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# Magnetically Recoverable Palladium(0) Nanocomposite Catalyst for Hydrogenation Reactions in Water

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An easy and straightforward strategy has been used for loading palladium(0) nanoparticles onto the magnetic surface of maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>), without the use of organic modifiers. The nanocomposite was fully characterized by TEM, XRD, <sup>57</sup>Fe Mössbauer spectroscopy, X-ray photoelectron spectroscopy, and superconducting quantum interference device measurements. The Pd<sup>0</sup>@ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanocatalyst has been investigated in various catalytic reactions, under mild conditions (100 kPa H<sub>2</sub>, RT), and in neat water. Relevant catalytic activities were

Introduction

In the guest for a sustainable chemistry,<sup>[1]</sup> the development of novel cost-effective cleaner catalytic technologies, as well as the use of environmentally safer solvents such as water or nonaqueous neoteric solvents (ionic liquids, supercritical CO<sub>2</sub>, fluorous media), remains of great interest.<sup>[2-3]</sup> Besides the properties of the catalysts, such as catalytic activity and selectivity, their recyclability remains essential for their applicability on an industrial scale.<sup>[4]</sup> Among the various catalytic systems, nanometer-sized metal particles proved to be relevant and sustainable catalyst candidates for synthetic transformations,<sup>[5-6]</sup> combining pertinent activities and selectivities with improved recovery potentialities.<sup>[7-9]</sup> Various strategies have been developed for the recoverability of these nanocatalysts, including decantation by using biphasic water/organic solvent or twophase systems with ionic liquids,<sup>[10-11]</sup> or filtration through their immobilization on inorganic supports.<sup>[12-13]</sup> In the last decade, superparamagnetic nanoparticles have emerged as novel supporting materials for catalysts immobilization to further facili-

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IMMM UMR CNRS 6283, Institut des Molécules et Matériaux du Mans LUNAM, Université du Maine 72085 Le Mans Cedex 9 (France) achieved in the hydrogenation of olefinic substrates, as well as in hydrodehalogenation reactions of halogenoarenes, that constitutes a promising process for wastewater treatment. These nanocatalysts proved also pertinent for the reduction of nitroarene derivatives into the corresponding anilines, which are promising substrates for fine chemistry. Finally, these catalysts proved to be easily recoverable through the use of an external magnet, without significant loss of activity.

tate their recovery<sup>[14–18]</sup> through the use of an external magnet or by magnetically assisted cross-flow filtration and centrifugation.<sup>[19]</sup> This magnetically driven separation approach could be considered as a clean, cheap, and highly scalable technology, avoiding filtration steps.<sup>[20]</sup> Bare magnetic nanoparticles (NPs) were successfully used as catalysts in some catalytic processes,<sup>[21]</sup> but could also be protected with inorganic supports<sup>[22-23]</sup> or directly "decorated" with transition-metal NPs. In the case of palladium nanospecies, many works have been reported regarding their immobilization on the magnetic surface, which was modified by external organic reagents.<sup>[24-25]</sup> However, the functionalization of the magnetic surface remains time-consuming and needs the use of organic reagents. Therefore, the direct immobilization of nanospecies on the unmodified surface of iron oxide, without the use of external modifiers, has been recently reported.<sup>[26-28]</sup> Herein we report the straightforward formation of palladium NPs on magnetic iron oxide supports, following an impregnation methodology and without the use of surface modifiers. After characterization, this novel magnetically recoverable nanocomposite (Pd<sup>0</sup>@Fe<sub>x</sub>O<sub>y</sub>) was first evaluated in a model reaction such as the hydrogenation of olefinic compounds in neat water and under mild conditions. The catalytic hydrodehalogenation of halogenated arenes was then investigated as an environmentally friendly and costsaving alternative for wastewater treatment, competing with oxidation processes.<sup>[29]</sup> Finally, the reduction of nitroarenes<sup>[30]</sup> was explored owing to the great potential of the resulting anilines as building blocks in the chemical industry.

#### **Results and Discussion**

Magnetic iron oxide NPs were synthesized through a usual coprecipitation method using aqueous  $Fe^{2+}/Fe^{3+}$  salt solutions.<sup>[31-32]</sup> The magnetic materials were characterized with a wide range of physicochemical techniques to determine the particle size and morphology, as well as their chemical composition, their crystalline structure, and their magnetic behavior. In the TEM images, relatively uniform iron oxide NPs with an average diameter of 11 nm were observed (Figure 1 a). The size



**Figure 1.** TEM analyses of iron oxide nanoparticles prepared by the coprecipitation method. a) TEM picture (scale bar = 100 nm). b) Size distribution. c) HRTEM picture of an isolated particle. d) Fast Fourier transformation spectrum ( $\emptyset$  = diameter).

distribution is relatively narrow, with 80% of the nanoobjects having a size between 6 and 15 nm (Figure 1b). Structural characterization of the magnetic particles was performed by means of high resolution (HR) TEM (Figure 1c) and selectedarea electron diffraction (SAED). The fast Fourier transformation diffraction patterns (Figure 1d) reveal the presence of interreticular distances of 0.252 and 0.161 nm, which are in good agreement with those of magnetite iron oxide (Fe<sub>3</sub>O<sub>4</sub>, JCPDS data 19-0629) and/or maghemite iron oxide ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, JCPDS data 39-1346). However, as repeatedly described in the literature, diffraction does not allow distinguishing magnetite from maghemite.<sup>[33]</sup>

The XRD patterns demonstrate that the particles display the typical spinel structure of iron oxide, which could be either magnetite or maghemite (Figure 2). The average particle size, calculated by using the Debye–Scherrer formula from the main reflection peak (311) at  $35.7^{\circ} 2\theta$ , is approximately 9.6 nm, consistent with the sizes obtained from the TEM pictures.

The magnetization curve of bare NPs at room temperature (Figure 3) is characteristic of a superparamagnetic sample and the saturation magnetization is approximately 66.7 emu g<sup>-1</sup>, in fair agreement with that recently reported for FeNPs exhibiting similar morphological characteristics.<sup>[14]</sup>

As previously reported,<sup>[34–35]</sup> XPS analyses constitute a promising tool for the discrimination of magnetite (Fe<sub>3</sub>O<sub>4</sub>) from maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>). The XPS spectrum in the Fe2p region for the magnetic particles obtained by the coprecipitation approach is shown in Figure 4. The peak positions of Fe2p<sub>3/2</sub> and Fe2p<sub>1/2</sub> are observed at 710.4 and 723.6 eV, respectively, which





Figure 2. XRD pattern of iron oxide particles.



**Figure 3.** Magnetization curve of the bare magnetic NPs measured at 300 K.  $M_{sat}$  = Saturation magnetization, Hc = coercive force.



Figure 4. Fe 2p XPS spectrum of the bare iron oxide particles.

agree well with literature values.<sup>[36]</sup> Moreover, the presence of an associated satellite peak for Fe2p<sub>3/2</sub>, located at 719 eV, at a binding energy approximately 8.5 eV higher than that of the main peak, constitutes an evidence of the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> form.<sup>[37]</sup>

To corroborate the XPS results, <sup>57</sup>Fe Mössbauer spectrometry was performed as a useful technique for determining the oxidation state of Fe species.<sup>[38]</sup> The Mössbauer spectra recorded at 300 and 77 K on the bare magnetic NPs are illustrated in Figure 5. The spectrum at 300 K exhibits a hyperfine complex



Figure 5. Mössbauer spectra on NPs samples recorded at 300 K (bottom) and 77 K (top), V = velocity.

structure consisting of a magnetic sextet with broadened lines and a central guadrupolar doublet: these two components are attributed to the larger and the smaller nanoparticles, which exhibit slower and faster superparamagnetic relaxation phenomena, respectively. In the spectrum at 77 K, only a sextet with fine and asymmetric lines was observed in agreement with rather blocked magnetic states. The values of the mean isomer, which give information on the valency state ( $\delta$ =0.32 and 0.42 mm s<sup>-1</sup> at 300 and 77 K, respectively), suggest the presence of rather exclusively Fe<sup>3+</sup> species and thus of maghemite form, according to previously reported works.<sup>[39]</sup> As already reported,<sup>[39]</sup> the obtained magnetic particles could not be labelled as magnetite, rather mainly as maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) as a result of the oxidation process of Fe<sub>3</sub>O<sub>4</sub>, which is facilitated by the very small particles that are characterized by a high surface/volume ratio.

The direct immobilization of palladium(0) NPs on the magnetic surface ( $Pd^0@\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) was performed by the wet impregnation method, according to the modified Mizuno's procedure used for ruthenium hydroxide on magnetite.<sup>[40]</sup> After redispersion of the magnetic particles in neat water, the palladium(0)



Figure 6.  $Pd^0@\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite. a) TEM image (scale bar = 50 nm). b) HRTEM image (scale bar = 2 nm).



Figure 7. X-ray photoelectron spectrum of Pd 3d of Pd<sup>0</sup>@γ-Fe<sub>2</sub>O<sub>3</sub>.

particles were deposited by chemical reduction of palladium chloride salts with sodium borohydride under basic conditions.

The palladium loading of the nanomaterials was determined by ICP analysis as 1.08 wt%, corresponding to the expected value. In the TEM images (Figure 6a), palladium(0) nanoparticles of 3 nm size are well dispersed on the magnetic surface. The analyses of the fast Fourier transformation of the HRTEM picture of an isolated  $Pd^0@\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite (Figure 6b) mainly reveal interreticular distances of 0.223 nm and 0.250 nm corresponding to the (111) plane lattice of palladium and (311) one of maghemite, respectively.

The X-ray photoelectron spectrum of the Pd3d core level in the  $Pd^0@\gamma$ -Fe<sub>2</sub>O<sub>3</sub> material is shown in Figure 7 The Pd 3d<sub>5/2</sub> and  $Pd 3d_{3/2}$  peaks, which were fitted by constraining the spin-orbit separation of 5.25 eV, could be resolved into two sets of spinorbit doublets.<sup>[41-42]</sup> Accordingly, the two peaks observed at 335.2 eV (Pd 3d<sub>5/2</sub>) and 340.45 eV (Pd 3d<sub>3/2</sub>) could be attributed to metallic Pd,<sup>[43]</sup> whereas those at 337.3 and 342.5 eV in the deconvoluted spectrum are assigned to the Pd3d<sub>5/2</sub> and  $Pd 3d_{3/2}$  peaks of  $PdO_2$ , respectively.<sup>[44]</sup> This result indicates that the surface of palladium particles was partially oxidized in air to PdO<sub>2</sub>. Additionally, the peaks corresponding to oxygen (O1s, 530 eV) and carbon (C1s, 285 eV) used as references were observed, contrary to those of chlorine (Cl 2p<sub>3/2</sub>, 198.2 eV) and boron (B1s, 187.3 eV) species issued from the Na<sub>2</sub>PdCl<sub>4</sub> precursor and the NaBH<sub>4</sub> reducing agent. The absence of the peaks corresponding to these species could be explained by several aqueous washings during the catalyst preparation.

Firstly, the magnetically separable  $Pd^0@\gamma$ -Fe<sub>2</sub>O<sub>3</sub> catalyst was investigated in hydrogenation reactions of linear or cyclic olefins under atmospheric hydrogen pressure and at room temperature. The reactions were performed in two different solvents in terms of polarity, water and hexane. The turnover frequencies (TOFs) were calculated, considering an optimized reaction time for complete conversion of the substrate and based on the total introduced amount of metal and not on the exposed surface metal. These TOFs were clearly underestimated but were suitable from an economic point of view.<sup>[45]</sup> As previously reported by Janiak et al.,<sup>[46]</sup> the catalytic activity re-

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<b>Table 1.</b> Hydrogenation of olefinic compounds with $Pd^0@\gamma$ -Fe <sub>2</sub> O <sub>3</sub> nanocatalyst in <i>n</i> -hexane or water. <sup>[a]</sup>								
Entry	Substrate	Product	TOF <sup>[b]</sup> [h <sup>-1</sup> ] in <i>n</i> -hexane in water					
1 2 3	cyclohexene 1-tetradecene styrene	cyclohexane tetradecane ethylbenzene	200 50 600	150 n.c. <sup>[c]</sup> (82 %) 100				
[a] Reaction conditions: catalyst $Pd^0@\gamma$ -Fe <sub>2</sub> O <sub>3</sub> (50 mg, 1% wt Pd, 4.6× $10^{-6}$ mol Pd), substrate (0.47 mmol), 100 kPa H <sub>2</sub> , 10 mL solvent, RT. [b] Determined by GC analysis and defined as the number of consumed H <sub>2</sub> per mole of introduced Pd per hour. [c] Not calculated; conversion determined by GC analysis shown in parentheses.								

sults not only from the exposed surface metal atoms because the surface can restructure, atoms can shift positions during the heterogeneous processes and partial aggregation could occur during catalysis, modifying the fraction of surface atoms. These changes in the surface render the determination of the number of surface atoms difficult. The results are gathered in Table 1.

Notably, the bare  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> particles are not active towards the reduction of unsaturated compounds. In contrast, the Pd<sup>0</sup>@ $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite presents remarkable activities towards the hydrogenation of linear and cyclic olefins (Table 1, entries 1–3) in both solvents. However, the catalytic system was more active in *n*-hexane, with TOFs up to 600 h<sup>-1</sup> for styrene (entry 3). These results could be attributed to a better solubilization of the substrate and product in organic solvents, and also to a better diffusion of the substrate towards the metallic surface, as already reported.<sup>[47]</sup> Concerning the 1-tetradecene (entry 2), the kinetics are slower owing to the hydrophobic nature of the substrate and to the isomerization of the terminal olefin, leading to the formation of more hindered olefins, which are more difficult to reduce. Finally, under these stan-

R       X       MNPs@Pd       R       +       HX         100 kPa H <sub>2</sub> , RT       RT       R       +       HX							
Entry	Substrate	Solvent	Product <sup>[b]</sup> [%]	t [h]	$TOF^{[c]}\left[h^{-1}\right]$		
1 2 3 4 5 <sup>[e]</sup> 6 7 8 9	chlorobenzene chlorobenzene 2-chloroanisole 2-chloroanisole 2-chloroanisole 4-chloroaniline bromobenzene 1,2-dichlorobenzene 2,4-dichloroanisole	n-hexane water n-hexane water water water water water water	benzene (98) benzene (100) anisole (13) anisole (100) anisole (0) aniline (100) benzene (100) benzene (100) anisole (100)	0.25 1.5 0.5 2.2 24 3.1 2 5.7 4.5	392 67 n.c. <sup>[d]</sup> 45 - 32 50 18 22		
[a] Reaction conditions: catalyst $Pd^0@\gamma$ -Fe <sub>2</sub> O <sub>3</sub> (50 mg, 1% wt Pd, 4.6× $10^{-6}$ mol Pd), substrate (0.47 mmol), 100 kPa H <sub>2</sub> , 10 mL solvent, RT. [b] Percentage of conversion determined by GC analysis. [c] Number of consumed H <sub>2</sub> per mole of introduced Pd per hour. [d] Not calculated. [e] $\gamma$ -Fe <sub>2</sub> O <sub>2</sub> .							

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dard mild conditions, no reduction of the aromatic ring was observed (entry 3).

Secondly, the Pd<sup>0</sup>@y-Fe<sub>2</sub>O<sub>3</sub> nanocatalyst was also studied in the dehalogenation reactions of halogenoarenes under the same conditions (100 kPa H<sub>2</sub>, RT). The results are reported in Table 2. In a first set of experiments (Table 2, entries 1-4), the influence of the solvent was studied. Whatever the solvent was, good activities were achieved with the  $Pd^0@\gamma$ -Fe<sub>2</sub>O<sub>3</sub> catalyst for the transformation of chlorobenzene into benzene (entries 1, 2), particularly with a TOF in *n*-hexane of approximately 400  $h^{-1}$ . However, the dehalogenation of 2-chloroanisole in *n*hexane (entry 3) led to poor conversion (13%) and destabilization of the  $Pd^0@\gamma$ -Fe<sub>2</sub>O<sub>3</sub> suspension. This result was attributed to the production of chlorine species in the reaction mixture, which acts as a poison towards the catalytic system, as already reported.<sup>[48-49]</sup> The addition of chlorohydric acid hydrochloric acid in the hydrogenation of 1-tetradecene in *n*-hexane after 5 min led to deactivation of the catalyst, with a 40% conversion after 2 h, instead of a complete transformation under classical conditions (Table 1, entry 2). Moreover, the maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) support was totally inactive towards the dechlorination reaction of 2-chloroanisole in water (Table 2, entry 5), with no production of anisole after 24 h. In a second set of experiments, the scope of the reaction was extended to other halogenoarenes in neat water (Table 2, entries 7-9). The reactivity of bromobenzene is lower than of the chloroarenes (Table 2, entry 7 vs. 2), as already reported.<sup>[49-51]</sup> This result could be explained by the lower electron affinity of Br (3.364 eV) than that of Cl (3.615 eV), which results in a less effective activation of the bromo reactant through surface  $\sigma$ -complex formation. The additional presence of a second chloro group (Cl or Br) on the ring leads to a deactivating effect, lowering the halogenoarene reactivity because the halogen substitution reduces the electron density associated with the ring carbons (entries 8–9).<sup>[51]</sup>

Thirdly, the reduction of nitroarenes into aniline was investigated by using the  $Pd^0@\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite under standard conditions (100 kPa H<sub>2</sub>, RT) in neat water (Table 3). As already observed in previous experiments, no reduction of the nitro groups was observed with the  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> support (Table 3, entry 2). However, the  $Pd^0@\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite was active towards the hydrogenation of nitrobenzene in neat water with a TOF up to 150 h<sup>-1</sup> (entry 1). Moreover, the tandem hydrogenation–dehalogenation reaction of 4-chloronitrobenzene was

Table 3. Hydrogenation of nitroarene derivatives into aniline with $Pd^0@\gamma\text{-}Fe_2O_3$ in water. $^{(a)}$							
Entry	Substrate	Time [h]	$TOF^{[b]}\left[h^{-1} ight]$				
1 2 <sup>[c]</sup> 3 4	nitrobenzene nitrobenzene 4-chloronitrobenzene nitrobenzene/4-chloronitrobenzene (1:1)	2 - 5 5	150 - 80 70				
[a] Reaction conditions: catalyst $Pd^0@\gamma$ - $Fe_2O_3$ (50 mg, 1% wt Pd, 4.6× $10^{-6}$ mol Pd), substrate (0.47 mmol), 100 kPa H <sub>2</sub> , 10 mL solvent, RT. [b] TOF determined by GC analysis and defined as the number of consumed H <sub>2</sub> per mole of introduced Pd per hour. [c] Reaction performed with $\gamma$ - $Fe_2O_3$ support.							

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Figure 8. Kinetics of the tandem hydrogenation–dechlorination reaction of 4-chloronitrobenzene in neat water with  $Pd^0@\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanocomposite.

performed, with a complete conversion into aniline in 5 h (entry 3). To understand the preferential reaction pathway, the kinetics of the reaction was investigated (Figure 8).

The kinetics profile (Figure 8) indicates a reaction pathway involving the reduction of the nitro group in a first step, producing 4-chloroaniline, followed by the dechlorination step. This hypothesis is reinforced by the fact that the nitro reduction (Table 3, entry 1) seems to be faster than the dehalogenation of 4-chloroaniline (Table 2, entry 6), thus explaining the low ratio of nitrobenzene observed during the reaction. Moreover, the conversion of 4-chloronitrobenzene seems to be directly correlated with the formation of 4-chloroaniline, which reaches a maximum with the complete conversion of the substrate. To confirm this preferential pathway, the hydrogenation of a 1:1 mixture of nitrobenzene and 4-chloronitrobenzene



Figure 9. Kinetics of the reduction of a nitrobenzene/4-chloronitrobenzene (1:1) mixture with the  $Pd^0@\gamma$ -Fe<sub>2</sub>O<sub>3</sub> catalyst.

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was performed (Table 3, entry 4). The kinetic profile is shown in Figure 9.

The kinetics study (Figure 9) reveals a rapid conversion of nitrobenzene into aniline after 1 h, whereas the 4-chloronitrobenzene ratio remains relatively constant. These results confirm the hypothesis that the reduction of nitro groups is favored over the dechlorination step and that the chlorinated compound is the preferential intermediate (Scheme 1).



**Scheme 1.** Proposed reaction pathway for the tandem hydrogenation–dechlorination reaction of 4-chloronitrobenzene. Dashed arrows: disfavored pathways.

Finally, the catalytic lifetime of  $Pd^0@\gamma$ -Fe<sub>2</sub>O<sub>3</sub> catalyst was investigated in water, through successive hydrogenations of three reference substrates, such as styrene, chlorobenzene, and nitrobenzene. The catalyst was easily separated from the reaction mixture, by using an external neodymium magnet, and washed with water before reuse under the same conditions. This method avoids loss of catalyst during the filtration step and a potential oxidation of active species. The results over five runs are reported in Figure 10. For hydrogenation reactions on styrene and nitrobenzene, the catalyst could be efficiently reused over five successive runs without loss of catalytic activity. In the case of styrene, the reuse has been performed up to 20 runs, showing the excellent catalytic lifetime of



Figure 10. Activities of the recycled  $Pd^{0}@\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanocatalyst over five runs in the hydrogenation of nitrobenzene, styrene, and chlorobenzene.

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 $Pd^{0}@\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanocatalyst. However, in the case of the dehalogenation reaction, the production of a co-product, hydrochloric acid, led to a progressive destabilization of the  $Pd^{0}@\gamma$ -Fe<sub>2</sub>O<sub>3</sub> suspension and a deactivation of the catalytic system in the fourth run. This phenomenon could be attributed to the dissolution of the magnetic support under acidic conditions, as already reported.<sup>[52]</sup> Nevertheless, the results prove the efficient adsorption of metallic nanospecies on the magnetic surface, with no metal leaching in the sequential reuse reactions in reduction reactions.

## Conclusion

We have developed a highly stable magnetically recoverable nanocomposite based on nanometer-sized palladium particles that are well dispersed on the magnetic support. XPS and Mössbauer analyses enabled us to conclude that the iron oxide particles were composed of maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>). This magnetic support was directly functionalized by zerovalent palladium nanoparticles having sizes of 3 nm, through a wet impregnation method and without the use of surface modifiers. The obtained nanocomposite (Pd<sup>0</sup>@γ-Fe<sub>2</sub>O<sub>3</sub>) exhibited excellent activities towards the reduction of olefinic compounds and nitro derivatives, as well as in dehalogenation processes. Moreover, this nanocatalyst could be easily recycled through magnetic separation from the reaction products, avoiding the use of organic solvents. The simple and straightforward methodology for immobilizing metallic nanospecies on magnetic iron oxide leads to the design of an attractive catalyst in terms of activity, selectivity, and recyclability in the drive towards sustainable processes.

## **Experimental Section**

#### General

FeCl<sub>2</sub>·4H<sub>2</sub>O, FeCl<sub>3</sub>·6H<sub>2</sub>O, and Na<sub>2</sub>PdCl<sub>4</sub> were purchased from Strem Chemicals. Sodium borohydride and all organic substrates were obtained from Aldrich, Acros, or Alfa Aesar and were used as received. Water was distilled twice by conventional methods before use. TEM images were performed at the Université Pierre et Marie Curie. They were recorded with a JEOL TEM 100CXII electron microscope operated at an acceleration voltage of 100 kV. The nanomaterial was dispersed in ethanol or water with ultrasounds and a drop of this solution was deposited on a carbon-coated copper grid and dried in air. HRTEM and energy-dispersive X-ray analysis were performed by using a JEOL JEM 2010 UHR microscope combined with a PGT-IMIX PC microanalyzer. Hysteresis cycles of the magnetic NPs were recorded at RT by using a MPMS XL5 magnetometer. XPS measurements were performed with an MgK<sub> $\alpha$ </sub> X-ray source (h $\nu$  = 1254 eV) by using a VSW HA100 photoelectron spectrometer with a hemispherical photoelectron analyzer, working at an energy pass of 22 eV. The experimental resolution was 1.0 eV. The binding energy for the main C-C peak was taken at 285.0 eV as an internal reference level for all measurements. Spectral analysis included a Shirley background subtraction and peak separation using mixed Gaussian-Lorentzian functions. 57Fe Mössbauer spectra were recorded at 300 and 77 K by using a conventional constant acceleration transmission spectrometer with a  $^{\rm 57}{\rm Co}$  (Rh) source. The spectra were fitted by means of the MOSFIT program and an  $\alpha\text{-}\text{Fe}$  foil was used as the calibration sample. The values of isomer shift are quoted to that of  $\alpha\text{-}\text{Fe}$  at 300 K.

#### Synthesis of Fe<sub>2</sub>O<sub>3</sub> magnetic NPs

Ferrous chloride hydrate (2.6 g, 13 mmol) was added to a hydrochloric acid solution (20 mL, 2 M). Ferric chloride hydrate (7.1 g, 26 mmol) was dissolved in nitrogen-purged water (200 mL), followed by the addition of the ferrous chloride solution. After 15 min of mechanic stirring, A 20 mL volume of nitrogen-purged aqueous NH<sub>3</sub> solution (20 wt%) was slowly introduced. The color of the solution turned from orange to dark brown and the stirring was maintained for 1 h. The nanoparticles were magnetically decanted and washed with deionized water.

#### Synthesis of maghemite-supported Pd<sup>0</sup> NPs (Pd<sup>0</sup>@\gamma-Fe<sub>2</sub>O<sub>3</sub>)

Maghemite particles (1 g) were redispersed in deionized water (50 mL) by sonication. The pH was adjusted at over 11 through addition of a NaOH solution (1 M). An aqueous solution of Na<sub>2</sub>PdCl<sub>4</sub> (27 mg,  $9.4 \times 10^{-6}$  mol, 10 mL) was slowly added and the stirring was maintained for 1 h. After cooling at 0°C, an aqueous solution of NaBH<sub>4</sub> (1 mg,  $2.6 \times 10^{-5}$  mol, 10 mL) was added dropwise. After 30 min at 0°C, the solution was stirred at RT for 2 h. The nanoparticles were magnetically decanted, washed with deionized water, and dried at 80°C over the night.

#### Catalytic tests and recycling

Catalysts (50 mg) were introduced in a glass recipient with a stirring bar and redispersed in deionized water (10 mL) by sonication. The adequate quantity of substrate was added. The solution was put under vacuum then hydrogen. The operation was renewed three times and the final pressure of hydrogen was adjusted to 1 atm. To recycle the catalyst, a neodymium magnet was applied under the recipient to precipitate the catalyst magnetically and remove the liquid phase. The catalyst was washed with water and precipitated three times before a new run.

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Magnetically Recoverable Palladium(0) Nanocomposite Catalyst for Hydrogenation Reactions in Water



Active, selective, and reusable! A magnetically Pd<sup>0</sup> nanocomposite was easily prepared and efficiently used in hydrogenation reactions of various substrates (nitro- and/or halogenoarenes) in neat water.