inconsistent with the theoretical prediction of $T_{KL} = 1$ K (13, 14). Further investigations, not only experimental but also theoretical, are necessary to clarify this fundamental issue.

References and Notes


Chemoselective Hydrogenation of Nitro Compounds with Supported Gold Catalysts
Avelino Corma* and Pedro Serna

The selective reduction of a nitro group when other reducible functions are present is a difficult process that often requires stoichiometric amounts of reducing agents or, if $H_2$ is used, the addition of soluble metals. Gold nanoparticles supported on TiO$_2$ or Fe$_3$O$_4$ catalyzed the chemoselective hydrogenation of functionalized nitroarenes with $H_2$ under mild reaction conditions that avoided the accumulation of hydroxylamines and their potential exothermic decomposition. These chemoselective hydrogenation gold catalysts also provide a previously unknown route for the synthesis of the industrially relevant cyclohexanone oxime from 1-nitro-1-cyclohexene.

Aromatic amines are generally produced by catalytic hydrogenation of nitro compounds. The reduction of simple nitro compounds is readily carried out with various commercial catalysts, but the selective reduction of a nitro group with $H_2$, when other reducible groups are present in the same molecule, is more challenging. Functionalized amines are industrially important intermediates for pharmaceuticals, polymers, herbicides, and other substances and fine chemicals (1, 2), so there is a strong incentive to develop chemoselective catalysts for the reduction of nitro groups.

Stoichiometric reducing agents such as sodium hydrosulfite (3), iron (2), tin (4), or zinc in ammonium hydroxide (5) have been successfully used to reduce aromatic nitro compounds containing olefinic bonds. However, these processes are not environmentally sustainable. Cobalt and ruthenium sulfide catalysts can selectively convert nitro compounds into amines in the presence of olefinic groups (6), but the yields are rather low, and sulfur-containing by-products are also formed that strongly limit the usefulness of these catalysts. Other catalytic systems, such as iron complexes (7) or doped Raney nickel (8), are not for general use and entail important practical drawbacks regarding the difficulty for reuse. Transition metal catalysts simultaneously hydrogenate both the nitro and olefinic or carbonyl functions (9), but Siegrist et al. (10) and Blaser et al. (11) have indeed shown that a catalyst of Pt on C (Pt/C), modified by $H_2$PO$_4$ or other low valent phosphorous additives, together with soluble vanadium compounds can be highly selective in apolar solvents. However, Pt-Pb/CaCO$_3$ catalysts, in the presence of FeCl$_3$ and tetramethyllummonium chloride in solution, were shown to be adequate for polar solvents (10). Siegrist et al. and Blaser et al. have achieved excellent chemoselectivity in apolar solvents by using the first catalyst and rather lower selectivity with the second type of catalyst and polar solvents. Although these catalytic systems are effective, catalyst preparation often remains critical, and the amount of the modifying agent must be precisely controlled (7). Moreover, the control of the Pt activity needed to improve the selectivity of the reaction produces an unavoidable accumulation of hydroxylamine intermediates, which makes the addition of soluble metal salts compulsory. Alternative heterogeneous catalysts for the chemoselective reduction of nitro groups that do not require soluble metal salts are highly desirable.

Noble metal catalysts can activate nitro groups as well as carbonyl and double bonds, leading to unselselective reductions (9). The most common solution to the selectivity problem has been to modify the metal adsorption characteristics by means of surface modifiers. This approach has been taken in the case of carbonyl and double bond hydrogenation by modifying Pt with Sn (12) and CeO$_2$ (13, 14) or, as described above for nitro groups, by introducing different Pt modifiers. In our case, we have approached the problem by investigating an alternative metal catalyst that directly activates nitro groups preferentially to other competing functional groups.

Gold in the form of nanoparticles is an active redox catalyst for oxygen-containing hydrocarbons, such as alcohols and carboxyls, but does not interact with olefinic groups (15, 16). For reduction, gold can hydrogenate, although at different rates, alkenes, alkynes, imines, and carboxyls (19, 20) in the presence of $H_2$. Gold exhibits some selectivity for the hydrogenation of C=O groups of $\alpha$, $\beta$-unsaturated aldehydes, producing allyl-type unsaturated alcohols (21–23). Because Pt and Pd are not chemoselective catalysts for the reduction of nitro groups...
and because olefins and NO₂ adsorb differently on Pt and Pd than on Au (24), we explored gold as a potential chemoselective catalyst for the reduction of nitro compounds in the presence of other reducible functional groups.

Two supported gold catalysts [1.5 weight percent (wt %) Au/TiO₂ and 4.5 wt % Au/Fe₂O₃], as well as Pt-, Pd-, Au-Pt-, and Au-Pd-supported catalysts were used (25) for the hydrogenation of 3-nitrostyrene with H₂ under mild reaction conditions (9 bar, 120°C). The results (Table 1) show that neither the Pt, Pd, Au-Pt, nor Au-Pd catalysts were selective for this reaction. However, the two supported gold catalysts gave conversions >98% with 96% selectivity to 3-vinylaniline, whereas the residual product was 3-ethylaniline (26). The evolution of the reaction products when Au/TiO₂ and Au/Fe₂O₃ are used as catalysts for the hydrogenation of 3-nitrostyrene (Fig. 1) shows only traces of hydroxylamine styrene, azostyrene, and azoxystyrene. These low levels are desirable, because the accumulated hydroxylamines can undergo exothermic decomposition; their toxicity and ability to form colored condensation products lead to reductions in quality (11). Results (fig. S2) show that hydroxylamines derivatives are also avoided for multiple turnovers of the catalyst. Therefore, if the aryly hydroxylamine can be formed on the gold catalysts, it apparently reacts rapidly to give the corresponding aniline, as illustrated in schemes S1 and S2.

The chemoselectivity reduction of the nitro group in the presence of a carbonyl group has been studied through the hydrogenation of 4-nitrobenzaldehyde. Results (Table 1) show that Au/Fe₂O₃ is an active catalyst for the chemoselective reduction of the nitro group, giving the corresponding aminobenzaldehyde (table S3). In this case, we have detected relatively high amounts of the azoxy intermediate species as a reaction product, but its presence can be reduced below 4 wt % by using TiO₂ as support. The nitrogen mass balances were close to 100%, probably because of the well-known polymerization of the 4-aminobenzaldehyde, which yields heavier products. However, neither 4-nitrobenzyl alcohol, 4-aminobenzyl alcohol, nor decarboxylated products were detected when supported Au was used as a catalyst. However, when Pt and Pd were tested, the results (Table 1) show that, contrary to the case for Au, the reduction of the nitro group with hydrogen was not chemoselective and large amounts of the products with reduced carbonyl groups were formed (26).

Nitro groups can also be reduced selectively in the presence of nitriles with gold catalysts. Thus, 4-nitrobenzonitrile was reduced to the corresponding amine with yields >96%, whereas much lower yields and selectivity (table S4) were obtained with Pt and Pd (Table 1).

Lastly, all of the noble metals studied were chemoselective for the hydrogenation of 4-nitrobenzamide. Nevertheless, the selectivity was still higher in the case of gold catalysts (Table 1).

### Table 1. Catalytic results of the chemoselective hydrogenation of nitro groups of aryl compounds (italic type in table) in the presence of several functional groups and for cyclohexanone oxime from 1-nitro-1-cyclohexene. Gold catalysts show notably better behavior for reducing nitro groups without modifying double bonds and carbonyl, nitrile, or amide groups. Pressure (P) refers to initial pressure (not isobaric conditions). Conversion was determined by gas chromatography (GC–mass spectrometry). T, temperature.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>% Metal (Mol)</th>
<th>T (°C)</th>
<th>P (bar)</th>
<th>Time (hours)</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/TiO₂</td>
<td>0.23</td>
<td>120</td>
<td>9</td>
<td>6.00</td>
<td>98.5</td>
<td>95.9</td>
</tr>
<tr>
<td>Au/Fe₂O₃</td>
<td>0.39</td>
<td>130</td>
<td>12</td>
<td>9.50</td>
<td>95.2</td>
<td>95.1</td>
</tr>
<tr>
<td>Pd/C</td>
<td>0.11</td>
<td>120</td>
<td>9</td>
<td>0.03</td>
<td>99.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Pt/C</td>
<td>0.12</td>
<td>120</td>
<td>9</td>
<td>0.03</td>
<td>96.7</td>
<td>2.9</td>
</tr>
<tr>
<td>Au-Au/Fe₂O₃</td>
<td>0.20</td>
<td>120</td>
<td>9</td>
<td>0.03</td>
<td>99.5</td>
<td>0.0</td>
</tr>
<tr>
<td>Au/Pt/TiO₂</td>
<td>0.31</td>
<td>120</td>
<td>9</td>
<td>0.02</td>
<td>93.0</td>
<td>1.8</td>
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<tr>
<td>4-Nitrobenzaldehyde</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Au/TiO₂</td>
<td>1.14</td>
<td>100</td>
<td>10</td>
<td>1.25</td>
<td>99.0</td>
<td>96.8</td>
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<tr>
<td>Au/Fe₂O₃</td>
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<td>100</td>
<td>10</td>
<td>1.00</td>
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<td>10</td>
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<td>Au/TiO₂</td>
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<td>1.25</td>
<td>99.0</td>
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<tr>
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<tr>
<td>1-Nitro-1-cyclohexene</td>
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<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>Au/TiO₂</td>
<td>0.27</td>
<td>110</td>
<td>15</td>
<td>0.50</td>
<td>99.6</td>
<td>90.9</td>
</tr>
<tr>
<td>Pd/C</td>
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<td>0.03</td>
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<td>67.1</td>
<td>52.6</td>
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</table>

**Scheme 1.**
Given the excellent chemoselectivity of gold for reducing nitro compounds, we explored this system as an alternative catalytic route for the production of cyclohexanone oxime, an important molecule in the production of e-caprolactam. Cyclohexanone oxime is currently obtained via two different routes (Scheme 1A).

In these processes, hydroxylamine, which is a toxic and unstable product, has to be used or otherwise synthesized in situ by the Sumitomo and ENICHEM procedure. However, the high activity and selectivity of gold catalysts open the possibility for an alternative process that would involve the steps given in Scheme 1B. This process requires a catalyst that selectively hydrogenates 1-nitro-1-cyclohexene into cyclohexanone oxime. Whereas Pt and Pd produce low selectivity even at relatively low levels of conversions, selectivity >90% is achieved at practically 100% conversion with the gold catalysts (Table 1).

References and Notes

25. Materials and methods are available as supporting material on Science Online.
26. Detailed product distributions with the different catalysts are given in tables S1 to S6.
27. We thank the World Gold Council for supplying the gold catalysts that were used as well as for the corresponding transmission electron microscopy images and F. Sánchez, M. Iglesias, and C. González-Arellano for useful comments. This work was supported by Ministerio de Educación y Ciencia (grant MAT2003-07945-C02-03).

Supporting Online Material

www.sciencemag.org/cgi/content/full/313/5785/332/DC1
Materials and Methods
SOM Text
Figs. S1 to S3
Tables S1 to S6
Schemes S1 and S2
References

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A Dielectric Polymer with High Electric Energy Density and Fast Discharge Speed

Baojin Chu,1,2 Xin Zhou,3 Kailiang Ren,2 Bret Neese,1,2 Minren Lin,2 Qing Wang,1,2 F. Bauer,4 Q. M. Zhang1,2,3*

Dielectric polymers with high dipole density have the potential to achieve very high energy density, which is required in many modern electronics and electric systems. We demonstrate that a very high energy density with fast discharge speed and low loss can be obtained in defect-modified poly(vinylidene fluoride) polymers. This is achieved by combining nonpolar and polar molecular structural changes of the polymer with the proper dielectric constants, to avoid the electric displacement saturation at electric fields well below the breakdown field. The results indicate that a very high dielectric constant may not be desirable to reach a very high energy density.

Dielectric materials are used to control and store charges and electric energies and play a key role in modern electronics and electric power systems. As the requirements dielectric materials becomes a major enabling technology (1–3). For example, high energy density dielectric capacitors would help to reduce the volume, weight, and cost of the electric power system in hybrid electric vehicles.

Among various dielectric materials, polymers are presently the material of choice for energy storage applications because of their relatively high energy density, high electric breakdown field ($E_b$), low dielectric loss, fast speed, low cost, and graceful failure (i.e., high reliability) (4–6). However, dielectric polymers that are currently used for high energy density capacitors show low (<3) dielectric constants (represented by $K$). Consequently, the high energy density in the dielectric polymers relies on the high $E_b$ (>500 MV/m). In general, the 21 JULY 2006 VOL 313 SCIENCE www.sciencemag.org 334