Supported Bimetallic AuPd Nanoparticles as Catalyst for the Solvent-Free Selective Hydrogenation of Nitroarenes

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Abstract:

Selective hydrogenation of nitrobenzene was carried out under solvent-free conditions using supported AuPd nanoparticles catalyst, prepared by modified impregnation method (M_{Im}), as efficient catalyst. >99% yield of aniline (AN) was obtained after 15 hours at 90 °C, 3 bar H₂ that can be used without any further purification or separation, therefore reducing cost and energy input. Supported AuPd nanoparticles catalyst, prepared by M_{Im}, was found to be active and stable even after 4 recycle experiments whereas the same catalyst prepared by S_{Im} deactivated during the recycle experiments. The most effective catalyst was tested for the chemoselective hydrogenation of 4-chloronitrobenzene (CNB) to 4-chloroaniline (CAN). The activation energy of CNB to CAN was found to be 25 kJ mol⁻¹, while that of CNB to AN was found to be 31 kJ mol⁻¹. Based on this, the yield of CAN was maximized (92%) by lowering the reaction temperature to 25 °C.

Keywords: bimetallic nanoparticles, solvent free hydrogenation, nitrobenzene and chloronitrobenzene.
Introduction:

Aniline (AN) is an industrially very important intermediate for the production of dyes, agricultural chemicals, pharmaceuticals, polymers, etc.[1-3] About 85% of aniline is produced via the catalytic hydrogenation of nitrobenzene (NB) using gaseous H₂ under either liquid or gas phase conditions as it is environmentally benign and water is the only by-product in this reaction.[4] Moreover nitration of aromatic compounds is a very well established and optimised technology that makes nitroarenes a readily available feedstock for the production of bulk and/or fine chemicals.[5,6] Solvents, such as ethanol,[1,7-12] methanol,[13] 2-propanol,[14] have been used to facilitate heat and mass transfer during liquid-phase reaction conditions. However, after the end of the reaction additional separation steps are always employed to separate the product, resulting in not only high cost and energy input but also higher E-factor of this process.[15] One way to circumvent this problem is to perform the reaction under solvent-free conditions, a green and atom-economical process. Sun and co-workers[4] developed an ultrafine Pt nanoparticles supported on multi-walled carbon nanotube catalyst for the “solvent-free” hydrogenation of nitrobenzene, however the target product AN was used as a solvent for this hydrogenation reaction. Recently Huang and co-workers[16] reported monometallic Pd nanoclusters supported on N-doped ordered mesoporous carbon catalyst for the solvent-free hydrogenation of NB. This monometallic catalyst has been reported to display good activity and selectivity for the reduction of various substituted nitro aromatics to their corresponding amines. However, the synthesis of this catalyst is complicated, which makes it challenging for
potential industrial application.

Recently, several groups including ours have reported supported Pd based bimetallic nanoparticles as very active and selective catalysts compared to their monometallic analogues for the direct synthesis of hydrogen peroxide from hydrogen and oxygen, selective oxidation, selective hydrodeoxygenation and many more transformation.[17-21] Similar to monometallic catalysts, the synthesis strategy plays a crucial role in determining the activity, selectivity and stability of supported bimetallic catalysts. We have developed a number of synthesis strategies to control the particle size, composition, size dependent composition and nanostructure of supported AuPd nanoparticles including wet impregnation, sol immobilization, modified impregnation, chemical vapour deposition etc.[22,23] The objective of this work is to develop very active, selective and stable supported bimetallic AuPd nanoparticulate catalysts for the solvent free hydrogenation of nitrobenzene.

Chloroaniline (CAN), an intermediate for the production of pesticides, drugs and dyes, is produced by the reduction of chloro nitrobenzene, which in turn is produced by the nitration of chlorobenzene. However, the hydrogenation of chloronitrobenzene (CNB) to chloroaniline is a challenging task as the weak carbon-halogen bond is highly susceptible for cleavage, resulting in the formation of AN thus lowering the selectivity of CAN.[24,25] Fine tuning of Pd-[26,27] Pt-[25,28] and Ni-based[29] catalysts through nanostructure modification, selective poisoning and other strategies have been reported. However, for a given catalyst, optimization of reaction condition to increase the selectivity of CAN has not been reported yet.
Based on these two themes, the aim of the present work is to develop an efficient and robust catalyst for the solvent-free hydrogenation of nitrobenzene and to investigate this system in detail through kinetic studies and activation energy calculation. The best catalyst will be utilized for the chemoselective hydrogenation of CNB to CAN and optimize the reaction condition to increase the selectivity of CAN.

2. Experimental

2.1 Catalyst preparation

The catalysts were prepared by modified impregnation, conventional impregnation and sol-immobilization methods, as reported by our group previously elsewhere.[30,31] The total metal loading used here was 1 wt.%. For bimetallic AuPd catalyst, the weight percentages of Au and Pd were both 0.5 wt%.

*Modified Impregnation (MIm):* Gold precursor solution was prepared by dissolving HAuCl₄·3H₂O (Sigma Aldrich) in deionized water and palladium precursor solution was prepared by dissolving PdCl₂ (Sigma Aldrich) in a 0.58 M aqueous HCl solution. The desired amounts of gold solution and/or palladium solution were placed into a 50 mL round-bottom flask. The total volume of the solution was filled up to 16 mL with deionized water. The flask then was put in an oil bath sitting on a hotplate with a magnetic stirrer. The solution was stirred at 1,000 rpm vigorously and heated from room temperature to 60 °C for 10 min. Then the support [1.98 g, TiO₂ (Degussa Evonik P25), carbon (Cabot Vulcan XC72R) or MgO (BDH)] was slowly added to the solution over a period of 10 min. The slurry was stirred for another 15 min, followed
by heating from 60 to 95 °C and being held for an additional 16 h with continuous stirring to evaporate the water. The solid powder was subsequently transferred to a mortar and grounded thoroughly for three times to form a uniform mixture. The sample was stored and denoted as “dried only” catalyst. Before reaction, a portion of the dried only sample (400 mg) was reduced using 5% H₂/Ar at 400 °C for 4 h in a furnace. The sample was finally denoted as Mᵢₘ catalyst.

*Conventional Impregnation (Cᵢₘ):* In this preparation procedure, PdCl₂ was dissolved in deionized water instead of aqueous HCl solution. Other procedures were the same as for the modified impregnation method.

*Sol Immobilization (Sᵢₘ):* Requisite amounts of gold solution, palladium solution and freshly prepared Polyvinylalcohol (PVA) [1 wt % aqueous solution, Sigma Aldrich, MW = 10000, 80% hydrolyzed, PVA/(Au+Pd) (w/w)=1:3] were dissolved in deionized water (400 mL) in a large beaker with vigorous stirring. A freshly prepared NaBH₄ solution (0.1 M, NaBH₄/(Au+Pd) (mol/mol)=5) was then quickly added to form a dark-brown sol. After continuous stirring for 30 min, the support material (TiO₂) was added into the beaker. Then 1 drop of concentrated H₂SO₄ was also added under vigorous stirring. After 2 h the slurry was filtered and the catalyst was washed with deionized water (2 L) and dried in an oven at 120 °C overnight.

Scanning Transmission Electron Microscopic characterization of 1%AuPd/TiO₂ catalyst prepared by Cᵢₘ, Sᵢₘ and Mᵢₘ was carried out using a JEOL JEM-2200FS aberration-corrected electron microscope at Lehigh University.
2.2 Catalytic testing

Solvent-free hydrogenation of nitrobenzene: nitrobenzene (78 mmol, ≥99.0%, Sigma Aldrich) and catalyst (0.1 g) were placed in a Colaver® glass reactor. The molar ratio of substrate/metal was 10,778. Before starting the reaction, the reactor was purged with N₂ first, followed by pressurizing with H₂ for five times. The reactor was then charged with 3 bar H₂ under isobaric condition and heated to 90 °C in an oil bath with a magnetic stirrer bar to start the reaction. After a selected reaction time, the reactor was cooled down to <5 °C using an ice bath, followed by depressurisation. The reaction mixture was then taken out, centrifuged to remove the solid catalyst and filtered before being injected into a gas-chromatographer (Varian 450-GC) equipped with a flame ionization detector (FID), a methaniser and a CP-SiL5CB column (50 m, 0.33 mm) in which He was used as the carrier gas. A calibration plot was utilized for the quantification of substrate and products.

Reusability test: Two batches of catalysts were used for the reusability test of the catalysts: batch A0: standard amount of catalyst (0.1 g); batch B0: an excess amount of catalyst (1.0 g). The reaction condition and operation procedure were identical with the solvent-free hydrogenation reaction. After 6 h reaction, the reaction mixture in batch A0 was analyzed by GC. The result was regarded as the activity for the fresh catalyst. The catalyst in batch B0 was taken out, stirred and washed with acetone for six times, followed by drying in the oven for 30 min at 110 °C. Then the standard amount of catalyst in batch B0 (0.1 g) was taken as batch A1, the rest was denoted as batch B1. Both batches were put for reaction. The result of batch A1 was regarded as
the activity for the first reuse. The catalyst in batch B1 was regenerated. The procedure was repeated until the 4\textsuperscript{th} reuse of the catalyst.

Kinetic study: For kinetic studies, ethanol (16 mL, ≥99.8\%, Sigma Aldrich) was used as the solvent for the hydrogenation reaction. Nitrobenzene (10 mmol) and catalyst (12.5 mg) were used for this test. Reaction temperature was selected as 40, 50 and 60 °C. The conversion was kept below 20\% to study the initial rate of the reaction. Other reaction conditions and operation procedures were the same with the solvent-free reaction.

Chemoselective hydrogenation of 4-chloronitrobenzene: ethanol (16 mL) was used as the solvent for this hydrogenation reaction. 4-chloronitrobenzene (10 mmol, 99\%, Sigma Aldrich) and catalyst (12.5 mg) were used. Reaction temperature was selected as 20, 40, 50 and 60 °C. Other reaction conditions and operation procedures were the same with the solvent-free reaction hydrogenation of nitrobenzene.

3. Results and discussion

The solvent-free hydrogenation of nitrobenzene was performed using 1\%AuPd/TiO\textsubscript{2} (M\textsubscript{Im}) catalyst at different temperatures (30, 60 and 90 °C) (Table 1). Poor NB conversion and high AN selectivity was observed at 30 °C after 2 h reaction. Increasing the reaction temperature, obviously, increased the NB conversion while maintaining high AN selectivity. At 90 °C, the NB conversion was 24\% and AN selectivity was 98\% after 2 h. Hence, 90 °C was selected as the standard reaction temperature for further NB hydrogenation studies reported in this article.
Table 1  Effect of reaction temperature for the solvent-free hydrogenation of nitrobenzene over 1%AuPd/TiO$_2$ (M$_{Im}$) catalyst$^a$

| Catalysts              | Reaction temperature / °C | NB conversion / % | AN selectivity / % |
|------------------------|---------------------------|-------------------|---------------------|
| 1%AuPd/TiO$_2$ (M$_{Im}$) | 30                        | 1                 | >99                 |
|                        | 60                        | 11                | 97                  |
|                        | 90                        | 24                | 98                  |

$^a$ reaction conditions: nitrobenzene: 78 mmol, catalyst: 100 mg, H$_2$ pressure : 3bar , time:2h.

In an effort to find the best metal, support and synthesis method combination we prepared different catalysts and tested them for the solvent-free hydrogenation of NB at 90 °C. We prepared monometallic 1%Au/TiO$_2$ (M$_{Im}$) and 1%Pd/TiO$_2$ (M$_{Im}$) catalysts and their catalytic activities were compared with the bimetallic 1%AuPd/TiO$_2$ (M$_{Im}$) catalyst (Table 2). As expected bimetallic 1%AuPd/TiO$_2$ (M$_{Im}$) catalyst was found to be more active (54%) compared to the monometallic catalysts (3% and 41% for Au and Pd respectively) under identical reaction conditions. In previous reports published by our group, similar phenomenon was observed also for other reactions like selective oxidation,[21,32] direct synthesis of H$_2$O$_2$[33] and hydrogenation of levulinic acid to $\gamma$-valerolactone.[19]

Then we checked the effect of support. AuPd supported on carbon showed only 14% conversion of nitrobenzene and 76% selectivity towards aniline. When MgO was used
as support, NB conversion was 36% with 94% selectivity of aniline. Nevertheless, in both cases the catalytic performances, including NB conversion and AN selectivity, were less than that of AuPd supported on TiO$_2$. Thus, TiO$_2$ was selected as the best support.

Synthesis strategy of supported metal nanoparticles play crucial role in determining the structural parameters such as particle size, composition and nanostructure and hence their catalytic properties like activity, selectivity and stability.[30] As shown in entries 6 and 7 in Table 2, the AuPd/TiO$_2$ catalysts prepared by S$_{Im}$ and C$_{Im}$ showed similar NB conversions (39 and 38% respectively) and AN selectivities, while both were less than those of the M$_{Im}$ catalyst (54%). From the data presented in Table 2, it is clear that 1%AuPd/TiO$_2$ (M$_{Im}$) is the best catalyst for the solvent-free hydrogenation of NB to AN.

*Table 2* Effect of different metals, supports and synthetic strategies for the solvent-free hydrogenation of NB$^a$

| Entry | Catalysts | Conversion / % | Selectivity / % | 
|-------|-----------|----------------|-----------------| 
|       |           |                | Aniline | Azobenzene | Azoxybenzene | 
| 1     | AuPd/TiO$_2$(M$_{Im}$) | 54 | 98    | 0.5 | 0.9 | 
| 2     | Au/TiO$_2$ (M$_{Im}$) | 3  | 98    | 0   | 0   | 
| 3     | Pd/TiO$_2$ (M$_{Im}$) | 41 | 97    | 0.2 | 0   | 
| 4     | AuPd/MgO (M$_{Im}$) | 36 | 94    | 0   | 0.5 |
Time on line evolution of products was studied using 1% AuPd/TiO$_2$ (M$_{im}$) catalyst at 90 °C, and the result was shown in Figure 1a. After 15 h reaction, the entire NB was converted and the GC yield of aniline was ca. 99% (GC did not show any other peak).

To further confirm the formation and purity of aniline, we compared the $^1$H-NMR spectra of crude reaction mixture after 15 h of the reaction, without any purification, with that of commercial aniline (≥99.5% purity from Sigma Aldrich) as shown in Figure 1b. From this $^1$H NMR spectra comparison it is clear that the crude reaction product is as pure as commercial AN standard, hence the crude reaction mixture can be used for further application without any modification or purification.
Figure 1  

Figure 1 a: Time-on-line plot for the solvent-free hydrogenation of nitrobenzene over 1%AuPd/TiO$_2$ (M$_{Im}$) catalyst. Reaction conditions: nitrobenzene: 78 mmol, catalyst: 100 mg, temperature: 90 °C, $H_2$ pressure: 3 bar. b: comparison of the $^1$H-NMR spectra of the crude reaction mixture after 15 h without any purification and commercial aniline standard from Sigma Aldrich (>99.5% Purity).

One of the crucial requirements of a heterogeneous catalyst to be used for industrial applications is its stability and reusability. Keeping that in mind, we studied the reusability of 1%AuPd/TiO$_2$(M$_{Im}$) and 1%AuPd/TiO$_2$(S$_{Im}$) catalysts (Figure 2). For the 1%AuPd/TiO$_2$(S$_{Im}$) catalyst, the yield of aniline decreased from 38% to 17% after 4 cycles. However, for the 1%AuPd/TiO$_2$(M$_{Im}$) catalyst, the aniline yield changed only slightly from 53% to 51%, indicating that M$_{Im}$ catalyst is more stable and reusable than S$_{Im}$ catalyst. A similar observation was previously reported by our group for the solvent-free selective oxidation of benzyl alcohol to benzaldehyde.[34] During that study, we observed that the PVA, used in the synthesis of 1%AuPd/TiO$_2$(S$_{Im}$),
blocked the active sites of the catalyst. We believe a similar phenomenon might be present hindering the reusability of 1% AuPd/TiO$_2$(S$_{im}$) catalyst. On the contrary, 1% AuPd/TiO$_2$(M$_{im}$) does not contain any stabilising ligands, hence this catalyst is more stable and reusable.

![Comparison of stabilities and reusability of 1% AuPd/TiO$_2$(M$_{im}$) and 1% AuPd/TiO$_2$(S$_{im}$) catalysts for the solvent free hydrogenation of NB to AN. Reaction conditions: nitrobenzene: 78 mmol, catalyst: 100 mg, temperature: 90 °C, H$_2$ pressure: 3 bar, time: 6 h.](image)

**Figure 2** Comparison of stabilities and reusability of 1% AuPd/TiO$_2$(M$_{im}$) and 1% AuPd/TiO$_2$(S$_{im}$) catalysts for the solvent free hydrogenation of NB to AN. Reaction conditions: nitrobenzene: 78 mmol, catalyst: 100 mg, temperature: 90 °C, H$_2$ pressure: 3 bar, time: 6 h.

For the kinetic studies, ethanol was used as a solvent to determine the concentrations of substrate and product accurately. For all experiments, the conversion of nitrobenzene was kept below 20% so that the time dependency of nitrobenzene concentration was linear and to eliminate the role of products in the rate of the reaction. To ensure that the data was obtained under kinetically controlled region, we performed the reactions at different agitation speed and selected an appropriate
parameter (result not presented) to eliminate the effect of mass transfer. The initial rate of the reaction was calculated at 40, 50 and 60 °C and the results are presented in Figure S1. The apparent activation energy ($E_a$) was calculated to be 37 kJ mol$^{-1}$ from the dependence of $\ln(k)$ on $1/T$ with $R^2 > 0.99$ (Figure S1). This value is similar to the values reported recently (37 kJ mol$^{-1}$ over Pt/$\gamma$-Al$_2$O$_3$ by Peureux et al.[35] 28±5, 33±5 and 45±5 kJ mol$^{-1}$ over Ru/FeO$_x$ by Easterday et al.[14] 35±1 kJ mol$^{-1}$ over Pd/C by Turáková et al.[36]) for this reaction. This activation energy value also gives evidence that the reaction was carried out under kinetic regime, otherwise the value should be in the range of 5-15 kJ mol$^{-1}$ if the diffusion played an important role.[36]

**Chemoselective hydrogenation of 4-chloronitrobenzene**

The most active and stable catalyst (1%AuPd/TiO$_2$(M$_{Im}$)) was tested for the chemoselective hydrogenation of chloronitrobenzene (CNB) to chloroaniline (CAN) because CAN is industrially very important for the synthesis of dyes, agricultural chemicals, pharmaceuticals and polymers.[37] This reaction is also challenging because under hydrogenation conditions, typically hydrodechlorination occurs, leading to the formation of AN, hence lower CAN yield. The 1%AuPd/TiO$_2$ catalysts prepared by different synthesis strategies (M$_{Im}$, S$_{Im}$ and C$_{Im}$) were initially tested for the hydrogenation of CNB.
Table 3 Selective hydrogenation of 4-chloronitrobenzene over AuPd/TiO$_2$ catalyst$^a$

| Entry | Catalysts            | Reaction time / h | Conversion / % | Selectivity / % |
|-------|----------------------|-------------------|---------------|-----------------|
|       |                      |                   | CAN | AN | CAN | AN |
| 1     | AuPd/TiO$_2$ (C$_{Im}$) | 1                | 96  | 83  | 17  |
| 2     | AuPd/TiO$_2$ (S$_{Im}$) | 1                | 100 | 70  | 30  |
| 3     | AuPd/TiO$_2$ (M$_{Im}$) | 1.5              | 100 | 85  | 15  |
| 4     | AuPd/TiO$_2$ (M$_{Im}$)$^b$ | 8                | 100 | 92  | 8   |

$^a$ reaction conditions: 4-chloronitrobenzene: 10 mmol, ethanol: 16 mL, catalyst: 12.5 mg, temperature: 60°C, H$_2$ pressure: 3 bar.

$^b$ reaction temperature 25°C.

As shown in Table 3 entries 1-3, the 1%AuPd/TiO$_2$(M$_{Im}$) catalyst gave the best yield (85%) of CAN among all the catalysts tested. Using this catalyst, we then optimized the reaction conditions to increase the CAN yield. As shown in Figure 3, we performed the reactions at different temperatures at the initial stages (CNB conversion < 20%) and calculated the formation rates of 4-chloroaniline and aniline. Using these data, we calculated the apparent activation energies for CNB to CAN and CNB to AN reactions independently using the Arrhenius plot (Figure S2). The activation energy of CNB to CAN is 25 kJ mol$^{-1}$, lower than that of CNB to AN (31 kJ mol$^{-1}$). This result suggests that lower reaction temperature would be beneficial for enhancing the selectivity of CAN. Based on this data, we performed the hydrogenation of CNB at a much lower temperature (25 °C) and after 8 h of reaction time, a CAN yield of 92%
was achieved (Table 3, entry 4). This is one of the highest yields of CAN reported in the literature.

![Graph showing the rate of formation of 4-chloroaniline (CAN) and aniline (AN) during the hydrogenation of 4-chloronitrobenzene (CNB) over 1%AuPd/TiO₂ (M₅₉) catalyst at different temperatures. Reaction conditions: 4-chloronitrobenzene: 10 mmol, ethanol: 16 mL, catalyst: 12.5 mg, H₂ pressure: 3 bar.]

**Figure 3:** Rate of formation of 4-chloroaniline (CAN) and aniline (AN) during the hydrogenation of 4-chloronitrobenzene (CNB) over 1%AuPd/TiO₂ (M₅₉) catalyst at different temperatures. Reaction conditions: 4-chloronitrobenzene: 10 mmol, ethanol: 16 mL, catalyst: 12.5 mg, H₂ pressure: 3 bar.

Figure 4 shows representative high angle annular dark field (HAADF) images of 1% AuPd/TiO₂ catalysts prepared by (a, b) S₅₉, (c, d) C₅₉ and (e, f) M₅₉, respectively. From the lower magnification images in Figure 4 (a), (c) and (e), the C₅₉ gives particles with 10-20 nm in size, while both the S₅₉ and M₅₉ produce particles largely within 2-5 nm range. From the higher magnification HAADF images of individual particles, it can be seen that 10-20 nm particles produced by C₅₉ show clear signs of a
Pd-rich shell structure (Figure 4 (d)). While the particles produced by S_{Im} (Figure 4 (b)) and M_{Im} (Figure 4 (f)) appear to be random alloys without a distinctive core-shell morphology. Some 1 nm or sub-nm clusters can also be occasionally found in the catalyst prepared by the C_{Im} method (inlet of Figure 4(d)). Those are Pd-rich clusters that are probably strongly bonded to the oxide support and therefore did not merge to form bigger particles.

**Figure 4.** Representative HAADF-STEM images of 1% AuPd/TiO\textsubscript{2} catalyst prepared by (a, b) sol-immobilization; (c, d) conventional impregnation; (e, f) modified impregnation.

This microscopy results suggest that the combination of smaller particles, absence of stabilizer ligands (PVA) and random alloy morphology could be the reason behind the
observed higher catalytic activity and stability of 1% AuPd/TiO$_2$(M$_{Im}$) catalyst for the solvent free hydrogenation of NB to AN and the chemoselective hydrogenation of CNB to CAN.

4. Conclusions

In summary, we have successfully developed a 1% AuPd/TiO$_2$ (M$_{Im}$) catalyst for the solvent-free hydrogenation of nitrobenzene to aniline and chemoselective hydrogenation of 4-chloronitrobenzene to 4-aniline. Some important conclusions that we report in this article are

(1) Through systematic catalyst screening, 1% AuPd/TiO$_2$ catalyst prepared by modified impregnation method is the most active and stable catalyst for the solvent-free hydrogenation of nitrobenzene to aniline. After 15 hours reaction, 99% yield of aniline was obtained at 90 °C. The activation energy of nitrobenzene reduction to aniline was calculated to be 37 kJ mol$^{-1}$.

(2) 1% AuPd/TiO$_2$ (M$_{Im}$) catalyst also showed a good selectivity for the chemoselective hydrogenation of 4-chloronitrobenzene to 4-chloroaniline. Using kinetic studies, we found that the activation energy of CNB transformation to CAN was calculated to be 25 kJ mol$^{-1}$, lower than that of CNB to AN (31 kJ mol$^{-1}$). Thus by decreasing the reaction temperature from 60 °C to 25 °C, a 92% yield of CAN was achieved.
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