

Nanoheterogeneous Catalytic Hydrogenation of Arenes: Evaluation of the Surfactant-Stabilized Aqueous Ruthenium(0) Colloidal Suspension

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Abstract: The hydrogenation of various aromatic compounds by a surfactant-stabilized aqueous ruthenium(0) colloidal suspension was investigated. The nanocatalysts in the size range of 2.5–3.5 nm were synthesized by reducing ruthenium trichloride salt with sodium borohydride and were stabilized by the highly water soluble *N,N*-dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium chloride salt according to our classical approach. The efficient catalytic reactions

were performed at room temperature and under hydrogen pressure. The effect of the stirring, namely magnetic stir bar or gas projection impeller, was also studied. A comparison with an analogous rhodium nanocatalyst is described.

Keywords: arenes; colloids; gas effect; hydrogenation; impeller speed rotation; ruthenium

Introduction

The complete or partial hydrogenation of benzene and its derivatives represents an important research area for the synthesis of cyclohexane/cyclohexene derivatives including intermediates for chemicals and pharmaceuticals.^[1] Partial hydrogenation is not only of academic interest but also the process developed by Asahi Chemical Industry in Japan is an industrial example of the selective formation of cyclohexene.^[2] Total hydrogenation has also industrial applications such as the conversion of benzene to cyclohexane, a key intermediate in adipic acid production,^[3] the removal of aromatic compounds from fuels^[4] which are responsible for health diseases.^[5]

Among the controversial active catalytic species,^[6–8] soluble noble metal nanoparticles are considered as a reference catalyst in monocyclic arene hydrogenation under mild conditions and several stabilized systems have been largely reported.^[1,9]

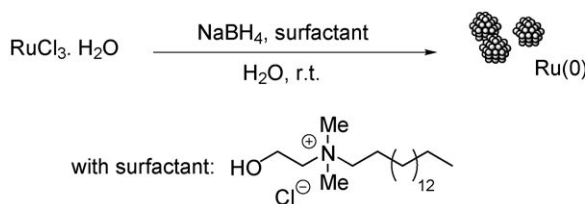
The protective agent is chosen according to the “organic” or “aqueous” nature of the media which generally depends on the nature of the precursor, namely organometallic compounds or metals salts. Our approach is to use ionic surfactants to prepare and stabilize aqueous colloidal suspensions of metallic particles. Previously, we have described the easy synthesis of *N,N*-dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium salts HEA16X with X = Br, Cl, I, CH₃SO₃, BF₄.^[10]

Among these compounds, the chloride salt HEA16Cl has largely been studied as a protective agent for rhodium and iridium particles for the hydrogenation of benzene derivatives.^[11,12] To complete our investigation on the noble metal efficiency in aromatic ring hydrogenation, we report the original synthesis of ruthenium nanocatalysts in aqueous suspension and their size distribution. We describe the complete hydrogenation of various benzene compounds in biphasic liquid-liquid (water/hydrocarbon) systems at room temperature and under 30 bar of hydrogen pressure. The ruthenium surfactant stabilization and the catalytic lifetime have been evaluated through an aqueous recycling process in three successive hydrogenation runs of several substrates at room temperature. In this paper, we also report the influence of the stirring and show the efficiency of a gas projection impeller. Finally, we compare our ruthenium system with previously described rhodium aqueous suspensions in the anisole hydrogenation.

Results and Discussion

Preparation and Characterization of Ru(0) Colloids

The catalytically active aqueous suspension consists of metallic ruthenium(0) particles prepared in the open air and room temperature by chemically reducing



Scheme 1. Surfactant-stabilized ruthenium nanoparticles synthesis.

ruthenium trichloride salt with sodium borohydride in dilute aqueous solution of our usual surfactant *N,N*-dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium chloride salt, HEA16Cl (Scheme 1).

First, the molecular ratio $R = \text{HEA16Cl}/\text{Ru}$ has been optimized to avoid aggregation and to provide a good stability after catalysis in order to investigate the potential recycling of the aqueous phase. The stability of the suspension before catalysis was visually observed after 24 h. As previously described for rhodium nanoparticles synthesis, a molar ratio of 2 was sufficient to maintain stable Ru colloids.

Transmission electron microscopy (TEM) observations show that the particles are well-dispersed on the grid and monodispersed in size with an average diameter of 3 nm with 70% of nanoparticles between 2.50 nm and 3.50 nm, as shown on the size histogram which results from the measurement of about 200 particles found in an arbitrarily chosen area. Figure 1 shows the obtained particle size distribution, which can be well fitted by a Gaussian curve. These Ru(0) aqueous suspensions are highly stable and can be stored without special precautions.

Catalytic Performances

The so-obtained system Ru(0)/HEA16Cl/water is active for the hydrogenation of various aromatic compounds. Preliminary experiments have shown that the

conversion of toluene at atmospheric pressure was very slow. Consequently, all reactions were carried out at room temperature (20 °C) and under 30 bar of hydrogen pressure. The conversion was determined by gas chromatographic analysis after an arbitrarily chosen time. The turnover frequency (TOF) was established according to the amount of introduced ruthenium, taking into account the true number of active metal sites. Thus, we could presume that TOF may be underestimated.^[13,14] Firstly, we have hydrogenated benzene and some monoalkylated derivatives under biphasic conditions (Table 1). In all cases, the conversion was complete after two hours. No aggregates were visually observed at the end of the catalytic reactions. We have also compared the effect of the stirring device, namely a magnetic stir bar (1500 min⁻¹) or a gas projection impeller (GPI 1000 min⁻¹). The kinetics of the reaction were significantly increased using the impeller system. In fact, turnover frequencies of 600 h⁻¹ were obtained for benzene and toluene hydrogenation and were 4 times higher than those obtained with a magnetic stirring. This phenomenon could be explained by a more efficient gas diffusion in the aqueous phase.

In a second series of studies, we have investigated the hydrogenation of functionalized arenes (Table 2). The nature of the arene substituents has a strong effect on the reaction time. In addition to the hydrogenation of the aromatic ring, the *exo* C=C or C=O double bonds of styrene or acetophenone, respectively, were also reduced. A rapid hydrogenation has also been observed with anisole (TOF = 300 h⁻¹). In this study, the significant influence of the stirring device (stir bar or GPI) has also been demonstrated. The hydrogenation of *o*-xylene leads to a complete conversion with a major formation of the *cis*-diastereoisomers (95%). A slow destabilisation with black ruthenium formation was obtained during the hydrogenation of aniline. Finally, the hydrogenation of chlorobenzene and bromobenzene shows the formation of a small amount of benzene and cyclohexane suggesting

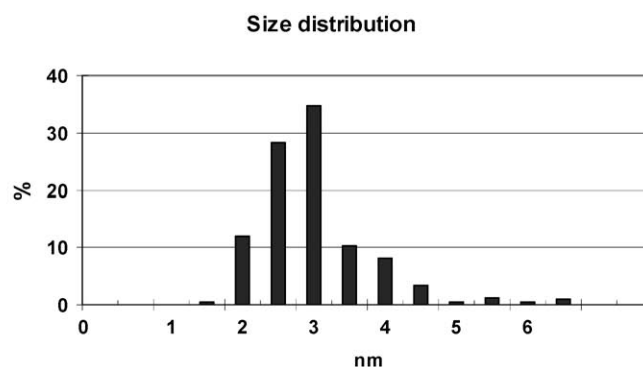
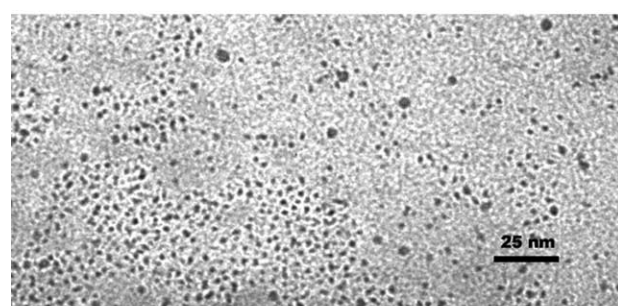


Figure 1. Transmission electron micrograph [scale bar = 25 nm] and size distribution histogram of Ru/HEA16Cl suspension before catalysis.

Table 1. Hydrogenation of benzene and monoalkylated substituted derivatives with ruthenium aqueous suspension. Effect of stirring device on activity.^[a]

Substrate	Stirring	Product (conv. %) ^[b]	Reaction time ^[c] [h]	TOF [h ⁻¹] ^[d]
Benzene	Stir bar	Cyclohexane (100)	2	150
Benzene	GPI ^[e]	Cyclohexane (100)	0.5	600
Toluene	Stir bar	Methylcyclohexane (100)	2	150
Toluene	GPI ^[e]	Methylcyclohexane (100)	0.5	600
Ethylbenzene	Stir bar	Ethylcyclohexane (100)	2	150
Ethylbenzene	GPI ^[e]	Ethylcyclohexane (96)	1	288
Isopropylbenzene	Stir bar	Isopropylcyclohexane (100)	2	150
Isopropylbenzene	GPI ^[e]	Isopropylcyclohexane (94)	1	282
<i>tert</i> -Butylbenzene	Stir bar	<i>tert</i> -Butylcyclohexane (100)	2	150
<i>tert</i> -Butylbenzene	GPI ^[e]	<i>tert</i> -Butylcyclohexane (100)	1.5	200

^[a] Conditions: ruthenium (3.8×10^{-5} mol), substrate (3.8×10^{-3} mol), HEA16Cl (7.6×10^{-5} mol), substrate/Ru = 100 (molar ratio), water (10 mL), 30 bar H₂, temperature (293 K), R = [HEA16Cl]/[Ru] = 2.

^[b] Determined by GC analysis.

^[c] The reaction was stopped after an estimated time for total hydrogenation and conversion was checked by GC

^[d] Turnover frequency defined as number of mol of consumed H₂ per mol of introduced ruthenium per hour.

^[e] Gas projection impeller at 1000 min⁻¹

Table 2. Hydrogenation of functionalized arene derivatives with ruthenium aqueous suspension.^[a]

Substrate	Stirring	Product (conv. %) ^[b]	Time ^[c] [h]	TOF [h ⁻¹] ^[d]
Styrene	GPI ^[e]	Ethylcyclohexane (100)	1.5	266
Anisole	GPI ^[e]	Methoxycyclohexane (100)	1	300
Anisole	Stir bar	Methoxycyclohexane (93)	1.25	223
Ethyl benzoate	GPI ^[e]	Ethyl cyclohexanoate (66)	2	99
Bromobenzene	GPI ^[e]	Benzene(4)/Cyclohexane (3)	16	nd ^f
Chlorobenzene	GPI ^[e]	Benzene(3)/Cyclohexane (8)	7	nd ^f
Aniline	GPI ^[e]	-	-	- ^g
<i>o</i> -Xylene	GPI ^[e]	1,4-Dimethylcyclohexane (Z/E:95/5)	1.5	200
<i>o</i> -Methylanisole	GPI ^[e]	2-Methylmethoxycyclohexane (Z/E:73/0)	19	12
Acetophenone	GPI ^[e]	Cyclohexylethan-1-ol (100)	3.5	115

^[a] Conditions: ruthenium (3.8×10^{-5} mol), substrate (3.8×10^{-3} mol), HEA16Cl (7.6×10^{-5} mol), substrate/Ru = 100 (molar ratio), water (10 mL), 30 bar H₂, temperature (293 K), R = [HEA16Cl]/[Ru] = 2.

^[b] Determined by GC analysis.

^[c] The reaction was stopped after an estimated time for total hydrogenation and conversion was verified by GC

^[d] Turnover frequency defined as number of mol of consumed H₂ per mol of introduced ruthenium per hour.

^[e] Gas projection impeller at 1000 min⁻¹

^[f] Not determined

^[g] The aqueous suspension was destabilized.

the hydrogenolysis of the C–Cl and C–Br bond, respectively. In a recent investigation of the C–Cl cleavage of chloroarenes with Pd and Rh nanoparticles,^[15] we have reported the efficient hydrogenolysis with palladium species and the consecutive dehalogenation/aromatic hydrogenation with rhodium systems under 10 bar H₂. We can conclude that ruthenium nanoparticles under 30 bar H₂ were less efficient than previous colloidal systems due to a poisoning phenomenon with substrate or induced chloride or bromide species.

To complete these results, the durability of the catalytic system has been checked. Similar to previously

reported studies with rhodium and iridium nanoparticles, we have investigated the recycling process in three successive hydrogenation runs by reusing the aqueous phase containing ruthenium nanoparticles after simple decantation in a separating funnel. Four representative substrates such as ethylbenzene, anisole, acetophenone and *o*-xylene were chosen as typical monoalkylated, monofunctionalized, partly hydrophilic and disubstituted benzene derivatives, respectively. Under 30 bar of hydrogen and reaction times based on the first run, we have observed total conversion indicating analogous turnover activity for all runs. Consequently, we demonstrate the efficient sta-

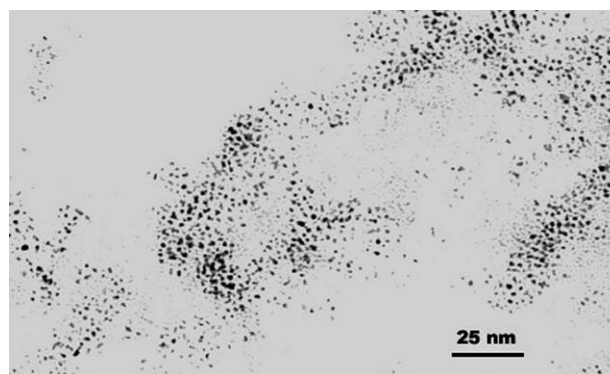
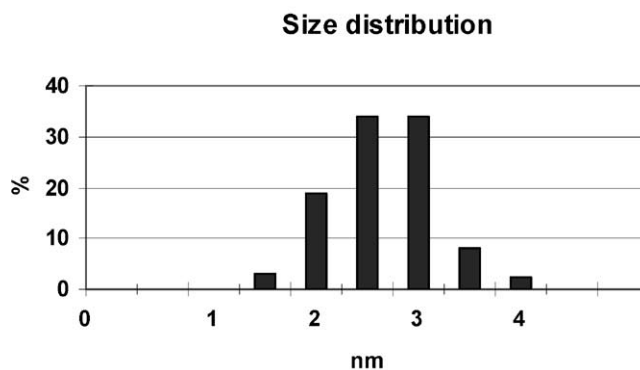


Figure 2. Transmission electron micrograph [scale bar = 25 nm] and size distribution histogram of Ru/HEA16Cl suspension after catalysis.



bility of the catalytically active ruthenium suspension for both hydrophobic and hydrophilic compounds as previously observed with rhodium and iridium nanoparticles. Moreover, transmission electron microscopy (TEM) observations show that, after a first run, the particles are always well-dispersed with an average diameter of 3 nm with 70 % of nanoparticles between 2.50 nm and 3.50 nm, as shown on the size histogram (Figure 2).

We have also studied the effect of the stirring, in particular the kinetic effect of the impeller speed rotation on the anisole hydrogenation activity. These experiments are summarized in the Figure 3. In the same catalytic conditions (hydrogen pressure, temperature, catalyst and substrate molar ratios), the activity significantly increases with the speed rotation (800 min^{-1} , 1000 min^{-1} and 1300 min^{-1}). We could presume that the solubility of the hydrogen efficiently increases in the aqueous media compared to the classical magnetic stirring. Moreover, the hydrogen is directly brought close to the ruthenium nanocatalysts in water in comparison to the slow diffusion due to the diffusion cone.

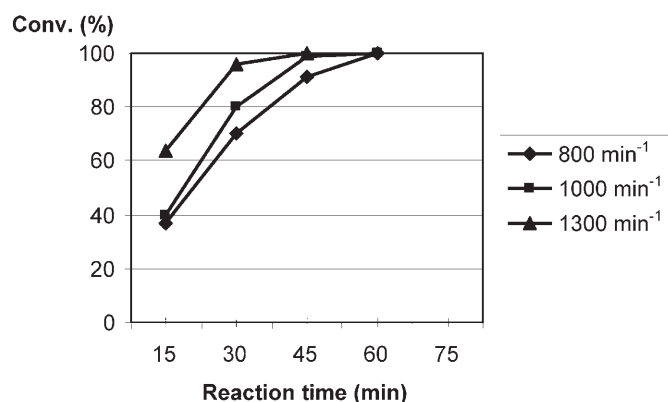


Figure 3. Kinetic effect of the impeller speed rotation on the anisole hydrogenation activity.

Finally, the preparation and the stabilization of ruthenium and rhodium nanoparticles are similar with a molar ratio surfactant/metal of 2 to prevent aggregation. Generally, various alkylated, functionalized and/or disubstituted benzene derivatives were completely hydrogenated in a few hours at room temperature. Nevertheless, the catalytic efficiencies of these two metallic species are really different: significant TOFs have only been observed under hydrogen pressures with ruthenium species, whereas arene hydrogenations could be performed at 1 bar of H_2 with rhodium nanocatalysts. In similar catalytic conditions (room temperature, 30 bar H_2 , magnetic stirring), the hydrogenation of anisole was complete after 15 min ($\text{TOF} = 1200\text{ h}^{-1}$) with rhodium nanoparticles as previously described^[10] and 1.25 h ($\text{TOF} = 223\text{ h}^{-1}$) with ruthenium nanocatalysts. Here, we demonstrate the efficient activity of rhodium species and justify the rhodium choice for benzene derivatives hydrogenations.

Conclusions

Based on the classical approach developed in our laboratory, the present work reports catalytic activities of an aqueous suspension of ruthenium(0) nanoparticles in the hydrogenation of various benzene derivatives. The chloride salt HEA16Cl has been used to efficiently stabilize ruthenium colloids. These colloidal suspensions display an efficient activity under mild hydrogen pressure (30 bar) and at room temperature. We have demonstrated the significant influence of the stirring, namely the use of a magnetic stir bar or a gas projection impeller. In all cases, the use of a gas effect system substantially increases the catalytic activity. Finally, we have compared rhodium and ruthenium as metal species in the anisole hydrogenation as a typical substrate. We report that the rhodium species are more efficient to reduce aromatic rings.

Experimental Section

Materials

Ruthenium chloride hydrate was obtained from Strem Chemicals. Sodium borohydride and all arenes were purchased from Aldrich or Acros and used without further purification. Water was distilled twice before use by conventional method. The surfactant HEA16Cl was prepared as previously reported and was fully characterized.^[10]

Analytical Procedures

TEM analysis: The transmission electronic microscopic studies were conducted using a Philips CM 12 transmission electron microscope at 100 keV (UMR CNRS 6026 – University of Rennes I). Samples were prepared by a dropwise addition of the stabilized ruthenium 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 is obtained at $\times 80,000$. Measurement of about 200 particles was made with the program SCION Image (NIH) and was analyzed with the Excel program providing the histograms of the nanoparticles size distribution

Gas chromatography: All analyses were performed using a Carlo Erba GC 6000 with an FID detector equipped with a Factor Four column (30 m, 0.25 mm i.d.). Parameters were as follows: initial temperature, 40 °C; initial time, 10 min; ramp, 10 °C min⁻¹; final temperature, 80 °C; final time, 30 min; injector temperature, 220 °C; detector temperature, 250 °C.

Catalytic Tests

Synthesis of the aqueous ruthenium(0) suspension: The aqueous suspensions of ruthenium nanoparticles were prepared according to our previously described rhodium suspension synthesis.^[11]

An aqueous solution of surfactant HEA16Cl (544 mg, 1.7×10^{-3} mol L⁻¹ in 40 mL H₂O) was added in a flask containing 16 mg of sodium borohydride (4.2×10^{-4} mol). Then this solution was quickly added under vigorous stirring to an aqueous solution (10 mL) of RuCl₃·1.8H₂O (50 mg, 1.7×10^{-4} mol) to obtain an aqueous Ru(0) colloidal suspension (50 mL). The reduction occurs instantaneously and is characterized by a color change from yellow-brown to black. The obtained suspensions are stable for several weeks.

General Procedure for Hydrogenation under Hydrogen Pressure

The stainless steel autoclave was charged with the previously prepared aqueous suspension of Ru(0) (10 mL) and a magnetic stirrer. The appropriate substrate (3.8×10^{-3} mol, 100 equivs.) was added into the autoclave and dihydrogen was admitted to the system at constant pressure (up to 30 bar). The mixture was stirred with a magnetic stir bar or with a magnetic stirrer of powerful torque up to 95 Ncm equipped with a gas projection impeller (Top-Industries SA). Samples for gas chromatographic analysis were removed from time to time. The TOF was determined for 100 % conversion.

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