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Simultaneous photocatalytic degradation of nitrate and oxalic acid over gold promoted titania

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ABSTRACT

The photocatalytic degradation of nitrate in aqueous solution has been examined using different Au/TiO_2 photocatalysts with oxalic acid as hole scavenger. Although complete elimination of oxalic acid was possible under conditions employed, complete nitrate removal was not achieved and the extent of conversion showed a dependence on hole scavenger concentration. The reacting stoichiometry was greater than predicted from the corresponding redox equations and suggests competitive reaction between protons and nitrate for conduction band electrons. The different photocatalysts exhibited different temperature sensitivities with the Hombikat supported Au showing the highest apparent activation energy, probably reflecting the stronger adsorption of carbon dioxide as reaction product.

1. Introduction

The complex nature and relatively low levels of components which are present in ground water require complex treatments and potential treatments have been reviewed in a recent book chapter [1] and the state of catalytic removal summarised in a recent paper [2]. In addition to reagents of an organic nature, nitrates are also of increasing concern in areas of extensive use of soluble nitrate fertilizers. The World Health Organisation (WHO) introduced standard recommended levels of nitrates, nitrite and ammonium concentration in drinking water to be 50 ppm NO_3^-, 3 ppm NO_2^- and 0.5 ppm NH_4^+. Catalytic hydrogenation over noble/base metal combinations, usually based on Pd shows some promise in terms of rates of nitrate removal (e.g. [2,3]) but are usually limited in terms of the selectivity required to avoid undesired nitrite and ammonium formation. Photocatalysis is particularly suitable for the abatement of contaminants including nitrates since it offers low cost operation and provides the possibility of installation at remote locations. Limited literature exists concerning photocatalytic nitrate removal in contrast to the extensive extent to which organic reagent destruction has been investigated [1] and the potential exploitable nature of this methodology makes it ideal for further, more throughout assessment.

Studies concerning the potential photocatalytic reduction of nitrates in solution using organic hole scavengers have been reported [4–6,14], and a recent paper has compared non-photocatalytic and photocatalytic reduction of nitrates over the same catalyst [7]. Despite the potential advantages of the latter approach, including reduced levels of ammonium produced [7], the reported activities and selectivites are usually lower and far from the desired values. Titania alone is reported to show either no activity for this reaction [8] or shows low activity but high nitrogen selectivity [9] or generates mainly ammonia [10]. Initial studies involving titania modified by metals (including Cu, Pt, Pd, and Ag [11], Pt [12], and Ru [13]) and the use of dopant ions including Fe^{3+}, Cr^{3+}, Co^{3+} and Mg^{2+} [14] had shown poor selectivity towards nitrogen and only when mixed metals were employed did the selectivity to nitrogen improve [7,11]. A more recent paper concerning the catalytic performance of Ag/TiO_2 [9] illustrated that this route shows great potential as a selectivity of ca 100% to N_2 and an activity of 24 mmol/g_{Ag} min were reported. The latter value is an order of magnitude higher than the activities generally reported for nitrate removal via use of hydrogenation catalysts. The validity of the finding has been confirmed for Ag/TiO_2, and the work expanded by assessing a number of other metals including Fe and Cu [15]. In the present study, the use of Au has been assessed. This metal offers the potential added advantage that it might be excited in the visible range rather than relying on the use of a UV source [16] to activate the semiconductor oxide. The role of metals as modifiers in the main, is based upon a capacity to collect electrons [17] which reduces the rate of hole–electron pair recombination and enhances the probability of the electrons being used in nitrate reduction. However, differences in both selectivity and activities between different metals [15] and by combing metals [7,11] sug-

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gest more complex roles and thus as yet, metal selection is far from being an optimised component of the system.

Organic substances such as humic acids which are naturally occurring may be used as hole scavengers [4], as they may co-exist with nitrates in contaminated waters. Additionally, there are many other organic species ranging from pesticides and insecticides to endocrine disrupting reagents which might be selected for study. However, it is known that advanced oxidation technologies (AOT) often fail to yield complete mineralisation of the organic substrate and produce instead aliphatic carboxylic acids. For example formic and oxalic acids are the main refractory compounds created by the Fenton reaction during phenol destruction [18]. Selection of hole scavenger may be important in determining catalyst performance for nitrate removal [1,8,8,15] and formic acid has often been observed to be effective in this role [7,8,15]. Here oxalic acid is selected as hole scavenger as part of an assessment to evaluate a secondary stage water purification treatment which simultaneously removes nitrates along with aliphatic acids generated during a prior partial mineralisation using AOTs. The role of titania particle size has received attention in the case of oxidation reactions [19] but this was not one of the factors assessed in previous photocatalytic studies of nitrate reduction [4–6]. In this study we directly compare the performance of Au supported on two different (P25 and Hombikat) titania materials, and compare with a commercially available Au/TiO_2 sample. The inclusion of a commercial sample provides a means of comparison with the laboratory prepared Au/P25 sample and then a contrast with the Hombikat based sample. This allows an assessment as to whether any differences in performance are related to the different supports or characteristics of the Au due to subtle differences in preparation. Secondly, as this is a commercially available catalyst which could in principle be employed in such a reaction, it makes sense to compare its performance with laboratory prepared samples.

2. Experimental

2.1. Catalyst preparation

The materials used for the synthesis of the catalysts were TiO_2 P25 (Degussa) and TiO_2 Hombikat UV 100 (Sachtleben Chemie) [20]. The ratio used for the synthesis was 5 g of support for 100 ml of distilled water and the target loading of gold for catalysts was 1 wt%. Gold supported on TiO_2 was synthesized by slowly dropping a NaOH 0.01 M solution into the solution containing the support and the salt, chloroauric acid ($HAuCl_4$) while it was being stirred. The pH was raised from 6 until 10 in order to slowly and uniformly precipitate the gold hydroxide, $Au(OH)_3$ through the liquid phase, with the support surface acting as nucleating agent. The resulting catalysts were filtered and dried at 60 °C during 24 h. A commercial gold catalyst, also prepared using P25 as support, was kindly donated by project AuTEK and is referred to as Au/Autek.

2.2. Catalyst characterisation

The BET surface areas of samples were obtained on samples which were outgassed in situ at 523 K and measured using N_2 adsorption/desorption isotherms at 77 K and using the P/P_0 range of 0.02–0.2 using a Coulter SA3100.

2.3. Photocatalytic removal of nitrates

Photocatalytic degradation of nitrates was performed in a stirred, batch reactor with a primary cooler (Fischer Scientific 30165) circulating cooled water to maintain the reactor temperature and an inner jacket also allowing passage of cooled water to remove heat generated by the UV light source. Any infrared radiation generated by the lamp would also be removed before exposure to the sample using such a set-up. Temperature was continually monitored using a probe connected to a Logger pro 3.3 system data analyser. Double distilled water (1200 ml, $R \sim 18\,M\Omega$) was transferred to the reaction vessel (after being degassed to remove oxygen) along with 250 mg of photocatalyst which was then irradiated with a 400 W UV light (Osram Supratec HSC 400-221, 400 W, 230 V) to allow time to ensure the system had thermally equilibrated was prepared before the addition of the nitrate and oxalic acid solutions. Nitrogen was bubbled continuously through the solution. Addition of solutions to provide initial nitrate and oxalic acid concentrations of 100 ppm and 0.008 M, respectively (unless otherwise stated) was performed and then samples were periodically extracted and analysed by ion chromatography (Dionnex DX-120, with an ASA4 anion column). The samples were analysed for the species of interest (NO_3^-, NO_2^-, oxalic acid) using the programme Dionex peaknet 5.1, and concentrations calculated from linear calibration profiles. Ammonia was determined using the Sepctroquant Kit (Merck) and measured on a Varian Cary 50 scan UV–vis spectrophotometer.

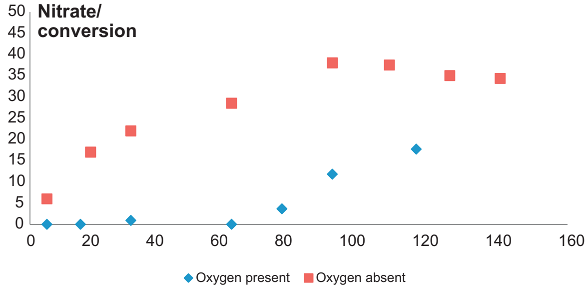


Fig. 1. Nitrate conversion as a function of time over Au/P25 at 15 °C using oxalic acid with nitrogen bubbled through the solution (squares) or without (diamonds) bubbling nitrogen.

3. Results and discussion

The measured BET surface areas for P25 (54 $m^2\,g^{-1}$) and Hombikat (286 $m^2\,g^{-1}$) were consistent with expectations and upon incorporation of 1 wt% Au gave surface areas of 53 and 252 $m^2\,g^{-1}$, respectively. XRD analysis confirmed the presence of anatase only in the case of Au/Hombikat but both anatase and rutile phases in the cases of both the Au/P25 and Au/Autek samples. TEM images show the Au/Autek sample to consist of evenly distributed small Au particles, whereas the Au distribution was much more heterogeneous in the case of Au/Hombikat with some particles as large as 50 nm being detected. The catalyst supplied by Autek, contained 1 wt% of metal and had an average particle size of 2.1 nm as measured by TEM (value provided by supplier). The XPS spectrum for Au/Autek showed signals which correspond to binding energies of 83.8 and 87.4 eV, due to Au $4f_{7/2}$ and Au $4f_{5/2}$, respectively [17], and characteristic of metallic gold. The good dispersion of gold over the Au/Autek sample was consistent with a Au:Ti ratio of 0.027 as determined by XPS.

In the absence of UV irradiation, no evidence was obtained over a 3 h period for consumption of nitrate or oxalic acid. When the reaction was performed without the continuous nitrogen spargeing of the solution, nitrate conversion was not observed during the first 60 min of irradiation (Fig. 1) although following this elapsed time period, nitrate removal commenced but at a slower rate that that observed in cases where nitrogen was bubbled from the onset. These results suggest competition between oxygen and nitrate for the conduction band electrons and that nitrate is unable to compete effectively in the presence of dissolved oxygen even at the

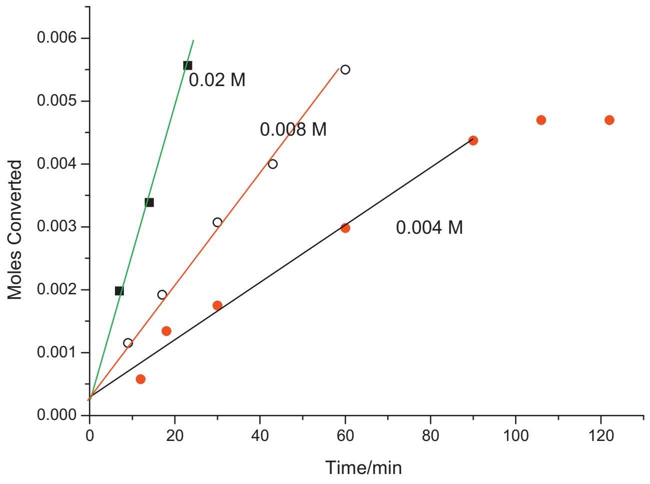


Fig. 2. Oxalic acid removal as a function of time using Au/P25 at 15 °C and initial oxalic acid concentrations of: 0.004 (filled circles), 0.008 (open circle), and 0.02 M (filled squares).

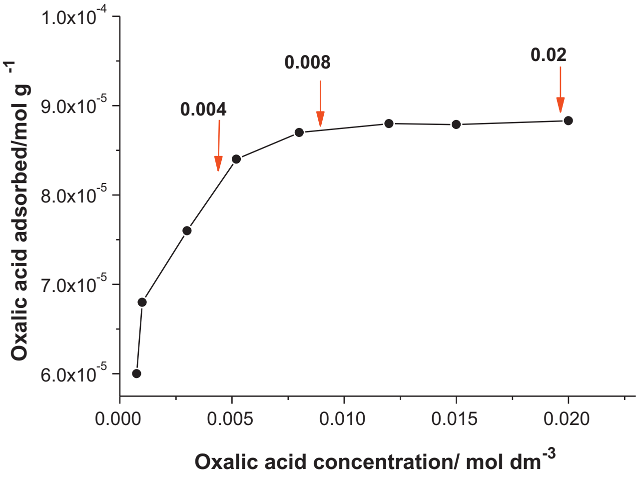


Fig. 3. . Adsorption isotherm for oxalic acid over Au/P25 at 15 °C.

low levels present after consumption over a 1 h period. The amount of oxalic acid consumed during this 60 min period was 2.99 mmol the same whether continuous purging with nitrogen took place or not indicating that the oxidation reaction proceeded at the same rate irrespective of the chemical nature and concentration of the electron scavenger.

The rate of nitrate removal was not increased when the initial concentration of nitrate was increased from 100 to 300 ppm. The extent to which nitrate was removed as a function of time was studied at 15 °C for initial oxalic acid concentrations of 0.004, 0.008, and 0.02 M using Au/P25 as an example of the Au/TiO_2 samples. Conversion in all cases failed to surpass a limit of ca 40% and there was a high degree of similarity between the conversion profiles suggesting that nitrate conversion was independent of oxalic acid concentration within the range employed.

Plots of oxalic acid removal as a function of concentration are shown in Fig. 2. At the lowest (0.004 M) concentration employed, complete conversion of oxalic acid was achieved after ca 100 min irradiation. Until this conversion, the concentration showed a linear relationship with time consistent with expectation for a reaction following overall zero order behaviour. This is consistent with kinetic studies of oxalic acid degradation using oxygen as electron scavenger at an acid concentration of 0.0085 M over titania supported Ag and Pt photocatalysts where the removal of acid followed zero order kinetics [21]. However, when the initial oxalic acid concentration was increased (doubled) to 0.008 M the rate of removal increased from 4.50×10^{-5} to 9.14×10^{-5} mol min^{-1} with the enhancement factor (2.03) consistent with the expectation based on a first order dependence on acid concentration. Similarly, increasing the initial oxalic acid concentration from 0.008 to 0.02 M (i.e. by a factor of 2.5) increased the rate of acid removal to 2.4×10^{-4} mol min^{-1} (i.e. by a factor of 2.62) again consistent with expectation for a first order dependence on oxalic acid concentration. It is clear that although the overall reaction follows zero order kinetics, consistent with previous studies of oxalic acid and oxygen [21], the order with respect to oxalic acid is first.

The isotherm for oxalic acid adsorption on Au/P25 in the absence of irradiation is shown in Fig. 3.The maximum uptake of ca 8.7×10^{-5} mol g^{-1} was obtained for solution concentrations of ca 0.0075 mol dm^{-3} and above. This data is consistent with studies using P25 titania at 22 °C, where a maximum uptake of 8.8×10^{-5} mol g^{-1} of oxalic acid was attained with initial solution concentrations of 5.2×10^{-3} M and above [10]. However, at 8.5×10^{-3} M, Iliev et al. report an uptake almost 6 times as great although this capacity was reduced by ca 50% (to 22.5×10^{-5} mol g^{-1}) after doping with 1% metal [21]. The isotherm suggests that at least for the two highest oxalic acid concentrations employed (Fig. 3), surface coverage by the hole scavenger should be at a maximum.

The Langmuir–Hinshelwood kinetic model (Eq. (1)) is often used to express the rate of degradation of organic pollutants;

$$r = k\vartheta = k\left(\frac{KC}{1+KC}\right) \tag{1}$$

where r is the initial rate of degradation of the organic substrate, k is the limiting step rate constant at maximum coverage under the given experimental conditions, K is the reactant adsorption constant and C is the bulk-solute concentration. From the individual plots in Fig. 2, the straight line conversion vs time plots suggests that we are operating in a regime where $\text{KC} \gg 1$ despite the fact that the lowest concentration employed (0.004 M) lies below the concentration for our isotherm (Fig. 3) and that of others [21] which show coverage to become independent of concentration. On the other hand, the increased rate as the initial oxalic acid concentration is increased from 0.004 to 0.008 and then 0.02 M, suggests that $1 + \text{KC} \sim 1$ so that 1st order behaviour with respect to acid concentration is exhibited. Malato et al. [22] and Friedmann et al. [23] highlight the fact that although Langmuir–Hinshelwood isotherm is useful in modeling the process, rate constants and orders should be seen as “apparent.” It is also possible that the overall rate is governed, not only by concentration of oxalic acid, but also by coverage of a reaction product, which leads to the need to insert a denominator term into Eq. (1). This will be discussed further after dealing with the temperature dependent nature of the reaction rate.

The removal of nitrate at 15 °C over the three Au/TiO_2 photocatalysts as a function of irradiation time was compared using 0.008 M oxalic acid as hole scavenger. The two P25 based samples initially showed very similar behaviour, reacting 31% conversion at 90 min before then diverging from the behaviour of the commercial Au/Autek sample reaching 44% conversion at 180 min and the laboratory prepared Au/P25 reaching only 34% (Fig. 4). The Au/Hombikat sample performed poorer than the P25 based photocatalysts giving only 16% nitrate conversion after 180 min. When the reactions were repeated at 30 °C rather than 15 °C, the P25 and Hombikat based samples performed very similarly (Fig. 5) indicating that the later had been most affected by the operating temperature.

The apparent activation energy, E_a, for a photocatalytic reaction may be around 20 kJ mol^{-1} due to the enthalpies of adsorption of reactant and product [24] although the true rate constant in

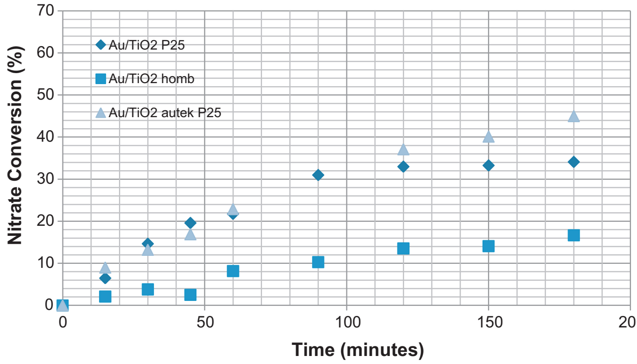


Fig. 4. Conversion of nitrate at 15 °C over Au/P25, Au/Autek and Au/Hombikat using 0.008 M oxalic acid as hole scavenger.

photocatalysis is independent of temperature [22,24,25]. At the low temperatures employed here, desorption of the final product becomes the rate limiting step and so the value of E_a tends to the value of the heat of adsorption/desorption of the product [22]. Differences in terms of temperature sensitivity between P25 and Hombikat based Au photocatalysts, were assessed by performing reactions using 0.008 M oxalic acid and 100 ppm nitrate at three temperatures between 15 and 30 °C. Plots of the natural logarithm of the rate constants obtained against reciprocal of the absolute temperature were made. The Au/Autek sample gave a good straight line correlation consistent with expectation for Arrhenius behaviour while the data fit is not of the same quality for the Au/Hombikat. Nonetheless, the relationships permit an estimation of the apparent activation energy for both samples and the values obtained were $E_a = 34\ \text{kJ mol}^{-1}$ for Au/Autek and $E_a = 42\ \text{kJ mol}^{-1}$ for Au/Hombikat [26]. Differences might be attributed to the heats of adsorption of CO_2 on the two different titania support materials as no other carbon containing products were detected. Similarity in the behaviour between our own Au/P25 sample and the commercial Au/Autek sample, also based on P25 as support, is consistent with this proposal. To support this conclusion, samples of the solids extracted from the reactor were measured using DRIFTS in a wet state. However, they did not provide strong evidence for adsorbed CO_2 either in molecular bound form or as carbonate. Spectra show (Fig. 6a) that for conversions of oxalic acid up to ca 80% oxalic acid bands at 1720, 1696, 1386 and 1231 cm^{-1} were found which can be attributed to vibrations of molecularly bond oxalic acid. The bands at 1720 and 1696 cm^{-1} are due to νC=O of the carbonyls interacting with the solution, and surface, respectively. The 1386 cm^{-1} feature is assigned to the C–OH stretching mode and the 1231 cm^{-1} band to O–H deformation mode. It has been assumed that under conditions of excess oxalic acid, the titania surface should be populated by oxalate species [10]. Only at higher oxalic acid conversion (Fig. 6b), did spectra display features at 1667, 1560 and 1410 cm^{-1} which are consistent with the presence of oxalate species. It has been reported [23] that oxalic acid from aqueous solution appears to preferentially adsorb in bidentate configuration on rutile but as a monodentate complex on anatase. Theoretical calculations suggest that both forms of adsorbed carboxylates may lead to CO_2 formation although monodentate forms may generate CO_2 or adsorbed formate [23]. From the above discussion it is apparent that the overall reaction kinetics are governed by a 1st order dependence on oxalic acid concentration and a negative order in product coverage which combine to show the overall zero order behaviour observed (Fig. 2). Reactions at the Au surface do not appear to be rate determining hence the lack of response when nitrate concentration was increased.

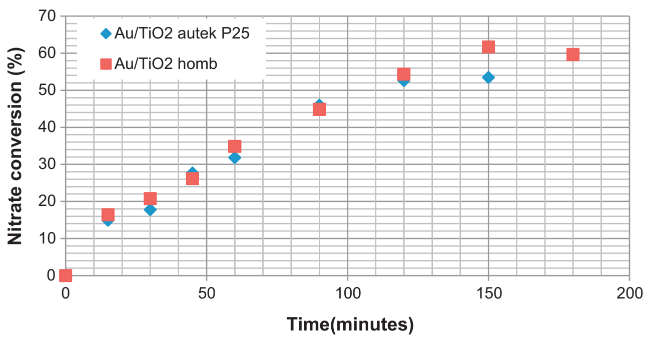


Fig. 5. Nitrate conversion at 30 °C over Au/Autek and Au/Hombikat using 0.008 M oxalic acid as hole scavenger.

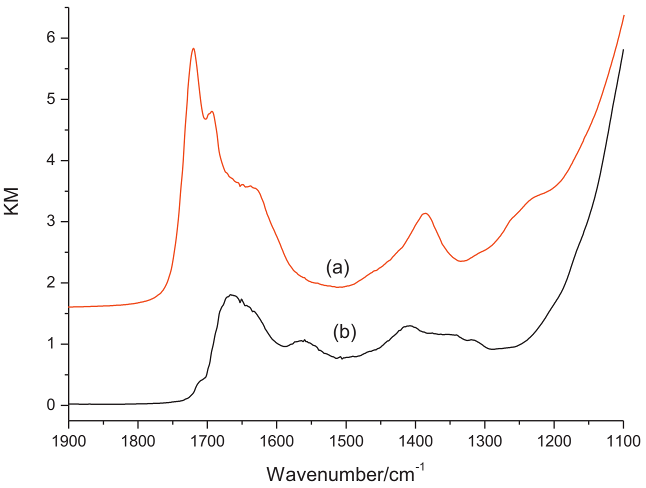


Fig. 6. DRIFT spectra of Au/P25 following removal from solution after performing photocatalytic reaction of oxalic acid (0.008 M) and nitrate solution (100 ppm) at 15 °C and having attained (a) 80% and (b) ca 95% degradation of the oxalic acid in solution.

Data relating the removal of oxalic acid and nitrate for two different temperatures are shown for Au/Autek and Au/Hombikat (Fig. 7) using an initial oxalic acid concentration of 0.008 M and 100 ppm nitrate. Data obtained for the different temperatures lie on the same line for each sample showing that the reacting stoichiometry was independent of temperature but a characteristic of the different samples. The relationship between rate of oxalic acid removal and rate of nitrate removal was 9.13 for Au/Autek, close

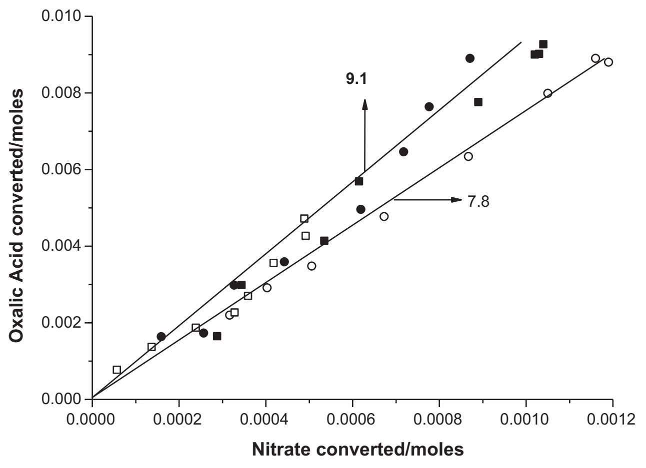


Fig. 7. Relationship between nitrate conversion and oxalic acid removal over Au/Autek at 15 °C and 30 °C (filled symbols) and over Au/Hombikat (open symbols) at 20 and 30 °C using initial oxalic acid concentrations of 0.008 M and 100 ppm nitrate.

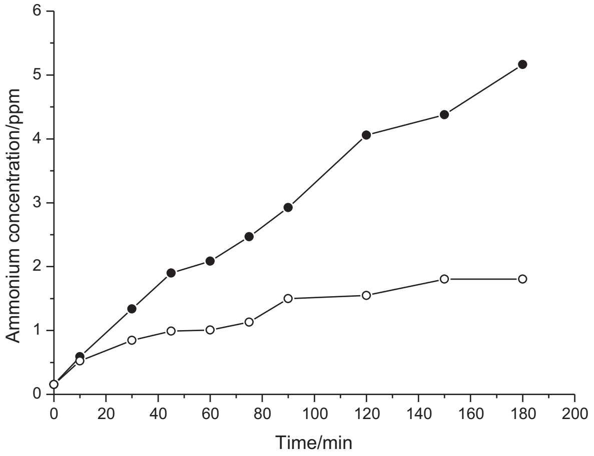
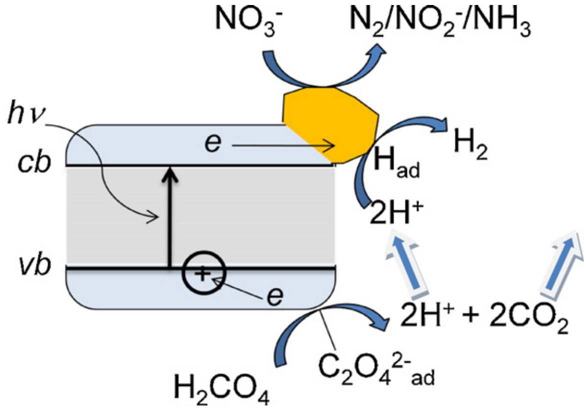


Fig. 8. Ammonium formation as a function of reaction time at 15 °C using initial oxalic acid concentrations of 0.008 M and 100 ppm nitrate over Au/Autek which was previously untreated (open symbols) or calcined at 250 °C (filled symbols).

to the 9.8 value for Au/P25 (not shown) for the same initial oxalic acid concentration. The ratio (gradient) was 7.8 for Au/Hombikat, indicating a more effective use of the hole scavenger although still approximately 3 times greater than the reaction stoichiometry (Eq. (2)) for the 5 electron reduction of nitrate and 2 electron oxidation of oxalic acid.

$$5H_2C_2O_4(aq) + 2NO_3{}^- + 2H^+ \rightarrow 10CO_2(g) + N_2 + 6H_2O \tag{2}$$

The reacting stoichiometries can be understood on the basis of the competing processes which give rise to products other than nitrogen and CO_2 during the reaction. Nitrite formation (2 electron reduction) took place during the first 15 min of reaction but then after, levels remained constant (at ca 5 ppm). If the reaction was performed using nitrite rather than nitrate, then the nitrite was readily removed. This suggests that nitrite is readily reduced by conduction band electrons, however, it is either formed and removed at similar rates in order to maintain a steady state concentration or that it is formed early during initial stages of irradiation due to non-selective reduction and then is unable to effectively compete with nitrate for electrons localised on the Au. There are contrasting observations regarding the generation and removal of nitrite by photocatalytic means in the presence of nitrates. For metal free titania, nitrite is either formed in amounts directly related to the amount of nitrate reduction [4] or is not detected at all, but may be a potential intermediate in the selective transformation of nitrate to ammonia [10]. Doping of titania by metals may enhance nitrite adsorption [14] which may facilitate its reduction although the amount adsorbed may be low (ca 10%) [7] and this may be diminished to ca 0 if the solution pH is increased above 5 [6]. Previously, for metal doped titania [11] only small amounts of nitrite were observed during the initial stages of photoirradiation which was then diminished as a function of time. However, other studies show that nitrite may be the dominant reaction product [8] or that the yield of nitrite is strongly dependent on the choice of metal [6,11]. The only previous published data for Au/TiO_2 [11] reported that at 16% nitrate conversion, selectivity was 75% to nitrite. In experiments here where further aliqouts of oxalic acid were added after the complete removal of hole scavenger, nitrate levels could be reduced to zero, but only at this point, was it possible to remove nitrite. On balance, it would appear that nitrite is formed at an early stage in the reaction but then it fails to compete effectively in the presence of nitrate for conduction band electrons on Au. However, complete reduction is possible when nitrite is removed. Such a scenario is not dissimilar to the formation of intermediate nitrite in solution during catalytic hydrogenation of nitrate and then further conversion as the process proceeds [1–3,27].



Scheme 1. Schematic representation of the simultaneous removal of nitrate and oxalic acid of titania supported Au.

Ammonia is commonly observed as a product of photocatalytic nitrate reduction [6,11] although its yield may [10] or may not [6,28] be higher in the case of titania alone than in the case of metal doped titanias. However this, like nitrite formation, shows some dependence on the choice of metal [6,11,12,14,28]. Ammonia formation was similarly found in this study for all Au/TiO_2 samples and the selectivity to ammonia was always higher in the case of Hombikat based samples (6 ppm) compared to P25 supported Au (Fig. 8) which was 2 ppm after 3 h reaction. This observation might be surprising in the first instance given the higher reductant/oxidant ratios observed for P25 based samples compared to Hombikat supported sample (Fig. 7), however, in any case, the yield to ammonia (8 electron transfer) does not fully account for additional hole scavenger consumed compared to the predicted values based on Eq. (2). It is clear that some oxalic acid must be consumed which does not lead to nitrate reduction. Using undoped P25, significant conversion of oxalic acid was observed in the absence of nitrate although the removal of hole scavenger was enhanced in the presence of nitrate [10]. Evolution of hydrogen gas was detected here and in previous studies [11,12,28] and the amount evolved was diminished in the presence of nitrate suggesting that hydrogen is formed through competing reactions for conduction band electrons i.e. photogenerated electrons are captured by H^+. Hydrogen was liberated from aqueous alcohol solutions and attributed to an efficient reduction of H^+ by e^- on the metal component surface [29]. A similar scenario is envisaged here (Scheme 1) where nitrate and protons compete for the photogenerated electrons [11] on the Au surface. It has been observed, that metals such as Cu with high hydrogen overvoltages [11] tend to yield ammonia whereas metals such as Pt and Pd which have a low overpotential for hydrogen, tend to give rise to low yields of ammonia [11,14]. However, the latter may also exhibit low activity for photocatalytic nitrate and nitrite reduction [11,14] and instead give rise to evolution of hydrogen. Such a scenario would consequently lead to reaction stoichiometries (oxalic acid consumed: nitrate reduced) greater than those predicted by Eq. (2), but consistent with observations in Fig. 7. The lower ratio observed for Au/Hombikat (ca 7.5) compared with Au/P25 or Au/Autek (ca 9.5) suggests less photogenerated electrons are used in the reduction of protons to yield hydrogen gas than leading to nitrate reduction to nitrogen. Clearly the ability to form and stabilise H_{ads} [7,14] may be key to the selectivity and effective use of hole scavenger. Differences between the Au/TiO_2 samples in terms of the behaviour of the Au are not clear at this stage however, Au exhibits a hydrogen overpotential [11] which lies between those metals which mainly generate ammonia (e.g. Cu) and those which produce significant amounts of hydrogen (e.g. Pt and Pd). It is also known that the position of the Fermi level (and consequently the reduction potential) following Fermi level equilibration with the titania semiconductor depends on the Au particle size [30–32]. One might speculate therefore that Au particle size may be crucial and may explain differences between the behaviour of the two different photocatalyst systems. In this context, when a sample of Au/Autek was calcined at 250 °C to induce sintering of Au particles, the ammonia concentration after 180 min was 5 rather than 2 ppm observed for the uncalcined sample under otherwise identical conditions (Fig. 8). Subsequently, the higher ammonium selectivity of the Au/Hombikat sample may be attributed to the presence of the larger Au particles present in the sample compared to Au/Autek as confirmed by TEM data. Note that bimetallic systems have so far received little attention although those based on PdCu/TiO_2 show promise, particularly with regards to low propensity to form ammonia [7,11]. The intermediate position of Au with respect to hydrogen overvoltage suggests that modification by addition of a second metal may give rise to an active and selective photocatalyst which makes effective use of hole scavenger for the reduction of nitrate.

A concluding remark involves the representation in Scheme 1 which infers that oxalic acid is in an adsorbed state while undergoing reaction rather than being oxidised by OH radicals in solution, formed by valence band holes reacting with surface hydroxyls. Infrared spectra recorded here (Fig. 6) show that oxalic acid is adsorbed during the course of the reaction and theoretical calculations provide a possible mechanism for the degradation of oxalic acid from an adsorbed state [23]. While this does not provide evidence that this is in fact the mechanistic path, data provided here do not rely on an assumption that oxalic acid is either in an adsorbed state or is oxidised in solution. However, there is experimental evidence that a few acids including oxalic acid are oxidised directly by valence band holes via a photo-Kolbe process [33].

4. Conclusions

Nitrate and oxalic acid and can be simultaneously degraded to produce predominantly CO_2 and nitrogen over Au/TiO_2. The selection of titania support leads to different temperature sensitivities which is ascribed to the relative strengths of adsorption of CO_2. Differences between reacting ratios of hole scavenger to nitrate were also observed between the two samples and this has been attributed to the relative efficiencies of the Au to either activate hydrogen to reduce nitrate or to form hydrogen gas and is probably linked to Au particle size.

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