

Stabilized Rhodium(0) Nanoparticles: A Reusable Hydrogenation Catalyst for Arene Derivatives in a Biphasic Water–Liquid System

Jürgen Schulz, Alain Roucoux,* and Henri Patin^[a]

Abstract: A colloidal system based on an aqueous suspension of rhodium(0) nanoparticles proved to be an efficient catalyst for the hydrogenation of arene derivatives under biphasic conditions. The rhodium nanoparticles (2–2.5 nm) were synthesized by the reduction of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ with sodium borohydride and were stabilized by highly water-soluble *N*-alkyl-*N*-(2-hydroxyethyl)am-

monium salts (**HEA-C_n**). These surfactant molecules were characterized by measurements of the surface tension and the aqueous dispersions with rhodium were observed by transmission

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electron cryomicroscopy. The catalytic system is efficient under ultramild conditions, namely room temperature and 1 atm H_2 pressure. The aqueous phase which contains the protected rhodium(0) colloids can be reused without significant loss of activity. The microheterogeneous behavior of this catalytic system was confirmed on a mercury poisoning experiment.

Introduction

For economic and ecological reasons, biphasic catalysis based on two immiscible liquid phases, water and hydrocarbons, have attracted increasing attention.^[1] In fact, such catalytic systems offer a way to separate and recycle the catalyst by simple decantation. The most classical approaches use water-soluble homogeneous catalysts coordinated to phosphines which contain hydrophilic functional groups (carboxylate, sulfonate, hydroxy, etc.). Thus, several industrial processes are essentially based on the exceptional water-solubility of ligands such as the triphenylphosphinetrisulfonate sodium salt (TPPTS-Na).

Our alternative is to use metallic nanoparticles that are finely dispersed in water to allow an easy separation of the catalyst from the reaction product.^[2] During the last decade, nanoparticles dispersed in liquid media have been studied^[3] in catalytic reactions, such as hydrogenation,^[4–7] oxidation,^[8] hydrosilation,^[9] or more recently, C–C coupling.^[10] These microheterogeneous systems show a great potential because of the large surface area of the particles. These small metal particles can work efficiently as a catalyst if aggregation does not occur. To prevent this phenomenon and to facilitate recycling, particles must be stabilized by a highly water-soluble protective agent. Three main methods are known to

prevent colloids from aggregating in water: i) electrostatic stabilization with ionic species,^[2a] ii) steric protection based on the use of polymers,^[11] and iii) electrosteric stabilization generated by surfactants or polyoxoanions.^[12]

We have chosen an ionic surfactant to prepare and to protect the aqueous colloidal suspension of metallic particles. We have synthesized *N*-alkyl-*N*-(2-hydroxyethyl)ammonium salts (**HEA**), which provide sufficiently hydrophilic character to maintain the catalytic species within aqueous phase.^[2c]

The hydrogenation of benzene derivatives represents an important industrial catalytic transformation.^[13] Generally, this reaction is carried out with heterogeneous catalysts.^[14] Some pure homogeneous^[15] or microheterogeneous^[5] systems have been reported, but they require in many, if not most, cases drastic conditions (high pressure and/or temperature). However, colloidal catalysts do give satisfactory results for the benzene/arene reduction in organic mixtures.^[5e] In this paper, we show that our catalytic system (Rh/protective agent) can efficiently catalyze the hydrogenation of arenes in biphasic liquid–liquid (water/organic phase) media at room temperature and under 1 atm H_2 pressure. We demonstrate that surfactant-protected colloids can be used in pure biphasic conditions with a satisfactory recycling process.

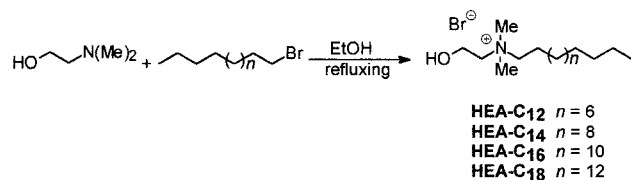
Results and Discussion

We have already demonstrated that aqueous dispersions of rhodium particles can efficiently catalyze alkene hydrogenation in biphasic systems with i) electrostatic stabilization by the use of trisulfonated triphenylphosphine oxide^[2a] or

[a] Dr. A. Roucoux, J. Schulz, Prof. Dr. H. Patin
Laboratoire de Chimie Organique
et des Substances Naturelles—CNRS ESA 6052,
Ecole Nationale Supérieure de Chimie de Rennes
Avenue du Gal Leclerc, 35700 Rennes (France)
Fax: (+33) 299-871-332
E-mail: alain.roucoux@ensc-rennes.fr

ii) electrosteric stabilization based on the use of trisulfonated molecules that contain a lipophilic side-chain and a bulky trianionic hydrophilic group.^[2b]

In this context, we have studied a new series of easily synthesized surfactants that stabilize an active catalytic system in the hydrogenation of arenes in a biphasic (liquid–liquid) medium.^[2c] Thus, *N*-alkyl-*N*-(2-hydroxyethyl)ammonium salts, **HEA-C_n**, have been prepared with an alkyl chain bearing *n* = 12–18 carbon atoms. These molecules are obtained by quaternization of *N,N*-dimethylethanolamine with the appropriate bromoalkanes (Scheme 1).^[16] All the **HEA-C_n** compounds are highly soluble in water, but their properties



Scheme 1. Synthesis of *N*-alkyl-*N*-(2-hydroxyethyl)ammonium salts, **HEA-C_n**.

depend on the number of carbons in the alkyl chain. Surface tension measurements (Figure 1) demonstrated that all **HEA-C_n** compounds which bear a lipophilic alkyl chain of more

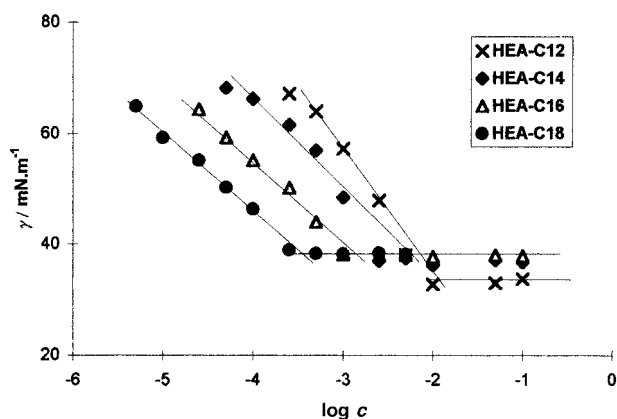


Figure 1. Surface tensions of aqueous solutions of surfactants **HEA-C_{12–18}**.

Abstract in French: *Un système catalytique colloïdal constitué d'une suspension de nanoparticules de rhodium(0) a montré une bonne efficacité pour l'hydrogénation de dérivés d'arènes en milieu biphasique. Des particules de rhodium d'environ 2 nm sont obtenues par réduction de RhCl₃·3H₂O par le borohydrure de sodium en présence de sels hydrosolubles de N-alkyl-N-(2-hydroxyéthyl)ammonium (HEA-C_n). Ces molécules tensioactives ont été caractérisées par des mesures de tension de surface et les suspensions aqueuses de rhodium observées par cryomicroscopie électronique à transmission. Le système catalytique est actif dans des conditions douces de température et de pression (20 °C, 1 atm d'H₂). La suspension aqueuse de rhodium(0) séparée par simple décantation peut être réutilisée sans perte notable d'activité. Enfin, le caractère microhétérogène du système a été confirmé par un test d'empoisonnement au mercure.*

than 12 carbon atoms are surfactants and self-aggregate into micelles above the critical micellar concentration (cmc) of 1×10^{-2} , 2.5×10^{-3} , 1×10^{-3} , and 2.5×10^{-4} mol L⁻¹ for **HEA-C₁₂**, **HEA-C₁₄**, **HEA-C₁₆**, and **HEA-C₁₈**, respectively. The decrease in the surface tension of aqueous solutions of these surfactants below the cmc (from 72 mN m⁻¹ for pure water to about 35 mN m⁻¹ for the surfactant-containing solutions) is related to their adsorption at the water/air interface by the Gibb's law.^[17] These series of **HEA-C_n** salts exhibited classical behavior: the cmc values decreased from 1×10^{-2} to 2.5×10^{-4} as the hydrocarbon chain length increased and we observed an usual linear variation of log cmc versus the number of carbon atoms (Figure 2).

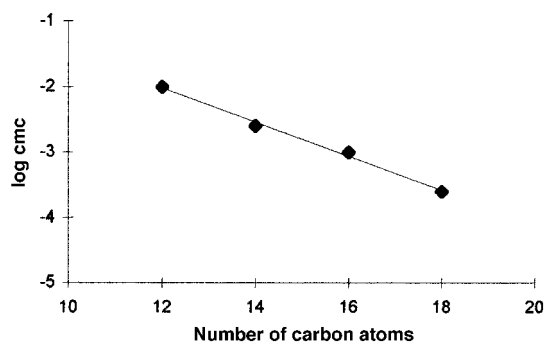


Figure 2. Plot of log cmc versus alkyl chain length.

Based on these results, catalytically active aqueous suspensions were made of metallic rhodium(0) colloids prepared at room temperature by the reduction of rhodium trichloride with sodium borohydride in dilute aqueous solutions of **HEA-C_n** salts. Nevertheless, only the surfactants **HEA-C₁₆** and **HEA-C₁₈** gave rise to stable monodispersed colloidal dispersions. With the compounds **HEA-C₁₂** and **HEA-C₁₄** the rhodium suspensions were less stable and the metal particles quickly aggregated. Accordingly, an effective electrosteric stabilization requires a sufficiently lipophilic substituent, namely, it must contain at least 16 carbon atoms in the side-chain attached to the head group, a highly hydrophilic *N*-(2-hydroxyethyl)ammonium salt.

The particle size of the optimized system Rh/**HEA-C₁₆** was determined by transmission electron cryomicroscopy. We compared the rhodium suspensions prior to catalysis and after the first run (Figure 3). The histograms of the size distribution of the nanoparticles were estimated after the original negative had been digitally scanned for more accurate resolution. Measurement of about 300 particles was made with a program that counted the objects automatically based on shape recognition.^[18] The comparative TEM studies showed that the catalytic suspensions had a similar average diameter (2.1 nm versus 2.2 nm) and thus confirmed the conservation of the size distribution (Figure 3). The “nearly monodispersed” colloidal suspension in water was highly stable under our mild catalytic conditions (1 atm H₂, 20 °C); this justifies a comparison of catalytic behavior during recycling. More specifically, our catalytic suspensions have good stability and can be used up to 60 °C without degradation; although it should be noted that the stability of our particles is somewhat less than that of

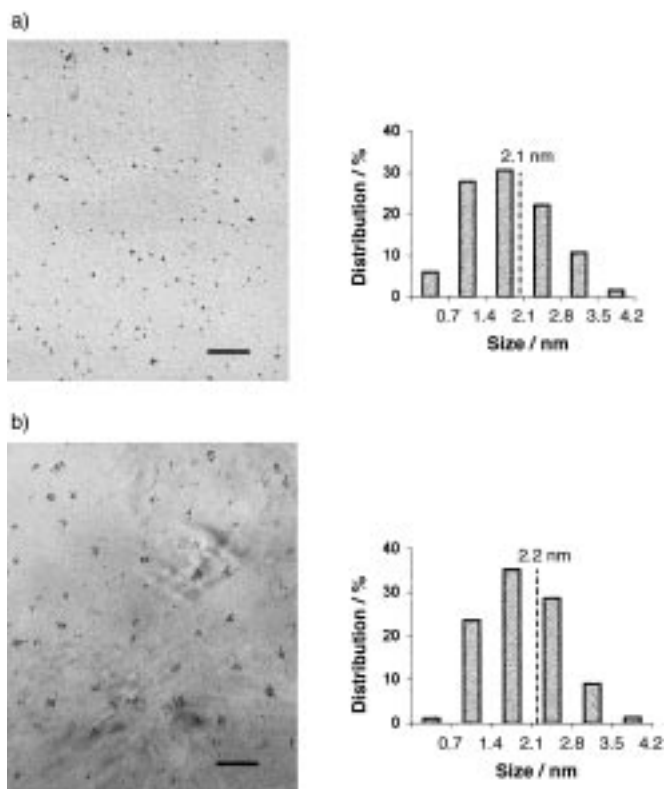


Figure 3. Comparison of colloids stabilized by **HEA-C₁₆** a) before and b) after catalysis (scale bar = 50 nm).

nanoclusters previously reported which are stable up to 100 °C.^[19]

Rhodium(0) colloids are known to reduce arenes,^[20] but as far as we know, our results provide the first example of an efficient conversion under pure biphasic conditions, with recycling at room temperature, and under 1 atm hydrogen pressure. In preliminary studies, we compared the new colloidal rhodium system with a standard Rh/C heterogeneous catalyst and with the classical water-soluble Rh/polyvinylpyrrolidone and Rh/poly(vinyl alcohol) systems synthesized in hydroalcoholic media by Hirai.^[21] These catalytic systems were investigated by means of the reduction of anisole; each reaction was performed under identical conditions (Table 1). Our colloids exhibited the best catalytic activity. Furthermore, only Rh/**HEA-C₁₆** can be reused for further runs. The Rh/polyvinylpyrrolidone or Rh/poly(vinyl

Table 1. Comparison of standard catalysts versus the Rh/**HEA-C₁₆** catalyst for the hydrogenation of anisole.^[a]

Catalyst	1st Run		2nd Run	
	<i>t</i> [h]	TOF [h ⁻¹] ^[b]	<i>t</i> [h]	TOF [h ⁻¹] ^[b]
Rh/C (5 wt.%; Degussa-type DG 10)	15	20	[d]	—
Rh/PVA (M.W. 22000) ^[c]	9	33	[e]	—
Rh/PVP (M.W. 40000) ^[c]	6.4	47	[e]	—
Rh/ HEA-C₁₆	5	60	5.3	57

[a] Reaction conditions: metal (3.8×10^{-5} mol), anisole (3.8×10^{-3} mol), water (10 mL), hydrogen pressure (1 atm), temperature (20 °C), stirred at 1500 min⁻¹. [b] Turnover frequency defined as number of moles of consumed H₂ per mole of rhodium per hour. [c] Rh colloids synthesized as previously described by Hirai.^[21] [d] The Rh/C cannot be easily recycled by filtration. [e] Cannot be recycled by decantation.

alcohol) catalysts gave a monophasic system and, consequently, cannot be separated by simple decantation for the purpose of recycling.

The molecular ratio $R = \text{HEA-C}_{16}/\text{Rh}$ was optimized to prevent aggregation and to provide a good activity. Specifically, the hydrogenation of anisole to the corresponding methoxycyclohexane was studied with different ratios of **HEA-C₁₆**/Rh (Figure 4). Below a molar ratio $R=2$, the rhodium particles aggregated with a total loss of activity for hydrogenation. A molar ratio $R=2$ gave better activity and was sufficient to maintain stable nanoparticles within the aqueous phase during the catalytic process and hence allowed its recycling. The activity decreased when $R > 2$ was used. In this case, the quantity of surfactant present around the metal particles was somewhat excessive and therefore prevented the access of the substrates to the active site(s).

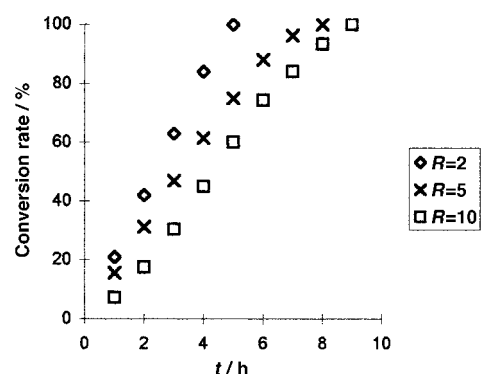


Figure 4. Hydrogenation of anisole with various amounts of **HEA-C₁₆** ($R = \text{HEA-C}_{16}/\text{Rh}$).

The durability of the catalytic system was investigated by employing it in several successive hydrogenations. For this, anisole was again selected as a reference substrate. After a first cycle (TOF = 60 h⁻¹), the aqueous phase containing the monodispersed colloidal suspensions of rhodium was separated from the methoxycyclohexane product by slow (overnight) decantation and then reused in a second run. In the same way, the catalytic suspension was recovered for a third, fourth, and fifth hydrogenation cycle. Figure 5 shows a comparable turnover activity for all runs. We have observed

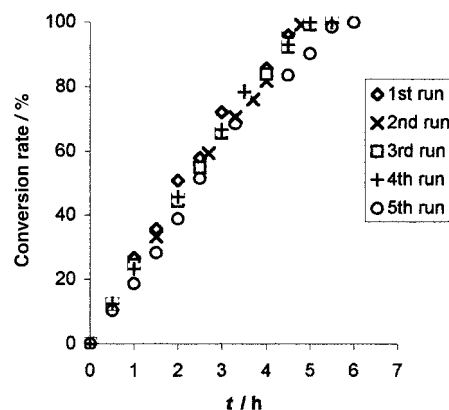


Figure 5. Activity of the recycled aqueous phase in the reduction of anisole.

Table 2. Hydrogenation of benzene and monosubstituted derivatives under biphasic conditions.^[a]

Substrate	Stabilizing agent	Substrate/Rh ⁰	Product (yield %) ^[b]	1st Run		2nd Run	
				<i>t</i> [h]	TOF [h ⁻¹] ^[c]	<i>t</i> [h]	TOF [h ⁻¹] ^[c]
benzene	HEA-C₁₆	100	cyclohexane (100)	5.3	57	5.9	51
benzene	HEA-C₁₆	200	cyclohexane (100)	6.6	91	7.1	85
benzene	HEA-C₁₈	100	cyclohexane (100)	9.1	33	13.3	23
toluene	HEA-C₁₆	100	methylcyclohexane (100)	5.7	53	6.3	48
toluene	HEA-C₁₆	200	methylcyclohexane (100)	6.5	92	7.6	79
toluene	CTAB	100	methylcyclohexane (100)	7.8	38	9.8	31
ethylbenzene	HEA-C₁₆	100	ethylcyclohexane (100)	6.9	43	7.4	40
propylbenzene	HEA-C₁₆	100	propylcyclohexane (100)	7.1	42	7.6	39
cumene	HEA-C₁₆	100	isopropylcyclohexane (100)	7.9	38	8.6	35

[a] Reaction conditions: catalyst (3.8×10^{-5} mol), surfactant (7.6×10^{-5}), water (10 mL), hydrogen pressure (1 atm), temperature (20 °C), stirred at 1500 min⁻¹. [b] Determined by GC analysis. [c] Turnover frequency defined as number of moles of consumed H₂ per mole of rhodium per hour.

that the conservation of the TOF value during recycling depends primarily on the amount of stable nanoparticles remaining in the aqueous phase after separation; hence, a meticulous and slow decantation is necessary in order to conserve an efficient catalytic activity. Additionally, we correlated the catalytic activity with the amount of rhodium within the aqueous phase. An atomic absorption analysis (by means of a rhodium lamp) of dilute solutions showed that the concentration of the metal in the aqueous phase before and after catalysis was similar. A small loss (1.4 ± 0.1 mg L⁻¹) was observed between the original catalytic solution (11.7 mg L⁻¹) and that after the fifth run (10.3 mg L⁻¹); this corresponds to a rhodium loss of $\approx 10\%$. Consequently, these water-soluble surfactants **HEA-C₁₆₋₁₈** satisfactorily maintain the colloidal rhodium particles within the aqueous phase during the catalytic process and thus allow the reuse of the aqueous suspensions in biphasic catalytic systems (water/hydrocarbon) to within $\pm 10\%$.

We have also hydrogenated benzene and some of its monoalkyl-substituted derivatives under biphasic conditions (Table 2). The reaction was monitored by the volume of hydrogen consumed and a gas chromatographic analysis. The turnover frequency (TOF), defined as number of moles of consumed H₂ per mole of rhodium per hour, was determined for the first run and for recycling after separation of the aqueous phase. No induction period was observed. The very

selective catalytic reaction gave good results and the conversion was usually complete after 7 h for a ratio S/Rh = 100 (S = substrate). Most importantly the ratio S/Rh (= 100 or 200) has little effect on the reaction time. In contrast with the *N*-alkyl-*N*-(2-hydroxyethyl)ammonium salt, cetyltrimethylammonium bromide (**CTAB**) gave poor results. The turnover frequency decreased during the first and second run as can be seen for toluene. These results justify the use of the hydroxyammonium function as the hydrophilic head group. Unfortunately, we did not observe any cyclohexene or cyclohexadiene derivatives as intermediates which ideally would have been desirable. Nevertheless, steric substituent effects of the arene influenced the reaction time. The increasing steric hindrance of the alkyl group in the series benzene, toluene, ethylbenzene, propylbenzene, and cumene is clearly indicated by the increase in the reaction time and the decrease in the catalytic TOF.

In a second series of studies, we investigated the hydrogenation of functionalized arenes (Table 3). The reaction was influenced by the electronic effects of the arene substituents. Thus, arenes substituted by electron-withdrawing groups reacted more slowly, whereas those with electron-donating groups reacted more quickly. Here, electron-rich substrates should be preferentially adsorbed on the rhodium colloids and thus the reaction is accelerated^[5d] for arenes such as anisole (5 h). Surprisingly, halogenated benzenes were not hydro-

Table 3. Hydrogenation of functionalized derivatives under biphasic conditions.^[a]

Substrate	Stabilizing agent	Substrate/Rh ⁰	Product (yield %) ^[b]	1st Run		2nd Run	
				<i>t</i> [h]	TOF [h ⁻¹] ^[c]	<i>t</i> [h]	TOF [h ⁻¹] ^[c]
anisole	HEA-C₁₆	100	methoxycyclohexane (100)	5	60	5.3	57
anisole	HEA-C₁₆	200	methoxycyclohexane (100)	6.2	97	7.1	85
anisole	HEA-C₁₆	500	methoxycyclohexane (100)	10	150	11.4	132
anisole	HEA-C₁₆	1000	methoxycyclohexane (100)	17	188	20	150
anisole	HEA-C₁₈	100	methoxycyclohexane (100)	8.4	36	11.5	26
anisole	CTAB	100	methoxycyclohexane (100)	5.1	59	24	13
phenol	HEA-C₁₆	100	cyclohexanol (100)	5.2	58	5.7	53
phenol	HEA-C₁₈	100	cyclohexanol (100)	5.6	54	8.4	36
ethyl benzoate	HEA-C₁₆	100	ethyl cyclohexanoate (100)	9.5	32	11.9	25
bromobenzene ^[d]	HEA-C₁₆	100	–	–	–	–	–
aniline	HEA-C₁₆	100	cyclohexylamine (100)	10	30	–	–
styrene	HEA-C₁₆	100	ethylcyclohexane (100)	7.3	55	8.4	48
α -methylstyrene	HEA-C₁₆	100	isopropylcyclohexane (100)	9.2	43	10.1	40
allylbenzene	HEA-C₁₆	100	propylcyclohexane (100)	10.3	39	11.2	36

[a] Reaction conditions: catalyst (3.8×10^{-5} mol), surfactant (7.6×10^{-5}), water (10 mL), hydrogen pressure (1 atm), temperature (20 °C), stirred at 1500 min⁻¹. [b] Determined by GC analysis. [c] Turnover frequency defined as number of moles of consumed H₂ per mole of rhodium per hour. [d] Similarly, PhI, PhCl, and PhF are not reduced.

generated, not even slowly, as a consequence of catalyst deactivation. Under our standard conditions, no selective catalytic hydrogenation to afford a cyclohexyl product was observed with i) a mixture of iodobenzene and benzene, or ii) a recycled catalytic suspension which was used for the hydrogenation of a halogenated compound; hence, the electron-withdrawing effect of the halogen is *not* responsible for the lack of reaction. Instead, it must be caused by a poisoning effect of the substrate.

The chemoselectivity was good: for example, ester and ether functions remained unaffected. Another case in point is the hydrogenation of aniline which gave the cyclohexylamine; here the catalyst cannot be recycled, since the colloidal aqueous phase was insufficiently stable and generally aggregated. We believe that the ammonium functionality was reacting with the product, which resulted in a loss of stabilization. In addition to the hydrogenation of the aromatic ring, reducible components of the substituents can also be hydrogenated, for example, *exo*-C–C double bonds of styrene, α -methylstyrene, and allylbenzene. In all cases, we observed the reduction of the double bond prior to the hydrogenation of the aromatic cycle. Nevertheless in the last case, we detected (in addition to the hydrogenation of the double bond to form propylbenzene) the partial isomerization of the double bond with formation of β -methylstyrene. This compound was then hydrogenated to propylbenzene and finally to propylcyclohexane.

In a third set of studies, we examined the hydrogenation of disubstituted benzene derivatives, such as xylene or methyl-anisole compounds, with the optimized system **HEA-C₁₆**/Rh = 2. A complete conversion was obtained in all cases (Table 4). The *cis* products were largely the major products, as is usually observed in heterogeneous catalytic systems.^[22]

Finally, we tested the behavior of our catalytic system by means of mercury poisoning experiments. Mercury is a well-known heterogeneous-catalyst poison on account of its classical adsorption onto the surface of transition metal(0) catalysts.^[5c] A large excess of Hg⁰ was added after 50% conversion to a catalytically active solution containing anisole. After stirring for 1 h, the solution was reconnected to the hydrogenation apparatus. No catalytic activity was detected, which indicated that Hg had completely inactivated

the catalyst (Figure 6). In light of prior reports,^[5c] these results provide good evidence that the Rh⁰ nanoparticles are the true catalysts.

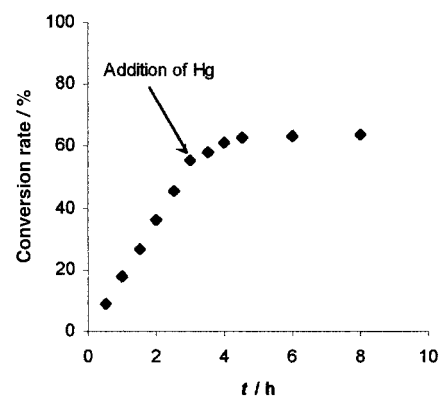


Figure 6. Hg⁰ poisoning of the catalyst in the reduction of anisole.

Conclusions

The results presented herein confirm that the Rh⁰ nanoparticles protected by *N*-alkyl-*N*-(2-hydroxyethyl)ammonium salts are a very efficient catalyst for the reduction of arenes; the results further demonstrate that our microheterogeneous system can be used to catalyze hydrogenation in two liquid phases, under mild conditions, and with recycling. These experiments confirm that microheterogeneous colloidal catalysis at room temperature and 1 atm hydrogen pressure, as demonstrated by TEM observations and mercury poisoning experiments, is a real alternative to biphasic liquid–liquid homogeneous catalysis, provided that the monodispersed colloidal suspensions of the rhodium particles are prepared and correctly stabilized with the correct, highly water-soluble protecting agent.

Experimental Section

Starting materials: Rhodium chloride hydrate and mercury were obtained from Strem Chemicals. Rh/C (5 wt.%; Degussa-type G10), poly(vinyl

Table 4. Hydrogenation of disubstituted benzene derivatives under biphasic conditions.^[a]

Substrate	Stabilizing agent	Substrate/Rh ⁰	Product (yield %) ^[b]	1st Run		2nd Run	
				t [h]	TOF [h ⁻¹] ^[c]	t [h]	TOF [h ⁻¹] ^[c]
<i>o</i> -xylene	HEA-C₁₆	100	1,2-dimethylcyclohexane <i>cis</i> (95), <i>trans</i> (5)	7.5	40	8.9	48
<i>m</i> -xylene	HEA-C₁₆	100	1,3-dimethylcyclohexane <i>cis</i> (87), <i>trans</i> (13)	7.3	41	8.5	35
<i>p</i> -xylene	HEA-C₁₆	100	1,4-dimethylcyclohexane <i>cis</i> (70), <i>trans</i> (30)	7.1	42	8.2	37
<i>o</i> -methylanisole	HEA-C₁₆	100	1-methoxy-2-methylcyclohexane <i>cis</i> (97), <i>trans</i> (3)	9.5	32	10.3	29
<i>p</i> -methylanisole	HEA-C₁₆	100	1-methoxy-4-methylcyclohexane <i>cis</i> (92), <i>trans</i> (8)	9.2	33	10	30
<i>m</i> -cresol	HEA-C₁₆	100	3-methylcyclohexanol <i>cis</i> (99), <i>trans</i> (1)	8.2	37	9.1	33

[a] Reaction conditions: catalyst (3.8×10^{-5} mol), surfactant (7.6×10^{-5}), water (10 mL), hydrogen pressure (1 atm), temperature (20 °C), stirred at 1500 min⁻¹. [b] Determined by GC analysis. [c] Turnover frequency defined as number of moles of consumed H₂ per mole of rhodium per hour.

alcohol) (PVA; MW = 22 000), polyvinylpyrrolidone (PVP; MW = 40 000), sodium borohydride, various bromoalkanes, *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 a conventional method. The surfactants HEA-C₁₂₋₁₈ were prepared and fully characterized as previously reported.^[16]

Analytical procedures: The surface tension measurements were performed at 20 °C by means of the ring method with a Du Nouy tensiometer (Krüss K10T).

The transmission electronic cryomicroscopic studies were conducted on a PHILIPS CM12 transmission electron microscope at 100 KeV. Samples were prepared by a dropwise addition of the stabilized colloid in water onto a Cu mesh covered with carbon. The colloidal dispersion was removed after 1 min with cellulose and the samples were quickly frozen in liquid ethane before their transfer to the microscope.

Gas chromatography was performed on a Carlo Erba GC 6000 with a FID detector equipped with an Alltech AT1 column (30 m long, 0.25 mm inner diameter). Parameters were as follows: initial temperature 40 °C; initial time 3 min; ramp 8 °C min⁻¹; final temperature 140 °C; final time 5 min; injector temperature 220 °C; detector temperature 250 °C; injection volume 0.3 µL.

The atomic absorption measurements were performed on a Varian AA-1275 spectrometer with the following parameters: lamp current 12 mA, $\lambda_{\text{Rh}} = 343.5$ nm, slit width 0.5 mm, air/acetylene flame. The sample (3 mL) was diluted in water (100 mL). The concentration (mg L⁻¹) was determined by means of a calibration graph.

Synthesis of the aqueous Rh⁰ colloidal suspensions: The suspensions were prepared under nitrogen at 20 °C. Sodium borohydride (36 mg, 9.5 × 10⁻⁴ mol) was added to an aqueous solution of surfactant (95 mL) with various concentrations (7.6 × 10⁻³ mol L⁻¹ gave the best results). This solution was quickly added, under vigorous agitation, to an aqueous solution (5 mL) of the precursor RhCl₃ · 3H₂O (100 mg, 3.8 × 10⁻⁴ mol) to give an aqueous Rh⁰ colloidal suspension (100 mL). The reduction occurred instantaneously and was characterized by a color change from red to black. The suspensions obtained were stable for months, as confirmed by TEM (the sizes of the particles remain unmodified over this time frame).

General hydrogenation procedure: All hydrogenation reactions were carried out under standard conditions (20 °C, 1 atm of H₂). A round-bottom flask (25 mL), charged with the chosen aqueous suspension of Rh⁰ (10 mL) and a magnetic stirrer, was connected to 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 (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 reused in a second run. The turnover frequencies (TOF) were determined for 100% conversion.

Mercury poisoning experiment:^[5e] A standard hydrogenation was conducted with anisole (411 mg, 3.8 × 10⁻³ mol) as the reference substrate. Subsequently, a second hydrogenation of anisole (411 mg, 3.8 × 10⁻³ mol) was conducted. After 50% conversion, the reaction was stopped and mercury was added (2.29 g, 1.14 × 10⁻² mol, 300 equiv; as described elsewhere^[5e]). The mixture was stirred for 1 h and was then reconnected to the hydrogenation apparatus. The two hydrogenation reactions were compared.

Acknowledgments

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