Polyhydroxylated ammonium chloride salt: a new efficient surfactant for nanoparticles stabilisation in aqueous media. Characterization and application in catalysis

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A trihydroxyammonium chloride has proved to be an efficient protective agent for Rh(0) nanoparticles and the hydrogenation of arene compounds has been investigated. Significant formation of cyclohexanone in the reduction of anisole has been demonstrated.

In the drive towards sustainable and environmentally friendly chemistry, aqueous biphasic catalysis has received an increasing interest.1 Such catalytic systems, based on two immiscible phases (water/hydrocarbon), provide an easy method for the separation and recycling of the catalyst by simple decantation and could be compared to heterogeneization of catalysts on supports in terms of recycling.² A prerequisite for aqueous biphasic catalysis is the solubility of the catalyst within water. The most classical approach is the design of water-soluble homogeneous catalysts coordinated to phosphines containing hydrophilic moieties.³ Our original method relies on the use of metallic nanoparticles finely dispersed in water, which offers an easy method to remove the catalyst from the reaction product.⁴ During the last decade, soluble nanoparticles have proved to be highly active nanocatalysts in hydrogenation,⁵ hydrosilylation⁶ or carbon-carbon coupling⁷ reactions. Considerable efforts have been devoted to their synthesis in order to prevent their aggregation and to control the particle size.8 For that purpose, various stabilizers have been developed according to the nature of the reaction media, which generally depends on the metallic precursors. Our general approach relies on the stabilization of metallic nanoparticles by highly watersoluble protective agents, such as ionic surfactants. Previously, we have described the easy synthesis of N,N-dimethyl-N-cetyl-N-(2-hydroxethyl) ammonium (HEAX) salts, which have proved to be efficient stabilizing agents of Rh, Ir, Ru colloids for arene hydrogenations under mild conditions,9 of Pt nanoparticles for asymmetric hydrogenation of ethylpyruvate¹⁰ and also of Pd nano species for dehalogenation reactions¹¹ and carbon-carbon couplings.¹² Herein, we report the synthesis of a new ammonium surfactant, namely N-hexadecyl-N-tris-(2-hydroxyethyl) ammonium chloride (THEA16Cl), as a protective agent for Rh(0) nanoparticles and their use in arene hydrogenation.†

THEA16Cl has been easily synthesized by quaternarization of hexadecylamine with chloroethanol in an aqueous solution of NaOH at reflux from a procedure adapted from the literature (Scheme 1).¹³ The reaction proceeds with a non-optimized 44% yield and the obtained ionic surfactant is highly soluble in water.



Scheme 1 Synthesis of THEA16Cl.

Catalytic aqueous suspensions of Rh(0) nanoparticles have been easily prepared by chemical reduction of rhodium trichloride with sodium borohydride in dilute aqueous solution of THEA16Cl. First, the molecular ratio R = THEA16Cl/Rh has been optimized to avoid aggregation and to provide an efficient stabilization. As previously described for HEAX-Rh nanoparticles, a molar ratio of 2 was used to maintain stable THEA16Cl-Rh nanoparticles.

Transmission electron microscopic (TEM) observations show that the particles are well-dispersed on the grid and near monodispersed with an average diameter of 3 nm, as shown on the size histogram resulting from the measurement of about 250 particles found in an arbitrarily chosen area (Fig. 1). 87 percent of nanoobjects are included between 2.5 and 3.5 nm. These Rh(0) aqueous suspensions are highly stable and can be stored without special precautions.

Surface tension measurements have been performed on THEA16Cl and also on the THEA16Cl-stabilized Rh(0) nanoparticles in the same conditions as in catalytic reactions (Fig. 2). Firstly, the studies on THEA16Cl demonstrated that this ammonium surfactant self-aggregates into micelles above the critical micellar concentration (CMC) of 7×10^{-4} mol L⁻¹. The interfacial tension of aqueous solutions decreases from 55 to 35 mN m⁻¹. This new protective agent exhibits a classical behaviour similar to HEAX. Secondly, measurements of THEA16Cl in the presence of nanoparticles, which give the surface tension of the free surfactant, have proved that the surfactant does not possess a critical micellar concentration. We could assume that THEA16Cl is all around the particles, forming a double layer at the surface, as previously characterized by Chen¹⁴ and El Sayed¹⁵ with ammonium salts stabilized Cu and Ni NPs or Au nanorods.

Hydrogenation of benzene derivatives using THEA16Clstabilized Rh(0) nanoparticles has been performed under biphasic conditions at atmospheric hydrogen pressure and room temperature. The reaction was monitored by gas chromatographic analysis and the turnover frequency (TOF) was defined as the number of moles of consumed H₂ per mole of rhodium per hour. The results are summarized in Table 1.

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 Table 1
 Hydrogenation of benzene derivatives with THEA16Cl-stabilized Rh(0) nanoparticles^a

Entry	Substrate	Product (%) ^b	TOF $(h^{-1})^c$
1	Benzene	Cyclohexane (100)	300
2	Toluene	Methylcyclohexane (100)	100
3	Anisole	Methoxycyclohexane/cyclohexanone (78/22)	120
4	Ethylbenzoate	Ethylcyclohexanoate (100)	86
5	o-Xylene	1,2-Dimethylcyclohexane ($cis/trans = 92/8$)	81
6	<i>m</i> -Xylene	1,3-Dimethylcyclohexane ($cis/trans = 80/20$)	81
7	<i>p</i> -Xylene	1,4-Dimethylcyclohexane ($cis/trans = 66/34$)	83

^{*a*} Reaction conditions: Rh (3.8×10^{-5} mol), THEA16Cl (7.6×10^{-5} mol), substrate (3.8×10^{-3} mol), H₂O (10 mL), 1 bar H₂, RT. ^{*b*} Determined by GC analysis. ^{*c*} Turnover frequency defined as mol of H₂ per mol of Rh per h.



Size distribution



Fig. 1 Transmission electron micrograph and size distribution of Rh/THEA16Cl suspension.

Benzene (entry 1) and monofunctionalized arene derivatives (entries 2–4) have been totally hydrogenated with quite interesting TOFs, ranging from 300 h^{-1} to 86 h^{-1} . A reaction was carried out without metal and no hydrogenation product was detected. The reduction of the metal in the absence of a surfactant shows the formation of aggregates, proving the decrease in catalytic



Fig. 2 Tensiometry of THEA16Cl and THEA16Cl-stabilized Rh(0) nanoparticles.

activity. Indeed, only 12% of the toluene was reduced in 3 h. Steric and electronic effects have been observed as arenes substituted with electron-withdrawing groups (entry 4) react slower than compounds possessing electron-donating group (Entry 3). A complete hydrogenation is also achieved with disubstituted benzene derivatives (entries 5-7), leading to the formation of the thermodynamically less favourable *cis* compounds, as usually observed in heterogeneous systems.¹⁶ Finally we have observed the formation of methoxycyclohexane and of about 22% of cyclohexanone in the reduction of anisole (entry 3). This formation, not previously described in the literature to our knowledge, has been explained by further NMR experiments to elucidate the mechanism. THEA16Cl-stabilized Rh(0) nanoparticles were prepared in D₂O. A 25 mL round bottom flask was charged with this colloidal solution, and then anisole was added dropwise. Anisole was hydrogenated at atmospheric pressure and room temperature. After hydrogenation, nanoparticles were adsorbed on silica and the filtered aqueous phase was analyzed by ¹H NMR. The formation of MeOH was proved by a peak found at 3.2 ppm, which was confirmed by the addition of $2 \mu L$ of methanol in the NMR tube. On the basis of these results, we have proposed the following mechanism (Scheme 2). Cyclohexanone was formed in acid conditions from the partially hydrogenated product, which leads in water to the formation of hemiacetal. This last compound decomposes in cyclohexanone and methanol.



Scheme 2 Proposed mechanism of cyclohexanone formation during the hydrogenation of anisole.

In conclusion, THEA16Cl, a trihydroxyalkylammonium salt possessing an alkyl chain of 16 carbons, provides an efficient electrosteric stabilization for Rh(0) nanoparticles in aqueous media. The aqueous catalytic systems have proved to be active in the hydrogenation of various arene derivatives with interesting TOFs. Relevant result has been explained as the cyclohexanone formation starting methoxybenzene.

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Notes and references

† NMR: 1H NMR and 13C NMR spectra were recorded on a BRUCKER Avance III 400 spectrometer at 400.13 MHz for ¹H and 100.61 MHz for ¹³C. Chemical shifts are given in δ -units (ppm) measured downfield from tetramethylsilane (TMS) as external reference. Chromatography: all gas chromatographic analyses were performed using a Carlo Erba GC 6000 with a FID detector equipped with an Alltech AT1 column (30 m, 0.25 mm i.d.). Helium was used as a carrier gas and the inlet pressure depend on the nature of the substrate. The injections were done at 220 °C and the temperature detector was fixed at 250 °C. TEM: TEM study was conducted using a Philips CM 12 Transmission Electron microscope at 100kV (UMR CNRS 6026-Université de Rennes I). The sample was prepared by a dropwise addition of the stabilized rhodium colloids in water onto a copper sample mesh covered with carbon. The colloidal dispersion was partially removed after 1 min using cellulose before transferring to the microscope. The picture was obtained at X 100000. Measurement of about 250 particles was made with a program SCION Image (NIH) and was analysed with Excel® program providing histogram of the nanoparticles size distribution. Tensiometry: surface tension of aqueous colloidal solutions was measured with a drop tensiometer. A syringe with a U-shaped needle was lowered into a sample cell containing an aqueous solution of rhodium nanoparticles protected by the surfactant. An air bubble was produced from the syringe. The dynamic surface tension was measured by filming the rising bubble and analysing the contour of the bubble with a Tracker instrument from IT Concept. The surface tension was thus determined at room temperature for several concentrations of surfactants. N-Hexadecyl-N-tris-(2-hydroxyethyl) ammonium chloride THEA16Cl. In a two necked flask, hexadecylamine (16.7 g, 62 mmol) and chloroethanol (19.5 g, 230 mmol) were heated to reflux. Then, NaOH (8.16 g, 204 mmol) in distilled water (75 mL) was added dropwise via an additional funnel. After 24 h at reflux, the reaction mixture was cooled down and extracted with chloroform $(3 \times 50 \text{ mL})$. The organic phase was dried on MgSO4 and chloroform was removed. The residue was recrystallized from EtOH-EtOAc to give the final product as a white powder with a moderate yield (44%). M.p. 94-96 °C. 1H NMR (400 MHz, DMSO-d₆, 25 °C, TMS) δ /ppm: 0.84 (t, J = 7 Hz, 3 H, H₁₆), 1.17–1.32 (m, 26 H, H_{3'-15'}), 1.66–1.68 (m, 2 H, H_{2'}), 3.38–3.40 (m, 2 H, H_{1'}), 3.48–3.50 $(m, 6 H, H_2), 3.73-3.79 (m, 6 H, H_1), 5.44 (t, J = 6 Hz, 3 H, OH).$ ¹³C NMR (100 MHz, DMSO-d₆, 25 °C, TMS) δ/ppm: 13.91 (C_{16'}), 21.32–31.25 (C_{2'}- $C_{15'}$), 54.51 (C_1), 60.13 (C_2), 60.61 ($C_{1'}$). IR (KBr) v/cm⁻¹: 3300 (C–OH). HRMS: C₂₂H₄₈NO₃ m/z calcd: 374.36342, m/z found: 374.3625 (2 ppm). Synthesis of THEA16Cl-stabilized Rh(0) nanoparticles. The suspensions were prepared under nitrogen at 20 °C. To an aqueous solution of the surfactant THEA16Cl (312 mg, 7.6 × 10⁻² mol, 2 equiv., in 90 mL H₂O) was added in a flask containing 36 mg of sodium borohydride (9.5×10^{-2} mol, 2.5 equiv.). Then this solution was quickly added under vigorous stirring to an aqueous solution (10 mL) of the precursor RhCl₃·6H₂O (100 mg, $3.8 \times$ 10⁻² mol) to obtained an aqueous Rh(0) colloidal suspension (100 mL). The reduction occurs instantaneously and is characterized by a change colour from red to black. The solutions are stable under stirring for several months. General procedure for hydrogenation under atmospheric hydrogen **pressure.** A 25 mL round bottom flask, charged with 10 mL of aqueous colloidal Rh(0) suspension and aromatic substrate ([substrate]/[metal] = 100), is connected to a gas burette (500 mL) and a flask to balance pressure. Then, the system is filled with hydrogen and the mixture is magnetically stirred at 1500 mn⁻¹. The reaction is monitored by gas chromatography analyses. Turnover frequency (TOF) is determined for 100% conversion.

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