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Introduction

Among metal catalyzed reactions, rhodium represents one of the most versatile and active metal catalysts in a plethora of transformations.¹ In the field of metal nanoparticles (MNPs), the activity attained by rhodium is related to its great π -acidic character, applied in the activation of dihydrogen and in hydrogenation reactions.² The use of stabilizers of MNPs to avoid the formation of bulk metals can increase the selectivity towards the hydrogenation of different functional groups.^{3–7} Ligands, polymers, non-conventional media and a combi-

RhNPs supported on *N*-functionalized mesoporous silica: effect on catalyst stabilization and catalytic activity[†]

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Amine and nicotinamide groups grafted on ordered mesoporous silica (OMS) were investigated as stabilizers for RhNPs used as catalysts in the hydrogenation of several substrates, including carbonyl and aryl groups. Supported RhNPs on functionalized OMS were prepared by controlled decomposition of an organometallic precursor of rhodium under dihydrogen pressure. The resulting materials were characterized thoroughly by spectroscopic and physical techniques (FTIR, TGA, BET, SEM, TEM, EDX, XPS) to confirm the formation of spherical rhodium nanoparticles with a narrow size distribution supported on the silica surface. The use of nicotinamide functionalized OMS as a support afforded small RhNPs (2.3 \pm 0.3 nm), and their size and shape were maintained after the catalyzed acetophenone hydrogenation. In contrast, amine-functionalized OMS formed RhNP aggregates after the catalytic reaction. The supported RhNPs could selectively reduce alkenyl, carbonyl, aryl and heteroaryl groups and were active in the reductive amination of phenol and morpholine, using a low concentration of the precious metal (0.07–0.18 mol%).

nation of two or more of these stabilizers impact the catalytic activity and selectivity observed in colloidal rhodium nanoparticles.^{4,5} Varying the rhodium nanoparticle setup favors the formation of anilines from nitroarene,^{8–10} secondary aryl alcohols from acetophenone¹⁰ and the complete hydrogenation of aryl derivatives,⁷ to name a few examples.

Despite the great performance of RhNPs in colloidal systems, their actual industrial application requires ease of separation and recyclability of the RhNPs, enabled when the nanoparticles are supported on solids.² RhNPs have been supported over amorphous to highly ordered materials (graphene, CNTs, mesoporous inorganic oxides). Other types of MNP approaches have used the architecture of ordered mesoporous materials (OMS) in order to form ultrafine metal nanoparticles.^{11,12} The most common methodologies used to support MNPs comprise impregnation (wet or dry), deposition/ precipitation or laser deposition, whilst chemical methods make use of the infiltration of metal salts in OMS followed by a reaction with borohydrides, urea or hydrazine to reduce the metal salts. The advantages of supporting MNPs include stability towards sintering,13-15 as well as an active role in the catalytic transformation, among other possibilities that to date are the focus of several investigations both in industry and academia. Overall, the catalytic performance of the supported MNPs



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[†]Electronic supplementary information (ESI) available: Characterization spectra of NAM (NMR, 2D), silicas (TGA, IR, BET), and RhNPs (IR, TGA, BET, SEM, TEM, XPS, EDX) and the tables of selected catalytic reactions. See DOI: 10.1039/ d0dt04213g

strongly depends on the nature of the interaction of MNPs with the support and solvent.^{16–18} Thus, RhNPs can be found within the pores of ordered mesoporous supports (OMS) showing remarkable activity.

Regarding the catalytic applications, rhodium has been immobilized on silica type MCM (Mobil Composition of Matter No. 41) by an ionic exchange reaction of Rh(III) with the template cation,¹⁹ and more recently an organometallic chemistry approach was used to support RhNPs with phosphine ligands grafted on silica.²⁰ One important challenge to address is the formation of stable metal nanoparticles that do not change throughout the catalytic reactions to extend the shelf life. The robustness of the supported RhNPs has been assessed by studying the recyclability of the catalyst through several catalytic runs, or by observing morphological changes on the catalyst after the reaction.

Among the catalytic applications of supported RhNPs, it is possible to obtain important products such as amines through a sustainable catalysis approach using one-pot methodologies (Scheme 1). In this regard, the production of amines from nitroarenes and benzaldehydes (I in Scheme 1),21,22 or from amines and phenols (II in Scheme 1), 2^{23} has been explored. Moreover, the selective hydrogenation of phenol to cyclohexanone by RhNPs is favored by specific sites of rhodium nanoparticles. It is crucial to control the reactivity of the RhNPs' sites that could favor the complete hydrogenation of aryl groups. The latter was demonstrated by the use of substituted triethoxysilanes grafted onto silica that bond to RhNPs selectively, deactivating them towards aryl hydrogenation.¹⁶ In this regard, thiolate and amine groups grafted onto RhNP-silica catalysts could modulate the selectivity towards the partial hydrogenation of phenol to cyclohexanone in 8-10 hours (TOF 14 h^{-1} calculated as mmol of cyclohexanone × (mmol of $Rh \times h)^{-1}$).

Given the efforts towards the development of active and stable catalysts based on RhNPs supported on ordered mesoporous materials, in the present work a methodology for the preparation of RhNPs based on our previous experience in the formation of colloidal RhNPs is proposed.^{9,10,24} The catalytic systems were prepared through the controlled reduction of a well-defined and readily prepared complex [Rh(μ -OMe)(1,5-COD)]₂ with dihydrogen in the presence of *N*-functionalized silicas. Considering that the selectivity in hydrogenation reac-



Scheme 1 One-pot methodologies to produce amines.

tions by supported RhNPs is influenced by the coordinating groups grafted on silica supports and that partial removal of these groups by pyrolysis is needed to afford active and selective catalysts, an approach without thermal treatment is proposed. In this regard, amine or pyridine functional groups grafted on the surface of silica were evaluated towards the stabilization of RhNPs after the catalytic hydrogenation of different functional groups as well as multistep transformations, with the focus on the selectivity and the recyclability of the catalytic systems.

Experimental

General

All manipulations were carried out under a dry, oxygen-free nitrogen atmosphere using standard Schlenk techniques. Organic solvents were distilled from an appropriate desiccant under a nitrogen atmosphere and stored over activated 3 Å molecular sieves. Unless otherwise stated, all reagents were acquired from commercial suppliers and used as received. The precursor methoxy(1,5-cyclooctadiene)rhodium(1) dimer [Rh $(\mu$ -OMe)(1,5-COD)]₂ was prepared following a previously reported method.²⁵ Infrared spectra were recorded on a PerkinElmer FTIR/FIR Spectrum 400 spectrometer. ¹H NMR, {¹H} COSY (Correlation Spectroscopy), ¹³C{1H}, 2D ¹H-¹³C HSOC (Heteronuclear Single-Quantum Correlation spectroscopy) and 2D ¹H-¹³C HMBC (Heteronuclear Multiple Bond Correlation spectroscopy) spectra were recorded on a Varian VNMRS spectrometer at 9.4 T (400.13 MHz for ¹H) and chemical shifts (δ , ppm) were calibrated relative to the residual solvent peak. Thermogravimetric analysis (TGA) data were recorded on a PerkinElmer TGA 4000 analyzer from room temperature to 900 °C with a speed of 1 °C min⁻¹. For surface area analysis a Micromeritics TriStar 3000 surface area and pore size analyzer was used to obtain nitrogen physisorption isotherms at 77 K on the synthesized silicas; the data were fit using a Brunauer-Emmett-Teller (BET) model to determine the apparent surface areas of the materials. The average pore diameter and cumulative pore volumes were calculated using the Barrett-Joyner-Halenda (BJH) model for mesopores and the Non-Local Density Functional Theory model for micropores (Tarazona NLDFT, Cylindrical Pores, E_{sf} = 30.0 K). Samples were degassed under vacuum at 130 °C for 18 h prior to the analysis. Scanning electron microscopy (SEM) images of the synthesized materials were obtained on a JEOL JSM-5900-LV microscope. The particle diameter was determined by counting at least 100 individual particles with the software package Digimizer 4.6.1.²⁶ High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and transmission electron microscopy (TEM) bright field images of the synthesized materials before and after recycling were obtained on a JEOL ARM200F microscope operating at an accelerating voltage of 200 kV. Nanoparticle measurements were performed with the software package DigitalMicrograph 3.30.2017.0.27 X-Ray photoelectron spectroscopy (XPS)

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measurements were performed using a Thermo Scientific K-Alpha spectrometer, with a MAGCIS ion source for depth profiling analysis and surface cleaning. The assignment of the chemical components of core level Rh 3d was made by comparison to the referenced values reported in the literature.^{28–30} The synthesis of supported rhodium nanoparticles was carried out in a 100 mL Fisher-Porter vessel. Microwave Plasma Atomic Emission Spectroscopy (MP-AES) was used to determine the Rh content on the samples before and after catalytic experiments and was performed on an Agilent MP-AES 420 equipment, after digesting the sample with nitric acid and microwaves (CEM MDS 2000). Catalytic reactions were performed in a Parr Multi Reactor 500 system. Catalytic conversions were determined on a Varian 3800 gas chromatograph with a capillary column DB-WAX (30 m \times 0.32 mm \times 0.25 mm) coupled to an FID detector, using decane as an internal standard.

Synthesis of N-(3-(triethoxysilyl)propyl)nicotinamide (NAM)

This compound was synthesized according to a previous report³¹ with some modifications. In a Schlenk vessel, nicotinic acid (1.99 g, 16.10 mmol) was cooled in an ice bath under a nitrogen atmosphere for 10 min. Subsequently, thionyl chloride (5 mL, 68 mmol) was added dropwise at 0 °C. The resulting mixture was stirred for 24 h at 25 °C. The respective acid chloride was obtained as a white solid after the removal of volatiles under reduced pressure and was used without any further purification. A suspension of the corresponding acid chloride in dry THF (60 mL) under nitrogen at 25 °C was treated with (3-aminopropyl)triethoxysilane APTES (3.8 mL, 16.23 mmol) and triethylamine (7 mL, 50.2 mmol). After the addition, the mixture was heated at reflux temperature and stirred for 24 h. The reaction mixture was cooled to room temperature, and the suspension was filtered through a fritted funnel under nitrogen, obtaining an orange solution. After the removal of all volatiles at reduced pressure, a highly viscous orange oil was obtained. Yield (4.27 g, 81%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.98 (1H, s, *Py*), 8.64 (1H, dt, ^{3,4} $J_{H,H}$ = 4.7, 1.3 Hz, Py), 8.12 (1H, dq, ${}^{3,4}J_{H,H}$ = 7.9, 1.6 Hz, Py), 7.37-7.32 (1H, m, Py), 7.14 (1H, br, (-CO)-NH-), 3.77 (6H, qd, ${}^{3,4}J_{\rm H,H}$ = 7.0, 0.9 Hz, $-SiO-CH_2-CH_3$), 3.43 (2H, q, ${}^{3}J_{\rm H,H}$ = 6.3 Hz, -CH₂-NH(CO)-), 1.73 (2H, p, ³J_{H,H} = 7.1 Hz, Si-CH₂-CH₂-CH₂-), 1.16 (9H, td, ${}^{3,4}J_{H,H}$ = 7.0, 0.9 Hz, $-SiO-CH_2-CH_3$), 0.66 (2H, t, ${}^{3}J_{H,H}$ = 7.9 Hz, $-Si-CH_{2}-CH_{2}-$). ${}^{13}C$ NMR (101 MHz, CDCl₃) δ (ppm): 165.60 (*C*=*O*), 151.74 (*C*_{Pv}), 148.03 (*C*_{Pv}), 135.05 (C_{Py}), 130.56 (C_{Py}), 123.30 (C_{Py}), 58.40 (CH_2), 42.30 (CH₂), 22.71 (CH₂), 18.18 (CH₃), 7.77 (CH₂). These data were consistent with the previous report³¹ and were confirmed with 2D NMR experiments (ESI S1-S5[†]).

General synthesis of *N***-functionalized mesoporous silica.** Silica MCM-41 type was synthesized according to a previous report³² with some modifications. In a 1 L plastic container, cetyltrimethyl ammonium bromide CTAB (1.0 g, 2.74 mmol) was dissolved in 500 mL of deionized water, stirred for 15 min and sonicated for another 30 min. Subsequently, 2 M NaOH solution (3.5 mL, 7 mmol) was added to CTAB solution and stirred for 5 min. Tetraethyl orthosilicate TEOS (5 mL, 23.8 mmol) was then added using a syringe pump with a speed of 3 mL h^{-1} under vigorous stirring. After the addition, the solution was heated at 80 °C for 2 hours and stirred for another 12 h at room temperature. The resulting suspension was filtered via a cannula and the resulting solid was washed with cold methanol (2 \times 50 mL). The white solid obtained was dried under vacuum for 12 h to afford a fine white powder. In a Schlenk flask, the synthesized silica (1 g) was suspended in dry toluene (70 mL) under nitrogen and treated with the corresponding silicate (NAM 1.6 g, 5.1 mmol or APTES 1 g, 4.5 mmol). The mixture was heated at reflux temperature and stirred for 24 h. The reaction mixture was cooled to room temperature. Subsequently ammonium nitrate NH₄NO₃ (60 mg, 0.75 mmol) and EtOH (60 mL) were added to remove the residual surfactant,33 and this mixture was heated to 60 °C and stirred for 24 h. The reaction mixture was cooled to room temperature and the solid was separated by centrifugation (300 000 rpm for 10 min), washed with ethanol five times and isolated by centrifugation. The resulting white solid (SiO₂-APTES or SiO₂-NAM) was dried under reduced pressure for 12 h.

General synthesis of supported RhNPs on *N*-functionalized silicas. In a Fisher–Porter reactor, $[Rh(\mu-OMe)(1,5-COD)]_2$ (23.5 mg, 0.049 mmol) and 90 mg of functionalized silica (SiO₂–APTES, SiO₂–NAM or non-functionalized SiO₂) were suspended in dry THF (50 mL) under a nitrogen atmosphere. This mixture was sonicated for one min to obtain a homogeneous pale-yellow suspension. The reactor was then charged with 3 bar of H₂ at room temperature and allowed to stir for 18 h. After the reaction, the reactor was depressurized, and the resulting black homogeneous suspension was transferred to a Schlenk flask. All volatiles were removed under reduced pressure to afford a black solid. The supported RhNPs (black solid) obtained were dried under vacuum at 80 °C for 24 h and stored under a nitrogen atmosphere.

General procedure for catalytic hydrogenation reactions with supported RhNPs. To a 25 mL stainless steel reactor flask equipped with a glass vessel and a stirring magnet were added supported catalyst (5 mg), heptane (2 mL), and substrate(s) (2 mmol). The reaction mixture was then pressurized with hydrogen (5 or 40 bar) and stirred at 100 °C for the specified time. After the reaction was completed, the reactor vessel was cooled in an ice bath and depressurized. The crude reaction residue was filtered through a column prior to being analyzed by GC.

General procedure for recycling of supported RhNPs. After the reaction was completed, cooled and depressurized, all volatiles were removed under reduced pressure and collected in a nitrogen trap for GC analysis. More solvent and substrate were added to the reactor vessel containing the catalyst and the procedure for the catalytic reaction was repeated.

Results and discussion

Catalyst characterization

Two different catalysts were prepared to evaluate the presence and nature of grafted capping agents in the stabilization of RhNPs. Porous silicas were functionalized with (3-aminopropyl)triethoxysilane (APTES) or *N*-(3-(triethoxysilyl)propyl)nicotinamide (NAM). The functionalization took place after the synthesis of porous silicas using TEOS and the templating agent CTAB in basic aqueous solution (NaOH 2 M). After *N*-functionalization, the removal of the surfactant was performed using NH₄NO₃. This type of functionalization locates the functional groups on the external surface and at the pore mouth, as suggested in previous reports for coumarin functionalized silicas.^{34,35}

The formation of supported RhNPs (Scheme 2) was achieved by the reduction of the metal precursor $[Rh(\mu-OMe) (1,5-COD)]_2$ with dihydrogen in the presence of the corresponding porous support SiO₂ (**RhNPs-A**), SiO₂–APTES (**RhNPs-B**) or SiO₂–NAM (**RhNPs-C**). The initial yellow suspension turned black within minutes after pressurization with dihydrogen. The resulting catalysts **RhNPs-(A–C**) were thoroughly characterized by different techniques (IR, TGA, SEM, TEM, BET and XPS) to assess the effect of the different amine-stabilizers grafted on mesoporous silicas.

The presence of functional groups was examined by FT-IR where the signals of the grafted aminopropyl or nicotinamide propyl groups were observed in addition to the expected signals for siloxane, silanol groups and physisorbed water. In the case of **RhNPs-B**, a slight change in the frequencies of the corresponding rhodium-free silica support corroborated the coordination of rhodium (Fig. 1a). In the case of SiO₂–NAM, a strong band at around 1640 cm⁻¹ is observed; it could be attributed to the carbonyl group of the nicotinamide (NAM) functional group, as well as IR bands were assigned to the alkyl, pyridine and amine groups (Fig. 1b). For **RhNPs-C**, an

interaction of rhodium with pyridine and amine of the nicotinamide group was indicated by the presence of bands at 1429 and 1463 cm⁻¹ (Fig. 1b). The carbonyl interaction with rhodium was discarded with the appearance of an upfield signal at 1648 cm⁻¹ as previously observed for several metal complexes with NAM as a ligand.^{36,37}

The interaction between RhNPs and the support was further corroborated by X-ray photoelectron spectroscopy (XPS). The Rh $3d_{5/2}$ region from the high resolution XPS spectra of **RhNPs-C** shows a chemical environment made up of Rh(0), Rh(1) and Rh(m) (Fig. 2).^{28–30} The presence of oxidized Rh is due to the anchoring of Rh nanoparticles onto the silica surface, which takes place *via* oxygen bonding, as previously reported.³⁸ Considering the structural magic numbers for a face-centered cubic closed-packed Rh nanoparticle, around 63% of atoms are on the surface for a nanoparticle without imperfection of 1.9 nm, and 52% of atoms for a particle of 2.4 nm.³⁹ For this reason, the presence of Rh(1) and Rh(m) is mostly on the nanoparticle surface. Comparable high-resolution spectra were observed for **RhNPs-B** (ESI S7 and S8†).

Thermal analyses of the silicas without rhodium showed the loss of organic material between 150 and 450 °C (ESI S10 and S11†). The amount of the organic fraction in SiO₂–APTES was determined to be 21 wt% and 27.4 wt% for SiO₂–NAM. Two important fragmentations in SiO₂–NAM were observed probably due to NH–(CO) bond cleavage (ESI S11†). For all the catalysts **RhNPs-(A–C)**, the presence of Rh enhanced the weight loss during thermogravimetric analyses (Fig. 3 and ESI S12–S14†) that could arise from the weakening of organic bonds upon an interaction with rhodium. The rhodium content on each support was determined by microwave plasma



Scheme 2 Synthesis of RhNPs supported on N-functionalized silicas.



Fig. 1 IR spectra of functionalized silicas and the respective supported RhNPs. (A) SiO₂-APTES and **RNPs-B**, (B) SiO₂-NAM and **RhNPs-C**. (Legend: \blacklozenge SiO₂ lattice, o physisorbed water, $\textcircled{o} \nu$ (N-H), $\bigstar \nu$ (-CH₂-), $\textcircled{o} \nu$ (-Co), $\blacklozenge \nu$ (-Co)), $\blacklozenge \nu$ (-Co)), $\blacklozenge \nu$ (-Co)), $\blacklozenge \nu$ (For **RhNPs-A** and SiO₂ see ESI S6.†)



Fig. 2 High resolution-XPS Rh 3d of RhNPs-C.

atomic emission spectroscopy (MP-AES) and it was 4.3 wt% for **RhNPs-A**, 2.9 wt% for **RhNPs-B** and 7.6 wt% for **RhNPs-C**. The small amount of Rh in SiO₂–APTES found in **RhNPs-B** com-



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Fig. 3 Thermogravimetric data of **RhNPs-(A–C)**. (For parent functionalized silicas see ESI S10 and S11.[†])

pared to the amount in pristine silica in **RhNPs-A** could be explained considering the presence of coordinating groups grafted onto silica. In the absence of functional groups such as propylamine, RhNPs aggregate and the amount of rhodium incorporated in pristine silica could be higher than the amount of rhodium incorporated when propylamine is present. Propylamine stabilizes smaller RhNPs and this could account for the low concentration of rhodium.

The synthesized materials were also characterized by electronic microscopy techniques. The size of silicas without rhodium was characterized by scanning electron microscopy (SEM), showing particles with a mean diameter of 206 ± 20 nm for pristine silica, 40 393 \pm 74 nm for SiO₂–APTES and 767 \pm 137 nm for SiO₂-NAM (ESI S15-S18[†]). The pore diameter of the silicas was measured by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), showing a size of around 1.4 nm for pristine silica, 3.5 nm for SiO₂-APTES and 3.3 nm for SiO₂-NAM (ESI S19, S20 and S22[†]). Upon the formation of RhNPs supported on the silicas, transmission electron microscopy (TEM) analyses showed the presence of nanoparticles exclusively at the silica external surface (Fig. 4 and 5) and in the cases of RhNPs-B and RhNPs-C, energy dispersive X-ray (EDX) mapping showed the presence of Rh homogeneously dispersed at the silica surface, as well as N. The morphology of RhNPs was influenced by the nature of the functional group at the silica surface. In the absence of functional groups like in RhNPs-A, mainly metal agglomerates were observed by TEM on the silica surface (ESI S24[†]). RhNPs-B showed the presence of small aggregates of Rh over the surface (Fig. 4A), while RhNPs-C presented a better dispersion (Fig. 5A). The size of the silicas was not modified after supporting Rh. The mean diameter of the supported RhNPs was determined by HAADF-STEM, obtaining 3.2 ± 0.5 nm for RhNPs-B (Fig. 4B) and 2.3 ± 0.3 nm for RhNPs-C (Fig. 5B). The formation of homogeneously dispersed spherical metal nanoparticles of smaller size in RhNPs-C compared to RhNPs-B, could be a consequence of the stronger coordination capabilities of nicotinamide groups. HR-TEM and FFT evidenced the



Fig. 4 TEM images of RhNPs-B (A); HAADF-STEM image; (B) TEM image of RhNPs; (C) size distribution of RhNPs (3.2 \pm 0.5 nm); (D) HR HAADF-STEM image with FFT of a single nanoparticle, an interplanar distance of 2.2 Å; (E) EDX mapping of a section of the catalyst, (F) Si, (G) O, (H) Rh and (I) N.



Fig. 5 TEM images of RhNPs-C (A); HAADF-STEM image; (B) TEM image of RhNPs; (C) size distribution of RhNPs (2.3 \pm 0.3 nm); (D) HR HAADF-STEM image, an interplanar distance of 2.2 Å; (E) EDX mapping of a particle of the catalyst, (F) Si, (G) O, (H) Rh and (I) N.

presence of a crystalline structure of Rh with an interplanar distance of 2.2 A, typical of the {111} planes of a face-centered cubic closed-packing in both **RhNPs-B** and **RhNPs-C** (Fig. 4D and 5D, respectively).

Concerning the textural properties of the supported RhNPs in functionalized OMS, the catalysts presented nitrogen adsorption–desorption curves of Type II (Fig. 6),⁴¹ and no hysteresis, characteristic of nonporous materials, with more gradual curvature (indistinguishable knee) indicating monolayer accumulation and the onset of multilayer adsorption resulting in a small apparent surface area (S_{BET}) for **RhNPs-B** (16 m² g⁻¹) and for **RhNPs-C** (9 m² g⁻¹). Interestingly, the parent silica material SiO₂–APTES presented a typical curve of mesoporous materials with a surface area (S_{BET}) of 415 m² g⁻¹ and a pore diameter of 2 nm (ESI S37†). A decrease in the



Fig. 6 Adsorption-desorption isotherms of RhNPs-B (red circles) and RhNPs-C (green triangles). Filled figures correspond to adsorption and hollow figures correspond to desorption.

apparent surface area in **RhNPs-B** compared to SiO_2 -APTES is associated with the blockage of the pore mouth (aperture) of the original functionalized silica by the metal nanoparticles. This loss of porosity was further corroborated by the pore width calculated using the NLDFT data treatment.

Catalytic activity in the hydrogenation of different substrates

The initial assessment in the hydrogenation of different substrates was performed using the RhNPs-B catalyst, and the results are summarized in Table 1. High conversion and selectivity were achieved in the hydrogenation of nitrobenzene (1), terminal and internal alkenes (2-4), 4-phenyl-3-buten-2one (5), benzylidene aniline (6) and acetophenone (7) (Table 1, entries 1-7). In comparison with other catalysts with heterogenized Rh on magnetic silica⁴² or hollow nano-mesosilica spheres with N-doped carbon⁴³ used as catalysts at 1 bar H₂ pressure, the activity towards the conversion of 1 was higher for RhNPs-B at 5 bar H₂ pressure. The activity and selectivity of RhNPs-B in the hydrogenation of 5 (entry 5 in Table 1) were superior to those of RhNPs supported on phosphine-functionalized silica.²⁰ RhNPs-B showed very low conversion of benzaldehyde (8) and toluene (9) under similar reaction conditions (Table 1, entries 8 and 9), whereas alkyl derivatives such as nitro-decane, 1-octene, nonanal and cyclohexanone were not hydrogenated (see ESI Table S6†). The catalytic results of RhNPs-B in hydrogenation reactions suggested that for the hydrogenation to take place, π -conjugated and constrained geometry substrates are required. The latter has been observed for ligand-capped colloidal metal nanoparticles9,10,44 where π -conjugated substrates favor the formation of metal di- σ bonded species and enhance the hydrogenation of one unsaturated group. This could explain why 3 is hydrogenated to ethylbenzene (3a) by RhNPs-B and 1-octene is not transformed.

The reuse of the **RhNPs-B** catalyst in the hydrogenation of cyclohexene was evaluated after product separation by simple distillation, and the catalyst was active for up to 5 catalytic runs (Fig. 7). The reused **RhNPs-B** catalyst was further analyzed

Table 1 Catalytic hydrogenation by RhNPs-B at low H_2 pressure in toluene

Entry	Substrate	Product	Conv. ^{<i>a</i>} (sel.) ^{<i>a</i>} %	$TOF (h^{-1})$
1	NO ₂	NH ₂	>99 (92) ^c	649
2		1a	>99 (100)	706
3	2	2a	>99 (92) ^c	649
4	3	3a	85 (100)	600
5	4	4a O	95 (100)	670
6	5a	5	67 (100)	473
7	6 C	6a OH	98 (81) ^d	560
8	7	7а ОН	6 (n. d.)	n.d.
9 ^e	8 	8a	1 (n. d.)	n.d.
10 ^{<i>f</i>}	e e	9a OH	81 (93)	219
11 ^g	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	7a OH	10 (80)	48
	7	79		

Reaction conditions: 2 mmol substrate, 5 mg of **RhNPs-B** (0.07 mol%), 2 mL of toluene, H₂ (5 bar), 100 °C, 2 h. ^{*a*} Determined by GC using decane as an internal standard. ^{*b*} TOF = mmol of the principal product × (mmol of Rh × h)⁻¹. ^{*c*} Completely hydrogenated byproduct. ^{*d*} Cyclohexyl ethanol (8%) and acetyl cyclohexane (11%) were detected by GC. ^{*e*} Performed in EtOH. ^{*f*} **RhNPs-C** (0.18 mol%) used as the catalyst. ^{*g*} **RhNPs-A** (0.10 mol%) used as the catalyst.

by HAADF-STEM, showing the formation of rhodium aggregates separated from the support as well as at the support, as a result of metal sintering. The coordination ability of alkyl amines used as stabilizers of metal nanoparticles changes under hydrogen pressure, leading to nanoparticle aggregates as previously shown for PdNPs.⁴⁵ The observed catalytic activity in the hydrogenation of cyclohexene by reused **RhNPs-B** could be feasible due to the presence of small rhodium nanoparticles.

Under similar reaction conditions, the **RhNPs-C** catalyst with nicotinamide groups grafted on silica as the stabilizer of rhodium nanoparticles was evaluated in the hydrogenation of



Fig. 7 (A) Recycling hydrogenation of cyclohexene in toluene with RhNPs-B, and (B) TEM images of catalysts after the recycling reactions. (Reaction conditions: 2 mmol cyclohexene, 5 mg of RhNPs-B (0.07 mol%), H_2 (5 bar), 100 °C, 2 h.)

acetophenone (7) in toluene (Table 1, entry 10). High activity with high selectivity for ketone hydrogenation to form 1-phenylethanol (7a, 93%) was observed. In the case of **RhNPs-A**, a catalyst with poor stability for RhNPs due to the lack of aminefunctional groups (as shown in the previous section) showed poor conversion of acetophenone with a high selectivity to 7a (Table 1, entry 11).

To apply the supported catalysts **RhNPs-B** and **RhNPs-C** in the hydrogenation of more challenging substrates, a higher dihydrogen pressure and heptane as an innocuous solvent were used. In general, the activity observed for both catalysts was similar. The hydrogenation of acetophenone (7) at 40 bar (Table 2, entry 1) afforded the fully reduced product cyclohexyl ethanol (7b) with moderate selectivity with acetyl cyclohexane as the remaining product. This suggested that none of the catalysts can reduce the initially formed acetyl cyclohexane into cyclohexyl ethanol.

The stability of **RhNPs-B** and **RhNPS-C** was assessed after the hydrogenation of acetophenone in heptane at 40 bar of H₂. HAADF-STEM analyses and EDX mapping of the samples revealed the formation of Rh aggregates at the surface in the case of **RhNPs-B** (Fig. 8A), whereas **RhNPs-C** preserved the homogeneous distribution of RhNPs over the functionalized silica surface (Fig. 8D) with a similar nanoparticle size distribution (2.3 ± 0.3 nm, ESI S42†). Moreover, rhodium loss from **RhNPs-C** during the hydrogenation of acetophenone was discarded by the MP-AES analysis of the organic phase collected after the catalytic reaction took place (0.19 ppm of rhodium detected, corresponding to 0.2×10^{-3} % of supported rhodium leaching.).

Both catalysts, **RhNPs-B** and **RhNPs-C**, were active in the hydrogenation of benzaldehyde (8) and quinoline (10) at high H_2 pressure with high selectivity to benzylic alcohol (8a) and 1,2,3,4-tetrahidroquinoline (10a), respectively (Table 2, entries 2 and 3). When toluene (9) was used as the substrate, it was moderately converted to methylcyclohexane (9a) (Table 2, entry 4). Benzonitrile (11) was converted entirely to 5 different products, with aryl benzyl imine (11a) as the major product and both catalysts showed similar behavior (Table 2, entry 5).

We further studied the hydrogenation of phenol (12) by the supported RhNPs at high H_2 pressure (40 bar) and observed

Entry	Substrate	Main product	H ₂ pressure (bar)	RhNPs-B		RhNPs-C	
				Conv. ^{<i>a</i>} (sel.) ^{<i>a</i>} %	$\operatorname{TOF}^{b}\left(\mathbf{h}^{-1}\right)$	Conv. ^{<i>a</i>} (sel.) ^{<i>a</i>} %	$\operatorname{TOF}^{b}\left(\mathbf{h}^{-1}\right)$
1		OH C	40	99 (78) ^c	545	99 (76) ^c	203
2	7	7ь ОН	40	$65(89)^d$	408	96 (91) ^d	235
3	8 N	8a N	40	99 (95)	664	94 (>99)	251
4		10a	40	61 (>99)	430	45 (>99)	120
5 ^e	g N		40	>99 (48)	335	97 (56)	147
6 ^{<i>f</i>}	11 OH		40	>99 (75 for 12b)	524	>99 (54 for 12a)	144
7 ^{<i>f</i>}	12 OH		5	87 (77)	473	25 (66)	44
	12	12a					

Reaction conditions: 2 mmol substrate, 5 mg of catalyst (RhNPs-B (0.07 mol%), RhNPs-C (0.18 mol%)), 2 mL of heptane, 100 °C, 2 h. ^{*a*} Determined by GC using decane as an internal standard. ^{*b*} TOF = mmol of the principal product × (mmol of Rh × h)⁻¹. ^{*c*} Acetyl cyclohexane as byproduct. ^{*d*} Benzoic acid as byproduct. ^{*e*} Products were determined by GC-MS, and benzylidene imine and dibenzyl amine were detected as byproducts. ^{*f*} Reaction run for 4 h yielding cyclohexanone and cyclohexanol.



Fig. 8 HAADF-STEM image and EDX mapping of **RhNPs-B** after acetophenone hydrogenation at 40 bar of pressure: (A) HAADF image; (B) EDX Rh mapping; (C) EDX N mapping, HAADF-STEM image and EDX mapping of **RhNPs-C** after acetophenone hydrogenation; (D) HAADF image; (E) EDX Rh mapping; (F) EDX N mapping.

the complete conversion of **12**. The use of **RhNPs-B** afforded a mixture of cyclohexanone (**12a**) and cyclohexanol (**12b**) in a 3 : 1 ratio, respectively, whereas **RhNPs-C** favored a 46 : 54 ratio of products (Table 2, entry 6). At low H₂ pressure (5 bar), both catalysts showed similar selectivity to **12a** and in the case of

RhNPs-B the activity was superior (Table 2, entry 7). The latter has been observed for colloidal RhNPs stabilized with N-heterocyclic carbene ligands, and it was suggested that the selectivity for cyclohexanone in the hydrogenation of phenol at low H₂ pressure is a result of the difference in the rates between the isomerization and hydrogenation of the enol intermediate.⁴⁶ Considering the amount of supported Rh in both catalytic systems, a similar TOF was calculated at 40 bar H₂ pressure (TOF 89 h⁻¹ for **RhNPs-B** and 76 h⁻¹ for **RhNPs-C**, calculated as mmol of cyclohexanone × (mmol of Rh × h)⁻¹), and at 5 bar H₂ pressure the difference was remarkable (239 h⁻¹ for **RhNPs-B** and 23 h⁻¹ for **RhNPs-C**). The latter are among the best catalytic results for the hydrogenation of phenol to cyclohexanone by supported RhNPs.¹⁶

Overall, the different catalytic activities of **RhNPs-B** and **RhNPs-C** depend on the coordination ability of amine or nicotinamide groups at the silica surface towards rhodium. The strong coordination of nicotinamide to the rhodium surface in **RhNPs-C** affords a more robust catalytic system, however with a low conversion rate in the hydrogenation of phenol.

Given the activity and selectivity shown by the supported RhNPs in the hydrogenation of phenol, the catalytic systems were applied in the reductive amination of phenol with morpholine as a one-pot methodology to produce tertiary amines (Scheme 3). In this multistep reaction, phenol is catalytically reduced to cyclohexanone, which reacts with morpholine to form an enamine intermediate; the latter is catalytically reduced to afford the desired tertiary amine. The reductive amination of phenol and morpholine catalyzed by both supported catalysts **RhNPs-B** and **RhNPs-C** at low H_2 pressure showed high conversion to the tertiary amine. In the reaction catalyzed by **RhNPs-C**, a positive effect of the added morpholine on the conversion of phenol was observed.

Conclusions

The controlled reduction of $[Rh(\mu-OMe)(1,5-COD)]_2$ using dihydrogen in the presence of functionalized porous silica afforded the formation of supported RhNPs. The supported catalyst was thoroughly characterized through diverse analytical techniques (FT-IR, TGA, XPS, SEM and TEM) to confirm the formation of spherical RhNPs with a narrow size and homogeneous distribution on the surface of ordered functionalized silicas.

RhNPs supported on amine-functionalized silica, RhNPs-B, were active in the hydrogenation of several substrates and showed remarkable selectivity to alkene, nitro, ketone and imine groups at low hydrogen pressure. The catalytic activity and selectivity of the supported RhNPs reached after only 2 hours of the hydrogenation reaction using less than 0.2 mol%, are among the most active supported catalysts based on RhNPs. RhNPs-B suffered from morphological changes after the catalytic reduction of cyclohexene as well as after the reduction of acetophenone. The presence of nicotinamide groups grafted on ordered mesoporous silica stabilized spherical and homogenously distributed RhNPs. The dispersion and morphology of RhNPs supported on the nicotinamide functionalized ordered silica, RhNPs-C, were preserved after the catalytic reduction of acetophenone at high hydrogen pressure. In addition, the selective reduction of acetophenone could be tuned by varying the hydrogen pressure from 5 to 40 bar, achieving 1-phenylethanol at low pressure and cyclohexylethanol at high pressure.

The strong interaction between nicotinamide and rhodium did not affect the reduction of several substrates. The catalyst could selectively hydrogenate benzaldehyde, quinoline and toluene, whereas benzonitrile and phenol showed moderate selectivity to benzyl imine and cyclohexanone, respectively.

Finally, the catalysts **RhNPs-B** and **RhNPs-C** showed a remarkable selectivity in the reductive amination of phenol and morpholine to afford tertiary amines under a low hydrogen pressure (5 bar).



Scheme 3 Reductive amination of phenol and morpholine. Reaction conditions: 2 mmol phenol, 2 mmol morpholine, 5 mg of catalyst, H₂ (5 bar), 2 mL of heptane, 100 °C, 6 h. Conversion and selectivity were determined by GC using decane as an internal standard.

Conflicts of interest

The authors have no competing interests to declare.

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