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1 Introduction

In catalysis, metal nanoparticles are very interesting systems due to their high number of surface atoms giving rise to numerous active sites.¹ In the past years, nanocatalysis has emerged as a domain at the border between homogeneous and heterogeneous catalysis, with the expectation that nanomaterials should be able to show the benefits of both types of catalysts, namely high efficiency and selectivity. Metal nanoparticles can be used in solution or deposited onto a support. When supported on materials, metal nanoparticles can be handled as classical heterogeneous catalysts, and in particular, an easier recovery can be envisaged.

Studies on solid materials to be used as supports in catalysis present a significant importance; alumina, silica, and carbon are the most commonly used solid supports, in order to immobilize the active catalyst phase, as for example, metal

Taking advantage of a terpyridine ligand for the deposition of Pd nanoparticles onto a magnetic material for selective hydrogenation reactions[†]

Miguel Guerrero,^{*ab} Natalia J. S. Costa,^c Lucas L. R. Vono,^c Liane M. Rossi,^{*c} Elena V. Gusevskaya^d and Karine Philippot^{*ab}

A hybrid terpyridine ligand was designed to functionalize a magnetic support constituted of magnetite cores surrounded by a silica shell with the aim of improving the stabilization of supported-palladium nanoparticles for the later application of the obtained composite nanomaterial in hydrogenation catalysis. The preparation of the nanomaterial was performed by direct decomposition of the organometallic complex $[Pd_2(dba)_3]$ on the terpyridine-modified magnetic support providing well-dispersed Pd NPs of 2.5 \pm 0.6 nm mean size. This new nanomaterial is a highly active catalyst for the hydrogenation of cyclohexene under mild conditions reaching turnover frequencies up to *ca.* 58 000 h⁻¹ or 129 000 h⁻¹ when corrected for surface Pd atoms. Furthermore, in the hydrogenation of β -myrcene, this nanocatalyst is highly selective for the formation of monohydrogenated compounds. When compared to a similar nanocatalyst consisting of palladium nanoparticles supported on an amino-modified magnetic support or on Pd/C, the activity and selectivity of the nanocatalyst are largely increased. These results show how the design of an appropriate hybrid ligand used to functionalize the support can strongly influence the catalytic properties of supported metal nanoparticles.

nanoparticles, to later facilitate the catalyst recovery and recycling.² Introducing a magnetic core inside the support renders the recovery of the nanocatalyst after liquid-phase reactions much easier than by cross-flow filtration or centrifugation.³ Furthermore, functionalization of the solid supports with suitable chelating ligands is emerging as a viable strategy to circumvent metal catalyst deterioration and leaching,⁴ as it improves the stabilization of the nanoparticles, thus allowing the adjustment of their catalytic efficiency and/or selectivity.⁵

The strong binding affinity of 2,2':6',2"-terpyridine (tpy) ligand and its derivatives to transition and rare earth metal ions is well known and, in consequence, they have attracted wide-spread interest in diverse areas.⁶ Nevertheless, the use of tpy derivative ligands in nanotechnology is less developed⁷ and their applications have been mainly focused on electronic devices.⁸

Hydrogenation of organic substrates is an important step in the preparation of various fine chemicals, with palladium being one of the metals most frequently used to catalyze these reactions. Monoterpenic compounds are the main components of various essential oils and represent an important renewable hydrocarbon feedstock for the flavour and fragrance industry.⁹ In this context, myrcene, a naturally occurring acyclic monoterpene, is a particularly attractive substrate to produce synthetic substitutes for natural aromas. Myrcene is industrially manufactured by the pyrolysis of β -pinene, one of the major

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^aCNRS, LCC (Laboratoire de Chimie de Coordination), 205, Route de Narbonne, BP44099, F-31077 Toulouse Cedex 4, France. E-mail: karine.philippot@lcc-toulouse.fr ^bUniversité de Toulouse, UPS, INPT, LCC, F-31077 Toulouse Cedex 4, France

^cInstituto de Química, Universidade de São Paulo, Av. Prof. Lineu Prestes 748, São Paulo 05508-000, SP, Brazil

^dDepartamento de Química, Universidade Federal de Minas Gerais, 31270-901 Belo Horizonte, MG, Brazil

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constituents of pine turpentine oil.¹⁰ For several years, some of us have been interested in the catalytic transformations of myrcene to more valuable oxygenated derivatives *via* oxidation¹¹ and hydroformylation¹² processes. Achievement of high selectivity has been found to be a major problem in the metal catalyzed functionalization of this polyolefin, which contains three different olefinic bonds, two of which are conjugated. The monohydrogenation of myrcene could produce diolefins which could be further transformed to oxygenated compounds with better selectivity than myrcene itself. However, the selective hydrogenation of myrcene has been little studied hitherto.¹³

The hydrogenation of myrcene has been performed over Co,¹⁴ Cr,¹⁵ Cu/Cr,¹⁶ Ru,¹⁷ Rh,¹⁸ Pt¹⁹ and Pd²⁰ catalysts; however, in most of the reported studies, monohydrogenated products were observed only at the beginning of the reaction because of their further hydrogenation to give a fully saturated product, 2,6-dimethyloctane. So, the development of catalysts for the partial hydrogenation of myrcene, especially those that allow for quenching the reaction after the consumption of the first hydrogen molecule, still remains a challenge.

In this paper we describe a novel and efficient approach for the deposition of palladium nanoparticles (Pd NPs) onto a magnetic support giving rise to a nanomaterial of interest in the field of nanocatalysis, while taking advantage of the coordination properties of a special bifunctional ligand. The designed hybrid terpyridine bifunctional ligand (L) bears in one extremity a tpy function able to stabilize palladium nanoparticles and in the second extremity an amino group able to link with the magnetic support through the principle of supramolecular chemistry. The magnetic properties of the support made possible an easy and fast separation of the catalyst from the reaction medium by the simple application of a magnet, thus both saving time and avoiding catalyst exposure to air during recycling. The designed ligand has been evaluated at the same time (i) as an effective stabilizing agent during the synthesis of supported Pd NPs through an organometallic approach and (ii) as a compelling linkage to the magnetic support to improve the recovery of the catalyst. Moreover, a discriminating role in the selective hydrogenation of myrcene was observed. The results obtained with this novel nanomaterial show how the design of an appropriate ligand used to functionalize a support can strongly influence the catalytic properties of supported metal nanoparticles.

2 Results and discussion

2.1 Synthesis of the terpyridine ligand

The hybrid terpyridine ligand (L) was synthesized by a modification of a two-step procedure reported elsewhere (Scheme 1).²¹ First, 6-amino-1-hexanol was reacted with KOH in dry dimethyl sulfoxide (DMSO) to give the corresponding potassium alkoxide. In the second step, this potassium salt was converted to L by reacting it with 4'-chloro-2,2':6',2''-terpyridine in dry DMSO. According to previous studies,²² the coordination of L on the Pd NPs surface is expected to occur through the terpyridine nitrogen atoms. However, the L ligand contains a free $-NH_2$ group available for the grafting of the ligand on the silica surface of the magnetic support by covalent bonding.

Ligand L has been fully characterized by elemental analysis, mass spectrometry, and IR and ¹H and ¹³C{¹H} NMR spectroscopy (see Experimental section). The NMR signals were assigned by reference to the literature²³ and from DEPT, COSY and HMQC NMR experiments. Elemental analysis, mass spectrometry and all spectroscopic data for L are consistent with the proposed structure.

2.2 Synthesis of the supported nanocatalyst

The magnetic support (**S**) chosen for this study is a core-shell material formed by magnetite NPs covered with a uniform layer of silica, with an average size of 35 nm and was synthesized following a previously described procedure.²⁴ The thermal stability as well as the fact that several organic groups can be robustly anchored to the surface makes this material an ideal candidate to provide immobilization of catalytic species.

In order to evaluate the potential influence of ligand L on Pd nanoparticle immobilization on the support and, further, on the catalytic properties of the obtained supported nanocatalyst, the material was previously functionalized by covalent attachment of L onto the silica surface (Scheme 2). For that purpose, the support S was reacted with 3-chloropropyltrimethoxysilane in toluene to obtain the chloropropyl-modified support, S_{Cl} . Then, the reaction of S_{Cl} with the amine group of L was performed in chloroform, under reflux, for 24 h, giving rise to the L-functionalized support, S_L . After that, the solid was purified by washing with chloroform and methanol, to remove the non-reacted L ligand. The presence of the ligand on the support has



Scheme 1 Organic synthesis of the ligand L.



been confirmed by ATR-IR spectroscopy (Fig. S1; ESI[†]). The most characteristic absorption bands of L (ESI, S1(b)[†]) correspond to the pyridine, ether and amine groups.²⁵ The nonfunctionalized support (S) displays IR bands at 3390 (O–H stretch, broad band), 1052 (Si–O–Si asymmetric stretch, the most intense band), and 630 and 425 cm⁻¹ (Si–O–Si symmetric stretch and Si–O–Si bend, respectively) (ESI, S1(a)[†]). The IR spectrum of S_L support (ESI, S1(c)[†]) exhibits new bands at 3326 (NH), 2927 and 2854 (aliphatic CH), and 1605 and 1464 cm⁻¹ (C=C and C=N) which seems indicative of the grafting of ligand L onto the surface of the support.

The supported Pd nanoparticles were prepared by impregnation of the L-functionalized support (S_L) with a THF solution of the palladium(0) organometallic precursor tris(dibenzylideneacetone)palladium(0) ([Pd₂(dba)₃]) followed by its decomposition with molecular hydrogen (3 bar; room temperature), giving rise to the solid S_LPd . This new nanocatalyst was characterized by flame atomic absorption spectroscopy to determine the metal loading (Pd content = 2.3 wt%), transmission electron microscopy (TEM and HRTEM) and FT-IR spectroscopy.

To confirm the role of **L** in the control of the Pd nanoparticles' size and dispersion onto the magnetic support, the same synthetic procedure followed to prepare S_LPd was applied using the non-functionalized solid (**S**) and the chloropropylfunctionalized solid (S_{Cl}) instead of S_L . After impregnation of these solids with $[Pd_2(dba)_3]$ and its decomposition with molecular hydrogen, only large aggregates of palladium were found in the TEM images of both systems (Fig. 1a and b, respectively). The TEM analysis of S_LPd revealed a uniform dispersion of the Pd NPs onto the surface of the magnetic support (Fig. 1c). In addition, the Pd NPs display a narrow particle size distribution centered at 2.5 \pm 0.6 nm, indicating a



Fig. 1 TEM micrographs of palladium deposited on the three different supports: (a) SPd, (b) $S_{CI}Pd$ and (c) $S_{L}Pd$.

good size control (Fig. S2; ESI⁺) that can only result from the stabilization efficiency of the terpyridine ligand L grafted onto the silica surface. Further characterization of S_LPd by high resolution transmission electron microscopy (HRTEM) (see Fig. S3; ESI[†]) revealed a lattice spacing of 2.27 Å, which can be attributed to the Pd(111) lattice plane of cubic metallic palladium (fcc structure). Energy-dispersive X-ray spectroscopy (EDS) analysis confirmed the presence of Pd as well as Si and Fe in the magnetic support (Fig. S4; ESI⁺). In all cases, the features of the support consisting of ca. 35 nm core-shell nanostructures containing magnetite NPs of ca. 10 nm surrounded by an amorphous silica shell were also observed. All these results clearly suggest that the terpyridine ligand grafted onto the magnetic material acts as an efficient stabilizer for the controlled synthesis of well-dispersed and narrow size distributed Pd nanoparticles on S₁Pd.

The same synthetic procedure used to prepare S_LPd was also applied using an amino-functionalized support (S_{NH2}) instead of S_L . This synthesis also gave rise to well-dispersed and narrow size distributed Pd nanoparticles $(S_{NH2}Pd)$ having a nearly spherical shape and a mean size of 1.8 ± 0.4 nm (Fig. S5; ESI[†]). Although this nanomaterial $(S_{NH2}Pd)$ also contained small Pd NPs, it was shown in the catalytic studies that these catalysts differed in terms of stability (*vide infra*). Indeed, as in the last case the stabilization of Pd NPs is performed through monodentate amine functions instead of the terpyridine moieties, we can expect variation in the stabilization of NPs and consequently different catalytic behaviours.

The so-obtained S_LPd and $S_{NH2}Pd$ supported catalysts can be easily dispersed in various organic solvents such as THF and CHCl₃ and various olefin substrates upon stirring, resulting in clear dark-brown-coloured dispersions. They can also be easily attracted to the reactor walls by applying a simple magnet. During the catalytic hydrogenation tests, magnetic separation was the only separation technique used, which has the advantage of keeping the solid catalysts inside the reactor during recycling avoiding catalyst mass loss and exposure to air.

2.3 Catalytic experiments

2.3.1 HYDROGENATION OF CYCLOHEXENE. We studied the ability of our Pd-based hybrid nanomaterials to catalyze the hydrogenation of a model olefin substrate, namely cyclohexene. In a typical experiment, the nanocatalyst S_LPd and the cyclohexene (palladium/olefin molar ratio of *ca.* 1/5500 or 1/11 000) were mixed in the reactor under an inert atmosphere without any solvent. Then the reactor was pressurized with hydrogen

(6 atm) and placed in an oil bath at 348 K under stirring (700 rpm). The reactor was kept connected to a hydrogen gas supply tank and the consumption of hydrogen was recorded as a function of time by the drop of pressure in the H_2 gas supply. At the desired time the reaction was quenched by cooling down the reactor in an ice bath, the remaining hydrogen released and the solid catalyst recovered magnetically by placing a magnet on the reactor walls. The organic phase was easily separated and analyzed by gas chromatography. The catalytic activity of each nanomaterial was expressed in turnover frequency (TOF) determined using the data from the hydrogenation curves transformed into conversions. From these curves we could obtain, for each reaction, the time required for the complete conversion (>99%, confirmed by GC) of a given substrate to metal ratio under the chosen reaction conditions. From the slope of the conversion versus time curves at initial rates and the turnover numbers (mole of substrate converted per mole of catalyst), we obtained the TOF, in h^{-1} , as shown in Tables 1 and 2. However, considering that (i) the number of surface palladium atoms is much lower than the total metal atoms present in the sample, and (ii) the Pd NPs are deposited on the support, the values given in Tables 1 and 2 are certainly underestimated. For example, if we consider the formation of full-shell clusters of palladium, the Pd NPs of 2.5 \pm 0.6 nm (catalyst S_LPd) and 1.8 \pm 0.4 nm (catalyst S_{NH2}Pd) have an approximate dispersion (D; the fraction of exposed Pd) value of ca. 0.45 and 0.52, respectively, indicating that about half of the total amount of Pd atoms are on the surface.²⁶ Thus, we used these values to estimate TOF corrected by the fraction of surface metal atoms, given in brackets in Tables 1 and 2 and in the text.

We observed an initial TOF of 12 100 h^{-1} (26 890 h^{-1}) in the first reaction cycle for the S_LPd catalyst in the hydrogenation of cyclohexene into cyclohexane. After recovering the catalyst by the simple application of a magnet on the reactor walls, the catalyst was reused in successive runs, by the addition of new portions of cyclohexene under an inert atmosphere; the initial TOF in the second cycle is two times the value of the first reaction, and was maintained in the third cycle. Interestingly,

Table 1	Hydrogenation of cyclohexene over $Pd(0)$ catalysts ^{a,d}						
Entry 1	Catalyst	Reaction cycle	$t^{b}(\mathbf{h})$	$\operatorname{TOF}^{c}(\mathrm{h}^{-1})$			
	S _T Pd	1 st	1.70	12 100 (26 890)			
	2	2 nd	0.50	24 575 (54 610)			
		3 rd	0.35	24 330 (54 070)			
2	S _L Pd*	1^{st}	0.90	22 680 (50 400)			
		2 nd	0.37	50 600 (112 435			
		3 rd	0.22	58 100 (129 120			
3	S _{NH2} Pd*	1 st	0.20	79 960 (153 770			
		2 nd	0.38	68 090 (130 940			
		3 rd	0.40	53 100 (102 110			

^{*a*} Reaction conditions (solventless): cyclohexene (10 mmol (entry 1) or 20 mmol (entries 2 and 3)), catalyst (1.8 µmol of Pd), 348 K, 6 atm of H₂. ^{*b*} Time interval required for the completion of each reaction cycle estimated by H₂ consumption curves (>99% conversion as determined by GC). ^{*c*} Initial turnover frequency (TOF) is expressed as moles of the substrate transformed per mole of catalyst per h and in brackets TOF is corrected per mole of surface Pd atoms. ^{*d*} *Catalysts pre-activated for 30 min under 6 atm of H₂ and at 348 K.

introducing a pre-activation step of the solid S_LPd catalyst under hydrogen gas (6 atm; 348 K; 30 min), before adding the substrate to the reactor for the catalytic tests, caused a marked increase of the initial TOF to 22 681 h^{-1} (50 400 h^{-1}), which is very close to the value observed in the second reaction cycle of the original catalyst. As this behaviour could be due to the storage conditions of the nanomaterial, namely in air, we decided to perform a pre-activation step before using the catalysts. Higher activities were obtained with the pre-activated catalyst S_LPd* (* denotes a pre-activation step), leading to the initial TOF in the range of 50 000 h^{-1} (100 000 h^{-1}) in the second and third reaction cycles (Table 1, entry 2). For the preactivated catalyst, the initial TOF in the second cycle is again two times the value of the first reaction, which suggests that the remaining oxidized Pd species in the pre-activated catalyst S_LPd* differed from those in the original S_LPd. We then observed the behaviour of the S₁Pd catalyst during 10 cycles of reaction (see ESI, Fig. S6[†]). After the fourth reaction cycle, the initial TOF was in the range of 30 000–35 000 h^{-1} , and did not reach the TOFs of SLPd*. This is strong evidence that the difference in the activity of SLPd and SLPd* should not be related to the oxidation of Pd nanoparticles; after 10 catalytic cycles, palladium in S_LPd is probably completely reduced.

The catalytic properties of the SLPd* nanomaterial were compared with a Pd catalyst prepared similarly using an aminefunctionalized support (S_{NH2}Pd*). An initial TOF value of 79 960 h^{-1} (153 770 h^{-1}) (Table 1, entry 3) was observed in the first reaction cycle, which was significantly higher than that observed for S_LPd*. However, a slight decrease in the catalytic activity was observed in the second and third reaction cycles, which suggests that the amine ligand is a poor stabilizer for the Pd nanoparticles in comparison with the terpyridine ligand.^{5b} Indeed, we can expect a less stabilizing character for the amine group in comparison with the terpyridine group which contains three oriented donating pyridines in the same direction, thus acting as a strong donating and pincer ligand. It is noteworthy that the TEM micrographs of the S_LPd nanomaterial after successive hydrogenation reactions have no evidence of coalescence or formation of large metal particles. Additionally, the core-shell morphology of the magnetic support did not change after exposure to the reaction conditions and the magnetic properties were preserved, allowing an easy and rapid procedure for the recovery of the catalyst that avoids conventional time-consuming techniques such as centrifugation, decantation, or filtration. Moreover, after catalyst separation, all the organic phases were collected and the Pd content was determined by ICP OES analysis leading to <0.01 ppm of metal. This result shows that Pd leaching is negligible.

The effects of temperature and hydrogen pressure on the hydrogenation reaction rates are presented in Table 2. As a general trend, it appears that changes in the hydrogen pressure affect less the initial TOF than changes in the temperature. For example, the TOF values obtained in the first hydrogenation cycle at 348 K are similar at 3 and 6 atm H_2 (*ca.* 22 600 h⁻¹) and reduced to 60% of this value at 1 atm (Table 1, entry 2 and Table 2, entries 5 and 6, respectively). The decrease of temperature from 348 to 298 K is detrimental to the catalytic activity at both 6 and 1 atm H_2 .

Table 2 Hydrogenation of cyclohexene over $S_L Pd^{\star}$ under various reaction conditions^{a,c}

Entry	P H ₂ (bar)	T (K)	Reaction cycle	$\operatorname{TOF}^{b}(\operatorname{h}^{-1})$			
4	6	298	1 st	15 400 (34 220) 16 200 (26 420)			
5	3	348	2 1 st 2 nd	22 605 (50 230)			
6	1	348	2 1 st	29 590 (85 760) 13 660 (30 360)			
7	1	298	1^{st}	25 190 (55 980) 5850 (13 000)			

^{*a*} Reaction conditions (solventless): cyclohexene (20 mmol) and catalyst (1.8 μ mol of Pd). ^{*b*} Initial turnover frequency is expressed as moles of the substrate transformed per mole of catalyst per h and in brackets TOF is corrected per mole of surface Pd atoms. ^{*c*} *Catalysts preactivated for 30 min under 6 atm of H₂ and at 348 K.

The reaction performed at 298 K has an initial TOF of 15 400 h⁻¹ (Table 2, entry 5), compared to 22 680 h⁻¹ at 348 K. Moreover, in the catalyst recycling, the reactivity does not increase at a lower temperature. A higher negative effect on activity was observed when both temperature and pressure were decreased to 298 K and 1 atm, respectively, resulting in a TOF of 5850 h⁻¹.

Poisoning tests with Hg (excess) were also carried out in an attempt to identify whether the Pd nanoparticles behave as a heterogeneous catalyst. Molecular active species are not expected to be affected by the presence of Hg, while a metallic surface is poisoned by mercury amalgam formation.²⁷ Comparing the hydrogenation curves of standard hydrogenation reactions (Fig. 2) and the curves in which the reactions stopped after the addition of Hg (Fig. 2), we can conclude that the catalysis occurs at the surface of the heterogeneous Pd(0) catalyst.

2.3.2 HYDROGENATION OF MYRCENE. We next examined the ability of our palladium-based nanocatalysts to catalyze selective hydrogenation reactions, taking as a reference the β -myrcene molecule. Several concurrent transformations of this poly-unsaturated substrate are expected under hydrogenation conditions giving a wide variety of products as shown in Scheme 3.

The S_LPd^* and $S_{NH2}Pd^*$ materials catalyzed the hydrogenation of β -myrcene (1) under mild conditions and without solvent



Fig. 2 Hydrogenation of cyclohexene by S_LPd^* catalyst under standard solventless conditions (\bullet) and hydrogenation of cyclohexene by S_LPd^* catalyst under similar conditions with the addition of Hg (300 equivalents) at <50% of conversion (\bigcirc).





(Table 3). The hydrogenation reactions were monitored by measuring the H_2 consumption over time (Fig. 3). For comparison purposes, in the first set of experiments, the GC analysis of the reaction mixture was performed just after the significant decrease of the hydrogen consumption rate (inset of Fig. 3). A second GC analysis was performed after longer reaction times, even though we noticed no further consumption of hydrogen. To our surprise, virtually only one hydrogen consumption regime was noticed for both nanocatalysts, with negligible amounts of hydrogen being consumed after the consumption of nearly 1.2 mol of hydrogen per mol of the substrate for $S_{\rm NH2}Pd^*$.

The products detected after the fast hydrogen consumption step in the reaction over the **S_LPd*** catalyst were mainly mono-hydrogenated compounds (86% selectivity, 96% substrate conversion) (Table 3, entry 8). It is important to mention that at longer reaction times (without noticeable consumption of hydrogen) the product distribution did not change significantly, with only a slight increase in the amount of di-hydrogenated product 3 being noticed (Table 3, entry 9). Thus, the **S_LPd*** nanomaterial is very efficient for the partial mono-hydrogenation of myrcene. The reaction occurs under mild and solvent free conditions and shows a high initial hydrogen consumption rate of *ca.* 51 000 mol_{H2} mol_{cat}⁻¹ h⁻¹ during the fast consumption step (Table 3, entry 8).

The kinetic curve for the myrcene hydrogenation over the $S_{NH2}Pd^*$ catalyst also exhibited only one hydrogen consumption

Table 3 Hydrogenation of myrcene over Pd catalysts ^a										
			~		a (Selectivity (%)				
Entry	Catalyst	Time (h)	Conv. (%)	(h^{-1})	S _{mono} " (%)	2	3	4	5	6 [(Z)/(E)]
8	S _L Pd*	0.3	96	51 060	86	2	12	7	21	58 (2.05/1)
9^d	S _L Pd*	3.5	98		80	2	18	2	18	60 (1.73/1)
10	S _{NH2} Pd*	0.6	98	22 340	75	3	22	1	17	57 (1.85/1)
11 ^e	S _{NH2} Pd*	4.0	>99		68	5	27	tr.	5	63 (1.17/1)
12 ^f	S _{NH2} Pd*	24	>99		64	6	30	tr.	4	60 (1.07/1)
13 ^g	Pd/C	0.3	>99	38 300	77	4	19	tr.	46	31(0/1)
14^{g}	Pd/C	3.5	>99		51	15	34	tr.	22	29 (0/1)
15^{g}	Pd/C	21	>99		tr.	48	52	tr.	tr.	tr.

^{*a*} Reaction conditions (solventless): β-myrcene (1 mL, 5.8 mmol), catalyst (5 mg, 0.9 µmol of Pd), 348 K, 6 atm of H₂. Conversion and selectivity were determined by GC. Catalysts were pre-activated for 30 min under 6 atm of H₂ and at 348 K before use. ^{*b*} Initial turnover frequency (TOF) is expressed as moles of H₂ consumed per mole of catalyst per h. ^{*c*} Selectivity for mono-hydrogenated products **4–6**. ^{*d*} The hydrogenation curve showed no H₂ consumption after 25 min. ^{*e*} The hydrogenation curve showed negligible H₂ consumption after 80 min. ^{*f*} The continuation of run 11. ^{*g*} Reaction conditions similar to that described in (^{*a*}) except for the catalyst (Pd/C 10 wt% (3.3 mg, 3 µmol of Pd)). tr. = traces.



Fig. 3 Hydrogen consumption curve obtained during the hydrogenation of β -myrcene by S_LPd^{\star} (\odot), $S_{NH2}Pd^{\star}$ (\odot) and Pd/C (Δ) for 3.5 h. The inset shows independent experiments stopped for analysis just after the hydrogen consumption step.

regime, but the initial hydrogen consumption rate was about 40% of that shown by the S_LPd^* material (*ca.* 22 340 *vs.* 51 000 h⁻¹). Additionally, the selectivity for mono-hydrogenation after the fast hydrogen consumption step over the $S_{NH2}Pd^*$ catalyst was lower than that with the S_LPd^* catalyst (75% in entry 10 *vs.* 86% in entry 8, Table 3). The di-hydrogenated product 3 and the totally hydrogenated product 2 were formed with 23% and 3% selectivity, respectively. At longer reaction times, neither significant hydrogen consumption nor a significant change in the product distribution was observed, with only a slight increase in the amounts of products 2 and 3 being noticed (Table 3, entry 11).

For comparison, Pd/C (10 wt%, commercially available) was employed as a reference catalyst in the hydrogenation of β myrcene under the same reaction conditions used for **S_LPd***; in this case, after the first H₂ consumption regime (fast),

continuous consumption of H₂ was noticed (Fig. 3). The GC analysis performed after the fast hydrogen consumption step showed a total conversion of β -myrcene and 77% selectivity to monohydrogenated products (Table 3, entry 13). However, at longer reaction times, further hydrogenation gradually occurred changing significantly the product distribution (Table 3, entries 14 and 15). After 21 h, the reaction gave exclusively polyhydrogenated products 2 and 3. During the reaction over Pd/C, the monohydrogenated products 4 and 6a were not observed at all in the reaction solutions, with the amount of products 2 and 3 being always higher when compared with that over the S_LPd* and S_{NH2}Pd* catalysts at the same reaction times. Thus, the conventional Pd/C catalyst tends to promote the complete hydrogenation of myrcene giving polyhydrogenated products. This observation is also in agreement with the results obtained in our previous work, in which the Pd/C catalyst had also promoted the exhaustive hydrogenation of β-myrcene.14

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For both S_LPd^* and $S_{NH2}Pd^*$ nanocatalysts studied, high selectivity for monohydrogenation was obtained at very high conversions (>99%) and, differently from the Pd/C material, the product distribution was not changed significantly even after keeping the products under the reaction conditions for 24 h (Table 3, entry 12). This finding is very interesting, because over conventional hydrogenation catalysts the intermediate products are usually highly sensitive to further hydrogenation giving a fully saturated product 2. These selectivity trends can be related to the accessibility of the double bonds for surface Pd species. The presence of bulky ligands close to Pd on the surface of S_LPd* and S_{NH2}Pd* materials makes the activation of the disubstituted and trisubstituted double bonds in compounds 5 and 6 more difficult as compared to the Pd/C catalyst. As a result, the selectivity for monohydrogenation drastically decreases with the reaction time over the Pd/C catalyst but not over the S_LPd* and SNH2Pd* catalysts. On the other hand, compound 4, which has an



Scheme 4 Mechanistic scheme for the hydrogenation of myrcene (1).

easily accessible monosubstituted double bond, undergoes further hydrogenation over all three materials.

The mechanistic scheme proposed for the hydrogenation of myrcene²⁰ could rationalize the formation of the observed products (Scheme 4). The products could arise from the absorbed σ -alkyl (**c** and **e**) and/or η^3 -allyl intermediates (**d** and **f**) formed by the reaction of surface Pd species with the terminal double bonds of myrcene. Both isomers of the main product **6** could result from only η^3 -allyl complexes, whereas the minor products **4** and **5** could result from both types of intermediates, σ -alkyls and η^3 -allyls, as shown in Scheme 4. The total amounts of products **4** and **5** do not exceed one-third of all mono-hydrogenated products; therefore, the η^3 -allyl mechanism seems to operate mainly (if not exclusively) in our systems.

A preferential formation of mono-hydrogenated products 5 and **6a** (nearly 60% combined selectivity) compared to **4** and **6b** (*ca.* 25%) is an expected result, since **5** and **6a** arise through the interaction of the surface Pd with the less substituted double bond. The predominant formation of the (*Z*)-isomer **6a** rather than the thermodynamically more stable (*E*)-isomer **6b** (**6a**/**6b** \approx 2/1) should be controlled kinetically (Table 3, entries 8 and 10). However, at longer reaction times, the **6a**/**6b** ratio decreases due to a higher reactivity of the (*Z*)-isomer **6a** towards further hydrogenation and/or its Pd catalyzed isomerization to a more stable (*E*)-isomer **6b**.

Thus, the S_LPd^* nanomaterial is an efficient magnetically recoverable catalyst for the selective hydrogenation of one of the conjugated olefinic bonds of myrcene to give diolefins 5 and 6 in high combined selectivity. On the other hand, this nanomaterial is much less effective in the activation of non-conjugated double bonds, which allows for the selective synthesis of mono-hydrogenated products. This can be of interest for the hydrogenation of myrcene into monoterpenic diolefins, which could be further converted into oxygenated fragrance compounds with better selectivity than myrcene itself.

3 Experimental

3.1 General procedures and materials

All manipulations were carried out under an argon atmosphere using standard Schlenk tube or Fischer-Porter reactor and vacuum line techniques, or in a glove-box. [Pd₂(dba)₃] was purchased from Strem Chemicals. L was synthesized following methodologies previously described.21 Solvents were purchased from SDS and dried through a purification machine (MBraun MB SPS-800) or distilled prior to use: THF over sodium/benzophenone, toluene over sodium. All materials were of analytical grade and commercially available (Aldrich), including ferric chloride hexahydrate (FeCl₃·6H₂O), ferrous chloride tetrahydrate (FeCl₂·4H₂O), ammonium hydroxide (25%[w/w]), tetraethyl orthosilicate (TEOS), 4'-chloro-2,2':6',2"-terpyridine, 6-amino-1-hexanol, and (3-chloropropyl)trimethoxysilane. Cyclohexene and myrcene were previously distilled before use.

Elemental analyses (C, H, and N) were run on a Perkin Elmer 2400 II instrument. Infrared spectra were run on a Perkin Elmer FT spectrophotometer, series 2000 cm⁻¹ in the range 4000–150 cm⁻¹. 11 H, 13 C { 11 H}, HSQC, COSY and NOESY NMR spectra

were recorded on a Bruker AVANCE 350 MHz NMR spectrometer in CDCl₃ solutions at room temperature. All chemical shift values (δ) are given in ppm. Electrospray mass spectra were obtained with an MS/MS API-365 spectrometer from Perkin Elmer Sciex.

Samples for TEM/HRTEM analyses were prepared by slow evaporation of a drop of crude colloidal solution deposited onto holey carbon-covered copper grids under argon (in glove-box) for THF solutions. Transmission Electron Microscopy analyses at low (TEM) and high resolution (HRTEM) were performed at the "Service Commun de Microscopie Electronique de l'Université Paul Sabatier" (UPS-TEMSCAN). TEM images were obtained using a JEOL 1011 electron microscope operating at 100 kV with a resolution point of 4.5 Å. HRTEM observations were carried out with a JEOL JEM 2010 electron microscope working at 200 kV with a resolution point of 2.5 Å and equipped with X-ray analysis PGT (light elements detection, resolution 135 eV). The size distributions were determined through a manual analysis of enlarged micrographs with Imagetool software Version 3.0 to obtain a statistical size distribution and a mean diameter. FFT treatments have been carried out with Digital Micrograph Version 1.80.70.

3.2 Synthesis of ligand 6-aminohexyl 4'-(2,2':6',2''terpyridinyl)ether (L)

To a stirred suspension of powdered KOH (1.05 g, 18.7 mmol) in dry DMSO (180 mL) at 353 K, 6-amino-1-hexanol (0.35 g, 2.91 mmol) was added. After 30 min, 4'-chloro-2,2':6',2"-terpyridine was added (0.78 g, 2.91 mmol) and the mixture was stirred for 24 h at 353 K and then poured into 2 L of distilled water. The aqueous phase was extracted with CH_2Cl_2 (3 \times 200 mL). The combined organic phases were dried over Na2SO4 and evaporated in vacuo to give 0.91 g (74%) of L. ¹H NMR [400 MHz, CDCl₃]: δ 8.75 (2H, H6,6"), 8.62 (2H, H3,H3'), 8.05 (2H, H3',5'), 7.89 (2H, H4,4"), 7.31 (2H, H5,5"), 5.34 (2H, NH2), 4.14 (2H, OCH2), 2.74 (2H, CH2NH), 1.84 (2H, OCH2CH2), 1.53 (4H, CH2CH2CH2CH2NH), 1.44 (2H, CH2CH2CH2NH). ¹³C NMR [400 MHz, CDCl₃]: δ 167.2 (C4'), 159.3 (C1',5'), 157.4 (C2,2"), 149.6 (C6,6'), 137.3 (C4,4"), 124.5 (C3,3"), 120.8 (C5,5"), 107.3 (C3',5'), 67.8 (O-CH₂), 42.7 (CH₂-NH₂), 29.2, 26.8, 25.9, 25.5 (-CH₂-). IR (KBr); cm⁻¹: 3325, 3280 (NH), 3050 (ArH), 2926-2746 (aliphatic -CH), 1604 (C=C, C=N)_{ar}, 1464 (δ(C=C), δ(C= N))_{ar}, 1057 (O). MS (*m*/*z*) 349.2 $[L+H]^+$ (calcd *m*/*z* = 348.2). Elemental analysis: calculated for C₂₁H₂₄N₄O: C, 72.39; H, 6.94; N, 16.08% and found: C, 72.35; H, 6.84; N, 16.34%.

3.3 Synthesis of silica-coated magnetic support (S)

The synthesis of the magnetic support comprised the preparation of magnetite nanoparticles by the co-precipitation method followed by silica coating using a reverse microemulsion process as reported elsewhere.²⁴

A mixture of aqueous solutions of 10 mL FeCl₃ (1 mol L^{-1}) and 2.5 mL FeCl₂ (2 mol L^{-1}) in HCl (2 mol L^{-1}) was added to 250 mL NH₄OH (0.7 mol L^{-1}) under N₂ and mechanical stirring. After 30 min the magnetite NPs were magnetically recovered and washed 3 times with 250 mL of distilled water. Then, the magnetite NPs were dispersed again in 250 mL of distilled water, and 5 mL of 1 mmol L^{-1} solution of oleic acid in acetone was added dropwise under vigorous mechanical stirring. The resulting material was washed with acetone and finally dispersed in 50 mL of cyclohexane. The final solution was centrifuged (2000 rpm, 30 min) to remove the non-stabilized particles and was stocked under air.

The silica coating was obtained by means of a reverse microemulsion process when 178.4 g of Igepal CO-520, 800 mg of magnetite cyclohexane solution (around 32 mL of a solution containing 25.0 mg.mL⁻¹ of magnetite NPs) and 38.0 mL of ammonium hydroxide (29%) were dispersed in 2.8 L of cyclohexane. Then 30.8 mL of tetraethyl orthosilicate (TEOS) was added dropwise and the mixture was kept under slow mechanical stirring for 16 h. Then the NPs were precipitated with methanol, recovered by centrifugation (7000 rpm, 60 min) and washed 3 times with ethanol. The resulting solid was dried in an oven at 373 K for 20 h. FT-IR (KBr); cm⁻¹: 3379 (Si–OH), 1052 (Si–O–Si), 630, 427 (Si–O).

3.3.1 SYNTHESIS OF CHLOROPROPYL-MODIFIED SILICA (S_{CL}). A mixture of silica support (S) (1.5 g) and (MeO)₃Si(CH₂)₃Cl (3.0 g, 15.0 mmol) in toluene (100 mL) was refluxed for 16 h.²⁸ The solvent was removed *in vacuo* and the residue was admixed again with (MeO)₃Si(CH₂)₃Cl (3.0 g, 15.0 mmol) and toluene (100 mL) and refluxed for 16 h and the solvent again removed *in vacuo*. The resulting residue was washed with dichloromethane (3 × 25 mL) and dried at 333 K for 24 h, to afford S_{CI} (1.8 g). FT-IR (KBr); cm⁻¹: 3348 (Si-OH), 1053 (Si-O-Si), 630, 425 (Si-O).

3.3.2 SYNTHESIS OF TERPYRIDINE-MODIFIED SILICA (S_L). A mixture of L (1.0 g, 2.36 mmol) and S_{Cl} (1.5 g) in CHCl₃ (100 mL) was refluxed for 24 h, and the solvent was then removed *in vacuo*. The residue was washed with chloroform (3 × 25 mL) and methanol (3 × 25 mL), before drying under vacuum to lead to S_L (1.7 g). IR (KBr); cm⁻¹: 3350 (Si–OH), 3326 (NH), 2927, 2854 (aliphatic CH), 1605, 1464 (C=C and C=N), 1054 (Si–O–Si), 631, 429 (Si–O).

3.3.3 SYNTHESIS OF S_LPd . $[Pd_2(dba)_3]$ (20 mg, 0.02 mmol) and 200 mg of S_L were dispersed in THF (150 mL) in a Fischer-Porter reactor under argon and vigorous stirring at 196 K. The solution was then pressurized under 3 bar of hydrogen and left at room temperature. After 1 h the color of the solution turned from purple to black, showing the formation of Pd NPs. The hydrogen pressure and the temperature were maintained for 20 h to ensure total decomposition of the palladium complex. The hydrogen was then evacuated and the resulting solid was washed with dichloromethane (5 × 25 mL) and dried under vacuum at 333 K for 24 h leading to S_LPd (ICP OES analysis: 2.3% Pd).

3.3.4 SYNTHESIS OF $S_{NH2}Pd$. $[Pd_2(dba)_3]$ (20 mg, 0.02 mmol) and 200 mg of S_{NH2} were dispersed in THF (150 mL) in a Fischer-Porter reactor under argon and vigorous stirring at 196 K. The solution was then pressurized under 3 bar of hydrogen and left at room temperature. After 1 h, the color of the solution turned from purple to black, indicating the formation of Pd NPs. The hydrogen pressure and the temperature were maintained for 20 h to ensure total decomposition of the palladium complex. The hydrogen was then evacuated and the resulting solid was washed with dichloromethane (5 × 25 mL) and dried under vacuum at 333 K for 24 h leading to $S_{NH2}Pd$ (ICP OES analysis: 2.1% Pd).

3.4 Hydrogenation reactions

The catalytic reactions were carried out in a modified Fischer-Porter glass reactor connected to a pressurized hydrogen tank. In a typical experiment, the nanocatalyst (10 mg) and the desired quantity of substrate were added to the reactor under an inert atmosphere. When indicated, a pre-activation step of the catalyst was performed by keeping the powder catalyst under H₂ pressure (6 atm) for 30 min inside the reactor before adding the substrate with a syringe under N2. The reactor was thus attached to the hydrogenation apparatus. The reactor was then purged with H₂ and the pressure was set to the required working pressure (6 atm) via a gas regulator. The pressure was maintained constant for the entire course of the reaction by leaving the reactor open to the H₂ supply tank. The reaction was conducted under magnetic stirring (700 rpm). The temperature was controlled using an oil bath and a hot-stirring plate connected to a digital controller (ETS-D5 IKA). The fall in the H₂ pressure in the H₂ tank was monitored with a pressure transducer interfaced through a Novus Field Logger converter to a computer. The pressure versus time data were collected by FieldChart Novus software. The catalyst was recovered magnetically by placing a magnet on the reactor wall. The organic phases were transferred into a glass vessel with a cannula and analyzed by gas chromatography (GC) and GC-MS. The catalyst was reused by adding to the reactor a new amount of substrate. The identification of the products resulting from the hydrogenation of myrcene (compounds 2-6) by MS and NMR Spectroscopy has been reported previously and used here for comparison.20

3.5 Hg(0) poisoning test

For the Hg poisoning experiments, the catalytic reactions were carried out in the same standard hydrogenation conditions as previously described, apart from the addition of elemental Hg (0.12 g, 300 equiv.) that was performed at 10% conversion of cyclohexene to cyclohexane. The reaction was monitored by the fall in hydrogen pressure in the H_2 reservoir as a function of time before and after the addition of Hg. The products were separated by decantation of the nanocatalyst with a magnet and the organic phase was transferred by cannula and analyzed by GC and GC-MS.

4 Conclusions

In this work, we report a novel and successful approach for the efficient deposition of palladium nanoparticles onto a magnetic silica support and the potential of the so-obtained nanomaterial in hydrogenation catalysis. The driving force of our strategy is the design of a hybrid bifunctional terpyridine ligand, whose role, in turn, is two-fold: (1) to functionalize the silica coated magnetite solid support and (2) control the size and stability of the deposited palladium nanoparticles. The obtained nanomaterial displays well-dispersed and size-controlled Pd

nanoparticles of 2.5 nm on the silica support. This nanomaterial has proved to be highly active for the hydrogenation of olefins using model substrates such as cyclohexene, with a high reusability without losing activity upon recycling. Actually, compared to a similar Pd catalyst, the terpyridine ligand provided a highly stable catalytic system, the activity of which increased upon reuse reaching a TOF of *ca.* 58 000 h⁻¹ or 129 000 h⁻¹ when corrected for surface Pd atoms. Furthermore, the high selectivity to the mono-hydrogenated products observed with myrcene constitutes promising results. In terms of *Green Chemistry*, the magnetic character of this nanocatalyst makes it an easily recoverable catalyst. Thus, further extensive scope for the Suzuki–Miyaura cross-coupling reaction and the application of this nanocomposite to other organic transformations are presently envisaged.

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