

Gold nanoparticles supported on titania for the reduction of *p*-nitrophenol

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Received 8 November 2012; revised and accepted 17 January 2013

Supported gold nanoparticles on titania have been prepared using the deposition-precipitation method at several *pH* levels. The effects of *pH* on gold loading, particle size and particle size distribution are studied, both below and above the isoelectric point of TiO₂. The effects of adjusting the *pH* before and after the addition of the support to gold chloride solution are also investigated. Gold particles with diameters of less than 10 nm have been obtained. The results reveal dependence of the gold particle size, and loading and distribution on the *pH*. The supported Au nanoparticles have been tested for the reduction of *p*-nitrophenol and found to exhibit particle size-dependent behavior. The highest rate constant of $16.9 \times 10^{-3} \text{ s}^{-1}$ has been obtained for the Au particles size between 4 and 5 nm.

Keywords: Catalysts, Deposition-precipitation, Reduction, Nanoparticles, Gold nanoparticles, Titania, Electron microscopy

Gold (Au) used to be considered an inert and chemically uninteresting metal that was not catalytically useful^{1,2}. This changed in the 1980s when small gold particles supported on metal oxides were successfully prepared and proved to be active in the oxidation of carbon monoxide at low temperatures³. This breakthrough significantly changed the role of gold in catalysis. Catalysis using supported gold nanoparticles often involves Au particles between 3 and 5 nm in size to optimally catalyze selected chemical reactions⁴. In addition to Au particle size, the support materials can also influence catalytic behavior toward a corresponding reaction. The supported materials can be carbon, polymers or metal oxides^{5,6}, which can be prepared by sol-gel^{7,8}, hydrothermal and conventional heating⁹, anodization¹⁰ and deposition-precipitation^{11,12} methods. Supported Au nanoparticles have been found effective in carbon monoxide (CO) oxidation¹³⁻²¹, epoxidation of propylene²², water gas-shift reaction^{23,24}, hydrogenation of unsaturated hydrocarbons^{25,26} and reduction of the nitro group²⁷. The Au supported on titania (TiO₂) catalyst system is well studied, and exhibits excellent catalytic activity in many oxidation reactions^{28,29}.

The *p*-nitrophenol (*p*-NP), also known as 4-nitrophenol (4-NP), is among the most common organic pollutants found in industrial and agricultural wastewaters. The

release of *p*-nitrophenol into the environment causes harmful effects to biological systems. Many methods have been developed to overcome this problem, including photocatalytic degradation³⁰, adsorption³¹, microbial degradation³² and catalytic reduction^{6,33-37}. Herein, we present the reduction of a nitro group, *p*-nitrophenol, over an Au/TiO₂ catalyst using hydrazine hydrate as the reducing agent. For the Au/TiO₂ catalyst system, there is relatively little literature concerning this catalyst in reduction reactions³⁸⁻⁴¹. Therefore, this study attempts to highlight the catalytic reduction of *p*-nitrophenol over Au/TiO₂ catalysts prepared by deposition-precipitation (DP) method at several *pH* levels.

The catalytic reduction of *p*-nitrophenol has been reported on three types of Au catalyst systems, including Au-poly(methyl methacrylate), PMMA⁶, an Au@SiO₂ yolk/shell structure³³ and magnetically recoverable Au⁴², which exhibited promising activities with rate constant (*k*) values of $7.2 - 7.9 \times 10^{-3} \text{ s}^{-1}$, $1.4 \times 10^{-2} - 3.9 \times 10^{-3} \text{ s}^{-1}$ and $1.25 \times 10^{-2} \text{ s}^{-1}$, respectively. These Au catalysts also showed good reusability and required only mild reaction conditions⁴². These factors make gold catalysts preferable to many other metal catalysts, such as Ni supported on metal oxides (alumina⁴³ and titania⁴⁴), which need reaction temperatures above 100 °C and the application of pressure⁴⁵.

Materials and Methods

Gold(III) chloride trihydrate (HAuCl₄·3H₂O), gold atomic absorption standard solutions and titanium (IV) oxide (anatase) were all obtained from Sigma-Aldrich (Switzerland). Sodium hydroxide (NaOH), silver nitrate (AgNO₃), hydrochloric acid (HCl) and nitric acid (HNO₃) were obtained from R&M Chemicals, UK. Sodium borate (Na₂B₄O₇·10H₂O), hydrazine hydrate (N₂H₄·H₂O) and *p*-nitrophenol were obtained from BDH Chemicals (England), Scharlau (Spain) and Merck (Germany), respectively. All reagents were of analytical grade and were used without further purification.

Preparation of gold nanoparticles supported on TiO₂

Gold nanoparticles supported on TiO₂ (Au/TiO₂) were prepared by the deposition-precipitation method (DP) with two adjustments of pH (DP2) i.e., before and after the addition of support to gold precursor⁴⁶. HAuCl₄·3H₂O was used as the gold precursor. In a typical preparation, 100 mL of HAuCl₄ solution (4.2×10^{-3} M) was heated to 80 °C, and the pH was adjusted to the desired value by dropwise addition of 0.5 M NaOH. Approximately 1.00 g of the titania support was dispersed into the solution. Insertion of the support resulted in change in pH and pH was kept constant by the dropwise addition of 0.5 M NaOH. The suspension was maintained at 80 °C and stirred vigorously for 2 hours. The precipitate was then washed several times with distilled water to remove residual sodium and chloride ions and unreacted Au species. The washing was considered complete when no AgCl precipitate was detected with AgNO₃ solution. The precipitate was gathered by centrifugation and dried at 100 °C overnight. The calcination procedure was carried out at 450 °C in air for 4 hours. The preparation of gold nanoparticles supported on TiO₂ at pH values 5 and 7 (which are below and above the isoelectric point (IEP) of titania⁴⁷ (IEP of anatase = 6) was repeated using the same procedure. The effects of pH adjustments were investigated in two ways: (1) one-time adjustment at pH 7, i.e., only after the addition of TiO₂ to the HAuCl₄ solution, denoted as DP1, and (2) without pH adjustment, denoted as DP0.

The Au/TiO₂ obtained were analyzed by diffuse reflectance UV-visible spectroscopy (DR UV-vis), powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). TEM images were obtained for the samples dried on carbon-coated copper grids. The

size distribution of the Au nanoparticles was determined from at least about 200 particles. The elemental composition of Au was analyzed using a Perkin Elmer AAnalyst 200 atomic absorption spectrometer at a wavelength of 243 nm (ref. 48). The Au loading of the samples⁴⁶ is expressed in grams of Au per gram of sample: %wt Au = $[m_{\text{Au}}/(m_{\text{Au}} + m_{\text{TiO}_2})] \times 100$. The specific surface area of the sample was measured by nitrogen adsorption on a Perkin Elmer ASAP 2000 instrument.

Catalytic reduction of *p*-nitrophenol

A solution of *p*-nitrophenol (1.5 mL, 0.1 mM) was added to a suspension of 1 mg of supported Au nanoparticles and 1.5 mL of hydrazine solution (0.3 mM) in a 3 mL cuvette at room temperature. The catalytic activity was determined using a UV-vis spectrophotometer (Perkin Elmer Lambda 25 UV-vis) by measuring the change in absorbance at 400 nm for 600 seconds. All solutions were freshly prepared in 0.005 M sodium borate (pH 8-10).

Results and Discussion

Effect of the preparation of Au/TiO₂ at pH below and above the IEP of TiO₂

The TiO₂-supported gold nanoparticles were synthesized at pH 5 (DP2 C5 Au/TiO₂) and pH 7 (DP2 C7 Au/TiO₂), which represent the pHs below and above the IEP of titania, respectively (IEP of titania is at pH 6)⁴⁷. After drying in an oven for several hours, the Au/TiO₂ prepared at both pH 5 and 7 had a gray-purple color. After calcination, the color changed to purple and deep purple for DP2 C7 and DP2 C5 Au/TiO₂, respectively. Purple is the characteristic color of metallic Au particles⁴⁹. The existence of metallic Au (Au⁰) particles was confirmed by DR UV-vis spectra, which showed the surface plasmon resonance (SPR) band at around 530 nm for all the samples (Fig. 1). The intensity of the SPR band in the DP2 C5 sample was higher compared with that of the DP2 C7 sample, suggesting that a higher Au content was achieved in DP2 C5 Au/TiO₂.

For Au/TiO₂, the focus region of the Au diffraction peaks is in the 2θ range of 40° to 80°. There are three dominant Au peaks at 44°, 64° and 77°, corresponding to the gold crystal lattices of (2 0 0), (2 2 0) and (3 1 1), respectively. These peaks are important as they represent the important crystal lattices of gold in a face centered cubic (fcc) crystal system (ICDD: 03-065-8601) and do not overlap with the TiO₂ peaks.

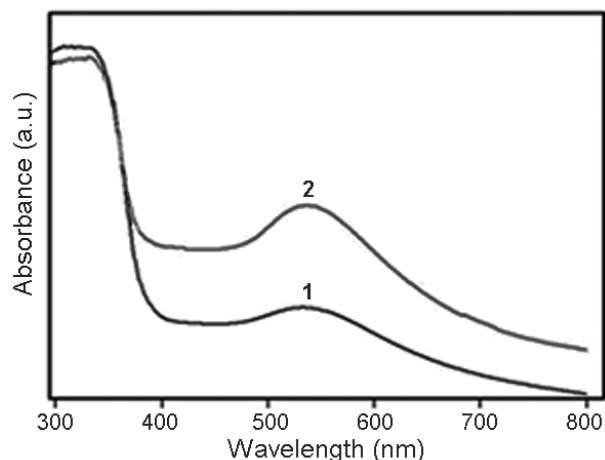


Fig. 1—DR UV-vis spectra of Au/TiO₂ prepared (1) below the IEP of titania (DP2 C5) (1), and, (2) above the IEP of titania (DP2 C7).

The XRD for DP2 C5 exhibited all three peaks for Au (Fig. 2a). However, only two gold peaks, (at 44° and 64°) were observed for the DP2 C7 Au/TiO₂ (Fig. 2b). The disappearance of a peak at $2\theta = 77^\circ$ for Au/TiO₂ at pH 7 indicates the smaller size of the Au particles as compared to that in the Au/TiO₂ prepared at pH 5. These findings are in agreement with the work of Moreau and Bond²⁸, who reported the decrease and finally the disappearance of the peak at $2\theta = 77^\circ$ due to the decrease in Au particle size with the increase of pH. They also reported that fine Au particles with a 2 nm size at pH 9 were obtained, while the size increased to 10 nm as the pH was reduced to 6.

Gold in the TEM images (Fig. 3) is represented by the small dark particles, while the TiO₂ is visible as the larger particles with less intense color. The TEM images clearly show the Au particles deposited on the supports. The obvious difference in gold particle size prepared at different pH levels can be seen from the TEM micrographs. The average of the Au particle size for DP2 C5 and DP2 C7 Au/TiO₂ are 6.95 ± 2.17 nm and 4.76 ± 1.50 nm, respectively. As the mean particle size decreases, the standard deviation also decreases and leads to a narrower Au particle size distribution. The Au particle size distributions are shown in Fig. 3.

The SEM images of the Au/TiO₂ samples show titania as grey cloud-like features, while the gold particles are visible as shiny white dot particles (Fig. 4). For DP2 C5, the image of agglomerated Au particles is observed at a high magnification of 50 K, as shown in Fig. 4a, while a better distribution of Au particles on TiO₂ is observed for DP2 C7 at the same

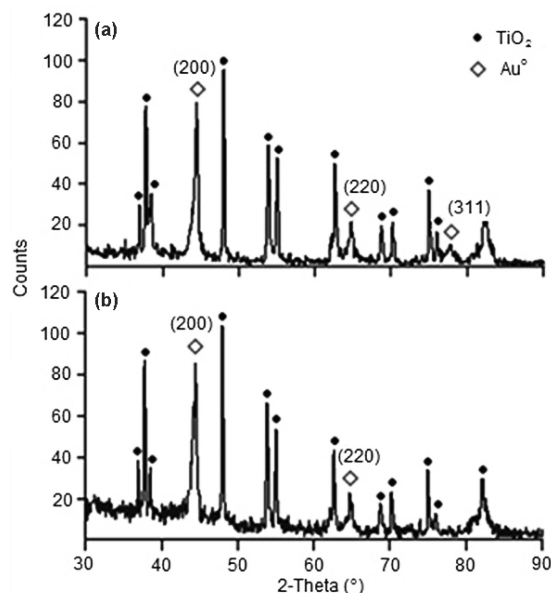


Fig. 2—XRD diffractograms of Au/TiO₂ prepared at pH (a) below the IEP of titania (DP2 C5), and, (b) above the IEP of titania (DP2 C7).

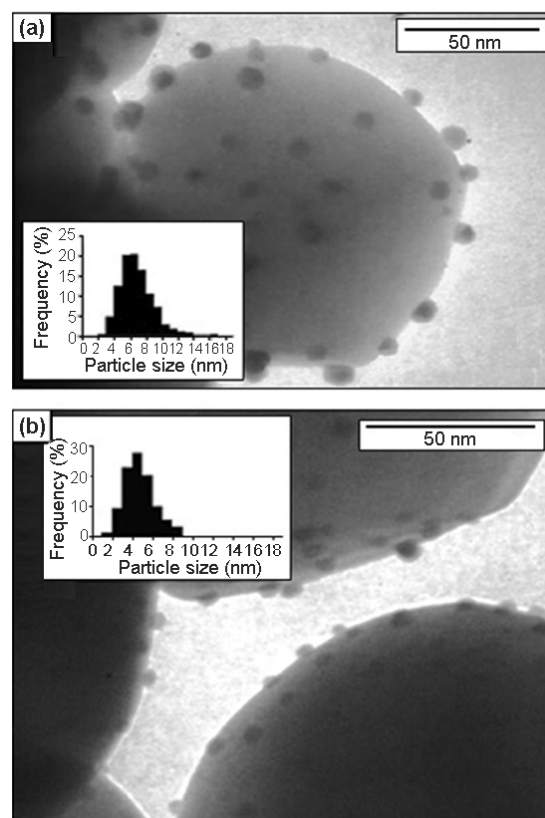


Fig. 3—TEM micrographs of Au/TiO₂ prepared at pH (a) below the IEP of titania (DP2 C5), and, (b) above the IEP of titania (DP2 C7). [Scale bar: 50 nm. The inserted images are the Au particle size distributions].

magnification (Fig. 4b). The elemental analysis by EDX confirms the presence of gold and titania. A small percentage of carbon was detected and is believed to originate from the carbon tape used to place the sample. A maximum amount of Au, obtained for Au/TiO₂ at pH 5, also exhibited a higher surface area compared to DP2 C7. The overall characteristics of the samples are tabulated in Table 1.

The above findings indicate that preparation of supported Au particles at pH lower than the IEP caused the formation of larger Au particles. This result can be explained by the direct dependence of the hydrolysis of the AuCl₄⁻ precursor in the solution on pH (refs 1, 50, 51). Fully hydrolyzed Au(OH)₄⁻ ions dominate at pH levels greater than 8, while below pH 8,

gold precursors that contain chloride ions, including AuCl₄⁻, AuCl₃(OH)⁻, AuCl₃(H₂O), AuCl₂(OH)₂⁻ and AuCl(OH)₃⁻ are present. The retention of the chloride ions in the solution causes aggregation of the particles into larger clusters during drying and forms larger Au particles after calcination. Removal of Cl⁻ after calcination is confirmed by TGA-IR analysis, which shows the disappearance of peak at 700 cm⁻¹.

The fact that pH above the IEP of titania leads to minimal gold loadings can be explained based on the surface properties of the support⁵⁰. Generally, the surface of the metal oxide is covered with surface hydroxyl species in solution (i.e., Ti-OH) because of its amphoteric character. At the IEP, both positive and negative charges are balanced. At a higher pH, the dominating surface species are negatively charged (i.e., Ti-O⁻), while at pH less than the IEP, positively charged species dominate (i.e., Ti-OH₂⁺) as a result of the protonation of the surface hydroxyl group. Thus, below the IEP, electrostatic adsorption of the anionic gold chloride precursors occurs as a direct anion exchange that leads to higher gold loadings. On the other hand, above the IEP the surface is negatively charged due to the removal of protons from the surface. Therefore, the interaction between the gold chloride precursors and the support involves only physical adsorption that direct to the minimal Au loadings.

Effect of the pH adjustment

The preparation of gold particles via the DP method generally requires two adjustments of the pH, with one adjustment before and one after the addition of the support, referred to as DP2. For comparison, gold particles were prepared using a single pH adjustment after insertion of the support (DP1) and without any pH adjustment (DP0). The pH of the solution was monitored at three intervals, specifically. The initial pH before the introduction of the support is labeled as pH_i and that after the insertion of the support as pH_f. The final pH after all of the adjustments is referred as pH_f. Table 2 tabulates the corresponding pH of the gold solution during the preparation method. Preparation of supported Au nanoparticles without any pH adjustment means that this preparation is at a pH close to the initial pH of

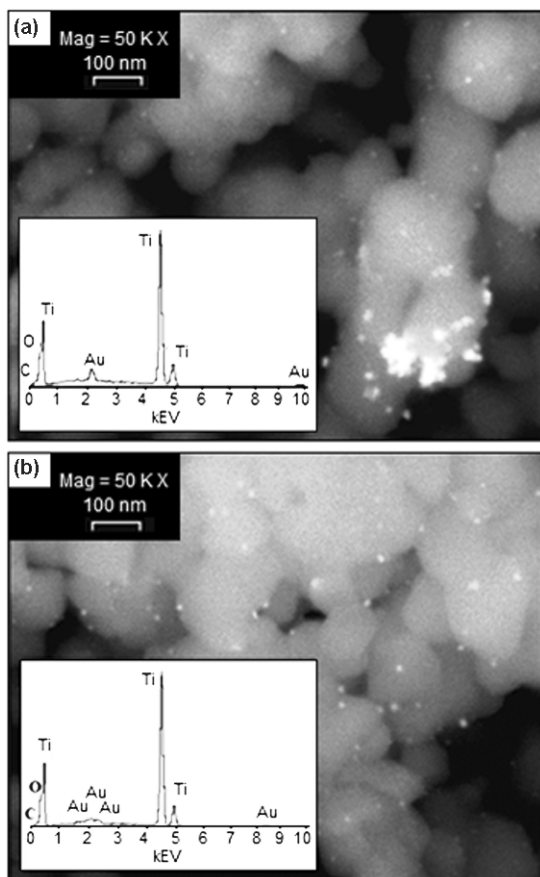


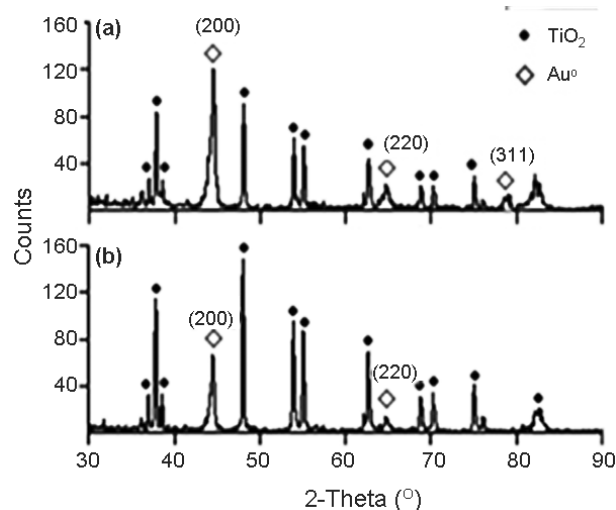
Fig. 4—SEM images of Au/TiO₂ prepared at pH (a) below the IEP of titania (DP2 C5), and, (b) above the IEP of titania (DP2 C7). [Scale bar: 100 nm. The inserted images are the spectra of the EDX analysis].

Table 1 — The physical properties of Au, loadings and surface area for Au/TiO₂ prepared at pH 5 and 7

Samples	pH	Particle size (nm)	Au particle distributions (nm)	Au loadings (% wt)	Surface area (m ² g ⁻¹)
DP2 C5 Au/TiO ₂	5.12	6.95 ± 2.17	2 – 16	4.026	9.17
DP2 C7 Au/TiO ₂	7.15	4.76 ± 1.50	1 – 8	2.341	8.68

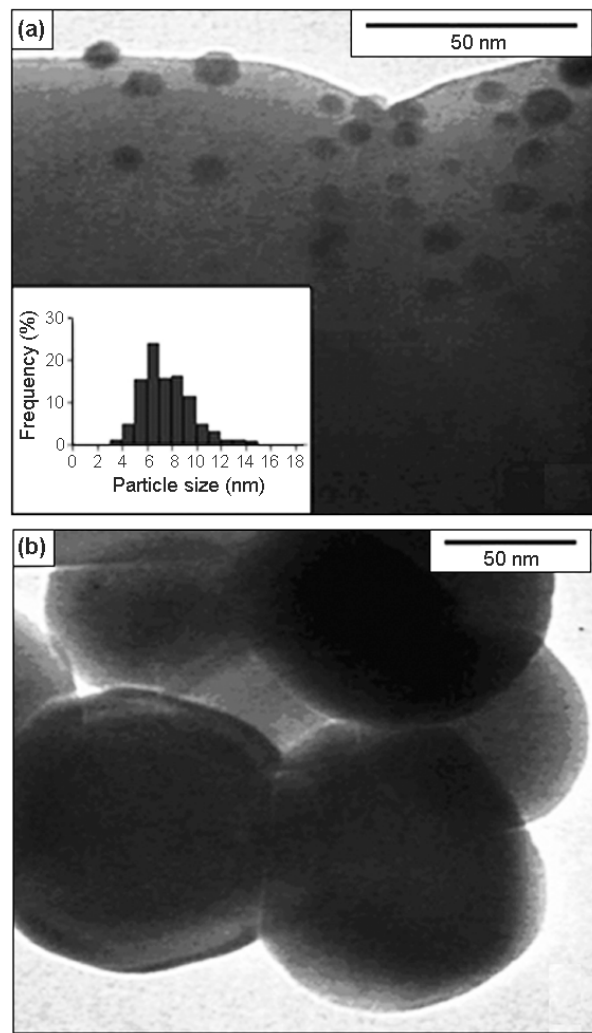
Table 2 — The pH of gold solution observed during the preparation method

Samples	pH of HAuCl ₄	First adjustment ^a	Initial pH (pH _i)	pH after addition of support (pH _i)	Second adjustment ^b	Final pH (pH _f)
DP2 Au/TiO ₂	1.75	✓	7.35	7.20	✓	7.15
DP1 Au/TiO ₂	1.75	-	1.75	1.68	✓	7.27
DP0 Au/TiO ₂	1.75	-	1.75	1.68	-	1.68

^aadjustment of pH of gold chloride solution before addition of support.^badjustment of pH of gold chloride solution after addition of support.Fig. 5—XRD diffractograms of Au/TiO₂ for (a) one-time pH adjustment (DP1 C7), and, (b) without pH adjustment (DP0).

gold chloride precursors (pH 1.75). However, the insertion of TiO₂ leads to a slight change in the pH due to the acidic property of the support. Therefore, for Au/TiO₂ obtained from both the DP1 and the DP0, a decreased of pH_i to 1.68 is observed. Without pH adjustment for Au/TiO₂ (DP0), the final pH is maintained at 1.68.

Figure 5 displays the XRD diffractograms for DP1 and DP0 Au/TiO₂. The Au peak at $2\theta = 77^\circ$ is not observed when no adjustment of the pH was made (DP0). The TEM micrographs for Au/TiO₂ prepared at pH 7 with a single pH adjustment (DP1) show a clear attachment of Au onto the TiO₂ surface with larger Au particles size (Fig. 6a) and wider distribution as compared to the Au/TiO₂ from DP2. The DP1 Au/TiO₂ has an average Au particle size of 7.62 nm with a particle size distribution of 3 – 14 nm. The standard deviation of the mean Au particle size also increases to ± 2.00 nm. These results indicate that a single pH adjustment does not adequately control the Au particle size and distribution. The TEM image for the DP0 sample did not show any Au particles (Fig. 6b), most probably due to the minimal loadings.

Fig. 6—TEM micrographs of Au/TiO₂ for (a) one-time pH adjustment (DP1 C7) with the inserted image of particles size distribution, and, (b) without pH adjustment (DP0). [Scale bar: 50 nm].

The AAS analysis detected the content of Au in the sample at only 0.081 wt%. We found that after the insertion of the support, pH adjustment is critical as pH_i determines the Au particle size. Herein, small gold particles < 6 nm were obtained when the pH_i was above 7 (Table 3).

Table 3 — The physical properties of Au, loadings and surface area for Au/TiO₂ prepared by the DP1 and DP0 methods

Samples	Au particle size (nm)	Au particle distributions (nm)	Au loadings (% wt)	Surface area (m ² g ⁻¹)
DP1 C7 Au/TiO ₂	7.62 ± 2.00	3 – 14	1.424	8.41
DP0 Au/TiO ₂	N/A	N/A	0.081	8.12

Tables 1 and 2 also show that the *pH* after the insertion of the support (*pH_i*) is critical as it determines the Au particle size. The preparation method in which the *pH_i* was above 7 resulted in smaller Au particle sizes (DP2 C7). It should be noted that above *pH* 7, the surface hydroxyl group of titania is dominated by negatively charged species⁵¹. The gold precursor species in the solution are [AuCl(OH)₃]⁻ and [Au(OH)₄]⁻, and hence electrostatic adsorption is unlikely to occur. However, between *pH* 6 and 10, Au(OH)₃ was formed from the solution and deposited on the support according to Chang *et al.*⁵² and Haruta *et al.*¹. In fact, the deposition of Au(OH)₃ on the support was related to the synthesis of smaller Au particle sizes as compared to the deposition by partially hydrolyzed Au precursors. Therefore, above *pH_i* 7, Au particles smaller than 5 nm in size were obtained.

Significant differences are observed in terms of Au loadings and distribution for the Au/TiO₂ prepared via the DP2 (wt%: 2.341) and DP1 (wt%: 1.424) adjustment at *pH* 7. The nature of the gold precursor species at the time the support is introduced is essential as the deposition step occurs at this stage⁵³. The DP1 C7 has a *pH_i* around 1.68, when the gold precursor species is [AuCl₄]⁻. The adjustment of *pH* to 7 after the addition of support to the gold solution for this sample changes the nature of the adsorbed species as follows²⁸: [AuCl₄]⁻ → AuCl₃(H₂O) → [AuCl₃(OH)]⁻ → [AuCl₂(OH)₂]⁻ → [AuCl(OH)₃]⁻. The evolution of these species opens up the possibility for re-adsorption when the *pH* is increased⁴⁸. It is suggested that the adsorption process causes an increase in the Au particle size and also the standard deviation for DP1 C7 Au/TiO₂.

It is important to note that with more Au precursors attached to the support, an enhancement of Au loadings is achieved. In addition, attachment of the Au precursor species starts after the addition of the support, which is at *pH_i*. For the DP1 method, the addition of the support changes the *pH_i* to 1.68, which is not favorable for the attachment of Au precursor ([AuCl₄]⁻). However, the occurrence of other Au precursor species as the *pH* is raised to 7 allow for the re-adsorption to occur^{28,48}. Therefore, reasonable Au

loadings are still obtained, although it is lower than Au/TiO₂ prepared at *pH* 7 by the DP2 method. According to the results tabulated in Table 3, for all of the Au/TiO₂ samples, *pH_i* plays a crucial effect in influencing the Au loadings.

The synthesis of Au/TiO₂ without *pH* adjustment results in the deposition of gold on TiO₂ when [AuCl₄]⁻ remains in the dominant form^{15,26}. The [AuCl₄]⁻ complex cannot be exchanged, but it is weakly adsorbed onto the surface of the support. This leads to the loss of gold particles during the washing and therefore as expected minimal Au loadings, (0.081 wt%) was found.

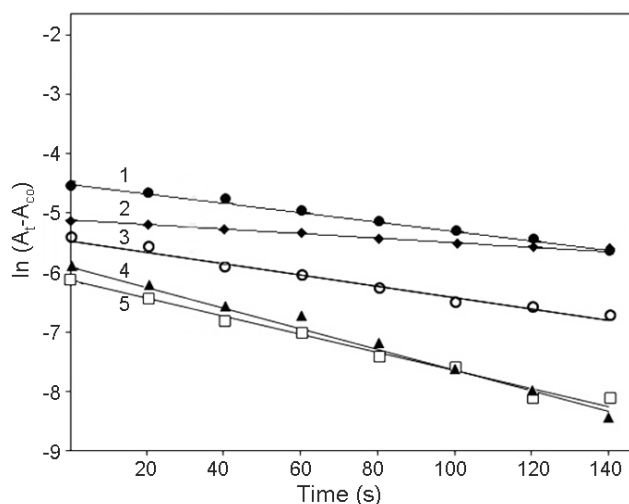
Catalytic reduction of *p*-nitrophenol

The catalytic activity of the prepared supported Au nanoparticles was tested in the reduction of *p*-nitrophenol (*p*-NP) with hydrazine (N₂H₄H₂O). The ratio of [*p*-NP] to [N₂H₄H₂O] is 1:30. Since an excess amount of hydrazine was used in this reaction, its concentration remains constant during the reaction. Therefore the overall reaction is monitored under pseudo-first order conditions³⁴. *p*-Nitrophenol and hydrazine were prepared in a 0.005 *M* sodium tetraborate solution (~ *pH* 8 buffer) to provide a basic and stable condition for the catalytic reaction. The basic condition was chosen because hydrazine reacts optimally at this environment⁵⁴.

While λ_{max} for 4-nitrophenol is observed at 317 nm⁴², the preparation of *p*-NP in sodium borate solution resulted in the shift of the absorbance peak to 400 nm due to the formation of *p*-nitrophenolate ions under alkaline conditions^{35,42}. Without the gold catalyst, the intensity of this peak remains unchanged during the reaction, which further indicates that the reduction of *p*-NP does not take place. The results of the rate constants (*k*) for all Au/TiO₂ catalysts were evaluated in terms of a pseudo-first order kinetic model and are tabulated in Table 4. The plot of ln *A_t* versus time yielded a linear correlation, as shown in Fig. 7. A control reaction with TiO₂ alone was also carried out. As expected TiO₂ catalyzed the reaction with a *k* value of 3.0 × 10⁻³ s⁻¹. This result is expected since titania is a photocatalyst that can degrade *p*-NP³⁰. However, with the Au/TiO₂ catalysts an enhancement of the *k* value by as much as 5.6 times was achieved.

Table 4 — The k values for TiO_2 and Au/TiO_2 series

Catalysts	k (s^{-1})
TiO_2	3.0×10^{-3}
DP2 C7 Au/TiO_2	16.9×10^{-3}
DP2 C5 Au/TiO_2	15.7×10^{-3}
DP1 C7 Au/TiO_2	9.8×10^{-3}
DP0 Au/TiO_2	9.0×10^{-3}

Fig. 7—Plots of $\ln(A_t/A_0)$ versus time for the reduction of p -NP with Au/TiO_2 catalysts. [1-DP1 C7, 2- TiO_2 , 3-DP0, 4-DP2 C5 and 5-DP2 C7].

The reduction reaction of p -nitrophenol by hydrazine in the presence of an Au/TiO_2 catalyst is a fast reaction and the observed absorbance remained constant after approximately 150 seconds for most of the catalysts. The best k value was obtained for Au/TiO_2 with two $p\text{H}$ adjustments, DP2 C7, which had a k value of $16.9 \times 10^{-3} \text{ s}^{-1}$. A trend of increasing k value with the decreasing Au particle size was also observed, which proves that this reaction is size-dependant. Conclusively, the reduction reaction with Au/TiO_2 catalysts highlights the importance of two $p\text{H}$ adjustments followed by Au particle size and loadings.

Recharacterization of the catalysts after the reaction showed minimal Au leaching into the reaction mixture, as confirmed by TEM and AAS analyses (Supplementary Data, Fig. S1). The supported Au nanoparticles can also be reused without a significant change in the catalytic activity, after even 3 cycles (Supplementary Data, Fig. S1). The first reuse of the Au/TiO_2 at $p\text{H}$ 7 has the k value of $16.5 \times 10^{-3} \text{ s}^{-1}$, followed by $15.7 \times 10^{-3} \text{ s}^{-1}$ and $16.6 \times 10^{-3} \text{ s}^{-1}$ for the second and third uses, respectively. Overall the small decrease in the k value

after reuse is possibly due to the loss of a small amount catalyst during centrifugation and washing. Since the activity of the catalyst is dependent on the amount of the gold catalyst this contributes to the observed small loss in activity. The k values achieved herein were higher as compared with other reported Au nanoparticles deposited on polymer^{6,55} or other template materials^{33,56}. These findings also prove that Au nanoparticles supported on metal oxides are efficient catalysts for these types of reactions.

Conclusions

Titania supported Au nanoparticles were prepared via deposition-precipitation method using various $p\text{H}$ adjustment approaches. The supported Au nanoparticles were found to be an effective catalyst for the reduction of p -NP with a noticeable effect of Au particle size and $p\text{H}$ adjustment on the catalytic activity. The highest k value obtained was $16.9 \times 10^{-3} \text{ s}^{-1}$, and the Au catalyst could be reused without causing significant changes in the rate constant even after 3 cycles. Moreover, the leaching of Au nanoparticles into the reaction solution occurred only minimally and further proved that the Au catalyst prepared was stable. The supported gold catalysts show potential as catalyst for such reactions.

Supplementary Data

Supplementary data associated with this article, viz., Fig. S1, is available in the electronic form at [http://www.nisclair.res.in/jinfo/ijca/IJCA_52A\(02\)184-191_SupplData.pdf](http://www.nisclair.res.in/jinfo/ijca/IJCA_52A(02)184-191_SupplData.pdf).

Acknowledgement

Financial support from Universiti Sains Malaysia (USM), Malaysia, under FRGS grant 203/PKIMIA/6711147 and PRGS grant 1001 /PKIMIA/831002 as well as The World Academy of Science (TWAS) are gratefully acknowledged.

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