Bimetallic Pd–Au/TiO₂ Nanoparticles: An Efficient and Sustainable Heterogeneous Catalyst for Rapid Catalytic Hydrogen Transfer Reduction of Nitroarenes

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ABSTRACT: Anilines are one of the important chemical feedstocks and are utilized for the preparation of a variety of pharmaceuticals, agrochemicals, pigments, and dyes. In this context, the catalytic reduction of nitro functionality is an industrially vital process for the synthesis of aniline derivatives. Herein, we report an efficient nanosized bimetallic Pd–Au/TiO₂ nanomaterial which is proved to be quite efficient for rapid catalytic hydrogen transfer reduction of nitroarenes into corresponding amines. Significantly, the reduction process is successful under solvent-free and mild green atmospheric conditions. Bimetallic Pd–Au nanoparticles served as the active center, and TiO₂ played as a support in hydrogen transfer from the source hydrazine monohydrate. Typical results highlighted that the reactions were very rapid and the products were obtained in good to excellent yields. Significantly, the process was successful in the presence of a very low amount catalyst (0.1 mol %). Furthermore, the reaction showed good chemoselectivity and compatibility with double or triple bond, aldehyde, ketone, and ester functionalities on the aromatic ring. Typical results indicated the true heterogeneous nature of the Pd–Au/TiO₂ nanocatalyst, where the catalyst retained the activity, without loss of its activity.

INTRODUCTION

Development of a green protocol for organic transformations is a great challenge to the synthetic community. A catalyst is a necessary element of any sustainable development.¹ In this context, development of stable, highly active, recyclable, and environmentally benign catalysts is highly desirable. Nanomaterial-based catalysts act as viaducts between homogeneous and heterogeneous catalysts and promote the advantages, namely, selectivity and recyclability.²,³ Therefore, nanocatalysts play an important role in the development of sustainable processes.²,⁵ Novel metal-containing nanomaterials have attracted a significant consideration because of their unique physicochemical properties, which exhibit versatile applications in organic transformations.⁶–⁸ It is desirable to have high dispersion of noble metals such as Pd, Au, Pt, and so forth, which is an important issue in the field of heterogeneous catalysis.⁹ Bimetallic nanomaterials have recently attracted an extensive consideration because of their enhanced catalytic properties when compared to monometallic nanoparticles for several catalytic reactions.¹⁰–¹¹ The catalytic reduction of nitroarenes is rather preferred with regard to high yields and selectivity over traditional metal-mediated reductions (iron, zinc, and tin).¹² In addition, heterogeneous catalytic reduction of nitroarenes, particularly, working under ligand and solvent-free and at milder reaction conditions is advantageous than those that make use of high pressure reactors of hydrogen gas,²⁶,²⁷ toxic organic solvents, ligands, and high temperatures.²⁴,²⁵ The catalytic reduction of nitroarenes mediated by homogeneous transition-metal catalysts has also been well-established (i.e., Pd,²⁹,³⁰ Ru,³¹ Rh,³² Ir,³³ and Ni³⁴). However, the main limitation of homogeneous catalysts is recyclability and reusability, whereas the commercially available heterogeneous catalysts (Pd/C) are less efficient because a high amount of noble metals is required.³⁵ However, the separation of nanocatalysts is difficult because of its small size.³⁶,³⁷ To overcome this problem, nanoparticles supported on high surface area materials is often practiced. To the best of our knowledge, a few reports are accessible for the combination of bimetallic metals and metal oxide supports for nitroarenes reduction reactions.¹⁶,¹⁷

Herein, we report a highly active bimetallic Pd–Au supported by a TiO₂ heterogeneous catalyst, which exhibits higher activity on the reduction of nitroarenes into anilines.
The catalytic activity of bimetallic Pd–Au/TiO₂ has been studied on hydrogenation of nitroarenes under mild and solvent-free green atmospheric conditions. The efficacy of the developed Pd–Au/TiO₂ catalyst has been confirmed by comparing with monometallic Pd/TiO₂ and Au/TiO₂ catalysts. In addition, chemoselectivity and recyclability of the Pd–Au/TiO₂ catalyst has also been examined.

■ RESULTS AND DISCUSSION

Synthesis of TiO₂-Supported Pd Nanoparticles. A mixture of PdCl₂ (0.56 mmol, 100 mg) and NaCl (1.5 mmol, 88 mg) was taken in 10 mL of methanol and stirred continuously for 24 h at room temperature. It was then diluted with 40 mL of methanol and stirred for 5 min at room temperature, and TiO₂ nanoparticles (6.26 mmol, 500 mg) were added into this solution. Further, the resultant mixture was stirred continuously for 1 h at 60 °C. Finally, the reaction mixture was cooled to room temperature, and sodium acetate (9.26 mmol, 0.76 g) and 0.5 mL of hydrazine monohydrate were added to into the mixture and stirred for 1 h. At the end, the mixture was centrifuged with methanol, water, and acetone. It was kept in the oven for drying, followed by grinding to obtain a fine powder.

Synthesis of TiO₂-Supported Pd–Au Nanoparticles. A mixture of PdCl₂ (0.56 mmol, 100 mg), HAuCl₄ (0.56 mmol, 190 mg), and NaCl (1.5 mmol, 88 mg) was taken in 10 mL of methanol and stirred continuously for 24 h at room temperature. It was then diluted with 40 mL of methanol and stirred for 5 min at room temperature, and TiO₂ nanoparticles (6.26 mmol, 500 mg) were added into this solution. Further, the resultant mixture was stirred continuously for 1 h at 60 °C. Finally, the reaction mixture was cooled to room temperature, and sodium acetate (9.26 mmol, 0.76 g) and 0.5 mL of hydrazine monohydrate were added to into the mixture and stirred for 1 h. At the end, the mixture was centrifuged with methanol, water, and acetone and kept in the oven for drying.

Characterization of As-Prepared Catalysts. X-ray Diffraction (XRD). The powder XRD patterns of pure TiO₂, Pd/TiO₂, and Pd–Au/TiO₂ are shown in Figure 1, which confirmed the formation of the catalysts. By using the JCPDS no.: 89–4921 (TiO₂), 89–4897 (Pd), and 89–3697 (Au), the presence of the active components is identified. The diffraction peaks of pure TiO₂ showed d-spacing values of 2.245, 1.948, 1.375, and 1.663 Å corresponding to (111), (200), (220), and (311) crystalline planes, respectively. In a similar manner, the peaks of Pd showed d-spacing values of 2.245, 1.948, 1.375, and 1.663 Å corresponding to (111), (200), (220), (311), and (222) crystalline planes, respectively.

Raman Analysis. The Raman spectra of TiO₂, Pd/TiO₂, and Pd–Au/TiO₂ indicated E₆g, B₁₉g, and A₁g peaks. The E₆g peak is due to the symmetrical stretching vibrations of O–Ti–O, whereas the B₁₉g peak is due to the symmetrical bending vibrations of O–Ti–O and the A₁g peak is due to asymmetric bending vibrations of O–Ti–O in the TiO₂ nanoparticles. In Figure 2, fresh TiO₂ has five Raman active modes in the vibrational spectrum centered at 143, 196, 395, 514, and 636 cm⁻¹, which are assigned to the E₆g, E₆g, B₁₉g, A₁g, and E₆g symmetries of the anatase phase of TiO₂. Pd impregnated on TiO₂ showed Raman vibrational modes centered at 152, 205, 237, 268, 330, 401, 562, 617, and 692 cm⁻¹ because of A₁g, B₁₉g, A₁g, B₃g, B₁₉g, A₁g, B₃g, A₁g, and A₅g symmetries of the

Figure 1. XRD pattern of TiO₂, Pd/TiO₂ and Pd–Au/TiO₂ nanomaterials.

Figure 2. Raman spectra of TiO₂, Pd/TiO₂, and Pd–Au/TiO₂ nanomaterials.
Brookite phase of Pd/TiO2, respectively, whereas Pd–Au-impregnated TiO2 showed the Raman vibrational modes at 149, 264, 401, and 601 cm⁻¹ corresponding to the E_g and two phonon scattering E_g and A_1g modes of the rutile phase of Pd–Au/TiO2, respectively. The phase transformation of TiO2 in Pd/TiO2 and Pd–Au/TiO2 is due to the presence of NaCl and NaOAc in the synthesis, which favors the anatase–brookite and anatase–rutile phases of TiO2. With the introduction of NaCl and NaOAc, the Na⁺ ions locally stop the direct closure of titanate layers at their adjacent positions, which induces the brookite- and rutile-like structures.

**XPS Analysis.** The valence states of the Pd–Au/TiO2 nanocatalyst were analyzed by X-ray photoelectron spectroscopy (XPS). The XPS spectra shown in Figure 3 show the characteristic Pd 3d₅/₂ and Pd 3d₃/₂ peaks at 339.6 and 335.7 eV, respectively, corresponding to Pd(0). The XPS core level spectra of the Au 4f are shown in Figure 3. The binding energies (BEs) of Au 4f₇/₂ and Au 4f₅/₂ electrons are 83.2 and 86.8 eV, respectively, corresponding to Pd(0). The XPS spectra shown in Figure 3 show the characteristic Pd 3d₅/₂ and Pd 3d₃/₂ electrons at 83.2 and 86.8 eV, respectively. It is reliable with the reports on gold metallic state (Au(0)). The valance state of nonstoichiometric TiO₂ in Pd–Au/TiO2 is due to the presence of NaCl and NaOAc, which favors the anatase–brookite and anatase–rutile phases of TiO2. With the introduction of NaCl and NaOAc, the Na⁺ ions locally stop the direct closure of titanate layers at their adjacent positions, which induces the brookite- and rutile-like structures.

**Transmission Electron Microscopy (TEM) Analysis.** Figure 4 shows the morphological characteristics of Pd–Au nanoparticles on TiO2 nanoparticles. The average particle size of Pd–Au nanoparticles is 5 nm, and TiO2 nanoparticles exhibited a wide range of sizes. We observed from the images that the the particles mostly have spherical shape.

**Catalytic Activity.** In an oven-dried 10 mL test tube, nitroarenes (1 mmol), reductant [hydrazine monohydrate (0.5 mL)], and Pd–Au/TiO2 nanoparticles (0.1 mol % of Pd–Au) were added. The resulting neat reaction mixture was stirred in an open vessel and at room temperature. The progress of the reaction was monitored by thin-layer chromatography. After completion of the reaction, the reaction mixture was diluted with an aqueous NH₄Cl solution (approximately 10 mL) and extracted with ethyl acetate (3 × 3 mL). The organic layers were dried (Na₂SO₄) and concentrated under reduced pressure. Purification of the residue by silica gel column chromatography using petroleum ether/ethyl acetate as the eluent furnished the corresponding amines 2, as a solid/viscous yellowish liquid.

**Optimization of the Reaction Conditions.** In order to find out the optimal reaction conditions, the hydrogenation of nitroarenes 1 (1 mmol) in the presence of various catalysts was studied in various parameters such as the effect of different conditions, and the results are summarized in Table 1. Initially, the reaction was carried out on nitrobenzene 1a with hydrazine monohydrate as the reductant under solvent-free conditions, with different Zn-based mono/bimetallic catalysts such as ZnO, ZnO₂MnO₃, and ZnFe₂O₄ (Table 1, entries 1–3). However, no progress was noticed except for the recovery of the starting material. The reaction did not show any progress even with other metal transition-metal oxides NiFe₂O₄, CuFe₂O₄, SnO₂, and TiO₂ (Table 1, entries 4–7). On the other hand, the reaction with Pd/C furnished aniline 2a in moderate yields (Table 1, entry 8). Notably, the reduction reaction in the presence of Pd/TiO₂ and Au/TiO2 proved to be efficient and gave product 2a in 82 and 80% yields, respectively, in shorter reaction times (Table 1, entries 9 & 10). Gratifyingly, the bimetallic Pd–Au/TiO2 nanocatalyst turned out to be the best and afforded aniline 2a just in 5 min in excellent yields under mild and solvent-free open vessel conditions (Table 1, entry 11). The catalytic activity of the catalyst depends on strong metal–support interaction (SMSI).

The small size metal nanoparticles have more SMSI effect compared with large size metal nanoparticles. Therefore, Pd–Au/TiO2 exhibited high catalytic activity due to small size of Pd–Au nanoparticles (for particles size see Figure S7).

The reaction was also explored with various solvents, such as methanol, ethanol, dichloromethane (DCM), ethyl acetate, and water, as depicted in Table 2. The protic solvents such as...
MeOH and EtOH seemed to be good and furnished 2a in very good yields (Table 2, entries 1 & 2), whereas the solvents DCM and ethyl acetate were also good (Table 2, entries 3 & 4). Water was also found to be the useful solvent (Table 2, entry 5). On the other hand, the reaction with other reductants, such as NaBH₄ and H₂ balloon, furnished the product aniline 2a in 76 and 64% yields, respectively (Table 2, entries 6 & 7).

Further to optimize the reaction with regard to the amount of hydrazine monohydrate (N₂H₄·H₂O), for the formation of aniline 2a, it was planned to carry out the reduction on nitrobenzene 1a with varying amounts of N₂H₄·H₂O. Thus, the reaction was carried out with 0.1, 0.2, 0.3, 0.4, and 0.5 mL of hydrazine monohydrate (N₂H₄·H₂O) for 10 min at room temperature and in an open vessel. However, it was observed that product yields were less with 0.1, 0.2, 0.3, and 0.4 mL of N₂H₄·H₂O when compared to that of 0.5 mL of N₂H₄·H₂O (Table 3, entries 1—5). Therefore, it was concluded that Pd−Au/TiO₂ (0.1 mol %) and N₂H₄·H₂O (0.5 mL) under the mild open vessel and solvent-free reaction conditions were best for the formation of aniline 2a reduction (Table 1, entry 11).

With these best conditions in hand (Table 1, entry 11), next, to check the scope and generality of the method, the hydrogenation reaction was explored with various nitroarenes 1a−r. Gratifyingly, the reaction was found to be amenable and general and furnished 2a in 80−96% yields. For the sake of clarity, Table 2 summarizes the results of solvent−reductant optimization studies, whereas Table 3 provides the optimization with regard to the amount of reductant for the formation of aniline 2a.

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**Figure 4.** TEM images of as-prepared Pd–Au/TiO₂.

**Table 1. Catalyst Optimization Studies for the Formation of Aniline 2a**

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst (mol %)</th>
<th>time</th>
<th>yield 2a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ZnO (2.5 mol %)</td>
<td>12 h</td>
<td>c</td>
</tr>
<tr>
<td>2</td>
<td>Zn₃MnO₃·δ (2.5 mol %)</td>
<td>12 h</td>
<td>c</td>
</tr>
<tr>
<td>3</td>
<td>Zn₃Fe₃O₃·δ (2.5 mol %)</td>
<td>12 h</td>
<td>c</td>
</tr>
<tr>
<td>4</td>
<td>NiFe₂O₄ (2.5 mol %)</td>
<td>12 h</td>
<td>c</td>
</tr>
<tr>
<td>5</td>
<td>CuFe₂O₄ (2.5 mol %)</td>
<td>12 h</td>
<td>c</td>
</tr>
<tr>
<td>6</td>
<td>SnO₂ (2.5 mol %)</td>
<td>12 h</td>
<td>c</td>
</tr>
<tr>
<td>7</td>
<td>TiO₂ (2.5 mol %)</td>
<td>12 h</td>
<td>c</td>
</tr>
<tr>
<td>8</td>
<td>Pd/C (2.5 mol %)</td>
<td>1 h</td>
<td>46</td>
</tr>
<tr>
<td>9</td>
<td>Pd/TiO₂ (0.1 mol %)</td>
<td>15 min</td>
<td>82</td>
</tr>
<tr>
<td>10</td>
<td>Au/TiO₂ (0.1 mol %)</td>
<td>10 min</td>
<td>80</td>
</tr>
<tr>
<td>11</td>
<td>Pd−Au/TiO₂ (0.1 mol %)</td>
<td>5 min</td>
<td>96</td>
</tr>
</tbody>
</table>

*aReaction conditions: nitrobenzene (1 mmol), hydrazine monohydrate (0.5 mL), and catalyst. *bIsolated yields of product 2a. *cStarting material 1a recovered. *dPd/C (palladium on activated charcoal).

**Table 2. Solvent & Reductant Optimization Studies for the Formation of Aniline 2a**

<table>
<thead>
<tr>
<th>entry</th>
<th>reductant</th>
<th>solvent</th>
<th>yield 2a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N₂H₄·H₂O</td>
<td>MeOH</td>
<td>82</td>
</tr>
<tr>
<td>2</td>
<td>N₂H₄·H₂O</td>
<td>EtOH</td>
<td>85</td>
</tr>
<tr>
<td>3</td>
<td>N₂H₄·H₂O</td>
<td>DCM</td>
<td>75</td>
</tr>
<tr>
<td>4</td>
<td>N₂H₄·H₂O</td>
<td>E.A</td>
<td>76</td>
</tr>
<tr>
<td>5</td>
<td>N₂H₄·H₂O</td>
<td>water</td>
<td>84</td>
</tr>
<tr>
<td>6</td>
<td>NaBH₄</td>
<td>water</td>
<td>76</td>
</tr>
<tr>
<td>7</td>
<td>H₂ balloon</td>
<td>water</td>
<td>64</td>
</tr>
</tbody>
</table>

*aReaction conditions: nitrobenzene (1 mmol), hydrazine monohydrate (0.5 mL), NaBH₄ (10 mmol), Pd−Au/TiO₂ (0.1 mol % of Pd−Au), and solvent (1 mL). *bIsolated yields of product 2a. *cClosed vessel with atmospheric pressure.

**Table 3. Optimization with Regard to the Amount of Reductant for the Formation of Aniline 2a**

<table>
<thead>
<tr>
<th>entry</th>
<th>N₂H₄·H₂O (mL)</th>
<th>yield 2a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1</td>
<td>65</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>72</td>
</tr>
<tr>
<td>3</td>
<td>0.3</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>0.4</td>
<td>85</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>96</td>
</tr>
</tbody>
</table>

*aReaction conditions: nitrobenzene (1 mmol) and Pd−Au/TiO₂ (0.1 mol % of Pd−Au). *bIsolated yields of product 2a.
afforded the corresponding amines 2a–i, in good to excellent yields (Table 4). Significantly, the reaction was completed in a reasonably short span of time. Interestingly, the reaction was successful with simple and methyl-substituted nitrobenzenes 1a–c and furnished the reduced anilines 2a–c in excellent yields (Table 4). However, the reaction with halo-substituted nitrobenzenes 1c–l (i.e. with Cl, Br, and I) not only reduced the nitro group but also removed the halide moieties reductively and thus furnished the products 2a–c in good to very good yields (Table 4). The reductive removal of halide groups along with the reduction of nitro functionality is due to the reactive nature of the catalyst. Quite interestingly, when the chloride/fluoride functionality belongs to other aromatic of biaryl nitro compound, the reaction was found to be chemoselective and gave the corresponding biaryl amines without affecting the halide moiety (Table 4). The reductive removal of halide groups along with the reduction of nitro functionality is due to the reactive nature of the catalyst. Quite interestingly, when the chloride/fluoride functionality belongs to other aromatic of biaryl nitro compound, the reaction was found to be chemoselective and gave the corresponding biaryl amines without affecting the halide moiety (Table 4). The reductive removal of halide groups along with the reduction of nitro functionality is due to the reactive nature of the catalyst. Quite interestingly, when the chloride/fluoride functionality belongs to other aromatic of biaryl nitro compound, the reaction was found to be chemoselective and gave the corresponding biaryl amines without affecting the halide moiety (Table 4).

Table 4. Synthesis of Anilines 2a–i from Nitroarenes 1a–r

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate (1)</th>
<th>Product (2)</th>
<th>Time (min)</th>
<th>Yield 2 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>2a</td>
<td>5</td>
<td>96</td>
</tr>
<tr>
<td>2</td>
<td>1b</td>
<td>2b</td>
<td>5</td>
<td>95</td>
</tr>
<tr>
<td>3</td>
<td>1c</td>
<td>2c</td>
<td>5</td>
<td>93</td>
</tr>
<tr>
<td>4</td>
<td>1d</td>
<td>2a</td>
<td>30</td>
<td>82</td>
</tr>
<tr>
<td>5</td>
<td>1e</td>
<td>2a</td>
<td>30</td>
<td>78</td>
</tr>
<tr>
<td>6</td>
<td>1f</td>
<td>2a</td>
<td>10</td>
<td>85</td>
</tr>
<tr>
<td>7</td>
<td>1g</td>
<td>2a</td>
<td>10</td>
<td>83</td>
</tr>
<tr>
<td>8</td>
<td>1h</td>
<td>2a</td>
<td>10</td>
<td>88</td>
</tr>
<tr>
<td>9</td>
<td>1i</td>
<td>2a</td>
<td>10</td>
<td>77</td>
</tr>
</tbody>
</table>

“Reaction conditions: nitrobenzene (1 mmol), hydrazine monohydrate (0.5 mL), and Pd−Au/TiO2 (0.1 mol % of Pd−Au)." Isolated yields of product 2a–r.

afforded with nitroanilines 1q–r and yielded the products 2q–r in good yields (Table 4).

To further check the compatibility and applicability of the method, it was aimed to explore the reduction reaction with other nitroarenes. Thus, the reaction was performed on aldehyde-, ketone-, ester-, and double and triple bond-containing nitroarenes 1s–w (Table 5). To our delight, the method showed excellent compatibility and chemoselectivity and furnished the corresponding anilines 2s–w without affecting the aldehyde, ketone, ester, olefin, and alkyne groups (Table 5). Thus, this reveals the importance of the present protocol.

It is worth mentioning that the catalyst retains its activity, which is evident with nearly no loss of activity even after the fifth reaction cycle (Figure 5). This was done by recovering the catalyst by centrifugation and washing with ethyl acetate and acetone, followed by drying in a hot air oven at 60 °C for 12 h. The recovered Pd−Au/TiO2 nanocatalyst was then subjected to the next catalytic cycles. The marginal loss of activity after the fifth cycle (<3%) may be due to loss of some amount of the catalyst during the recovery of the Pd−Au/TiO2 nanocatalyst. The catalyst was recycled five times without an appreciable change in the product 2a yield, under the established conditions.
conditions. Thus, on the basis of the above results, it was confirmed that the Pd−Au/TiO₂ nanocatalyst is stable enough and can be reused.

**CONCLUSION**

In summary, we did a comparative study with as-synthesized various nanomaterials among all the catalysts and bimetallic Pd−Au nanoparticles impregnated on TiO₂ were found to exhibit excellent catalytic activity for various nitroarenes rapid hydrogenation reactions. On the other hand, this catalyst exhibits chemoselective nitroarenes hydrogenation under green atmospheric conditions. The Pd−Au/TiO₂ catalyst could be reused several times without any loss of activity. Typical results indicated the heterogeneous nature of the catalyst with good reusability.

**EXPERIMENTAL SECTION**

**Instruments Used.** Structural characterization of the catalyst was done on PANalytical, X’pertPRO with Cu Kα-radiation. Raman spectroscopy also corroborated the various phases of TiO₂ and thus the confirmation of various phases of TiO₂ was done by using Raman spectroscopy. Raman spectroscopy is analyzed in the Raman shift ranging from 70 to 900 cm⁻¹ at the excitation line of 532 nm at room temperature. The oxidation state and the elemental composition of the as-prepared catalyst were confirmed by XPS with a

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**Table 5. Chemoselective Synthesis of Anilines 2s−w from Nitroarenes 1s−w**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate (1)</th>
<th>Product (2)</th>
<th>Time (min)</th>
<th>Yield 2 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>O₃N-RCHO</td>
<td>H₂N-RCHO</td>
<td>15</td>
<td>89</td>
</tr>
<tr>
<td>20</td>
<td>NH₃-R</td>
<td>NH₂-R</td>
<td>15</td>
<td>82</td>
</tr>
<tr>
<td>21</td>
<td>O₃N-RCHO</td>
<td>H₂N-RCHO</td>
<td>5</td>
<td>72</td>
</tr>
<tr>
<td>22</td>
<td>NH₃-R</td>
<td>NH₂-R</td>
<td>5</td>
<td>68</td>
</tr>
<tr>
<td>23</td>
<td>NH₃-R</td>
<td>NH₂-R</td>
<td>5</td>
<td>70</td>
</tr>
</tbody>
</table>

aReaction conditions: nitrobenzene (1 mmol), hydrazine monohydrate (0.5 mL), and Pd−Au/TiO₂ (0.1 mol % of Pd−Au).
bIsolated yields of product 2s−w.

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**Figure 5. Recyclability of the Pd−Au/TiO₂ nanocatalyst in nitrobenzene hydrogenation reaction.**
Kratos axis ultra-spectrometer with an Al Kα source at 1498.5 eV, by fixing the emission current and applied a voltage at 10 mA and 15 kV. The weight percentages of metals in the catalysts were confirmed by X-ray fluorescence spectrometry and energy-dispersive X-ray spectroscopy. High-resolution TEM was performed by using a JEOL JEM 2100FX TEM instrument. 1H and 13C NMR spectra were recorded using a Bruker AVANCE instrument 400 & 100 MHz, respectively.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02064.

Details of catalyst synthesis and characterization studies and 1H, 13C NMR spectra of all isolated products (PDF)

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Notes

The authors declare no competing financial interest.

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