

New approach for the preparation of well defined Rh and Pt nanoparticles stabilized by phosphine-functionalized silica for selective hydrogenation reactions

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In this work, a new methodology for the synthesis of well defined metallic nanoparticles supported on silica is described. This methodology is based on the surface control provided by SOMC. The nanoparticles are formed via the organometallic approach and are catalytically active in the hydrogenation of *p*-xylene, 3-hexyne, 4-phenyl-2 butanone, benzaldehyde, and furfural.

Nowadays, the synthesis of well defined metallic nanoparticles (M-NPs) has become a major challenge since they are utilized in a variety of fields with applications in biomedicine, optical electronics and catalysis.¹ M-NPs are constituted by several metallic atoms, possess a nanometric scale (1-100 nm of diameter)² and can be stabilized by a wide range of compounds such as polymers, surfactants, ionic liquids, silane³ or electron donor ligands.⁴ The main disadvantage when dealing with soluble nanoparticles in catalysis is the loss of activity caused by agglomeration and the impossibility of their recycling and reuse. The use of supported catalysis is therefore required to ensure the sustainability of the processes. Several approaches were reported for the immobilization of metal nanoparticles such as impregnation, co-precipitation or deposition.⁵ Nevertheless, low control on the size and distribution of the supported species is often observed following these methodologies. For example, classical impregnation on conventional supports usually provides various dispersions of the metal and the size of the obtained species can be limited by the pore size of the supports.⁶ Surface Organometallic Chemistry (SOMC) is an established methodology that affords well defined heterogeneous catalysts through the grafting of organometallic species on surface hydroxyls of classical supports such as alumina, silica, mesoporous silica, silica-alumina, etc...⁷ On the other hand,

phosphorus based ligands have been extensively used in homogeneous catalysis and recently, their use as efficient stabilizers of soluble Pd, Ru, Ir and Rh nanoparticles was reported.^{8,9,10,11,12} These catalysts have controllable size and shape and show interesting activities and selectivities in various catalytic reactions. It was therefore thought that the treatment of the support by efficient M-NPs stabilizing groups through SOMC could provide well defined and monodispersed materials.

Several examples of supported metallic nanoparticles on silica are reported in the literature.¹³ However, in this work, a new methodology combining the surface control provided by SOMC and the advantages of the organometallic approach is described, producing supported nanoparticles with controlled size, shape and environment. The catalytic performance of the resulting materials was examined in the hydrogenation of *p*-xylene, 3-hexyne, 4-phenyl-2-butanone, benzaldehyde, and furfural. This latter substrate is an abundant feedstock derived from biomass.¹⁴

Initially, the silica supported rhodium nanoparticles were synthesized under the conditions previously reported for non-supported systems.¹² The amount of rhodium was calculated as 5 wt%, in analogy with the classical heterogeneous supported catalysts. The rhodium precursor [Rh(η^3 -C₃H₅)₃] was reduced under 4 bar of hydrogen at 40 °C in the presence of triphenylphosphine (PPh₃) and silica previously dehydroxylated at 700 °C (SiO₂₋₇₀₀) (Figure 1). The solution turns black after a few hours and after washings with pentane and drying under vacuum, the material **Rh-NPs@SiO₂** was obtained.

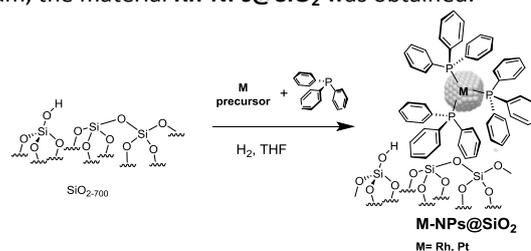


Figure 1 Scheme of the synthesis of silica supported rhodium PPh₃ stabilized NPs M-NPs@SiO₂.

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According to TEM analysis, the nanoparticles **Rh-NPs@SiO₂** were formed with spherical shape, a mean size of 2.55 ± 0.42 nm and moderate distribution (Figure 2, left).

Based on the size obtained by TEM and the VHH model,¹⁵ it was calculated that 45 % of the rhodium atoms are at the surface of these nanoparticles. A corresponding experiment in the absence of silica provided nanoparticles with smaller size and narrower distribution (1.52 ± 0.21 , Figure S5). Note that **Rh-NPs@SiO₂** contains a small fraction of formed nanoparticles with no interaction with the support (Figure 2, right). The same methodology was applied to obtain platinum nanoparticles (Figure 1). The organometallic precursor Pt(dba)₃ was reduced in THF under 3 bar of H₂, at 25 °C in the presence of PPh₃ and silica previously dehydroxylated at 700 °C (SiO₂₋₇₀₀). The solution darkened after a few hours. The resulting material, **Pt-NPs@SiO₂**, was then washed three times with pentane. After evacuation of the volatiles and drying under vacuum, a brown powder was obtained. TEM microscopy confirmed the formation of the platinum nanoparticles **Pt-NPs@SiO₂** that exhibited spherical shape and a narrow size distribution, with a mean diameter of 1.60 ± 0.40 nm (figure S7). However, as previously observed for rhodium, some metal particles were observed outside the support.

The synthesis of the nanoparticles **Rh-NPs@SiO₂** and **Pt-NPs@SiO₂** stabilized by PPh₃ in silica₇₀₀ was thus completed. However, the presence of supported and unsupported NPs in both cases was expected to constitute an issue in catalysis.

In view of these results, it was thought that the appropriate functionalisation of the support could overcome this issue.

Recently, a method was used for the anchoring of functionalized groups on silica surface, leading to new hybrid materials used as supports.¹⁶ Since phosphines efficiently stabilized such Rh NPs, the use of a silica support containing grafted triphenylphosphine units at the surface was explored. The use of such material as catalyst was recently published by our groups.¹⁷ This functionalized support, defined in this work as **P-SiO₂**, was therefore used for the grafting of the rhodium nanoparticles. Initially, [Rh(η^3 -C₃H₅)₃] and Pt(dba)₃ organometallic precursors were reduced under the same previously described conditions in the presence of the phosphine modified silica **P-SiO₂**. TEM measurements confirmed the formation of the nanoparticles. However, a significant increase in size was observed for both systems, *ca.* 4 nm for Rh and 1.9 nm for Pt (see S3). Moreover, some degree of agglomeration was detected. It was concluded that the high dispersion of phosphine at the surface could not ensure an efficient stabilization of the nanoparticles alone.

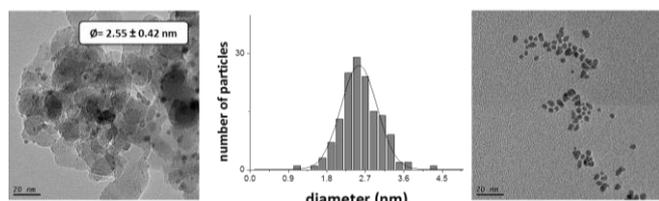


Figure 2 TEM micrographs and size distribution of nanoparticles Rh-NPs@SiO₂. (20 nm scale bar)

To enhance the nanoparticles stabilization, triphenylphosphine ligand was added in addition of the phosphine contained on the support. The phosphine modified silica support **P-SiO₂**, excess triphenylphosphine and [Rh(η^3 -C₃H₅)₃] were placed in THF and treated overnight under 4 bar of hydrogen at 40 °C. The solution turned black after a few hours. Washings with pentane were performed and after evacuation of the volatiles a black powder corresponding to the material **Rh-NPs@P-SiO₂** was obtained.

The new material **Rh-NPs@P-SiO₂** was characterized by TEM (Figure 3) and a homogeneous distribution of the nanoparticles on the support was observed. It is noteworthy that for this sample, all the NPs detected were situated onto the **P-SiO₂** support, in contrast with the results obtained for unfunctionalized silica (Figure 2). In addition, using this new strategy, NPs with spherical shape, a mean diameter of 1.17 ± 0.18 nm and narrow size distribution were obtained. Interestingly, the supported NPs were slightly smaller than the non-supported analogous previously reported (1.5 nm),¹² indicating the potential stabilizing role of the phosphine modified silica surface **P-SiO₂**. This result is in agreement with previous reports describing that supported nanoparticles are usually smaller than the corresponding unsupported systems.¹⁸

The material was also analyzed by ³¹P CP MAS solid state NMR, revealing a main signal at 21 ppm, a small resonance at 26 ppm and a very broad signal at 42 ppm (Figure S8). The chemical shift of the main peak was attributed to Rh coordinated phosphorus atoms surrounded by phenyl moieties based on reported data.¹⁹ However, a contribution of the oxidized form of the stabilizing ligand could be present in this broad band as previously observed for ruthenium nanoparticles.²⁰ The broad signal at 42 ppm could correspond to partially reduced ligand interacting with the nanoparticles (Figure S8). Hydrogenation of the stabilizing ligands and stabilization by their oxidized form were previously reported for rhodium and ruthenium nanoparticles.^{21,22} Significantly, the peak corresponding to the **P-SiO₂** at *ca.* -6 ppm was not observed, revealing the complete interaction of the phosphine anchored to the support with the rhodium nanoparticles. The elemental analysis of this material revealed a content of 1.27 wt% in phosphorus and 4.36 wt% in rhodium. Based on the VHH model,¹⁵ the **Rh-NPs@P-SiO₂** system contains 76 % of the Rh atoms at their surface. This value is considerably higher than that of the non-modified silica **Rh-NPs@SiO₂** (45%).

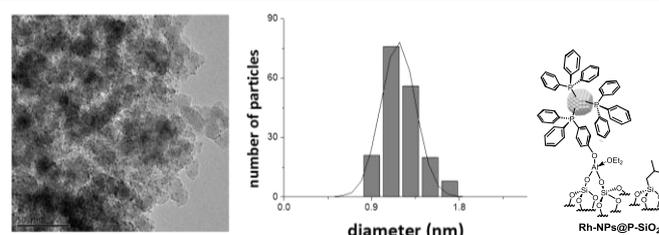


Figure 3 TEM micrograph and size distribution of nanoparticles Rh-NPs@P-SiO₂, scheme of the material. (50 nm scale bar)

The same procedure was employed for the synthesis of the corresponding platinum nanoparticles with 5 wt% in metal. The organometallic precursor $\text{Pt}(\text{dba})_3$ was reduced in THF under 3 bar of H_2 at 25 °C in the presence of PPh_3 and the material P-SiO_2 . The solution turned dark after a few hours. The resulting material Pt-NPs@P-SiO_2 was then washed with pentane and dried under vacuum. A brown powder was obtained. TEM microscopy confirmed the formation of the platinum nanoparticles Pt-NPs@P-SiO_2 homogeneously distributed on the support. These NPs exhibited spherical shape, a diameter of 1.47 ± 0.25 nm and a narrow size distribution (Figure S9). All the NPs detected were onto the support. The material Pt-NPs@P-SiO_2 was also characterized by solid state NMR spectroscopy (Figure S10). The elemental analysis of this material revealed a content of 0.61 % in phosphorus and 3.46 % in platinum. The number of surface atoms for the Pt-NPs@P-SiO_2 is of 68 %, which smaller than the Rh system due to the slightly larger diameter of these nanoparticles.

These results indicated that the phosphine anchored on the silica support plays an important role in the stabilization of both Rh- and Pt-NPs. The synthesis of the nanoparticles described in this work can therefore be considered an optimal methodology to obtain controlled systems of supported nanoparticles of small size and well distributed.

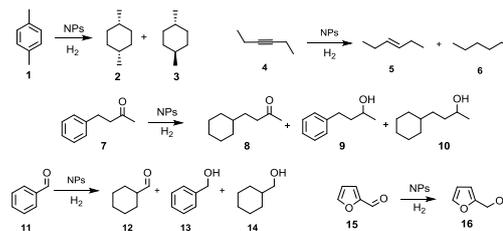
To evaluate their catalytic performance, the supported nanoparticles Rh-NPs@P-SiO_2 and Pt-NPs@P-SiO_2 were tested in the hydrogenation of *p*-xylene, 3-hexyne, 4-phenyl-2 butanone, benzaldehyde, and furfural. The reactions were carried out at 80 °C under 40 bar of H_2 during 4h using 2 mol % catalyst. The preliminary results using *p*-xylene **1** as substrate are summarized in table 1.

When the rhodium nanoparticles Rh-NPs@P-SiO_2 were used, full conversion was obtained under these conditions (entry 1). The products were detected by GC-MS in a 58/42 *cis/trans* ratio. In contrast, the platinum catalyst only provided 32 % conversion but with total selectivity to the *cis* product, in agreement with reported results (entry 10).²³

The Rh-NPs@P-SiO_2 catalyst was therefore more active than the Pt-NPs@P-SiO_2 counterpart and in both cases, the *cis* isomer was the preferred product. However, the platinum system only formed this product. No partially hydrogenated products were obtained using these catalysts, in contrast with previous work on colloidal phosphine stabilized rhodium nanoparticles.¹²

In view of the high activity of the Rh-NPs@P-SiO_2 catalyst, a recyclability test was performed. The catalyst was reused (entries 2 and 3), observing a slight decrease in the conversion after the third run (entry 3), no significant differences in terms of selectivity were detected. Additionally, the stability of the system was studied: after the third run, the catalyst was filtered and more substrate was added to the remaining solution, and the same catalytic conditions were applied (entry 4). The metal leaching in the solution was also measured by ICP OES as <0.035 ppm, confirming no Rh leaching during catalysis. In this experiment, no conversion was observed, indicating the absence of leached nanoparticles in solution.

Table 1 Catalytic hydrogenation using the supported Rh and Pt-NPs.



entry	NPs	Subs.	% Conv.	% a ^a	% ket.	% full hyd.	(Cis/Trans) ^b
1	Rh-NPs@P-SiO ₂	1	100	-	-	100	58/42
2	Rh-NPs@P-SiO ₂	1	100	-	-	100	61/39
3	Rh-NPs@P-SiO ₂	1	95	-	-	100	62/38
4	-	1	0	-	-	-	-
5	Rh-NPs@P-SiO ₂	4	100	-	-	100	-
6	Rh-NPs@P-SiO ₂	7	97	5	53	42	-
7	Rh-NPs@P-SiO ₂	11	99	-	97	3	-
8	Rh-NPs@P-SiO ₂	15	16	-	100	-	-
9	Pt-NPs@P-SiO ₂	1	32	-	-	100	100/0
10	Pt-NPs@P-SiO ₂	7	100	-	87	13	-
11	Pt-NPs@P-SiO ₂	15	100	-	100	-	-

General conditions: 2 mol % NPs, 2 ml of heptane, T = 80 °C, P = 40 bar H_2 , t = 4 h; Determined by GC. ^a% a: amount of product from the hydrogenation of the arene group; % ket.: % of product from the hydrogenation of the ketone group; % full hyd.: amount of fully hydrogenated product; ^bCis/trans selectivity

When 3-hexyne **4** was tested as substrate (entry 5), full conversion was observed and the only product detected was hexane **6**. Next, the substrate 4-phenyl-2 butanone **7**, which contains two reducible groups, namely a ketone and an aromatic ring, was tested using both catalysts. The results obtained are summarized in Table 1 (entries 6 and 10). When the rhodium nanoparticles Rh-NPs@P-SiO_2 were used, almost full conversion was obtained (97%) providing 53 % of 4-phenyl-2 butanol **9**, 42 % of the completely reduced product **10** and only 5 % of the cyclohexylketone derivative **8**. It was concluded from this results that there was no significant preference for the hydrogenation of the ketone or that of the aromatic ring using this Rh catalyst. Using the platinum catalyst, full conversion was observed with 87 % selectivity for 4-phenyl-2-butanol **9** and 13 % to the completely hydrogenated product **10**. No traces of the cyclohexyl derivative **8** were detected using this catalyst. In the case of the platinum catalyst, there is clearly a preference for the hydrogenation of the ketone group over that of the aromatic ring. Benzaldehyde **11**, that contains an aromatic and an aldehyde was used as substrate with the Rh system (entry 7). In this case, excellent conversion (99 %) was observed with preferential hydrogenation of the aldehyde group, producing benzyl alcohol as main product (97 %). In view of the selectivity obtained with these systems as catalysts, the more challenging substrate furfural **15** was

tested.¹⁴ The hydrogenation of furfural can provide furfuryl alcohol that is an important precursor in the synthesis of a wide variety of chemicals.²⁴ The selective formation of this product by hydrogenation of furfural is still a challenge. Several authors have explored the modification of supported catalysts by tuning the size, shape, supports and surface modifiers to promote this selectivity. For example, the modification of silica supported Pt nanoparticles with Sn improves the selectivity from 36 to 98 % to furfuryl alcohol **16** by poisoning the sites responsible for the side reactions.²⁵

In this work, we investigated whether the phosphine units present in our systems could have an analogous effect. Both systems showed remarkable selectivities to the desired product (Table 1, entries 8 and 11), showing a beneficial effect of the phosphorus present in our systems. Both catalytic systems provided total selectivity to furfuryl alcohol **16** although **Rh-NPs@P-SiO₂** provided lower conversion (16 %) than the **Pt-NPs@P-SiO₂** system that fully converted the substrate under the same conditions.

In conclusion, a new methodology for the preparation of silica supported rhodium and platinum nanoparticles has been successfully developed using a phosphine functionalized support prepared by SOMC methodology. The NPs were synthesized in a one-pot manner using the organometallic approach. The characterization of these systems showed a homogeneous distribution of the metallic nanoparticles on the support, exhibiting a small size of ca. 1.2 and 1.5 nm for Rh and Pt respectively.

These new supported systems were active in the hydrogenation of aromatics and ketones. Remarkably, promising results were obtained for the selective hydrogenation of furfural to furfuryl alcohol, with high activities in the case of the Pt catalyst. The phosphine stabilized moiety could play an important role in the selectivity of this reaction by blocking some surface sites.

This new approach to surface organometallic chemistry will thus pave the way to a wealth of new directions in well-defined heterogeneous catalysts, and contribute to the development of catalytic systems of improved performances compared to the current state-of-the-art.

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