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Photocatalytic Oxidation of Aqueous Ammonia (Ammonium Ion) to Nitrite or Nitrate at TiO_2 Particles

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Summary. The photocatalytic oxidation of ammonia (ammonium ion) in the presence of air or pure oxygen at titanium(IV) oxide powder surfaces and induced by UV light was investigated. Experimental conditions were varied and the effect of *pH*, sparging gas, as well as the concentration of both ammonia (ammonium ion) and photocatalyst were investigated. It has been established that the principal product of photocatalytic oxidation depends on *pH*, and is either nitrite or nitrate. A gas-diffusion flow injection analysis system with conductivity detection was used for on-line monitoring of ammonia concentration. In addition, ion-chromatography with UV detection was utilized for off-line monitoring of nitrite and nitrate concentrations. The use of a photocatalyst such as TiO_2 may prove to be a viable method for conversion of ammonia (ammonium ion) to either nitrite or nitrate.

Keywords. Ammonia; Nitrate; Oxidation; Photocatalysis; Titanium(IV) oxide.

Photokatalytische Oxidation von wäßrigem Ammoniak (Ammoniumion) zu Nitrit oder Nitrat an TiO_2 Partikeln

Zusammenfassung. Es wurde die photokatalytische Oxidation von Ammoniak (Ammoniumion) mittels Luft oder reinem Sauerstoff an Titan(IV)oxid-Pulveroberflächen unter Induktion von UV-Licht untersucht. Die experimentellen Bedingungen wurden variiert, wobei der Effekt des *pH*-Wertes, des Spülgases und sowohl die Ammoniak- als auch die Photokatalysator-Konzentration berücksichtigt wurde. Dabei ergab sich, daß das Hauptprodukt der photokatalytischen Oxidation vom *pH* abhängt und entweder Nitrit oder Nitrat ist. Ein Gasdiffusions-Fließinjektions-Analysensystem wurde zur on-line-Kontrolle der Ammoniak-Konzentration verwendet. Off-line-Ionenchromatographie mit UV-Detektion wurde zur Konzentrationsbestimmung für Nitrit und Nitrat herangezogen. Die Verwendung von Photokatalysatoren wie Titanoxid könnte sich als gangbarer Weg erweisen, um Ammoniak (Ammoniumion) entweder zu Nitrit oder zu Nitrat umzusetzen.

Introduction

Titanium(IV) oxide is one of the most interesting catalysts whose function can be activated by UV light. We have recently shown [1] that it is possible to oxidize cyanide all the way to nitrate using this photocatalyst. Since the nitrogen atom in ammonia (ammonium ion) has the same formal oxidation number as in the cyanide ion, we wished to examine whether it would be possible to oxidize the former to nitrate under similar experimental conditions.

There is relatively little information in the literature on the photocatalytic oxidation of ammonia, and most of the research was done with ammonia in the gas phase. It has been reported [2] that a gaseous mixture of NH_3 and O_2 in the presence of dry TiO_2 produced small amounts of N_2O and of surface NO_2^- ions. It was later corroborated [3, 4] that oxidation of gaseous ammonia induced by UV irradiation in the presence of TiO_2 produces N_2O, but it was also shown that N_2 was formed as the other oxidation product. It is interesting to note that NO_3^- surface ions have been observed [5] by IR spectroscopy when NH_3 was photocatalytically oxidized at pretreated (high temperature) γ-Al_2O_3.

Recently, Tennakone et al. [6] studied reductive and oxidative photocatalytic nitrogen fixation in hydrous iron(III) oxide loaded nafion films and found that N_2 is fixed reductively and oxidatively at the same time. The reduction and oxidation products were found to be NH_3 and NO_2^-/NO_3^-, respectively.

Even less has been published concerning the photocatalytic oxidation of ammonia in aqueous solutions. In one of the first publications on heterogeneous photocatalysis using TiO_2 [7] it was established that an aqueous solution of ammonia was oxidized to nitrite. After 40 hours of irradiation of a 0.2 *M* ammonia solution, about 0.9 $g\,l^{-1}$ of nitrite was produced, as determined by a Hellige-Dubosq colorimeter. We have been unable to find any reference in the literature on the photocatalytic oxidation of ammonium ion.

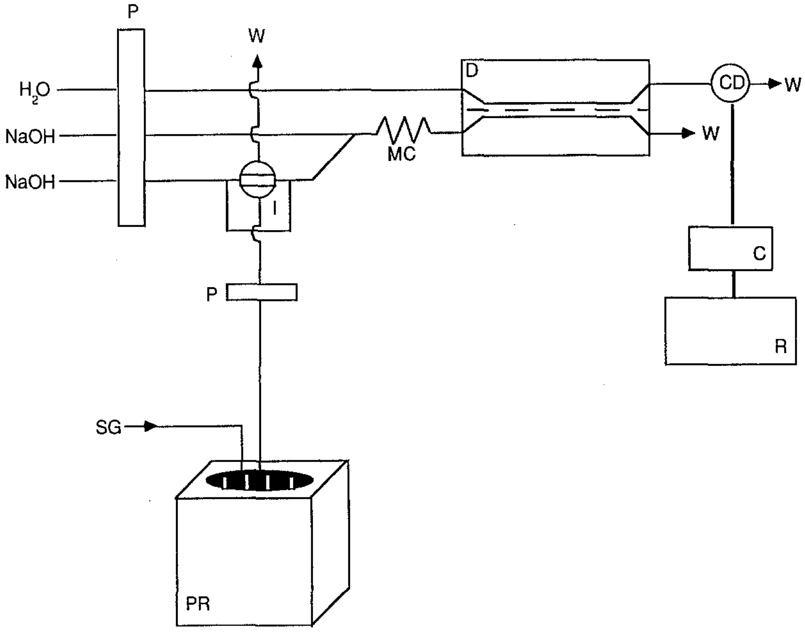

Fig. 1. Schematic diagram of the experimental setup utilized for investigating photocatalytic oxidation of ammonia (ammonium ion). *PR* photochemical reactor, *SG* sparging gas, *P* peristaltic pumps, *I* injection valve, *MC* mixing coil, *D* diffusion cell, *CD* conductivity flow-through cell, *C* conductivity meter, *R* recorder, *W* waste. All flow rates were 1 $ml\,min^{-1}$

This communication presents results which show that it is possible to photocatalytically oxidize ammonia (ammonium ion) in the presence of air or pure oxygen at a TiO_2 semiconductor via nitrite to the nitrate ion.

Experimental

The anatase form of titanium(IV) oxide was obtained from Degussa as material P-25. This material was previously characterized [8] as consisting of fused spherical particles with a diameter of 0.014 µm, hydrodynamic radius of 0.6 µm and surface area of $50 \pm 15\,m^2\,g^{-1}$. If not otherwise stated, 0.0400 g of TiO_2 per 500 ml of solution were used. All other chemicals were reagent grade and solutions were prepared using distilled deionized water.

The experimental setup is illustrated in Fig. 1. A Rayonet Photochemical Reactor (Model RPR-100), equipped with a circular bank of sixteen 253.7 nm low pressure mercury lamps, was used for UV irradiation of the 500 ml samples placed in a 30 cm × 5 cm i.d. quartz reaction vessel. During irradiation oxygen or air was bubbled through the solution at a rate of $1\,l\,min^{-1}$. In experiments with air, carbon dioxide was removed by a sodium hydroxide solution. A flow injection analysis (FIA) system was used for online monitoring of ammonia (ammonium ion). Its construction utilized a Tecator 5020 FIAstar Analyzer equipped with two peristaltic pumps and a Tecator Chemifold V gas-diffusion cell. The membrane used was PTFE supplied with the Chemifold. A Tecator L-100-1 variable volume injector with a 100 µl sample loop was used for sample injections. A Dionex conductivity detector was used to monitor the conductance of the acceptor solution, which was recorded on a Honeywell Electronic 195 recorder. The analytical procedure (see Fig. 1) is based on increasing the *pH* of the injected sample. Ammonia formed in the donor stream diffuses through a microporous membrane to the acceptor solution, increasing the conductivity of the latter. The height of the FIA peak obtained is proportional to the concentration of ammonia (ammonium ion) in the injected sample. Concentrations of nitrite and nitrate ions were followed off-line by ion-chromatography with UV detection at 205 nm. For this purpose, a Dionex Model 4000 i Ion Chromatograph, equipped with a Dionex AG4A guard column, AS4A separator column, 100 µl sample loop, and Dionex Variable Wavelength Detector were used to obtain chromatograms. The eluent was 1.80 m*M* and 1.70 m*M* in Na_2CO_3 and $NaHCO_3$, respectively, and its flow rate in most runs was $1.0\,ml\,min^{-1}$. The output data were recorded on a Spectra Physics SP 4270 Integrator, which was programmed to simultaneously determine both peak areas and peak heights.

Results and Discussion

The results of irradiating a 0.1 *M* ammonia solution in the presence of TiO_2 for four hours with continuous sparging of oxygen at a rate of $1\,l\,min^{-1}$, are illustrated in Fig. 2. During the irradiation the *pH* of the solution decreased from 10.12 to a final value of 9.32*. Under these conditions the principal product of photo-oxidation is the nitrite ion, which is in agreement with previous findings. However, contrary to the same research [7], substantial amounts of nitrate ion were also formed. The concentrations of nitrite and nitrate at the end of the four hour irradiation experiment were 211.4 and $13.3\,\mu g\,ml^{-1}$, respectively. These concentrations correspond to a 4.80% conversion of the initial ammonia to oxidized species.

As was stated in the introductory section, as far as we know, there are no

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* The decrease of the *pH* value is in contrast to Eq. (4/4 a), however, concurrently with conductance band reduction processes, the valence band oxidation processes are also occuring (Eqs. (2) and (3)). In addition, evaporation of NH_3 would also cause a decrease in *pH*.Therefore, the decrease reflects the sum-total of various processes.

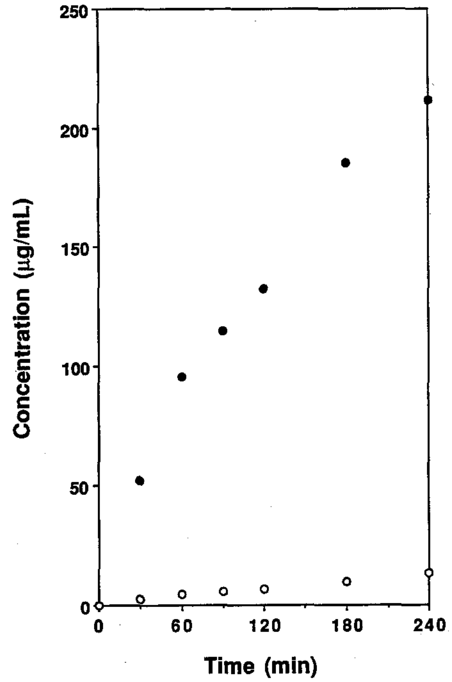

Fig. 2. Results of irradiation of a 0.1 *M* ammonia solution; concentrations of NO_2^- (●●●), and NO_3^- (○○○) as a function of irradiation time

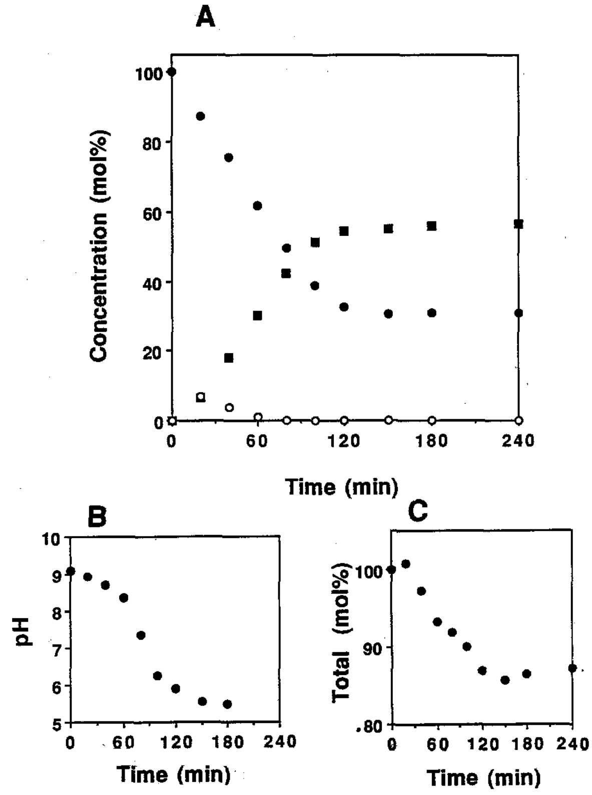

Fig. 3. Results of irradiation of an ammonium ion/ammonia solution ($10.0\,\mu g\,ml^{-1}$); initial *pH* was adjusted to 9.1. (**A**) Concentrations (mol%) of NH_4^+/NH_3 (●●●), NO_2^- (○○○), and NO_3^- (■■■) as a function of the irradiation time; (**B**) *pH* as a function of irradiation time; (**C**) total concentration (mol%) of all nitrogen containing species detected as a function of the irradiation time

reports of the photocatalytic oxidation of ammonium ion. Thus, it was of interest to establish what effects the initial *pH* of the NH_3/NH_4^+ solution would have on the rate and products of the corresponding photo-oxidation reactions. The results of the speciation studies when a 10.0 µg ml^{-1} ammonium ion solution was irradiated in the presence of a TiO_2 photocatalyst are illustrated in Fig. 3. In this experiment oxygen was also bubbled through the solution at a rate of 1 l min^{-1}. The solution *pH* was adjusted by a sodium-hydroxide solution to 9.1 at the beginning of the experiment. At this *pH* value the ratio of the concentrations of NH_4^+ to NH_3 should be about 1.4. As may be seen from Fig. 3 A, in which the concentration profiles for ammonium ion (ammonia), NO_2^- and NO_3^- are shown, the nitrate concentration reaches a level of 54.3 mol% within 120 minutes of irradiation and then stays essentially constant for the duration of the experiment. The concentration of ammonium ion (ammonia) decreases from an initial 100 mol%, within the same time span of 120 minutes, to approximately 33 mol%. Concurrently, the NO_2^- concentration only increases for the first 20 minutes of irradiation, and after about an hour it drops back to a 0 mol% level. The increase in NO_2^- concentration occurs at relatively high *pH* values (Fig. 3B). As soon as the *pH* decreases below 8.3, the concentration of NO_2^- decreases to zero. This is in agreement with a recent finding [9] that NO_2^- in neutral aqueous solution is relatively rapidly oxidized in the presence of TiO_2 to NO_3^-. As may be seen from Fig. 3C, mass balance calculations indicate that the species analyzed for (NH_4^+/NH_3, NO_2^- and NO_3^-) account for between 101 – 86% of the initial amount of NH_4^+/NH_3. The substantial rate of decrease in total mol% concentration coincides with higher *pH* values, when it is plausible that some of the ammonia may be lost from the solution by volatilization.

Figure 4 shows the NO_3^- ion concentration profiles for different initial *pH* values for 10.0 µg ml^{-1} ammonium ion solutions. The corresponding concentration profile for the *pH* 6.95 experiment is not shown since it was nearly identical to the

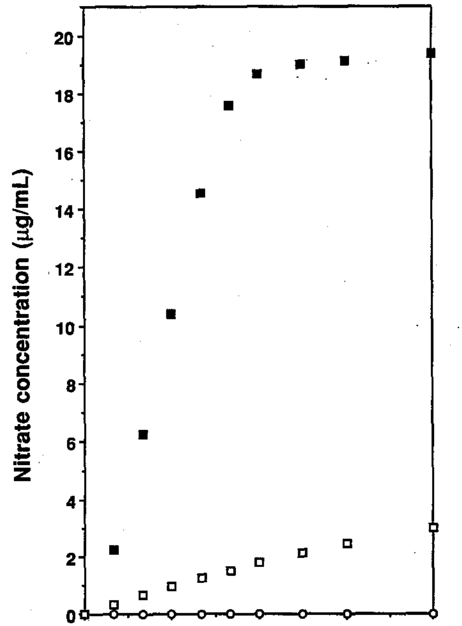

Fig. 4. Effect of *pH* on the rate of nitrate formation. Results of irradiation of ammonium ion/ammonia solutions (10.0 µg ml^{-1}) differing in the initial *pH* value; *pH* 9.1 (■■■), *pH* 4.8 (□□□), and *pH* 1.6 (○○○)

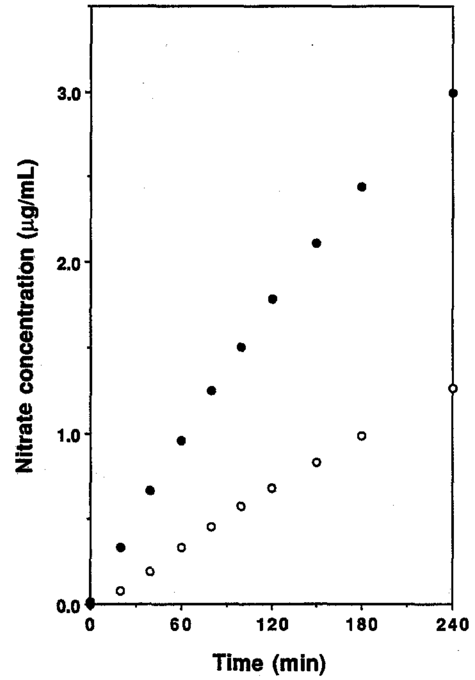

Fig. 5. The effect of the apparent concentration of the catalyst on the rate of nitrate formation. Results of irradiation of ammonium ion/ammonia solutions (10.0 µg ml^{-1}) differing in the amount of a TiO_2 photocatalyst added; 0.040 g (●●●), and 0.400 g (○○○)

pH 4.8 profile. All of these experiments lasted four hours and oxygen was bubbled through the solution continuously at a rate of 1 l min^{-1}. As may be seen from Fig. 4, the highest rate of NO_3^- ion formation and highest efficiency for the conversion of ammonium ion was obtained when the initial *pH* was adjusted to 9.1. This was the only experiment in which nitrite ion was also detected. As expected, the photo-oxidation reaction does not occur at all at the lowest *pH* value (1.6).

The effect of the apparent catalyst concentration on the rate of NO_3^- formation when oxygen was used as a sparging gas is illustrated in Fig. 5. Surprisingly, increasing the amount of TiO_2 from 0.040 to 0.400 g decreases the efficiency of the photocatalytic oxidation process. This unexpected phenomenon may be due to an increase in the opacity of the medium. It is also noteworthy that the same rate of NH_4^+ photo-oxidation was obtained irrespective of whether pure oxygen or air stripped of CO_2 was used as a sparging gas. This indicates that the partial pressure of oxygen is not a crucial factor in the photo-oxidation studied, as long as it is at or above the level achieved with air sparging.

The photocatalytic oxidation of NH_3 to NO_3^- changes the formal oxidation state of the N atom from −III to +V. From the data presented, the following reaction scheme summarizes the photocatalytic oxidation of ammonia:

$$TiO_2 + h\nu \Rightarrow (TiO_2) + h^+ + e^- \tag{1}$$

$$NH_3 + 2\,H_2O + 6\,h^+ \Rightarrow NO_2^- + 7\,H^+ \tag{2}$$

$$NO_2^- + H_2O + 2\,h^+ \Rightarrow NO_3^- + 2\,H^+ . \tag{3}$$

The conduction band reductive processes are usually represented by the following equations:

$$O_2+2e^- + 2H_2O \Rightarrow H_2O_2 + 2OH^- \text{ or} \tag{4}$$

$$\tfrac{1}{2}O_2+2e^- + H_2O \Rightarrow 2OH^- \tag{4a}$$

It is clear that reaction (2) which requires transfer of six holes summarizes two or more primary steps. Another possible pathway for the oxidation of ammonia to NO_2^- would be the reaction between adsorbed (chemisorbed) NH_3 and O_2 at the surface of the photocatalyst:

$$NH_3+O_2+2h^+ \Rightarrow NO_2^- + 3H^+. \tag{2a}$$

This process involves transfer of only two holes and is similar to the mechanism suggested recently [6] for the oxidative fixation of N_2.

Conclusion

The use of photocatalytic oxidation in the presence of a semiconductor may prove to be a viable method for conversion of ammonia (ammonium ion) to nitrite or nitrate, which may have significant implications regarding the obviation of ammonium ions in wastewater and, perhaps, chemical production of nitrates. Also it is clear that high *pH* values, at which the predominant species is ammonia, favor the formation of nitrite ion, whereas, when ammonium ion dominates (lower *pH*), the principal photo-oxidation product is nitrate ion.

Acknowledgements

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