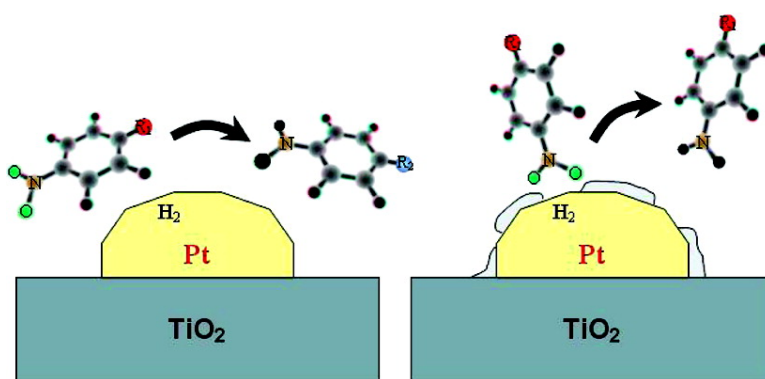


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Transforming Nonselective into Chemoselective Metal Catalysts for the Hydrogenation of Substituted Nitroaromatics

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Abstract: It is generally accepted that good hydrogenation noble and nonnoble metal catalysts such as Pt, Ru, or Ni are not chemoselective for hydrogenation of nitro groups in substituted aromatic molecules. We have found that it is possible to transform nonchemoselective into highly chemoselective metal catalysts by controlling the coordination of metal surface atoms while introducing a cooperative effect between the metal and a properly selected support. Thus, highly chemoselective and general hydrogenation Pt, Ru, and Ni catalysts can be prepared by generating nanosized crystals of the metals on the surface of a TiO₂ support and decorating the exposed (111) and (100) crystal faces by means of a simple catalyst activation procedure. By doing this, it has been possible to change the relative rate for hydrogenating competitive groups present in the molecule by almost 2 orders of magnitude, increasing the chemoselectivity from less than 1% to more than 95%.

Introduction

Catalysis is a key discipline for sustainability since it allows chemical transformations to be performed at lower temperatures while avoiding or minimizing the formation of byproduct. The impact is not only on energy saving but also for preserving a cleaner environment, provided that more active, and especially more selective, catalysts could be prepared. Selectivity becomes crucial when molecules present two or more reacting groups and only one of them has to be transformed. Thus, a selective catalyst has to “recognize” and preferentially interact with the desired chemical group, while avoiding the transformation of the others. This is, for instance, the case for chemoselective hydrogenations, for which noble metals are frequently used as catalysts.^{1–3} However, the problem often arising is that the highly active noble metals are not chemoselective and they must be modified by alloying or poisoning with other metal oxides or molecules that improve selectivity, but in most cases at the expenses of activity. The chemoselective hydrogenation of substituted nitroaromatics to the corresponding substituted anilines, which are important products for pharmaceuticals, pesticides and dyes, among others, is a difficult scientific and technological problem. It is generally accepted that commercially available Ni or Pt catalysts cannot be used to hydrogenate substituted nitrobenzenes with H₂, since they are not chemoselective. Because of this lack of selectivity, it is common to see that stoichiometric reducing agents such as sodium hydrosulfite,⁴

iron,⁵ tin,⁶ or zinc in ammonium hydroxide⁷ are still being used, with the concomitant formation of at least 1 mol of residue per mole of desired product. Researchers have attempted to overcome this limitation by use of H₂ as reducing agent and addition of PbO or H₃PO₂ to supported Pt catalysts. Then, though the total catalytic activity decreased, the selectivity to substituted aromatic amines was increased.⁸ However, the chemoselective hydrogenation of substituted nitroaromatics is an especially complex case, since one type of byproduct formed with Pt–PbO or Pt–H₃PO₂ catalysts was phenylhydroxylamine derivatives, which can be explosive even at low levels. Intelligently, Siegrist et al.⁸ used Pt–H₃PO₂ and Pt–PbO and added vanadium or iron salts, respectively, to the reaction media in amounts of up to 20 wt % to convert the hydroxylamines and improve the final process. By using these catalytic systems, the authors have presented a large number of examples comprising differently functionalized nitroaromatics, showing that a broad spectra of substitutes anilines can be synthesized through a chemoselective hydrogenation.⁹ Despite the important advance achieved, the resultant catalyst, which involves large amounts of transition metal salts in solution, should be improved by designing a fully heterogeneous chemoselective catalyst.

Recently, the reaction was studied from another direction by starting with a less active hydrogenation catalyst, such as gold,¹⁰ that gave very high selectivity to substituted anilines.¹¹ Nev-

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(1) Bond, C. G. *Chem. Soc. Rev.* **1991**, 20 (4), 441.

(2) Gallezot, P.; Richard, D. *Catal. Rev. Sci. Eng.* **1998**, 40, 81.

(3) Claus, P. *Appl. Catal., A* **2005**, 291, 222.

(4) Kovar, R. F.; Armond, F. E. (U.S. Air Force). U.S. Patent 3,975,444, 1976.

(5) Suchy, M.; Winternitz, P.; Zeller, M. (Ciba-Geigy). WO Patent 91/02278, 1991.

(6) Butera, J.; Bagli, J. (American Home Products). WO Patent 91/09023, 1991.

(7) Burawoy, A.; Critchley, J. P. *Tetrahedron* **1959**, 5, 340.

(8) Siegrist, U.; Baumeister, P.; Blaser, H.-U. *Chem. Ind. (Dekker)* **1998**, 75, 207.

(9) Blaser, H. U.; Siegrist, U.; Steiner, H.; Studer, M. In *Fine Chemicals Through Heterogeneous Catalysis: Aromatic Nitro Compounds*; Sheldon, R. A., van Bekkum, H., Eds.; Wiley: New York, 2001; p 389.

ertheless, a catalyst with the same selectivity as gold but with a higher activity would be desired for industrial application,¹² and there is a scientific and technological challenge to transform active but nonselective noble metals (Pt, Ru) and a nonnoble metal (Ni) into highly active and chemoselective catalysts.

In this paper, we will show that control of the crystal dimensions of the metal and the corresponding exposed domains, together with proper selection of the support, are key issues to directly transform nonselective Ni, Pt, or Ru into highly active and chemoselective catalysts for the hydrogenation of substituted nitroaromatics to the corresponding anilines, without forming hydroxylamine derivatives while avoiding the addition of transition metal salts.

Experimental Section

Catalyst Preparation. Pt/Al₂O₃, Pt/C, Pt/TiO₂, Ni/TiO₂, and Ru/TiO₂ samples were prepared by incipient wetness technique at the desired metal contents. H₂PtCl₆ (hexahydrate, Aldrich, >37.5% as Pt), Ni(NO₃)₂ (hexahydrate, Fluka, >98.5%), and RuCl₃ (Aldrich, Ru content 45–55%) precursors were used to impregnate the γ -Al₂O₃ (Merck), C (activated carbon, Aldrich), and TiO₂ (Degussa P-25) supports. As an example, 20 mL of an aqueous solution containing 53.1 mg of H₂PtCl₆·6H₂O was impregnated on 10 g of TiO₂ to prepare the 0.2 wt % Pt/TiO₂ catalyst. After a perfect mixing of the corresponding slurries, samples were always dried at 373 K for 5 h and then reduced under pure H₂ flow at 473 or 723 K for 3 h. Only in the case of Ni catalysts, a calcination process in air atmosphere was performed at 823 K for 3 h before the reduction of the sample. The Au/TiO₂ catalyst has been supplied by the World Gold Council and was prepared by a deposition–precipitation procedure.

Catalyst Characterization: A. FTIR Experiments. Infrared transmission spectra were recorded with a Bio-Rad FTS-40A spectrometer equipped with a mercury–cadmium–telluride (MCT) detector. The infrared cell was designed to treat the samples in situ under vacuum or under flow conditions. CO adsorption experiments were performed at room temperature at increasing CO pressure (2–100 mbar). Prior to adsorption, the samples were evacuated at 298 K and 10^{−5} mbar for 1 h.

B. Electron Microscopy. Studies have been performed in a JEOL 2010F microscope operating at 200 kV in both transmission (TEM) and scanning–transmission modes (STEM). This microscope has a structural resolution of 0.19 nm and allows formation, in STEM mode, of electron probes with diameters down to 0.5 nm suitable for high-spatial resolution analytical investigation. High-resolution transmission electron microscopic (HRTEM) images were acquired digitally on a 1024 × 1024 CCD camera and analyzed by the routines of the Diffpack module of Gatan Digital Micrograph software. Crystallographic phase analysis has been performed on the basis of FFTs applied on small selected areas of the HRTEM micrographs. Particle size distributions were obtained by use of a program developed at UCA. STEM images were obtained by use of a high-angle annular dark field detector (HAADF), which allows Z-contrast imaging. Electron energy loss spectra (EELS) were recorded on a GIF2000 spectrometer. To monitor the presence of TiO_x moieties on top of the Pt metal particles in the Pt/TiO₂ catalysts, the spectrum-line mode was employed. In this operation mode, a fine electron probe (about 0.5 nm diameter) is rastered along a predefined path on the sample. EELS spectra, spanning a defined energy-loss window, are collected at successive points on this path; in our case with a separation slightly larger than that of the probe diameter, 0.7 nm. Changes in the EELS spectra allow performing element distribution mapping. Collecting EELS spectra along electron-beam paths going from vacuum through surface positions of the metal particles and ending in the bulk of the metal particles has allowed us to detect the presence of patches of support (fingerprint of Ti L_{2,3} edge) covering the metal nanoparticles.

Samples for electron microscopic studies were prepared by depositing small amounts of the powders directly onto holey carbon-coated Cu grids. Excess powder was removed from the grids by gentle blowing with a nozzle.

C. Hydrogenation of Nitroaromatics. Catalytic testing was performed in reinforced glass reactors equipped with a temperature and pressure control. For each reaction, a 1 mL mixture of reactants and solvent was placed into the reactor (2 mL capacity) together with an appropriate amount of catalyst. All the reactants used in this paper were commercially available from Sigma–Aldrich Co. with purities above 96%. *o*-Xylene was always used as internal standard for the determination of conversion level and yields. Details on the composition of feed for the different substrates tested can be found in Table S1 in Supporting Information. After the reactor was sealed, air was purged by flushing two times with 10 bar of hydrogen. Then the autoclave was heated up to the required temperature, and finally it was pressurized with H₂ at the selected set point. During the experiment, the pressure was maintained constant and the stirring rate was fixed at 1000 rpm (magnetic stirring). Aliquots were taken from the reactor at different reaction times until the end of the experiment. The product composition was determined by means of gas chromatography, once the catalyst particles were removed from the solution by centrifugation at 12 000 rpm. The products were identified by gas chromatography/mass spectrometry (GC-MS) and also by comparison with commercially pure products (Sigma–Aldrich Co.). Only experiments with mass balances >95% were considered.

Results and Discussion

Structure of Pt Nanoparticles and Catalytic Behavior. It is well recognized that different crystallographic planes of metals exhibit different catalytic performance. On the other hand, it is also known that the nature of the support strongly affects the shape of the metal particles, and this can influence which crystallographic planes participate in the reaction. For instance, it has been found that the hydrogenolysis activity of Ni particles on silica is a function of the relative percentage of (100) and (111) facets on the particle surfaces.¹³ Also, during the NO + CO reaction over Pd catalysts, it was demonstrated that the stabilization of inactive atomic nitrogen species occurred on highly reactive undercoordinated sites, which are more abundant on smaller particles.^{14,15} In the case of Ni metal catalysts, the formation of thin hexagonal morphologies generated on graphite nanofibers strongly increases the selectivity of partial hydrogenation of 1,3-butadiene to 1-butene.¹⁶ An important effect of the metal particle morphology was also reported for hydrogenation of crotonaldehyde,^{17–19} indicating that the reaction tends to occur on Pt(111), Pt(100), and Pt(110) terraces. While there is an important amount of work on the influence of different crystallographic planes of metals on the activation of alkenes, alkynes, carbonyl groups, or α,β -unsaturated carbonyls, only a few examples²⁰ dealing with nitro-group activation on the

- (10) Corma, A.; Boronat, M.; González, S.; Illas, F. *Chem. Commun.* **2007**, 32, 3371.
- (11) Corma, A.; Serna, P. *Science* **2006**, 313, 332.
- (12) Blaser, H.-U. *Science* **2006**, 313, 312.
- (13) Rainer, D. R.; Goodman, D. W. *J. Mol. Catal. A: Chem.* **1998**, 131, 259.
- (14) Rainer, D. R.; Xu, C.; Koranne, M.; Oh, W. S.; Goodman, D. W. *J. Catal.* **1997**, 167, 234.
- (15) Vesecky, S. M.; Rainer, D. R. *J. Vac. Sci. Technol. A* **1996**, 14, 1457.
- (16) Park, C.; Baker, R. T. K. *J. Phys. Chem. B* **1998**, 102, 5168.
- (17) Englisch, M.; Jentys, A.; Lercher, J. A. *J. Catal.* **1997**, 166, 25.
- (18) Delbeq, F.; Sautet, S. *J. Catal.* **1995**, 152, 217.
- (19) Beccat, P.; Bertolini, J. C.; Gauthier, Y.; Massardier, J.; Ruiz, P. *J. Catal.* **1990**, 126, 451.
- (20) Zhao, F.; Ikushima, Y.; Aray, M. *J. Catal.* **2004**, 224, 479.

surface of these particles have been presented, showing that this process goes from a non-structure-sensitive relationship to a moderate dependency under different reaction conditions. Moreover, our previous research on gold catalysts²¹ showed that the adsorption of nitro groups is very slightly modified when working with nanoparticles of different morphologies. When all the above factors are taken into account, it could be expected, in a first approximation, that if one is able to prepare Pt catalysts with a smaller fraction of metal atoms in faces with respect to Pt atoms in corners of the crystallites, it could be possible to decrease the reaction rate of a structure-sensitive reaction, such as the hydrogenation of a double bond or a carbonyl, while maintaining the activity for the reduction of the nitro group. This effect would certainly produce an increase of the chemoselectivity toward the reduction of the nitro group in substituted nitroaromatics containing olefinic or carbonyl groups. To check this hypothesis, a series of Pt/Al₂O₃ catalysts have been prepared containing different amounts of Pt, in which the average metal crystallite size, as determined by STEM, decreases when decreasing the Pt content is decreased (see Figure S1 in Supporting Information). The electron microscopic results have been complemented with a structural characterization of the Pt metal surface by adsorption of CO followed by IR spectroscopy. This was done in order to characterize the relative amount of Pt atoms located on corners and terraces in the different Pt/Al₂O₃ samples. It has been reported²² that CO adsorbs in a bridge form mainly on large Pt particles, while linear adsorbed CO predominates on small particles. More specifically, in the case of 0.2 wt % Pt/Al₂O₃ sample, with the smallest average metal crystallite size according to STEM measurements (Figure S1), an intense CO adsorption band is observed at 2056 cm⁻¹ (Figure S2 in Supporting Information), which is related to CO linearly adsorbed on low-coordination Pt surface sites.^{23–25} No bands at higher frequencies (2110–2070 cm⁻¹) related to extended Pt surfaces, such as Pt(111) and Pt(100), have been observed on this sample, and a much less intense IR band appears at 1823 cm⁻¹, which can be associated with CO adsorbed in a bridge form on larger particles. We can then conclude from STEM and IR characterization that, in the 0.2 wt % Pt/Al₂O₃ sample, most of the Pt atoms are within very small particles (~2 nm), and consequently the ratio of Pt on low-coordinated sites (corners and steps) to metal atom on terraces is high.

When the Pt content is increased, the particle sizes increases (Figure S1) together with the intensity of IR bands of CO associated with Pt in Pt(111) and Pt(100) faces, while the intensity of the IR bands associated with low-coordinated surface sites decreases (Figure S2). If this is so, we should expect that the specific activity, that is, the activity per metal atom, for a well-proven structure-sensitive reaction such as styrene hydrogenation to ethylbenzene, would decrease with decreasing metal dispersion. Indeed, this can be clearly observed in Figure 1. On the contrary, in the case of the reduction of nitrobenzene to aniline we observe no influence of crystal size on the specific catalytic activity (Figure 1), in agreement with our previous hypothesis. From the results presented above, we could expect

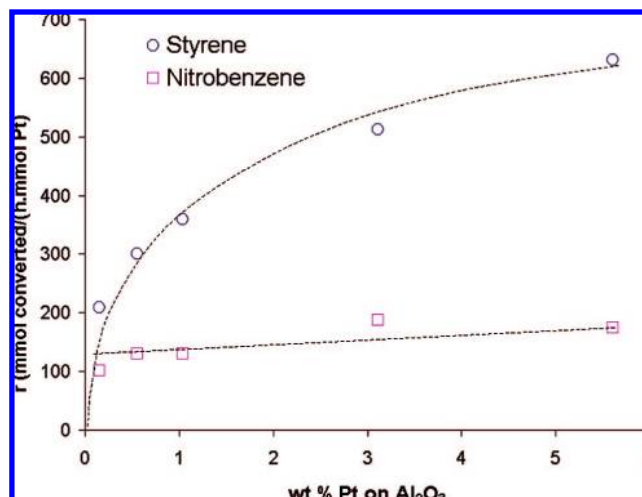


Figure 1. Effect of Pt loading on the intrinsic reaction rate of Pt/Al₂O₃ catalysts in the hydrogenation of (○) styrene and (□) nitrobenzene. Reaction conditions: 313 K, 3 bar of hydrogen, 0.0044 mol of Pt/mol of substrate. Feed composition: 94.75 mol % toluene, 4.25 mol % styrene or nitrobenzene, 1 mol % *o*-xylene.

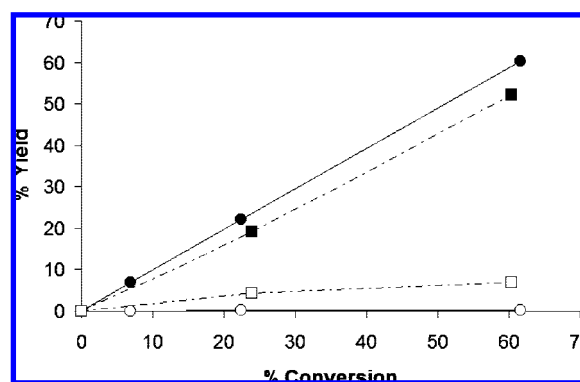


Figure 2. Effect of the support in hydrogenation of 3-nitrostyrene with 0.2 wt % Pt/C [0.00124 mol of Pt/mol of 3-nitrostyrene; (■) yield of 3-aminostyrene, (□) yield of hydroxylamine derivatives] and with 0.2 wt % Pt/TiO₂ [0.00310 mol of Pt/mol of 3-nitrostyrene; (●) yield of 3-aminostyrene, (○) yield of hydroxylamine derivatives] reduced at 450 °C. Reaction conditions: 313 K, 3 bar of hydrogen. Feed composition: 90.5 mol % toluene, 8.5 mol % 3-nitrostyrene, 1 mol % *o*-xylene.

that the chemoselective reduction of 3-nitrostyrene to 3-aminostyrene will increase when the crystallite size of Pt is decreased. Results from Table S2 in Supporting Information confirm this hypothesis, though the maximum 3-nitrostyrene selectivity with the best Pt/Al₂O₃ catalyst (0.2 wt % Pt/Al₂O₃) is still not high enough (~60%) when working at high levels of conversion. Nevertheless, these results already show that the direction we should follow to increase the chemoselectivity of Pt catalysts is to further decrease the metal crystallite size. This was done by preparing a catalyst with a low Pt content (0.2 wt %) on a high-surface-area support such as activated carbon (~850 m²·g⁻¹). Under the preparation conditions used here, a very large metal dispersion should be obtained. STEM analysis of this sample reveals a rather large number of very small Pt particles (particle diameters in the range 0.5–1.7 nm) as well as a much smaller fraction of larger ones (3–4 nm) (Figure S3 in Supporting Information). The large fraction of crystallites with very small size is in agreement with the IR results of adsorbed CO (Figure S4 in Supporting Information), which shows only one IR band at 2040 cm⁻¹ that is associated with

(21) Boronat, M.; Concepción, P.; Corma, A.; González, S.; Illas, F.; Serna, P. *J. Am. Chem. Soc.* **2007**, *129* (51), 16230.

(22) Sarkany, J.; Gonzalez, R. D. *Appl. Catal.* **1983**, *5*, 85.

(23) Jin, T.; Zhou, Y.; Mains, G. J.; White, J. M. *J. Phys. Chem.* **1987**, *91*, 5931.

(24) Raskó, J. *J. Catal.* **2003**, *217*, 478.

(25) Bocuzzi, F.; Chiorino, A.; Guglielminotti, E. *Surf. Sci.* **1996**, *368*, 264.

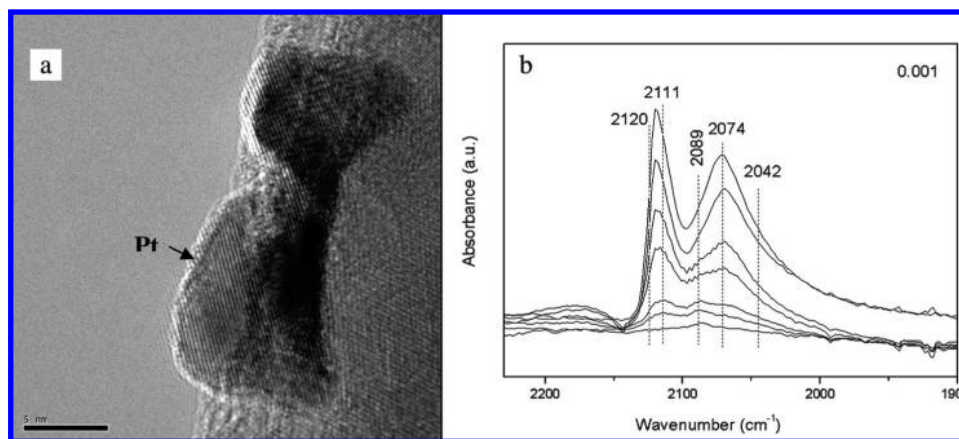


Figure 3. (a) HRTEM images of 0.2 wt% Pt/TiO₂ catalyst after reduction at 473 K. The surface of the crystallites appears free from any support material. (b) IR spectra of CO adsorbed on this sample reveal the presence of Pt terraces Pt(111) and Pt(100), as well as oxidized metal sites.

Table 1. Product Distribution for Hydrogenation of 3-Nitrostyrene in Toluene by Different Catalytic Systems^a

catalytic system	reduction temp (K)	% X	% S _a	% S _b	% S _c	% S _d
1.5% Au/TiO ₂		98.5	95.9	0.0	3.9	0.2
5% Pt/C	723	95.6	29.0	7.8	63.1	0.1
0.2% Pt/C	723	95.1	90.5	3.0	3.9	2.6
0.2% Pt/TiO ₂	473	89.3	41.5	6.4	52.1	nd
0.2% Pt/TiO ₂	723	95.1	93.1	0.1	6.8	nd
5% Ni/TiO ₂	473	1.0	55.3	4.0	35.6	5.1
5% Ni/TiO ₂	723	93.0	90.2	0.2	7.3	2.3
1% Ru/TiO ₂	473	85.0	71.4	4.3	20.7	3.6
1% Ru/TiO ₂	723	95.1	96.3	0.2	2.8	0.7

^a a, 3-aminostyrene; b, 3-nitroethylbenzene; c, 3-ethylaniline; d, hydroxylamine derivatives.

CO adsorbed on highly uncoordinated Pt sites. This result explains the fact that 90% selectivity to 3-aminostyrene at 95% conversion is obtained with the 0.2 wt % Pt/C catalyst. Interestingly, 0.2 wt % Pt/C is much more active than the Pt-PbO/CaCO₃ or Au/TiO₂ catalysts previously reported,^{8,11} since the former works at 313 K and 3 bar, while the others require 393 K and H₂ pressures between 9 and 20 bar. In other words, by controlling the crystallite size of Pt, we can make selective the nonselective Pt without the necessity of poisoning the metal surfaces, while avoiding the corresponding decrease in activity. Unfortunately, with the 0.2 wt % Pt/C catalyst, an important amount of the highly undesired phenylhydroxylamine intermediates (up to 25% at low conversion levels; Figure 2) is produced, which makes the catalyst unsuccessful, at least from an industrial point of view.

Importance of the Support. From our previous work on gold catalysis,^{11,21} we learned that a proper selection of the support could improve selectivity through a cooperative effect between the support (TiO₂) and the metal, avoiding the formation of hydroxylamine derivatives. If this could be extrapolated to Pt, a highly active and selective catalyst that will not produce phenylhydroxylamine intermediates could be achieved with small crystallites of Pt on a TiO₂ support. Following this hypothesis, 0.2 wt % Pt/TiO₂ catalyst was prepared and reduced at 473 K. HRTEM images show that Pt particles preferentially grow along TiO₂ interphases, resulting in larger particles than expected (Figure 3a, and Figure S5 in Supporting Information). The IR spectrum of adsorbed CO shows bands at 2120, 2111, 2089, 2074, and 2042 cm⁻¹ (Figure 3b). The high-frequency band at 2120 cm⁻¹ has been assigned to CO adsorbed on oxidized Pt surface sites, while IR bands in the 2111–2086

cm⁻¹ region correspond to CO molecules adsorbed on Pt(111) terraces (sites with coordination number 9). The IR bands in the 2077–2071 cm⁻¹ region have been related to CO molecules adsorbed on Pt(100) (Pt sites with coordination number 8). The IR bands at lower frequencies (2066, 2050, and 2040–2020 cm⁻¹) indicate the presence of Pt sites of low surface coordination, like steps and corners.^{23–25} In other words, the metal crystallites on the Pt/TiO₂ catalyst are larger than in the case of Pt/C and contain a larger proportion of Pt atoms on terraces. It is not surprising, then, that the selectivity at 90% conversion is lower with this 0.2 wt % Pt/TiO₂ catalyst than with 0.2 wt % Pt/C (see Table 1). Remarkably, and as was also observed with the Au/TiO₂ catalysts,²⁶ no phenylhydroxylamine was detected any more with Pt/TiO₂, and the only undesired observed products were 3-nitroethylbenzene and 3-ethylaniline.

At this point, and to further increase the selectivity of the Pt/TiO₂ sample, one should reduce the fraction of the Pt atoms in terraces and increase the Pt–Ti interface sites. It has been reported^{27,28} that high reduction temperatures of Pt/TiO₂ catalysts produce a decoration of the Pt crystal terraces with TiO_x, decreasing the number of Pt atoms exposed on terraces as well as increasing the number of Pt–Ti sites. Therefore, the 0.2 wt % Pt/TiO₂ sample was reduced at 723 K instead of 473 K, and the resultant sample was characterized by means of HRTEM (Figure 4a) and IR spectroscopy of adsorbed CO (Figure 4b). The presence of TiO_x species on top of the Pt particles reduced at 723 K has been observed by nanoanalytical techniques (STEM EELS; Figure S6 in Supporting Information). Evidence of Ti features in EELS spectra acquired at certain positions on top of the particles shows a partial coverage effect after reduction at high temperature. This was confirmed by CO adsorption results: only one band at 2048 cm⁻¹ due to CO adsorption on Pt–Ti interface sites is observed with the high temperature (723 K) activated 0.2 wt % Pt/TiO₂ catalyst, while CO adsorption on Pt terraces was mainly observed on the sample activated at 473 K. This decorated catalyst gives 93% selectivity at 95% conversion in 6.5 h under very mild reaction conditions (313 K, 3 bar of H₂ pressure) and without formation of phenylhydroxylamine (Table 1, Figure 2). Interestingly, in the

(26) Corma, A.; Concepción, P.; Serna, P. *Angew. Chem., Int. Ed* **2007**, *46* (38), 7266.

(27) Datye, A. K.; Kalakkad, D. S.; Yao, M. H.; Smith, D. J. *J. Catal.* **1995**, *155*, 148.

(28) Salama, T. M.; Hattori, H.; Kita, H.; Ebitani, K.; Tanaka, T. *J. Chem. Soc., Faraday Trans.* **1993**, *89* (12), 2067.

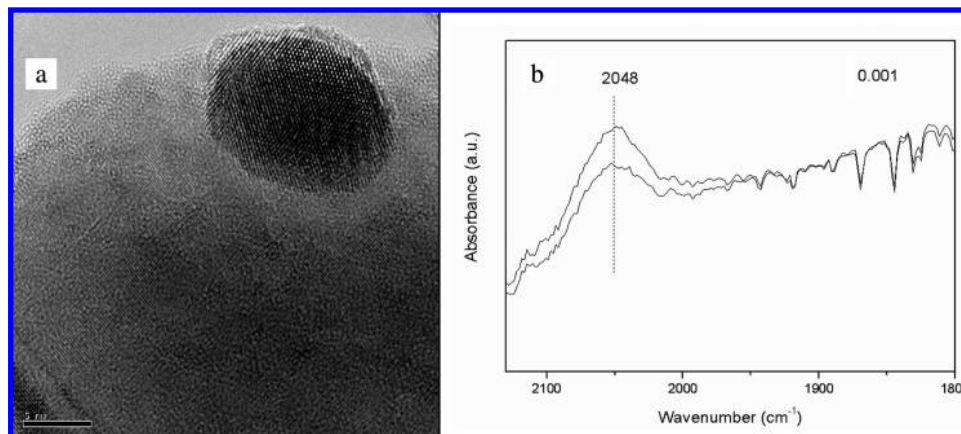


Figure 4. (a) HRTEM images of 0.2 wt % Pt/TiO₂ catalyst after reduction at 723 K. The Pt particle surface appears partially covered by TiO_x species as a decoration effect. (b) IR spectra of CO adsorbed on this sample show only one band corresponding to low surface coordination sites, indicating the absence of Pt terraces Pt(111) and Pt(100).

Table 2. Catalytic Results for 0.2 wt % Pt/TiO₂ Catalyst Reduced at 723 K for the Hydrogenation of Different Substituted Nitroaromatics

substrate	solvent	Pt/nitro (mol, × 10 ²)	T (K)	P (bar)	time (h)	conversion (%)	selectivity (%)
3-nitrostyrene	toluene	0.31	313	3	6.50	95.1	93.1
4-nitrobenzaldehyde ^a	THF	0.92	313	3	3.00	99.2	98.2
4-nitrobenzotrile	THF	0.40	323	6	2.20	99.5	98.6
4-iodonitrobenzene	THF	1.02	333	6	0.35	99.5	99.5
4-nitrophenylacetylene	toluene	0.24	313	3	5.60	98.9	90.1
3-chloronitrobenzene	THF	0.75	318	4	1.00	99.0	99.6

^a Mass balance ~85% because of an unavoidable polymerization of 4-aminobenzaldehyde

Table 3. Catalytic Results of Chemoselective Hydrogenation of Substituted Nitroaromatics into the Corresponding Aminoaromatics on Various Catalysts^a

catalysts ^b	Pt/nitro (mol, × 10 ²)	T (K)	P (bar)	time (h)	conversion (%)	selectivity (%)
3-Nitrostyrene in Toluene						
Au/TiO ₂	0.23	393	9	6.00	98.5	95.9
Pt/TiO ₂	0.31	313	3	6.50	95.1	93.1
Ni/TiO ₂	2.06	393	15	3.00	93.0	90.2
Ru/TiO ₂	1.19	393	15	1.50	95.1	96.3
4-Nitrobenzaldehyde ^c in THF						
Au/TiO ₂	1.14	373	10	1.25	99.0	96.8
Pt/TiO ₂	0.92	313	3	3.00	99.2	98.2
Ni/TiO ₂	20.40	363	11	1.75	99.6	98.7
Ru/TiO ₂	8.89	363	11	2.17	98.4	96.5
4-Nitrobenzotrile in THF						
Au/TiO ₂	0.60	413	25	1.25	99.0	97.2
Pt/TiO ₂	0.40	323	6	2.20	99.5	98.6
Ni/TiO ₂	6.71	413	15	0.75	99.1	88.3 ^d
Ru/TiO ₂	2.92	413	15	3.75	90.0	85.4 ^d
4-Iodonitrobenzene in THF						
Au/TiO ₂	1.20	413	25	10.0	0.5	100.0
Pt/TiO ₂	1.02	333	6	0.35	99.5	99.5
Ni/TiO ₂	16.90	413	15	1.50	93.0	93.8
Ru/TiO ₂	5.89	413	15	1.75	98.0	98.8

^a Reactions were performed under isobaric conditions. Conversion was determined by gas chromatography (GC) with *o*-xylene as internal standard. Products were identified by means of GC-MS. ^b Catalysts were 1.5 wt % Au/TiO₂ and decorated 0.2 wt % Pt/TiO₂, 5 wt % Ni/TiO₂, and 1 wt % Ru/TiO₂. ^c Mass balances were between 80–90% because of an unavoidable polymerization of 4-aminobenzaldehyde. ^d Loss of selectivity through hydrolysis of nitrile function to the amide group.

case of chemoselective hydrogenation of α,β -unsaturated aldehydes (crotonaldehyde) it was found, contrary to the substituted

nitroaromatics, that Pt with larger crystallites was more selective.²⁴ Nevertheless, reduction of the Pt/TiO₂ catalysts at higher temperatures also improved the chemoselectivity for hydrogenation of crotonaldehyde.^{17,29,30} However, it has to be pointed out that chemoselectivity to crotyl alcohol on Pt/TiO₂ was always below 40% at high levels of conversion, while the optimized Pt/TiO₂ catalyst achieves a selectivity above 93% at 95% conversion in the case of nitrostyrene. We have also studied here the relative rate of hydrogenation of the nitro and carbonyl groups by reacting 4-nitrobenzaldehyde on 0.2 wt % Pt/TiO₂ catalyst reduced at 723 K. The results presented in Table 2 show a selectivity to 4-aminobenzaldehyde of 98% at 99% conversion level. These results indicate that, on this catalyst, the nitro reacts faster than the carbonyl group, probably due to a preferential adsorption through the former. We have seen that the optimized Pt/TiO₂ catalyst is of general application for the chemoselective reduction of substituted nitroaromatics, since it gives very high yields of the amino derivatives in the presence of double and triple bonds, carbonyl, nitriles, and halogens (Table 2).

Extension of the Concept to Other Metals. The first objective of this work was already achieved by converting the nonselective Pt catalyst while avoiding the formation of phenylhydroxylamine without using any other catalyst additive. A second objective was then to find if the concept could be generalized to other metals. Results from Table 1 show that Ru and Ni, which are not chemoselective for the reduction of 3-nitrostyrene, can now be converted into selective catalysts by supporting them on TiO₂ and reducing at 723 K. Notice that, with the preparation and activation procedures described here, Ru gives 96% selectivity at 95% conversion, and even Ni gives 90% selectivity to 3-aminostyrene at 93% conversion. These catalysts have also been tested in the hydrogenation of different substituted nitroaromatics, always showing high chemoselectivity toward the nitro group reduction. Table 3 summarizes the results of catalysts optimized in this paper for 3-nitrostyrene, 4-nitrobenzaldehyde, 4-nitrobenzotrile, and 4-iodonitrobenzene. (Detailed distribution of products can be observed in Tables S3–S5 in Supporting Information.)

In order to explain the strong effect of the catalyst activation conditions on Pt/TiO₂, as well as on the other metal catalysts,

(29) Vannice, M. A.; Sen, B. *J. Catal.* **1989**, *115*, 65.

(30) Claus, P.; Schimpf, S.; Schödel, R.; Kraak, P.; Mörke, W.; Hönicke, D. *Appl. Catal., A* **1997**, *165*, 429.

we can assume that a strong metal–support interaction (SMSI) occurs between the metals and the TiO₂ support.³¹ SMSI can be manifested by modifying the electron density of small clusters by charge transfer or polarization from partially reducible supports,³² through the unique properties of metal–support borderline sites,³³ and/or by decoration of the metal by mobile support.³⁴ In our case, we have seen that chemoselective reduction of nitro groups on supports such as γ -Al₂O₃ and carbon, in where SMSI are not to be expected. This should allow us to disregard electronic effects as being the main cause of the high selectivity observed with Pt/TiO₂ catalysts. In a similar way, it would be difficult to explain the high selectivity of the properly activated Ni/TiO₂ catalysts with large Ni crystallite sizes, on the bases of electronic effects. On the other hand, the fact that high chemoselectivity is observed when the formation of high-density metal plains is avoided and when the number of metal sites in corners and axes is increased leads us to assume that the main role of SMSI is, in our case, due to the decoration of metal surfaces by TiO₂. This decreases the assemblies of accessible metal atoms, with a strong effect on the adsorption of the substituted nitroaromatic, in such a way that a preferential adsorption through the nitro groups occurs. Molecular modeling and kinetic studies are in process to elucidate the selective surface interactions occurring between substituted nitroaromatics and decorated and nondecorated Pt/TiO₂ catalysts.

Conclusions

It is possible to transform nonchemoselective hydrogenation metals such as Pt, Ru, and Ni into chemoselective catalysts by supporting nanosized crystals of the metals on TiO₂ and decorating the exposed (111) and (100) crystal faces by means of a simple catalyst activation. The very high activity and

selectivity of some of the catalysts presented here breaks the previous paradigm that high chemoselectivity in the hydrogenation of substituted nitroaromatics was in parallel with a reduction of the intrinsic hydrogenation capacity of the catalyst, together with the requirement of a second catalytic function (iron or vanadium salts) to avoid the accumulation of undesired reaction products. These conclusions not only are relevant from a fundamental point of view but also have allowed preparation of very active, chemoselective, and environmentally friendly catalysts for the reduction of nitro groups in substituted nitroaromatics, which accomplishes the requirements for industrial application.

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Supporting Information Available: Characterization of Pt/Al₂O₃, Pt/C, and Pt/TiO₂ samples by FTIR of CO, STEM, HRTEM, STEM-HAADF, and STEM-EELS spectroscopy and detailed distribution of products for the hydrogenation of 3-nitrostyrene, 4-nitrobenzaldehyde, 4-nitrobenzaldehyde, and 4-iodonitrobenzene. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(31) Tauster, S. J.; Fung, S. C.; Garten, R. *J. Am. Chem. Soc.* **1978**, *100*, 170.

(32) Boudart, M.; Djega-Mariadasson, G. In *Kinetics of Heterogeneous Catalytic Reactions*; Princeton University Press: Princeton, NJ, 1984; p 157.

(33) Schwab, G. M. *Discuss. Faraday Soc.* **1950**, *8*, 166.

(34) Haller, G. L.; Resasco, D. E. *Adv. Catal.* **1989**, *36*, 173.