Effect of Noble Metal Nanoparticles on Photocatalytic Activity of TiO$_2$

A. M. Orlov, D. A. Jefferson, R. M. Lambert

Department of Chemistry, Cambridge University, Lensfield Road, Cambridge, CB2 1EW, UK

Fax: 44-1223-336-362, e-mail: ao220@cam.ac.uk

Modification of TiO$_2$ with noble metals has shown significant promise in increasing the activity of titania for a variety of catalytic processes. Even so, relatively few studies have been carried out on Au-modified TiO2 where metal particle sizes < 5 nm give rise to unique physico-chemical properties. In particular, the effect of Au nanoparticle size on TiO$_2$-induced photodegradation of organics in solution is largely unknown. Here we report the effects of washing and of gold particle size on the photocatalytic degradation of 4-chlorophenol. Characterization by TEM and EDS confirmed that the catalysts possessed a narrow gold particle size distribution with average particle size varying from 3.6 to 5.5 nm, depending on Au loading. It is found that addition of gold always significantly increased the photocatalytic activity, the optimum Au loading being 0.42 at. %.

Key words: photocatalytic, gold, 4-chlorophenol, TiO$_2$, HRTEM

1. INTRODUCTION

Titanium dioxide, commonly regarded as one of the most active and stable photocatalysts for environmental applications, has been studied extensively [1]. Efforts to improve the intrinsic efficiency of TiO$_2$ have included doping by transition metals, sensitisation, application of composite semiconductors, and addition of noble metals [2]. The latter strategy shows promise and most efforts have focused on Pt/TiO$_2$ systems, although Au/TiO$_2$, and Ag/TiO$_2$ systems have also been investigated [3-6]. However, these studies have involved relatively large metal particles (~ 10 nm or more) and have tended not to address the effects of metal particle size. Moreover, they were primarily concerned with the use of colloidal titania rather than P25 titania – which is one of the most active commercial materials available in large quantities at low cost.

Following the pioneering work of Haruta and his co-workers [7] it is now well known that ultra-dispersed Au particles ($\leq$ 3.6 nm) can display unusual catalytic properties for a range of reactions. However, the effect of Au nanoparticles of size < 5 nm on the photocatalytic activity of titania are largely unknown. Here we report on the photocatalytic decomposition by Au/TiO$_2$ of 4-chlorophenol in aqueous solution. 4-chlorophenol is one of the most well studied organic molecules in photocatalytic area, with significant number of papers published on the subject. However, improving activity of the catalyst still poses a significant challenge. We show that small Au particles can induce a significant improvement in performance even at small gold loadings.

2. EXPERIMENTAL METHODS

TiO$_2$ modified by gold particles was prepared by the deposition precipitation method established by Haruta et al. [17] P25-TiO$_2$ was obtained from Degussa Corporation (70% anatase and 30% rutile) and used without further treatment. After adjusting the pH of an aqueous solution of HAuCl$_4$ to the desired value with Na$_2$CO$_3$, the titania support was added and the mixture stirred for 3 hours. Preparations were carried out at pH 7

(intended to produce below 5 nm gold particles [7]). The solid product was washed with distilled water until the traces of chloride were undetectable by titration with silver nitrate. It was then calcined in air for 5 hours at 300 °C, ground and sieved to give catalyst grains below 45 mm. Unmodified TiO$_2$ was also subjected to similar heat and size separation procedures to serve as a benchmark of the activity. We also prepared sintered catalyst with significantly different gold particle size distribution.

The photocatalytic system was based on a 1000 W Xe lamp (ORIEL), the radiant flux from which was collimated, filtered once to remove infra red radiation, then again to eliminate radiation below 300 nm. Experiments in which a long-wavelength pass filter was used to eliminate UV radiation < 400 nm confirmed that no photocatalytic activity was induced by visible portion of the spectrum. Control experiments confirmed that (i) volatilisation of 4-chlorophenol from aqueous solution and (ii) photolytic reactions in the absence of the catalyst were negligible. An on-line intensity monitor was used to compensate for intensity variation due to aging of the lamp.

Reactions were carried out in a well-mixed heterogeneous batch reactor, which incorporated ports for sampling, oxygen injection, and a thermocouple. The system temperature was stabilized at 20°C by a water recirculation bath connected to the outer jacket of the reactor. Oxygen was delivered to the reactor at constant rate of 18 ml/min by means of a mass flow controller

In a typical experiment, the reactor was loaded with 100 ml of 200 mg/l of 4-chlorophenol solution and 100 mg of catalyst. The system was stirred in the dark for approximately 1.5 hours to establish sorption/desorption equilibria before switching the lamp on. After starting the photocatalytic reaction, 0.4 ml aliquots were periodically withdrawn from the reactor over the course of the reaction, filtered through an acetate membrane, and transferred to vials for analysis of the amount of 4-chlorophenol remaining. 5 ml samples were analysed by liquid chromatography-mass spectrometry (HP-1050). The composition of mobile phase was 95%

H_2O with 0.1% of trifluoroacetic Acid (TFA), and 5% acetonitrile with 0.1 % of TFA; the flow rate was 0.6 ml/min. Analysis was carried at two wavelengths (282 and 254 nm) with a column temperature of 22° C. 4-chlorocatechol was identified by HPLC as one of the reaction products by comparing with a retention time of standards.

Specimens for electron microscopy were prepared by suspending them in acetone and transferring to a copper grid coated with an amorphous carbon support. HRTEM images were recorded on a JEOL JEM-3011 electron microscope operated at 300 keV. The JEM-3011 was fitted with a PGT energy-dispersive X-ray (EDX) solid-state detector incorporating Excalibur software. Particle size was determined by counting at least 50 particles.

Infra-red spectroscopy experiments were performed with a Perkin-Elmer GX2000 spectrometer equipped with an MCT detector and a high temperature DRIFTS cell (Thermo Spectra-Tech). Spectra were acquired at a resolution of 4 cm^{-1} typically averaging 32 scans. Catalyst samples were conditioned at 250° C in flowing helium prior to data acquisition in order to remove weakly adsorbed water (the broad O-H stretch peak associated with this masked other spectral features in this region.

Surface area measurements were carried out with Micromeretics Gemini 2360 surface area analyser. Samples were degassed for at least 12 hours prior to the measurements. BET surface area measurements on the catalyst samples and on pure untreated P25 titania showed that the deposition precipitation technique had no measurable effect on the total surface area, which was ~ 48 m^2/g in every case.

3. RESULTS

3.1 Catalyst characterization

TEM analysis of the samples showed that the titania support was decorated with gold nanoparticles, primarily cubo-octahedral, although a significant number of hemispherical particles were also observed. Figure 1.
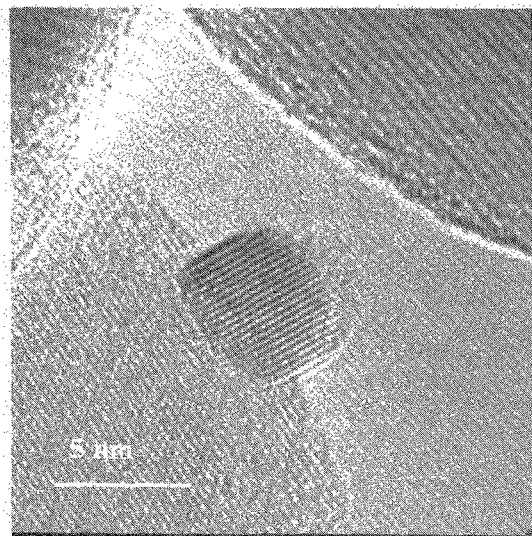

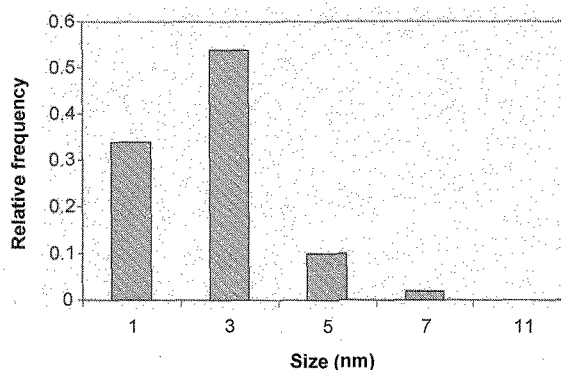Fig. 1 TEM image of 5.58 Au at. % sample

Fig. 2 TEM image of 0.55 Au at. % sample and particle size distribution

shows a representative image obtained with 5.58 at. % Au. EDX analyses indicated no detectable impurities Figure 2 shows an HRTEM image and the corresponding gold particle size distribution obtained with a 0.55 at. % Au sample. The average gold particle size for this sample was 3.6 nm—with increasing gold loading the average gold particle size increased to 5.1 nm. For all the samples, the Au particle size distributions were quite narrow, except at the highest loading (5.58 Au at. %) where significant agglomeration of gold nanoparticles was observed. DRIFTS data show that increased gold loading resulted in attenuation of the 3651 cm^{-1} band intensity, indicating progressive elimination of hydroxyl groups from the titania surface. This conclusion is strongly supported by the accompanying decrease in intensity of the 3413 cm^{-1} band, which is due to hydrogen bonded water in interaction with surface hydroxyl groups [8]. Surface area measurements demonstrated that the specific surface areas of pure P-25 titania and those of the Au-loaded catalysts derived from this material were similar. Additionally, no significant changes in adsorption properties of the catalysts were observed.

3.2 Catalytic activity

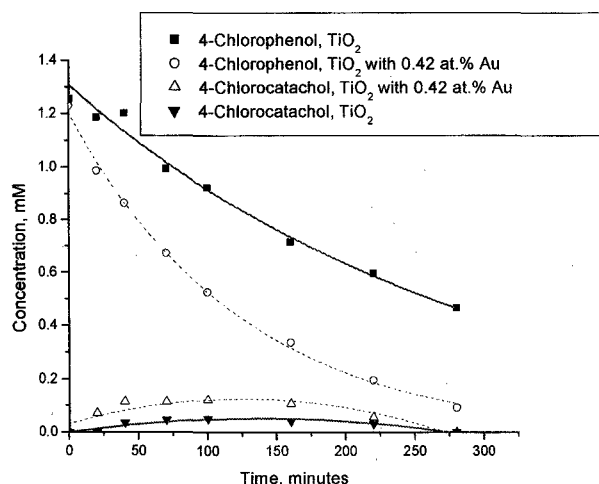A significant increase in catalytic activity relative to unmodified titania was observed for all

Fig. 3 Disappearance of 4-chlorophenol and appearance of 4-chlorocatechol on unmodified TiO_2 (closed symbols) and 0.42 Au at. % modified TiO_2 (open symbols).

gold modified samples. Equally, there was a significant enhancement in 4-chlorocatechol production (one of the reaction intermediates). Figure 3 shows corresponding trends of 4-chlorophenol disappearance and 4-chlorocatechol production for a 0.42 at. % Au sample and an unmodified TiO_2 sample. In total, eight samples with different gold loadings were prepared for testing. A maximum in catalytic activity was observed at 0.42 Au at. %, with pseudo first order reaction rate exceeding that of bare titania by a factor of two (Figure 4). Even small loadings of gold had a significant effect on the photocatalytic reaction. At the highest gold loadings the activity fell, approaching that of unmodified titania. Recall that the observed changes in the pseudo first-order rate constants are not merely due to variations in intrinsic surface area between the different samples as confirmed by surface area measurements.

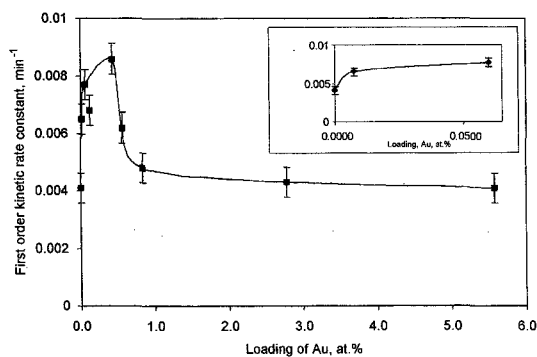Significant variations of activities of Au containing

Fig. 4 Dependence of rate of photocatalytic degradation of 4-chlorophenol on gold loading.

samples prepared by different research groups has often been attributed to impurities resulting from incomplete elimination of gold precursors. Given that chloride impurity can adversely affect the catalytic activity of

Au/TiO_2 catalysts for certain reactions[7], one sample that was *not* subjected to the extensive washing/chloride elimination procedure was used for comparison. A small statistically insignificant increase in activity of the unwashed sample was observed, indicating that chloride does not substantially impact the present experimental results.

3.3 Effects of gold particle size on catalytic activity.

The activities of two catalysts—freshly prepared 0.42 Au at. % and a sintered catalyst with the same gold loading—were remarkably different. The average gold particle size of the fresh catalyst was around 3.6 nm, whereas the sintered one had an average particle size of about 15 nm. This sintering caused the activity of the catalyst to decrease by a factor of three.

4. DISCUSSION

Based on Figure 4 one can suggest that Au particle density is likely to be one of the important parameters determining the catalytic performance. The general explanation of the positive effect of gold on photocatalytic performance is based on role of Au acting as a sink for photo-generated electrons. A Schottky junction between metal and oxide phases reduces the e-/h+ recombination rate increasing the lifetime of charge carriers [2]. Photoluminescence data [9] indicate that this mechanism indeed plays a significant role in catalytic rate enhancement. However, one needs to be cautious in extending this explanation to small Au particles. Au particles size 3 nm and below are no longer metallic but semiconducting [10]. The difference in activities between fresh and sintered catalysts further indicates that particle size effect is not unimportant. In this case one may invoke an alternative mechanism [2] based on semiconductor-semiconductor contact in which photo-excited electrons are injected from Au into the TiO_2 conduction band creating separated electrons and holes which then undergo charge transfer reactions with adsorbates.

Increase in gold loading above 0.42 at. % resulted in an activity decrease. Two possible factors are: (1) increased Au loading reduces the titania surface area available for 4-chlorophenol adsorption and (2) increased Au loading decreases the concentration of surface hydroxyl groups. These groups are efficient hole traps, and their elimination should decrease the photo-catalytic rate. The first possibility seems unlikely on simple geometrical grounds. However, DRIFTS spectra show a substantial decrease (by ~ 40 %) in the intensity of the OH band at 3650 cm⁻¹ when the Au loading increases from 0.12% to 5.58%, suggesting that this is likely to be an important effect.

The conclusions above are based on the assumptions that neither 4-chlorophenol adsorption nor light absorption properties of the materials were changed due to gold deposition. Based on the experiments conducted with different light sources it is feasible to conclude that the reaction was occurring under light saturated conditions, where the variation of adsorptive properties of the catalyst might play a pronounced role. However, surface area and 4-chlorophenol adsorption measurements demonstrate that adsorption characteristics of the catalysts were not substantially

altered due to gold deposition. Additionally, TEM images confirmed that a significant area of TiO_2 is not covered by Au nanoclusters, even at the highest gold loadings employed in this study. Therefore, it is likely that catalytic properties, rather than adsorptive properties are of the outmost significance to explain the phenomena described above. Additional experiments, such as diffuse reflectance Uv-vis spectroscopic measurements are currently being conducted to gather supplementary information on optical characteristics of the catalysts.

5. CONCLUSIONS

At very low metal loadings, gold nano-particles significantly enhance the catalytic activity of P-25 titania towards the photo-degradation of 4-chlorophenol. With increasing Au loading, the activity falls again towards a value characteristic of unmodified titania. TEM and DRIFTS results indicate that progressive elimination of hole-trapping OH groups on the TiO_2 surface, and titania surface blocking with gold particles are the main causes of catalyst deactivation.

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