

# A simple and reproducible method for the synthesis of silica-supported rhodium nanoparticles and their investigation in the hydrogenation of aromatic compounds

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Colloidal suspensions of rhodium nanoparticles have been easily prepared in aqueous solution by chemical reduction of the precursor  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  in the presence of the surfactant *N,N*-dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl)ammonium chloride (HEA16Cl) and further used to immobilize rhodium nanoparticles on silica by simple impregnation. The obtained silica-supported rhodium nanoparticles have been investigated by adapted characterization methods such as transmission electron microscopy and X-ray photoelectron spectroscopy. A particle size increase from 2.4 to 5 nm after the silica immobilization step and total elimination of the surfactant has been observed. This “heterogeneous” catalyst displayed good activities for the hydrogenation of mono-, di-alkylsubstituted and/or functionalized aromatic derivatives in water under atmospheric hydrogen pressure and at room temperature. In all cases, the catalyst could be recovered several times after a simple decantation or filtration and reused without any significant loss in catalytic activity. This supported catalyst has also been tested under higher hydrogen pressure giving rise to TOFs reaching  $6430 \text{ h}^{-1}$  at 30 bar and in terms of catalytic lifetime 30 000 TTO in 8.5 h for pure anisole hydrogenation at 40 bar.

## Introduction

Among active areas of academic and industrial research, total and partial hydrogenation of benzene derivatives still attracts increasing interest, more particularly, with the industrial demand for cyclohexane,<sup>1</sup> the most important precursor to adipic acid used to produce nylon-6,6, and cyclohexene, an important intermediate in organic synthesis produced by the Asahi Chemical Industry process.<sup>2</sup> Moreover, hydrogenation of aromatic compounds becomes more and more of an industrial challenge as refineries attempt to reduce emissions of volatile organic matter (VOM) during combustion of diesel oil.<sup>3</sup> The catalytic transformation is generally carried out in drastic conditions with heterogeneous catalysts of group VIII metals.<sup>4</sup> In the past few years, the concept of arene homogeneous hydrogenation catalysis has been reviewed since some catalysts originally assigned as homogeneous have proved to be precursors to colloidal or nanoparticulate catalysts.<sup>5</sup> Consequently, relevant hydrogenation catalytic systems have been investigated using noble metal nanoparticles stabilized in water or organic media.<sup>6</sup> These nanoheterogeneous systems

tend to be more active than classical heterogeneous systems under mild conditions.

For economical and environmental reasons, the development of efficient catalysts in water, limiting the use of volatile organic solvents, seems to be of fundamental interest for the future.<sup>7</sup> Therefore, the synthesis of colloidal nanoparticles stabilized in aqueous solution may lead to significant progress in green chemistry. These aqueous systems are potentially excellent starting materials for the preparation of new supported catalysts, which are largely more active and selective than commercially available analogous catalysts. Indeed, several papers relate the effective catalytic activities of such metal nanoparticles after their immobilisation in rigid matrices ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,...).<sup>8</sup> In most cases, the particles have been synthesized by reduction of a metallic precursor in the presence of an appropriate support. Only some research relates the anchoring of pre-stabilized metal nanoparticles on an inorganic support. The immobilization of polymer-stabilized colloids by a modified coordination capture described by Liu and co-workers<sup>9</sup> led to supported metal nanoparticles with singular catalytic activity for olefinic and nitro compound hydrogenation but no aromatic ring hydrogenation has been observed. The deposition of trioctylamine (TOA)-stabilized ruthenium nanoparticles over  $\gamma\text{-Al}_2\text{O}_3$  has been described by Marconi and co-workers<sup>8i</sup> for the reduction of methylbenzoate to methylhexanoate at 80 °C under 20 atm hydrogen pressure and the authors have reported higher activities with supported-nanoparticles prepared in the presence of TOA as a stabilizer in comparison to the direct reduction of the precursor in the presence of  $\gamma\text{-Al}_2\text{O}_3$ . Based on a similar

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approach, we report, in this paper, an easy way to synthesize supported rhodium nanoparticles by simple addition of silica under vigorous stirring to a pre-stabilized rhodium aqueous colloidal suspension. The rhodium nanoparticles embedded in rigid matrices have been characterized by adapted methods such as TEM after microtomy preparation and XPS experiments. The catalytic activity of these supported systems has been evaluated in the classical hydrogenation of various aromatic substrates under mild conditions. Moreover, these supported catalysts allow an easy product separation and an easy catalyst recycling as well as the catalytic hydrogenation of pure substrates in the absence of co-solvents and associated environmental problems.

## Results and discussion

### Synthesis of silica supported rhodium(0) nanoparticles

The immobilization of metal nanoparticles on supports to obtain nanocatalysts has already been reported. Most of the time, the supported nanocatalyst preparation methods require severe conditions involving repeated oxidation and reduction steps at high temperature. The approach described here combines in *one pot* stabilization of metal nanoparticles and their deposition onto an inorganic support in the same aqueous media.

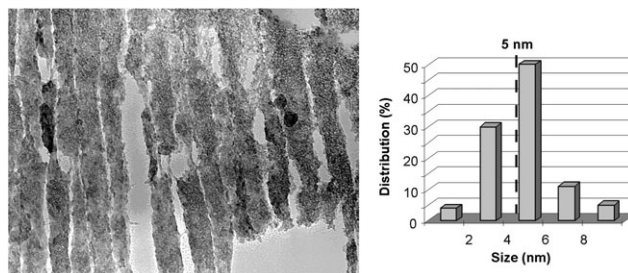
Indeed, we have developed an easy way to immobilize rhodium nanoparticles on silica from our previously reported aqueous colloidal rhodium(0) suspension<sup>9</sup> prepared by chemical reduction of an aqueous solution of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  in the presence of highly water soluble ammonium chloride salts as stabilizing agents.<sup>10</sup> The optimized results have been obtained with the *N,N*-dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl) ammonium chloride salts (HEA16Cl) which efficiently prevent particle aggregation. Then, the nanoparticle adsorption on a support (about 0.1%wt Rh) has been performed by the addition of an adequate amount of silica to this latter colloidal suspension under vigorous stirring. After 2 h, the coloration of the aqueous phase turned from black to colorless evidencing a total adsorption of the particles at the silica surface. After filtration, the dark-brown powder was washed several times with clean water to eliminate the surfactant and dried overnight at 60 °C leading to a solid corresponding to silica-supported rhodium nanoparticles. It should be noticed that all the reactions have been carried out at ambient temperature, under air, without neither use of gas treatment nor a calcination step.

### Characterization of the supported nanoparticles

This silica-supported rhodium nanoparticle system has been characterized by several techniques (TEM, XPS) in order to evaluate the size and the nature of deposited rhodium nanoparticles.

Fig. 1 shows a transmission electron micrograph and a particle size histogram obtained by observation of the central zone of the silica spheres containing metal nanoparticles after microtomy preparation.

We can observe a homogeneous dispersion of the rhodium particles in the silica matrix although a few aggregates are

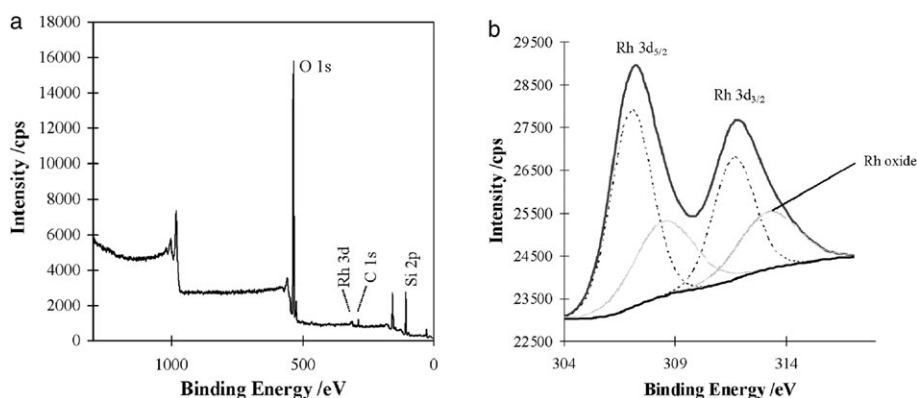


**Fig. 1** TEM realized on the central zone of  $\text{Rh}_{\text{coll}}/\text{SiO}_2$  at 100 kV and metal particle size distribution.

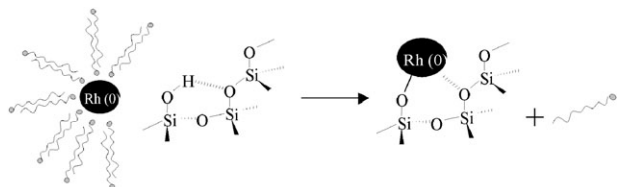
visible in certain areas. The mean diameter of the Rh nanoparticles, calculated from about 300 particles found in an arbitrary chosen area, corresponds to an average diameter of 5 nm indicating that a weak clustering has occurred during the immobilization step since the mean diameter of the rhodium particles in the initial aqueous colloidal suspension was 2.4 nm. The microtomy experiments show that surfactant-stabilized Rh nanoparticles have homogeneously diffused inside the silica pores during the immobilization step. Moreover, the pore sizes of the silica matrix certainly contribute inside to limit this aggregation phenomenon and finally allow the control of the particle size.

The silica-supported rhodium nanoparticles have also been analyzed by X-ray photoelectron spectroscopy to examine the oxidation state and the chemical environment of the deposited Rh nanoparticles. Fig. 2 shows the photpeak related to the Rh 3d core level recorded on Rh nanoparticles embedded in silica.

Two contributions corresponding to different rhodium species can be isolated after mathematical decomposition according to the procedure described in the Experimental section. The low binding energy signal (BE of  $3d_{3/2}$  at 311.8 eV and Rh  $3d_{5/2}$  at 307.9 eV) is consistent with rhodium metal whereas the higher one (BE of  $3d_{3/2}$  at 313.8 eV and Rh  $3d_{5/2}$  at 308.8 eV) agrees with the presence of oxidic rhodium species. Subsequent comparisons with earlier investigations are consistent with  $\text{Rh}^{3+}$  species suggesting the formation of  $\text{Rh}_2\text{O}_3$  on the surface.<sup>11</sup> Consequently, a partial oxidation during the sample preparation and/or the introduction into the spectrometer occurs. Same observations concerning the presence of the rhodium oxidized form could be made between the supported rhodium nanoparticles ( $\text{Rh}_{\text{coll}}/\text{SiO}_2$ ) and the aqueous colloidal rhodium suspension ( $\text{Rh}$ -HEA16Cl) with a similar atomic ratio between the two different forms of rhodium. On the other hand, no specific core-level peaks associated with N 1s, C 1s and Cl 2p relative to the surfactant HEA, used to prepare the aqueous colloidal rhodium suspension, were noticed (Fig. 2) and the Si 2p and O 1s corresponding to the silica support were found, respectively, at 103.8 eV and 533.1 eV. Absence of the Cl signal (BE at 200 eV) indicates that the surface is not contaminated by ionic species. Therefore, we suggest that the particles were totally adsorbed on the support during the preparation and that the surfactant was totally removed after the washing step. This result justifies the investigation of the effect of chlorine as already reported<sup>12</sup> by a catalytic comparison with the aqueous suspension stabilized by the ammonium



**Fig. 2** (a) X-Ray photoelectron spectra of isolated silica-capped rhodium nanoparticles. (b) X-Ray photoelectron spectra of rhodium 3d core level in  $\text{Rh}_{\text{coll}}/\text{SiO}_2$ .



**Scheme 1** Scheme proposed for the anchoring of rhodium nanoparticles on silica surface.

chloride salts (*vide infra*). Moreover, in the literature, experimental and theoretical attention has been devoted to understanding the interactions between metal and supports.<sup>13</sup> Based on recent work,<sup>14</sup> including XAFS experiments coupled with the density functional theory, we suggest that rhodium nanoparticles might be anchored to silica *via* oxygen bonding (Scheme 1).

### Catalytic activity in the hydrogenation of aromatic derivatives

The silica-supported rhodium nanocatalyst ( $\text{Rh}_{\text{coll}}/\text{SiO}_2$ ) previously described has been tested in the hydrogenation of various aromatic compounds under mild conditions in a

triphasic system ( $\text{H}_2\text{O}/\text{hydrocarbon}/\text{silica}$ ). The catalytic reactions were carried out at room temperature and monitored by the hydrogen volume consumption and gas chromatography analysis. The catalytic performances of the  $\text{Rh}_{\text{coll}}/\text{SiO}_2$  nanocatalyst in the hydrogenation of mono- or di-alkylsubstituted and/or functionalized benzene derivatives are reported in Table 1.

In all cases, a total conversion of the substrate has been observed with quite interesting turn over frequencies (TOF), ranging from  $93 \text{ h}^{-1}$  to  $129 \text{ h}^{-1}$ . In the series of benzene, toluene, ethylbenzene, propylbenzene and cumene (Entries 1–5), the increased reaction time and decreased catalytic TOF observed are typical of the increasing steric hindrance influence of the alkyl group as usually observed with other catalysts.<sup>15</sup> Moreover, cumene (Entry 5) which is usually difficult to reduce under mild conditions has been hydrogenated with a TOF of  $93 \text{ h}^{-1}$ . In addition, the hydrogenation of functionalized aromatic compounds such as anisole, phenol, ethylbenzoate, aniline or styrene (entries 6–10) has been performed with complete conversion. Nevertheless, arenes substituted by electron-withdrawing groups such as an ester group react more slowly (entry 8) whereas the reaction is accelerated for electron rich substrates such as anisole which is

**Table 1** Hydrogenation of aromatic compounds with  $\text{Rh}_{\text{coll}}/\text{SiO}_2^a$

Entry	Substrate	Product (%) <sup>b</sup>	<i>t</i> /h	TOF/ $\text{h}^{-1c}$
1	Benzene	Cyclohexane (100)	3.8	113
2	Toluene	Methylcyclohexane (100)	4	107
3	Ethylbenzene	Ethylcyclohexane (100)	4.3	100
4	Propylbenzene	Propylcyclohexane (100)	4.4	97
5	Cumene	Iso-propylcyclohexane (100)	4.6	93
6	Anisole	Methoxycyclohexane (100)	3.2	129
7	Phenol	Cyclohexanol (100)	3.2	129
8	Ethylbenzoate	Ethylcyclohexanoate (100)	5.3	80
9	Aniline	Cyclohexylamine (100)	14	31
10	Styrene	Ethylcyclohexane (100)	4.5	127
11	<i>o</i> -Xylene	1,2-Dimethylcyclohexane ( <i>cis/trans</i> : 95/5)	6.8	63
12	<i>m</i> -Xylene	1,3-Dimethylcyclohexane ( <i>cis/trans</i> : 90/10)	6.1	71
13	<i>p</i> -Xylene	1,4-Dimethylcyclohexane ( <i>cis/trans</i> : 75/25)	5.4	79
14	<i>o</i> -Methylanisole	1-Methoxy-2-methylcyclohexane ( <i>cis/trans</i> : 98/2)	6.4	67
15	<i>m</i> -Methylanisole	1-Methoxy-3-methylcyclohexane ( <i>cis/trans</i> : 95/5)	5.9	73
16	<i>p</i> -Methylanisole	1-Methoxy-4-methylcyclohexane ( <i>cis/trans</i> : 90/10)	5.1	77

<sup>a</sup> Conditions:  $\text{Rh}_{\text{coll}}/\text{SiO}_2$  (1 g, 0.07 wt% Rh),  $[\text{S}]/[\text{M}] = 100$ , 10 ml  $\text{H}_2\text{O}$ , 1 atm  $\text{H}_2$ , 20 °C, stirred at  $1500 \text{ min}^{-1}$ . <sup>b</sup> Determined by GC analysis. <sup>c</sup> Turnover frequency defined as mol of  $\text{H}_2$  per mol of rhodium per h.

hydrogenated in less than 4 h (entry 6). Moreover, the hydrogenation of aniline with the supported catalyst has been achieved after 14 h (entry 9) and  $\text{Rh}_{\text{coll}}/\text{SiO}_2$  could be reused after simple filtration with no significant loss of activity ( $\text{TOF} = 30 \text{ h}^{-1}$  for the second run). This activity is relevant since a destabilization of the catalytic system and particle agglomeration were observed after the first run for aniline hydrogenation with our classical aqueous colloidal rhodium suspension.<sup>10a</sup> Thus, the adsorption of metal nanoparticles on silica is an alternative to solve this problem. Finally, the hydrogenation of di-substituted arenes has also been performed with complete conversion (entries 11–16). In all cases, the selectivity of the reaction was unchanged. Indeed, as usually observed with pure heterogeneous catalysts and with our classical aqueous rhodium colloidal suspension,<sup>10a</sup> the hydrogenation of xylenes and methylanisoles yields the kinetically favoured *cis*-product with a ratio of up to 98% in 1-methoxy-2-methylcyclohexane (entry 14) with silica supported rhodium nanoparticles. The *cis*-product is also the major product with *p*-xylene but the ratio of the *trans*-isomer increases in the same range with colloidal and supported systems (30 and 25%, respectively). In this case, this ratio could be explained by a successive dissociation and re-association phenomenon of a partially hydrogenated intermediate on the catalyst surface.

The deposition of the surfactant-stabilized rhodium nanoparticles on silica appears as a rapid and easy way for preparation of active heterogeneous catalysts under mild conditions. The so-obtained supported nanocatalyst has shown an interesting activity in the hydrogenation of various aromatic compounds at 20 °C and under atmospheric hydrogen pressure. However, in order to explore the limits of this catalyst, other anisole hydrogenation experiments have been carried out at higher hydrogen pressure (Table 2).

Silica-capped rhodium nanoparticles reveal an efficient activity at higher hydrogen pressure for anisole hydrogenation since a TOF of  $6430 \text{ h}^{-1}$  at 20 °C and 30 bar  $\text{H}_2$  has been obtained. This result is certainly one of the most important Turnovers described in the literature for immobilised metal nanoparticles (entry 19). Moreover, 30 000 total turnover (TTO) in 8.5 h were also obtained in terms of catalytic lifetime under 40 bar  $\text{H}_2$  (entry 22).

For comparison, three other catalytic systems have been tested in anisole hydrogenation at 20 °C and under 1 bar of  $\text{H}_2$  (Table 3). These catalysts are: the heterogeneous catalyst Rh/C from Degussa (5 wt%), our classical aqueous rhodium nanoparticles Rh-HEA16Cl suspension and a similar catalyst containing supported metal nanoparticles,  $\text{Rh}^{\text{III}}\text{-NaBH}_4/\text{SiO}_2$ , adapted from the literature.<sup>16</sup> In this latter case, the rhodium salt was adsorbed on the support before chemical reduction. This comparative study evidences that the best activities are obtained with the catalyst resulting from immobilization on silica on the pre-stabilized Rh-HEA16Cl nanoparticles.

Finally, recycling experiments have been investigated on catalytic systems containing typical substrates such as benzene, anisole and styrene at 20 °C and under 1 atm  $\text{H}_2$  (Fig. 3). After each run, the catalyst was recovered by simple filtration and dried at 60 °C before another run with new addition of substrate. Five runs could be performed at least with no significant loss of activity. These results point out the efficient

**Table 2** Hydrogenation of anisole with  $\text{Rh}_{\text{coll}}/\text{SiO}_2$  under hydrogen pressure<sup>a</sup>

Entry	Substrate/ Rh	$\text{PH}_2$ / bar	Product (%) <sup>b</sup>	TOF/ $\text{h}^{-1c}$
17	100	10	Methoxycyclohexane (100)	1714
18	100	20	Methoxycyclohexane (100)	4286
19	100	30	Methoxycyclohexane (100)	6429
20	300	10	Methoxycyclohexane (100)	1929
21	1000	10	Methoxycyclohexane (100)	951
22	10 000	40	Methoxycyclohexane (100)	5069

<sup>a</sup> Conditions:  $\text{Rh}_{\text{coll}}/\text{SiO}_2$  (1 g, 0.07 wt% Rh), water (10 mL), 1 atm  $\text{H}_2$ , 20 °C, stirred at  $1500 \text{ min}^{-1}$ . <sup>b</sup> Determined by GC analysis. <sup>c</sup> Turnover frequency defined as mol of  $\text{H}_2$  per mol of rhodium per h.

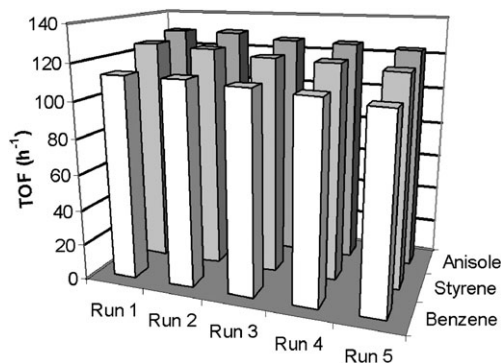
**Table 3** Comparison of traditional catalysts versus the  $\text{Rh}_{\text{coll}}/\text{SiO}_2$  for the hydrogenation of anisole<sup>a</sup>

Catalyst	1st run <i>t</i> /h	TOF/ $\text{h}^{-1c}$	2nd run <i>t</i> /h	TOF/ $\text{h}^{-1c}$
Rh/C 5 wt% (Degussa type DG 10)	8	38	—	—
$\text{Rh}^{\text{III}}\text{-NaBH}_4/\text{SiO}_2$ 0.1 wt%	6	50	7	42
$\text{Rh}_{\text{coll}}/\text{SiO}_2$ 0.07 wt%	3.2	129	3.2	129
Rh-HEA16Cl <sup>b</sup>	3.6	83	3.9	77

<sup>a</sup> Reaction conditions: Substrate/Rh = 100 (molar ratio), anisole ( $3.8 \times 10^{-3}$  mol), water (10 mL), 1 atm  $\text{H}_2$ , 20 °C, stirred at  $1500 \text{ min}^{-1}$ . <sup>b</sup> Rhodium ( $3.8 \times 10^{-5}$  mol), HEA16Cl ( $7.6 \times 10^{-5}$  mol). <sup>c</sup> Turnover frequency defined as mol of  $\text{H}_2$  per mol of rhodium per h.

adsorption of the particles on the silica surface since in the case of weak interaction between particles and support, a loss of activity is usually observed due to metal leaching. In our case, a slight loss of activity is noticed (e.g.  $\text{TOF} = 129 \text{ h}^{-1}$  for the first run of anisole hydrogenation and  $120 \text{ h}^{-1}$  for the fifth run) that can be attributed to the loss of a small quantity of the catalyst during the filtration step.

The efficiently obtained activities can be attributed to the very homogeneous dispersion of rhodium nanoparticles inside silica pores due to the initial surfactant-stabilization of the particles, thus avoiding aggregation and allowing a better control of the particle size. Moreover, the substrate diffusion rate to rhodium active sites might be increased thanks to the



**Fig. 3** Catalytic lifetime of silica-capped rhodium nanoparticles for benzene, anisole and styrene hydrogenation at 20 °C and under 1 atm  $\text{H}_2$ .



large covering of the silica matrix in contrast with classically supported nanoparticles which are usually concentrated on a localised area of the support.

## Conclusions

In summary, we have shown that an aqueous solution containing pre-stabilized Rh nanoparticles can be used easily for particle deposition onto silica through simple impregnation. The so-obtained silica supported-rhodium nanoparticles displayed an unexpected activity under atmospheric hydrogen pressure and at room temperature for the hydrogenation of various aromatic compounds and could be reused at least for five runs without significant loss of activity. Moreover, this catalytic system appears as a good way to solve the problem of destabilisation which occurs with rhodium nanoparticles in aqueous suspension towards N-substrates. Finally, since the preparation of the catalyst has been carried out at ambient temperature without necessitating neither a calcination step nor a high hydrogen pressure, the method described in this paper is an easy way to prepare a heterogeneous nanocatalyst.

## Experimental

### Starting materials

Rhodium chloride hydrate was obtained from Strem Chemicals. Rh/C (5 wt%; Degussa-type G10), Sodium borohydride, 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-16-Cl was prepared as previously described in the literature and was fully characterized.<sup>10</sup> Commercial Silica Si 60 (Merck) was used as received (surface area  $S_{\text{BET}} = 364 \text{ m}^2 \text{ g}^{-1}$ ).

### Analytical procedures

**TEM-analysis.** After embedding the sample in a resin (Spurr R1032) and treatment at 70 °C overnight for polymerization, the solid was cut into thin lamellae (50 nm) with a microtome. Analysis of the sample was then realized after deposition of a lamella onto a carbon covered copper grid using a Hitachi HU-12 A microscope operating at 120 kV with a resolution of 4.5 Å, at the service “Centre de Microscopie Électronique Appliqué à la Biologie de la Faculté de Médecine” in Toulouse.

**Gas chromatography.** All analysis 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.).

**X-Ray photoelectron spectroscopy analysis.** XPS measurements were performed using a Vacuum Generators Escalab 220XL spectrometer. A monochromatized aluminium source was used for excitation ( $\text{Al K}\alpha = 1486.6 \text{ eV}$ ). The binding energies were referenced to the photopeak C 1s at 285 eV. The decomposition of the Rh 3d photopeak was achieved according to a ratio Gaussian/Lorentzian equal to 0.3 and accounting for the relative intensity  $I(\text{Rh } 3d_{5/2})/I(\text{Rh } 3d_{3/2})$  and the

difference in binding energy levels between both signals as constraints.

### Synthesis and characterization of the aqueous rhodium(0) suspension

To an aqueous solution of surfactant HEA-16-Cl (95 mL,  $7.6 \times 10^{-3} \text{ mol l}^{-1}$ ) was added sodium borohydride (36 mg,  $9.5 \times 10^{-4} \text{ mol}$ ). Then this solution is quickly added under vigorous stirring to an aqueous solution (5 mL) of the precursor  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  (100 mg,  $3.8 \times 10^{-4} \text{ mol}$ ) to obtain an aqueous Rh(0) colloidal suspension (100 mL). The reduction occurs instantaneously and is characterized by a color change from red to black. The obtained suspensions are stable for several months as confirmed by TEM (the sizes of the particles remain unmodified over this time frame). The transmission electronic microscopic studies were conducted using a FEI Technai G2 Sphera at 200 kV (cathode LaB6). Samples were prepared by a dropwise addition of the stabilized nanoparticles 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 X 80.000 with a video GATAN USC1000 (CCD detector 2048X2048) and associated software DIGITAL Micrograph. Measurement of about 300 particles was made with the program SCION Image (NIH) and was analyzed with the KaleidaGraph program providing histograms of nanoparticle size distribution.

### Synthesis of the silica supported-rhodium nanoparticles

Silica (18.5 g) was added under vigorous stirring to 40 ml of deionized water. After 2 h, 50 ml of Rh(0)-HEA-16-Cl ( $1.9 \times 10^{-4} \text{ mol}$  of Rh) was added under vigorous stirring to this suspension. The system was kept under stirring for 2 h, afterwards the black power obtained after filtration was dried overnight at 60 °C. Anal. found: Si, 41.72; Rh, 0.07.

### General procedure for hydrogenation under atmospheric hydrogen pressure

Reactions were carried out under standard conditions (20 °C, 1 atm of  $\text{H}_2$ ). A 25 ml round bottom flask, charged with appropriated Rh(0) catalyst (10 mL for aqueous suspension and 1 g in 10 ml of water for Rh/SiO<sub>2</sub>) 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 ( $[\text{Substrate}]/[\text{Rh}] = 100$ ) was injected through the septum, and the mixture was stirred at  $1500 \text{ min}^{-1}$ . The reaction was monitored by the volume of gas consumed and by gas chromatography. Turnover frequency (TOF) was determined for 100% conversion.

## Acknowledgements

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