

DEVELOPMENT OF NEW CATALYSTS FOR THE ENHANCED REMOVAL OF CHLOROPHENOL FROM WATER

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Photocatalysis is a useful method for the removal of organic contaminants from water, in which the contaminants are in general mineralised, i.e. converted to inorganic materials. The efficiency of the catalyst is most important, and the improvement of activity of conventional catalysts for photocatalytic degradation of organic contaminants remains a significant challenge. Modification of titanium dioxide, the most commonly used photocatalyst, with metal nanoparticles offers a very effective way of enhancing its activity. This paper presents the results of modification of titanium dioxide with gold nanoparticles. A range of catalysts with different amount of gold loading was prepared. It was found that the photocatalytic activity towards decomposition of chlorophenol increased substantially in comparison with unmodified catalyst. Even at very low loadings of gold, which only fractionally increases the cost of the catalyst, the improvement of the photocatalytic performance for degradation of organic contaminants was significant. The paper also presents the results of catalyst characterization by surface area measurements, transmission electron microscopy, and energy dispersive x-ray spectroscopy.

Introduction

Chlorinated phenolic compounds constitute an important class of pollutants, because of their widespread use in industry, and their toxicity and persistence in the environments. Photocatalysis offers an attractive way to completely decompose organic substances to the harmless inorganic materials. 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 TiO₂ 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/TiO₂ systems, although Au/TiO₂, and Ag/TiO₂ systems have also been investigated (3). However, these studies have involved relatively large metal particles (~ 10nm or more) and have tended not addressed 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 (5) it is now well known that ultra-dispersed Au particles (≤ 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/TiO₂ of 4-chlorophenol in aqueous solution. We show that small Au particles can induce a significant improvement in performance even at small gold loadings.

Methods

1.1 Catalyst preparation

TiO₂ modified by gold particles was prepared by the deposition precipitation method established by Haruta et al. (5) P25-TiO₂ was obtained from Degussa Corporation (70% anatase and 30% rutile) and used without further treatment. After adjusting the pH of an aqueous solution of HAuCl₄ to the desired value with Na₂CO₃, the titania support was added and the mixture stirred for 3 hours. Most preparations were carried out at pH 7 (intended to produce below 5 nm gold particles (5)); some were also performed at pH less than 7 in order to vary the Au particle size. 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 nm. Unmodified TiO₂ was also subjected to similar heat and size separation procedures to serve as a benchmark of the activity.

1.2. Photocatalytic experiments

The photocatalytic system was based on a 1000 Wt 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 that 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% H₂O 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 (284 and 254 nm) with a column temperature of 22°C.

1.3. HRTEM, DRIFTS, and BET surface area measurement

Specimens for electron microscopy were prepared by suspending them in acetone and transferring to a copper grid coated with an amorphous carbon support. Transmission Electron Microscopy (TEM) 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 removed adsorbed water. Surface area measurements were carried out with Micromeritics 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 $\sim 48 \text{ m}^2/\text{g}$ in every case.

Results

2.1 Catalysts characterization

Catalysts with a range of gold loadings were prepared at pH 7, and four of these with loadings of 0.55, 0.83, 2.78, and 5.58 at.% Au were characterized by TEM/EDX, yielding information about chemical composition and metal particle size distributions. Figure 1 shows a representative image obtained with a 5.58 atomic % Au catalyst. EDX analyses indicated no detectable impurities. Figure 2 shows HRTEM image obtained with 0.55 atomic % Au sample, which was examined in detail to obtain metal particle size distribution, which is also shown in the figure. The DRIFTS data (Figure 3) 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 hydrogen bonded water in interaction with surface hydroxyl groups. The mean Au particle size varied from 3.6 (lowest Au loading) to 5.1 nm (highest loading).

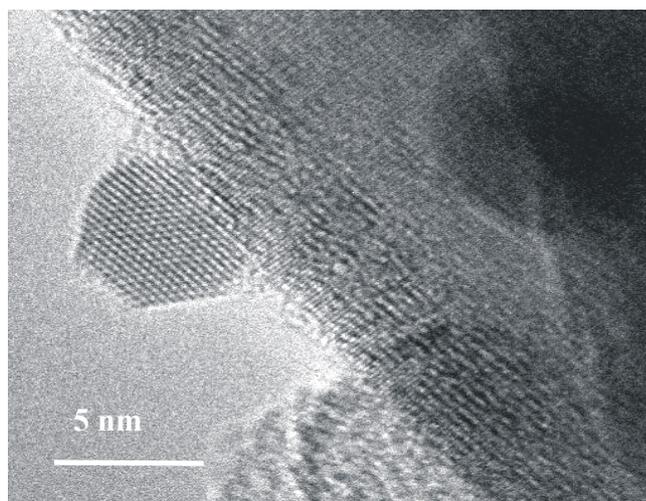


Figure 1. (a) TEM spectra of 5.58 Au at. % sample.

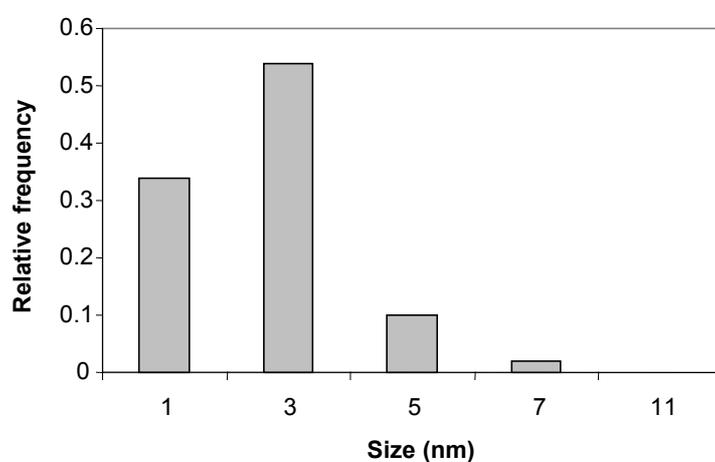
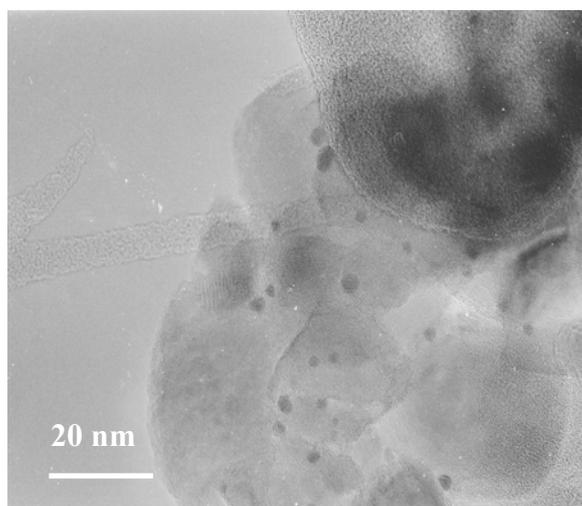


Figure 2. TEM image of 0.55 Au at. % sample and particle size distribution.

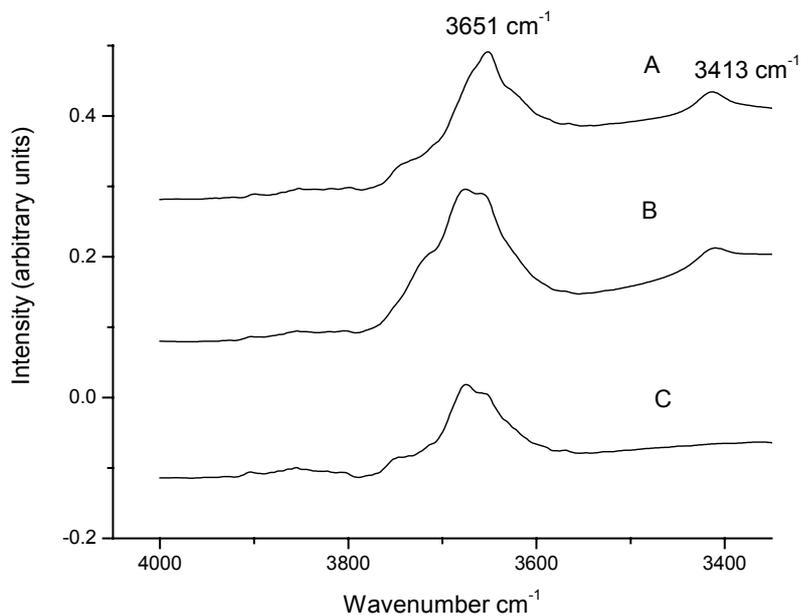


Figure 3. DRIFTS spectra of (a) TiO_2 . (b) 0.42 Au at. % sample. (c) 5.58 at. % sample.

2.2 Catalysts testing

Eight samples, synthesised at pH 7, but with different gold loadings, were prepared for testing: 0.0074, 0.06, 0.12, 0.42, 0.55, 0.83, 2.77, and 5.58 at.% Au. A significant increase in catalytic activity relative to unmodified titania was observed for all samples, as illustrated in Figure 4. Enhancement of 4-chlorophenol degradation was detectable, even at extremely low gold loading. A maximum in catalytic activity was observed at 0.42 Au at.%, the pseudo first order reaction rate exceeding that of bare titania by a factor of two.

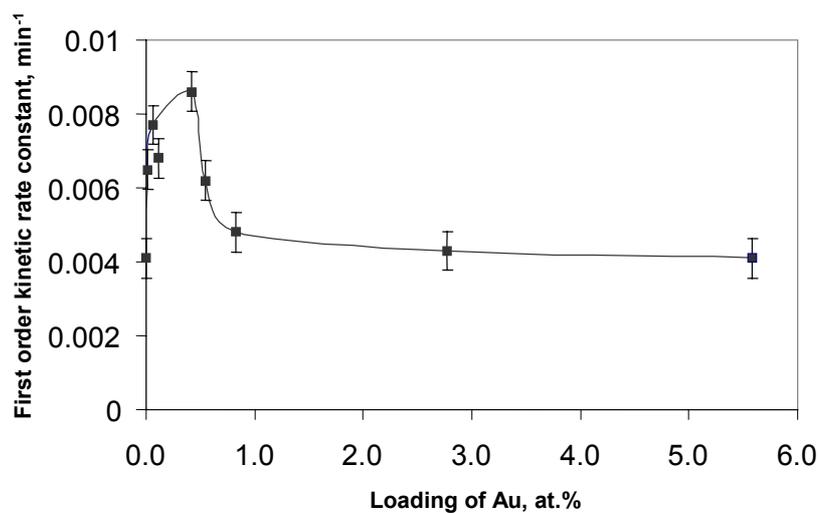


Figure 4. Dependence of rate of photocatalytic degradation of 4-chlorophenol on gold loading.

Note that this corresponds to a very significant enhancement of performance and is of the same order or better than results reported by others for degradation of organics on Pt-loaded P25 titania (2). At the highest gold loadings the activity fell, approaching that of unmodified titania.

Discussion

The reactor and TEM results obtained with catalysts indicate that Au particle size is likely to be an important factor in determining performance. A significant enhancement of the reaction rate (about 2 times) can be explained by formation of a Schottky junction between titania and gold so that the metal and oxide phases are in electronic communication (2). A gold particle could act as a sink for photo-generated electrons, thus reducing the e⁻/h⁺ recombination rate and enhancing the photocatalytic rate. Further increase in gold loading resulted in an activity decrease. Several factors may contribute to this trend. First, increasing the amount of Au reduces the titania surface area available for 4-chlorophenol adsorption. Second, increasing the gold loading also reduces the amount of illuminated titania surface, although this factor is not independent of the first. A third contributing factor is suggested by the DRIFTS spectra which 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%. Hydroxyl groups are efficient hole traps, and since holes are thought to initiate the oxidative processes that lead to degradation of adsorbed organic species (1), their elimination should decrease the photo-catalytic rate.

Conclusions

Novel materials with significant enhanced photocatalytic properties have been developed. 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. The observed Au particle size distributions indicate that it is the very smallest Au particles that are responsible for the enhanced catalytic performance – probably by increasing the rate of production of separated electrons and holes.

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