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Dendrimer-Stabilized Metal Nanoparticles as Efficient Catalysts for Reversible Dehydrogenation/Hydrogenation of N-Heterocycles

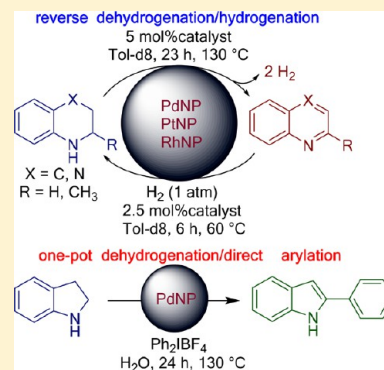
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S Supporting Information

ABSTRACT: Nanoparticles (Pd, Pt, Rh) stabilized by G4OH PAMAM dendrimers and supported in SBA-15 (MNPs/SBA-15 with M = Pd, Pt, Rh) were efficiently used as catalysts in the acceptorless dehydrogenation of tetrahydroquinoline/indoline derivatives in toluene (release of H₂) at 130 °C. These catalysts are air stable, very active, robust, and recyclable during the process. The reverse hydrogenation reaction of quinoline derivatives (H₂ storage) was also optimized and successfully performed in the presence of the same catalysts in toluene at 60 °C under only 1 atm of hydrogen gas. Such catalysts may be essential for the adoption of organic hydrogen-storage materials as an alternative to petroleum-derived fuels. Hot filtration test confirmed that the reaction follows a heterogeneous pathway. Moreover, PdNPs/SBA-15 was an excellent catalyst for the direct arylation at the C-2 position (via C–H activation) of indole in water in the presence of a hypervalent iodine oxidant. Thus, a one-pot dehydrogenation/direct arylation cascade reaction between indoline and an arylated agent was efficaciously performed in water, demonstrating the potential of the system to catalyze tandem heterogeneous/homogeneous processes by choice of the appropriate oxidant/reductant.



INTRODUCTION

Catalytic dehydrogenation of alkanes has received significant attention because it converts low-value hydrocarbon feedstocks into valuable alkenes and arenes that are important in organic synthesis, polymer synthesis, and widely used in many industry processes.¹ N-containing compounds have been experimentally and computationally shown to undergo dehydrogenation more readily than cyclic alkanes, because the nitrogen atom decreases the endothermicity of the reaction. Moreover, acceptorless dehydrogenation of saturated N-heterocycles provides one of the most atom-efficient processes to produce heterocycles, such as indole and quinolone, that are found in numerous pharmaceutical and bioactive compounds.² Therefore, tremendous effort has been aimed at identifying and improving catalytic methods for the dehydrogenation of N-heterocycles. Homogeneous catalysts (Ir,³ Rh,⁴ Ru,⁵ and Co⁶ pincer complexes, air-sensitive in most cases), heterogeneous catalysts (Au, Rh, Pt, Pd, Cu nanoparticles)⁷ have been applied in the catalytic dehydrogenation processes, but these methods may require additional oxidizers (O₂, TEMPO), bases, hydrogen acceptors (ethylene or *t*-butylethylene (TBE)), and/or require harsh conditions.⁸ In addition to the formation of valuable dehydrogenated N-heterocycles, the catalytic dehydrogenation is also applicable to the field of liquid organic hydrogen storage materials and commercial fuel cells.⁹ However, examples of catalysts describing activity for both the dehydrogenation of N-heterocycles (release of hydrogen H₂) and the reverse hydrogenation (storage of H₂) of the dehydrogenated N-

heterocycles, are exceedingly rare. In 2009 Fujita et al. reported a homogeneous Ir-pincer complex capable of catalyzing the dehydrogenation of 1,2,3,4-tetrahydroquinoline to quinoline in *p*-xylene under reflux for 20 h. The reverse reaction was possible in the presence of the same catalyst (4 mol %) at 110 °C for 20 h under 1 atm of hydrogen gas.¹⁰ The same dehydrogenation/hydrogenation sequence was described by Kaneda et al. using Cu nanoparticles supported on TiO₂ as catalysts. In this case, the dehydrogenation step was carried out at 150 °C in mesitylene for 16 h, while the hydrogenation reaction required 6 h under 1 atm of hydrogen.¹¹ More recently Jones et al. described the use of an homogeneous cobalt pincer catalyst in the reverse dehydrogenation/hydrogenation of 1,2,3,4-tetrahydroquinoline/quinolone and derivatives.⁶ The dehydrogenation reaction was only efficient in the presence of 10 mol % of catalyst at 150 °C in xylene for 4 days (no reaction was detected at 120 °C in toluene). The same catalyst (5 mol %) allowed the hydrogenation of the quinoline derivatives at 120 °C in THF in the presence of 10 atm of hydrogen. Toyao et al. synthesized different metallic nanoparticles supported on carbon. They found that only 0.1 mol % of their Pt/C was necessary to catalyze the dehydrogenation of 2-methyl-1,2,3,4-tetrahydroquinoline, but under these catalyst loading, the reaction required refluxing xylene for 60 h. The

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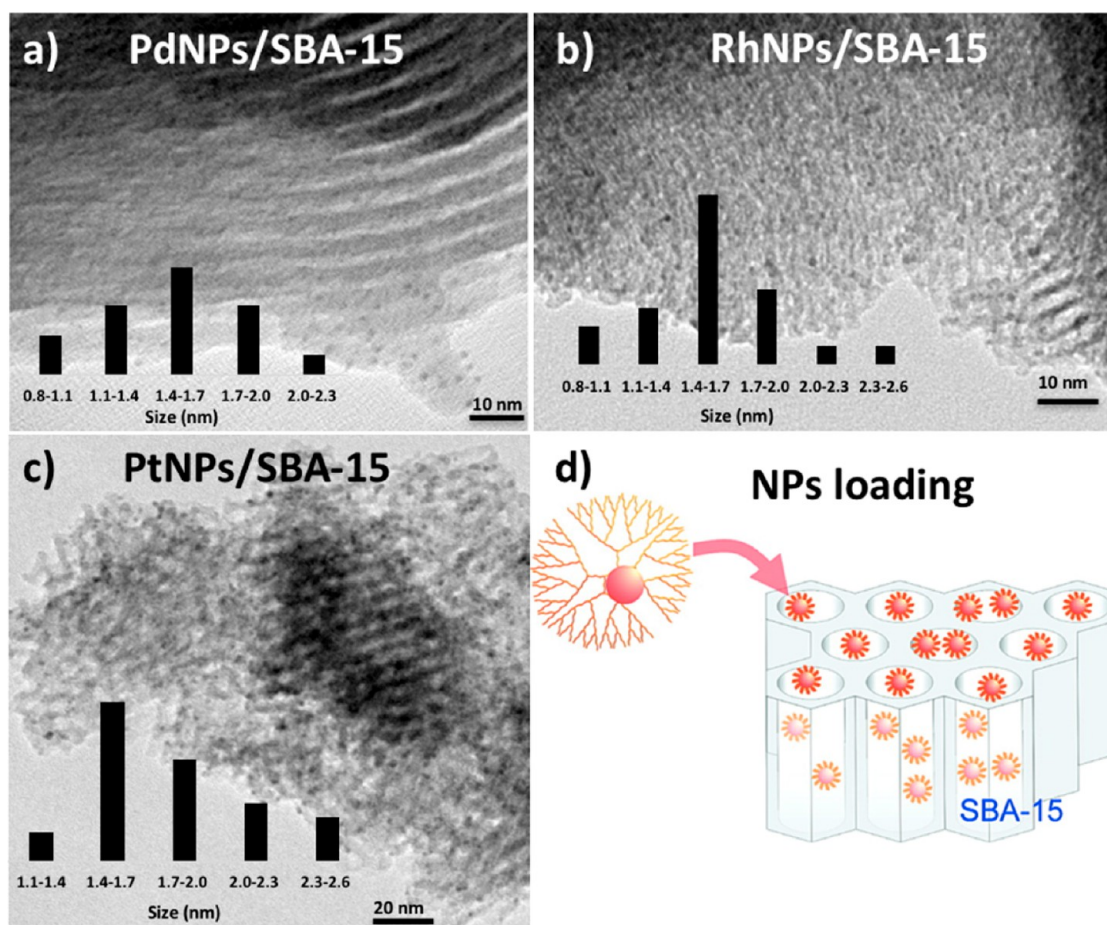
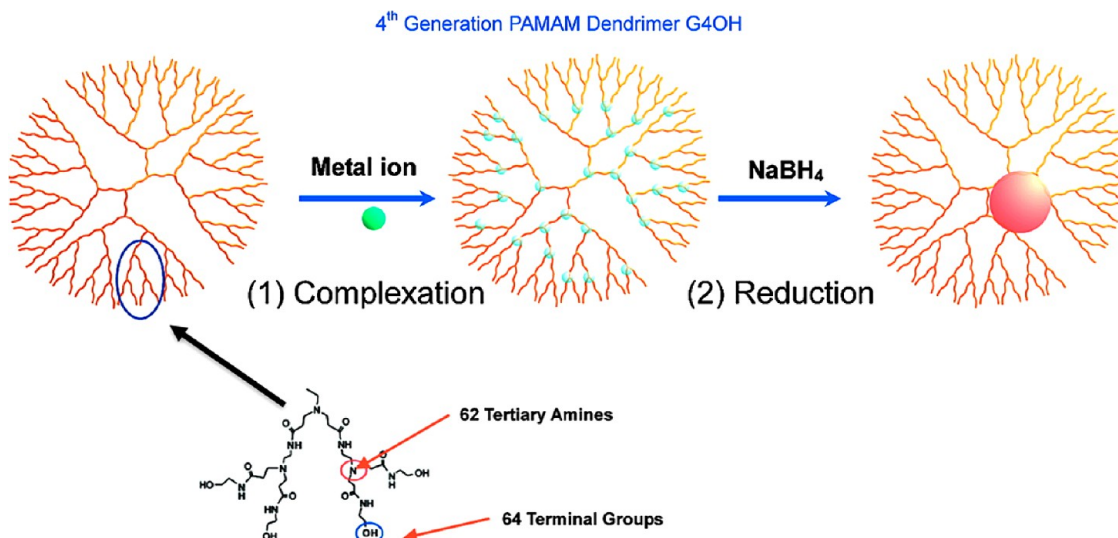
Scheme 1. Synthesis of MNPs Stabilized by PAMAM-G4OH Dendrimer^{13a}

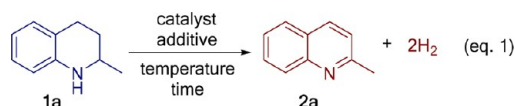
Figure 1. NPs loading. TEM images of PdNPs/SBA-15 (average size = 1.5 ± 0.3 nm) (a), RhNPs/SBA-15 (average size = 1.6 ± 0.4 nm) (b), and PtNPs/SBA-15 (average size = 1.8 ± 0.4 nm) (c). Schematic of NPs loading (d).

reverse reaction was promoted by the same catalyst, but only at 160 °C with 3 bar of hydrogen.¹²

We have developed the synthesis of heterogeneous metallic nanoparticles stabilized by PolyAMido AMine (PAMAM) dendrimers supported on SBA-15 (MNPs/SBA-15).¹³ While the unsupported MNPs have been reported as competent catalysts for C–C cross coupling reactions (Suzuki, Heck,

Sonogashira, Stille), hydrogenation of double bonds, selective hydrogenation of triple bonds, nitrophenol/methyl blue/methyl orange hydrogenation,¹⁴ our MNPs/SBA-15 catalysts were also efficient in promoting other reaction classes,¹³ such as cyclization reactions via π -bond activation,^{13a–d} ring opening reaction of strained 3-membered rings,^{13e} and aldol reactions of methyl isocyanoacetate.^{13f} In this article, we report on our

Table 1. Selective Dehydrogenation of 2-Methyl-1,2,3,4-tetrahydroquinoline into 2-Methyl Quinoline



entry	catalyst ^a	solvent	additive	temperature (°C)	time (h)	conversion (%)
1	PdNPs/SBA-15			110	15	10.3
2	PdNPs/SBA-15		TBE (300%)	110	15	9.6
3	PdNPs/SBA-15		TBE (600%)	110	15	15
4	PdNPs/SBA-15		PhICl ₂	110	15	5.6
5	PdNPs/SBA-15	Tol- <i>d</i> ₈		110	15	7.8
6	SBA-15	Tol- <i>d</i> ₈		130	23	<0.2
7		Tol- <i>d</i> ₈		130	23	<0.2
8	PdNPs/SBA-15 ^b			130	23	>99.9
9	RhNPs/SBA-15 ^b			130	23	>99.9
10	PtNPs/SBA-15 ^b			130	23	>99.9
11	PtNPs/SBA-15 ^c			130	23	>99.9

^a0.5 mol % catalysts. ^b5 mol %. ^c1 mol %. Conversion (formation of the desired product) was calculated by ¹H NMR.

studies of the dehydrogenation/hydrogenation reaction of tetrahydroquinoline/quinoline derivatives in the presence of MNPs/SBA-15 (M = Pd, Pt, Rh). PdNPs/SBA-15, PtNPs/SBA-15, and RhNPs/SBA-15 show activities in the dehydrogenation of these N-heterocycles in toluene (or without solvent) at 130 °C that are higher than their unsupported MNP homologues, or their metallic salt precursors. These catalysts also operated under mild conditions (20–60 °C, 1 atm of H₂) for the hydrogenation of quinolines derivatives. Moreover, PdNPs/SBA-15 showed remarkable activity toward the C–H arylation at the C-2 position of indole. The mild conditions allowed for the PdNPs/SBA-15-catalyzed direct conversion of indoline to 2-phenylindole through a one-pot cascade involving indoline dehydrogenation step followed by direct arylation.

RESULT AND DISCUSSION

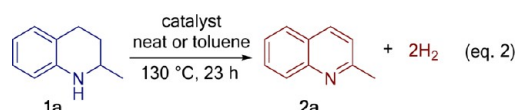
Synthesis of the Catalysts. The catalysts studied in the reverse dehydrogenation/hydrogenation were prepared in two steps. The first step consisted of synthesizing the homogeneous MNPs (M = Pd, Pt, Rh) stabilized by the fourth generation G4OH PAMAM dendrimer in water as described by Crooks.¹⁵ This step is composed of two parts (see Scheme 1): complexation of the metallic ions to the tertiary amines of the dendrimer and subsequent reduction of these metallic ions to the NPs. Briefly, PdNPs were prepared by addition of an aqueous solution of K₂PdCl₄ (0.1 mmol in 10 mL of deionized water) to an aqueous solution of PAMAM G4OH (2.5 μmol of in 10 mL of deionized water) in order to achieve a ratio 40/1 Pd atoms/dendrimer. The resulting solution was diluted by 4-fold, which is necessary to avoid aggregation during the reducing step (no dilution is required for the synthesis of PtNPs or RhNPs). The solution was degassed with argon for 30 min, allowing for complete complexation of Pd(II) by the tertiary amines of the dendrimer (complexation for the formation of RhNPs and PtNPs required one night or 3 days, respectively). Fresh sodium borohydride NaBH₄ (10 equiv per Pd) dissolved in 4 mL of deionized water at 5 °C, was added dropwise to the Pd(II)/PAMAM-G4OH solution with rapid stirring, leading to an instantaneous change of solution color from yellow to dark black. The solution was stirred for an additional 3 h prior to the purification/washing step (i.e., dialysis).

The final supported catalyst (second step, heterogenization of the homogeneous catalyst) was obtained by mixing a mesoporous SBA-15 support with the nanoparticle water solution in an ultrasonic bath for 3 h at room temperature, in order to achieve 1.0 wt % Pd loading. The catalyst solution was centrifuged and then dried in an oven at 80 °C for 2–3 days. The success of the impregnation was evaluated using ICP-OES, and TEM: ICP-OES revealed that the loading was 100% successful and TEM images showed that the MNP size remained unchanged after loading (1.5 ± 0.3 nm). Using this technique, we also produced supported MNPs of 1.0 wt % Rh and 2.0 wt % Pt (1.6 ± 0.4 nm, 1.8 ± 0.4 nm respectively), see Figure 1.

Dehydrogenation Process. 2-Methyl-1,2,3,4-tetrahydroquinoline **1a** was chosen as a model substrate for the investigation of the catalytic dehydrogenation (eq 1). As the reaction typically requires a high temperature and a long reaction time, 110 °C and 15 h were chosen accordingly (see Table 1). Under these conditions, approximately 10% of **1a** was converted into 2-methyl-quinoline **2a** when the reaction was carried out using 0.5 mol % PdNPs/SBA-15 as catalyst without solvent and or additives (entry 1). No significant enhancement was observed by adding an excess of t-butylethylene (TBE) as a hydrogen acceptor (entries 2, 3). The use of dichloro iodobenzene (PhICl₂), an oxidizer,^{13d} resulted in a decrease in the conversion to the desired product (entry 4). No trace of 2-methyl-quinoline **2a** was detected by ¹H NMR or by GC–MS when SBA-15 alone was used as catalyst or when no catalyst was used during the reaction. By increasing the temperature to 130 °C and the time of reaction to 23 h, a significant improvement was observed. A catalyst loading of 1 mol % or 5 mol % was necessary to induce the complete conversion of **1a** into **2a** using PdNPs/SBA-15, PtNPs/SBA-15 and RhNPs/SBA-15, at 130 °C during 23 h (entries 8, 9, 10, 11). Only PtNPs/SBA-15 quantitatively catalyzed the dehydrogenation of **1a** into **2a** with 1 mol % catalyst loading (entry 11, only 59.9% and 24% of conversion were observed with RhNPs/SBA-15 and PdNPs/SBA-15 respectively). No trace of partial dehydrogenated product was detected by GC–MS or ¹H NMR with any of the conditions tested.

The dehydrogenation of 2-methyl-1,2,3,4-tetrahydroquinoline **1a** was also evaluated using Pt, Pd, Rh ionic salts (0.5–5 mol %) as catalysts at 130 °C for 23 h in toluene-*d*₈ or without

Table 2



entry	catalyst	amount (mol %)	conversion ^a (tol- <i>d</i> ₈) ^b
12	RhCl ₃	0.5	13.3% (8.9%)
13	RhCl ₃	5	26.3%
14	Rh(acac) ₃	0.5	3.9% (0.5%)
15	K ₂ PtCl ₄	0.5	6.1% (0.8%)
16	Pt/C	0.5	6.1% (8.1%)
17	K ₂ PdCl ₄	0.5	8.4% (3.8%)
18	K ₂ PdCl ₄	5	15.4% (11%)
19	PdCl ₂	0.5	7.7% (4%)

^aAll the reactions were carried out with 1 mmol of reactant, at 130 °C, for 23 h without solvent. ^bConversion to product when carried out in toluene-*d*₈. The conversion (formation of desired product) was calculated by ¹H NMR.

solvent; however, low conversions were observed in all cases (Table 2). The low efficiency was attributed to reduction of the ionic species to the corresponding metallic form during the reaction (black metallic particles were observed inside the solution and on the wall of the vessel).

The scope of the reaction was studied (Table 3). As expected, the three catalysts were also efficient for dehydrogenation of similar *N*-heterocycles in toluene. 1,2,3,4-Tetrahydroquinoline **1b**, 2-methyl-1,2,3,4-tetrahydroquinoxaline **1c** and 1,2,3,4-tetrahydroquinoxaline **1d** were quantitatively dehydrogenated using PdNPs/SBA-15 and RhNPs/SBA-15 as catalysts. The dehydrogenation of **1c** and **1d** in the presence of PtNPs/SBA-15 reached only 77% and 72% of conversion, respectively, in toluene. However, performing the reaction under neat conditions allowed for almost complete transformation of the starting materials in both cases. The lower activity observed in this case is likely a result of the increase of absorption strength of the reactants (presence of an additional nitrogen atom) onto the PtNPs/SBA-15 catalyst. The dehydrogenation of cycloalkane is more endothermic than *N*-

Table 3

Reactant ^a	product	catalyst	Conversion (neat) ^b	Yield ^c
		PdNPs/SBA-15 ^e	>99.9%	98%
		RhNPs/SBA-15	>99.9%	98%
		PtNPs/SBA-15	>99.9%	98%
		PdNPs/SBA-15	>99.9%	92%
		RhNPs/SBA-15	>99.9%	91%
		PtNPs/SBA-15	>99.9%	93%
		PdNPs/SBA-15	>99.9%	99%
		RhNPs/SBA-15	>99.9%	99%
		PtNPs/SBA-15	77% (95%)	77%
		PdNPs/SBA-15	>99.9%	99%
		RhNPs/SBA-15	>99.9%	99%
		PtNPs/SBA-15	72% (>93%)	72%
		PdNPs/SBA-15	10% (60%)	(50%)
		RhNPs/SBA-15	<2% (<2%)	-
		PtNPs/SBA-15	<2% (<2%)	-
		PdNPs/SBA-15 ^d	>99.9%	96%
		RhNPs/SBA-15 ^d	>99.9%	97%
		PtNPs/SBA-15 ^d	>99.9%	96%
		PdNPs/SBA-15 ^d	>99.9%	96%
		RhNPs/SBA-15 ^d	>99.9%	94%
		PtNPs/SBA-15 ^d	>99.9%	96%
		PdNPs/SBA-15	5% (>99.9%)	(89%)
		RhNPs/SBA-15	0% (0%)	-
		PtNPs/SBA-15	0% (0%)	-

^aAll the reactions were carried out with 0.1 mmol of reactant, 5 mol % catalyst, 1 mL of toluene-*d*₈ at 130 °C for 23 h. ^bConversion to product in reaction conducted without solvent. ^cThe yield was calculated by ¹H NMR using of mesitylene as an internal standard. ^dCatalyst loading lowered from 5 to 2 mol %. ^eThe reaction was also carried out in H₂O, and identical conversion of the reaction was observed.

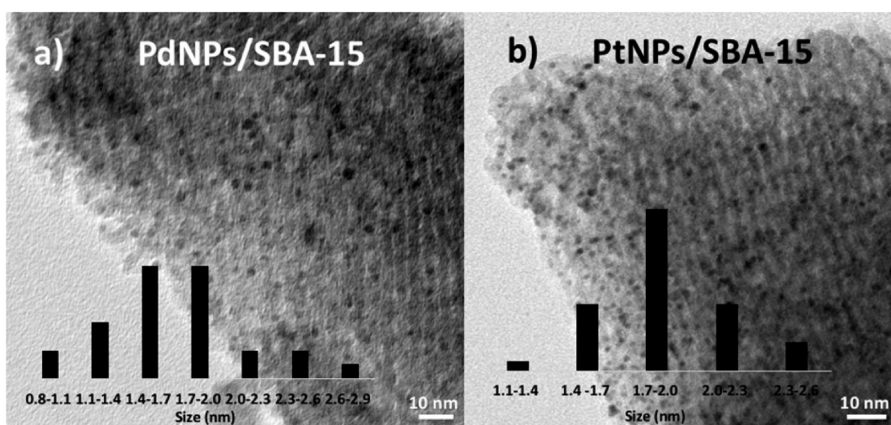


Figure 2. TEM images of PdNPs/SBA-15 (a) and PtNPs/SBA-15 (b) after reaction.

heterocycles; therefore, as expected, 1,2,3,4-tetrahydronaphthalene **1e** underwent slower dehydrogenation to afford naphthalene **2e** in 60% conversion under neat conditions (only 10% were observed in toluene). The dehydrogenation of indoline derivatives (**1f** and **1g**) under the optimized conditions with only 2% mol of any of the three catalysts, gave quantitative conversion into indole derivatives (**2f** and **2g**) as detected by ^1H NMR and GC–MS. Finally, dehydrogenation of 2,3-dihydrobenzofuran **1h** was successful only with PdNPs/SBA-15.

In order to investigate whether the catalyst leaching occurred during the reaction, the catalyst was filtered after reaction (dehydrogenation of **1a** into **2a**) and the supernatant analyzed by ICP-AES. The metal content of the solution was below the limit of detection of the apparatus (0.1 ppm), consistent with a minimal or no metal leaching under reaction conditions. Moreover, spent catalysts analyzed by TEM showed roughly no change in particle size (1.7 ± 0.4 nm instead of 1.5 ± 0.3 nm for PdNPs/SBA-15, Figure 2a). Additionally, the PdNPs/SBA-15 catalyst was used an additional two times without a significant loss in activity (95% of conversion was detected after 3 runs). PtNPs/SBA-15 and RhNPs/SBA-15 were also analyzed by TEM after reaction, and no change in size for the nanoparticles (1.8 ± 0.3 nm for PtNPs/SBA-15) was observed (Figure 2b and SI). Finally, the catalysts were analyzed before and after reaction using X-ray photoelectron spectroscopy (XPS). Analysis of the XPS data is consistent with the three catalysts becoming reduced (more metallic) at the end of the reaction, as hydrogen gas is forming from the substrates.

The mechanism of the dehydrogenation reaction likely follows that of previous reported palladium-catalyzed processes.¹⁶ Consistent with these reports, release of hydrogen gas was detected with gas buret connected to the reactor. In the case of tetrahydroquinoline derivatives, two successive dehydrogenation reactions are required; as no intermediate was observed by ^1H NMR and GC–MS, it is likely that the second dehydrogenation reaction, which forms an aromatic molecule, is the faster of the two steps.

Hydrogenation Process. The hydrogenation reaction (i.e., “hydrogen storage” step) of 2-methyl quinoline **2a** into **1a** was investigated in order to examine whether the catalyst systems could be applied in a reversible dehydrogenation/hydrogenation system (eq 3). The hydrogenation reaction can be challenging to perform under mild conditions; typically the hydrogenation of N-heterocycles requires between 10 to 70

atm of hydrogen or elevated temperature; relatively few examples of this transformation operating under low temperatures and only 1 atm of hydrogen have been disclosed.^{7f,10,11,17} Gong et al. reported that Pd nanoparticles supported on graphitic carbon nitrides catalyzed the hydrogenation of quinoline derivatives under 1 atm of H_2 in ethanol at 60 °C.^{17a} More recently, Bai et al. described that 1.2 nm PtNPs supported on silica spheres presented the highest reported activity for the hydrogenation of quinoline derivatives. The hydrogenation occurred at 30 °C with 1 atm of hydrogen and 5% mol catalyst loading.^{17d} As mentioned in the introduction Fujita et al.^{10a} and Kaneda et al.¹¹ described the synthesis of catalysts (homogeneous and heterogeneous, respectively) capable of catalyzing both the dehydrogenation and hydrogenation. In these studies, the hydrogenation step was performed under only 1 atm of hydrogen, but required elevated temperature of 110 °C–150 °C.

The catalytic hydrogenation of 2-methylquinoline was examined in various solvents (see Table 4) at 60 °C for 24 h

Table 4. Hydrogenation of 2-Methylquinoline^a

entry	catalyst	solvent	yield (%)
20	PtNPs/SBA-15		87
21	PtNPs/SBA-15	CD_3OD	65
22	PtNPs/SBA-15	D_2O	98.4
23	PtNPs/SBA-15	THF	86
24	PtNPs/SBA-15	Tol- d_8	>99.9
25	PdNPs/SBA-15	Tol- d_8	>99.9
26	RhNPs/SBA-15	Tol- d_8	48
27	PdNPs solution	H_2O	16

^aThe reactions were carried out with 0.1 mmol of 2-methylquinoline. The yield was calculated by ^1H NMR using mesitylene as an internal standard.

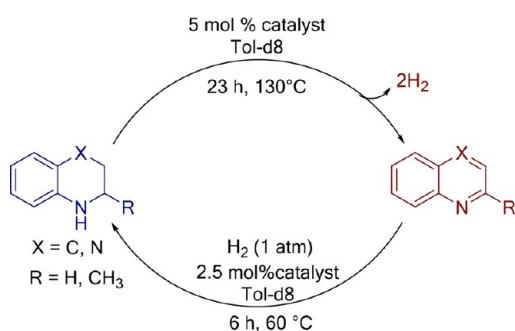
under 1 atm of hydrogen (via a balloon). The reaction in toluene, catalyzed by PtNPs/SBA-15 (entry 24) or PdNPs/SBA-15 (entry 25), provided the optimal results, furnishing complete conversion to 2-methyl-1,2,3,4-quinoline **1a** as detected by ^1H NMR and GC–MS). The unsupported PdNPs catalyst was not efficient for the hydrogenation reaction

affording only 16% of conversion to the tetrahydroquinoline (entry 27)

Further reaction optimization revealed that **2a** to **1a** underwent quantitatively hydrogenation catalyzed by PdNPs/SBA-15 or PtNPs/SBA-15 after only 6 h under reaction conditions of entries 24 and 25. On the other hand, decreasing the catalyst to 1 mol %, produced **2a** with 92% and 73% conversion at 60 °C in 24 h in the presence of PdNPs/SBA-15 or PtNPs/SBA-15, respectively; however, the hydrogenation of **2a** with 2.5 mol % of PtNPs/SBA-15 was quantitative at 40 °C after 24 h and almost quantitative at 20 °C (91% of conversion) for the same time of reaction.

The scope of the hydrogenation reaction was also studied in the presence of PdNPs/SBA-15 or PtNPs/SBA-15 as their activity for the reaction was higher than RhNPs/SBA-15. The hydrogenation of quinolone derivatives (**2a–2d**) was quantitative under optimized conditions with both catalysts (Scheme 2). However, only traces of indoline **1f** or 2-methyl indoline **1g**

Scheme 2. Reversible System for Hydrogen Storage/Release



were detected when the hydrogenation was tested on indole **2f** or 2-methyl indole **2g**. Notably, low hydrogen pressure was not sufficient to hydrogenate indole derivatives, even at elevated temperatures (110 °C) where indole was cracked/destroyed.

The three catalysts were recovered after the hydrogenation of 2-methyl-quinoline **2a**, and analyzed by TEM. No change of particle size was observed (see Figure 3). As before, ICP analysis of the supernatant (<0.1 ppm), after filtration of the catalyst, suggested that significant leaching of the catalysts during the reaction was absent.

To confirm that the reaction takes place at the interface between the solid catalyst and the liquid medium, a hot filtration test was performed during hydrogenation process. After 1 h of hydrogenation of 2-methylquinoline **2a** at 60 °C in toluene, the catalyst (PdNPs/SBA-15 or PtNPs/SBA-15) was quickly filtered, and the reaction solution was allowed to stir for an additional 5 h at 60 °C. The conversion of the reaction was analyzed by ¹H NMR after 3 h and 6 h of reaction (Figure 4). After filtration of the catalyst, the hydrogenation seems to stop. Indeed, after 1 h of reaction with PdNPs/SBA-15, extra 5 more hours of stirring of the filtrate under H₂ after filtration, the conversion of the reaction remains the same as after 1 h of reaction (Figure 4a). The same phenomenon has been observed for the hot filtration test in the presence of PtNPs/SBA-15 (Figure 4b). The reaction is stopped after filtration, confirming the heterogeneous role of the catalyst during the reaction. The catalysts were reused three times without apparent loss of activity. Indeed, only 88% conversion of **2a** into **1a** was detected by ¹H NMR in the presence of PdNPs/SBA-15 after 3 reuses and 6 h of reaction, instead of >99.9%. Two more hours were necessary to achieve a quantitative

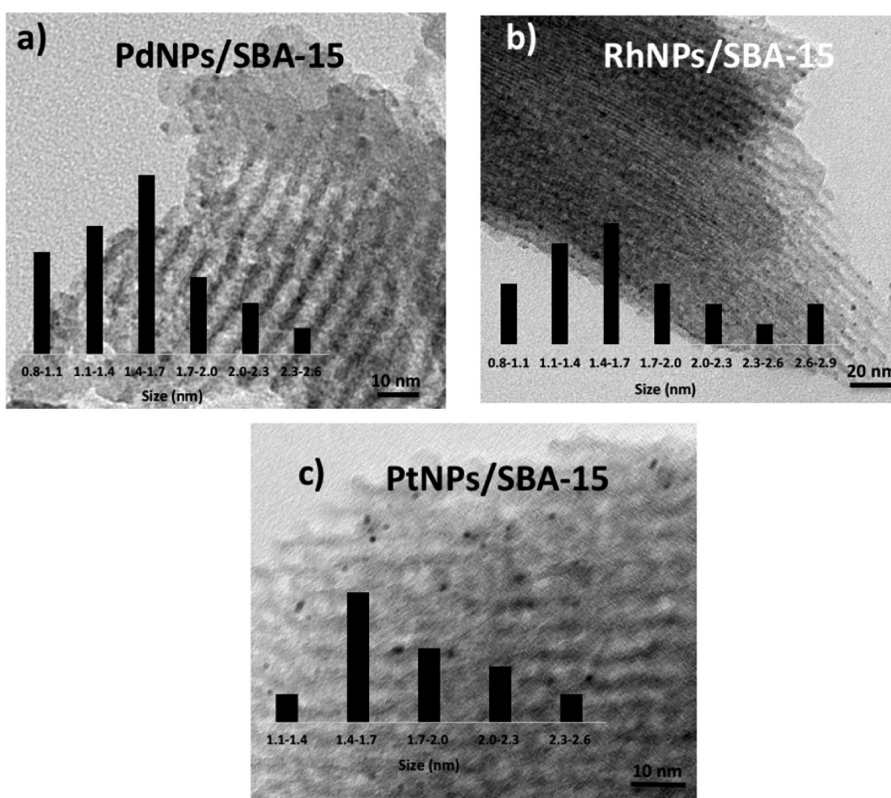


Figure 3. TEM images of PdNPs/SBA-15 (average size 1.5 ± 0.6 nm) (a), RhNPs/SBA-15 (average size 1.6 ± 0.6 nm) (b), and PtNPs/SBA-15 (1.8 ± 0.4 nm) (c) after reaction.

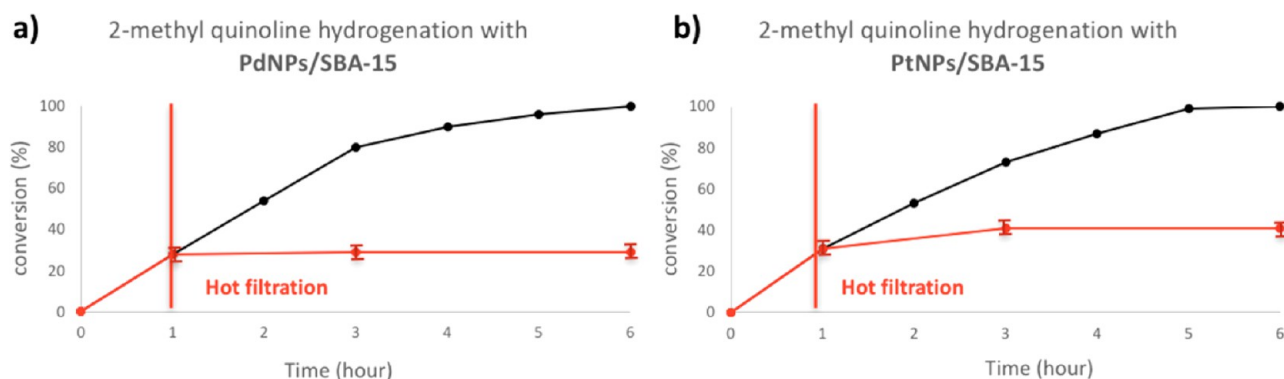


Figure 4. Kinetics of the reaction and hot filtration test results with PdNPs/SBA-15 (a) and PtNPs/SBA-15 (b) (see Experimental Section).

conversion. This “loss” of activity was attributed to a diffusion problem linked to the higher concentration of **2a** and **1a** after the fourth reaction as the catalyst was used 4 times in a row. The filtration of the catalyst plus the drying under vacuum allows the total recovery of the catalyst.

The product selectivity for the hydrogenation of quinoline derivatives depends on how quinoline adsorbs to the metal surface.¹⁸ As only one product was detected by ¹H NMR and GC–MS during the hydrogenation, this observed selectivity implies exclusive absorption of the quinoline derivatives to metal through the *N*-heterocycle. While at this stage it is difficult to conclusively explain the absorption behavior of the quinoline on the metal, it is reasonable to posit that the absorption is impacted by specific microenvironment of the metal in these catalysts. Previous studies have reported that the *N*-heterocycle of quinoline can interact with hydroxylated supports through hydrogen bonding.^{17d,e,19} In the MNPs/SBA-15 catalyst system, the amine, amide, hydroxyl groups of the dendrimer capping agent, as well as the hydroxyl group of the support SBA-15, all have the potential to engage in this type of interaction. Accordingly, while NP catalysts supported on SBA-15 were not effective catalysts, the combination of metal/dendrimer/SBA-15 provided very active and stable catalysts.

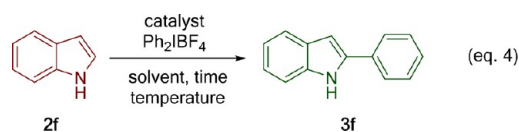
C–H Activation of Indole. Given that indole could be effectively produced with this catalyst system, we further investigated the potential activity of PdNPs/SBA-15 in the C–H functionalization of indole. While there have been numerous reports of palladium salts as catalysts for C–H bond arylation at position C-2 or C-3 of indole **2f**,²⁰ examples of nanoparticle-catalyzed C–H functionalization have only recently been described.^{20d} We have previously reported the MNP/SBA-15 can be oxidized using hypervalent iodine reagents. Moreover, while in nonpolar solvents the oxidized catalysts retain their heterogeneous nature, in polar solvents they are best considered homogeneous molecular catalysts.²¹ Therefore, we envisioned that the heterogeneous catalyst employed in the dehydrogenation reaction could be subsequently leveraged to catalyze a homogeneous C–H functionalization reaction by treatment with the appropriate oxidant in a polar solvent. In the event, reaction of PdNPs/SBA-15 with Ph₂IBF₄ allowed for a highly efficient direct arylation of indole **2f** leading to the exclusive formation of the 2-phenyl-indole **3f** with 100% of conversion at 60 °C in water for 22 h (Table S, entry 28). Two equivalents of Ph₂IBF₄ were necessary to transform quantitatively the indole **2f** into the desire product (entries 28, 29). The amount of catalyst was reduced to 0.75 mol % and a very high activity was still observed. Consistent with the hypothesis that a

Table S. C–H Activation of Indole

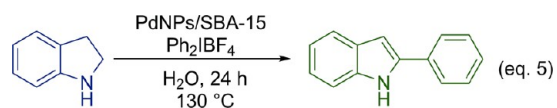
entry ^a	catalyst (mol %)	time (h)	selectivity (%)	conversion (%)	yield ^c (%)
28	PdNPs/SBA-15 (3.8)	22	>99.9	>99.9	98
29	PdNPs/SBA-15 (3.8) ^b	22	>99.9	73.9	70
30	PdNPs/SBA-15 (0.75)	24	>99.9	>99.9	97
31	PdNPs (0.75) ^c	24	>99.9	90	89
32	K ₂ PdCl ₄ (0.75)	24	>99.9	84.7	80
33	Pd(OAc) ₂ (0.75)	24	>99.9	93.9	92

^aThe reactions were conducted with 1 mmol of indole **2f** and 2 mmol of Ph₂IBF₄ in water at 60 °C. ^bThe reaction was conducted with 1 mmol of **2f** and 1 mmol of Ph₂IBF₄. ^cThe yield was calculated by ¹H NMR using mesitylene as an internal standard.

homogeneous catalyst was being formed, the catalyst lacking the support (water solution of PdNPs stabilized by dendrimers) was also tested with the same conditions as for PdNPs/SBA-15, and revealed to only be slightly less efficient (entry 31). Moreover, Pd(OAc)₂ is a classic homogeneous catalyst for this reaction, provided similar activity to that observed with the oxidized nanoparticles (entry 33).



Finally, the one-pot reaction sequential dehydrogenation/C–H arylation reaction of the indoline **1f** and Ph₂IBF₄ in the presence of 5 mol % PdNPs/SBA-15 was examined. The dehydrogenation/C–H activation/C–C cross coupling reaction was successful as only the final product 2-phenyl-indole **3f** was observed at the end of the reaction (plus byproducts coming from Ph₂IBF₄). No starting material indoline **1f** or intermediate indole **2f** was detected by ¹H NMR or GC–MS.



CONCLUSION

Metallic nanoparticles stabilized by G4OH PAMAM dendrimer are very active catalysts for the dehydrogenation of tetrahydroquinoline/indoline derivatives, combining efficiency, air

compatibility, and robustness/recyclability/reuse of the catalyst. The hydrogenation of quinoline derivatives catalyzed by PdNPs/SBA-15 and PtNPs/SBA-15, under one hydrogen atmosphere, was also found to be efficient. The catalysts tested here showed higher activity for this hydrogenation/dehydrogenation sequence than the tested homogeneous homologues and reported catalysts. As a consequence, the combination of these catalysts for quinoline derivatives raises the possibility that this system might be applied to hydrogen storage through reversible dehydrogenation/hydrogenation processes. Finally, we found that the heterogeneous catalyst, PdNPs/SBA-15, can readily be oxidized with Ph₂IBF₄ to generate an efficient catalyst for the C-2 arylation of indole. This observation suggests a strategy in which a single catalyst precursor can be employed to promote sequential hetero- and homogeneous process by the choice of the appropriate oxidant/reductant.

EXPERIMENTAL SECTION

Chemicals. Information about chemicals, including synthesis of supported NPs and characterization methods, can be found in the Supporting Information.

Representative Procedure for Catalytic Reactions. *Dehydrogenation Reactions.* To 1 or 0.1 mmol of *N*-heterocycle, in a Schlenk flask or closed vial, was added the corresponding amount of a catalyst in 1 mL of toluene-*d*₈. The system was closed in order to avoid the vaporization and allowed to stir for 24 h. At the end of the reaction, the solution was filtered and used directly for ¹H NMR or GC-MS analysis. Mesitylene was introduced in the NMR tube as an external standard for calculation of the reported conversions.

Hydrogenation Reactions. To 1 or 0.1 mmol of *N*-heterocycle, in a Schlenk flask or closed vial, was added the corresponding amount of a catalyst in 1 mL of toluene-*d*₈. The system was closed, degassed, and then placed under 1 atm of hydrogen gas. The reaction was allowed to stir for the necessary time. At the end of the reaction, the solution was filtered and used for ¹H NMR or GC-MS analysis. Mesitylene was introduced in the NMR tube as an external standard for calculation of the reported conversions.

Direct Arylation of Indole. To 0.1 mmol of indole and 0.2 mmol of Ph₂IBF₄, in a Schlenk flask or closed vial, was added the corresponding amount of a catalyst in 1 mL of water. The reaction was allowed to stir for the necessary time. At the end of the reaction, the solution was filtered and used for ¹H NMR or GC-MS analysis. Mesitylene was introduced in the NMR tube as an external standard for calculation of the reported conversions.

Recyclability Test. The catalyst was recycled by simple centrifugation at 3900 rpm for 6 min.

Hot Filtration Test. In the case of Figure 4b: 3 reactions were performed simultaneously. The first reaction was stopped after 1 h and the conversion was checked by ¹H NMR (32%). The second reaction was filtered to remove the catalyst after 1 h. The supernatant was allowed to stir under reaction conditions and the conversion checked by ¹H NMR after an additional 2 h and 5 h (41% conversion in both cases). The third reaction was checked every hour for 6 h.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b10768.

Detailed information on synthesis of catalysts, materials characterization, and catalysis (PDF)

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Notes

The authors declare no competing financial interest.

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