Arene Hydrogenation with a Stabilised Aqueous Rhodium(0) Suspension: A Major Effect of the Surfactant Counter-Anion

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Abstract: A reduced aqueous colloidal suspension of rhodium shows an efficient activity in the catalytic hydrogenation of various benzene derivatives under biphasic conditions at room temperature and under atmospheric hydrogen pressure. The rhodium nanoparticles in the size range of 2–2.5 nm have been synthesised by reducing $RhCl_3 \cdot 3\,H_2O$ with sodium borohydride and were stabilised by highly water-soluble *N*,*N*-dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium salts (HEA16X, X = Br, Cl, I, CH_3SO_3, BF_4). The major influence of the counter-ion of these surfactants on catalytic activity and recycling is described. The best results have been obtained with chloride ammonium salts HEA16Cl.

Keywords: biphasic catalysis; colloids; counter-ions; hydrogenation; rhodium; surfactants

Introduction

The complete hydrogenation of benzene derivatives represents an important industrial catalytic transformation due to the increasing industrial demand for low-aromatic diesel fuels.[1] Moreover, the conversion of benzene to cyclohexane still represents the most important industrial hydrogenation reaction.[1–8] In some cases, the partial arene hydrogenation to cyclohexenes is desired and in others observed during the reduction.[9–13] Undoubtedly, in the future, this reaction will be an active area of research. Traditionally, monocyclic arene hydrogenation is performed with heterogeneous catalysts[14–23] such as Rh/Al_2O_3 and Raney Nickel or metal sulfides. Nevertheless, some pure homogeneous systems have been reported.[7,24–28] These systems require in many if not most cases drastic conditions (high pressure and/or temperature). In a few cases, these homogeneous catalysts have been shown to be microheterogeneous catalysts.[29–31] Consequently, the use of nanoparticles as catalysts has received increased attention and now some colloidal catalysts give satisfactory results for benzene/arene reduction in organic mixtures. The use of rhodium and ruthenium nanoparticles for arene derivative hydrogenation has been largely reported.[4,5,31–39]

Our original approach is to use colloidal metallic particles finely dispersed in water.[40] The colloidal suspension must be stabilised by protective agents. Several stabilisers are used in the hydrogenation of arene derivatives to prevent aggregation such as tetraalkylammonium salts,[4,5,31,34,38,39,41–43] polymers,[35] surfactants[31,40,44,45] or polyoxoanions.[12–13,46] In this context and to facilitate recycling, particles must be stabilised by a highly water-soluble protecting agent. We have chosen an ionic surfactant to prepare and to protect the aqueous colloidal suspension of metallic particles. Previously we have described the easy synthesis of *N*,*N*-dimethyl-*N*-alkyl-*N*-(2-hydroxyethyl)ammonium bromide salts (**HEAC$_{12-18}$Br**). The best system has been defined as R=2=**HEAC$_{16}$Br**/Rh which gives sufficiently hydrophilic behaviour to maintain catalytic species within the aqueous phase and to prevent aggregation.[44] In this paper, we describe the effect of the counter-ion to ammonium on the catalytic system. In fact, its influence on the rhodium nanoparticle size and on the hydrogenation of various arene derivatives was investigated.

Results and Discussion

The catalytically active aqueous suspension was made of metallic rhodium(0) particles prepared by reducing rhodium trichloride with sodium borohydride in dilute aqueous solutions of **h**ydroxy**e**thyl**a**mmonium salts **HEA16X** (**X** = Br, Cl, I, CH_3SO_3, BF_4). These compounds are easily synthesised by quaternisation of *N*,*N*-dimethylethanolamine with the appropriate functionalised cetylalkanes or by ion exchange (Scheme 1).

Surface tension measurements demonstrate that **HEA16X** self aggregates into micelles above the critical micellar concentration (cmc) of 1.1×10^{-3}, 1.4×10^{-3}, 9.3×10^{-4}, 1.3×10^{-5} and 2.8×10^{-4} mol · L^{-1} for **X** = Br, Cl, Ms, I, BF_4, respectively. The decrease of the surface tension of aqueous solutions of these surfactants

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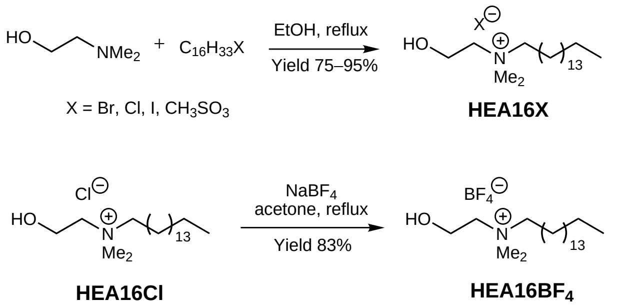
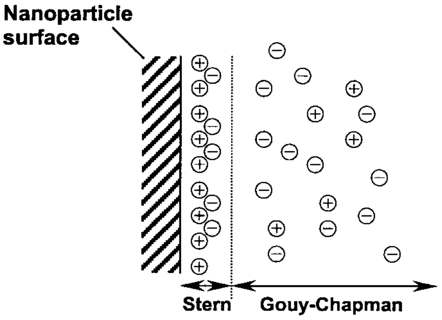


Scheme 1. Synthesis of *N*,*N*-dimethyl-*N*-alkyl-*N*-(2-hydroxyethyl)ammonium salts **HEA16X.**



Scheme 3. Schematic representation of the double-layer around particles.

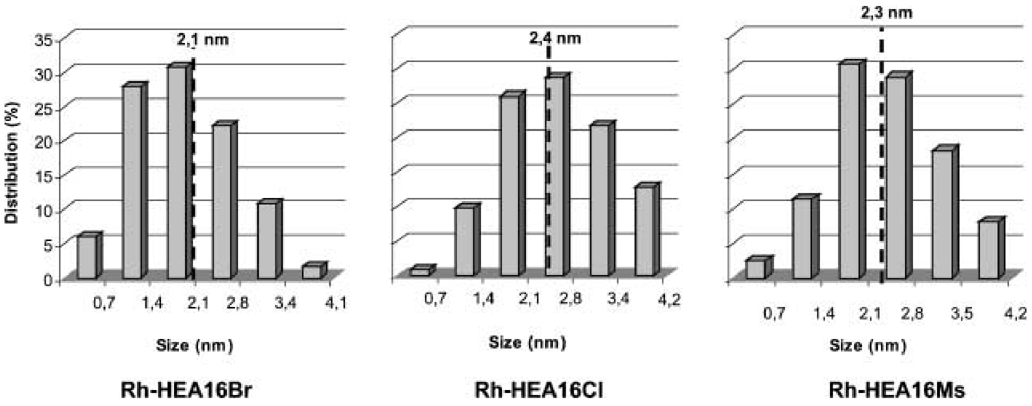
below the cmc (from 72 mN · m^{-1} for pure water to about 38 mN · m^{-1}) is related to their adsorption at the water/air interface by the Gibb's law.[47] The cmc values decreased from Cl > Br > BF_4 > Ms > I. The larger counter-ions are more polarisable and contribute to decreased electrostatic repulsions between head groups and consequently promote the micelle formation.

Based on this study, catalytically active aqueous suspensions are made of metallic rhodium(0) colloids prepared at room temperature by reducing rhodium trichloride with sodium borohydride in dilute aqueous solutions of **HEA16X** salts. The particle size of the Rh-**HEA16X** systems have been determined by transmission electron cryomicroscopic observations. The histograms (Scheme 2) of the nanoparticles size distribution were estimated once the original negative had been digitally scanned for more accurate resolution. Measurement of about 300 particles was made with an automatic counting objects program based on shape recognition.[48] The average particles size was 2.1 to 2.4 nm.

These comparative TEM studies show that the counter-ion of the surfactant does not seem to present a major influence on the average particle size of colloidal suspensions. Finally, no evolution of distribution was observed after catalysis as we have previously reported with the Rh-**HEA16Br** system.[44] Consequently, these nearly monodispersed colloidal suspensions were highly stable and can be used under our mild catalytic conditions. The zeta potential measurements have been performed to find the apparent charge of a nanoparticle in solution. The surfactants form with their counter-ions an electrical double-layer around the rhodium(0) particles (Scheme 3). The subshell (Stern layer) characterises the ionic species adsorbed on nanoparticles surface and the outershell (Gouy – Chapman layer) is a disperse layer where salt concentration decreases with increasing distance.

These values characterise the difference of potential between the solution far from the metal/solution interface and the mobile part of the double-layer. The results of zetametric studies of catalytic suspensions are summarised in Table 1. In all cases, rhodium(0) nanoparticles give an apparently positive charge in solution from 40 to 100 mV. This phenomenon has already been observed with cationic stabilisers.[49] The measured values show the important role of the electrostatic repulsion (coulombic interaction) for the stabilisation of nanoclusters.

In preliminary catalytic studies, we compared the colloidal rhodium systems Rh-**HEA16X** (**X** = Br, Cl, I, Ms, BF_4) in the reduction of anisole under atmospheric pressure and at room temperature (Scheme 4). All aqueous catalytic suspensions were sufficiently stable



Rh-HEA16Br Rh-HEA16Cl Rh-HEA16Ms

Scheme 2. Size distribution histograms of rhodium(0) suspensions.

Table 1. Zeta potential measurements versus **X**$^-$ stabiliser.

Surfactant	ζ [mV][a]
HEA16Cl	+40.0
HEA16Ms	+100.0
HEA16BF$_4$	+55.5
HEA16Br	+50.0

[a] Measurements performed in catalytic conditions: rhodium (3.8×10^{-5} mol), surfactant (7.6×10^{-5}), water (10 mL), temperature (20 °C).

Table 2. Influence of hydrogen pressure on anisole reduction[a]

Surfactant	10 bar/15 min		30 bar/15 min	
	1st run[b]	2nd run[b]	1st run[b]	2nd run[b]
HEA16Cl	58	56	100	100
HEA16Ms	44	- [c]	100	- [c]
HEA16BF$_4$	44	42	100	100
HEA16Br	30	27	80	77
HEA16I	–	–	–	–

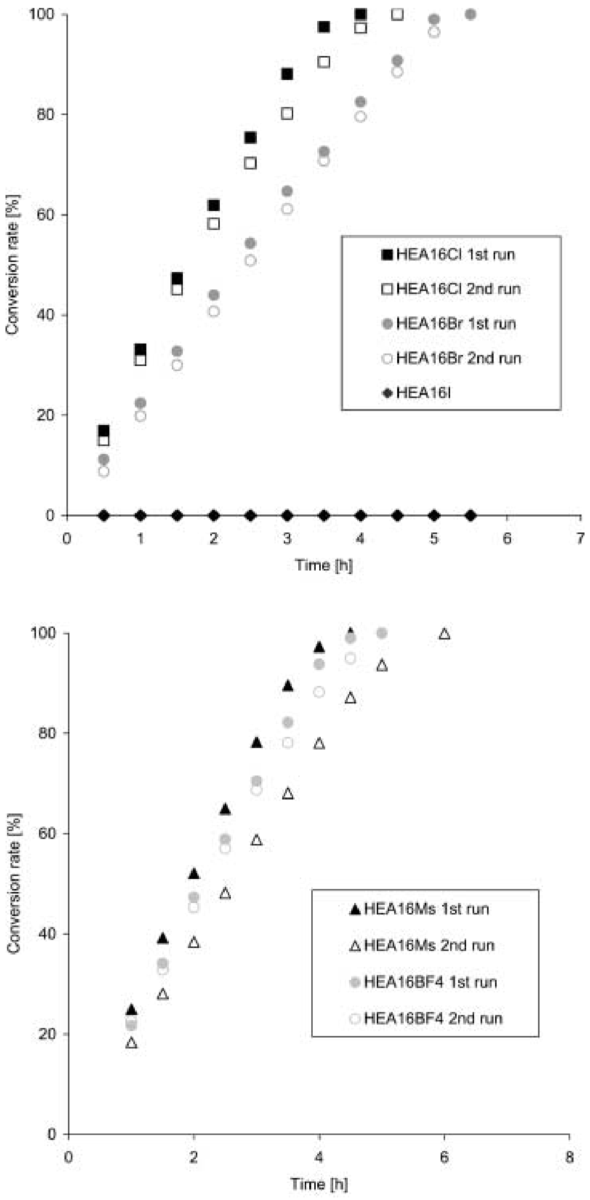
[a] Conditions: reaction time (15 min), catalyst (3.8×10^{-5} mol), anisole (3.8×10^{-3} mol), surfactant (7.6×10^{-5}), water (10 mL), hydrogen pressure (1 atm), temperature (20 °C), stirred at 1500 min^{-1}.

[b] Percent of methoxycyclohexane after 15 min determined by GLC analysis.

[c] Emulsion, cannot be recycled by decantation.

during the hydrogenation to allow their recycling after a meticulous decantation of the biphasic mixture. Each reaction and its recycling were performed under identical conditions.

The results show that the counter-ion (**X**$^-$ stabiliser) significantly influences the catalytic activities. The rhodium suspensions stabilised by **HEA16Cl**, **HEA16BF$_4$** and **HEA16Ms** give analogous activities during the first run. The reaction time varies between 3.6 and 4.3 h. Nevertheless, the CH_3SO_3 anion gives an emulsion generating a small metal loss. In this case, the aqueous phase cannot be easily recycled justifying an increasing of the reaction time during the recycling in contrast to the use of Rh-**HEA16Br** and Rh-**HEA16Cl** which give better results. Surprisingly, no anisole hydrogenation was observed with the use of **HEA16I** as surfactant. This phenomenon can be explained by a redox reaction between the Rh^{3+}/Rh ($E = 0.758$ V) and I_2/I^- ($E = 0.536$ V) couples giving iodine during the preparation of the rhodium suspension. We tested the behaviour of the more efficient Rh-**HEA16Cl** system after addition of iodine (Scheme 5). To a traditional catalytically active solution containing anisole, 760 μL (7.6 mmol) of I_2 were added after 2 hours of reaction time (about 65%) and the solution was reconnected to the hydrogenation apparatus.



Scheme 4. Influence of counter-ion on activity and recycling.

No hydrogen consumption was detected indicating that I_2 had completely killed the catalytic system. This experiment confirms that iodine is a poison of rhodium nanoparticles and justifies the absence of reactivity when **HEA16I** was used.

The efficiency of the catalytic system modified by different surfactants was tested under hydrogen pressure. The results obtained in anisole hydrogenation after 15 min of reaction time under 10 and 30 bars are summarised in Table 2.

In most of cases the increasing hydrogen pressure gave rise to an activation of the catalytic suspension and the conversion determined by GLC analysis was usually complete after 15 min under 30 bar. We also observed a good conservation of the conversion rate during the recycling. Finally, the relative activities of different

Table 3. Hydrogenation of benzene and monosubstituted derivatives[a]

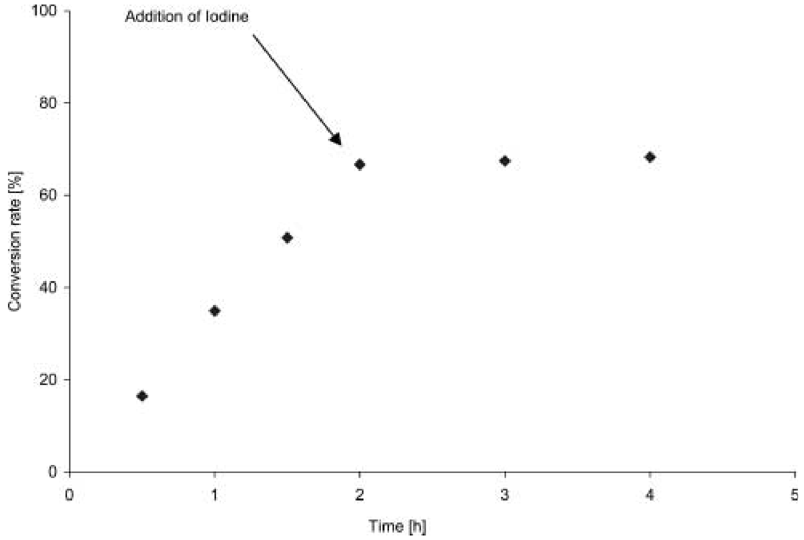
Substrate	Surfactant	Products (yields %)[b]	1st run t [h]	1st run TOF [h^{-1}][c]	2nd run t [h]	2nd run TOF [h^{-1}][c]
Benzene	**HEA16Cl**	Cyclohexane (100)	3.6	83	3.9	77
Benzene	**HEA16Br**	Cyclohexane (100)	5.3	57	5.9	51
Benzene	**HEA16Ms**	Cyclohexane (100)	3.7	81	4.1	73
Benzene	**HEA16BF$_4$**	Cyclohexane (100)	3.7	81	4.0	75
Cumene	**HEA16Cl**	Isopropylcyclohexane (100)	5.2	58	5.7	53
Cumene	**HEA16Br**	Isopropylcyclohexane (100)	7.9	38	8.6	35
Cumene	**HEA16Ms**	Isopropylcyclohexane (100)	6.4	47	– [d]	–
Cumene	**HEA16BF$_4$**	Isopropylcyclohexane (100)	5.2	58	– [d]	–
Toluene	**HEA16Cl**	Methylcyclohexane (100)	3.6	83	4.0	75
Toluene	**HEA16Br**	Methylcyclohexane (100)	5.7	53	6.3	48
Ethylbenzene	**HEA16Cl**	Ethylcyclohexane (100)	3.7	81	3.9	77
Ethylbenzene	**HEA16Br**	Ethylcyclohexane (100)	6.9	43	7.4	40
Propylbenzene	**HEA16Cl**	Propylcyclohexane (100)	3.9	77	4.3	70
Propylbenzene	**HEA16Br**	Propylcyclohexane (100)	7.1	42	7.6	39

[a] Conditions: catalyst (3.8×10^{-5} mol), substrate (3.8×10^{-3} 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 mol of H_2 per mol of rhodium per h.

[d] Emulsion, cannot be recycled by decantation.



Scheme 5. I_2 poisoning experiment.

rhodium suspensions did not change with hydrogen pressure, in fact the Rh-**HEA16I** system stays inactive whereas the Rh-**HEA16Cl** system reacts more quickly.

We also hydrogenated benzene and some of its classical monoalkyl-substituted derivatives under biphasic conditions at room temperature and under atmospheric hydrogen pressure (Table 3). This comparative study shows the major influence of the counterion of the surfactant on the conversion rate. The reaction was monitored by the volume of hydrogen consumed and a gas chromatographic analysis. The turnover frequency, defined as mol of H_2 per mol of rhodium per h, has been determined for the first run and for recycling after separation of the aqueous phase.

In all cases, the colloidal suspension of rhodium(0) stabilised by **HEA16Cl** gave the better turnover frequencies compared with **HEA16Br**, **Ms** and **BF$_4$**. Moreover, **HEA16Ms** and **BF$_4$** compounds lead at the end of the reaction to an emulsion which prevents, in some cases, the recycling of the aqueous phase. As previously described with bromide stabiliser,[44] whatever the counter-ion of **HEA16** we observed i) no cyclohexene or cyclohexadiene derivatives as intermediates, and ii) a steric effect of the arene substituents on the reaction time.

We also investigated the hydrogenation of functionalised arenes (Table 4). The reaction is influenced by the electronic effects of the arene substituents. The arenes substituted by electron-withdrawing groups react slowly

Table 4. Hydrogenation of functionalised arene derivatives.[a]

Substrate	Surfactant	Products (yields %)[b]	1st	run	2nd	run
			t [h]	TOF [h^{-1}][c]	t [h]	TOF [h^{-1}][c]
Anisole	**HEA16Cl**	Methoxycyclohexane (100)	3.6	83	3.9	77
Anisole	**HEA16Br**	Methoxycyclohexane (100)	5	60	5.3	57
Anisole	**HEA16Ms**	Methoxycyclohexane (100)	4.2	71	5.5[d]	55
Anisole	**HEA16BF$_4$**	Methoxycyclohexane (100)	4.5	67	4.7	64
Phenol	**HEA16Br**	Cyclohexanol (100)	5.6	54	8.4	36
Phenol	**HEA16Cl**	Cyclohexanol (100)	5.2	58	5.7	53
Ethyl benzoate	**HEA16Br**	Ethyl cyclohexanoate (100)	9.5	32	11.9	25
Ethyl benzoate	**HEA16Cl**	Ethyl cyclohexanoate (100)	4.7	64	5.3	57
Styrene	**HEA16Br**	Ethylcyclohexane (100)	7.3	55	8.4	48
Styrene	**HEA16Cl**	Ethylcyclohexane (100)	4.0	100	4.2	95
α-Methylstyrene	**HEA16Br**	Isopropylcyclohexane (100)	9.2	43	10.1	40
α-Methylstyrene	**HEA16Cl**	Isopropylcyclohexane (100)	5.4	74	5.7	70
Allylbenzene	**HEA16Br**	Propylcyclohexane (100)	10.3	39	11.2	36
Allylbenzene	**HEA16Cl**	Propylcyclohexane (100)	5.0	80	5.4	74
Acetophenone	**HEA16Cl**	Cyclohexylethan-1-ol (80) Cyclohexyl methyl ketone (20)	8.8	36	9.2	35

[a] Conditions: catalyst (3.8×10^{-5} mol), substrate (3.8×10^{-3} 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 mol of H_2 per mol of rhodium per h.

[d] Recycling after centrifugation of the emulsion.

Table 5. Hydrogenation of disubstituted benzene derivatives.[a]

Substrate	Surfactant	Products (yields %)[b]	1st	run	2nd	run
			t [h]	TOF [h^{-1}][c]	*t* [h]	TOF [h^{-1}][c]
o-xylene	**HEA16Br**	1,3-dimethylcyclohexane *cis* (95), *trans* (5)	7.5	40	8.9	34
o-xylene	**HEA16Cl**	1,3-dimethylcyclohexane *cis* (97), *trans* (3)	5.3	57	6.1	49
m-xylene	**HEA16Br**	1,3-dimethylcyclohexane *cis* (87), *trans* (13)	7.3	41	8.5	35
m-xylene	**HEA16Cl**	1,3-dimethylcyclohexane *cis* (90), *trans* (10)	4.3	70	5.1	59
p-xylene	**HEA16Br**	1,4-dimethylcyclohexane *cis* (67), *trans* (33)	7.1	42	8.2	37
p-xylene	**HEA16Cl**	1,4-dimethylcyclohexane *cis* (70), *trans* (30)	4.0	75	4.6	65
o-methylanisole	**HEA16Br**	1-methoxy-2-methylcyclohexane *cis* (97), *trans* (3)	9.5	32	10.3	29
o-methylanisole	**HEA16Cl**	1-methoxy-2-methylcyclohexane *cis* (98), *trans* (2)	5.3	57	6.2	48
p-methylanisole	**HEA16Br**	1-methoxy-4-methylcyclohexane *cis* (92), *trans* (8)	9.2	33	10	30
p-methylanisole	**HEA16Cl**	1-methoxy-4-methylcyclohexane *cis* (94), *trans* (6)	4.8	63	5.2	58
m-cresol	**HEA16Br**	3-methylcyclohexanol *cis* (99), *trans* (1)	8.2	37	9.1	33
m-cresol	**HEA16Cl**	3-methylcyclohexanol *cis* (99), *trans* (1)	8.0	38	8.6	35

[a] Conditions: catalyst (3.8×10^{-5} mol), substrate (3.8×10^{-3} 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 mol of H_2 per mol of rhodium per h.

in contrast with those with electron-donating groups. In all cases we observed the reduction of the double bond prior to the hydrogenation of the aromatic ring.

The catalytic activity was most influenced by the choice of counter-ion (**X** = Br, Cl, CH_3SO_3, BF_4). In numerous cases, the reaction is twice as active when the Rh(0) nanoparticles are stabilised by **HEA16Cl** than the other standard surfactants **HEA16Br**, **Ms** or **BF$_4$.**

In a third series of studies, we examined the hydrogenation of disubstituted benzene derivatives such as xylene, methylanisole or cresol compounds. Based on our preliminary results, we essentially compared the two halogenated systems **HEA16Cl** and **HEA16Br.** In all cases, a complete conversion was obtained (Table 5). The *cis* diastereomers are largely the major products (up to 99%) as is usually observed in heterogeneous catalytic systems.[42,50,51]

The *cis*/*trans* ratio was not modified by the choice of the stabiliser, however the chloride anion gives better reaction times and turnover frequencies. The reaction time is affected by the nature and the position of the substituents. Thus, the reactivity decreases in the series *para* > *meta* > *ortho* positions. Complementary laboratory studies have shown that the increasing hydrogen pressure contributes to activating the catalytic process but increases also the *cis/trans* ratio.

The results described in Tables 2–5 demonstrate that the stabilised aqueous dispersions of rhodium particles can efficiently catalyse various monoalkyl-substituted, disubstituted, and functionalised benzene derivatives. We have studied the influence of the anion stabiliser (**X** = Br, Cl, CH_3SO_3, BF_4) on the catalytic activity characterised by the turnover frequency (TOF) defined as number of moles of consumed H_2 per mol of introduced rhodium per hour. Here, this parameter was sufficient to compare results but, as recently reported by Finke, the TOF should, ideally, be corrected for the true number of actives site. Except for some works,[53,54] determining the number of actives sites for a colloid is not frequent and in a first approximation can be estimated by the number of surface atoms on a particle. For example, a nanocluster with an average diameter of 2.1 nm is expected to have about 50% of the atoms on the surface. In this condition it is necessary to divide by 0.5 to give a corrected TOF.

Our work is essentially focused on the influence of the counter-anion in the catalytic reaction. We have shown that, in all cases, the chloride stabiliser gives the best result. The usual literature of colloid stabilisation described that nanoparticles can be in part stabilised by the adsorption of anions to the electron-deficient metal surface.[55–58] The zeta potential measurements of the catalytic system ($\zeta = +40$ to 100 mV, Table 1) only show that the sum of the partial positive charge and ammonium salt exceeds the amount of surface-bound anion present. The difference between catalytic activities cannot be correlated with the particle size because the various histograms of the size distribution show a similar average. However, we can suggest that the weakly basic, small and non-chelating Cl^- stabiliser binds less strongly to colloid surface, affording a higher TOF. Probably, stabilised nanoparticles present a more "naked surface" increasing the catalytic activities. In this context the research on clean-surface colloids should be a focused goal. To our knowledge, the first "anion series" approach for stabilising abilities recently described by Finke[59,60] for Ir(0) nanoclusters showed the basic polyoxoanions as the best stabiliser.

Conclusion

The results described herein confirm that Rh(0) nanoparticles are a very efficient catalyst for the reduction of arenes under mild conditions. The best activities are obtained with particles stabilised by the highly water-soluble *N*,*N*-dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium chloride salt. As previously reported,[45] the control of the surfactant concentration gives rise to high catalytic activities (up to 5-fold more active), therefore the combination of three parameters i) the use of the ammonium chloride salt, ii) a surfactant concentration around the critical micellar concentration and iii) the recycling of the aqueous phase containing the catalyst and its reuse for further runs, should give the best catalytic lifetime.

Experimental Section

Starting Materials

Rhodium chloride hydrate was obtained from Strem Chemicals. Sodium borohydride and fluoride, various functionalised cetylalkanes, *N,N*-dimethylethanolamine, and all aromatic substrates were purchased from Aldrich or Fluka and were used without further purification. Water was distilled twice by conventional methods before use.

Analytical Procedures

The surface tension measurements were performed at 20 °C using the ring method with a Du Nouy tensiometer (Krüss K10T).

Zeta potential measurements were performed on catalytic suspensions of rhodium(0) under catalytic conditions: catalyst (3.8×10^{-5} mol), surfactant (7.6×10^{-5}), water (10 mL), temperature (20 °C) with Zêtasizer 3000 Malvern.

The transmission electronic cryomicroscopic studies were conducted using a Philips CM 12 transmission electron microscope at 100 keV. Samples were prepared by a dropwise addition of the stabilised colloid in water onto a copper sample mesh covered with carbon. The colloidal dispersion was removed after 1 min using cellulose, the samples were then quickly frozen in liquid ethane before transfer to the microscope.

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

Synthesis of Surfactants HEA16X

The surfactants HEA16X were prepared as previously described in the literature or after adapted modification and were fully characterised.[52]

N,*N*-Dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium Bromide HEA16Br: yield: 92%; white powder; M_R: 394.47 g · mol^{-1}; $C_{20}H_{44}BrNO$; R_f (MeOH): = 0.15; mp 207–208 C; ^{1}H NMR: $\delta = 0.85$ (t, $J = 7$ Hz, 3H, H-16′), 1.23 (m, 24H, H-15′–H-4′), 1.32 (m, 2H, H-3′), 1.73 (m, 2H, H-2′), 3.36 (s, 6H, H-3), 3.56 (m, 2H, H-1′), 3.74 (m, 2H, H-2); 4.10 (m, 2H, H-1); 5.0 (t, $J = 5.3$ Hz, 1H, O$\underline{H}$); ^{13}C NMR: $\delta = 14.1$ (C-16′), 22.6–31.9

(C-15–C-2′), 52.1 (C-3), 55.8 (C-1), 65.6 (C-2), 66.0 (C-1′); IR (KBr): ν = 3245 cm^{-1} (C-OH); Anal. calcd.: C 60.89, H 11.24%; found: C 60.56, H 11.34%.

N,*N*-Dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium Chloride HEA16Cl: yield: 92%; white powder; M$_R$: 350.02 g · mol^{-1}; $C_{20}H_{44}ClNO$; R$_f$ (MeOH): 0.13; mp 203–205 °C; ^{1}H NMR: δ = 0.84 (t, *J* = 7.1 Hz, 3H, H-16′), 1.17 (m, 24H, H-15′–H-4′), 1.30 (m, 2H, H-3′), 1.71 (m, 2H, H-2′), 3.34 (s, 6H, H-3), 3.51 (m, 2H, H-1′), 3.68 (m, 2H, H-2), 4.06 (m, 2H, H-1), 5.8 (m, 1H, OH); ^{13}C NMR: δ = 14.2 (C-16′), 22.7–31.9 (C-15′–C-2′), 52.0 (C-3), 55.9 (C-1), 65.7 (C-2), 66.0 (C-1′); IR (KBr): ν = 3291 cm^{-1} (C-OH); Anal. calcd.: C 68.63, H 12.67%; found: C 68.59, H 12.69%.

N,*N*-Dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium Mesylate HEA16Ms: yield: 84%; white powder; M$_R$: 409,66 g · mol^{-1}; $C_{21}H_{47}NO_4S$; R$_f$ (MeOH): 0.11; mp 68–72 °C; ^{1}H NMR: δ = 0.84 (t, *J* = 7 Hz, 3H, H-16′), 1.21 (m, 24H, H-15′–H-4′), 1.30 (m, 2H, H-3′), 1.69 (m, 2H, H-2′), 2.68 (s, 3H, H-4), 3.21 (s, 6H, H-3), 3.38 (m, 2H, H-1′), 3.59 (m, 2H, H-2), 4.03 (m, 2H, H-1), 4.27 (m, 1H, OH); ^{13}C NMR: δ = 14.1 (C-16′), 22.7–31.9 (C-15′–C-2′), 39.6 (C-4), 51.6 (C-3), 56.1 (C-1), 65.6 (C-2), 65.7 (C-1′); IR (KBr): ν = 3358 (C-OH), 1190 cm^{-1} (CH_3-S); anal. calcd.: C 61.57, H 11.56%; found: C 61.74, H 11.78%.

N,*N*-Dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium Iodide HEA16I: yield: 84%; white powder; M$_R$: 441.47 g · mol^{-1}; $C_{20}H_{44}INO$; R$_f$ (MeOH): 0.13; mp 176–178 °C; ^{1}H NMR: δ = 0.85 (t, *J* = 7.1 Hz, 3H, H-16′), 1.23 (m, 24H, H-15′–H-4′), 1.34 (m, 2H, H-3′), 1.75 (m, 2H, H-2′), 3.36 (s, 6H, H-3), 3.55 (m, 2H, H-1′), 3.76 (m, 2H, H-2), 4.14 (m, 3H, H$_1$-OH); ^{13}C NMR: δ = 14.2 (C-16′), 22.7–31.9 (C-15′ - C-2′), 52.5 (C-3), 55.8 (C-1), 65.6 (C-2), 66.4 (C-1′); IR (KBr): ν = 3276 cm^{-1} (C-OH); Anal. calcd.: C 54.41, H 10.04%; found: C 54.27, H 10.23%.

N,*N*-Dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium Tetrafluoroborate HEA16BF4: yield: 83%; white powder; M$_R$: 401.37 g · mol^{-1}; $C_{20}H_{44}BF_4NO$; R$_f$ (MeOH): 0.12; mp = 113–115 °C; ^{1}H NMR: d = 0.87 (t, *J* = 7 Hz, 3H, H-16′), 1.24 (m, 24H, H-15′–H-4′), 1,32 (m, 2H, H-3′), 1.71 (m, 2H, H-2′), 3.13 (s, 6H, H-3), 3.32 (m, 2H, H-1′), 3.47 (m, 2H, H-2), 3.58 (m, 1H, OH), 4.04 (m, 2H, H-1); ^{13}C NMR: δ = 14.2 (C-16′), 22.8–32.0 (C-15′–C-2′), 51.4 (C-3), 56.3 (C-1), 65.5 (C-2), 66.1 (C-1); ^{19}F NMR: d = – 150.60, (s, 1F, BF_4), – 150.65 (3s, 3F, BF_4); IR (KBr): ν = 3327 (C-OH); 1074 cm^{-1} (BF_4); Anal. calcd.: C 59.84, H 11.05%; found: C59.57, H 10.92%.

Synthesis of the Aqueous Rh(0) Colloidal Suspensions

The suspensions were prepared under nitrogen at 20 °C. To an aqueous solution of the appropriate surfactant (95 mL, 7.6 × 10^{-3} mol · L^{-1}) was added sodium borohydride (36 mg, 9.5 × 10^{-4} mol). Then this solution was quickly added under vigorous stirring to an aqueous solution (5 mL) of the precursor $RhCl_3 \cdot 3\,H_2O$ (100 mg, 3.8 × 10^{-4} mol) to obtain an aqueous Rh(0) colloidal suspension (100 mL). The reduction occurs instantaneously and is characterised by a colour 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).

General Procedure for Hydrogenation

Classical hydrogenation reactions were carried out under standard conditions (20 °C, 1 atm of H_2). A 25 mL round-bottomed flask, charged with the chosen aqueous suspension of Rh(0) (10 mL) 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 meticulous and slow 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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