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Photocatalytic nitrate reduction over Au/TiO_2

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ABSTRACT

The photocatalytic degradation of nitrates in aqueous solution has been examined using different Au/TiO_2 photocatalysts and using 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 greatest apparent activation energy.

1. Introduction

Provision of clean drinking water is a primary concern to those living in both developing and developed nations. The complex nature and relatively low levels of components which are present in EU ground water require complex treatments. The range of potential treatments has been reviewed in a recent book chapter [1]. 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 metals combinations, usually based on Pd show some promise in terms of rates of nitrate removal (e.g. [2]) 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. There is a limited amount of literature dealing with photocatalytic nitrate removal (in contrast to the huge volume of accessible data for organic reagent destruction [1]) and the potential exploitable nature of this methodology makes it appear ideal for further, more extensive study.

Several studies concerning the potential photocatalytic reduction of nitrates in solution using organic hole scavengers have been reported [3–14], and a recent paper has directly compared non-photocatalytic and photocatalytic reduction of nitrates over the same catalyst [6]. Despite the potential advantages of the latter approach, including reduced levels of ammonium formed [6], the reported activities and selectivities are usually lower and far from the desired values. Titania alone is reported to show no activity for this reaction [7] or shows low activity but high nitrogen selectivity [8] or generates mainly ammonia [9]. Initial studies involving titania modified by metals (including Cu, Pt, Pd, and Ag [10,11], 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 selectivity to nitrogen improve [6,10]. Despite these earlier findings, a more recent paper concerning the catalytic performance of Ag/TiO_2 [8] 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 work presented here, we extend these studies to the use of Au which 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 use of metals as modifiers in the main, is based upon a role as an electron collector [17] which reduces the rate of hole–electron pair formation 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 combining metals [6,10] suggest more complex roles and thus as yet, metal selec-

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tion is far from being an optimised component of the system. The role of titania particle size has received attention in the case of oxidation reactions [18] but this was not one of the factors assessed in previous photocatalytic studies of nitrate reduction [3–5]. In this study we directly compare performance of Au supported on two different titania materials.

Naturally occurring organic substances such as humic acids may be considered as a potential hole scavengers [3], as they may co-exist with nitrates in contaminated waters. Additionally, there are many other organic species ranging from pesticides and insecticides through to endocrine disrupting reagents which might be selected for study. However, it is known that advanced oxidation technologies (AOT) often fail to yield complete mineralization 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 [19]. Selection of hole scavenger may be important in determining catalyst performance for nitrate removal [1,7,15] and formic acid has often been observed to be effective in this role [6,7,15]. 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 mineralization using AOTs.

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 characterization

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.

XPS spectra were run on a PerkinElmer F 5600 ci spectrometer using standard Al Ka radiation (1486.6 eV) working at 350 W. The working pressure was $<5 \times 10^{-8}$ Pa. The spectrometer was calibrated by assuming the binding energy (BE) of the Au 4f7/2 line at 83.9 eV with respect to the Fermi level.

2.3. Photocatalytic removal of nitrates

Photocatalytic degradation of nitrates was performed in a stirred, batch reactor with a cooling system where water was used as the coolant. Double distilled water (1200 mL R ~18 MΩ) was transferred to the reaction vessel (after being degassed) along with 250 mg of photocatalyst which was then irradiated with a 400 W UV light to allow time to ensure the system 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^-, and 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 WPA Septrawave S 1000 Diode Array UV–vis spectrophotometer.

3. Results and discussion

Table 1 compiles the key characteristics of the supported Au photocatalysts. The P25 and Hombikat surface areas were consistent with expectations and were not significantly modified by the introduction of 1% Au.

A number of blank reactions were performed. In the absence of UV irradiation, no nitrate or oxalic acid was consumed over a 3 h period. When the reaction was performed without the continuous bubbling of nitrogen through the solution, no nitrate conversion was observed during the first 60 min of irradiation 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 low levels present after consumption over a 1 h period. The amount of oxalic acid consumed during this 60 min period was the same whether nitrogen bubbling was conducted or not indicating that the oxidation reaction proceeded at the same rate irrespective of the chemical nature and concentration of the electron scavenger.

The extent of nitrate removal as a function of time over Au/P25 at 15 °C is shown in Fig. 1 for initial oxalic acid concentrations of 0.004, 0.008, and 0.02 M. 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. The rate of nitrate removal was not increased when the initial concentration of nitrate was increased from 100 to 300 ppm.

Plots of oxalic acid removal as a function of concentration are shown in Fig. 2. It is assumed that CO_2 was the only product of reaction as no other species were determined by ion chromatography and CO_2 could be trapped and detected by GC (TCD). At the

Table 1
Support and Au catalyst characteristics.

	Au loading (%)	BET surface area ($m^2\,g^{-1}$)	Langmuir surface area ($m^2\,g^{-1}$)	Au:Ti[a]
P25	–	54	57	–
Au/TiO_2 (P25)	1	53	54	
Hombikat	–	286	250	–
Au/TiO_2 (Hombikat)	1	252	216	–
Au/TiO_2 (Autek)	1			0.027

[a] Measured by XPS.

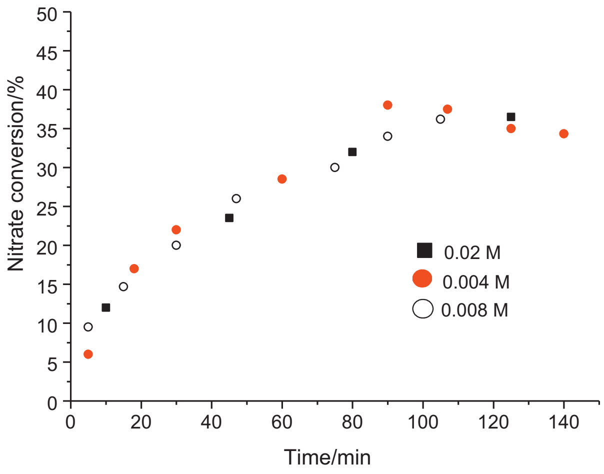


Fig. 1. Plot of nitrate conversion as a function of time over Au/P25 at 15 °C using oxalic acid concentrationsof 0.004 (filled circles), 0.008 (open circle), and 0.02 M (filled squares).

lowest (0.004 M) concentration, complete conversion of oxalic acid was achieved after *ca.* 100 min irradiation. Up to this conversion, the concentration showed a linear relationship with time consistent with expectation for a reaction following overall zero order behaviour. Previous 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 indicated that the removal of acid follows zero order kinetics [21]. However, increasing the initial oxalic acid concentration here to 0.008 M increased the rate of removal from 4.50×10^{-5} to 9.14×10^{-5} mol min^{-1} with the increase in rate (2.03) consistent with the expectation of doubling the acid concentration where the order with respect to acid is first. Similarly, increasing the initial oxalic acid concentration from 0.008 to 0.02 M (i.e. 2.5×) increased the rate of acid removal to 2.4×10^{-4} mol min^{-1} (i.e. 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.

Previous studies using P25 titania in the dark, show that at 22 °C, a maximum uptake of 8.8×10^{-5} mol g^{-1} of oxalic acid can be attained and this is achieved with initial solution concentrations of 5.2×10^{-3} M and above [9]. However, at 8.5×10^{-3} M, Iliev et al. [21] report an uptake value almost 6 times as great. This capacity was reduced by *ca.* 50% to 22.5×10^{-5} mol g^{-1} after depositing 1% metal [21]. The rate of degradation of organic pollutants is often expressed by the Langmuir–Hinshelwood kinetic model as indicated in Eq. (1):

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

where *r* is the initial rate of disappearance 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 *versus* time plots suggest that we are operating in a regime where $KC \gg 1$ despite the fact that the lowest concentration employed (0.004 M) lies below the concentration for which Li and Wasgestian [21] showed 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 $1 + KC \sim 1$ 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 aslo 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 reation rate.

Fig. 3 shows the relationship between nitrate consumption and oxalic acid removal at 15 °C using Au/P25 using initial oxalic acid concentrations of 0.004 and 0.008 M. The dashed line shows the theoretical reaction stoichiometry based on the 2 electron oxidation of oxalic acid and 5 electron reduction of nitrate to nitrogen. At the lower of the two oxalic acid concentrations, the ratio of removal rates approximates to the theoretical reaction stoichiometry but then as the period of irradiation progresses, the relative rate of oxalic acid to nitrate removal is increased, leading to increased deviation from the 2.5:1 relationship and leading to the exponential relationship observed (Fig. 3). On the other hand, an initial oxalic acid concentration of 0.008 M, led to a straight line relationship between the removal rates of both reagents with a gradient indicating a removal stoichiometry of 9.8:1, approximately 4 times the

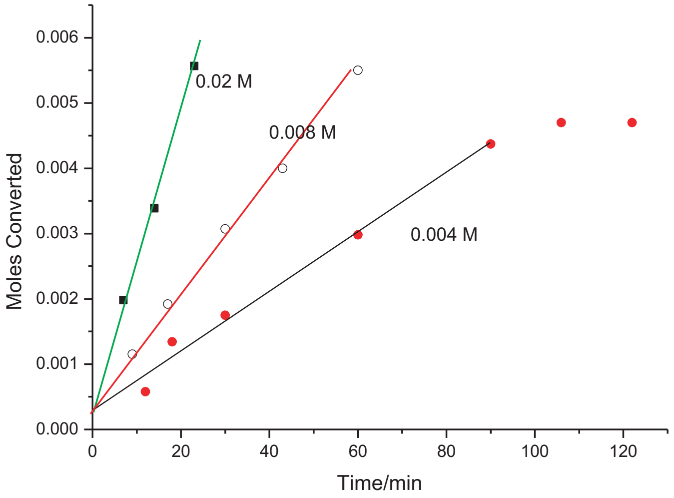


Fig. 2. Plot of oxalic acid removal as a function of time over Au/P25 at 15 °C using initial oxalic acid concentrations of 0.004 (filled circles), 0.008 (open circle), and 0.02 M (filled squares).

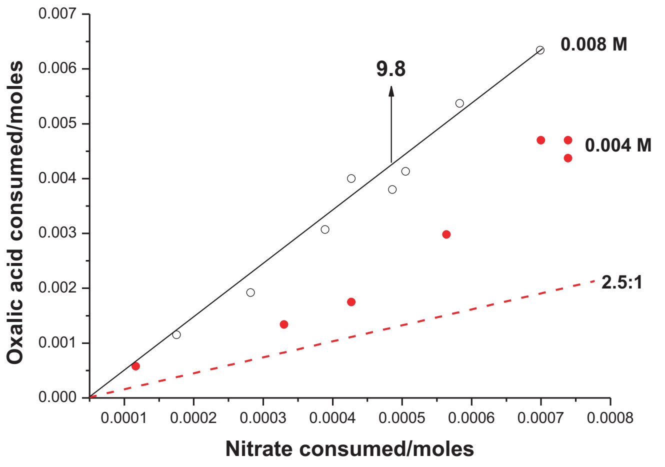


Fig. 3. Correlation between nitrate conversion and oxalic acid removal over Au/P25 at 15 °C using initial oxalic acid concentrations of 0.004 (filled symbols) and 0.008 (open circles). The dashed line shows the reaction stoichiometry based on the 2 electron oxidation of oxalic acid and 5 electron reduction of nitrate to nitrogen.

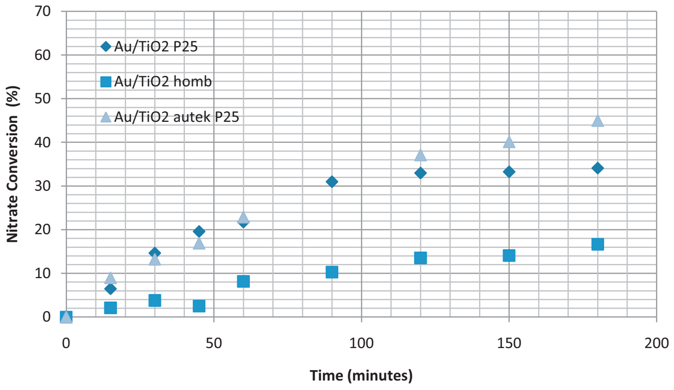


Fig. 4. Comparison of the conversion of nitrate at 15 °C over Au/P25, Au/Autek and Au/Hombikat using 0.008 M oxalic acid as hole scavenger.

value expected if one assumes:

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

Although ammonium (and nitrite) was formed during the process (see later), the amounts formed do not account for the additional oxalic acid consumed beyond the theoretical stoichiometry predicted by Eq. (2).

Fig. 4 shows the removal of nitrate over the three Au/TiO_2 photocatalysts at 15 °C as a function of irradiation time using 0.008 M oxalic acid as hole scavenger. The two P25 based samples initially show very similar behaviour, reacting 31% 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 reaching only 16% after 180 min. When the reactions were repeated at 30 °C, the P25 and Hombikat based samples performed very similarly (Fig. 5) indicating that the later had been most affected by the operating temperature.

Although the true rate constant in photocatalysis is independent of temperature [22,24,25], the apparent activation energy, E_a, may be around 20 kJ mol^{-1} as this will include terms for the enthalpies of adsorption of reactant and product [24]. At low temperatures such as those 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]. To investigate differences between P25 and Hombikat based Au photocatalysts, reactions using 0.008 M oxalic acid and 100 ppm nitrate were performed at three temperatures between 15 and 30 °C. Plots of the natural logarithm of the rate constants obtained against reciprocal of the absolute temperature are shown in Fig. 6. The Au/Autek sample gives 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 kJ mol^{-1} for Au/Autek and E_a = 42 kJ mol^{-1} for Au/Hombikat. This might be attributed to differences in the heats of adsorption of CO_2 on the two different titania support materials. No other carbon containing molecules other than oxalic acid/oxalate were detected on the solid surface by DRIFTS and CO_2 was the only carbon containing reaction product detected (by GC of gas phase). Similarity in behaviour between our own Au/P25 sample and the commercial Au/Autek sample, also based on P25 as support, is consistent with this proposal. Samples of the solids extracted from the reactor and measured using DRIFTS in a wet state did not provide strong evidence for adsorbed CO_2 either in molecular bound form or as carbonate. At up to *ca.* 80% oxalic acid conversion, the samples gave spectra which showed bands at 1720, 1696, 1386 and 1231 cm^{-1} which can be attributed to molecularly bond oxalic acid. Previous authors have assumed that under excess oxalic acid conditions, the titania surface should be populated by oxalate species [9]. At higher acid conversion, spectra showed main features at 1667, 1560 and 1410 cm^{-1} which can be attributed to oxalate species. Note that it has been reported that oxalic acid from aqueous solution appears to preferentially adsorb in bidentate configuration on rutile but as a monodentate complex on anatase [23]. Theoretical calculations suggest that both may lead to CO_2 formation while the latter 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 leading to 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.

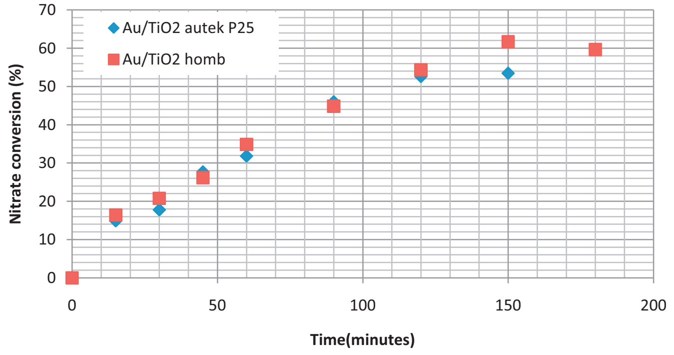


Fig. 5. Comparison of the conversion of nitrate at 30 °C over Au/Autek and Au/Hombikat using 0.008 M oxalic acid as hole scavenger.

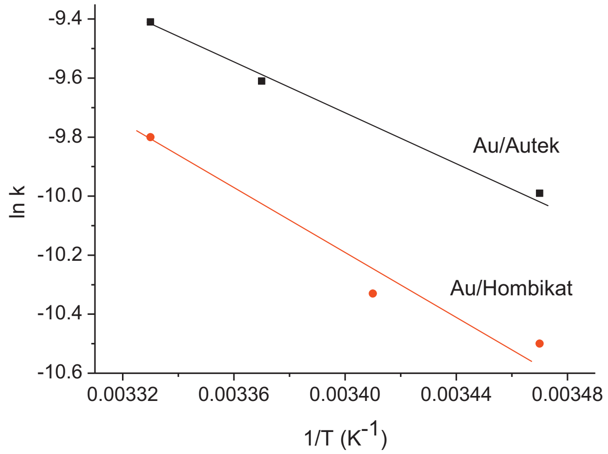


Fig. 6. Arrhenius plots for Au/Autek and Au/Hombikat in the temperature range 15–30 °C.

Data relating the removal of oxalic acid and nitrate for two different temperatures are shown for Au/Autek (Fig. 7) and Au/Hombikat (Fig. 8) 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 individual sample showing that the reacting stoichiometry was independent of temperature. The gradient (and relationship between rate of oxalic acid removal to rate of nitrate removal) was 9.13 for Au/Autek, close to the 9.8 value for Au/P25 shown in Fig. 3 for the same initial oxalic acid concentration. The ratio (gradient) was 7.5 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.

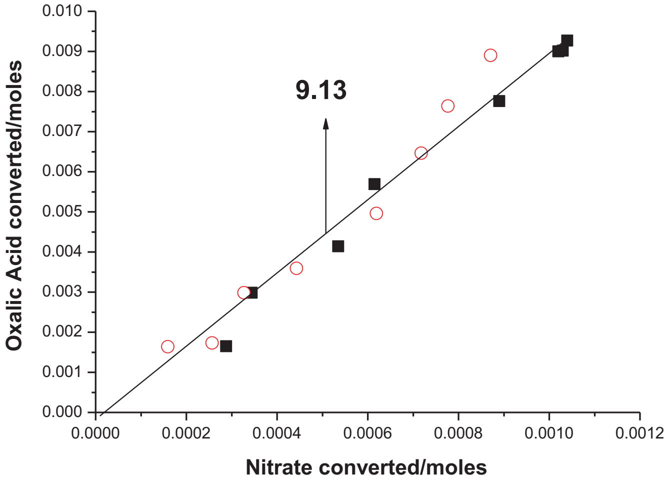


Fig. 7. Correlation between nitrate conversion and oxalic acid removal over Au/Autek at 15 °C (open circles) and 30 °C (filled squares) using initial oxalic acid concentrations of 0.008 M and 100 ppm nitrate.

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 for both samples. 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 [3] or is not detected at all, but may be a potential intermediate in the selective transformation of nitrate to ammonia [9]. Doping of titania by metals may enhance nitrite adsorption [14] which may facilitate its reduction although the amount adsorbed may be low (*ca.* 10%) [6] and this may be diminished to *ca.* 0 if the solution pH is increased above 5 [5]. For metal doped titania, Kominami et al. [10] observed only small amounts of nitrite 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 [7] or that the yield of nitrite is strongly dependent on the choice of metal [5,10]. Previously published data for Au/TiO$_2$ [10] reported that at 16% nitrate conversion, selectivity was 75% to nitrite or at 56% nitrate conversion, gave 0.11% nitrite selectivity to [11]. This might suggest nitrite undergoing further reaction as a course of irradiation time. In experiments here where further aliquots 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 for conduction band electrons on Au in the presence of nitrate. However, complete reduction is possible when nitrate 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 [1,2,26].

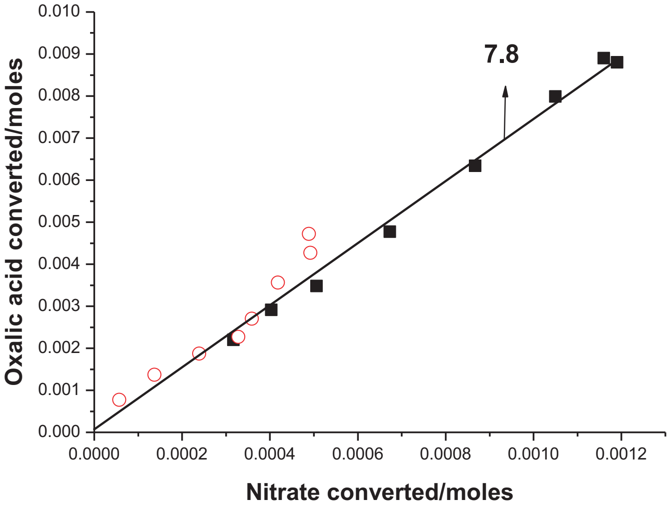
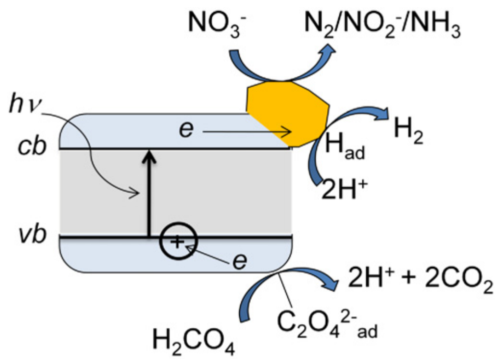


Fig. 8. Correlation between nitrate conversion and oxalic acid removal over Au/Hombikat at 20 °C (open circles) and 30 °C (filled squares) using initial oxalic acid concentrations of 0.008 M and 100 ppm nitrate.

Ammonia formation is also commonly observed as a product of photocatalytic nitrate reduction [5,10] although yield to ammonia may [9] or may not [5,27] be higher in the case of titania alone than in the case of metal doped titanias although this, like nitrite formation, shows some dependence on the choice of metal [5,10,12,14,27]. 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 P25 based samples (2%) compared to Homikat supported Au (5%). While this may be linked to the observed high reductant/oxidant ratios observed for P25 based samples (Figs. 3 and 7) and Hombikat supported sample (Fig. 8), 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. Li and Wasgestian [9] using undoped P25, observed significant conversion of oxalic acid in the absence of nitrate although the removal of hole scavenger was enhanced in the presence of nitrate. Hydrogen was detected in the gas phase here and in previous studies [10,12,27] 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 [28]. A similar scenario is envisaged here and is represented in Scheme 1 where nitrate and protons compete for the photogenerated electrons [10] on the Au surface. It has been observed, that metals such as Cu with high hydrogen overvoltages [10,11] tend to produce ammonia whereas metals such as



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

Pt and Pd which have a low overpotential for hydrogen, tend to give rise to low yields of ammonia [10,11,14]. However, the latter may also exhibit low activity for photocatalytic nitrate and nitrite reduction [10,14] 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 Figs. 3, 7 and 8. 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 and ammonia than leading to nitrate reduction to nitrogen. Clearly the ability to form and stabilise H_{ads} [6,14] 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 [10,11] which lies between those metals which mainly generate ammonia (e.g. Cu) and those which produce significant amounts of hydrogen (e.g. Pt, 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 [29–31]. One might speculate therefore that Au particle size may be crucial and may explain differences between the behaviour of the two different photocatalyst systems. 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 [6,10]. The intermediate position of Au with respect to hydrogen overvoltage suggests that modification by addition of a second metal may give rise an active and selective photocatalyst which makes effective use of hole scavenger for the reduction of nitrate.

One final point 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. Spectra recorded here show that oxalic acid is adsorbed during the course of the reaction and theoretical calculations provide a possible mechanism for 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 [32].

4. Conclusions

Oxalic acid and nitrate can be simultaneously degraded over Au/TiO_2 to produce predominantly CO_2 and nitrogen. The reactions show temperature sensitivity which is ascribed to desorption of CO_2 from the titania surface with differences noted between the two titania supports employed. Differences between reacting ratios of hole scavenger to nitrate were also observed between the two samples and this has been attributed the relative efficiencies of the Au to either activate hydrogen to reduce nitrate or to form hydrogen gas.

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