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# **Rh(0)** colloids supported on TiO<sub>2</sub>: a highly active and pertinent tandem in neat water for the hydrogenation of aromatics

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 $\text{TiO}_2$ -supported Rh(0) nanoparticles were easily prepared in one step without calcination by a room temperature impregnation of the inorganic support with a prestabilized colloidal Rh(0) suspension. They are highly active and reusable catalysts for the hydrogenation of aromatics and chloroanisole derivatives in neat water with TOFs up to 33000 h<sup>-1</sup>. The comparison with the analogous silica system Rh@SiO<sub>2</sub> was discussed showing higher catalytic selectivities and activities with Rh(0) colloids supported on TiO<sub>2</sub>.

# Introduction

Nanometer-sized transition metal particles have been intensively pursued as potentially pertinent catalysts as their particular properties lie between mononuclear metal complexes and heterogeneous bulk catalysts.<sup>1,2</sup> Their large surface area-tovolume ratio, which increases when decreasing particle size, could greatly increase their specific catalytic activity.3-5 In that context, the control of the structural parameters such as size, composition and morphology is of crucial importance to tune their catalytic activities and selectivities.<sup>6,7</sup> The most usual approach for the particle synthesis relies on the chemical reduction of metallic precursors (organometallic complexes or metal salts) in the presence of protective agents such as polymers, ligands, surfactants, ionic liquids according to the nature of the reaction media.<sup>8-11</sup> Among the various catalytic applications, metallic nanospecies have particularly proved to be pertinent catalysts for arene hydrogenation in mild conditions.<sup>12-14</sup> However, particle aggregation and catalyst deactivation could occur during catalytic reactions with particle suspensions and the catalyst separation from the reaction products, which represents a crucial parameter in the search for clean processes, could sometimes be problematic. Among the approaches towards stabilizing metal nanoparticles for heterogeneous catalysis,15 their deposition on solid supports (such as metal oxides, carbon or zeolites) provides a great scope for the development of highly active, robust and potentially recyclable catalysts.<sup>16</sup> Supported nanocatalysts are widely recognized as a mainstay of industrial catalysts, being used in petrochemical industries and in the manufacturing of fine and speciality chemicals.17 Many preparation methods have

been reported in the literature, being divided into physical (e.g. sonication, microwaves, UV) or chemical (e.g. electrochemical, impregnation, fluidized bed) routes.<sup>16,18</sup> Classical methods for the preparation of supported nanocatalysts usually involve repeated oxidation and reduction steps under severe conditions. However, in the drive towards environment-friendly processes, the synthesis of supported metal particles should be promoted in a more sustainable way with room-temperature aqueous solution protocols, improving manufacturing safety as well as decreasing production costs.<sup>19</sup> Moreover, nanomaterialscatalyzed transformations in an aqueous reaction media remain one of the most ideal solutions for the development of green and sustainable protocols.<sup>20</sup> In that context, we developed a clean methodology in mild conditions for the preparation of SiO<sub>2</sub>-supported metal nanoparticles and their investigation in arene hydrogenation in neat water. Our approach is based on the wet<sup>21</sup> or dry<sup>22,23</sup> (fluidized bed) impregnation onto silica of prestabilized colloidal suspensions, which were well-characterized in terms of size, distribution and organization.<sup>24</sup> More recently, this relevant approach was extended to the use of TiO<sub>2</sub> anatase as a new support and preliminary investigation with TiO<sub>2</sub>supported Rh(0) particles proved to be highly active catalysts in model arenes hydrogenation.<sup>25</sup> The choice of this support was governed by its various advantages such as good stability, low cost, non-toxicity and photocatalytic properties.<sup>26</sup> In this paper, we describe the convenient preparation of Rh@TiO<sub>2</sub> nanocatalyst and the further investigations in the hydrogenation of functionalized or disubstituted arene compounds in neat water. Moreover, a comparison in terms of activities and selectivities of Rh@TiO2 and Rh@SiO2 systems was performed on various aromatic compounds.

# **Results and discussion**

In the drive towards a sustainable and green chemistry, we have developed an easy and reproducible method, based on

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the simple impregnation of the anatase TiO<sub>2</sub> support by a pre-stabilized aqueous rhodium(0) suspension (Fig. 1).25 More precisely, colloidal solutions of rhodium(0) were easily prepared, as previously described, by chemical reduction of rhodium chloride salts in the presence of N,N-dimethyl-N-cetyl-N-(2hydroxyethyl) ammonium chloride (HEA16Cl) surfactant as protective agent, which prevents from particle aggregation through electrosteric stabilization.<sup>24,27</sup> Then, the addition of the adequate amount of titania under vigorous stirring leads to the adsorption of the Rh(0) nanospecies on the support, which is evidenced by the color change from black to colorless. After filtration and several water washings, the powder was dried overnight at 60 °C, leading to titania-supported Rh(0) nanoparticles as a fine grey powder. This one-step preparation was performed at ambient temperature, under air without any gas treatment or calcination step. The metal loading of the nanomaterials was determined by ICP analysis as 0.09 wt%, corresponding to the expected one.



Fig. 1 One pot TiO<sub>2</sub>-supported Rh(0) nanoparticles preparation.

The titania-supported rhodium(0) nanoparticles system was characterized by High Resolution Transmission Electron Microscopy (HRTEM) and Energy Dispersive X-ray spectrometry (EDX) to identify the location and size of the metallic nanospecies. The rhodium(0) particles, observed on the micrograph 2a (zone contrasted), present an average size of 3-4 nm, very close to anatase one. The analyses of the fast Fourier transformation (FFT) of the HRTEM pictures mainly revealed the interplanar distances of 0.352 and 0.233 nm corresponding to the (101) and (112) lattice planes of anatase as shown on the magnification area (Fig. 2b). However, the intereticular distances of 0.2196 and 0.1902 nm, which are characteristic of the (111) and (200) planes lattice of Rh(0) were not clearly observed. The presence of Rh(0) particles was confirmed by EDX (Fig. 2c red line) by focusing the electron beam at about 10 nm size and the deconvolution of the Rh signal (blue line) was calculated to prove its presence. The Cl signal was clearly observed at 2.62 keV near to the Rh signals at 2.696 and 2.834 keV. Finally, as shown by these microtomy experiments of a cross section of titania spheres, the surfactant-stabilized Rh(0) colloidal suspension is well-diffused into the matrix.

The  $\text{TiO}_2$ -supported nanomaterials were evaluated in the catalytic hydrogenation of various aromatic compounds in water under hydrogen pressure (1 or 30 bar H<sub>2</sub>) and at room temperature. The conversion was determined by gas chromatography analysis. The turnover frequencies (TOFs) were calculated considering an optimized reaction time for complete conversion of the substrate and based on the introduced amount of metal and not on the exposed surface metal and thus may be underestimated. As previously reported by Janiak *et al.*,<sup>28</sup> the catalytic activity results not only from the exposed surface metal



Fig. 2 HRTEM micrographs a)  $Rh@TiO_2$  (Scale bar is 2 nm). b) Magnification of an area showing the lattice planes of anatase. c) EDX spectrum of Rh(0) particles proved by deconvolution analysis.

atoms since the surface can restructure, atoms can shift positions during heterogeneous processes and partial aggregation could occur during catalysis, modifying the fraction of surface atoms. These changes in the surface render the determination of the number of surface atoms difficult. The catalytic performances of the Rh@TiO<sub>2</sub> nanocatalyst in the hydrogenation of mono- or di-alkylsubstitued and/or functionalized arene derivatives are reported in Table 1.

First, the Rh@TiO<sub>2</sub> catalyst is very active at atmospheric pressure. In all cases, a total conversion of the substrate in the totally hydrogenated compound was observed with quite interesting TOFs ranging from 72 h<sup>-1</sup> to 476 h<sup>-1</sup>. In the series of benzene, toluene, o-xylene (entries 1, 3, 5), the increased reaction time and decreased catalytic activity are typical of the increasing steric hindrance of the alkyl groups, which hamper the approach of the substrate towards the metallic nanospecies. This could also be explained by the difference of solubility of these arenes in water (benzene > toluene > *p*-xylene) as reported by Matsumoto *et al.*<sup>29</sup> In addition, the hydrogenation of functionalized arene derivatives such as anisole and ethylbenzoate (entries 11 and 13) was performed with complete conversion. Moreover, in the case of anisole, the formation of phenol or cyclohexanone as by-products was not observed, contrary to the Rh(0) colloidal suspension which gives a significant ratio of cyclohexanone (20-30%).<sup>30</sup> The hydrogenation of di-substituted benzene derivatives was also performed with total conversion (entries 5, 7, 9). In all cases, the selectivity of the reaction remained unchanged. Indeed, as usually observed with pure heterogeneous catalysts<sup>22,31</sup> and with our classical aqueous Rh(0) suspension,<sup>13,27</sup> the hydrogenation

Entry	Substrate	Products <sup>b</sup> (%)	P (bar H <sub>2</sub> )	t (h)	$\mathrm{TOF}^{c}\left(\mathrm{h}^{\mathrm{-1}} ight)$
1	Benzene	Cyclohexane (100)	1	0.7	476
2	Benzene	Cyclohexane (100)	30	0.01	33300
3	Toluene	Methylcyclohexane (100)	1	1.5	222
4	Toluene	Methylcyclohexane (100)	30	0.03	11100
5	o-Xylene	1,2-Dimethylcyclohexane cis (90)/trans (10)	1	4	83
6	o-Xylene	1,2-Dimethylcyclohexane cis (95)/trans (5)	30	0.25	1333
7	<i>m</i> -Xylene	1,3-Dimethylcyclohexane cis (80)/trans (20)	1	4.6	72
8	<i>m</i> -Xylene	1,3-Dimethylcyclohexane cis (85)/trans (15)	30	0.42	793
9	<i>p</i> -Xylene	1,4-Dimethylcyclohexane cis (64)/trans (36)	1	4.6	72
10	<i>p</i> -Xylene	1,4-Dimethylcyclohexane cis (67)/trans (33)	30	0.42	793
11	Anisole	Methoxycyclohexane (100)	1	1.8	185
12	Anisole	Methoxycyclohexane (100)	30	0.07	4761
13	Ethylbenzoate	Ethylcyclohexanoate (100)	1	2	167
14	Ethylbenzoate	Ethylcyclohexanoate (100)	30	0.09	3704
15	Diphenylmethane	Dicyclohexylmethane	1	20	33 <sup>d</sup>
16	Diphenylmethane	Dicyclohexylmethane	30	3	222
17	Naphtalene	Decalin cis (91)/trans (9)	1	24	23 <sup>d</sup>
18	Naphtalene	Decalin cis (92)/trans (8)	30	3	185 <sup>d</sup>
19	Pyridine	Piperidine	1	20	$17^{d}$
20	Pyridine	Piperidine	30	3	$111^{d}$

 Table 1 Hydrogenation of non halogenated aromatic compounds under 1 or 30 bar H<sub>2</sub><sup>a</sup>

<sup>*a*</sup> Reaction conditions: Rh@TiO<sub>2</sub> (1 g, 0.09% wt, 8.8 × 10<sup>-6</sup> mol), substrate (9.6 × 10<sup>-4</sup> mol), H<sub>2</sub>O (10 mL), RT, stirred at 1700 min<sup>-1</sup>. <sup>*b*</sup> Determined by Gas Chromatography analysis. <sup>*c*</sup> Turnover frequency defined as the number of moles of consumed H<sub>2</sub> per mole of introduced rhodium per hour and calculated considering 100% conversion of the substrate after an optimized time. <sup>*d*</sup> Underestimated value according to a total conversion but a non-optimized time. <sup>*e*</sup> 50% conversion after 6 h.

of xylenes yields the kinetically favoured *cis*-product with a ratio ranging from 65 to 90% according to the isomer. The cis-product is also the major product with p-xylene but the ratio of the trans-isomer increases in the same range as with colloidal and supported systems (35 and 36% respectively). The formation of the *trans* isomer, commonly observed as the minor product, could be explained by a successive dissociation and re-association phenomenon of a partially hydrogenated intermediate on the catalyst surface. Whatever isomer of xylene is considered, it can be noticed that the values of cis/trans ratio are higher than unity and increase with hydrogen pressure, suggesting that trans products are formed through a "roll-over" mechanism.32 The selective hydrogenation was also carried out with bicyclic arenes. The diphenylmethane was totally converted into dicyclohexylmethane after 20 h (entry 15); the conversion was complete after 3 h into a 1:1 mixture of mono-and dihydrogenated products. The hydrogenation of naphthalene was observed with a total conversion after 24 h (non optimized time) in the decalin isomers with a *cis/trans* ratio of 91/9 (entry 17), which is quite consistent with the one observed in the literature with Rh nanoparticles entrapped in aluminium oxyhydroxide nanofibers.<sup>33</sup> After 6 h, all the naphthalene was converted in a mixture of tetralin (68%) and decalins (32%). It is interesting to notice that the substrate did not strongly interact with the particle surface, limiting the tetralin hydrogenation, as observed with the  $Pt/TiO_2$  system described by Kurokawa *et al.*<sup>34</sup> The pyridine was also investigated as an heteroaromatic compound and shows a total conversion into piperidine in 20 h (entry 19). The increase in hydrogen pressure up to 30 bar  $H_2$  (entries 2, 4, 6, 8, 10, 12, 14) dramatically increases the catalytic activity, with TOFs up to 33000 h<sup>-1</sup> observed in the case of benzene. Finally, the Rh@TiO<sub>2</sub> catalyst is also more active on bicyclic substrates such as diphenylmethane and naphthalene (entries 16 and 18) and heteroaromatics such as pyridine (entry 20).

The selective hydrogenation is also possible for anthracene (Scheme 1). Some results have been described in the literature with Rh(0) nanocatalysts.<sup>35,36</sup> Due to the non-solubility of the substrate in water, the reaction was performed in a cyclohexane/water mixture. After 20 h, a yield of 87% was observed and the three formed products were analyzed by GC-MS: the one produced by the hydrogenation of the central ring **2**, the two side rings **3** and only one side ring **1**.



Scheme 1 Anthracene hydrogenation with Rh@TiO<sub>2</sub> catalyst.

The hydrogenation of chloroanisole isomers were also investigated in neat water under hydrogen pressure (1 or 30 bar  $H_2$ ) and room temperature. The reaction leads to the formation of two products, which were identified by Gas Chromatography analysis: the expected methoxycyclohexane 1 and also small traces of cyclohexanone 2. The results are gathered in Table 2.

First, in all cases, the substrate is totally converted in methoxycyclohexane (95–98%) with TOF around 70–80 h<sup>-1</sup> at atmospheric pressure (entries 1, 3, 5). Very small traces (<5%) of cyclohexanone were detected, compared with the results obtained with classical colloidal Rh(0) suspensions which gave

Table 2 Hydrogenation of chloroanisoles with Rh@TiO2<sup>a</sup>



<sup>*a*</sup> Reaction conditions : Rh@TiO<sub>2</sub> (1 g, 0.09% wt, 8.8 × 10<sup>-6</sup> mol), substrate (9.6 × 10<sup>-4</sup> mol), H<sub>2</sub>O (10 mL), RT, stirred at 1700 min<sup>-1</sup>. <sup>*b*</sup> Determined by Gas Chromatography analysis. <sup>*c*</sup> Turnover frequency defined as number of moles of consumed H<sub>2</sub> per mole of introduced rhodium per hour and calculated considering 100% conversion of the substrate after an optimized time.

a higher ratio of cyclohexanone.<sup>30</sup> The increase in hydrogen pressure to 30 bar  $H_2$  leads to a dramatic increase in catalytic activities, with TOFs up to 11000 h<sup>-1</sup>, and in selectivity with 100% methoxycyclohexane (entries 2, 4, 6).

Recycling experiments were carried out with the Rh@TiO<sub>2</sub> catalyst in the hydrogenation of typical substrates such as toluene, anisole and *o*-xylene at room temperature and atmospheric pressure in water (Fig. 3). After each run, the catalyst was easily recovered by filtration and dried at 60 °C before another run with new addition of the substrate. Three runs were performed with no significant loss of activity. Moreover, we have checked in the case of toluene the absence of catalytic activity with the aqueous phase after filtration of the solid catalyst which could be due to putative metallic species obtained by desorption.



Fig. 3 Recycling experiments.

These results prove again the efficient adsorption of the metallic nanospecies on the titania surface since a loss of catalytic activity due to metal leaching is usually observed in the case of weak interactions between the particles and the support. Moreover, the absence of lixiviation was checked by elemental analysis of the supported catalyst after hydrogenation, which presents a same metal ratio (0.09%) after the recycling experiments.

Finally, the catalytic activities of  $Rh@TiO_2$  system were compared to those of  $Rh@SiO_2$  catalyst prepared by the same methodology in the hydrogenation of the same monoor di-substitued and/or functionalized arene derivatives at room temperature and under atmospheric pressure in water (Table 3). In all cases, the hydrogenation of aromatic compounds proceeds with higher TOFs using the  $Rh@TiO_2$  catalyst than the  $Rh@SiO_2$  one. In the case of xylenes (entries 5– 10), whatever the isomer is, the *cis/trans* ratio is higher with

 Table 3
 Hydrogenation of arene derivatives: Rh@TiO2 vs. Rh@SiO2<sup>a</sup>

Entry	Catalyst	Substrate	Products <sup>b</sup> (%)	t (h)	$\mathrm{TOF}^{c}\left(\mathbf{h}^{-1}\right)$
1	Rh@TiO <sub>2</sub>	Benzene	Cyclohexane (100)	0.7	476
2	Rh@SiO <sub>2</sub>	Benzene	Cyclohexane (100)	3.8	113
3	Rh@TiO <sub>2</sub>	Toluene	Methylcyclohexane (100)	1.5	222
4	Rh@SiO <sub>2</sub>	Toluene	Methylcyclohexane (100)	2.5	149
5	Rh@TiO <sub>2</sub>	o-Xylene	1,2-Dimethylcyclohexane cis (90)/trans (10)	4	83
6	Rh@SiO <sub>2</sub>	o-Xylene	1,2-Dimethylcyclohexane cis (95)/trans (5)	4	93
7	Rh@TiO <sub>2</sub>	<i>m</i> -Xylene	1,3-Dimethylcyclohexane cis (80)/trans (20)	4.6	72
8	Rh@SiO <sub>2</sub>	<i>m</i> -Xylene	1,3-Dimethylcyclohexane cis (90)/trans (10)	4	93
9	Rh@TiO <sub>2</sub>	<i>p</i> -Xylene	1,4-Dimethylcyclohexane cis (64)/trans (36)	4.6	72
10	Rh@SiO <sub>2</sub>	<i>p</i> -Xylene	1,4-Dimethylcyclohexane cis (75)/trans (25)	4	93
11	Rh@TiO	Anisole	Methoxycyclohexane (100)	1.8	185
12	Rh@SiO2	Anisole	Methoxycyclohexane (100)	3	124
13	Rh@TiO <sub>2</sub>	Ethylbenzoate	Ethylcyclohexanoate (100)	2	167
14	Rh@SiO <sub>2</sub>	Ethylbenzoate	Ethylcyclohexanoate (100)	2.3	162
15	Rh@TiO <sub>2</sub>	o-Chloroanisole	Methoxycyclohexane (95)/Cyclohexanone (5)	0.7	72
16	Rh@SiO <sub>2</sub>	o-Chloroanisole	Methoxycyclohexane (64)/Cyclohexanone (36)	5.5	68
17	Rh@TiO <sub>2</sub>	<i>m</i> -Chloroanisole	Methoxycyclohexane (96)/Cyclohexanone (4)	1.5	83
18	Rh@SiO <sub>2</sub>	<i>m</i> -Chloroanisole	Methoxycyclohexane (60)/Cyclohexanone (40)	5	75
19	Rh@TiO2	<i>p</i> -Chloroanisole	Methoxycyclohexane (98)/Cyclohexanone (2)	4	72
20	Rh@SiO <sub>2</sub>	<i>p</i> -Chloroanisole	Methoxycyclohexane (65)/Cyclohexanone (35)	5.5	68

<sup>*a*</sup> Reaction conditions : Rh@TiO<sub>2</sub> or Rh@SiO<sub>2</sub> (1 g, 0.09% wt,  $8.8 \times 10^{-6}$  mol), substrate (9.6 × 10<sup>-4</sup> mol), H<sub>2</sub>O (10 mL), 1 bar H<sub>2</sub>, RT, stirred at 1700 min<sup>-1</sup>. <sup>*b*</sup> Determined by Gas Chromatography analysis. <sup>*c*</sup> Turnover frequency defined as the number of moles of consumed H<sub>2</sub> per mole of introduced rhodium per hour and calculated considering 100% conversion of the substrate after an optimized time.

Rh@SiO<sub>2</sub>. The hydrogenation of chloroanisole isomers (entries 15-20) leads to the formation of two products: the expected methoxycyclohexane and small (<5%) or significant (35–40%) quantities of cyclohexanone according to the catalyst, respectively Rh@TiO<sub>2</sub> or Rh@SiO<sub>2</sub>. The methoxycyclohexane was obtained from the tandem dehalogenation-hydrogenation reaction. The cyclohexanone has already been observed in acidic media via the formation of an hemiacetal during the hydrogenation of anisole with aqueous colloidal Rh(0) suspensions.<sup>30</sup> In contrast, no cyclohexanone was observed in the hydrogenation of anisole with the Rh@SiO<sub>2</sub> or Rh@TiO<sub>2</sub> catalyst (entries 11-12). In this case, the formation of cyclohexanone during the hydrogenation of chloroanisole isomers could be explained by the release of HCl in the reaction media during the dehalogenation, which constitutes the first step of the tandem dehalogenation-hydrogenation reaction (Scheme 2).37 The difference of cyclohexanone ratio between both catalysts could be explained by a pH value of the aqueous phase near 6.5 with Rh@TiO2 and near 5 with Rh@SiO2. The initial pH difference value between both catalysts and the release of HCl in the reaction media are responsible for a more acidic solution (pH = 3.9) with the  $Rh@SiO_2$  system, which favours the formation of cyclohexanone. As the kinetics of the hydrogenation reaction is faster with the Rh@TiO<sub>2</sub> catalyst, compared to Rh@SiO<sub>2</sub>, the formation of cyclohexanone is not favoured.



Scheme 2 Formation of cyclohexanone during the chloroanisole hydrogenation.

In conclusion,  $TiO_2$ -supported Rh(0) nanoparticles were easily prepared by a simple, environmentally-friendly and reproducible procedure based on wet impregnation of the support with a pre-stabilized colloidal suspension, under mild conditions without calcination step in water. The nanocatalysts presenting low metal loading (0.09 wt%) proved to be very active and recyclable in the hydrogenation of mono- or di-substituted and/or functionalized arene derivatives at atmospheric pressure with TOF up to 470  $h^{-1}$  in neat water at atmospheric hydrogen pressure and room temperature. A dramatic increase in catalytic activities with TOF up to 33000 h<sup>-1</sup> were achieved when increasing the pressure up to 30 bar H<sub>2</sub>. The catalytic activities of the Rh@TiO<sub>2</sub> system proved to be higher than those of Rh@SiO<sub>2</sub> on a large variety of aromatic derivatives. The use of TiO<sub>2</sub> anatase, well-known for its high photocatalytic activity,<sup>38</sup> offers great opportunities for the development of photocatalytic processes and further investigations are ongoing concerning the remediation of toxic arene compounds from aqueous effluents, combining tandem dehalogenation-hydrogenation reaction and photocatalytic activity using metallic nanoparticles doped-TiO<sub>2</sub>

materials. These new properties are under current investigation in the laboratory.

## Experimental

## a) General

RhCl<sub>3</sub>·3H<sub>2</sub>O was obtained from Strem Chemicals. All the organic compounds were purchased from Acros Organics or Sigma-Aldrich-Fluka and used without further purification. The titania was purchased from Millenium Chemicals. The photocatalyst PC500 has a BET-surface area of 287 m<sup>2</sup> g<sup>-1</sup> with 100% anatase and a primary particle size of 5-10 nm.<sup>39,40</sup> The silica Si80 was obtained from Merck and presents the following characteristics: mean diameter: 80 µm, pore diameter 5.4 nm, specific area 490 m<sup>2</sup> g<sup>-1</sup>, pore volume 0.77 cm<sup>3</sup> g<sup>-1</sup> and internal porosity 58%. Water was distilled twice before use by conventional method. The hydroxyethylammonium chloride salt HEA16Cl, which was used as a protective agent for the Rh(0) nanoparticles in aqueous solution, was synthesized as previously described in the literature and fully characterized.<sup>27,41</sup> All gas chromatography analyses of catalytic reactions were performed using a Carlo Erba GC 6000 with a FID detector equipped with a Factor Four column (30 m, 0.25 mm i.d.).

#### b) Preparation of Rh@TiO<sub>2</sub>

A suspension of titania (19 g) in 40 mL of deionized water is stirred vigorously during two hours. Furthermore, 50 mL of surfactant-stabilized Rh(0) suspension<sup>13</sup> ( $1.9 \times 10^{-4}$  mol of Rh) are added under vigorous stirring. The system is kept under stirring during two hours. After filtration and three water washings, the grey powder is dried overnight at 60 °C. Anal. found: Rh, 0.09.

#### c) Preparation of Rh@SiO<sub>2</sub>

Silica (18.5 g) was vigorously stirred in 40 mL of deionized water during 2 h. Furthermore, 50 mL of Rh(0)@HEA16Cl (1.9 ×  $10^{-4}$  mol of Rh) were added under vigorous stirring and the system was kept under stirring for two hours. The catalyst was recovered by filtration, then washed several times with distilled water and dried at 60 °C overnight. Previous TEM analyses<sup>22</sup> have evidenced well-dispersed Rh(0) particles with an average size of 5 nm. Anal. found: Rh, 0.09.

## d) General procedure for hydrogenation under atmospheric hydrogen pressure

Reactions are carried out under standard conditions (20 °C, 1 atm of H<sub>2</sub>). A 25 mL round bottom flask, charged with Rh@TiO<sub>2</sub> catalyst (1 g, 10 mL of water) and a magnetic stirrer, is connected with a gas burette (500 mL) with a flask to balance the pressure. The flask is closed by a septum, and the system is filled with hydrogen. The appropriate aromatic substrate ([Substrate]/[Rh] = 100) is injected through the septum and the mixture is stirred at 1700 min<sup>-1</sup>. The reaction is monitored by gas chromatography analyses. Based on the amount of introduced rhodium, turnover frequencies (TOFs) are calculated for 100% conversion.

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## e) General procedure for hydrogenation under hydrogen pressure

The stainless steel autoclave was charged with the  $Rh@TiO_2$  catalyst (1 g, 10 mL of water) and a magnetic stirrer. The appropriate substrate ([Substrate]/[Rh] = 100) was added into the autoclave and dihydrogen was admitted to the system at constant pressure (up to 30 bars). The conversion was determined by gas chromatography analysis. Based on the amount of introduced rhodium, the TOF was determined for 100% conversion.

## d) Transmission electron microscopy (TEM) analysis

After embedding of the sample in a resin (AGAR 100) and treatment at 70 °C during 48 h for polymerization, the solid has been cut into ultrathin lamellas (70 nm) with a diamond knife (Leica Ultracut UCT). A TEM analysis was then realized after deposition of the lamellas onto a carbon covered copper grid using a microscope operating at 200 kV with a resolution of 0.18 nm (JEOL JEM 2011 UHR) equipped with an EDX system (PGT IMX-PC).

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