TiO_2-supported Rh nanoparticles: From green catalyst preparation to application in arene hydrogenation in neat water

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Received 10th March 2010, Accepted 21st May 2010
First published as an Advance Article on the web 7th June 2010
DOI: 10.1039/c004079g

TiO_2-supported Rh(0) nanoparticles were prepared by an easy method under mild conditions in neat water. They proved to be highly active catalysts for arene hydrogenation in water with TOFs up to 33 333 h^{-1}.

The use of metallic nanoparticles in catalysis has attracted a growing interest over the last few decades owing to their unique properties such as a large surface-to-volume ratio and tunable shapes.[1] The control of their size, shape and dispersity is essential for selective and enhanced activity in a desired application. Among the various catalytic applications, noble metal nanospecies are reference catalysts for the hydrogenation of arene derivatives,[2,3] thus leading to the formation of key intermediates for fine chemistry. In the drive towards sustainable and environmentally-friendly chemistry, catalyst recovery is a crucial parameter. The combination of metal nanoparticles with an heterogeneous support provides a powerful means for the development of new, highly active and recyclable catalysts,[4,5] leading to specific applications in catalysis. Supported metal nanoparticles are a mainstay of commercial heterogeneous catalysts with applications in various industrial reactions.[6,7] Different preparation routes have been developed over the last few years and are subdivided into physical (*e.g.* sonication, microwaves, UV) or chemical (*e.g.* electrochemical, impregnation, fluidized bed).[4,8] However, with respect to the sustainability criterion, the design and synthesis of supported nanomaterials is still an ongoing challenge.[9,10] In this context, the particles should ideally be prepared with less toxic precursors in green solvents in mild conditions and with few synthetic steps.[11] Among the various supports, metal oxides offer high thermal and chemical stabilities with a well-developed porous structure and high surface areas (>100 m^2 g^{-1}). Our approach relies on the deposition onto an inorganic support of pre-stabilized nanoparticles in aqueous suspensions, which have been well-characterized in terms of size and organization.[12] Interesting results in terms of catalytic activity and recycling have been obtained in arene hydrogenation using silica-supported rhodium(0) nanoparticles prepared by wet impregnation or in fluidized beds.[13,14] In this paper, we describe the easy synthesis of TiO_2-supported rhodium(0) nanoparticles and their efficient use in model arene hydrogenation. Titania materials offer many advantages such as good stability, low cost and nontoxicity,[15] and are widely used in oxidative reactions and photocatalysis due to their wide gap band. Metal-doped TiO_2 are also described in hydrogenation of various substrates, such as olefins, alkynes or nitro groups, but to our knowledge there is scarcely any report on arene reduction. Moreover, contrary to classical routes for the synthesis of supported nanocatalysts, which requires repeated oxidation and reduction steps under severe conditions, our approach relies on an impregnation methodology which consists of wetting the titania support with an aqueous solution containing preformed rhodium nanoparticles. Among the three main crystalline forms (brookite, rutile and anatase), the anatase form was chosen, offering the possibility to apply the method to photocatalysis.

Based on the method we have developed for silica-supported nanoparticles, the immobilization of rhodium(0) nanoparticles on titania has been performed from our previously reported aqueous colloidal rhodium(0) suspension prepared by chemical reduction of an aqueous solution of rhodium chloride salt in the presence of highly hydrosoluble ammonium chloride salts as stabilizing agents (Fig. 1).[16–18] Then, the addition of an adequate amount of titania under vigorous stirring leads to the nanoparticle adsorption on the support. The color change from black to colorless evidences the total adsorption of the metallic nanospecies on the titania surface. After filtration, the grey powder was washed several times with clean water and dried overnight at 60 °C. The metal loading of the nanomaterials was determined by ICP analysis as 0.09 wt% and corresponds to the expected one. Our method combines a one pot stabilization of metallic nanospecies and their deposition onto the inorganic support at room temperature, under air, without gas treatment or calcination step.

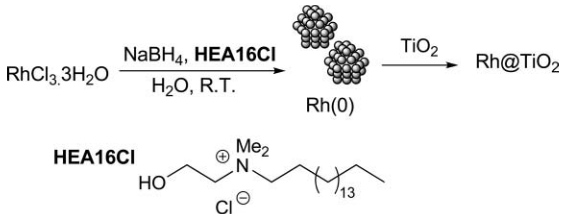

Fig. 1 One pot synthesis of TiO_2-supported Rh(0) nanoparticles.

The obtained Rh@TiO_2 materials were characterized by High Resolution Transmission Electron Microscopy (HRTEM) and

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compared to TiO_2 to identify the location and the size of the rhodium(0) nanoparticles (Fig. 2).

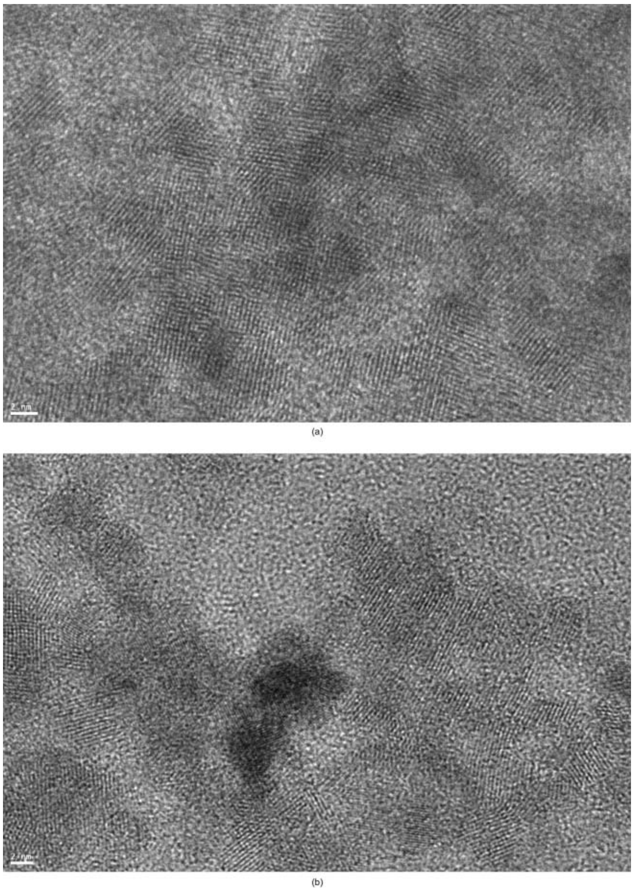

Fig. 2 HRTEM micrographs a) TiO_2 b) Rh@TiO_2. Scale bar is 2 nm.

The micrograph in Fig. 2b shows the presence of the rhodium(0) nanoparticles with an average size of 3–4 nm (zone contrasted), size very close to the anatase one. Analyses of the fast Fourier transformation (FFT) of the HRTEM images did not clearly reveal the presence of inter-reticular distances of 0.2196 nm and 0.1902 nm, which are characteristic of the (111) and (200) lattice planes of Rh(0). We mainly observed the interplanar distances of 0.352 and 0.233 nm corresponding to the (101) and (112) lattice planes of the anatase.

Due to the low metal loading of rhodium (0.09%) and the difficulties in observing it, the effective presence of the rhodium(0) nanoparticles was checked by Energy Dispersive X-ray spectrometry (EDX), as shown in Fig. 3 (red line), by focusing the electron beam at about 10 nm size. As an EDX spectrum obtained on an ultrathin section is very weak and generally polluted by a Cl signal from the resin, we have calculated the deconvolution of the Rh signal to prove its presence (blue line). Clearly, we observed the Cl signal at 2.62 keV near to the Rh signals at 2.696 and 2.834 keV. Moreover, these microtomy experiments of a cross section of titania spheres confirm the thorough diffusion of the surfactant-stabilized rhodium colloidal suspension into the titania matrix according to our silica methodology.[12]

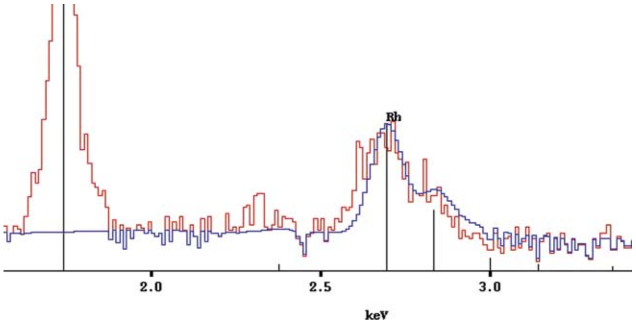

Fig. 3 EDX spectrum of rhodium species proved by deconvolution analysis.

The catalytic activity of the new supported nanomaterials Rh(0)@TiO_2 were evaluated in the hydrogenation of benzene and mono- or di-functionalized derivatives in water under two hydrogen pressures (1 or 30 bar H_2). The conversion was determined by gas chromatography analysis and the turnover frequency (TOF) was defined as the number of moles of consumed H_2 per mole of rhodium per hour. The results are gathered in Table 1. Moreover, the results are compared to those obtained in the hydrogenation of toluene with aqueous colloidal suspension of Rh(0) nanoparticles[17] and SiO_2-supported Rh(0) nanoparticles.[13]

Table 1 Hydrogenation of arene derivatives with TiO_2-supported Rh(0) nanoparticles[a]

Entry	Catalyst	Substrate	Product (%)[b]	P H_2/bar	t/h	TOF[c]/h^{-1}
1	Rh@TiO_2	Benzene	Cyclohexane (100)	1	0.7	476
2	Rh@TiO_2	Benzene	Cyclohexane (100)	30	0.01	33333
3	Rh@TiO_2	Toluene	Methylcyclohexane (100)	1	1.5	222
4	Rh@TiO_2	Toluene	Methylcyclohexane (100)	30	0.03	11111
5	Rh NPs[d]	Toluene	Methylcyclohexane (100)	1	5.7	53
6	Rh@SiO_2	Toluene	Methylcyclohexane (100)	1	2.3	163
7	Rh@TiO_2	Anisole	Methoxycyclohexane (100)	1	1.8	185
8	Rh@TiO_2	Anisole	Methoxycyclohexane (100)	30	0.07	4761
9	Rh@TiO_2	*o*-xylene	1,2-dimethylcyclohexane *cis* (90) *trans* (10)	1	4	83
10	Rh@TiO_2	*o*-xylene	1,2-dimethylcyclohexane *cis* (95) *trans* (5)	30	0.25	1333

[a] Reaction conditions: Rh@TiO_2 (1 g, 0.09 wt%, 9.6×10^{-6} mol), substrate (9.6×10^{-4} mol), H_2O (10 mL), RT. [b] Determined by GPC. [c] Turnover frequency defined as the number of moles of consumed H_2 per mole of rhodium per hour. [d] Rhodium aqueous colloidal suspension (3.8×10^{-5} mol).

The catalytic system Rh@TiO_2 is very active at atmospheric pressure whereas no hydrogenation occurred with TiO_2 alone, showing that Rh(0) nanoparticles are the active catalytic species. In all cases, with Rh@TiO_2 catalyst, the substrate is totally converted in the saturated product with quite interesting TOFs (entries 1, 3, 7, 9). The increase in substituents (benzene, toluene, xylene) seems to hamper the approach of the substrate towards the metallic nanospecies, decreasing the reaction rate (entries 1, 3, 9). The hydrogenation of *o*-xylene leads to the formation of 1,2-dimethylcyclohexane with a classical 90/10 *cis*/*trans* ratio, as already observed with heterogeneous catalysts[13,19] but also with nanoparticles in suspension.[16,17] In the hydrogenation of anisole (entry 7), no by-product such as phenol or cyclohexanone was detected, contrary to the aqueous colloidal suspension in which cyclohexanone was observed *via* the formation of an hemiacetal.[20] Compared to the surfactant-stabilized aqueous colloidal suspension (entry 5) or Rh@SiO_2 system (entry 6), higher TOF was obtained with Rh@TiO_2 (entry 3). The increase in hydrogen pressure to 30 bar (entries 2, 4, 8, 10) dramatically increases the catalytic activity, with TOF up to 33 333 h^{-1} in the case of benzene.

To check the efficiency of nanoparticle immobilization and the absence of leaching, recycling experiments were carried out with Rh@TiO_2 nanocatalysts in water at room temperature and under 1 bar H_2. The catalyst was recovered by simple filtration and dried at 60 °C before another run. The recycling experiments on three substrates (toluene, anisole, *o*-xylene) are reported in Fig. 4.

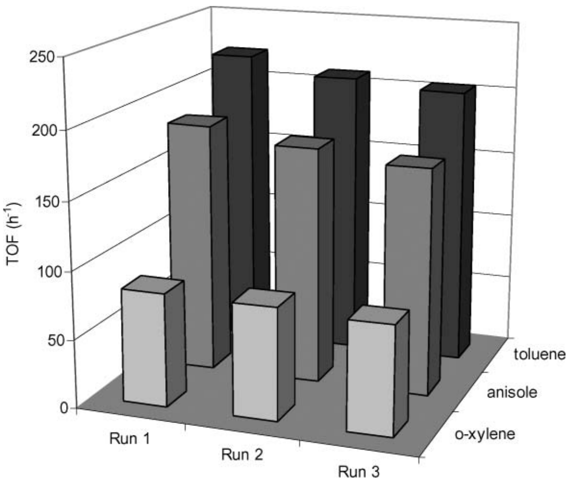

Fig. 4 Recycling experiments.

Whatever the substrate is, no significant loss of activity was observed, showing the efficient adsorption of the particles on TiO_2 support. Elemental analysis of the supported catalyst after hydrogenation indicates a same metal ratio, proving the absence of lixiviation.

In conclusion, we developed a simple procedure to prepare TiO_2-supported nanoparticles by wet impregnation from a surfactant-stabilized aqueous colloidal suspension under mild conditions without calcination step. The nanocatalysts proved to be very active in arene hydrogenations in neat water at atmospheric pressure with TOF up to 476 h^{-1}. Moreover, an increase in hydrogen pressure up to 30 bar leads to unprecedented TOFs up to 33 333 h^{-1}. The catalysts could be recycled without any loss of activity. These new nanomaterials supported on anatase, which is known for its higher photocatalytic activity than rutile,[21] are very promising candidates for use in photocatalytic processes and the mild conditions for the catalyst preparation prevent modification of the anatase structure which is a metastable form.[22]

Experimental section

a) Preparation of Rh@TiO_2

A suspension of titania (19 g) in 40 mL of deionized water is stirred vigorously for two hours. Furthermore, 50 mL of surfactant-stabilized Rh(0) suspension[17] (1.9×10^{-4} mol of Rh) are added under vigorous stirring. The system is kept under stirring for two hours. After filtration and three water washings, the grey powder is dried overnight at 60 °C. Anal. found: Rh, 0.09 wt%.

b) General procedure for hydrogenation under atmospheric hydrogen pressure

Reactions are carried out under standard conditions (20 °C, 1 atm of H_2). A 25 mL round bottom flask, charged with Rh@TiO_2 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 1500 min^{-1}. The reaction is monitored by gas chromatography. Turnover frequencies (TOFs) are calculated for 100% conversion.

c) 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 using a Carlo Erba GC 6000 with a FID detector equipped with a Factor Four column (30 m, 0.25 mm i.d.). 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).

Acknowledgements

We thank the Region Bretagne for financial support (Grant to C. Hubert) and the Université Européenne de Bretagne (UEB).

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