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Photocatalytic reduction of nitrate ions on TiO_2 by oxalic acid

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Abstract

Using oxalic acid as a hole scavenger, the photocatalytic reduction of nitrate in aqueous dispersions of TiO_2 has been investigated. Oxalic acid accelerates the reaction considerably compared to the reaction in the absence of oxalic acid. In the presence of nitrate, the oxidation of oxalate is also accelerated. The reduction product of the nitrate is mainly ammonia. The effects of concentrations of nitrate, of oxalate, and of pH were studied. The adsorption of the reactants on TiO_2 is an important factor for accelerating the reaction.

Keywords: Oxalic acid; Nitrate; TiO_2

1. Introduction

Agricultural effluents and sewage result in excessive amounts of nitrate in water supplies. High levels of nitrate in domestic water cause cyanosis in young babies [1]. The WHO standards recommend that NO_3^- in drinking water should be less than 45 mg/l [2].

The photocatalytic reduction of nitrate on TiO_2 loaded with noble metals has been studied [3–5]. These investigations showed that titanium dioxide itself has no or almost no photocatalytic efficiency. It has been stated that the presence of the metal on the semiconductor is necessary for the photocatalytic reduction of NO_3^-.

In the case of the photocatalytic oxidation of organic materials, quantum efficiencies are limited by the effective rate of interfacial reduction (electron transfer) [6,7]. We believe that the same may happen in the reduction of nitrate. Hoffmann et al. [8] have proposed a general mechanism for the heterogeneous photocatalysis on TiO_2. The recombination of photogenerated electrons or holes with surface trapped charge carriers occurs fast on the TiO_2 surface: for holes, the characteristic time is about 10 ns; for electrons, it occurs in 100 ns. However, the charge transfer is relatively slow from the surface of TiO_2 to the adsorbed species: for oxidation, the hole transfer occurs in 100 ns; for reduction, electron transfer needs milliseconds. It can be concluded from the above that the interfacial electron transfer is the primary rate limiting step for the photocatalytic reaction on TiO_2.

For the photocatalyst to be efficient, the recombination of electrons and holes on the TiO_2 surface must be suppressed. It was reported that in Degussa P25 TiO_2 the lifetimes of electrons were markedly increased in the presence of 2-propanol as a hole scavenger [9]. Therefore, if suitable adsorbed species react irreversibly with photogenerated holes (i.e., surface bound hydroxyl radicals) the lifetime of the electrons is increased and the photocatalytic reduction efficiency on the surface of TiO_2 will be enhanced. In order to increase the reaction rate and quantum efficiency an effective hole scavenger is necessary.

In the present paper, the choice of oxalic acid as a hole scavenger for this process is based on the fact that it is an efficient hole scavenger [10] and it is also a water pollutant resulting from some industrial processes [11]. It is shown in our work that nitrate is photoreduced on TiO_2, which was not loaded with noble metals.

2. Experimental section

Degussa P25 TiO_2 powder (70:30% anatase-to-rutile) was used as photocatalyst without further treatment. The detailed characterization of this TiO_2 has been described elsewhere [8,12]. Nessler's reagent was received from Merck. All other reagents were of analytical grade.

The photocatalytic reaction was carried out using a double wall cylindrical pyrex cell. The reaction mixture (80 ml) inside the cell was maintained in suspension by means of a

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magnetic stirrer. As a light source, a medium pressure Hg vapor lamp, Heraeus TQ150 (150 W) was used. The IR fraction of the beam was removed by water in the double wall of the quartz and pyrex cell. Prior to irradiation, argon was bubbled through the reaction mixture for 30 min to remove oxygen. Then an argon balloon was attached to the reactor. The reaction was carried out at room temperature (21–23°C).

After irradiation, the solution was made alkaline and kept for 1 h to desorb the oxalate from the TiO_2 particles [13]. The catalyst was removed by centrifugation. The unreacted oxalate was determined by conventional permanganate titration. Ammonia was determined spectrophotometrically at 436 nm by means of Nessler's reagent [14]. Nitrate was analyzed by an ultraviolet spectrophotometric method [15], and the interference of oxalate was taken into account by measuring the absorbance of oxalate under the same conditions. The amount of oxalate in the solution was determined by titration. The pH values were measured using the pH meter WTW pH 526.

3. Results

3.1. Decomposition of oxalic acid under UV illumination ($\lambda \geq 300$ nm)

Oxalic acid decomposes very slowly under UV illumination [16]. In order to establish this effect, we measured the decomposition of oxalic acid in deoxygenated solutions in the absence of TiO_2 (Table 1). The photochemical conversion of oxalic acid was negligible and depended on the concentration (compare Table 1 with Fig. 1). In the presence of nitrate, the effect was even smaller. Nitrate was found to be stable over an irradiation time of 6 h, but traces of nitrite were qualitatively detected in the solution by diazo coupling with sulfanilic acid and α-naphthylamine. In the photocatalytic reaction, UV light was absorbed predominately by the suspended TiO_2 powder. The uncatalyzed decomposition was negligible.

3.2. Adsorption measurements

Following Domenech and Peral [13], the adsorption of oxalate on P25 TiO_2 was measured at different concentrations (Table 2). The adsorption of nitrate on TiO_2 was weaker. The adsorbed amount of nitrate for 1.0×10^{-3} M initial concentration was about one order of magnitude smaller than for the same concentration of oxalic acid.

Table 1
Photochemical conversion of oxalic acid under UV illumination in the absence of TiO_2

Initial concentration (M)	Illumination time (h)	Conversion $\tau=(C_0-C)/C_0$ (%)
5.2×10^{-3}	6	2.2
2.0×10^{-3}	6	2.8
5.2×10^{-3a}	6	0.7

[a] In the presence of 1.0×10^{-3} M KNO_3.

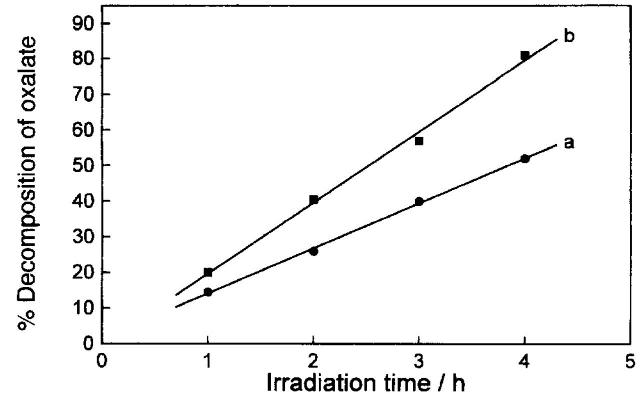

Fig. 1. Time course of the photocatalytic reaction; ●: reacted NO_3 and ■: formed NH_3. Reaction conditions: 80 ml solution containing 1.0×10^{-3} M NO_3^- and 5.2×10^{-3} M $H_2C_2O_4$, TiO_2: 0.2 g.

Table 2
Moles of oxalate adsorbed on TiO_2 after stirring 25 ml solution containing 0.25 g TiO_2 at different initial concentrations for 60 min in the dark at 22°C (natural pH)

Initial concentration of oxalic acid (M)	Moles of oxalate adsorbed on TiO_2
1.0×10^{-2}	2.2×10^{-5}
8.0×10^{-3}	2.2×10^{-5}
5.2×10^{-3}	2.1×10^{-5}
3.0×10^{-3}	1.9×10^{-5}
1.0×10^{-3}	1.7×10^{-5}
7.5×10^{-4}	1.5×10^{-5}

The adsorption of oxalate can be described by a Langmuir type isotherm [11] $\theta=KC/(1+KC)$. The data of Table 2 yielded $K=2.7\times10^3$ M^{-1}, which may be compared with $K=4.4\times10^3$ M^{-1} deduced from the oxidation kinetics with O_2 [11]. The stronger adsorption of oxalic acid could be attributed to the formation of oxalato complexes at the TiO_2 surface, since $C_2O_4^{2-}$ is a good bidentate ligand [17]. It can be assumed that in the presence of excess oxalic acid, the surface of the TiO_2 particles is mainly occupied by oxalate and the adsorption of nitrate is inhibited.

3.3. Time dependence of the photocatalytic reaction

Fig. 2 shows that the amounts of reacted NO_3^- and produced NH_3 increased proportionally to the irradiation time within 4 h of irradiation. The dark reaction was negligible during that time interval. The amount of formed NH_3 was consistent with the amount of reacted NO_3^-. This demonstrates that NH_3 is the principal product of the photocatalytic reaction. In the absence of oxalic acid, when 1.0×10^{-3} M KNO_3 or 1.0×10^3 M HNO_3 solutions with the suspended

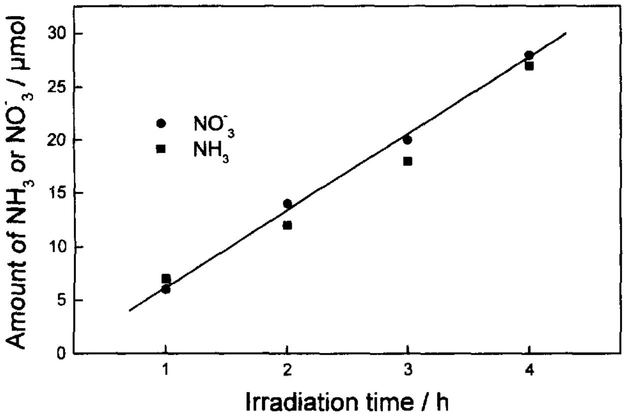

Fig. 2. Time course of the photocatalytic oxidation percentage. Reaction conditions: 80 ml 5.2×10^{-3} M oxalic acid solution, without (●) and with (■) 1.0×10^{-3} M nitrate, TiO_2: 0.2 g.

catalyst were irradiated for 4 h, only a small amount of NH_3 was formed (2.8 µmol and 2.2 µmol, respectively). It can be concluded that oxalic acid is an efficient hole scavenger.

Fig. 1 describes the time course of percentage of oxidized oxalic acid in the absence of nitrate (curve a) and in the presence of 1.0×10^{-3} M NO_3^- (curve b). The time dependence was linear up to 80% consumption of oxalic acid. Under the experimental conditions of Fig. 1 the nitrate induced reaction was consistent with:

$$NO_3^- + 4C_2O_4^{2-} + 10H^+ \rightarrow NH_4^+ + 8CO_2 + 3H_2O \qquad (1)$$

A ratio $-\Delta c_{ox}/-\Delta c_{nit} = 4.0\pm0.3$ with $-\Delta c_{ox}$ the nitrate induced decomposition of oxalic acid concentration (total conversion minus the conversion without nitrate) and $-\Delta c_{nit}$ the change in nitrate concentration was obtained from the data of Figs. 1 and 2 in agreement with Eq. (1). Hence, the oxidation of oxalic acid by nitrate does not compete with the other oxidation processes that take place in the absence of nitrate as for instance oxidation by H^+ and by residual O_2. It does, however, compete at lower oxalic acid concentrations. It is seen that nitrate enhances the oxidation of oxalate noticeably.

3.4. *Effect of the concentration*

Fig. 3 shows the effect of the initial nitrate concentration on the reduction of NO_3^-. With increasing concentrations of nitrate, NH_3 formation is increased. This may be attributed to increasing amounts of adsorbed nitrate or to a more successful competition with other oxalate oxidants. At high nitrate concentrations the yield of NH_3 approached a limiting value.

Fig. 4 presents the dependence of the NO_3^- reduction upon the oxalic acid concentration. At high concentrations the reduction yield approached saturation (11 µmol). In this area the oxalic acid consumption was constant ($\Delta m_{ox} = 155\pm5$ µmol). In the absence of nitrate, oxalic acid decomposition was 107 ± 3 µmol. These values yield a ratio of the NO_3^- induced oxalic acid oxidation (total conversion minus 107 µmol) to the nitrate consumption of 4.4 ± 0.3 in reasonable agreement with Eq. (1), from which follows a ratio of 4. On lowering the oxalic acid concentration the nitrate reduction yield reached a maximum of 25.6 µmol at $c_{ox} = 2.0$ mM, while the oxalic acid consumption remained constant. In this region the additional nitrate reduction has to compete with the other processes that oxidize oxalic acid (i.e., that occur in the absence of nitrate). The additional nitrate reduction (14.6 µmol) consumed $14.6\times4 = 58$ µmol oxalic acid, which is about half of the oxalic acid decomposition in the absence of nitrate. Beyond the maximum the oxalic acid was completely oxidized within the exposure time of 2 h. The ratio of the total oxalic acid oxidation to the consumption of nitrate was 5.4 ± 0.3. That means nitrate can successfully compete with the other oxidants at low oxalic acid concentrations.

Table 3 shows the change of the ammonia yield on varying the pH. The yield dropped in alkaline solution to 1/8 of the value at natural pH (pH: 2.37) in 5.2×10^{-3} M oxalic acid.

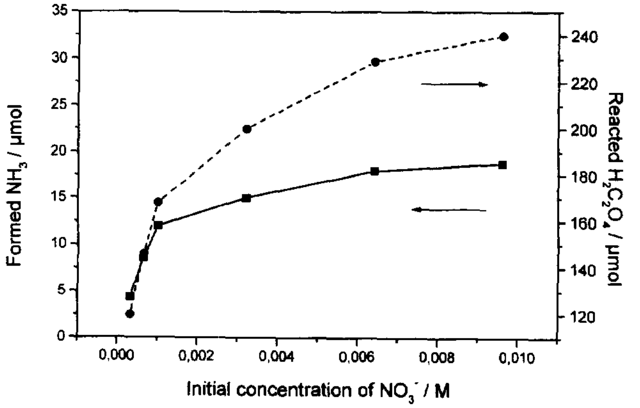

Fig. 3. Amount of produced NH_3 (■) and of reacted oxalate (●) as a function of the initial concentration of nitrate. 80 ml solution containing initially 5.2×10^{-3} M oxalic acid, irradiation time: 2 h, TiO_2: 0.2 g.

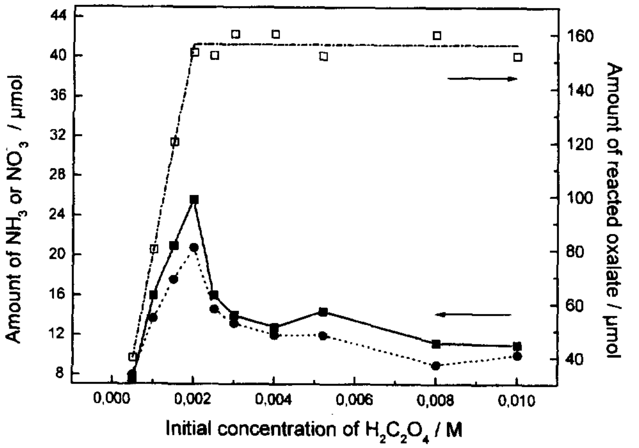

Fig. 4. Amount of produced NH_3 (●), of reacted NO_3^- (■) and of reacted oxalate (□) as a function of the initial concentration of oxalic acid. 80 ml solution containing initially 1.0×10^{-3} M nitrate, irradiation time: 2 h, TiO_2: 0.2 g.

Table 3
Amount of NH_3 produced at different initial pH after irradiating for 2 h, 80 ml solution containing 1.0×10^{-3} M nitrate and 5.2×10^{-3} M oxalate

pH of solution before the reaction	pH of solution after the reaction	Formed NH_3 μmol	Reacted oxalate μmol
10.83	[a]	1.5	4
7.08	[a]	5.2	40
5.74	8.25	6.6	67
5.00	8.01	11.4	143
4.82	7.76	13.2	187
3.92	5.14	12.7	147
2.37	2.64	12.0	160

[a] Not determined.

4. Discussion

Although nitrate reduction by oxalic acid is exergonic ($\Delta E°$1.37 V) a high reaction barrier is expected, because for the first step

$$NO_3^- + C_2O_4^{2-} \rightarrow NO_3^{2-} + C_2O_4^{\bullet -} \qquad (2)$$

an e.m.f., $\Delta E° = < -2.5$ V can be estimated from the normal potentials $E°(NO_3^-/NO_3^{2-}) < -0.4$ [18] and $E°(C_2O_4^{\bullet -}/C_2O_4^{2-}) = 2.1$ V [19,20].

The bulk of our experiments was done at the natural pH of 5.2×10^{-3} M oxalic acid, i.e., pH 2.37. Then the reacting species are NO_3^- and $HC_2O_4^-$ (pK_a 4.19 [21]) forming $HNO_3^{\bullet -}$ (pK_a 4.8 [22]) and again $C_2O_4^{\bullet -}$ (pK_a 1.4 of $C_2O_4H^\bullet$ [19]). Since the pK_a values for the protonated reactant and the protonated product are rather similar, the e.m.f. is not significantly changed ($\Delta E = 0.04$ V). The endergonic first step explains that a dark reaction is not observed.

The reaction barrier is easily surpassed with light energy. Anatase has a band gap of 3.2 eV and a valence band potential of ≈3 eV [23]. The band gap of rutile is slightly smaller (3.0 eV) [24]. Thus, it is able to oxidize adsorbed oxalate to the oxalate radical, which is sufficiently negative to reduce NO_3^-. Its decomposition product $CO_2^{\bullet -}$ (normal potential $E°(CO_2/CO_2^{\bullet -}) = -1.8$ V [18]) is also able to reduce NO_3^-. On the other hand, conductivity electrons can reduce adsorbed H^+ to $H^\bullet$ radicals [25], which also can reduce nitrate ($E°(H^+/H^\bullet) = -2.31$ V [18]).

Adsorption of species that can trap electrons or holes plays an important role in heterogeneous photocatalysis. At high concentrations of electron-hole pairs, the charge carriers recombine within a fraction of one nanosecond [26]. Therefore, the interfacial carrier trapping must be very rapid in order to achieve effective photochemical conversion. This requires the electron or hole trapping species to be preadsorbed on the catalyst surface [23,25]. The efficient adsorption of electron acceptors is expected to be more important, because the interfacial electron transfer occurs slower [8].

Kudo et al. [4] proposed that NH_3 was liberated via hydrogenation of NO_3^- on Pt–TiO_2. Ohtani et al. [3] held a converse view that reduction is initiated by 'unpaired electrons'. We think that these two mechanisms may be equally possible and depend on the reaction conditions. It has been known that P25 TiO_2 has a large surface proton exchange capacity (0.46 mmol/g) [27]. In acidic media, there is a large amount of adsorbed protons on the TiO_2 surface. The photogenerated electrons will be mainly trapped by these protons. In this case the reduction of NO_3^- would principally proceed via hydrogenation by $H_{ads.}^\bullet$. In alkaline media, the amount of adsorbed protons on TiO_2 is small. The decrease in the ammonia yield might be caused by the smaller surface concentration of hydrogen radicals. However, some of the various acid base equilibria might also play a role in the reduction mechanism. If adsorbed hydrogen radicals are not available, NO_3^- may be reduced by photogenerated electrons on TiO_2 directly, provided nitrate adsorption is not blocked by oxalate.

At high oxalic acid concentrations and low nitrate concentrations oxalate adsorption has reached saturation and nitrate adsorption is negligible. Nitrate, however, may be available in the double layer. In acid solution the TiO_2 surface is positively charged, due to the binding of protons at the hydroxyl groups. The negatively charged ions (oxalate and nitrate) accumulate in the outer layer, where nitrate can react with adsorbed radicals ($C_2O_4^{\bullet -}$, $CO_2^{\bullet -}$, $H^\bullet$ or their conjugate acids). The reaction with $CO_2^{\bullet -}$ radicals after their dissociation from the TiO_2 surface does not seem feasible, because their reaction would not increase the decomposition yield of oxalate. If the radicals are scavenged at the surface, charge recombination is inhibited and the oxalic acid oxidation yield is enhanced.

At low oxalic acid concentrations, nitrate may be adsorbed as well. Then it is capable to accept electrons from the conduction band directly. In this case, nitrate competes with the other oxalate oxidizing processes and the total oxalic acid oxidation yield should not be affected. At very low oxalic acid concentrations we found almost stoichiometric ratios of oxalic acid decomposition to nitrate consumption (Fig. 4).

Ranjit et al. [5] reported that during the photocatalytic reduction of nitrate, an increase in the yield of ammonia was observed, if nitrite was added. This suggests that nitrite is a possible intermediate in the photocatalytic reduction of nitrate. However, we failed to detect nitrite. Presumably any nitrate formed as an intermediate was rapidly reduced. Other possible intermediates such as hydroxylamine and hydrazine were also not detected.

The reduction steps following the formation of NO_3^{2-} are obviously all exergonic and lead almost quantitatively to ammonia. It seems that the partaking of hydrogen radicals in the reduction mechanism or coordination to transition metals is necessary for the reduction of nitrate to NH_3. While photochemical decomposition of NO_3^- yields NO_2^- [28,29], catalytic reduction of NO_3^- with H_2 at noble metals and the photo or electrocatalytic reduction with coordination compounds yield ammonia [29–31]. The increase in reduction yield that we found, if nitrate adsorption became feasible, may be caused by the coordination effect.

5. Conclusions

Nitrate can be effectively photoreduced to NH_3 on TiO_2 using oxalic acid as sacrificial electron donor. The reduction is favored at low oxalic acid concentration, when both reactants are adsorbed on the TiO_2 surface. It seems that noble metal coated TiO_2 is only necessary, if no reductants are available in solution. In this case, photochemically produced hydrogen acts as electron donor.

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