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Model arenes hydrogenation with silica-supported rhodium nanoparticles: The role of the silica grains and of the solvent on catalytic activities

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A B S T R A C T

Silica-supported rhodium-based nanoheterogeneous catalysts were easily prepared by impregnation with a pre-stabilized colloidal suspension. The resulting catalysts contain rhodium nanoparticles well-dispersed in the silica pores with a mean size of 5 nm. Influence of the silica grains size and of the solvent was investigated in arenes hydrogenation. It appeared that the size of the silica grains has a minimal influence on the reaction rate but the supported nanocatalysts displayed higher TOFs in hexane than in water.

1. Introduction

Transition-metal nanoparticle science is a strategic research area in material development due to their physical and chemical properties. In particular, the recent period has known a growing interest for the controlled synthesis of nanometric size metal species and their application in various academic or industrial areas. Compared with homogeneous catalytic systems, these nanospecies have for example proved to be efficient in the hydrogenation of arene derivatives [1]. From now on, noble metal nanoparticles constitute an unavoidable family of nanocatalysts for hydrogenation under mild conditions [2] at the border between homogeneous and heterogeneous chemistry, thus leading to the formation of key intermediates for fine chemistry [3].

For economical and environmental purposes, the catalyst recovery is of paramount importance in sustainable fine chemicals production. According to the approaches developed in homogeneous catalysis to easily recover catalysts; several techniques have essentially been developed through the heterogenization of the active species. In all cases, the first investigation is to immobilize the efficient species onto various support materials. This strategy offers the advantages to combine both high and specific activity with easy and environmentally friendly product separation.

In this context, the combination of metallic nanoparticles with a solid support provides a huge scope for the development of highly active and stable catalysts, which could potentially be recyclable [4]. Successful supported metal nanoparticles on inorganic oxides carriers are a mainstay of commercial heterogeneous catalysts and are employed in numerous industrial reactions [5] and fuel cell technologies [6]. Several authors have reported the development of supported metal nanoclusters on solid supports by methodologies such as adsorption [7], diffusion of pre-formed nanoparticles into pores via sonication [8], sol–gel [9], vapor-phase deposition of organometallic complexes [10]. Our methodology relies on the deposit onto an inorganic matrix of a pre-stabilized aqueous colloidal suspension, which has been well characterized in terms of organization and size [11]. Several authors have also reported modified wetness impregnation methods for the preparation of supported nanocatalysts [12]. In this paper, we describe the behaviour of pore-controlled silica-supported nanocatalysts in arenes hydrogenation. Particularly, we investigated the influence of solvents and grain sizes on the rate and kinetic effect in the hydrogenation of functionalized arene derivatives.

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2. Experimental

2.1. Starting materials

Rhodium chloride hydrate was obtained from Strem Chemicals. 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 method. The surfactant **HEA-16Cl** was prepared as previously described [13]. Two commercial silicas from Merck were used as received. They display similar physical properties (specific area: 500 m^2/g; porous volume: 0.8 cm^3/g; average pore diameter: 5.5 nm) but different grains sizes [80 μm (**Si80**) and 120 μm (**Si120**)].

2.2. Analytical procedures

2.2.1. TEM-analysis

After embedding of the sample in a resin (Spurr R1032) and treatment at 70 °C during one night for polymerization, the solid has been cut into thin lamellas (50 nm) with a microtom. A TEM-analysis was then realized after deposition of a lamella onto a carbon covered cupper grid using a Hitachi HU-12A 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" at Toulouse.

2.2.2. Gas chromatography

All 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.).

2.3. Synthesis of the aqueous rhodium(0) suspension

To an aqueous solution of surfactant HEA-16Cl (95 mL, 7.6×10^{-3} mol L^{-1}) sodium borohydride (36 mg, 9.5×10^{-4} mol) was added. Then, this solution was added under vigorous stirring to an aqueous solution (5 mL) of $RhCl_3$, $3H_2O$ (100 mg, 3.8×10^{-4} mol) to obtain an aqueous Rh(0) colloidal suspension (100 mL). The reduction occurs instantaneously as revealed 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 [13]).

2.4. Synthesis of the silica-supported rhodium nanoparticles

A suspension of silica (18.5 g) in 40 ml of deionized water was stirred vigorously during 2 h. Furthermore, 50 ml of Rh(0)-HEA-16Cl (1.9×10^{-4} mol of Rh) were added under vigorous stirring. The system was kept under stirring for 2 h. After filtration and three water washings, the grey powder was dried overnight at 60 °C. The rhodium loading of the materials were determined by ICP–AES in the CNRS center at Vernaison. Similar results were obtained before and after catalysis with 0.08 wt% of Rh showing the absence of metal leaching .These results were homogeneous what kind of silica used, namely **Si120** and **Si80**. In all cases, a reproducible value about 0.08 wt% was obtained by ICP-analysis near the theoretical value of 0.1 wt%.

2.5. General procedure for hydrogenation under atmospheric hydrogen pressure

Reactions were carried out under standard conditions (20 °C, 1 atm of H_2). A 25 ml round bottom flask, charged with SiO_2-supported Rh(0) catalyst (1 g, 10 ml of water) 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 filled with hydrogen. The appropriate aromatic substrate ([Substrate]/[Rh] = 100) was injected through the septum and the mixture stirred at 1500 min^{-1}. The reaction was monitored by gas chromatography analyses. Turnover frequencies (TOFs) were determined for 100% conversion.

3. Results and discussion

3.1. Preparation of silica-supported rhodium(0) nanoparticles

In opposition to classical preparation methods of supported nanocatalysts which involve repeated oxidation and reduction steps under severe conditions, our approach consists of the simple impregnation of silica particles using a pre-stabilized rhodium aqueous colloidal suspension.

Colloidal suspensions of rhodium nanoparticles were prepared by chemical reduction of an aqueous solution of $RhCl_3 \cdot 3H_2O$ in the presence of two equivalents of *N,N*-dimethyl-*N*-cetyl-*N*-(2-hydroxyethyl) ammonium chloride salt **1** as protecting agent (Fig. 1) [13]. Then, an adequate amount of silica was added to the colloidal suspension under vigorous stirring. The suspension coloration change from black to colorless evidences the quantitative adsorption of rhodium nanoparticles on the silica grains. After filtration, the surfactant was eliminated by water washings and the dark powder dried overnight at 60 °C, leading to silica-supported rhodium(0) nanoparticles as a fine grey powder. The metal loading of the composite materials was determined by ICP-analysis as 0.08 wt% whatever is the silica employed. This value corresponds well to the expected one showing that the metal is significantly deposited onto the silica support. During this preparation, all the steps were performed at room temperature, under air, without any gas treatment or calcination step. Two silica were used, namely **Si120** and **Si80**. These silica are quite similar in terms of specific area, porous volume and pores diameter (see § 2.1). The difference concerns the silica grains which are smaller for **Si80** than for **Si120** to estimate their impact during nanoparticles deposit, clustering and catalytic activities.

3.2. Catalytic activity in the hydrogenation of arene derivatives

3.2.1. Influence of the solvent and of the silica on the catalytic activity

We have examined the influence of several solvents (hexane, water, dichloromethane) in the hydrogenation of toluene as model substrate at room temperature and under atmospheric hydrogen pressure. The nature of catalytic species has previously been checked with mercury poisoning experiments. The results provide good evidence, in light of prior literature [13,14], that the Rh(0) nanoparticles are the true catalysts without leached molecular species. Consequently, nanoheterogeneous catalysts synthesized with silicas **Si80** and **Si120** were used to compare the influence of their grain size (80 μm and 120 μm, respectively).

The conversion was determined by gas chromatography analysis. The catalytic performances are reported in Table 1. The TOFs are defined as moles of H_2 consumed per moles of rhodium per hour.

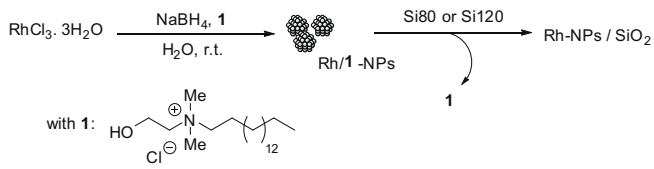
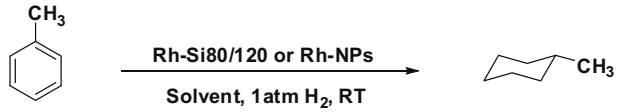


Fig. 1. Practical one-pot silica-supported rhodium nanoparticles synthesis.

Table 1
Influence of the solvent and the grain size of the silica in the catalytic hydrogenation of toluene.[a]



Entry	Catalyst	Solvent	Time (h)	Conv.[b] (%)	TOF (h^{-1})[c]
1	**Rh NPs**[d]	H_2O	5.7	100	53
2	**Rh-Si80**	H_2O	2.3	100	163
3	**Rh-Si120**	H_2O	2.5	100	150
4	**Rh-Si80**	Hexane	0.9	100	417
5	**Rh-Si120**	Hexane	0.83	100	452
6	**Rh-Si80**	CH_2Cl_2	5.5	31	21
7	**Rh-Si120**	CH_2Cl_2	5.5	33	23

[a] *Conditions.* Catalyst: 1 g of Rh-SiO_2, toluene, [S]/[M] = 100, 10 mL solvent, 1 atm H_2, RT.
[b] Determined by GC analysis.
[c] Turnover frequency defined as mol of H_2 per mol of rhodium per h.
[d] Rhodium suspension (3.8×10^{-5} mol).

In water, the total conversion of toluene was observed with higher TOFs (ca. 160 h^{-1}; Entries 2 and 3) than with the surfactant-stabilized aqueous suspension of rhodium nanoparticles (TOF = 53 h^{-1}, Entries 1). These results show the positive kinetic effect in aqueous media of the catalyst's heterogenization. However, dichloromethane does not constitute a good reaction medium for toluene hydrogenation since, only 24–30% conversion of toluene was achieved in 5.5 h in this solvent (Entries 6 and 7). Finally, very improved catalytic activity was obtained in hexane with a total conversion in methylcyclohexane and a TOF of 450 h^{-1} (Entries 4 and 5). Kinetic investigations have shown a linear variation of the conversion with time (25% and 50% in a reaction time of 12 and 25 mm, respectively) which corresponds to zero-order. Hexane is thus a good solvent compared to water. It may enable a better solubilization of substrate and product and also a better diffusion of the substrate towards the metallic surface. In the opposite, in water, the silica rhodium nanoparticles are surrounded by water molecules, slowing down the access of the lipophilic substrate to the metallic species. Besides these results, no significative difference was observed in terms of catalytic activity between the two supports **Si80** or **Si120** demonstrating that the silica grains size is not an important parameter in conditions used.

3.2.2. Hydrogenation of various arene derivatives in hexane and water

The catalytic study was extended to typical monofunctionalized and disubstituted arene derivatives, such as anisole and *o*-xylene, using Rh(0)-**Si80** and Rh(0)-**Si120** catalysts, in water and hexane (Table 2).

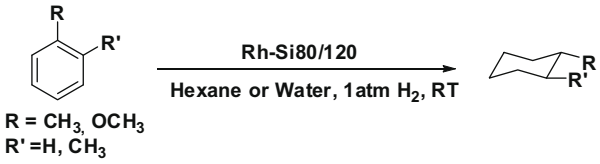
In all cases, whatever the silica and the solvent are, a total conversion of the substrate was observed. No real difference in catalytic activity was noticed between the two families of catalysts prepared with silica **Si80** and **Si120** showing here again the minimal influence of the silica grain size. As previously observed with toluene, for anisole and *o*-xylene hydrogenations, a better activity was obtained in hexane as in water due to better substrate solubility and a better diffusion to the active metal centers. In fact, TOFs are three times higher in hexane compared to water (Entries 5 and 7, 9 and 11). We obtained relevant TOFs (470 h^{-1}) in anisole hydrogenation without by-product such as phenol or cyclohexanone (Entries 5, 6). In all cases (Entries 9–12). The hydrogenation of *o*-xylene leads to the formation of 1,2-dimethylcyclohexane with a classical 92/8 cis/trans ratio for nanoheterogeneous catalysts A similar ratio (95/5) has already been observed with colloidal suspension of rhodium nanoparticles [13]. In comparison with monosubstituted substrates, reaction time for *o*-xylene hydrogenation significantly increased showing the steric hindrance impact.

3.3. Characterization of silica-supported rhodium(0) nanoparticles

Both silica-supported rhodium nanoparticle systems were characterized by TEM-analysis after microtomy preparation. The transmission electron micrographs and the particle size histograms obtained by observation of a cross section of silica spheres containing metal nanoparticles are shown on Fig. 2.

These experiments show that a well uniform diffusion of the surfactant-stabilized rhodium colloidal suspension in the silica matrix has occurred, leading to a homogeneous dispersion of rhodium particles with an average size of 5 nm. Whatever the grain size of silica is, we observed similar mean sizes and size distributions, thus justifying the low influence of the grain size during impregnation with the aqueous suspension. Compared to the size of the nanoparticles in the aqueous colloidal suspension (2.4 nm) [13], the particle size increase during the immobilization step, can be explained by their clustering inside the pores of the silica matrix, whose size is ca. 5.5 nm for the two silica studied. The

Table 2
Catalytic hydrogenation of arene derivatives in hexane and water with silica-supported rhodium nanoparticles.[a]



Entry	Substrate	Catalyst	Solvent	Product (%)[b]	Time (h)	TOF (h^{-1})[c]
1	Toluene	**Rh-Si80**	Hexane	Methylcyclohexane (100)	0.9	417
2	Toluene	**Rh-Si120**	Hexane	Methylcyclohexane (100)	0.83	452
3	Toluene	**Rh-Si80**	Water	Methylcyclohexane (100)	2.3	163
4	Toluene	**Rh-Si120**	Water	Methylcyclohexane (100)	2.5	150
5	Anisole	**Rh-Si80**	Hexane	Methoxycyclohexane (100)	0.8	469
6	Anisole	**Rh-Si120**	Hexane	Methoxycyclohexane (100)	0.8	469
7	Anisole	**Rh-Si80**	Water	Methoxycyclohexane (100)	2.5	150
8	Anisole	**Rh-Si120**	Water	Methoxycyclohexane (100)	2.5	150
9	*o*-Xylene	**Rh-Si80**	Hexane	1,2-Dimethylcyclohexane (cis/trans=92/8)	2.1	179
10	*o*-Xylene	**Rh-Si120**	Hexane	1,2-Dimethylcyclohexane (cis/trans=92/8)	2.1	179
11	*o*-Xylene	**Rh-Si80**	Water	1,2-Dimethylcyclohexane (cis/trans=92/8)	6.8	55
12	*o*-Xylene	**Rh-Si120**	Water	1,2-Dimethylcyclohexane (cis/trans=92/8)	7.5	50

[a] *Conditions.* Catalyst: 1 g of Rh-SiO_2, [S]/[M] = 100, 10 mL solvent, 1 atm H_2, RT, stirred at 1500 min^{-1}.
[b] Determined by GC analysis.
[c] Turnover frequency defined as mol of H_2 per mol of rhodium per h.

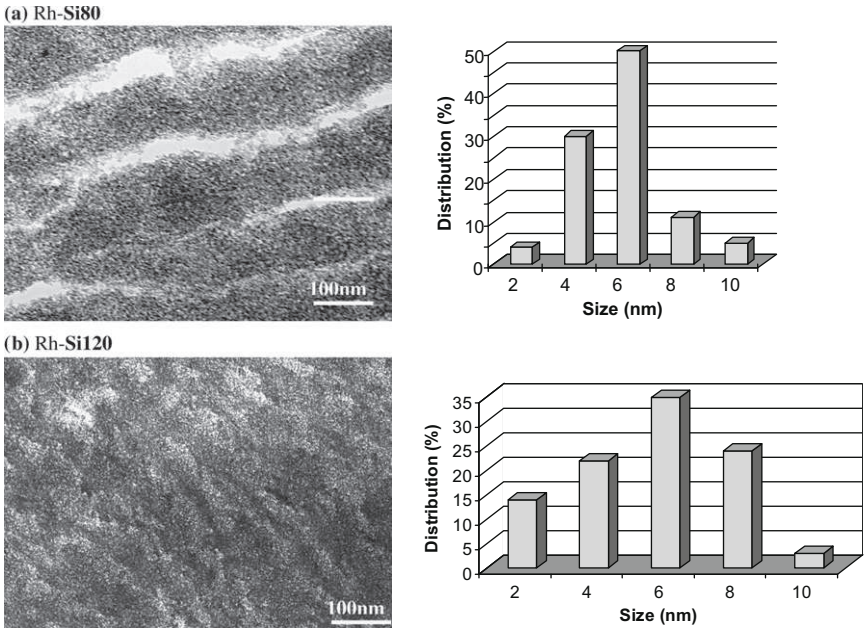


Fig. 2. Transmission electron microscopy of silica-supported rhodium nanoparticles performed on the central zone at 120 kV. Micrograph and metal size distribution of (a) Rh-Si80 and (b) Rh-Si120.

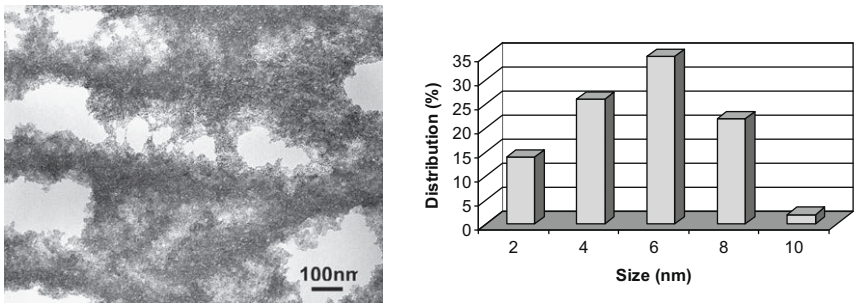


Fig. 3. TEM of Rh-Si120 after catalysis.

pores size of the matrix controls thus the rhodium nanoparticles size and further their catalytic activities in hydrogenation reactions.

To check the efficiency of the nanoparticles immobilization and the absence of leaching, recycling experiments were performed with silica-supported nanocatalysts **Rh-Si80** and **Rh-Si120** in toluene hydrogenation in both hexane and water at 20 °C and under 1 atm H_2. The catalyst was recovered by simple filtration and dried at 60 °C before another run with new addition of substrate. No significant loss of activity in both solvents was observed, showing the efficient adsorption of the particles on the silica and the reusability of our system. Similar catalytic lifetimes of silica-capped rhodium nanoparticles for model arenes hydrogenation have already been reported in a previous study [11]. Finally, TEM-analysis of Rh-**Si120** sample (Fig. 2b) after recycling showed no modification in particle size, with a similar average size of 5 nm (Fig. 3). This observation justifies the narrow catalytic activity observed in the second run.

4. Summary

In conclusion, we developed a simple procedure to synthesize silica-supported rhodium nanoparticles by wet impregnation from a surfactant-stabilized aqueous colloidal suspension. Catalysts were prepared without calcination step. The nanoclusters are well-dispersed with a homogeneous mean size of 5 nm controlled by the pores size of the silica. The obtained activities can be explained with the very homogeneous size dispersion of rhodium particles inside silica pores probably due to the initial surfactant-stabilization allowing a better control of the particle size in contrast with traditional supported catalysts which are usually concentrated on a localised area of the support. Indeed, a recent study has shown the influence of surfactant for dispersions of rhodium in mesoporous aluminosilicates [15]. Finally, they display an interesting activity in arenes hydrogenation in hexane and can be reused in successive runs. We also observed no real influence of silica grain size on the catalytic activity.

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