})	Selectivity to Alkene (%)
1	 **7**	Pd/C[a]	90	96	1490	95
		Pd@**1b**[b]	27	99	434	98
2	 **10**	Pd/C[a]	70	98.5	1970	95
		Pd@**1b**[b]	45	>99	263	95
3	 **11**	Pd/C[a]	60	88	2050	95
		Pd@**1b**[b]	20	83	491	95
4	 **12**	Pd/C[a]	70	91	1820	94
		Pd@**1b**[b]	70	94	159	95
5	 **13**	Pd/C[a]	60	80	1400	97
		Pd@**1b**[b]	50	77	182	97
6	 **14**	Pd/C[a]	80	98	1720	94
		Pd@**1b**[b]	60	>99	197	97
7	 **15**	Pd/C[a]	90	68	1060	95
		Pd@**1b**[b]	80	62	92	93

8	 **16**	Pd/C[a]	80	97	1700	90
		Pd@**1b**[b]	90	98	129	88

Experimental conditions: Reaction volume 3mL, H_2 1 atm, T 25°C. a) Pd/C 1.6 mg (0.0015 mmol Pd), substrate 3.5 mmol, solvent THF; b) $Pd(OAc)_2$ 1.6 mg (0.0071 mmol Pd), substrate 1.4 mmol, [**1b**] 100 mM, solvent H_2O.

If we analyze the behavior of the aryl alkynes reported in Table 5 with Pd/C it seems, as should be expected, that the presence of an electron-donating group in the *para* position increases the corresponding TOF (compare entry 1 with entries 2-4). Substrate solubility in micelles is a widespread parameter to rationalize the catalytic behavior of micellar catalysts with homologous substrates. For example we could duly rationalize the substrate selectivity properties of Pd@**1a** in the C=C double bond hydrogenation in a series of α,β-unsaturated aldehydes bearing increasingly long aliphatic tails, establishing a clear correlation between the lipophilicity of the substrate and its reactivity.[15] In the present case this guideline seems useless because the solubility of substrates in water decreases of about two orders of magnitude on going from substrate **7** to substrate **12**[26] which suggests that their lipophilicity, hence their solubility in **1b** should follow an opposite order.

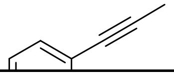
The solubility in water of aryl alkynes **7**, **10-12** is about four times higher than the corresponding alkenes,[26] which implies that in the course of the reaction the dissolution in the micelles of the alkene semi-hydrogenation products are higher than the corresponding alkyne reactants, a situation that is intrinsically unfavorable with respect to the same reaction carried out in e.g. THF. Nevertheless the selectivity to alkene in the micellar medium is as good as with Pd/C in THF.

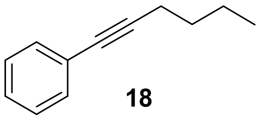
The same reaction carried out on aliphatic alkynes (Table 5, entries 5-8) showed a lower efficiency of both catalytic systems as demonstrated by the generally lower TOFs and in one case (entry 7) the need of a lower conversion to achieve high selectivity to alkene. The presence of hydrophilic substituents as in **16** led to a lower selectivity, while the aromatic ring in **14** allowed a better performance with Pd@**1b** which suggests the hypothesis of a possible π-π interaction of the substrate with **1b** explaining also the better performance shown by aryl alkynes.

As a further application of the catalytic systems to a wider range of substrates, we tested the activity of Pd@**1b** in the semi-hydrogenation reactions of internal triple bonds. Unfortunately many substrates of this family were excluded because they are solid under mild conditions and therefore they were hardly miscible in an aqueous micellar solution. For this reason we checked only **17** and **18** that are liquid under the mild conditions applied and with this substrates we investigated the properties of Pd@**1b** in the presence of internal alkynes characterized by different lipophilicity.

The data reported in Table 6 show very different results for the two substrates. Substrate **19** reacted very rapidly in the hydrogenation reaction, thus leading to high conversions but low selectivity to alkenes in the presence of both Pd@**1b** in water and Pd/C in THF. Elongating the aliphatic tail of the substrate as in **18** significantly slowed down the reaction allowing a better control and a better selectivity to alkene, even if in this case Pd@**1b** provided a less favorable *E:Z* ratio with respect to Pd/C.

Table 6. Semi-hydrogenation reaction of internal alkynes **17** and **18** with Pd@**1b** in water and with Pd/C in THF.

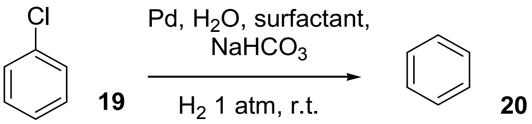
#	**Substrate**	**Catalyst**	**Time (min)**	**Conversion (%)**	**TOF (h^{-1})**	**Alkene (%)**	**Alkane (%)**	***Z:E***
1		Pd/C[a]	35	>99	4000	27	72	92 : 8

		Pd/**1b**[b]	40	>99	296	57	42	95 : 5
2	 **18**	Pd/C[a]	165	84	713	79	5	97 : 3
		Pd/**1b**[b]	360	85	28	77	8	86 : 14

Experimental conditions: Reaction volume 3mL, H_2 1 atm, T 25°C. a) Pd/C 1.6 mg (0.0015 mmol Pd), substrate 3.5 mmol, solvent THF; b) $Pd(OAc)_2$ 1.6 mg (0.0071 mmol Pd), substrate 1.4 mmol, [**1b**] 100 mM, solvent H_2O.

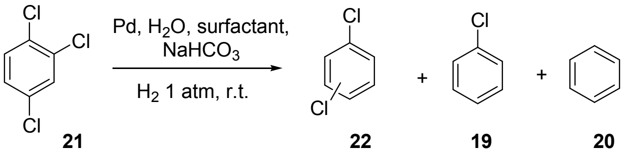
Catalytic hydrodechlorination of aromatic substrates

Many halogenated hydrocarbons are hazardous compounds that are quite persistent and difficult to decompose by biological degradation.[27] High amounts of these compounds are found in ground water in some industrial areas and they tend to accumulate in the environment. It is also known that their biological degradation can be considerably improved by previous de-halogenation. Several methods for the hydrogenolysis of chloroarenes using either stoichiometric and/or catalytic reagents have been developed, but most of them suffer from incomplete dechlorination, low catalytic activity, the need of low substrate/catalyst ratios or extreme conditions.[28] Nevertheless, catalytic hydrodehalogenation is still a convenient and promising method for the decontamination of water from this kind of waste.[29] Palladium-based catalysts showed high activity in the hydrodehalogenation reaction and this prompted us to test the above described Pd@surfactant systems as catalyst in the hydrodechlorination reactions of aromatic compounds in water because the presence of the surfactant would improve the dispersion of the aromatic substrate. Hence we investigated the catalytic activity of Pd-NP in the presence of **1a, 1b, 1c** and **1d** under conditions that could be of practical interest and verify their stability. Chlorobenzene **19** was taken as a benchmark substrate and all the Pd@surfactant systems were tested at room temperature, in water under H_2 at atmospheric pressure in the presence of 1 equivalent of sodium bicarbonate to quench the release of HCl during the reaction (Scheme 5).



Scheme 5. Hydrodechlorination reaction of chlorobenzene **19** leading to benzene **20**.

When **1a, 1b** and **1c** were tested in this reaction, precipitation of Pd-NP occurred rapidly and no conversion of the substrate was observed. Conversely, in the presence of surfactant **1d** the reaction led to quantitative conversion of **19** into benzene **20** in 24 hours. We believe that the presence of the PEG fragment in the structure of **1d**, that in the previous reactions showed to reduce the activity of the Pd@surfactant catalytic system, at the same time confers to the Pd-NP improved stability and avoids Pd aggregation under the experimental conditions. The latter catalytic system was further tested in the hydrodechlorination of a polychlorinated aromatic substrate like 1,2,4-trichlorobenzene **21** (Scheme 6).



Scheme 6. Hydrodechlorination reaction of the 1,2,4-trichlorobenzene derivative **21** leading to several possible products.

The reaction was optimized in order to obtain a quantitative conversion to **20**. As reported in Table 7 this result was achieved under mild conditions (room temperature and 1 atm of H_2) in 24 hours increasing five times the initial amount of Pd and adding an excess of base (Table 7, entry 7). Upon recycling, after extracting the reaction products with an apolar solvent such as pentane, this catalyst maintained its performance even reducing the base amount to stoichiometric (Table 7, entry 8). The catalytic system Pd@**1d** showed stability to pH changes and maintained its activity even in basic solutions. When the reaction was carried out under 5 atm of H_2 (Table 6, entry 6), the Pd@**1d** system showed high stability and a higher activity, observing a quantitative conversion in 24 hours even with a lower Pd loading.

In the liquid-phase hydrodehalogenation reactions of chlorinated aromatic compounds with molecular hydrogen, supported palladium catalysts are usually strongly deactivated by HCl formed during the reaction, but when the supports are doped with sodium hydroxide they lead to increased activity in the hydrodehalogenation reaction.[30] In this respect, Pd@**1d** showed two peculiarities for this reaction: (i) the property to work directly in water and (ii) the ability to maintain the catalytic activity simply by adding sodium bicarbonate.

Table 7. Hydrodechlorination reaction of 1,2,4-trichlorobenzene **21** with Pd@**1d**.

#	Cat/Sub	Sub/Base	H_2 (atm)	Conversion (%)	Yield 22 (%)	Yield 19 (%)	Yield 20 (%)
1	1/100	1/3	1	83	30	7	46
2	1/100	1/3[a]	1	71	36	5	30
3	2/100	1/3	1	90	33	7	50
4	2/100	1/6	1	90	24	6	60
5	2/100	1/9	1	95	17	3	75
6	2/100	1/6	5	>99	-	-	>99
7	5/100	1/6	1	>99	>1	-	99
8[b]	5/100	1/3	1	>99	-	-	>99

Experimental conditions: [Pd(OAc)$_2$] 2.4 mM, water 3 mL, [surfactant **1d**] 80mM, base = NaHCO$_3$, T 25°C. a) base K$_2$CO$_3$; b) Recycling test after products extraction with 3 aliquots of 15 ml of pentane.

Conclusions

In conclusion, we reported a straightforward preparation of Pd-NP in aqueous medium stabilized by commercial anionic sulfonated surfactants simply obtained by stirring micellar solutions of $Pd(OAc)_2$ under hydrogen atmosphere. These Pd-NP showed similar size range and distribution but different morphology as a function of the surfactant employed as well as the concentration and experimental conditions. This proved to be a facile, and inexpensive method to synthesize catalysts with modulated activities simply by changing the surfactant that can operate directly in water as the green solvent *par excellence*, thus avoiding the use of large amounts of toxic organic solvents. This did not affect the performance of the surfactant stabilized Pd-NP as they showed in some cases better efficiency with respect to commercial Pd/C in various hydrogenation reactions.

When catalyzed by Pd@**1d**, the hydrogenation reaction of benzaldehyde and some other aromatic derivatives showed a very high chemoselectivity towards the formation of the corresponding benzyl alcohols, while Pd/C as a benchmark comparison was more difficult to control causing the formation of de-oxygenation reaction products. However, when we used **1a** and **1c** we obtained catalytic systems with higher activity and their application in the de-oxygenation reactions of secondary and tertiary alcohols at room temperature and 1 atm of H_2 in the absence of acid co-catalysts gave quantitative conversions. Much lower conversions were obtained when these reactions were repeated with Pd/C in methanol. **1b** gave a catalytic system with controlled activity in the semi-hydrogenation reactions of alkynes to alkenes where a particular affinity of the catalytic system for compounds endowed with aromatic rings was observed probably due to π-π supramolecular interactions between the surfactant molecular structure and the substrates.

To demonstrate the generality of the catalytic system developed in water, we have reported also a possible application of these systems to the decomposition of hazardous chlorinated aromatic compounds directly in water. With this purpose we studied the catalytic activity of Pd-NP stabilized by sulfonated anionic surfactants in the reaction of 1,2,4-trichlorobenzene. In this way we demonstrated that Pd@**1d** could convert quantitatively the substrate under mild conditions in water and recycling of the catalytic system was possible without detrimental effects on its activity and selectivity.

As is clear from the data reported, the role of the surfactant is crucial to ensure, first of all, the necessary stability to Pd-NP under the catalysis conditions applied. It is interesting that even if the reaction environment is always the same (water, surfactant, hydrogen), the type of substrate analyzed in the individual cases can completely change the stability of the metal system (see e.g. the case of **1b** that leads to Pd metal precipitation with aldehydes while it gives the best catalyst with acetylenes) in a delicate balance between catalytic activity and stability that in some cases can be quite significant as in the case of the hydrodechlorination reaction with Pd@**1d** that can be even recycled.

In all these reactions, typical heterogeneous catalysis criteria like particle size/particle distribution correlations were poorly helpful in rationalizing catalytic activity and selectivity, rather, intriguing and somehow unpredictable "ligand" effect by the different surfactants capping the Pd-NP could be invoked to partly explain the sometimes large differences in activity observed. What is interesting is also that a benchmark catalyst like Pd/C can be often surpassed in activity and/or selectivity in the reactions tested by simply switching to the appropriate cheap and commercially available surfactant, thereby providing an easy to use, flexible and practical catalytic system capable of efficiently addressing a variety of synthetically significant hydrogenation reactions.

Experimental

General

^{1}H NMR spectra were recorded at 298 K, unless otherwise stated, on a Bruker AVANCE 300 spectrometer operating at 300.15 MHz. δ values in ppm are relative to $Si(CH_3)_4$. GC analyses were performed on HP SERIES II 5890 equipped with a HP5 column (30 m, I. D. 0.25 m, film 0.25 μm) using He as gas carrier and FID as detector. GC-MS analyses were performed on a GC Trace GC 2000 equipped with a HP5-MS column (30 m, I.D. 0.25 mm, film 0.25 μm) using He gas carrier, coupled with a quadrupole MS Thermo Finnigan Trace MS with *Full Scan* method. TLC analyses were performed on TLC Polygram ® Sil G/UV254 of 0.25 mm thickness. $Pd(OAc)_2$, 10% Pd/C, solvents, surfactants, reactants and products were all commercially available products (Aldrich) and were used as received without any further purification.

Synthesis of Pd-NP in micellar media

In a 10 ml round-bottomed flask, equipped with a magnetic stirrer, 1.6 mg of $Pd(OAc)_2$ (2.4 mM), followed by the appropriate amount of surfactant and 3 mL of double-distilled water were introduced under nitrogen. The mixture was stirred for 1 hour until complete dissolution of the metal complex to yield an orange homogeneous solution. Subsequently the solution was placed under hydrogen flow for variable times as a function of the surfactant employed observing a net color change from orange to grey as a proof of the formation of dispersed Pd-NP.

TEM Analysis

Size and morphology of the nanoparticles were studied through a JEOL JEM 3010 transmission electron microscope (TEM) operating at 300 kV; the powder specimens were suspended in isopropyl alcohol and then sonicated, 5μl of this suspension were deposited on a copper grid (300 mesh) coated with holey carbon film. The copper grids were allowed to dry in air.

Catalytic Studies

Pd/C: In a 10 ml round-bottomed flask, equipped with a magnetic stirrer were placed 3 ml MeOH (or THF) and the appropriate amount of 10% Pd/C followed by H_2 at atmospheric pressure at room temperature. The mixture was vigorously stirred for 5 min then the required amount of substrate was introduced. Substrate conversion over time was monitored by periodically sampling with a microsyringe followed by GC analysis. Hydrogenation products were identified by comparison with authentic samples and by GC-MS analysis.

Pd-NP: To a 10 ml round-bottomed flask, equipped with a magnetic stirrer containing the catalyst prepared according to the above procedure in 3 mL water was added the substrate in the required amount. Substrate conversion over time was monitored by periodically sampling 100 μL of mixture, extracted with 200 μL of ethyl acetate and the organic phase analyzed by GC analysis. Hydrogenation products were identified by comparison with authentic samples or by GC-MS analysis.

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: XXXXX. Experimental details on Pd NPs preparation and characterization, catalytic tests and characterization of compounds.

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