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Hydrogenation of quinolines, alkenes, and biodiesel by palladium nanoparticles supported on magnesium oxide[†]‡

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A new catalyst composed of Pd nanoparticles supported on MgO has been prepared by the room temperature NaBH₄ reduction of Na₂PdCl₄ in methanol in the presence of the support. TEM measurements reveal well-dispersed Pd particles of mean diameter 1.7 nm attached to the MgO surface. Further characterization was achieved by ICP-AES, XPS, XRD, H₂ pulse chemisorption and H₂-TPR. The new catalyst is efficient for the regioselective hydrogenation of the heterocyclic ring of quinolines, as well as for the mild reduction of a variety of alkenes representative of fuel components, and the partial saturation of biodiesel. The new material is considerably more reactive than commercial Pd/SiO₂ and Pd/Al₂O₃ catalysts under analogous reaction conditions.

1. Introduction

Catalytic hydrogenation continues to be of great interest in relation to a variety of industrially important processes. Partial or total saturation of N-heteroaromatic compounds is of relevance to hydrodenitrogenation (HDN), a key reaction routinely used for the removal of nitrogen impurities from refinery feedstocks.¹⁻⁴ There is also a growing interest in the hydrogenation of nitrogen heterocycles as a possible means to store hydrogen in organic liquids,⁵ and selective reduction of quinolines to 1,2,3,4-tetrahydroquinolines may lead to important intermediates for the synthesis of bioactive compounds.⁶ Selective alkene hydrogenation, in turn, is of interest in the conversion of fluid catalytic cracking (FCC) naphtha into gasoline,^{7,8} and selective hydrogenation of polyunsaturated fatty acid methyl esters (FAMEs) to the corresponding monounsaturated derivatives greatly enhances the storage stability and combustion properties of biodiesel.9-16

Although a number of catalysts are known for all these reactions, many do not display the desired activity and/or selectivity, require drastic reaction conditions, or are susceptible to poisoning by the substrates, the products, or impurities present in the feed. Therefore, there is a continuing need for new catalysts capable of hydrogenating various unsaturated substrates under mild reaction conditions, while being resistant to poisoning by common impurities. Metal nanoparticles (NPs) represent a promising alternative for the development of novel catalytic systems, due to their unique activity and selectivity features associated with the small and generally uniform particle size.¹⁷ Palladium nanoparticles, in particular, have been used in catalysis, in liquid suspensions, in ionic liquids, and supported on solids.^{18,19} Most reports are concerned with C-C coupling, but examples of hydrogenation reactions are also available; they include the reduction of simple alkenes by Pd NPs immobilized by ionic liquids on zeolites,²⁰ of butadiene by Pd NPs on porous alumina membranes,²¹ of the C=C bond of dihydrolinalool by Pd NPs on polystyrene-block-poly-4-vinylpyridine,²² and of cinnamaldehyde by Pd NPs inside multi-walled carbon nanotubes.²³ Pd NPs on polyvinylpyrrolidones have been used to selectively hydrogenate alkynes to alkenes²⁴ and nitrotoluenes to their corresponding anilines;²⁵ acetophenone is reduced to ethylbenzene via phenylethanol using Pd NPs supported on polymers.²⁶ Cascade reactions involving Heck coupling followed by C=C bond hydrogenation of the intermediate product have been reported with Pd/C,²⁷ Pd/TiO₂,²⁸ and with Pd nanoparticles stabilized by ionic liquids, either unsupported,²⁹ or supported in functionalized multi-walled carbon nanotubes.³⁰ Hydrogenation of benzene, benzylidene-acetone, phenylacetylene, diphenylacetylene, and quinoline was achieved by Pd NPs on hyperbranched aramids,³¹ while 5-membered N/O/S-heterocycles were reduced by Pd NPs supported on aminomethyl polystyrene modified with hyperbranched dendritic polyamidoamines.³² Phenanthrolines were hydrogenated by use of Pd nanoparticles supported on silica,³³ and phenol was reduced predominantly to cyclohexanone by use of Pd on MgO as the catalyst.^{34,35}

In previous work on Ru NPs supported on poly(4-vinylpyridine) (Ru/PVPy) we presented evidence indicating that the combination of small metallic particles and basic sites on the surface of the support leads to a nano-structure capable of promoting heterolytic hydrogen splitting and ionic hydrogenation

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[†]This paper is dedicated to Prof. David Cole-Hamilton on the occasion of his retirement and for his outstanding contribution to transition metal catalysis with many good memories (R.A. S.-D.) of our common time in Geoff Wilkinson's lab (1973–76).

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Scheme 1 Heterolytic hydrogen splitting and ionic hydrogenation of polar substrates by metal NPs on basic support.

mechanisms for N-heterocyclic substrates.³⁶ Heterolytic hydrogen activation and ionic hydrogenation pathways are very common in solution³⁷ but extremely rare on solid surfaces. Such outer sphere mechanisms (Scheme 1) do not require the binding of the substrate or the products to the active metal site and therefore they constitute a possible route to avoid catalyst poisoning.

Here we describe a new catalyst of this series, composed of palladium nanoparticles supported on magnesium oxide as the basic support; this material is an efficient catalyst for the hydrogenation of a variety of substrates of interest in relation with fuels and energy issues.

2. Results and discussion

2.1. Catalyst preparation and characterization

2.1.1. Preparation. The 1 wt% Pd/MgO catalyst used in this study was prepared by the room temperature reduction of Na₂PdCl₄ with excess NaBH₄ in methanol in the presence of suspended MgO, which had been previously calcined at 500 °C in the air for 2 h. Upon completion of the reaction, the solution became colorless and the initially white solid changed to gray; after appropriate work-up, the catalyst was stored under an inert atmosphere. For comparison and characterization purposes, analogous materials containing ca. 5 wt% and 10 wt% Pd/MgO were prepared by using the same procedure described above, except for the amount of Na₂PdCl₄ employed. The exact Pd loading in all three catalysts, determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), was 0.9 wt%, 4.4 wt% and 9.7 wt%, respectively. For convenience, hereafter we use 1 wt%, 5 wt%, and 10 wt% Pd/MgO notation to represent the different solids; nevertheless, the actual metal loadings from the ICP-AES analyses were used to calculate TOF values in the catalytic experiments described below.

2.1.2. TEM measurements. TEM analysis of the freshly prepared 1 wt% Pd/MgO solid (Fig. 1) revealed the presence of highly dispersed Pd particles with a narrow size distribution on the surface of the support, with an average diameter of 1.7 nm, calculated by measuring 350 particles chosen at random from several images.

Analysis of a sample of this catalyst after being used in a quinoline hydrogenation run (Fig. 1) at 150 °C and 40 atm H₂ shows that the average Pd particle diameter remains essentially unchanged (1.6 nm), although the particle size distribution is somewhat broader; these results indicate that the catalyst does not undergo sintering or other aggregation processes to an important extent under the harshest conditions employed for hydrogenation reactions. TEM analysis of analogous fresh 5 wt% and 10 wt% Pd/MgO (Fig. S1, ESI⁺₂) revealed particle size



Fig. 1 Transmission electron micrographs of a freshly prepared sample (top) and a used sample (bottom) of 1 wt% Pd/MgO with corresponding particle size distribution histogram.



Fig. 2 Pd 3d XPS spectrum of a freshly prepared sample of 10 wt% Pd/MgO.

distributions very similar to that of the 1 wt% material, with average diameters of 1.5 and 1.8 nm, respectively.

2.1.3. XPS analysis. The survey XPS scan of the 1 wt% Pd/MgO catalyst is shown in Fig. S2, ESI.[‡] No peaks are observed around 200 eV (Cl 2p), indicating that the catalyst surface is free of Cl contamination from the preparation process, as opposed to what is observed for a similar Pd/MgO catalyst prepared by the impregnation method.³⁴ The narrow scan for 1 wt% Pd/MgO in the Pd 3d region displayed extremely weak signals because of the very low metal loading, not allowing a reliable direct characterization by this method. The 3p region is highly interfered by large O peaks, making deconvolution invaluable. However, satisfactory XPS data were obtained in the 3d region for the two analogous solids containing 10 wt% Pd/MgO (Fig. 2) and 5 wt% Pd/MgO (Fig. S3, ESI[‡]). The presence of metallic palladium on these surfaces is clearly indicated by the signals at 335.2 and 339.3 eV, which correspond to Pd(0) $3d_{5/2}$ and Pd(0) $3d_{3/2}$,

respectively;³⁴ no evidence for any other Pd species was observed in the spectra of the two materials analyzed. With all preparation parameters being identical except for the amount of the Pd precursor, it is reasonable to conclude that the chemical composition on the surface of the 1 wt% catalyst would be similar. Furthermore, H₂-TPR measurements (section 2.1.4 below) also support the presence of Pd(0) as the only or predominant species on the surface.

2.1.4. XRD results. In order to further identify the crystalline phase of Pd in the catalyst, powder X-ray diffraction patterns of the three solids with different metal loadings were obtained, as shown in Fig. 3. Similarly to what we observed in the XPS experiments, the Pd diffraction pattern of the 1 wt% Pd/MgO material was essentially undetectable because of the very low metal loading; all five peaks are assigned to the MgO phase. When the metal loading is increased to 5 wt%, a small diffuse peak around $2\theta = 40^{\circ}$ starts to appear, which corresponds to the Pd (111) crystalline plane; the rest of the diffraction pattern of the 5 wt% Pd/MgO is still indistinguishable from that of MgO. However, samples of the analogous 10 wt% Pd/MgO displayed peaks associated with highly dispersed face centered cubic (fcc) crystalline Pd at 2θ values of 40.3°, 46.8° and 68.3°, assigned to the (111), (200) and (220) planes, respectively. These values are consistent with those in the standard diffractogram of Pd (40.1°, 46.7° and 68.1°).³⁸ The most intense peak at $2\theta = 43.0^{\circ}$ is MgO (200),³⁹ which was used as an internal standard to assign the other signals.

2.1.5. BET surface area, H₂ pulse chemisorption and temperature programmed reduction (TPR) experiments. Table 1 contains the data obtained from physisorption and chemisorption measurements. The MgO support (after calcination at 500 °C for 2 h) has a specific surface area of 88 m² g⁻¹, which is essentially retained (91 m² g⁻¹) after deposition of 1 wt% Pd NPs onto the surface. H₂ pulse chemisorption measurements for the 1 wt% Pd/MgO revealed *ca.* 5% metal dispersion on the surface. Similar measurements were performed on commercial 5% Pd/SiO₂ and 5% Pd/Al₂O₃ catalysts, which were used for catalytic activity comparison, leading to higher metal dispersion values of

11% and 18%, respectively. The metal dispersion values obtained from H_2 chemisorption experiments were subsequently used to calculate catalytic activities.

To provide further information concerning the reducibility of chemical species present on the surface of the Pd/MgO materials, H₂-TPR experiments were carried out for 1 wt%, 5 wt% and 10 wt% Pd/MgO, as well as for the MgO support itself. The TPR profiles for these four samples (Fig. 4) showed no positive peaks indicative of hydrogen consumption. The negative peaks observed around 360 K correspond to *desorption* from surface metallic Pd of the H₂ adsorbed at r.t. at the beginning of the analysis. The relative intensities of these peaks correlate with the amount of surface Pd in each sample, with the 10 wt% catalyst having the largest H₂ desorption peak.

These TPR profiles demonstrate that no significant reduction processes take place within the temperature range 400–700 K. This is in contrast to what was observed for Pd/MgO prepared by impregnation, which showed a positive TPR peak at about 450 K ascribed to the presence of PdO.³⁴ The TPR data for our three Pd/MgO samples are consistent with the XRD and XPS results presented above, which allows us to safely conclude that the Pd in our catalysts is exclusively or predominantly metallic, with no significant amount of PdO that can be detected by any of the three methods employed.

2.2. Catalytic hydrogenation

2.2.1. Hydrogenation of quinolines. The 1 wt% Pd/MgO catalyst is efficient and highly selective for the hydrogenation

Table 1 Physical and chemical adsorption measurement results

Material	BET surface area ^{<i>a</i>} (m ² g ^{-1})	Metal dispersion (%)		
MgO	88	_		
1% Pd/MgO	91	$4.7 \pm 0.4\%$		
5% Pd/SiO ₂		$11 \pm 2\%$		
5% Pd/Al ₂ \tilde{O}_3	—	$18\pm2\%$		

^a Single-point measurement.



Fig. 3 Powder X-ray diffraction pattern of 1, 5 and 10 wt% Pd/MgO.



Fig. 4 H_2 -TPR profile of the three Pd/MgO catalysts and MgO support.



Fig. 5 Hydrogenation of quinoline catalyzed by 1 wt% Pd/MgO (150 °C, 40 atm H₂; $n_{\rm Q}$: $n_{\rm Pd}$ = 1000; in THF; \triangle : quinoline; \blacktriangle : 1,2,3,4-tetrahydroquinoline.



Fig. 6 Hydrogenation of quinoline over 1 wt% Pd/MgO (n_{sub} : n_{Pd} = 1000 in THF). Left: influence of pressure on the hydrogenation rate, 150 °C; right: effect of temperature on the hydrogenation rate at 40 atm.

of quinoline to 1,2,3,4-tetrahydroquinoline under moderate reaction conditions (150 °C and 40 atm H₂) using THF or hexane as the solvent. A typical reaction profile is depicted in Fig. 5; the conversion reaches 100% after a few hours with no evidence for catalyst poisoning or inhibition by the substrate or the product. The linear hydrogen uptake observed during the first 1.5–2 h of the reaction was used to calculate an initial turnover frequency (TOF_{init}) of 300 h⁻¹.

This value was subsequently corrected for metal dispersion to yield a TOF_{corr} of 6400 h⁻¹, which is our measure of catalytic activity. The high selectivity of the Pd/MgO catalyst for the hydrogenation of the heterocycle, coupled with a total lack of activity toward toluene observed in independent experiments, is suggestive of an ionic mechanism for quinoline reduction, similar to the one proposed by us for the Ru/PVPy catalyst.³⁶

As shown in Fig. 6 (left), TOF_{corr} values increase steadily with H₂ pressure within the range 20–40 atm, indicating that the catalyst does not undergo metal sintering or any other deactivating processes to a significant extent at H₂ pressures of up to 40 atm, in agreement with our TEM observations (Fig. 1). The catalytic activity also increased with the temperature in the range 100–150 °C as depicted in Fig. 6 (right). Although it is likely that hydrogenation rates can be further increased by using higher pressures and temperatures, we consider the TOF values obtained within this range satisfactory.

The 1 wt% Pd/MgO catalyst is also efficient and highly selective for the hydrogenation of substituted quinolines under analogous reaction conditions, as summarized in Table 2. Introduction

Table 2 Hydrogenation of quinolines over 1 wt% Pd/MgO^a

Entry	Substrate	TOF (h^{-1})	$TOF_{corr}(h^{-1})$	Product
1		300	6400	
2		310	6600	
3		250	5300	
4		250	5400	

^{*a*} In *n*-hexane; n_{sub} : n_{Pd} = 1000; 150 °C, 40 atm H₂.

of a methyl group in the 3- or 8-position of quinoline results in lower hydrogenation rates, while no effect is apparent when the methyl group is located in the 2-position. All the substrates were exclusively hydrogenated at the heterocycle with no evidence for products of the hydrogenation of the carbocycle being observed in any experiment.

For comparison, commercial 5% Pd/SiO₂ and 5% Pd/Al₂O₃ catalysts displayed activities about four times lower than that of our 1 wt% Pd/MgO under analogous reaction conditions and equivalent amounts of Pd, yielding TOF_{corr} values of 1800 h⁻¹ and 1600 h^{-1} , respectively, for the hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline. To our knowledge, only one other quinoline hydrogenation catalyst containing Pd NPs (on hyperbranched aramids) is known.³¹ In that case, uncorrected TOF values of \sim 350 h⁻¹, comparable to ours, were achieved. We are not aware of any reported examples involving substituted quinolines. As mentioned in the introduction, the hydrogenation of N-heterocycles is of interest in connection with hydrodenitrogenation of fossil fuel feedstocks,^{1–4} and with hydrogen storage in organic liquids.⁵ The high selectivity for saturation of the heterocyclic ring observed could also be of use in the synthesis of valuable tetrahydroquinoline intermediates.⁶

2.2.2. Hydrogenation of alkenes. FCC naphtha represents about 36% of the gasoline pool composition in the US. It is produced with up to 40 vol% of C5–C7 alkenes of varied structures, but specifications for the final product allow at most about 12%.

The excess of alkenes in naphtha is usually lowered by hydrogenation that takes place during hydrodesulfurization (HDS) over standard solid catalysts. Excessive reduction of the olefin content, however, can result in a marked decrease in the octane rating of the fuel.^{7,8} Highly substituted and branched alkenes are responsible for most of the octane rating and therefore, it is desirable to hydrogenate predominantly the linear and unsubstituted components. In this context, we evaluated the behavior of our 1 wt% Pd/MgO catalyst in the mild hydrogenation (25 °C, 10 atm H₂) of C5–C6 olefins representative of naphtha components, with different degrees of substitution at the C==C bond. The results collected in Table 3 (entries 1–5) show that the

Table 3	Hydrogenation	of selected	alkenes	over 1	l wt%	Pd/MgO ^a
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Entry	Substrate	TOF (h^{-1})	$TOF_{corr} (h^{-1})$	Product at 2 h
1	\bigcirc	2300	50 000	\bigcirc
2	\sim	2800	60 000	\sim
3	\succ	180	3800	\succ
4	\rightarrow	90	1900	\succ
5	$\succ \prec$	70	1500	\succ
6	$\bigvee \\$	1800	39 000	\sim
^{<i>a</i>} $n_{\rm sub}$: $n_{\rm Pd} = 10$	000; r.t., 10 atm H ₂ .			

hydrogenation activity of our catalyst decreases sharply with increasing congestion around the double bond.

Such selectivity would leave the branched olefins essentially untouched when mixed with linear or unsubstituted analogues. Previous reports of C6-alkene hydrogenation using Pd NPs supported on silica indicated TOF values ranging from $4000-38\ 000\ h^{-1}$ under similar reaction conditions.^{40,41}

2.2.3. Partial hydrogenation of biodiesel. Biodiesel is an important alternative fuel most commonly produced by transesterification of vegetable oils catalyzed by sodium or potassium hydroxides or alkoxides, to yield mixtures of fatty acid methyl esters (FAMEs). Biodiesel is an attractive alternative to petroleum-based diesel because it displays similar combustion properties, viscosity, and cetane number but it is renewable, nontoxic, and sulphur free, and it is considered to have a negative CO₂ balance. Biodiesel production is increasing steadily, to be used in motor vehicles as a single fuel or in blends with petroleum-derived diesel.^{9,10,13,14} However, several problems related to ageing due to low oxidative stability, higher NO_x emissions in petrodiesel blends, and poor performance at low temperatures have been associated with a high proportion of polyunsaturated FAMEs; partial catalytic hydrogenation of the polyenes to monoenes has been proposed as an efficient way to improve the characteristics of biodiesel.^{14,16,42,43} Several catalytic systems have been reported for the hydrogenation of vegetable oils or biodiesel; for instance, metallic Ni suspended in oil can be used at 170-180 °C under atmospheric pressure;^{11,44} silica-supported Cu is active and selective at 180 °C and 20 atm H2.45,46 Liquid biphasic systems based on rhodium with sulfonated triphenylphosphine ligands operate at 50-100 °C and 10 atm H₂.^{42,43} Palladium supported on alumina was employed as a catalyst in the partial hydrogenation of sunflower oil at 40 °C and 10 atm H₂, as a pretreatment for biodiesel synthesis;⁴⁷ other metal oxide supports, including MgO, provided lower activities and/or selectivities. Recently, the partial hydrogenation of biodiesel catalyzed by Pd NPs dispersed in ionic liquids⁴⁸ or Pd NPs supported on Al₂O₃ in the presence of ionic liquids⁴⁹ has been reported; these systems are efficient at room temperature but require high H₂ pressures (75 atm).

Table 4 Biodiesel composition determined by GC-MS

%
9
5
31
48
7

^{*a*} In Cn: x, n indicates the number of carbons and *x* the number of C==C bonds in the FAMEs.

Since our 1 wt% Pd/MgO catalyst proved to be very active for the mild hydrogenation of 1-undecene (Table 3, entry 6), it seemed interesting to evaluate its efficacy in the partial hydrogenation of a biodiesel prepared by transesterification of soybean oil with methanol using KOH as the catalyst. The composition of the biodiesel, determined by GC-MS, is shown in Table 4; our aim was to transform the polyunsaturated FAMEs (C18 : 2 and C18 : 3), which represent over 50% of the biodiesel, into the more desirable monounsaturated (C18 : 1) ester, without increasing the proportion of the fully saturated components (C18 : 0 and C16 : 0, initially 14%).

After preliminary screening for optimal reaction conditions in the range 25–100 °C/1–7 atm H₂, we were able to rapidly and selectively convert the mixture of FAMEs into predominantly (>80%) the desired C18 : 1 product, under extremely mild conditions (100 °C and 1 atm H₂) (Fig. 7).

No further reduction to the fully saturated species was observed even at longer reaction times. The final composition achieved corresponds to an upgraded first-generation biodiesel with improved stability and performance, indicating that our 1 wt% Pd/MgO catalyst could be of practical use in this type of application.

2.3. Catalyst recyclability

In order to ascertain the stability and recyclability of our catalyst, three consecutive hydrogenation runs were performed using the same sample of 1 wt% Pd/MgO, for cyclohexene and for



Fig. 7 Partial hydrogenation of FAMEs over 5% Pd/MgO (100 °C, 1 atm; \blacksquare : C18:3; \bigcirc : C18:0; \spadesuit : C16:0; \triangle : C18:2; \blacktriangledown : C18:1).



Fig. 8 Activities of the 1 wt% Pd/MgO catalyst (100 mg) in three consecutive runs of hydrogenation; left: cyclohexene, r.t., 10 atm; right: quinoline, 150 $^{\circ}$ C, 40 atm.

quinoline. Fig. 8 shows the corrected TOF values for each hydrogenation cycle, together with the normalized hydrogenation activities. The hydrogenation activities for cyclohexene displayed about $\pm 10\%$ variation, which is in the order of the experimental error of our TOF measurements, suggesting that the catalyst is stable and reusable for alkene hydrogenation for at least three cycles without significant loss of catalytic activity. In contrast, recycling the catalyst in quinoline hydrogenation reactions resulted in about 30% loss of activity after the third run. Comparable results were obtained for commercial 5% Pd/SiO₂ and 5% Pd/Al₂O₃ catalysts during quinoline hydrogenation recycling under the same conditions.

ICP-AES analysis of the catalyst recovered from quinoline recycling experiments revealed essentially no loss of Pd from the catalyst (0.9 wt% used vs. 0.9 wt% fresh), while the liquid organic phase contained only very small amounts of Pd (<5% of total Pd); therefore, the observed loss of activity cannot be ascribed to leaching of the metal into the solution. TEM images of a used catalyst (Fig. 1) show no significant aggregation into larger Pd NPs that could account for a decrease in the catalytic efficiency. In independent experiments using a 50:50 quinoline/ 1,2,3,4-tetrahydroquinoline mixture as the substrate, the rate of hydrogenation observed was very similar to that of quinoline alone, which rules out the possibility of inhibition by the product 1,2,3,4-tetrahydroquinoline. The observed moderate decrease in activity is likely due to the presence of an unidentified trace impurity in quinoline, since such a deactivation effect is not observed during alkene hydrogenation.

3. Conclusion

We have synthesized a new catalyst composed of Pd nanoparticles supported on the basic support MgO. TEM measurements reveal well-dispersed Pd particles of about 1.7 nm. The catalyst was further characterized by XPS, XRD, hydrogen pulse chemisorption and H₂-TPR measurements. The new material is efficient for the regioselective hydrogenation of the heterocyclic ring of quinolines under moderate reaction conditions (150 °C, 40 atm H₂), as well as for the mild reduction (25 °C and 10 atm H₂) of a variety of alkenes representative of fuel components, and the partial saturation of biodiesel under atmospheric hydrogen pressure at 100 °C. The catalyst is about four times more active in the hydrogenation of quinoline than commercial Pd/ SiO₂ and Pd/Al₂O₃ catalysts, and it is recyclable for alkene hydrogenation for at least three cycles without significant loss of catalytic activity, while a 30% loss of activity was observed after three catalytic runs of quinoline hydrogenation, probably due to inhibition by trace impurities in the substrate.

4. Experimental

4.1. Materials

Na₂PdCl₄ (Pressure Chemicals, Inc.), 5% Pd/SiO₂ and 5% Pd/ Al₂O₃ (Strem Chemicals) were used as purchased. Solvents (analytical grade, Sigma-Aldrich) were purified using a PureSolv purification unit from Innovative Technology, Inc. and further deoxygenated with a nitrogen flow prior to use. Substrates and other reagents (Sigma-Aldrich) were purified by appropriate methods prior to use as necessary. Magnesium oxide (~325 mesh, ≥99% trace metals basis) (Sigma-Aldrich) was calcined prior to metal loading at 500 °C in the air for 2 h. Biodiesel was synthesized by a standard procedure: in short, a sonicated solution of KOH (0.875 g) in methanol (50 cm³) was added to commercial soybean oil (250 cm³) and the mixture was stirred at 60 °C for 75 min. The biodiesel phase was separated and then heated to 80 °C for 15 min to remove residual methanol. The product was washed six times with warm water to remove glycerol and the remaining KOH, then heated to 110 °C for 20 min and finally dried over sodium sulfate overnight.

4.2. Synthesis of Pd/MgO

To prepare the 1 wt% Pd/MgO catalyst, magnesium oxide (2.0 g) was placed in a 3-neck round bottom flask under nitrogen. Dry deoxygenated methanol (10 cm³) was added and the mixture was stirred. Two pressure-equalizing dropping funnels were attached to the flask, one containing Na₂PdCl₄ (0.055 g; 0.02 g Pd) in dry deoxygenated methanol (10 cm³) and the second containing NaBH₄ (0.142 g) in the same solvent (20 cm³). Approximately 10 cm³ of the borohydride solution was added quickly to the flask and the mixture was stirred for a few minutes. Subsequently, both the Na₂PdCl₄ and the remaining NaBH₄ solutions were added simultaneously to the flask at the rate of about one drop per second. After the addition was complete, the dark gray solution was stirred for 4 h under nitrogen at room temperature. The product was filtered under nitrogen, washed three times with methanol (10 cm³), and dried under vacuum at room temperature overnight. Analysis by ICP-AES (Micro-Analysis, Inc., Wilmington) confirmed a metal content of 0.9 wt%. Materials containing 5 wt% and 10 wt% Pd/MgO were prepared by use of the same procedure, adjusting the amount of Na_2PdCl_4 to 0.275 g and 0.550 g (0.10 g and 0.20 g Pd), respectively; the metal content was verified by ICP-AES analysis in both cases as 4.4% and 9.7%, respectively.

4.3. TEM studies

Transmission electron microscopy analysis was conducted at the Environmental Sciences Analytical Center (ESAC) of the Earth and Environmental Sciences Department of Brooklyn College using a JEOL TEM-2010 high-resolution microscope, operating at an accelerating voltage of 200 kV and providing a point-topoint resolution of 0.19 nm. Samples for analysis were prepared by placing a drop of a suspension of the catalyst in hexane on a copper grid and allowing it to air-dry. Images were captured using an AMT camera system.

4.4. XRD measurements

Powder X-ray diffraction (XRD) patterns were obtained at the Environmental Sciences Analytical Center (ESAC) of the Earth and Environmental Sciences Department of Brooklyn College on a Phillips X'PERT MPD diffractometer, using monochromatic Cu-K α radiation at 45 kV and 40 mA and 2 θ scanning from 20° to 90°. Samples were ground in a mortar prior to analysis in the air at room temperature.

4.5. XPS measurements

XPS spectra were recorded using an Omicron XPS spectrometer equipped with a multichannel hemispherical analyzer and a dual Al/Mg X-ray source using Mg K α excitation (1253.6 eV). The powdered sample was mounted on studs using a double-sided adhesive tape in air. The data analysis was performed by deconvoluting the XPS peaks by curve fitting using XPSPEAKS 4.1, applying Shirley background subtraction and Lorentzian–Gaussian functions (20% L, 80% G). The charging effect was corrected based on the literature value of 529.9 eV for the O 1s peak in MgO.⁵⁰

4.6. Hydrogen pulse chemisorption

Chemisorption measurements were performed using a Micromeritics ChemiSorb 2750 instrument, coupled to a TPx system controller. The fresh catalyst was reduced in 10% H₂/Ar at 150 °C for 30 min and then purged with Ar at 150 °C for 30 min to remove impurities; after which the sample was allowed to cool to room temperature. Doses of 10% H₂/Ar were repeatedly introduced into the sample tube until no further H₂ uptake was observed. The gas composition was analyzed by use of a TCD detector. The metal dispersion was determined by built-in software that detects the amount of hydrogen adsorbed for each atom of palladium, using a 1 : 1 H : Pd model.⁵¹

4.7. H₂-TPR analysis

Temperature programmed reduction (TPR) of catalyst samples was also conducted in the Chemisorb 2750 instrument equipped with a thermal conductivity detector (TCD). About 120 mg of the sample was first degassed at 200 °C in a flow of Ar gas (25 mL min⁻¹) for 1 h and then cooled down to room temperature. The carrier gas was then switched to a 9.9% H₂/Ar mixture; after 10 min when the baseline of the TCD signals was stable, the sample was heated linearly at a rate of 10° min⁻¹ to 700 K. The TCD signal change was displayed in real time on the computer interfaced to the instrument through the TPx system.

4.8. Catalytic tests

4.8.1. Hydrogenation of quinolines. Hydrogenation of quinolines was carried out in a glass-lined 5500 Parr reactor (100 cm^3) equipped with an internal stirrer, a thermocouple, a dip tube, and a sampling valve, coupled to a 4843 controller. Typically the reactor was loaded with the catalyst (100 mg) and the desired amount of the substrate in 30 cm³ of the solvent. The reaction mixture was deoxygenated by flushing with H₂ (20 atm) three times. The reactor was pressurized with H₂ at room temperature to 33 atm and then heated while stirring until the temperature reached 150 °C; at that point the pressure was adjusted to 40 atm and this was taken as the zero time for each reaction. The progress of the reaction was followed by monitoring the H₂ uptake. At the end of the run, a sample of the final mixture was analyzed by GC-MS using a Varian 3900 gas chromatograph fitted with a FactorFour VF-5ms capillary column and a Saturn 2100T mass detector. TOFinit values were calculated from the slope of the linear part of TON vs. t plots. Average TOF values were obtained from at least three experiments; the dispersion observed between individual measurements was less than 10%. Finally, TOF values were corrected for metal dispersion (TOF_{corr}) , using the data obtained from chemisorption.

4.8.2. Hydrogenation of alkenes. Experiments were carried out using a 5000 Parr multireactor (75 cm³) equipped with a magnetic stirrer and a thermocouple, and coupled to a 4871 controller. The reactor was loaded with the catalyst (100 mg) and the substrate (10 cm³), flushed with H₂ (5 atm) three times, and then pressurized to 10 atm H₂ at room temperature. Stirring was initiated at that point, which was taken as the zero time for the reaction. At the end of the run, a sample of the mixture was analyzed by use of a Shimadzu 2010 gas chromatograph fitted with an FID detector and an Agilent HP-Al/S capillary column. Each experiment was repeated at least three times in order to ensure reproducibility.

4.8.3. Partial hydrogenation of biodiesel. Partial hydrogenation of biodiesel was carried out in a low-pressure 5100 Parr glass reactor (160 cm³) equipped with a thermocouple and a stirrer, and coupled with a 4848 controller. The reactor was loaded with the catalyst (100 mg) and the biodiesel (75 cm³), and flushed three times with 1 atm H₂. The mixture was heated while stirring until the desired temperature was reached, which was taken as zero time for the reaction. The mixture was kept under a constant H₂ pressure of 1 atm and the hydrogenation progress was followed by taking samples every 10 min and

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immediately analyzing them by GC-MS on a Supelco SP-2330 capillary column.

4.8.4. Recycling experiments. A quinoline hydrogenation run was performed as described in Section 4.8.1, using 1 mL of quinoline and 30 cm³ hexane as the solvent. At the end of the reaction, the reactor was cooled to room temperature and the catalyst was allowed to settle down; the supernatant liquid was carefully withdrawn as much as possible and 1 mL of fresh quinoline and 30 cm³ of solvent were added. A second hydrogenation run was then started following the same procedure; further recycling steps were carried out by repeating the same procedure.

When using cyclohexene as the substrate, 10 mL of neat cyclohexene was used in the first run and the experiments were carried out at room temperature. After 3 h of reaction, another 10 mL of fresh cyclohexene was added and a second run was started. The hydrogenation was carried out for three runs in total.

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Notes and references

- H. Topsøe, B. S. Clausen and F. E. Massoth, *Hydrotreating Catalysis Science and Technology*, Springer-Verlag, New York, 1996.
- 2 The Desulfurization of Heavy Oils and Residua, ed. J. G. Speight, Marcel Dekker, New York, 2000.
- 3 R. A. Sánchez-Delgado, Organometallic Modeling of the Hydrodesulfurization and Hydrodenitrogenation Reactions, Kluwer Academic Publishers, Dordrecht, 2002.
- 4 K. Toshiaki, I. Atsushi and Q. Weihua, Hydrodesulfurization and Hydrodenitrogenation: Chemistry and Engineering, Wiley-VCH, Tokyo, 1999.
- 5 R. H. Crabtree, *Energy Environ. Sci.*, 2008, **1**, 134–138.
- 6 S.-I. Murahashi, Y. Imada and Y. Hirai, Bull. Chem. Soc. Jpn., 1989, 62, 2968–2976.
- 7 S. Brunet, D. Mey, G. Pérot, C. Bouchy and F. Diehl, *Appl. Catal., A*, 2005, **278**, 143–172.
- 8 P. J. Baricelli, E. Lujano, M. Modroño, A. C. Marrero, Y. M. García, A. Fuentes and R. A. Sánchez-Delgado, J. Organomet. Chem., 2004, 689, 3782–3792.
- 9 M. Di Serio, M. Cozzolino, M. Giordano, R. Tesser, P. Patrono and E. Santacesaria, *Ind. Eng. Chem. Res.*, 2007, **46**, 6379–6384.
- 10 M. Di Serio, R. Tesser, L. Pengmei and E. Santacesaria, *Energy Fuels*, 2007, 22, 207–217.
- 11 O. Falk and R. Meyer-Pittroff, Eur. J. Lipid Sci. Technol., 2004, 106, 837–843.
- 12 E. Lotero, Y. Liu, D. E. Lopez, K. Suwannakarn, D. A. Bruce and J. G. Goodwin, *Ind. Eng. Chem. Res.*, 2005, 44, 5353–5363.
- 13 J. A. Melero, J. Iglesias and G. Morales, *Green Chem.*, 2009, 1285– 1308.
- 14 S. Pinzi, I. L. Garcia, F. J. Lopez-Gimenez, M. D. Luque de Castro, G. Dorado and M. P. Dorado, *Energy Fuels*, 2009, 23, 2325–2341.
- 15 Y. C. Sharma, B. Singh and J. Korstad, Fuel, 2011, 90, 1309–1324.
- 16 R. Yang, M. Su, M. Li, J. Zhang, X. Hao and H. Zhang, *Bioresour*. *Technol.*, 2010, **101**, 5903–5909.

- 17 D. Astruc, F. Lu and J. R. Aranzaes, Angew. Chem., Int. Ed., 2005, 44, 7852–7872.
- 18 J. Durand, E. Teuma and M. Gómez, Eur. J. Inorg. Chem., 2008, 2008, 3577–3586.
- 19 I. Favier, D. Madec, E. Teuma and M. Gomez, *Curr. Org. Chem.*, 2011, 15, 3127–3174.
- 20 J. Huang, T. Jiang, H. Gao, B. Han, Z. Liu, W. Wu, Y. Chang and G. Zhao, Angew. Chem., Int. Ed., 2004, 43, 1397–1399.
- 21 H.-P. Kormann, G. Schmid, K. Pelzer, K. Philippot and B. Chaudret, Z. Anorg. Allg. Chem., 2004, 630, 1913–1918.
- 22 L. M. Bronstein, D. M. Chernyshov, I. O. Volkov, M. G. Ezernitskaya, P. M. Valetsky, V. G. Matveeva and E. M. Sulman, *J. Catal.*, 2000, **196**, 302–314.
- 23 J.-P. Tessonnier, L. Pesant, G. Ehret, M. J. Ledoux and C. Pham-Huu, *Appl. Catal.*, A, 2005, 288, 203–210.
- 24 C. Evangelisti, N. Panziera, A. D'Alessio, L. Bertinetti, M. Botavina and G. Vitulli, J. Catal., 2010, 272, 246–252.
- 25 J.-L. Pellegatta, C. Blandy, R. Choukroun, C. Lorber, B. Chaudret, P. Lecante and E. Snoeck, *New J. Chem.*, 2003, 27, 1528–1532.
- 26 A. Drelinkiewicza, A. Waksmundzka, W. Makowski, J. W. Sobczak, A. Król and A. Zieba, *Catal. Lett.*, 2004, 94, 143–156.
- 27 M. Gruber, S. Chouzier, K. Koehler and L. Djakovitch, *Appl. Catal.*, A, 2004, 265, 161–169.
- 28 M. J. Climent, A. Corma, S. Iborra and M. Mifsud, Adv. Synth. Catal., 2007, 349, 1949–1954.
- 29 S. Jansat, J. Durand, I. Favier, F. Malbosc, C. Pradel, E. Teuma and M. Gómez, *ChemCatChem*, 2009, 1, 244–246.
- 30 L. Rodríguez-Pérez, C. Pradel, P. Serp, M. Gómez and E. Teuma, *Chem-CatChem*, 2011, 3, 749–754.
- 31 D. Tabuani, O. Monticelli, A. Chincarini, C. Bianchini, F. Vizza, S. Moneti and S. Russo, *Macromolecules*, 2003, 36, 4294–4301.
- 32 Z. Guo, H. Feng, H.-c. Ma, Q.-X. Kang and Z.-W. Yang, Polym. Adv. Technol., 2004, 15, 100–104.
- 33 C. Bianchini, V. Dal Santo, A. Meli, S. Moneti, R. Psaro, L. Sordelli and F. Vizza, *Inorg. Chim. Acta*, 2008, 361, 3677–3680.
- 34 P. Claus, H. Berndt, C. Mohr, J. Radnik, E.-J. Shin and M. A. Keane, J. Catal., 2000, 192, 88–97.
- 35 N. Mahata, K. V. Raghavan, V. Vishwanathan, C. Park and M. A. Keane, *Phys. Chem. Chem. Phys.*, 2001, 3, 2712–2719.
- 36 M. Fang, N. Machalaba and R. A. Sánchez-Delgado, *Dalton Trans.*, 2011, 10621–10632.
- 37 C. A. Sandoval, T. Ohkuma, K. Muniz and R. Noyori, J. Am. Chem. Soc., 2003, 125, 13490–13503.
- 38 Powder Diffraction File, Card # 46-1043, PDF-2/Release 2004; International Center for Diffraction Data, Newton Square, PA, USA.
- 39 Powder Diffraction File, Card # 65-0476, PDF-2/Release 2004; International Center for Diffraction Data, Newton Square, PA, USA.
- 40 A. V. Biradar, A. A. Biradar and T. Asefa, *Langmuir*, 2011, 27, 14408– 14418.
- 41 O. Domínguez-Quintero, S. Martínez, Y. Henríquez, L. D'Ornelas, H. Krentzien and J. Osuna, J. Mol. Catal. A: Chem., 2003, 197, 185–191.
- 42 A. Bouriazos, K. Mouratidis, N. Psaroudakis and G. Papadogianakis, *Catal. Lett.*, 2008, **121**, 158–164.
- 43 A. Bouriazos, S. Sotiriou, C. Vangelis and G. Papadogianakis, J. Organomet. Chem., 2010, 695, 327–337.
- 44 B. R. Moser, M. J. Haas, J. K. Winkler, M. A. Jackson, S. Z. Erhan and G. R. List, *Eur. J. Lipid Sci. Technol.*, 2007, **109**, 17–24.
- 45 N. Ravasio, F. Zaccheria, M. Gargano, S. Recchia, A. Fusi, N. Poli and R. Psaro, *Appl. Catal.*, A, 2002, 233, 1–6.
- 46 F. Zaccheria, R. Psaro and N. Ravasio, Green Chem., 2009, 11, 462–465.
- 47 B. Nohair, C. Especel, G. Lafaye, P. Marécot, L. C. Hoang and J. Barbier, J. Mol. Catal. A: Chem., 2005, 229, 117–126.
- 48 M. S. Carvalho, R. A. Lacerda, J. P. B. Leao, J. D. Scholten, B. A. D. Neto and P. A. Z. Suarez, *Catal. Sci. Technol.*, 2011, 1, 480– 488.
- 49 B. S. Souza, D. M. M. Pinho, E. C. Leopoldino, P. A. Z. Suarez and F. Nome, *Appl. Catal. A.*, 2012, **433–434**, 109–114.
- 50 J. F. Moulder, W. F. Stickle, P. E. Sobol and K. D. Bomben, in *Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data*, ed. J. Chastain, Perkin-Elmer, Eden Prairie, MN, 1992.
- 51 C. Amorim and M. A. Keane, J. Colloid Interface Sci., 2008, 322, 196–208.