Aqueous Rhodium Colloidal Suspension in Reduction of Arene Derivatives in Biphasic System: a Significant Physico-chemical Role of Surfactant Concentration on Catalytic Activity

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Received: October 10, 2001; Accepted: December 28, 2001

Abstract: The hydrogenation of benzene derivatives represents an important industrial catalytic transformation. An original approach is to use transition metal nanoparticles that are finely dispersed in liquid media. During the last decade, these nanoparticles have been largely characterized by sophisticated techniques. Recently, we have described the hydrogenation of arene derivatives in liquid-liquid systems catalyzed by an aqueous suspension of rhodium nanoparticles stabilized by a cationic surfactant. Here, we demonstrate that the modulation of surfactant concentration fundamentally influences the turnover frequencies (TOF’s) in hydrogenation of classical benzene derivatives such as anisole, toluene and *p*-xylene. A maximum TOF is obtained when the surfactant concentration is about the critical micellar concentration. In this condition, the Rh(0) stabilized nanoparticles are up to 5-fold more active.

Keywords: biphasic catalysis; colloids; hydrogenation; interface; rhodium

Fine metal colloid nanoparticles dispersed in liquid media are today a hot research topic and regularly show novel catalytic and physical properties.[1] To understand these new properties, many characterization techniques – mainly drawn from solid state chemistry, metallurgy or molecular transition metal organometallic chemistry – have been used. For example, size and distribution of metallic nanoparticles can be determined by HREM[2] (high-resolution electron microscopy). The composition of such materials can be elucidated with the help of EDX[3] (energy dispersive X-ray spectroscopy) and XPS[2a,3b,4] (X-ray photoelectron spectroscopy) allows us to know the oxidation state of the metal. Finally, the structure of these small particles can be investigate with XRD[2a,3a,4c,5] (X-ray diffraction), WAXS[2a,2c,6] (wide-angle X-ray scattering), XANES[3b,4b,5a,7] (X-ray absorption near edge structure) or EXAFS[4b,5a,7,8] (extended X-ray fine structure). Fortunately, all these sophisticated techniques are complementary and allow us to develop new experimental procedure to have access to new structures at the microscopic scale.

Nevertheless, all these methods study the nanoparticles outside of their original liquid media. Indeed, in most of them we have to dry the nanoparticles to obtain analyzable powders and this process is liable to modify the structure of the particles. Furthermore, only few *in situ* catalytic reaction studies have been performed to understand the influence of the interfacial mechanism[9] between stabilized colloids and substrate and its impact on turnover activities.

Recently, we have described the hydrogenation of arene derivatives in liquid-liquid systems catalyzed by an aqueous suspension of rhodium nanoparticles stabilized by a cationic surfactant, cetyl(hydroxyethyl)(dimethyl)ammonium bromide (**HEA-C$_{16}$**), at room temperature and under atmospheric hydrogen pressure.[10]

In this paper, we report our study of this aqueous colloidal suspension and particularly the major influence of interfacial water-hydrocarbon tension in a pure biphasic catalytic liquid-liquid system. In fact, we demonstrate the main role of surfactant concentration to obtain high turnover activities for hydrogenation of arene derivatives under ultra-mild conditions.

The catalytically active aqueous suspension is made of metallic rhodium(0) particles prepared by reducing rhodium trichloride with sodium borohydride in a dilute solution of bromide surfactant. Surface tension measurements of this suspension show that the surfactant self aggregates into micelles above the critical micellar concentration (cmc) of 3.2×10^{-4} mol L^{-1}. Preliminary catalytic results show satisfactory turnover frequencies (TOF) with a good reproducibility during the recycling process.[10]

First of all, we studied the influence on catalytic activity of two different concentrations of surfactant (Table 1). The two concentrations studied were (i) 3.8×10^{-3} mol L^{-1} corresponding to our classical system preliminary described (Condition 1) and (ii) $3.04 \times$

Table 1. Comparison of activities in hydrogenation of typical aromatic substrates.

Liquid system	Catalyst	Condition[a]	Anisole		Toluene		*p*-Xylene	
			t [h]	TOF [h^{-1}][b]	t [h]	TOF [h^{-1}][b]	t [h]	TOF [h^{-1}][b]
Monophasic	Rh/C 5 wt % (Degussa type DG 10)[c]	1	15	40	16	38	23	26
	Rh/PVP (M. W. = 40000)[d]	1	16	38	18	33	21	29
	Rh/C 5 wt % (Degussa type DG 10)[c]	2	18	33	17	35	24	25
	Rh/PVP (M. W. = 40000)[d]	2	17	35	19	32	23	26
Biphasic	Rh-HEA-C_{16}	1	6.2	97	6.5	92	8.6	70
		2	1.4	429	2.3	256	4	149

[a] Reaction conditions : 1) substrate (3.8×10^{-3} mol), Rh (1.9×10^{-5} mol), and surfactant (3.8×10^{-3} mol L^{-1}) in biphasic system, 20 °C, 1 atm H_2, stirred at 1500 min^{-1}; 2) substrate (1.52×10^{-3} mol), Rh (7.6×10^{-6} mol), and surfactant (3.04×10^{-4} mol L^{-1}) in biphasic system, 20 °C, 1 atm H_2, stirred at 1500 min^{-1}.

[b] Turnover frequency defined as number of moles of consumed H_2 per mol of rhodium per hour.

[c] Catalyst preliminary dried over P_2O_5.

[d] Rhodium colloids synthesized as previously described by Hirai.[11]

10^{-4} mol L^{-1} corresponding to a concentration near the cmc of the surfactant in the catalytic suspension (Condition 2). In this study, the ratios r_1 = surfactant/Rh and r_2 = substrate/Rh were constant and, respectively, 2 and 200. Adequate concentrations were obtained by simple dilution of an original aqueous suspension containing typically 1.9×10^{-3} mol L^{-1} of rhodium and 3.8×10^{-3} mol L^{-1} of the bromide salt (Solution A, see experimental section). In a second phase, we compared the two conditions of reaction of our biphasic liquid-liquid system to the classical monophasic liquid system Rh/polyvinylpyrrolidone synthesized in hydroalcoholic media by Hirai[11] and to an Rh/C heterogeneous catalyst. In the latter system, r_2 is analogous to that of biphasic catalysis but r_1 cannot be defined because of the absence of surfactant.

These catalytic systems were investigated by means of reduction of typical monoalkyl-substituted, disubstituted, and functionalized benzene derivatives such as toluene, *p*-xylene and anisole, respectively. A complete conversion was obtained in all cases under Conditions 1 and 2. The comparative liquid system studies showed that the turnover frequency and the reaction time values for all substrates were similar in monophasic mixture whereas they are dependent on dilution in the biphasic liquid-liquid system with r_1 constant. Using a suitable surfactant, the TOF's are considerably increased. Most importantly, the dilution of the catalytic suspension and the thus decreasing surfactant concentration has a beneficial impact on the reaction time. Consequently, we present evidence that the interfacial tension of the catalytic suspension is a key factor in our system.

To elucidate this phenomenon, we have determined the profile of the catalytic efficiency of the aqueous rhodium suspension in various concentrations of surfactant around the cmc. The experimental results (Figure 1) show that the TOF, and thus the activity, largely depends on the amount of surfactant. In

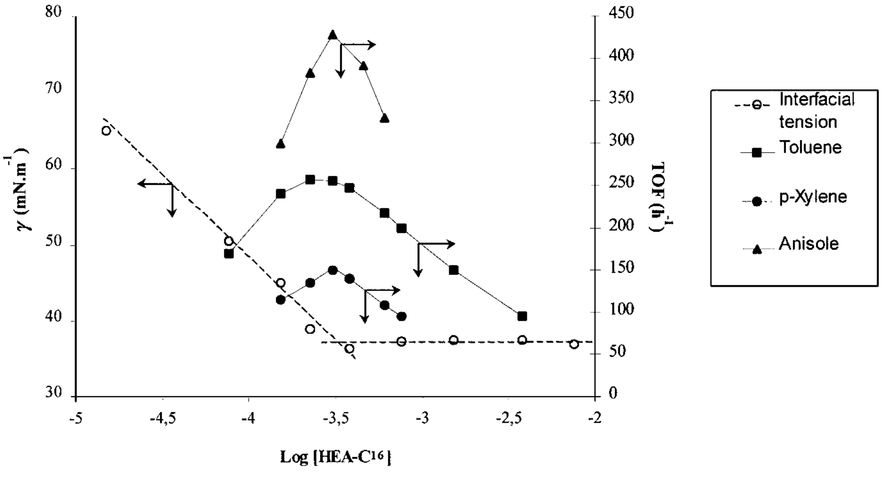

Figure 1. Plot of interfacial tension and turnover frequencies versus log concentration of **HEA-C$_{16}$**.

particular, when the interfacial tension remains constant, the TOF decreases with increasing surfactant concentration. The same profile is obtained for all of our substrates such as anisole, toluene, and *p*-xylene. In all cases, the maximum TOF is correlated with the cmc (429, 256, 149 h^{-1}, respectively). This clearly demonstrates that the activity of our colloidal catalyst in a biphasic liquid-liquid system depends on the concentration of surfactant and then on the value of the interfacial tension.

We can define two behaviors of the system from the surfactant concentration: (i) one before the cmc and (ii) one after the cmc. The decrease in surface tension of an aqueous solution of surfactant below the cmc is related to the adsorption at the water/air interface by the Gibb's law.[12] In our case, the value decreased from 72 mNm^{-1} for pure water to 37 mNm^{-1} for the surfactant-containing solution.

As we can see in Figure 1, before the cmc the TOF increases as the surface tension decreases. We can explain this observation if we consider that the increase of surfactant concentration permits a decrease in interfacial tension and then permits a better contact between substrate (in the organic phase) and catalyst (in the aqueous phase). Moreover, the lower activity at low surfactant concentration is not simply due to a decrease in colloid surface area by agglomeration because TEM studies have shown that the catalytic suspensions after catalysis conserved the same size distribution. Another concept is to consider the strong adsorption of the surfactant on the surface of the rhodium particles. The increasing surfactant concentration, below the cmc, can develop regionally on the surface hemimicelles or surfactant aggregates. This surface layer of surfactant would provide a hydrophobic region close to the surface of the catalyst in which aromatic hydrocarbons would dissolve, making their local concentration higher than in the absence of the surfactant layer and hence enable a more rapid hydrogenation rate.

After the cmc, the TOF decreases but the surface tension is constant. The addition of bromide salt contributes to form micelles in the aqueous phase and it is well known that micelles are able to solubilize part of organic substrates. Thus, molecules located within micelles become less accessible to the catalyst and hence the amount of aromatic hydrocarbon near the catalyst surface would be lowered with increasing surfactant concentration, compared to below the cmc. This phenomenon can justify the decrease of the catalytic activity. Another approach could be to consider that the surfactant added goes around the metal particles and therefore prevents the access of the substrate to the active sites.

In addition to our investigation in arene hydrogenation using colloidal metal particles, these results show that the control of the surfactant concentration and then of the interfacial tension parameters gives rise to high catalytic activities. We have demonstrated that the maximum TOF can be obtained when the surfactant concentration is about the critical micellar concentration. Under these conditions, the Rh(0) stabilized nanoparticles are 2- to 5-fold more active than our standard aqueous colloidal suspension preliminary described. Finally, surface tension measurements of aqueous solutions of the surfactant afford the possibility to choose the efficiency of catalytic systems with two liquid phases by using colloidal catalysts.

Experimental Section

Starting Materials

Rhodium chloride hydrate was obtained from Strem Chemicals. Rh/C 5 wt % (Degussa type G10), Poly(vinyl alcohol) (PVA; M.W. = 22000), polyvinylpyrrolidone (PVP; M.W. = 40000), sodium borohydride, 1-bromohexadecane, *N,N*-dimethylethanolamine, and all aromatic substrates were purchased from Aldrich or Fluka and were used without further purification. Water was distilled twice before use by conventional methods. The surfactant **HEA-C$_{16}$** was prepared as previously described in the literature and fully characterized.[13] The surface tension measurements were performed at 20 °C using the ring method with a Du Nouy tensiometer (Krüss K10T).

Typical Preparation of the Colloidal Suspensions

The suspensions were prepared under nitrogen at 20 °C. To an aqueous solution of surfactant (95 mL, 3.8×10^{-4} mol for Condition 1) was added sodium borohydride (18 mg, 4.75×10^{-4} mol). Then this solution was quickly added under vigorous agitation to an aqueous solution (5 mL) of the precursor $RhCl_3 \cdot 3\,H_2O$ (100 mg, 1.9×10^{-4} mol) to obtain an aqueous Rh(0) colloidal suspension (100 mL of Solution A). The reduction occurs instantaneously and is characterized by a color change from red to black. The suspensions obtained are stable for months as confirmed by TEM (the sizes of the particles remain unmodified over this time frame). In Condition 1, 10 mL of this solution A are used: 1.9×10^{-5} mol of Rh (1.9×10^{-3} mol L^{-1}), 3.8×10^{-5} mol of surfactant (3.8×10^{-3} mol L^{-1}). The substrate is finally added to have a ratio of 200. For Condition 2, 20 mL of solution A are diluted in 250 mL, surfactant = 3.04×10^{-4} mol L^{-1} and hence the rhodium concentration is 1.52×10^{-4} mol L^{-1} (7.6×10^{-6} mol in 50 mL of solution.).

General Procedure for Hydrogenation

All hydrogenation reactions were carried out under standard conditions (20 °C, 1 atm of H_2). A 25-mL, round-bottom flask, charged with the chosen aqueous suspension of Rh(0) (10 mL, Condition 1) and a magnetic stirrer, was connected with a gas burette (500 mL) with a flask to balance the pressure. The flask was closed by a septum, and the system was filled with hydrogen. The appropriate aromatic substrate (3.8×10^{-3} mol) was injected through the septum, and the mixture was stirred at

1500 min^{-1}. The reaction was monitored by the volume of gas consumed and by gas chromatography. At the end of the reaction, the two phases were separated by decantation and the aqueous phase was re-used in a second run. The turnover frequencies (TOF) were determined for 100% conversion.

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