Biphasic liquid–liquid hydrogenation catalysis by aqueous colloidal suspensions of rhodium: The choice of the protective-colloid agent and the role of interfacial phenomena

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Abstract

Microheterogeneous catalytic systems using aqueous suspensions of rhodium particles are proved to be efficient for alkene hydrogenation in biphasic liquid–liquid medium provided that the method of stabilization and the interfacial phenomena are properly chosen and controlled. Aqueous supensions stabilized by specially designed trianionic molecules or by hydrophilic polymer (PVA) have been studied. A series of trisulfonated molecules 1 with modulated solution behaviors (surfactant or hydrotrope) depending on the nature of the substituents has been used to stabilize aqueous suspensions of oxidized (polar) or reduced (non polar) rhodium particles. Stabilization of polar particles occurs whatever the substituents when stabilization of metallic apolar particles requires surfactants bearing a significant lipophilic part. In the former case, highly stable suspensions of rhodium nanoparticles with controlled size are obtained in micellar solutions. Both oxidized and reduced rhodium suspensions efficiently catalyzed octene hydrogenation in liquid–liquid medium and it is established that high activity and possible recovery and recycling of the catalyst can be achieved by the control of interfacial parameter e.g. the interfacial tension. In the same way, common polymer-protected colloidal suspensions of Rh(0) particles are proved to efficiently catalyze hydrogenation in two liquid phases systems provided that optimized amounts of surfactants are added to reduce the interfacial tension without emulsification. From these results a relationship between interfacial tension and catalytic activity in biphasic system is proposed.

1. Introduction

During the last decade, there has been a growing interest on biphasic catalytic systems consisting of two non miscible liquid phases, water (or more recently fluorocarbon [1]) and hydrocarbon, which offer a mean to separate and recycle the catalyst by simple decantation. The most widely studied approaches use water-soluble homogeneous catalysts coordinated to hydrophilic phosphines [2–7]. An other alternative, so-called 'microheterogeneous catalysis', is to use colloidal metallic particles finely dispersed in water. Indeed, protected metallic colloids are efficient catalysts mainly for alkenes hydrogenation in liquid media (water–alcohol,

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organic solvents and microemulsions) [8–12]. Immobilization of platinum metals colloids has also been described to perform heterogeneous catalysis allowing an easy separation of the catalyst from the reaction products and recyclings [13–16]. Biphasic liquid–liquid catalytic systems involving aqueous suspensions of colloidal metals, scarcely studied, are of great interest provided that the colloidal particles remain stable in the aqueous phase during the whole catalytic process. Such a condition may be achieved by the proper choice of protective-colloid agents which must be highly water-soluble. The most widely used methods to protect colloidal suspensions in water against aggregation are (i) electrostatic stabilization, generally obtained by surface adsorption of ionic species, (ii) steric stabilization by adsorption of polymer and (iii) electrosteric stabilization which combines both previous effects [17,18]. Thus, aqueous colloidal suspensions of metallic particles have been prepared in the presence of protective-colloid agents such as natural or synthetic polymers, ionic species and ionic or nonionic surfactants; the choice of the stabilizer depends on whether the surface of the particles is polar (metal oxide or hydroxide) or apolar (metal) [17,18].

In this paper, we wish to show that aqueous colloidal suspensions of rhodium particles can efficiently catalyze alkenes hydrogenation in biphasic liquid–liquid (water/organic phase) systems provided that the interfacial phenomena are properly controlled. In a first part, we describe catalytic systems based on aqueous suspensions of metallic or oxidized rhodium particles stabilized by specially designed highly water-soluble sulfonated tripods 1. In a second part, we demonstrate that common polymer-protected colloids can be used in biphasic system provided that the interfacial liquid–liquid tension is controlled and optimized.
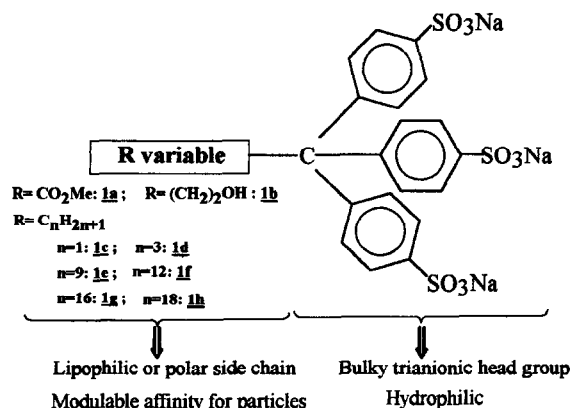
In every case, the catalytic medium is a tetraphasic (colloidal particles/ water/ organic/ gas) system in which diffusion obviously plays a significant role. In this paper, we focus on the 'macroscopic' catalytic activity of the aqueous supensions (particles + water + stabilizer) which includes diffusion enhancement.

2. Results and discussion

2.1. Hydrogenation of oct-1-ene catalyzed by aqueous suspensions of rhodium particles stabilized by sulfonated tripods 1

We have previously shown that aqueous dispersions of rhodium particles, electrostatically stabilized by sulfonated molecules like trisulfonated triphenylphosphine oxide, efficiently catalyze alkenes hydrogenation in biphasic system [19]. In order to optimize such catalytic systems and to estimate their scope and limitations, we have developed a new series of sulfonated tripods 1 with various polar, non-polar or lipophilic side chains [20] (Scheme 1). This series of compounds with a constant trianionic head group, allowing an efficient electrostatic stabilization, and various R substituents provides valuable information on the interactions with polar (metal oxide and/or hydroxide) or apolar (metal) particles and on the relationship between their surface activity and the catalytic effectiveness of the suspension.
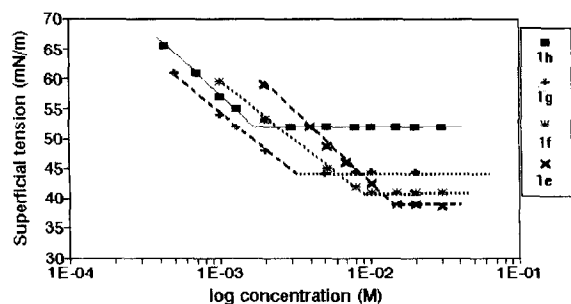

R variable

R= CO_2Me: **1a** ;   R= $(CH_2)_2OH$: **1b**
R= C_nH_{2n+1}
    n=1: **1c** ;   n=3: **1d**
    n=9: **1e** ;   n=12: **1f**
    n=16: **1g** ;   n=18: **1h**

Lipophilic or polar side chain
Modulable affinity for particles

Bulky trianionic head group
Hydrophilic

Scheme 1.

Fig. 1. Surface tensions of aqueous solutions of surfactants 1e, 1f, 1g, and 1h. Superficial tension (mN m^{-1}) versus log concentration (mol l^{-1}), 1e: cmc # 10^{-2} mol l^{-1}; 1f: cmc # 6.10^{-3} mol l^{-1}; 1g: cmc # 3.5×10^{-3} mol l^{-1}; 1h: cmc # 2×10^{-3} mol l^{-1}

Fig. 3. Conductivity of aqueous solutions of surfactant 1h. Conductivity (mS m^{-1}) versus concentration (mol l^{-1})

2.1.1. Surface activity and solution properties of compounds 1

The surface adsorption and solution properties of compounds 1 have been studied by surface tension and conductivity measurements. All compounds 1 are highly soluble in water but their properties depend on the substituent R. Surface tension measurements demonstrate that compounds 1e to 1h bearing an alkyl chain with nine to eighteen carbon atoms are surfactants and self aggregate into micelles above the critical micellar concentration (cmc) (Fig. 1) [21,22]. The decrease of the surface tension of aqueous solutions of these compounds below the cmc (from 72 mN m^{-1} for pure water to about 40 to 50 mN m^{-1}) is related to their adsorption at the water/air interface by the Gibbs' law [21,22]. This series of trisulfonated surfactants 1e to 1h has a classical behaviour: 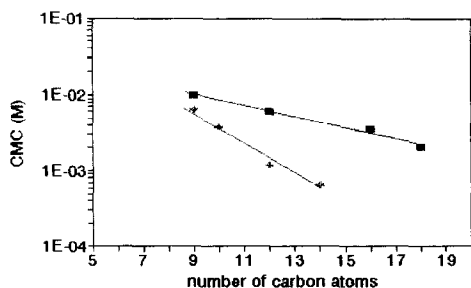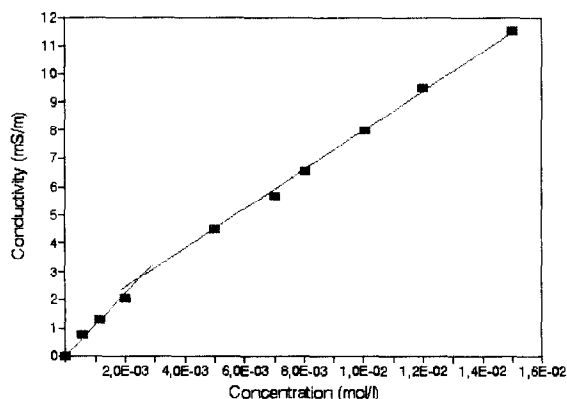the cmc value decreases when the hydrocarbon chain length increases with an usual linear variation of log cmc versus number of carbon atoms (Fig. 2) [21,22]. Compared to alkylbenzenesulfonates, the weak slope observed for the trisulfonated compounds 1 accounts for the bulk and the charge of the trianionic head group and consequently the weak contribution of the alkyl chain to the enthalpy of micellization [22]. Conductivity measurements show a break at the cmc which accounts for the association of the counterion to the surfactant aggregates (Fig. 3) [21–23]. The degree of association of counterions to the micelles, estimated from the ratio of the slopes (conductivity versus concentration) before and after the cmc, is fairly low (about 60%) demonstrating that surfactant aggregates bear a strong negative charge.

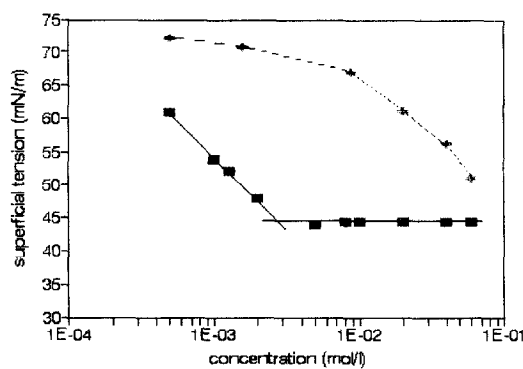Fig. 2. Log cmc (mol l^{-1}) versus alkyl chain length (number of carbon atoms). (■) 1f to 1g, (+) p-RC$_6$H$_4$SO$_3$Na.

Fig. 4. Surface tensions of aqueous solutions of surface active and hydrotropic compounds 1. Superficial tension (mN m^{-1}) versus log concentration (mol l^{-1}).(■) 1g: surfactant, (+) 1c: hydrotrope.

On the contrary, the surface tension of aqueous solutions of compounds **1a** to **1d** decreases much more slowly with the concentration and does not reach a minimum value thus demonstrating that saturation of the interface does not occur and that these compounds do not self-aggregate: compounds **1a** to **1d** are hydrotropes. Curves of Fig. 4 show how surface tension measurements allow to assign the two different, surfactant and hydrotrope, behaviors. One can notice that the concentration required to decrease the surface tension to a given value is much higher for a hydrotropic compound than for a surface active compound. The same behaviour is observed at a liquid–liquid interface.

2.1.2. Aqueous suspensions of polyhydroxylated rhodium particles: stabilization by tripods 1 and catalytic activity

In these systems, the catalytically active polynuclear hydroxylated Rh(III) particles are generated in situ by oxidative addition of water and molecular dioxygen on Rh(I) formed by previous reduction of rhodium trichloride with ethanol [24]. The catalytic system is thus generated by reduction of rhodium trichloride with a small amount of ethanol followed by dilution with an aqueous solution of stabilizer **1**; after addition of pure olefin (oct-1-ene) hydrogenation is performed under atmospheric pressure. The catalytic activity at the second run, e.g. after decantation and filtration of the aqueous phase on calibrated micropore, depends on the

amount of colloidal particles which remain in water and is therefore a measure of the stability of the suspension.

The trisulfonated compounds **1a** to **1h** have been used and compared to study the factors which govern the stabilization of the aqueous suspension of such polar particles and the catalytic activity. The results given in Table 1, for first runs and recyclings, demonstrate that stable catalytically active suspensions are obtained with all compounds **1** whatever their behaviour. On the other hand, the optimum amount of trisulfonated compound required to get high turn-over number at the first run and conservation of the activity during recycling depends on its solution properties, e.g. hydrotrope or surfactant. Thus, when hydrotropic compounds **1a** to **1d** are used, the best results are obtained with high trisulfonate concentrations and molar ratio (R) **1** per rhodium of about 30. On the contrary, the presence of high concentration, far above the cmc value, of surface active compounds **1e** to **1h** gives rise to an emulsified system which is almost inactive and does not allow recycling. For these compounds, efficient biphasic catalytic systems with good remaining activity at the second run are obtained with much lower concentration, far below the cmc value, and consequently a much lower molar ratio $R = 0.5$.

These results demonstrate that stabilization of aqueous suspensions of polyhydroxylated polar particles is obtained with the whole series of trisulfonated molecules **1** whatever the nature,

Table 1
Octene hydrogenation catalyzed by aqueous suspensions polyhydroxylated rhodium particles stabilized by compounds 1

	1a	**1b**	**1c**	**1d**	**1d**	**1d**	**1e to 1h**	**1g**	**1g**
Molar ratio R [a] 1/Rh	30 [b]	30 [b]	30 [b]	10 [c]	20 [d]	30 [b]	30 [b]	0.5 [e]	30 [f]
Medium [g]	2 ph	2 ph	2 ph	2 ph	2 ph	2 ph	em	2 ph	em
Turn-over number [h]									
First run	17	49	78	55	73	47	< 5	18	1
Second run [i]	16	37	61	6 [j]	18 [j]	29	N.S.	24	N.S.

[a] [Rh] constant = 1.9×10^{-3} mol l^{-1}.   [b] [1] = 5.7×10^{-2} mol l^{-1}.   [c] [1d] = 1.9×10^{-2} mol l^{-1}.   [d] [1d] = 3.8×10^{-2} mol l^{-1}.
[e] [1g] = 9.5×10^{-4} mol l^{-1} # 0.3 cmc.   [f] [1g] = 5.7×10^{-2} mol l^{-1} # 16 cmc.   [g] 2 Ph: two phases, Em: emulsion.
[h] Turn-over number (h^{-1}) = number of mole octene hydrogenated per mole rhodium initially introduced and per hour.
[i] After separation of the aqueous phase by decantation and filtration on 0.45 μm micropore. N.S.: No separation upon decantation, the aqueous phase cannot be reused.
[j] Aggregation occurs during catalysis, the aggregated large particles are removed by filtration.

polar, apolar or lipophilic, of the substituent R. Thus, the trianionic sulfonated head group affords an effective electrostatic stabilization. Moreover, the nature of the substituent R having no significant effect on the stabilizing power, the adsorption of the stabilizer on the particles implies hydrophilic interactions between the trisulfonated head group and the polar surface of the particles. Hydrotropic compounds 1a to 1d behave like polyanions and provide an electrostatic stabilization. Surfactants 1e to 1h, which may form bilayers at the surface of the particles, allow a so-called 'electrosteric stabilization' combining both an electrostatic stabilization via the trianionic head group and a steric stabilization via the lipophilic hydrocarbon chain. This electrosteric stabilization accounts for the stability of the suspension at low stabilizer concentrations (molar ratio versus rhodium about 0.5). On the other hand, the very large amount of hydrotropic trisulfonates 1a to 1d required to ensure the conservation of the catalytic activity (molar ratio versus rhodium: 30, about 30 to 40 g/l) is much higher than in usual electrostatically stabilized metal oxides suspensions with inorganic anions. One can thus assume that a major part of the trisulfonated molecules 1a to 1d are not involved in the stabilization process but nevertheless play an important role in the catalytic process. By comparison with surfactant molecules 1e to 1h, the excess of hydrotropic compounds appears necessary to reduce the liquid–liquid interfacial tension down to a value low enough to facilitate the contact between the aqueous catalyst and the organic substrate. Indeed, if one considers the surface tension of aqueous solutions of compounds 1 in the condition of an efficient catalysis, the surface tension is lowered to 52 mM m^{-1} in the presence of hydrotropic compound 1c at a concentration of 57 mM ($R = 30$) while the same value is reached with surfactant 1g at a much lower concentration of 0.95 mM ($R = 0.5$) (Fig. 4). Obviously, the same trend is observed for water/octene interfacial tension: in the presence of 0.95 mM of 1 g the interfacial tension is

decreased from 32 mN m^{-1} to 13 mN m^{-1} while a similar value (17 mN m^{-1}) is obtained with a much higher concentration 57 mM of 1c (for 20 mM of 1c, the interfacial tension is almost unchanged: 30 mN m^{-1}). Moreover, as shown by surface tension measurements, in the presence of surface active compounds (Figs. 1 and 4), the interfacial tension reaches a minimum value above a given surfactant concentration so that no further improvement of the catalytic activity is expected at high surfactant concentration. On the contrary, at high surfactant concentration, emulsification takes place making the contact very difficult between the substrate included within the oil droplets and the catalyst particles associated with the trisulfonated head group at the outer interfacial region [25].

These findings demonstrate a relationship between the interfacial tension and the catalytic activity in biphasic systems: such a relationship has already been proposed in phase transfer catalysis [26] and is much more easily establish with polymer-protected colloids (vide infra). Enhancement of solubility of hydrogen and octene in the aqueous phase may account for the increase of activity. Nevertheless, it is well known that the solubility of apolar molecules is nearly independent of the surfactant concentration below the cmc and increases almost linearly with the surfactant concentration above the cmc [27–30]. Moreover, the solubility of gas in micellar solution is considerably lower than in hydrocarbons because of the intramicellar Laplace pressure [28–30]. Thus, in our experiments, the catalytic activity does not appear to be limited by solubilization in the aqueous phase since it decreases when the surfactant concentration is reached above the cmc.

2.1.3. Aqueous suspensions of metallic rhodium particles: stabilization by tripods 1 and catalytic activity

In these systems, the catalytically active aqueous suspension is made of Rh(0) metallic particles with an apolar surface [31]. The sus-

pensions are prepared by reducing rhodium trichloride with sodium borohydride in dilute aqueous solutions of trisulfonated compounds 1. These suspensions are chemically stable and can be prepared beforehand and stored; the colloidal stability can thus be studied by classical methods apart from the catalytic point of view.

2.2. Preparation and stability of aqueous colloidal suspensions of rhodium particles

The stability of suspensions obtained in the presence of compounds 1 towards time, temperature (critical flocculation temperature: CFT), electrolytes (critical flocculation concentration: CFC) and the size of the particles has been determined; the main results are summarized in Table 2. When hydrotropic trisulfonated molecules 1a to 1d are used, large particles with a broad size distribution are obtained; these suspensions are poorly stable towards time, temperature and addition of electrolytes. Hydrotropic trisulfonated compounds 1a to 1d are poor protective colloid agents and do not prevent aggregation. On the other hand, highly stable aqueous suspensions of rhodium nanopar-

ticles are obtained in the presence of trisulfonated surfactants 1f to 1h. The remarkable stability in time towards electrolytes and temperature accounts for an effective electrosteric stabilization. Moreover, the use of trisulfonated surfactants allows the control of the particle size by the choice of the alkyl chain length and the surfactant concentration. Thus, as shown in Table 2, surfactants 1g and 1h bearing an alkyl chain with sixteen or eighteen carbon atoms, give rise to stable monodispersed suspensions of particles of about ten angstroms (20 to 50 Å), when surfactant 1e with a nonyl chain gives rise to less stable suspensions of larger particles. Consequently, an effective electrosteric stabilization requires a significant lipophilic substituent and at least a dodecyl side chain on the triphenylsulfonated skeleton. As emphasize in Table 2 for compound 1g, the size and the distribution of the particles depend on the surfactant concentration. Monodispersed suspensions of nanoparticles are obtained provided that the surfactant concentration is far above the critical micellar concentration cmc (entries S4 to S6, Table 2) thus demonstrating that the control of the particles size requires a preparation in micellar solution: a nucleation-growth

Table 2
Characterization and stability of aqueous suspensions of Rh(0) particles stabilized by compounds 1

No.	Stabilizer	[1] (mM)	R [a]	Particle size (T.E.M.)	Time stability	C.F.T. [b]	C.F.C. [c]
S1	1b	19	10	0.27 μm to 1 μm polydisperse	< 48 h	80°C	MgSO$_4$: 1.87 M
S2	1c	19	10	25 nm to 1 μm polydisperse	< 24 h	65°C	NaCl: 0.17 M, MgSO$_4$: 2.54 M
S3	1e	19 # 2 cmc	10	80 Å to 600 Å polydisperse	< 48 h	85°C	MgSO$_4$: 2.73 M
S4	1g	19 # 5 cmc	10	20 Å to 30 Å monodisperse	> months	100°C	saturated MgSO$_4$, saturated NaCl
S5	1g	9.5 # 3 cmc	5	50 Å monodisperse	> months	100°C	saturated MgSO$_4$, saturated NaCl
S6	1g	3.5 # 0.3 cmc	0.5	50 Å to 800 Å polydisperse	> months	100°C	saturated MgSO$_4$, saturated NaCl
S7	1h	19 # 10 cmc	10	20 Å to 30 Å monodisperse	> months	100°C	saturated MgSO$_4$ NaCl

[a] R = molar ratio 1/RhCl$_3$ initially introduced, [RhCl$_3$] = 1.9 × 10^{-3} mol l^{-1}.
[b] CFT: critical flocculation temperature.
[c] CFC: critical flocculation concentration.

process within the micellar core accounts for these observations. Moreover, in micellar solutions, the particle size depends on the surfactant concentration since an increase of the concentration gives rise to an increase of the number of micelles and consequently produces more isolated nuclei (entries S4 and S5). It is noteworthy, that, although micellar solutions are required to control the particles size, the suspensions remain stable at much lower surfactant concentration (far below the cmc) for example upon dialysis or dilution.

NMR studies confirm the location of the rhodium particles within the micellar core and lipophilic interactions involving the surfactant adsorption via its hydrocarbon chain. Thus, comparison of the ^{13}C NMR spectra of surfactant **1g** in aqueous solution before addition of rhodium (Fig. 5a) and in the colloidal suspension (Fig. 5b) show a shift of some signals of aliphatic carbon nuclei. Similar ^{13}C NMR spectra with additional peaks attributed to surfactant (CTAB) molecules bound to silver particles have been described [32].

In conclusion trisulfonated surfactants **1f** to **1h** are efficient protective colloid agents for Rh(0) aqueous suspensions and afford a mean to control the size of the particles provided that the preparation is performed in micellar solutions.

From the results obtained for polar oxidized rhodium particles (vide supra) and apolar reduced rhodium particles, it is clear that the effectiveness of a stabilizer is related to the nature of the interactions with the surface of the particles: the sulfonated tripods **1** are versatile protective colloid agents allowing the electrostatic stabilization of polar particles via hydrophilic interactions for the whole series **1a** to **1h** and apolar particles via hydrophobic interactions for surfactants **1f** to **1h**.

2.3. Catalytic activity of the aqueous suspensions of metallic rhodium particles

These suspensions have been used such as they were for catalytic hydrogenation of oct-1-
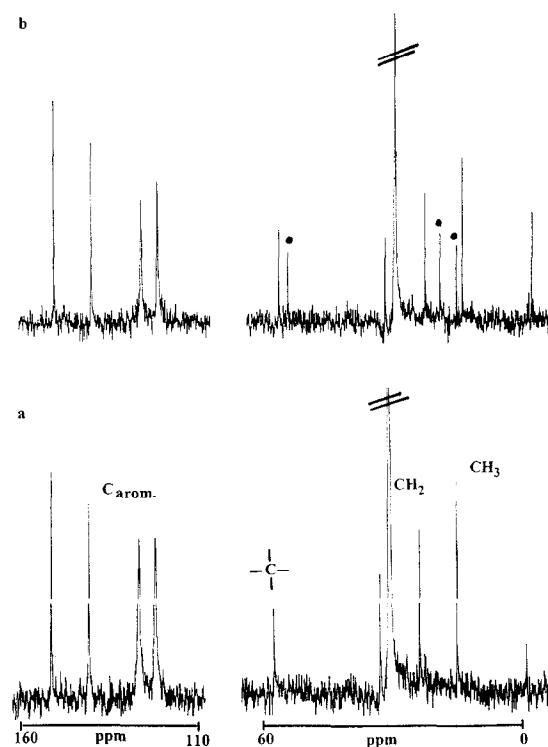

Fig. 5. ^{13}C NMR spectra (22.5 MHz, D$_2$O) of compound **1g**. (a) Solution of **1g** in pure water. (b) Aqueous colloidal suspension of Rh(0) particles stabilized by **1g**.

ene under atmospheric pressure and the turnover numbers determined at the first run and recycling after separation of the aqueous phase and filtration on micropore. The results given in Table 3 show, as expected, that the catalytic activity of poorly stable suspensions (S1, S2, S3) dramatically decreases at the second run since flocculation takes place during the first run. Stable suspensions prepared in the presence of surfactant **1g** or **1h** allow a better conservation of activity during recycling provided that the molar ratio 1/Rh (R) is high enough to prevent aggregation and the best results are obtained for $R = 10$ (entries S4 and S7). Nevertheless, in these systems using high concentrations of surfactants, emulsification occurs and makes the separation of the aqueous and organic phases slightly more troublesome and longer than simple two phases systems.

Table 3
Octene hydrogenation. Catalysis by aqueous suspensions of Rh(0) particles stabilized by compounds **1**

Suspension	[1]	Average particle size	R [a]	Medium	Turn-over number [b]		Remaining activity
					1st run	2nd run [c]	
S1	**1b**: 19 mM	0.5 μm	10 [f]	two phases	120 [d] (480000)	5 [d] (20000)	5%
S2	**1c**: 19 mM	0.1 μm	10 [f]	two phases	39 [d] (31200)	10 [d] (8000)	25%
S3	**1e**: 19 mM # 2 cmc	400 Å	10 [f]	emulsion	19 [e] (6080)	8 [e] (2560)	40%
S4	**1g**: 19 mM # 5 cmc	30 Å	10 [f]	emulsion	36 [e] (865)	28 [e] (670)	80%
S4/20	**1g**: 0.95 mM # 0.25 cmc	30 Å	10 [g]	two phases	247 (5930)	250 (6000)	99%
S4/50	**1g**: 0.38 mM # 0.1 cmc	30 Å	10 [h]	two phases	277 (6650)	275 (6600)	99%
S5	**1g**: 9.5 mM # 3 cmc	50 Å	5 [f]	emulsion	17 [e] (680)	5 [e] (200)	30%
S6	**1g**: 1 mM # 0.3 cmc	400 Å	0.5 [f]	two phases	60 [d] (19200)	11 [d] (3520)	20%
S7	**1h**: 19 mM # 10 cmc	30 Å	10 [f]	emulsion	38 [e] (910)	30 [e] (720)	80%
S7/20	**1h**: 0.95 mM # 0.5 cmc	30 Å	10 [g]	two phases	262 (6290)	260 (6240)	99%

[a] R = molar ratio $1/RhCl_3$ initially introduced.
[b] Turn-over number (h^{-1}) = number of mole octene hydrogenated per mole rhodium initially introduced and per hour; in brackets is given the number of mole octene hydrogenated per surface rhodium mole and per hour.
[c] After separation of the aqueous phase by decantation and filtration on 0.45 μm micropore.
[d] Aggregation occurs during catalysis, the aggregated large particles which are flocculated at the liquid/liquid interface are removed by filtration.
[e] Upon decantation a Winsor III system is observed, the lower aqueous phase was solely reused, a part of the rhodium particles are thus lost in the middle phase.
[f] $[Rh] = 1.9 \times 10^{-3}$ mol l^{-1}. [g] $[Rh] = 0.095 \times 10^{-3}$ mol l^{-1}. [h] $[Rh] = 0.038 \times 10^{-3}$ mol l^{-1}.

Efficient two phases catalytic systems can easily be obtained by dilution of the previous suspensions so that the surfactant concentration is low enough to prevent emulsification and the molar ratio per rhodium is held at a value high enough ($R = 10$) to prevent aggregation. Thus dilution of suspensions S4 (S4/20 and S4/50) or S7 (S7/20) gives rise to highly effective catalytic biphasic systems easily recycled by simple decantation with a complete conservation of activity. The catalytic activity of these diluted suspensions is close to those of polymer-protected colloidal suspensions in homogeneous medium [12] and higher than commercially available supported Rh catalyst.

It is noteworthy that, whatever the medium, high molar surfactant concentrations slow down the catalytic process probably because adsorption induces a steric hindrance [25]. Moreover, as previously noticed, high surfactant concentrations do not bring profit in terms of interfacial tension because a minimum value is reached from low concentrations (for example for compound **1g**, the interfacial tension is lowered to

less than 15 mN m^{-1} since 0.1 cmc). As already mentioned, solubilization of hydrogen and octene in the aqueous phase, which is expected to increase beyond the cmc [27–30], does not account for our experimental results.

Turn-over numbers calculated per surface rhodium atom are given in brackets in Table 3: whatever the nature of the surfactant when stable colloidal suspensions (S4 and S7) are used the activity is low at high surfactant concentration and increases to a nearly constant value when the surfactant concentration is lowered by dilution (S4/20, S4/50 and S7/20). When unstable suspensions (S1, S2, S3, S6) are used, large aggregates flocculate at the interface and high apparent activities are obtained: in these cases, the catalytic reaction takes place within the organic phase and is no more limited by phase transfer of octene and hydrogen solubility. The difference of activity per surface rhodium atom between stable aqueous suspensions and flocculated aggregates is with no doubt related to the diffusion and phase transfer limiting factors.

In conclusion, monodispersed colloidal suspensions of rhodium nanoparticles can be prepared and stabilized by using trisulfonated surfactants **1f** to **1h** taking advantages of both control of the nucleation-growth process in micellar solution and electrosteric stabilization. Moreover, these highly water-soluble surfactants **1** maintain the colloidal particles within the aqueous phase during catalytic processes and thus allow the use of aqueous suspensions in biphasic catalytic systems. The proper choice of the surfactant concentration and the surfactant per rhodium molar ratio gives rise to efficient biphasic catalytic systems with a good remaining of the activity during recyclings.

2.4. Hydrogenation of oct-1-ene catalyzed by polymer-protected aqueous suspensions of rhodium particles

The study of suspensions stabilized by specially designed trisulfonated molecules **1** has shed light on the influence of the interfacial tension parameter on the catalytic properties. Nevertheless, a clear relationship is hard to draw since the compounds responsible for the decrease of the interfacial tension are also involved in the colloid stabilization process. In order to dissociate both effects, we have chosen to use aqueous suspensions of polymer-protected particles and to modulate the interfacial tension parameter by addition of an auxiliary surfactant [33]. Moreover, this approach is of practical interest since polymer-protected rhodium suspensions, readily prepared from commercially available products, have been proved efficient for catalytic hydrogenations in homogeneous media but their usefulness is restricted by the separation and the lack of possible recyclings [8–12].

Thus, suspensions of Rh(0) particles have been prepared by reduction of rhodium trichloride with sodium borohydride in aqueous solutions of polyvinylalcohol (PVA). Transmission electron microscopy shows that these suspensions are made of particles of about 50 Å with a narrow size distribution. The catalytic activity of these suspensions has been tested after addition of oct-1-ene in the presence of various amounts of surfactant. Hydrophilic surfactants have been chosen in order to avoid the transfer of the colloidal particles from the aqueous phase to the organic phase: an anionic surfactant DBS (sodium dodecylbenzene sulfonate) and a non-

Table 4
Octene hydrogenation. Catalysis by aqueous suspensions of polymer-protected Rh(0) particles [a]

Auxiliary surfactant	Concentration (mol l^{-1})	Medium	Interfacial tension (mN m^{-1})	Turn-over number [d] 1st run	2d run [e]	Remaining activity
DBS [b]	1.5×10^{-2} # 10 cmc	emulsion	1.9	94 (3760)	N.S.	—
DBS [b]	1.5×10^{-3} # cmc	emulsion	4.9	75 (3000)	N.S.	—
DBS [b]	1.5×10^{-4} # cmc/10	two phases	7.5	57 (2280)	55 (2200)	96%
DBS [b]	3×10^{-5} # cmc/50	two phases	8.5	39 (1560)	38 (1520)	97%
NP20 [b]	4.8×10^{-4} # 3 cmc	emulsion	6.2	94 (3760)	N.S.	—
NP20 [b]	5.3×10^{-5} # cmc/3	emulsion	8.1	39 (1560)	N.S.	—
NP20 [b]	5.3×10^{-6} # cmc/30	two phases	11.8	28 (1120)	20 (800)	70%
None [b]		two phases	12.3	19 (760)	17 (680)	90%
None [c]				36 (1440)	—	—
Cosolvent methanol [b,f]		homogenous		38 (1520)	N.S.	—

[a] Particles size: 50 Å. [b] [PVA] = 3 g/l. [c] [PVA] = 0.3 g/l.
[d] Turn-over number (h^{-1}) = number of mole octene hydrogenated per mole rhodium initially introduced and per hour; in brackets is given the number of mole octene hydrogenated per surface rhodium mole and per hour.
[e] After separation of the aqueous phase by decantation and filtration on 0.45 μm micropore; N.S.: no separation upon decantation, the aqueous phase cannot be reused.
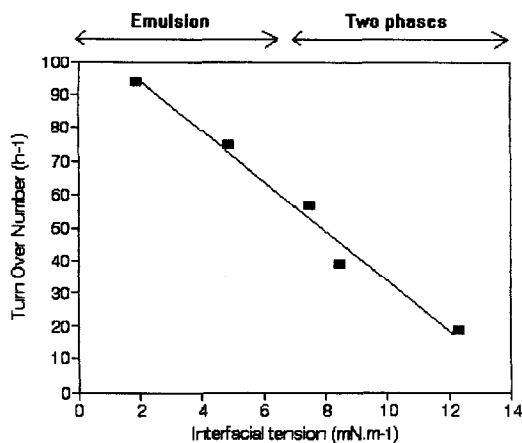[f] Methanol/water 50/50 (v/v).

Fig. 6. Hydrogenation of oct-1-ene catalyzed by an aqueous suspension of PVA-protected colloidal Rh(0) particles in the presence of various amounts of DBS. Turn-over number (h^{-1}) versus interfacial tension $(mN\ m^{-1})$.

ionic surfactant NP20 (polyethoxylated nonylphenol with about 20 ethoxy groups).

Obviously, the reaction medium, emulsion or two separated phases, depends on the nature and the concentration of the surfactant. The interfacial tension, measured before catalysis, and the turn-over numbers at the first run and second run (after filtration on calibrated micropore) have been determined for each experiment (Table 4). These experimental results clearly demonstrate that, whatever the medium and the auxiliary surfactant, the catalytic activity increases when the interfacial tension decreases: the almost linear relationship between the interfacial tension and the catalytic efficiency is depicted Fig. 6 in the presence of DBS. It is noteworthy that the relationship does not depend on the reaction medium, e.g. emulsion or biphasic system: the catalytic efficiency seems to be governed by interfacial tension rather than interfacial area which is obviously much higher in emulsified medium.

Therefore, it becomes quite easy to find a compromise between catalytic efficiency and recovery and recycling of the catalyst by performing the reaction in biphasic liquid–liquid system. Thus, such systems where the aqueous phase containing the colloidal catalyst can be reused with high efficiency are obtained at low

anionic or nonionic surfactant concentrations (Table 4). The best results, e.g. 90 to 100% of the initial activity, are obtained in the presence of the most water-soluble surfactant (DBS). In the presence of nonionic NP20, the leakage of rhodium particles in the organic phase accounts for the decrease of activity during the second runs. The modulation of the interfacial parameter affords a mean to obtain biphasic reusable systems which are as much efficient as usual homogeneous systems made of water/alcohol mixtures [12]. The efficiency of these catalytic systems could be optimized by lowering the amount of polymer protective colloid agent PVA. Indeed, in this study, the PVA concentration is fairly high (3000 ppm) and can be significantly decreased leading to less sterically hindered particles and consequently higher catalytic activities (Table 4).

3. Conclusion

The results described in this paper demonstrate that the 'microheterogeneous approach' is a promising alternative to liquid–liquid biphasic catalysis provided that the colloidal catalyst is effectively protected towards aggregation. Like homogeneous biphasic processes [1], these systems suffer from the fact that the two partners (catalyst and substrate) are located in separated phases. Our results show that this problem can be avoided by modulating the interfacial tension parameter. It is not surprising that such an effect has already been observed in phase transfer catalysis [26] and is expected to be of general significance. Moreover, one can take advantage of low interfacial tension to get high activity while allowing recovery and recycling of the aqueous colloidal catalyst. Lastly, this study shed light on the usefullness of the highly water soluble surfactants 1 which act both as protective-colloid agents and surface tension reducing agents and consequently avoid the addition of any auxiliary compound.

Nevertheless the significance of the measured

interfacial tension parameter in terms of diffusion coefficients, phase transfer and solubilization of the various components of such polyphasic systems remains unclear and is currently being studied.

4. Experimental

Commercially available $RhCl_3-3H_2O$, oct-1-ene, sodium dodecylbenzenesulfonate, NP20 (ICI) and PVA ($M_w = 49000$) were used as received. Water was distilled before use by conventional methods. Compounds **1** were prepared and purified according to the previously described procedure [20]. Surface tension (superficial tension: air/water and interfacial tension: octene/water) measurements have been performed at 20°C by the ring method with a Du Nouy Tensiometer (Kruss K10T). Conductivity measurements were performed with a Radiometer CDM 80 equipped with a CDC 104 type electrode. The critical micellar concentrations were determined from both surface tension and conductivity measurements.

4.1. General procedure for hydrogenation

The chosen aqueous suspension and 2 ml of oct-1-ene (1.3×10^{-2} mol) were placed in a standard ordinary pressure hydrogenator equipped with a magnetic stirrer: the same two-necked 50 ml flask, the same magnetic stir bar and the same rotational speed (500 rpm) were used for all the experiments. The reaction was monitored by the volume of hydrogen consumed and gas chromatography analysis. At the end of the reaction, the two phases were separated by decantation and the aqueous phase filtrated on 1.6 μm or 0.45 μm micropore before recycling. The turn-over numbers were determined for 100% conversion.

4.2. Aqueous suspensions of oxidized rhodium particles stabilized by compounds 1

8 mg (3.8×10^{-5} mol) of $RhCl_3-3H_2O$ were added to 1 ml of ethanol. 19 ml of an aqueous solution of compound **1** at the desired concentration and 2 ml oct-1-ene were added after a few minutes. The resulting mixture was placed under hydrogen (vide supra).

4.3. Aqueous suspensions of Rh(0) particles stabilized by compounds 1

The suspensions were prepared under nitrogen by addition of sodium borohydride (22 mg, 5.8×10^{-4} mol) to 150 ml of an aqueous solution of $RhCl_3-3H_2O$ (60 mg, 2.28×10^{-4} mol) and compound **1** at various concentration. The reduction occurs instantaneously. The suspensions were neutralized before characterization and catalytic reaction. The time stability was estimated macroscopically for unstable suspensions; for suspensions stable for a long period of time, the stability was confirmed by TEM since the sizes of the particles are not modified. The critical flocculation temperature and concentration (CFT and CFC) were determined upon progressive heating of the suspension or addition of salt by turbidity measurements (adsorption at 500 nm).

The catalytic reactions were performed with 20 ml of colloidal suspension using the experimental procedure described above.

4.4. Aqueous suspensions of polymer-protected Rh(0) particles

The suspensions were prepared under nitrogen by addition of sodium borohydride (103 mg, 2.7×10^{-3} mol) to 500 ml of an aqueous solution of $RhCl_3-3H_2O$ (180 mg, 6.8×10^{-4} mol) and PVA ($M = 49000$). All the preparations were performed with 1.5 g of PVA (34×10^{-3} mol as monomeric residue, [PVA] = 3 g/l) except one (labelled in Table 4) which has been performed with 0.15 g of PVA (3.4×10^{-3} mol as monomeric residue, [PVA] = 0.3 g/l). The reduction occurs instantaneously. The aqueous suspensions were neutralized and stored under nitrogen before characterization and catalytic reaction.

The catalytic reactions were performed according to the procedure described above using 20 ml of aqueous suspension. The desired amount of pure surfactant DBS (cmc = 1.5×10^{-3} mol l^{-1} determined by surface tension measurements) or NP20 (cmc = 1.6×10^{-4} mol l^{-1} determined by surface tension measurements) was added and the interfacial tension determined just before use. For reactions using methanol as a cosolvent, methanol has been added to the biphasic water/octene mixture until it became homogeneous. The volume ratio MeOH/water is 1/1.

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