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The effect of Pt oxidation state and concentration on the photocatalytic removal of aqueous ammonia with Pt-modified titania

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ABSTRACT

Platinum-modified titanium (IV) oxide (Pt-TiO_2) was used to photocatalytically oxidize aqueous ammonia selectively to nitrogen gas. The photocatalyst was solvent deposited on acrylic (PMMA) supports for use in simple distributive reactors. Pt was photodeposited on the titania surface within each reactor with concentrations ranging from 0.4% (w/w) to 5.1% (w/w) Pt. The oxidation state of the deposited Pt was subsequently modified using reduced phosphotungstic acid. Time-dependent kinetic studies were used to demonstrate the effect of oxidation state on the photocatalytic activity of the Pt-TiO_2. It was determined that treatment with reduced phosphotungstic acid enhanced the reaction rate and selectivity to nitrogen gas of the Pt-TiO_2 photocatalysts. Most significantly, treatment of Pt-TiO_2 with reduced phosphotungstic acid shifts the optimum Pt concentration to higher Pt loadings. The reactor containing 3.2% (w/w) post-treated Pt demonstrated the most favorable combination of NH_3 degradation rate and selectivity to N_2, resulting in the removal of 28.34% total nitrogen from 1.7 L of a 45.5 ppm NH_3-N solution within 72 h.

1. Introduction

Ammonia is a common water contaminant that has notable effects upon the environment and human health when present in excess amounts. Environmental sources of ammonia include fertilizers, herbicides, pesticides, and industrial solvents [1,2]. Due to ammonia's toxicity, the World Health Organization has set the maximum concentration of ammonia in drinking water at 1.24 ppm NH_3-N [3]. Most current methods used to remove aqueous ammonia, such as breakpoint chlorination and ion exchange, merely sequester the ammonia rather than truly removing it from the environment. Biological denitrification, which does truly remove aqueous ammonia, is limited to applications within certain temperature, pH, and toxicity ranges [4,5].

A relatively new method to remove ammonia that could overcome many limitations of existing methods is photocatalytic oxidation using titanium (IV) oxide (titania) [1,3,5,6]. Titania is activated by absorbing ultraviolet light ($\lambda < 375$ nm) (Eq. (1)).

$$TiO_2 + h\nu \rightarrow h^+ + e^- \tag{1}$$

The resulting valence band hole (h^+) and conduction band electron (e^-) can be consumed in the catalyzed oxidation and reduction reactions, respectively. Specifically, the hole can split an adsorbed water molecule producing a hydroxyl radical as shown in Eq. (2) [3].

$$h^+ + H_2O \rightarrow H^+ + {}^{\bullet}OH \tag{2}$$

The hydroxyl radical serves as the primary reactive species facilitating ammonia oxidation to nitrogen gas (Reaction Scheme 1.1) or to nitrate (Reaction Scheme 1.2) [3].

Reaction Scheme 1.1:

$$NH_3 + {}^{\bullet}OH \rightarrow NH_2 + H_2O$$

$$NH_2 + {}^{\bullet}OH \rightarrow NH + H_2O$$

$$NH + {}^{\bullet}OH \rightarrow N + H_2O$$

$$NH_x + NH_y \rightarrow N_2H_{x+y}(x, y = 0, 1, 2)$$

$$N_2H_{x+y} + (x+y)h^+ \rightarrow N_2 + (x+y)H^+$$

Reaction Scheme 1.2:

$$NH_3 + {}^{\bullet}OH \rightarrow HONH_2 + H^+$$

$$HONH_2 + {}^{\bullet}OH \rightarrow NO_2{}^- \rightarrow NO_3{}^-$$

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The presence of the intermediate NH_x and $HONH_2$ species in the production of N_2 and NO_3^-, respectively are important differentiators between the two mechanisms. Therefore, a determining factor for selectivity to N_2 is the formation and stabilization of these species [3].

A solvent deposition method was used to apply the titania to the surface of the acrylic [7]. Utilization of deposited titania is desirable because it precludes the need for post-use filtration to remove the photocatalyst. This benefit is significant in field applications where the cost in time and materials related to post-use filtration is a decided disadvantage for non-deposited photocatalytic materials. For the work reported here, the dependable deposition of the photocatalyst facilitated laboratory investigations because it permitted the time-dependent investigations of the oxidation of ammonia without altering the concentration of the photocatalyst by repeated sampling. While several reports have been published for the photocatalytic oxidation of gaseous ammonia with titania deposited on various support materials [8–10], previous reports of photocatalytic oxidation of aqueous ammonia with titania have involved suspended titania [1,3,5,6,11,12]. This is likely due to the higher adhesion strength and durability requirements for a titania-support composite material designed for use in an aqueous environment. The titania–acrylic composite materials reported herein have sufficient titania adhesion strength to facilitate the long-term durability needed for aqueous applications. The highly cross-linked nature of the acrylic materials used has been shown to resist the oxidation of the polymeric support that would otherwise be expected to rapidly occur [7]. Additional benefits of using these titania–acrylic composite materials include increased ultraviolet transmission of the acrylic support material, increased adhesion strength, and comparable photocatalytic activity of the deposited titania as compared to glass-supported titania [7].

Modification of titania with a metal is commonly practiced as it has been demonstrated to enhance titania's photocatalytic efficiency by altering substrate/photocatalyst interactions, permitting utilization of the visible spectrum, and trapping titania's conduction band electrons [3,12,13–22]. The deposited titania was modified with Pt because Pt adsorbs ammonia, stabilizes NH_x intermediates, and has a low overpotential to gasification [3,16].

The photocatalytic effectiveness of Pt-TiO_2 can be enhanced by controlling the Pt morphology, concentration, and oxidation state [12,19–22]. Studies to determine the optimum Pt concentration needed for the oxidation of ammonia via titania photocatalysis have concluded that low concentrations of Pt ($\leq$0.5%, w/w) yield optimal results [3,12]. The effect of the Pt oxidation state upon the ideal Pt concentration needed for ammonia oxidation has not been previously reported. A study noting the effect of platinum oxides (PtOx) upon the ability of Pt-TiO_2 to degrade percholoroethylene and 4-chlorophenol concluded that treating Pt with reduced phosphotungstic acid, a polyoxometalate (POM) which reduces the oxidation state of the Pt, greatly affects the photocatalytic degradation of perchloroethylene but does not influence the photocatalytic degradation of 4-chlorophenol [21]. Since the effects of the oxidation state of Pt were substrate-specific, it is difficult to draw general conclusions about the implications of oxidation state on other photocatalytic reactions. For this reason, the role of the oxidation state of Pt in the photocatalytic degradation of ammonia using platinized titania is reported here.

The morphology and oxidation state of the Pt can be varied depending upon the pH and time required for photodeposition. It has been shown that Pt photodeposition under high pH conditions results in optimum particle morphology, yet increases the concentration of Pt oxides during initial Pt photodeposition [21,22]. Treatment of the Pt-TiO_2 with reduced POM can be used to reduce the Pt photodeposited under high pH conditions [21]. When placed into contact with oxidized Pt, the reduced acid is oxidized and the deposited Pt is concomitantly reduced.

A complete study of the ideal metal loading on the titania surface should include the control of both the Pt amount and oxidation state. Ideally, the optimum concentration and oxidation state of Pt should not only result in a high degradation rate of aqueous ammonia, but should also maximize selectively to the production of nitrogen gas.

In this work, the effect of varying the oxidation state of Pt upon the concentration of Pt needed to efficiently and selectivity oxidize aqueous ammonia using titanium dioxide is reported. The degradation rate of ammonia and the selectivity to nitrogen gas for titania modified with a range of Pt concentrations, both before and after treatment of deposited Pt with POM, are reported herein. The selectivity and degradation rate are expressed in terms of rate constants derived from numerical fits to the experimental data.

2. Experimental methods

2.1. Materials

The titania powder (P-25) was provided by Degussa. All water (resistivity 18.6 MΩ/cm) used was from a Millipore MilliQ A-10 system. The acrylic, poly(methyl methacrylate), used was 4.76 mm thick Acrylite OP-4 from Cyro Industries. Chloroplatinic acid, phosphotungstic acid, ammonium hydroxide, dichloromethane (Optima grade), and methanol (HPLC grade) were purchased from Fisher Scientific. Glacial acetic acid was obtained from Mallinckrodt. Ethanol (95% (v/v)) from Mallinckrodt was used as the electron donor for all Pt photodeposition solutions. The sodium hydroxide (40% (w/v)) used for all experimentation was obtained from Ricca Chemical Company. The illumination sources were 400 W Hg-vapor lamps with glass jackets to minimize exposure of short-wave UV light. All reagents were used as received.

2.2. Titania–acrylic composite reactors

As described elsewhere, titania dispersions were prepared at a concentration of 2.6% (w/v) with a solvent consisting of 90% (v/v) dichloromethane and 10% (v/v) methanol and applied to the surface of the acrylic support [7]. A series of titania-containing reactors were fabricated from these titania–acrylic materials, and used for the photocatalytic degradation of ammonia. This simple distributive type reactor was constructed based on a prior design [7,23]. Fig. 1 shows the diagram of this reactor. The reactor was 19 cm × 8 cm × 6.4 cm and had a total internal solution volume of 408 mL. Nineteen internal fins (5.0 cm × 7.0 cm) were inserted alternately on each wall to allow the aqueous solution to flow through the reactor. The reactor was assembled using dichloromethane as the adhesive solvent. With the exception of the two 8.0 cm × 6.4 cm end pieces, every surface on the interior of the reactor was coated with titania. Titania having a mass of 1.0 g was spread over an internal surface area of approximately

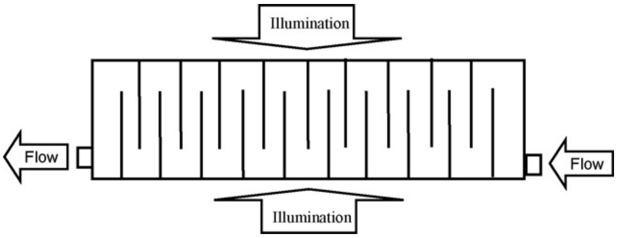

Fig. 1. Reactor schematic.

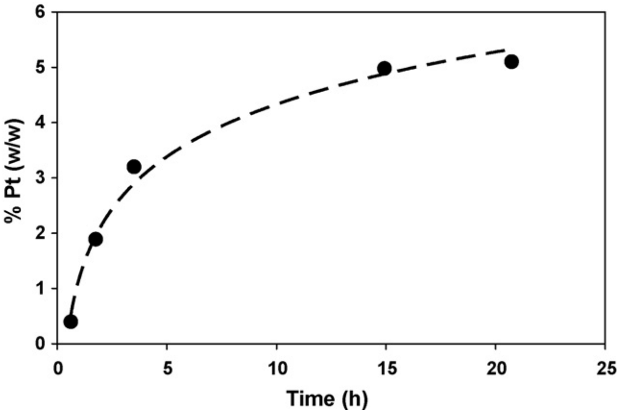

Fig. 2. % (w/w) Pt deposited as a function of illumination time. The line drawn through the data represents a logarithmic fit.

1740 cm^2 providing an average coverage of 0.57 mg/cm^2. The ends were assembled with hose barb fittings for connection to the pump and sample reservoir via vinyl tubing.

A lamp was placed 7 cm from both sides of the reactor so that the light was coupled directly into the acrylic walls and fins of the reactor. A submersible pump in a polypropylene solution reservoir was used to circulate the solution through the reactor with a flow rate of 5.8 L/min. The solution temperature in the reservoir was maintained at 29 °C throughout the reaction by pumping cooled water from a constant temperature bath through loops of vinyl tubing immersed in the reservoir.

2.3. *Surface modification with Pt*

The surface of the deposited titania was modified by the addition of Pt using a method adopted from a prior report [3]. A 50 ppm Pt solution was prepared from chloroplatinic acid and 58 mL of ethanol was added as the electron donor. In order to produce relatively small, monodisperse particles, the pH of the solution was adjusted to 12 with NaOH [22]. The resulting solution was pumped through the reactor using the aforementioned apparatus. The time required for photodeposition varied depending upon the concentration of Pt desired. The amount of residual Pt in the solution was quantified using atomic absorption spectroscopy and was used to determine the amount of Pt that was photodeposited on the titania surface.

2.4. *Chemical treatment of deposited Pt*

After the photocatalytic activity of the platinized titania was determined, the deposited Pt was chemically treated with reduced phosphotungstic acid. A 2.0 L solution of 4.5 mM POM containing 200 mL of ethanol and 10 mL of acetic acid was photocatalytically reduced (Eq. (3)) using titanium dioxide before being used to treat the deposited Pt.

$$PW_{12}O_{40}{}^{3-} + e^- \rightarrow PW_{12}O_{40}{}^{4-} \qquad (3)$$

The titania used for the reduction of the POM was supported in a reactor identical to those utilized in the photocatalytic oxidation of ammonia. The utilization of deposited titania for the POM reduction precluded the need to filter titania from the reduced POM solution prior to use. The reduced POM solution was then circulated through a platinized titania reactor and kept in the dark for 16 h while the reduced POM reduced the deposited Pt as follows:

$$n\mathrm{POM}^- + \frac{\mathrm{Pt}^{n+}}{\mathrm{TiO_2}} \rightarrow n\mathrm{POM} + \frac{\mathrm{Pt}^0}{\mathrm{TiO_2}} \qquad (4)$$

2.5. *Characterization of Pt-TiO$_2$*

The characteristics of the titania–acrylic interface and surface uniformity of the applied titania were assessed using scanning electron microscopy (Hitachi H-5000 SEM). Transmission electron microscopy (TEM) was performed with a Hitachi H-8100 TEM and was used to probe the morphology of the photodeposited Pt. The Pt-TiO_2 particles analyzed in this manner were removed from the acrylic support material, suspended in methanol, and loaded on TEM grids. Energy-dispersive analysis by X-rays (EDAX) was performed using a Hitachi S4300 SE/N SEM working at an accelerating voltage of 12–15 kV. EDAX was used to verify the metallic composition of the samples following chemical treatment with POM. Variation in the oxidation states of the deposited Pt before and after exposure to POM was investigated with X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra-Imaging X-ray Photoelectron Spectrometer) using mono(Al) as an excitation source. The reference peak used for all data was C 1s (284.5 eV).

2.6. *Photocatalytic ammonia oxidation using Pt-TiO$_2$ acrylic reactors*

A series of reactors, constructed from titania–acrylic materials, were modified with concentrations of Pt ranging from 0 to 5.1% (w/w). The oxidation rate of ammonia and selectivity to nitrogen gas were subsequently quantified for comparison between reactors of varying Pt oxidation states and/or concentrations using a kinetic model derived from Reaction Schemes 1.1 and 1.2.

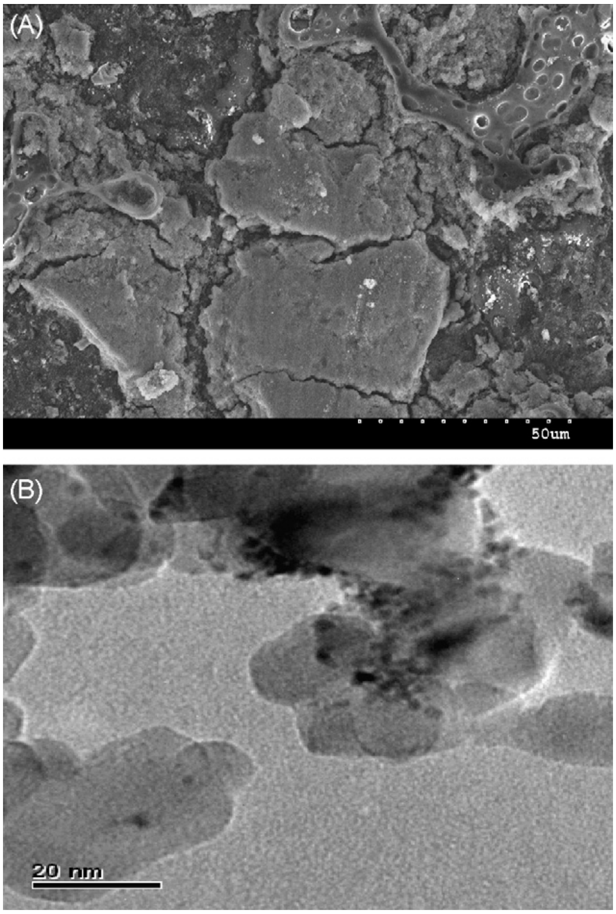

Fig. 3. (A) SEM image of platinized titania deposited on sanded acrylic. (B) TEM image of Pt deposited on titania under high-pH conditions.

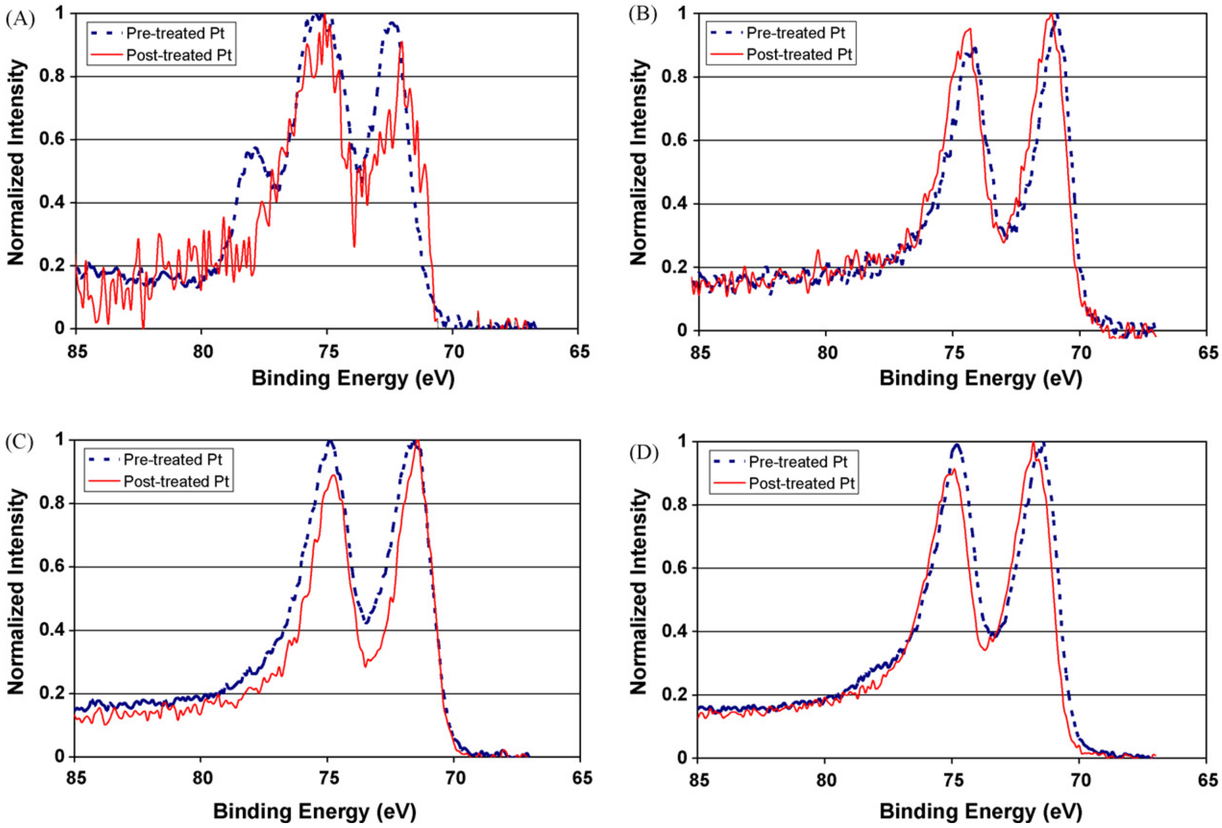

Fig. 4. Normalized XPS data for 0.78% (w/w) Pt (A), 2% (w/w) Pt (B), 4% (w/w) Pt (C), and 5% (w/w) Pt (D) before and after chemical reduction. The peaks at 71.5, 74.8, and 78.0 eV are assigned as Pt^0, Pt^{2+}, and Pt^{4+} respectively.

Reaction Schemes 1.1 and 1.2 can be summarized as shown in Eqs. (5)–(7),

$$NH_3 \rightarrow N_2, \quad k_1 \tag{5}$$

$$NH_3 \rightarrow NO_2^-, \quad k_2 \tag{6}$$

$$NO_2^- \rightarrow NO_3^-, \quad k_3 \tag{7}$$

where k_1, k_2, and k_3 are the rate constants for Eqs. (5)–(7), respectively. Rate constants k_1, k_2, and k_3 were determined using numerical fits to the experimental data. Since the degradation of NH_3 is accomplished through two presumably first-order processes (Eqs. (5) and (6)), the observed first-order rate constant (k_{obs}) can be interpreted as the sum of k_1 and k_2. k_{obs} was determined by a least-squares fit of the experimental time-dependent NH_3 concentrations (Eq. (8)).

$$[NH_3] = [NH_3]_0\, e^{-k_{obs}t} \tag{8}$$

Values for k_2 and k_3 were determined by least-squares fits to the time-dependent NO_2^- concentration (Eq. (9)).

$$[NO_2^-] = \frac{k_2}{k_3 - k_2}(e^{-k_2 t} - e^{-k_3 t})[NH_3]_0 \tag{9}$$

The value of k_1 was then calculated as the difference between the k_{obs} and k_2. The ratio of k_1 to k_{obs} was utilized as a metric for the selectivity of the reaction to N_2 since the relative magnitude of this ratio is indicative of the NH_3 degradation pathway followed. The sum of k_1 and k_2 (k_{obs}) was used to compare the overall rates of NH_3 oxidation for the various materials tested.

The pH of the reactant solutions probed were maintained at 10 with NaOH to ensure that the NH_3-N was present primarily in the form of NH_3 and not NH_4^+ ($pK_a = 9.3$). Samples were periodically collected over a 72 h period and the concentration of dissolved nitrogenous species at each sampling interval was determined. Ion selective electrodes were used to determine concentrations of NH_3-N (Denver Instruments, 300740.0) and NO_3-N (Orion 9700BNWP), while NO_2-N concentrations were determined spectrophotometrically (EPA method 353.3). The total aqueous nitrogen present was calculated as the sum of the nitrate, nitrite, and ammonia concentrations. It has been previously demonstrated that these three species, in addition to N_2, are the only detectable nitrogenous species involved in the photocatalytic oxidation of ammonia with $Pt\text{-}TiO_2$ [3].

2.7. *Control experiments*

Four control reactors were utilized to verify the role of Pt, pH, and light in the oxidation of ammonia. The influence of Pt was probed by determining the selectivity and degradation rate of a reactor containing unmodified titania. The photocatalytic activity of a reactor under neutral pH conditions was measured to determine whether or not ammonium could be degraded in the same manner as ammonia. The role of light in the oxidation of ammonia was investigated using two reactors, one that lacked any photocatalyst and a second that was kept in the dark for 72 h.

3. Results

3.1. *Surface modification with Pt*

The time required to deposit a desired amount of Pt depends on the concentration of Pt deposited (Fig. 2). Reactors containing higher concentrations of deposited Pt required a substantially longer time for photodeposition since the Pt concentration of the solution becomes depleted as the photodeposition proceeds.

3.2. *Characterization of Pt-TiO$_2$*

The interface between the Pt-TiO$_2$ and acrylic and the surface uniformity of the photocatalyst were assessed at a magnification of 900× using SEM (Fig. 3A). As seen in the TEM image (Fig. 3B), fairly monodisperse Pt particles (d = 3–4 nm) were photodeposited on the surface of the titania nanoparticles (d = 30–40 nm).

XPS analysis of Pt-modified samples before and after exposure to the POM was performed in order to confirm changes in Pt oxidation state due to POM. Fig. 4 displays these XPS spectra demonstrating that the effects of the POM on deposited Pt were not uniform at all metal loadings. The XPS peaks (Pt 4f) located at binding energies of 71.5, 74.8, and 78.0 eV are attributed to Pt^0, Pt^{2+}, and Pt^{4+}, respectively [21,22]. The spectra are normalized to yield a maximum peak height of 1.0 on each spectrum. This allows the effect of the POM to be observed by comparing the relative peak heights of the various Pt species before and after POM exposure. The most striking change in oxidation state observed was for the reactor containing 0.78% (w/w) Pt where the Pt^{4+} was reduced primarily to Pt^0. For samples which did not initially possess Pt^{4+}, substantial changes in oxidation state were observed at moderate metal loadings (4% (w/w)) with smaller relative differences at both higher and lower Pt concentrations. The 4% (w/w) Pt sample showed the greatest conversion from Pt^{2+} to Pt^0 after POM treatment as shown by the reduction in the Pt^{2+} peak. The presence of tungsten was identified by XPS and EDAX in reactors following chemical treatment with phosphotungstic acid. The amount of tungsten present was irrespective of the Pt concentration.

3.3. *Photocatalytic ammonia oxidation using Pt-TiO$_2$ acrylic reactors*

The concentration of ammonia in each reactor that contained Pt-TiO$_2$ decreased exponentially with time while the concentration of the intermediate (NO_2^-) increased before its conversion to NO_3^- began to deplete the NO_2^- concentration. The NO_3^- formation in each reactor is best described linearly (slope reported as m_4) as shown in Fig. 5. This figure shows the concentrations of NH_3, NO_2^-, and NO_3^- as a function of time for the reactor containing 3.2% (w/w) Pt both before and after POM treatment.

Fig. 6 shows the trends for k_1, k_2, k_3, and m_4 for all materials studied both before and after exposure to POM. As can be seen from Fig. 6, the photocatalytic activity of Pt-TiO$_2$ changed following POM treatment. In general, k_1 and k_2 both increased following treatment of the deposited Pt, but the change in k_1 exceeded the change in k_2. k_3 and m_4 both decreased after the Pt was exposed to POM (Fig. 6). The net result of these changes is that the selectivity and degradation rate of the reactors containing post-treated Pt is higher than that of their pre-treated counterparts.

Prior to treatment of the deposited Pt with POM, reactors containing Pt concentrations greater than 1.7% (w/w), exhibited lower k_1 and k_2 rate constants than that of unmodified titania. Following exposure to POM, reactors containing Pt in excess of 1.7% (w/w) exhibited higher k_1 and k_2 rate constants, but k_1 increased more than k_2 thereby making the post-treated Pt more selective than their pre-treated counterparts and more active than unmodified titania. k_3 also decreased after the Pt was exposed to POM. In general, post-treated Pt materials show a dependence of selectivity on the amount of Pt. This comes at the expense of a reduced reaction rate for metal loadings greater than 1.7% (w/w) Pt.

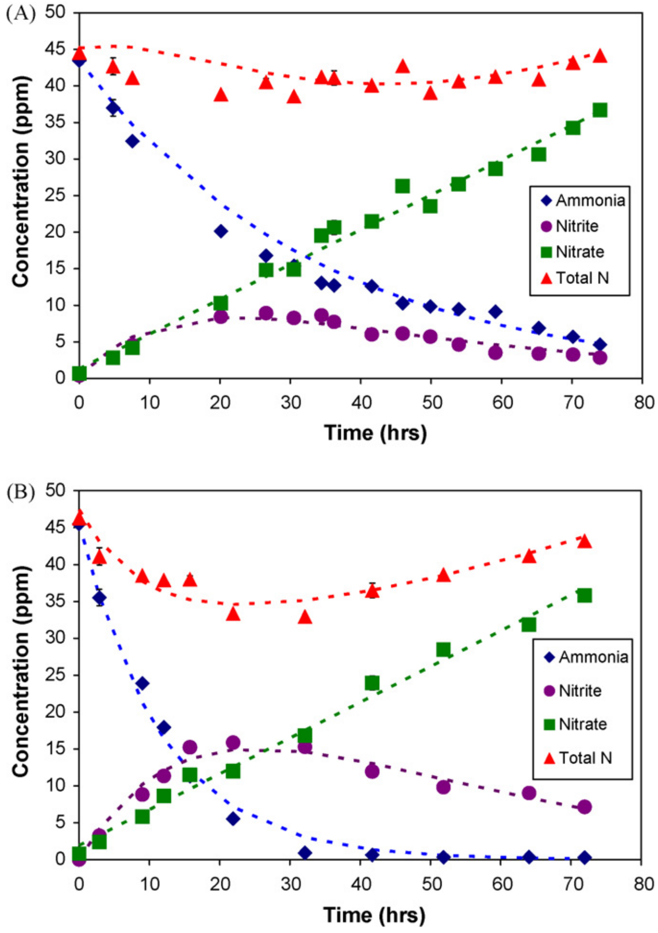

Fig. 5. Concentrations of nitrogenous species over a 72 h period for a reactor containing 3.2% (w/w) Pt. (A) NO_3^-, NO_2^-, and NH_3 before exposure to POM. (B) NO_3^-, NO_2^-, and NH_3 after exposure to POM. Dashed lines represent numerical fits to the data as described in the text. Error bars representing one standard deviation from replicate analysis are shown for nitrate, nitrite, ammonia, and total nitrogen concentrations at several reaction times.

3.4. *Durability*

To determine the durability of the reactors used for this study, a reactor containing 5.1% (w/w) Pt was exposed to the reaction conditions for a cumulative time of 1100 h. After this time period, the photocatalytic activity increased as compared to the initial run following exposure to POM. The rate constants k_1, k_2, and k_3 for the ammonia degradation experiment begun after 1100 h of reactor use were 0.115 h^{-1}, 0.0632 h^{-1}, and 0.0276 h^{-1}, respectively, as compared to the initial rate constants of 0.0397 h^{-1}, 0.0248 h^{-1}, and 0.0311 h^{-1}. The selectivity of the Pt therefore increased from 0.616 to 0.645 and the oxidation rate (k_{obs}) correspondingly increased from 0.0644 h^{-1} to 0.178 h^{-1} after 1100 h of use.

3.5. *Control reactors*

The control reactor consisting of sand-blasted acrylic with no photocatalyst indicated a slight decrease in total nitrogen with a slope of 0.060 ppm/h over a 72 h period. This reduction in total nitrogen was presumably due primarily to ammonia volatilization, although a slight oxidation of ammonia to nitrite (1.9 ppm) and nitrate (5.0 ppm) was also observed. The NH_3 concentration decreased by a total of 24.8% during this 72 h period. A control reactor tested with a 50 ppm NH_3 solution at neutral pH for 16 h showed

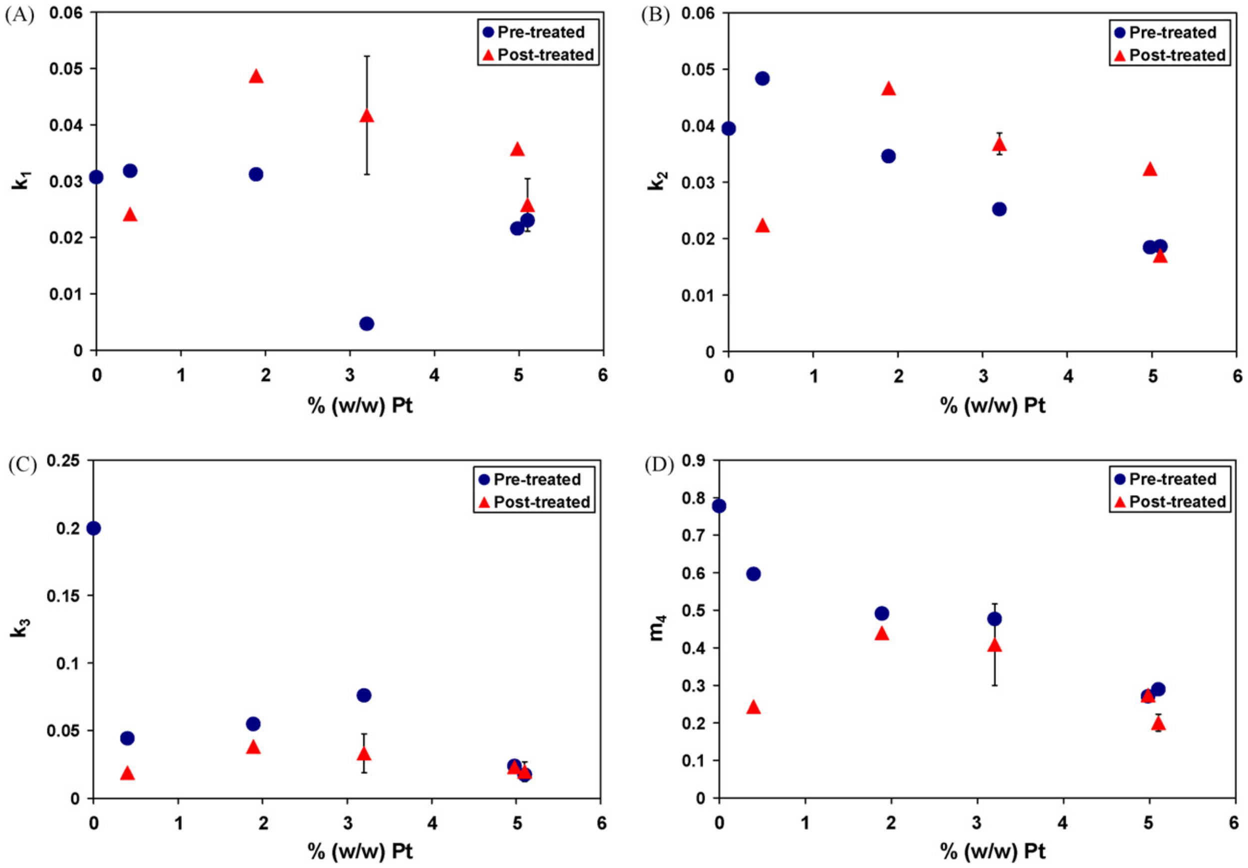

Fig. 6. k_1 (A), k_2 (B), k_3 (C), and m_4 (D) of Pt reactors tested before and after chemical reduction with POM. Error bars representing one standard deviation from replicate analysis are shown for 0.4%, 3.2%, and 5.1% (w/w) Pt following exposure to POM.

a concentration increase of dissolved nitrogenous species that was attributed to absorption of nitrogen gas into the solution [24,25]. A dark control reactor resulted in a total nitrogen degradation rate of 0.0401 ppm/h with a corresponding production of small amounts of nitrite (0.4 ppm) and nitrate (4.5 ppm) in a period of 73 h. The NH_3 concentration in the dark control reactor decreased by a total of 19% during the 73 h period.

4. Discussion

4.1. Characterization of Pt-TiO_2

Fig. 3(A) shows an SEM image of a titania–acrylic composite sample. The fissures evidenced on the surface of the acrylic are likely due to re-hardening of the acrylic upon evaporation of the solvent [7]. An important observation from this SEM image is that there is no evidence of significant burying of the titania within the support material as has been observed with other titania deposition techniques [7]. The titania was successfully adhered to the acrylic material with minimal loss of exposed titania surface area due to coverage with acrylic.

The TEM image of Pt-TiO_2 (Fig. 3(B) demonstrates the uniform deposition of Pt in an alkaline environment onto the titania–acrylic materials. This behavior has been attributed to the nature of the electrochemical interaction between the titania surface and anionic $PtCl_6^-$ species. At pH values higher than the isoelectric point of titania (pH 6.25), the $PtCl_6^-$ anions and dominant hydrolyzed products are repulsed by the negatively charged titania surface thus decreasing their local concentrations and corresponding deposition rate [22].

The lack of dependence of the concentration of tungsten (as determined with EDAX and XPS) upon the amount of Pt deposited, indicates that although the presence of tungsten may have an effect on the photocatalytic activity, the tungsten does not explain the dependence of the photocatalytic activity on the amount of Pt or the shift in this dependence accompanying treatment of Pt with POM.

4.2. Photocatalytic ammonia oxidation using Pt-TiO_2 acrylic reactors

In general, it seems that for the pre-treated Pt, low metal concentrations increase the selectivity and oxidation rate of ammonia. Further increases in the amount of Pt result in a decrease in k_1 and k_2. This reduction in k_{obs} indicates clearly that the overall photocatalyzed degradation of ammonia has been slowed by the presence of excessive Pt. The increase in k_1 at higher concentrations (greater than 3.2% (w/w) Pt) is indicative of the simultaneous importance of the amount of metal present and the oxidation state of the metal. The logarithmic nature of the time dependence of the Pt deposition shown in Fig. 2 results in exceedingly long deposition times required for the highest Pt concentrations. It has been previously shown that with long photodeposition times, the deposition of reduced Pt is increasingly favored [21]. The decrease in this photodeposition rate at higher concentrations (4–5% (w/w)) gives rise to increased concentrations of reduced Pt. A Pt concentration near 3–4% (w/w) is undesired as it is comprised mainly of PtOx which will favor k_2 rather than k_1, thereby decreasing selectivity and the rate of N_2 formation. Pt concentrations in the 4–5% (w/w) range, however, have higher con-

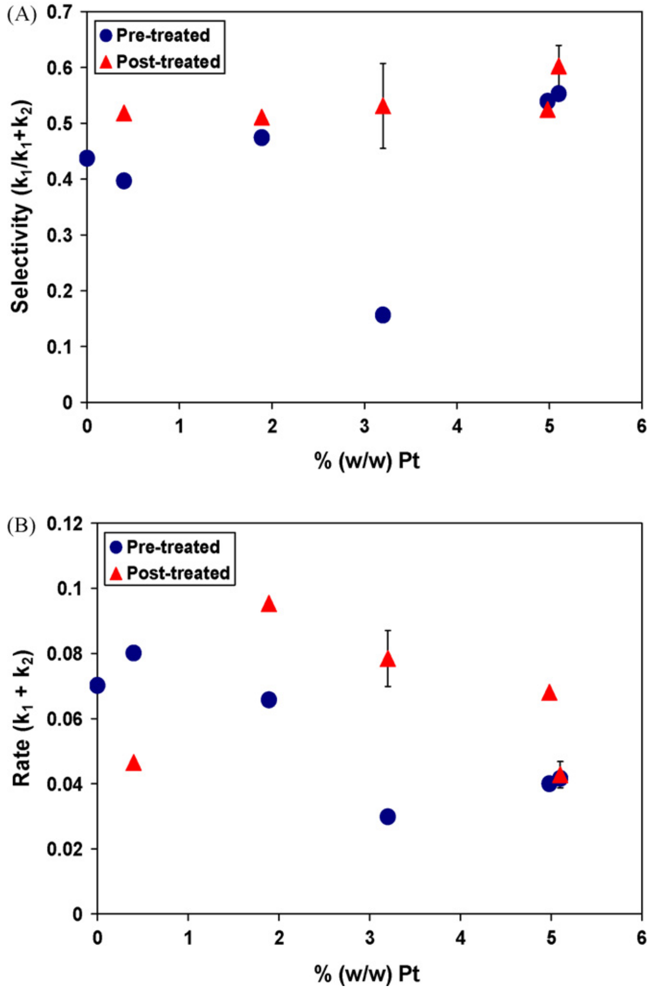

Fig. 7. Selectivity (A) and degradation rate (B) expressed in terms of k_1 and k_2 as a function of the concentration of Pt in various reactors tested before and after reduction of deposited Pt. Error bars representing one standard deviation from replicate analysis are shown for 0.4%, 3.2%, and 5.1% (w/w) Pt following exposure to POM.

centrations of Pt^0 and thus the value of k_1 increases at the expense of k_2.

Pt oxides have an inhibiting effect upon the oxidation rate and selectivity of titania-catalyzed ammonia oxidation due to their inability to stabilize intermediate NH_x species and their role as recombination centers for electron–hole pairs via the cyclic oxidation and reduction of Pt^{2+} and Pt^{4+} [21]. Recombination of electron–hole pairs inhibits the desired redox reaction by limiting the concentration of hydroxyl radicals produced. This reduction in the production of hydroxyl radicals not only depresses the reaction rate but may also have an effect on the selectivity. As seen in Reaction Schemes 1.1 and 1.2, the proposed mechanism for nitrate production via ammonia oxidation utilizes fewer hydroxyl radicals than that of the mechanism that results in nitrogen gas. Therefore, the production of NO_3^- should be increasingly favored as the concentration of hydroxyl radicals is limited. Such a hypothesis is supported by the decrease in the selectivity (k_1/k_{obs}) with increasing Pt loading (up to 3.2% (w/w)) for pre-treated Pt-TiO_2. The rate and selectivity for each Pt concentration is shown in Fig. 7.

An additional determining factor in the production of nitrogen gas is the formation and stabilization of NH_x species as evidenced in Reaction Scheme 1.2. It has been noted that Pt^0 is able to stabilize these intermediates thereby encouraging the production of nitrogen gas [3]. This increased affinity for NH_x intermediates is supported by the observed increase in k_1 after the Pt in a reactor is chemically treated with POM (Fig. 6).

As shown by the XPS data in Fig. 4, there is an increase in the amount of reduced Pt present particularly for Pt concentrations between 3% (w/w) and 4% (w/w) after exposure to POM. In Fig. 4(C), this change is evident in the relative decrease in the Pt^{2+} peak following POM exposure. The greatest changes in k_1 and k_2 following exposure to POM also occur at these same concentrations of Pt. The maxima in Fig. 7 can be explained by the extent of change in the oxidation state of the Pt before and after treatment with POM. At low concentrations of Pt, the Pt was quickly deposited as PtOx; but because the Pt concentration is low, the overall benefit of the presence of Pt is modest, regardless of the oxidation state of the Pt. At high Pt loadings (4–5% (w/w)), there is a significant amount of Pt^0 already present, thereby limiting the effect of POM. At intermediate Pt concentrations, there is a substantial amount of metal present, but its initial state is still highly oxidized. For this reason, the intermediate metal loadings benefit the most from treatment with POM.

It is clear from Fig. 4 that while some of the deposited PtOx was reduced, a significant portion was not affected by POM. Even if the entire surface of the Pt particles was reduced to Pt^0 by the POM solution, the core of the particles may remain in a higher oxidation state. The apparently limited success of the chemical reduction of the Pt by the POM as demonstrated by Fig. 4 may be partially explained by the expected penetration depth of the XPS technique (~10 nm) being greater than the Pt particles' size. It is likely that the Pt that is on the surface is more reduced than the Pt in the core of the nanoparticles. It is this surface Pt that would be the most directly relevant to the photocatalyzed reaction rates.

Since substantial increases in the photocatalytic activity of Pt have been observed with modest reduction of PtOx, it would seem that further reduction could yield greater improvements in degradation rate and selectivity to nitrogen gas. This hypothesis is supported by the increased degradation rate of the post-treated Pt in the reactor containing 5.1% (w/w) Pt that was used for a cumulative time of 1100 h. It has been reported that as Pt-TiO_2 is continually used to catalyze an oxidation reaction, it can be increasingly reduced as some of the electrons donated by the oxidized species are utilized for the reduction of the Pt in addition to the more dominant reduction of the hydroxyl radicals present [21]. This subsequent reduction of Pt would be expected to manifest as a higher degradation rate and increased selectivity to nitrogen gas. As noted earlier, this increase in degradation rate and selectivity was observed.

4.3. *Control reactors*

The data obtained from the neutral pH reactor indicates that the required ammoniacal species for the photocatalytic oxidation of ammonia with titania is NH_3. This difference in reactivity is likely due to the enhanced interaction strength of ammonia with titania as compared to ammonium [1,3,12].

The concentration trends from the dark reactor indicate that the extent of NH_3 volatilization and its possible adsorption on the surface of the titania are both moderate. The amount of NH_3 volatilization should be independent of the amount and oxidation state of the Pt present. The total amount of NH_3 volatilization that was evidenced in the control reactors is clearly larger than the amount of NH_3 volatilization that occurred in the illuminated titania reactors since the photocatalytic process resulted in the removal of NH_3 in the solution, minimizing the amount available for volatilization over the 72 h timescale of the experiment.

5. Conclusions

When the concentration, morphology, and oxidation state of the Pt deposited on the surface of the titania are simultaneously controlled, the apparent optimum Pt concentration shifts from the previously reported 0.5% (w/w) Pt to 3.2% (w/w) Pt due to reduction of the deposited Pt. When the Pt was treated with POM, the reactor containing 3.2% (w/w) Pt demonstrated the most favorable combination of NH_3 degradation rate and selectivity to N_2, resulting in the removal of 28.34% total nitrogen from 1.7 L of a 45.5 ppm NH_3-N solution within 72 h.

The solvent deposition of titania on acrylic supports used in this work greatly facilitated the time-dependent kinetic studies of the ammonia oxidation. These kinetic studies are crucial to the selection of the optimum Pt loadings since they allow the observation of not only the degradation rates of the ammonia, but also the rates of production of nitrite and nitrate. Alternative methods should be explored to more fully reduce the deposited Pt as it can be assumed that such reduction will result in an enhanced selectivity to nitrogen gas and oxidation rate of ammonia.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2008.07.016.

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