The Significant Effect of Interfacial Tension in Liquid–Liquid Catalysis: a New Way to Improve the Efficiency of Colloidal Metal Catalysts in a Biphasic System

Chantal Larpent* and Elisabeth Bernard

Laboratoire de Chimie Organique et des Substances Naturelles, associé au CNRS, ENSCR, Avenue du Général Leclerc, 35700 Rennes, France

The control of the interfacial tension gives rise to highly efficient biphasic liquid–liquid catalytic systems where the catalytically active aqueous suspension of colloidal metal is readily separated and recycled.

There has been much recent interest in catalysis by colloidal metals.[1–5] Protected colloids have been used mostly for catalytic hydrogenation of various alkenes or polyenes in liquid media (water–alcohol mixtures, organic solvents and microemulsions).[2–5] More recently, immobilization of platinum metal colloids for heterogeneous catalysis has been performed in order to allow an easy separation from the reaction products as well as repeated recycling.[2a,6–9] However, biphasic liquid–liquid catalytic systems, which provide an alternative to separate and to recycle the catalyst by using aqueous suspensions of colloidal metals, have so far been scarce. Recently, we have described the hydrogenation of alkenes in liquid–liquid systems catalysed by aqueous colloidal suspensions of Rh^0 particles stabilized by specially designed highly water soluble trianionic surfactants.[10]

In this paper, we demonstrate the main role of the interfacial water–organic phase tension in a biphasic catalytic system and we report a new method to obtain high catalytic efficiencies with readily prepared polymer protected colloids which is expected to be of universal significance.

Thus, an aqueous suspension of Rh^0 colloidal particles has been prepared by reducing rhodium trichloride with sodium borohydride in an aqueous solution containing suitable amounts of protective colloid agent (PVA: polyvinylalcohol). The catalytic efficiency of this sterically stabilized Rh^0 colloidal suspension for hydrogenation of oct-1-ene has been determined in a homogeneous medium in the presence of methanol, according to Hirai's procedure,[2] and in various water–alkene emulsified or biphasic systems in the presence of surfactants. The surfactant concentration, *i.e.* concentration higher or lower than the critical micelle concentration (cmc), has been chosen in order to select, respectively, an emulsion or a two liquid separated phases system when the substrate

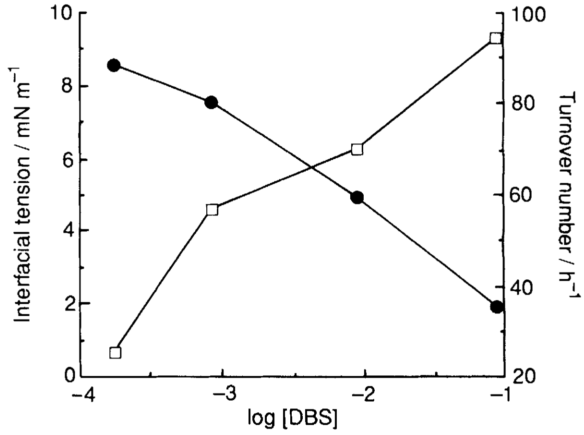

Fig. 1 Interfacial tension (mN m^{-1}) (—•—•—•—) and turnover number (h^{-1}) (—□—□—) *vs.* log concentration of DBS (mol dm^{-3})

Table 1 Catalytic activities of aqueous colloidal suspension of Rh^0 in various media for hydrogenation of oct-1-ene[a]

Additive	Conc./ cmc[b]	Interfacial tension/ $mN\ m^{-1}$	Medium	Turnover no./ h^{-1}[d,e]	
				Run 1	Run 2
DBS[b]	10.0	1.9	Emulsion	94	—
	1.0	4.9	Emulsion	70	—
	0.1	7.5	Two phases	57	55
	0.02	8.5	Two phases	25	25
NP20[b]	3.0	6.2	Emulsion	94	—
	0.333	8.1	Two phases	39	31
	0.033	11.8	Two phases	28	20
None	—	13.2	Two phases	19	17
Methanol[c]	—	—	One phase	38	—

[a] Experimental procedure: the colloidal suspension was prepared by adding under nitrogen $NaBH_4$ (103 mg, 2.7 mmol) to 500 ml of an aqueous solution containing $RhCl_3$, $3H_2O$ (180 mg, 0.68 mmol) and PVA (M_r = 49 000, 1.5 g, 34 mmol as monomeric residue). Reduction occurred instantaneously. The aqueous suspension was neutralized by addition of diluted HCl and stored under nitrogen before characterization and catalytic use. The particles sizes, determined by transition electron microscopy (TEM), are 30 Å (monodispersed). The catalytic reactions were performed according to the general following procedure: the desired amount of surfactant (DBS or NP20) was added to 20 ml of colloidal suspension, 2 ml ($1.3\ 10^{-2}$ mol) of oct-1-ene were added and the interfacial water-oct-1-ene tension was measured by the ring method with a Du Nouy Tensiometer (Kruss K10T). The catalytic reactions were carried out in a standard ordinary pressure hydrogenator equiped with a magnetic stirrer (20 °C, 1 atm H_2). At the end of the reaction, determined by the volume of hydrogen consumed and gas chromatography control, the mixture was allowed to stand 15 min. When the two liquid phases were separated, the product (organic layer) was eliminated by decantation and the aqueous colloidal suspension was filtered on a 0.45 μm micropore before recycling. [b] Technical grade DBS (Aldrich) and synperonic NP20 (ICI) were used without purification. The cmc, determined by surface tension measurements, are 1.5×10^{-3} and 1.6×10^{-4} mol dm^{-3}, respectively, for DBS and NP20. [c] Methanol has been added to the water–oct-1-ene mixture until the system became homogeneous. The resulting component ratio was $MeOH : H_2O = 1 : 1$. [d] Turnover number = mol product/mol Rh initially introduced h^{-1}, determined by GC analysis and hydrogen consumption. [e] The catalytic efficiency also depends on the amount of added protective polymer: the lower the PVA concentration the higher the catalytic activity. The turnover numbers for the first and second runs are three times higher when the PVA concentration is decreased to 300 ppm.

(oct-1-ene) is added to the aqueous colloidal suspension. An ionic surfactant (sodium dodecylbenzene sulfonate: DBS) and a non-ionic surfactant (nonylphenolpolyethoxylate with 20 ethoxy groups: NP20) have been used. These two highly hydrophilic surfactants have been chosen in order to avoid the transfer of the colloidal particles from the aqueous solution to the organic phase. The experimental results, given in Table 1, show that, whatever the nature of the surfactant, the catalytic efficiency largely depends on the amount of surfactant and consequently on the interfacial tension. The plots of turnover number and interfacial tension *vs.* surfactant concentration (Fig. 1) clearly demonstrate that interfacial tension is the main parameter. The catalytic efficiency increases when the interfacial tension decreases with approximately the same order of magnitude whatever the medium *i.e.* emulsion or biphasic system. Therefore, these results shed light, for the first time, on the fact that the efficiency of a catalyst in a two liquid phases system depends on the value of the interfacial tension rather than on the medium (emulsion or macroscopic interphase). A correlation between catalytic and interfacial activity of quaternary ammonium bromides phase transfer catalysts has already been described by Mason *et al.*[11] Moreover, we have previously observed the influence of the interfacial tension on the catalytic activity of surfactants stabilized colloidal suspensions.[12] In both cases, the surface active agent participates, *i.e.* catalyst or stabilizer, in the reaction so that the enhancement of the catalytic activity could be related to its interfacial location as well as to the interfacial tension parameter.

The tremendous effect of the interfacial tension is confirmed when the catalytic activity is compared to a homogeneous medium *i.e.* catalytic reaction performed in the presence of methanol. The control of the interfacial tension parameter affords a means by which higher catalytic activities in a two-separated-phases system than in a homogeneous medium can be obtained.

Moreover, one can take advantage of this occurrence to get efficient biphasic catalytic systems where the aqueous phase containing the colloidal catalyst can be reused. The catalytic activity remains almost unchanged (96 to 100% activity conserved) provided that the added surfactant is adequately water soluble. The slightly lower conservation of the catalytic activity (70 to 80%) observed when the non-ionic NP20 surfactant is used could indeed be explained by the leakage of colloidal rhodium particles in the organic phase since NP20 is slightly more soluble than the ionic DBS in hydrocarbons.

In conclusion, our results shed light on the effect of the interfacial tension on the efficiency of two liquid phases catalytic systems using colloidal catalysts. Moreover, we demonstrate that the proper choice of the nature, necessary highly hydrophilic, and of the concentration of the surfactant, and therefore both of the medium and of the interfacial tension, gives rise to highly efficient biphasic catalytic systems with easy separation and recyclic of the catalyst.

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