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

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S *Supporting Information*

ABSTRACT: 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 amounts of time. The aqueous Pd nanoparticle 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 semihydrogenation of alkynes leading to alkenes, and in the efficient hydrodechlorination of aromatic substrates. In all cases, the micellar media were crucial for stabilizing the metal nanoparticles, dissolving substrates, steering product selectivity, and enabling recycling. What is interesting is also that a benchmark catalyst like Pd/C can often be 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.
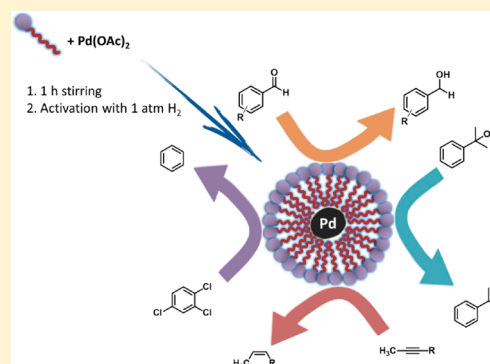
■ INTRODUCTION

Thanks to their peculiar properties, metal nanoparticles (NPs) are attracting significant interest in the field of catalysis as witnessed by the numerous reviews on this subject.[1] Usually, metal NPs in the catalysis field are prepared in proper solvents from a metal salt precursor and a reducing agent in the presence of a stabilizer to avoid aggregation. Examples of suitable stabilizers are numerous, including 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 aimed 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 solvent allows in principle easier product separation and catalyst recycling, but on the other hand, most organic substrates are insoluble in this solvent, causing lower reaction rates. Although 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 often require the use of polar cosolvents, 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 NPs 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 2-fold. This is the case of the nonionic 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] 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 semihydrogenation 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

Scheme 1. Sulfonated Anionic Surfactants Employed for the Stabilization of Pd-NPs in Water
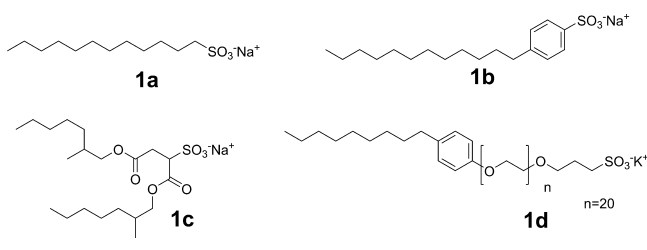
by a range of particle sizes, stabilities, and catalytic activities. We tested these Pd systems in water in the hydrogenation reactions of aromatic aldehydes, ketones, and aryl-alcohols in the hydrodechlorination reaction of aromatic substrates and in the chemoselective semihydrogenation reactions of alkynes to the corresponding alkenes, observing a modulation in catalytic activity of the product selectivity and recyclability by simply changing the surfactant.

RESULTS AND DISCUSSION

Preparation and Characterization of the Pd-NPs in the Presence of Surfactants. The preparation of the solutions containing the Pd-NPs was carried out consisting of the simple dissolution of $Pd(OAc)_2$ in water in the presence of a given surfactant subsequently left under a hydrogen atmosphere for a variable amount of time, observing a change in the solution color from orange to gray-black as evidence of the presence of Pd-NPs. The time required for this operation varied from 2 min, as in the case of **1d**, up to 10 min for **1b**. The concentration of surfactant employed was in all cases at least 1 order of magnitude higher than the corresponding c.m.c., and it was optimized to grant the system the highest stability using the lowest possible amount of surfactant.

The solutions of Pd-NPs 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 pseudospherical nanoparticles with an average diameter of ∼4−6 nm (Table 1) and a relatively narrow distribution between 2 and 9 nm. High-resolution electron microscopy (HREM) showed 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.

In the presence of surfactant **1c**, we obtained well-dispersed and rather small-sized nanoparticles, whereas with surfactants

Table 1. Pd-NP Average Size As Determined by TEM Analysis

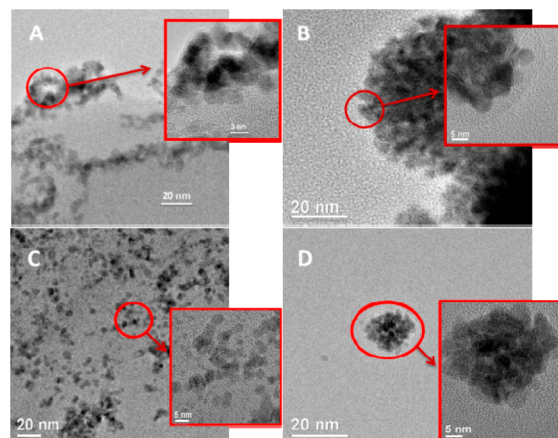| surfactant	Pd particle size (nm)
1a	4.4
1b	5.0
1c	5.1
1d	6.1

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

1a and **1b**, similarly sized Pd-NPs 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 NPs were still visible but highly aggregated into clusters that assumed a diameter of ∼25 nm.

The observed differences are likely to be due to the different interactions 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-NPs 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-NPs 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 NPs in clusters stabilized by the long polyethylene glycol chains. Furthermore, as will be clear afterward, 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 as to whether these differences also apply 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 semihydrogenation 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

Scheme 2. Hydrogenation of Aromatic Aldehydes and Ketone 2 Catalyzed by Pd-NPs in Water
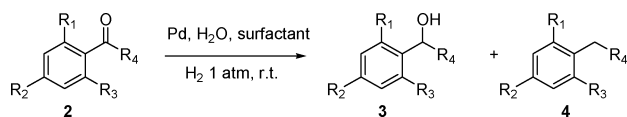
acidity, provided by a heterogeneous support[18] or by an acid cocatalyst,[19] is generally necessary to obtain the complete substrate deoxygenation when the reaction is carried out with molecular hydrogen. Preliminary experiments showed that catalysts made of Pd-NP in the presence of **1a**, **1c**, 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

Table 2. Hydrogenation Reaction of Aromatic Aldehydes 2a−d and Ketone 2e with Different Pd/Surfactants 1a,c,d in Water and with Pd/C in MeOH[a]

#	Substrate		Pd@1a[b]		Pd@1c[c]		Pd@1d[b]		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

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

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.

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 better control on the hydrogenation of individual benzaldehydes **2** selectively forming the corresponding benzyl alcohols **3** or alternatively leading to full deoxygenation by simply changing the surfactant and the reaction time.

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-NPs. This may result by the coordination of the oxygen atoms of **1c** to the metal centers that provide stability to the Pd-NPs but at the same time tend to reduce their activity. At variance, surfactant **1a** binds less strongly the Pd-NPs, and this results in a slightly more active catalytic system despite the higher aggregation observed.

Observing the results obtained in the hydrogenation reactions catalyzed by Pd/C, different reactivities of the aldehydes investigated can be noted. The presence of a methoxy group in the para position of the aromatic structure of **2d** makes this substrate more active compared to benzaldehyde **2a** in the hydrogenation and deoxygenation reactions. Compounds **2a** and **2c** showed comparable reactivities despite the higher steric hindrance of the latter, whereas 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**, which showed the lowest activity with Pd/C. The higher lipophilicity derived from the presence of the *tert*-butyl group in the para position of 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. Compound **2a** became the most reactive substrate followed by **2b**. The hydrogenation reaction of **2d** proceeded at a lower rate, and **2c** returned to being the least reactive substrate. The cause of this particular reactivity might likely be found in the PEG oxygen donors present in surfactant **1d** that stabilize the catalytic system and thus lower its activity, a recurring effect with these systems (vide infra).

Systems Pd@1a and Pd@1c seemed quite active also in the subsequent deoxygenation 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, whereas Pd@1a and Pd@1c gave results comparable to 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 deoxygenation reaction than Pd/C in methanol despite the higher solubility of hydrogen in the latter medium.

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

Scheme 3. Deoxygenation 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

Table 3. Deoxygenation Reaction of Benzyl Alcohols 5a−c with Pd@Surfactant 1a, 1c, and 1d in Water and Pd/C in THF[a]

#	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[b]	5c	Pd@1a	24	>99
		Pd@1c	24	>99
		Pd@1d	24	8
		Pd/C	24	40

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

methanol using the appropriate Pd/surfactant in water. When we performed the deoxygenation 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 h, whereas the same time allowed to obtain only 40% conversion of 5c even increased up to 5-times the amount of Pd/C. With the Pd@surfactant systems, the order of substrate reactivity was confirmed, but Pd@1a and Pd@1c systems proved to be very active also in the deoxygenation 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 clusters.

In no case was the addition of acid cocatalyst necessary to promote the reaction. Commercially 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 cocatalyze the deoxygenation reaction of the substrate.

Catalytic Semihydrogenation of Alkynes to Alkenes. The semihydrogenation reaction of alkynes to the corresponding alkenes is an extremely important chemical transformation[22] because the production of Z-alkenes starting from internal alkynes allows for obtaining 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 preorientation of the substrates, thus selectively leading to the Z products[25] even though sometimes possible isomerization to the E isomer was observed. In 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 to maximize the selectivity to alkenes and 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@

Scheme 4. Hydrogenation Reaction of Phenylacetylene 7 Leading to Styrene 8 and Eventually to Ethylbenzene 9
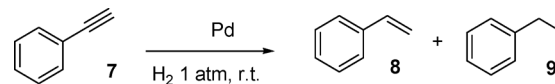
surfactant catalytic systems. Initially, the reaction was carried out in tetrahydrofuran with a commercial 10% Pd/C catalyst. For maximizing the selective conversion to styrene 8, the reaction was repeated with different amounts of catalyst, observing that interesting levels of both activity and selectivity were achieved working with 0.04 mol % of Pd compared to 7 in THF.

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.

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 to 0.5 mol % and the concentration of 1b was 100 mM (Table 4, entries 7−9),

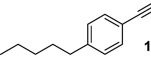**Table 4. Semihydrogenation Reaction of Phenylacetylene 7 with Pd/Surfactant 1a−c in Water and with 10% Pd/C in THF**

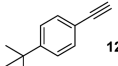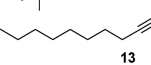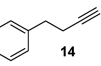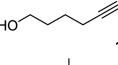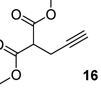| #	catalyst	[surfactant] (mM)	cat/subs (mol %)	solvent	time (min)	conversion (%)	selectivity to styrene (%)
1	Pd/C		1	THF	10	94	93
2	Pd/C		0.1	THF	50	88	97
3	Pd/C[b]		0.04	THF	90	96	95
4	Pd@1a[c]	80	1	H₂O	50	94	97
5	Pd@1b[c]	100	1	H₂O	25	86	98
6	Pd@1c[c]	80	1	H₂O	80	84	62
7	Pd@1b[d]	100	0.5	H₂O	27	99	98
8	Pd@1b[e]	100	0.33	H₂O	120	96	97
9	Pd@1b[d]	120	0.5	H₂O	75	85	98

[a]Experimental conditions: phenylacetylene (1.5 mmol), 3 mL reaction volume, 1 atm of H₂, T = 25 °C. [b]Phenylacetylene (3.5 mmol). [c]Phenylacetylene (0.7 mmol). [d]Phenylacetylene (1.4 mmol). [e]Phenylacetylene (2.1 mmol).

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 in 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

Table 5. Semihydrogenation of Phenyl Acetylene Derivatives 7−12 and Other Alkynes 13−16 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[b]	90	96	1490	95
		Pd@1b[c]	27	99	434	98
2	**10**	Pd/C[b]	70	98.5	1970	95
		Pd@1b[c]	45	>99	263	95
3	**11**	Pd/C[b]	60	88	2050	95
		Pd@1b[c]	20	83	491	95
4	**12**	Pd/C[b]	70	91	1820	94
		Pd@1b[c]	70	94	159	95
5	**13**	Pd/C[b]	60	80	1400	97
		Pd@1b[c]	50	77	182	97
6	**14**	Pd/C[b]	80	98	1720	94
		Pd@1b[c]	60	>99	197	97
7	**15**	Pd/C[b]	90	68	1060	95
		Pd@1b[c]	80	62	92	93
8	**16**	Pd/C[b]	80	97	1700	90
		Pd@1b[c]	90	98	129	88

[a]Experimental conditions: 3 mL reaction volume, 1 atm of H₂, T = 25 °C. [b]Pd/C = 1.6 mg (0.0015 mmol Pd), 3.5 mmol substrate, THF solvent. [c]Pd(OAc)₂ = 1.6 mg (0.0071 mmol Pd), 1.4 mmol substrate, [1b] = 100 mM, H₂O solvent.

concentrations were chosen to maximize selectivities to the intermediate alkenes in the consecutive reactions that are almost always in the ≥95% range with some minor exceptions (entries 5 and 10). For obtaining comparable performance in terms of conversion, the amount of Pd necessary with Pd@1b was ∼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.

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 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 ∼2 orders of magnitude on going from substrate 7 to 12,[26] which suggests that their lipophilicity, hence their solubility in 1b, should follow an opposite order.
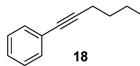
The solubility in water of aryl alkynes 7 and 10−12 is ∼4-times higher than the corresponding alkenes,[26] which implies that, in the course of the reaction, the dissolution in the micelles of the alkene semihydrogenation products are higher than the corresponding alkyne reactants, a situation that is 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 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, whereas 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, also explaining 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 semihydrogenation 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 these substrates, we investigated the properties of Pd@1b in the presence of internal alkynes characterized by different lipophilicities.

The data reported in Table 6 show very different results for the two substrates. Substrate 17 reacted very rapidly in the

**Table 6. Semihydrogenation Reaction of Internal Alkynes 17 and 18 with Pd@1b in Water and with Pd/C in THF[a]**

#	Substrate	Catalyst	Time (min)	Conversion (%)	TOF (h⁻¹)	Alkene (%)	Alkane (%)	Z:E
1	17	Pd/C[b]	35	>99	4000	27	72	92 : 8
		Pd/1b[c]	40	>99	296	57	42	95 : 5
2	18	Pd/C[b]	165	84	713	79	5	97 : 3
		Pd/1b[c]	360	85	28	77	8	86 : 14

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

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 the reaction, allowing better control and better selectivity to alkene even if in this case Pd@1b provided a less favorable E:Z ratio with respect to Pd/C.

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 groundwater 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 dehalogenation. 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−d under conditions that could be of practical interest and verify their stability. Chlorobenzene 19 was taken as a benchmark substrate, and all of the Pd@surfactant systems were tested at room temperature in water under H_2 at atmospheric pressure in the presence of 1 equiv of sodium bicarbonate to quench the release of HCl during the reaction (Scheme 5).

When 1a−c 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 to benzene 20 in 24 h. We believe that the presence of the PEG fragment in the

Scheme 5. Hydrodechlorination Reaction of Chlorobenzene 19 Leading to Benzene 20
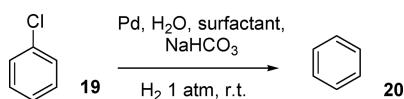
structure of 1d, which in the previous reactions were shown to reduce the activity of the Pd@surfactant catalytic system, at the same time confers to the Pd-NP improved stability and avoids Pd aggregation under the experimental conditions. The latter catalytic system was further tested in the hydrodechlorination of a polychlorinated aromatic substrate like 1,2,4-trichlorobenzene 21 (Scheme 6).

Scheme 6. Hydrodechlorination Reaction of 1,2,4-Trichlorobenzene Derivative 21 Leading to Several Possible Products
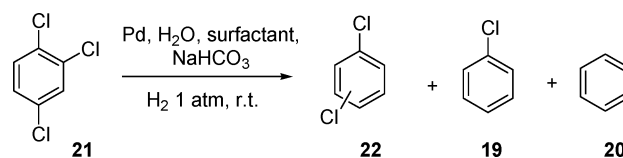
The reaction was optimized to obtain a quantitative conversion to 20. As reported in Table 7, this result was

Table 7. Hydrodechlorination Reaction of 1,2,4-Trichlorobenzene 21 with Pd@1d[a]

#	cat/sub	sub/base	H_2 (atm)	conversion (%)	yield of 22 (%)	yield of 19 (%)	yield of 20 (%)
1	1/100	1/3	1	83	30	7	46
2	1/100	1/3[b]	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[c]	5/100	1/3	1	>99			>99

[a]Experimental conditions: [Pd(OAc)$_2$] = 2.4 mM, 3 mL of water, [surfactant 1d] = 80 mM, base = $NaHCO_3$, $T = 25$ °C. [b]Base = K_2CO_3. [c]Recycling test after product extraction with 3 aliquots of 15 mL of pentane.

achieved under mild conditions (room temperature and 1 atm of H_2) in 24 h, increasing 5-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 h 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.

CONCLUSIONS

In conclusion, we reported straightforward preparation of Pd-NPs in aqueous medium stabilized by commercial anionic sulfonated surfactants simply obtained by stirring micellar solutions of Pd(OAc)$_2$ under a hydrogen atmosphere. These Pd-NPs showed a similar size range and distribution but different morphologies 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-NPs 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 toward the formation of the corresponding benzyl alcohols, whereas Pd/C as a benchmark comparison was more difficult to control, causing the formation of deoxygenation reaction products. However, when we used **1a** and **1c**, we obtained catalytic systems with higher activity, and their application in the deoxygenation reactions of secondary and tertiary alcohols at room temperature and 1 atm of H$_2$ in the absence of acid cocatalysts gave quantitative conversions. Much lower conversions were obtained when these reactions were repeated with Pd/C in methanol. Compound **1b** gave a catalytic system with controlled activity in the semihydrogenation reactions of alkynes to alkenes where a particular affinity of the catalytic system for compounds endowed with aromatic rings was observed probably due to $\pi-\pi$ 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 giving 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 even be 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 often be 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 SECTION

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 an HP5 column (30 m, 0.25 m I.D., 0.25 μm film) using He as gas carrier and FID as detector. GC-MS analyses were performed on a GC Trace GC 2000 equipped with an HP5-MS column (30 m, 0.25 mm I.D., 0.25 μm film) using a 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-NPs 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 h until complete dissolution of the metal complex to yield an orange homogeneous solution. Subsequently, the solution was placed under hydrogen flow for variable amounts of time as a function of the surfactant employed, observing a net color change from orange to gray as proof of the formation of dispersed Pd-NPs.

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; 5 μL of this suspension was deposited on a copper grid (300 mesh) coated with a 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$_2$ under atmospheric pressure at room temperature. The mixture was vigorously stirred for 5 min, and 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 at 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 was analyzed by GC analysis. Hydrogenation products were identified by comparison with authentic samples or by GC-MS analysis.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.8b00314.

> Experimental details on Pd-NP preparation and characterization, catalytic tests, and characterization of compounds (PDF)

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Notes

The authors declare no competing financial interest.

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