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A mechanism of the photocatalytic decomposition of 2,4-dinitrophenol on TiO_2 immobilized on a glass surface

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HIGHLIGHTS

- A mathematical model is proposed for photocatalytic DNP decomposition on immobilized TiO_2.
- Electrostatic interactions affect photocatalytic DNP decomposition on immobilized TiO_2.
- DNP decomposition obeys zero-order kinetics despite very low initial DNP concentrations.
- Produced nitrate ions inhibit DNP decomposition but not to the extent as in TiO_2 suspensions.
- DNP decomposition on immobilized TiO_2 is fundamentally different from that in TiO_2 suspensions.

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ABSTRACT

A reaction mechanism of the photocatalytic decomposition of 2,4-dinitrophenol (DNP) on TiO_2 immobilized on a glass surface is investigated both theoretically and experimentally. The experimental results show that (1) the DNP concentration decreases linearly in the same manner; (2) the initial rate of decomposition increases with an increase in the initial DNP concentration, *i.e.*, the reaction is not inhibited by DNP; and (3) product inhibition is present, but it is not as strong as that in the aqueous TiO_2 suspension. To elucidate the mechanism of the photocatalytic reaction, a mathematical model is constructed by taking into consideration an electrostatic interaction between positively-charged TiO_2 and negatively-charged DNP. The calculated results suggest that mixing a solution breaks down the DNP-aggregate layer formed in the neighborhood of TiO_2 film and removes reactant inhibition by DNP. The results are also compared with our previous result for the DNP decomposition in an aqueous TiO_2 suspension and the difference is identified.

1. Introduction

Titanium dioxide (TiO_2) excited by UV light can mineralize various organic compounds, a unique property that has been investigated worldwide to treat air and water containing harmful chemical compounds [1–6]. However, it is not easy to apply the photocatalytic treatments to practical applications. This is especially true in water purification processes, because the film-diffusion resistance produced near a TiO_2 surface dramatically decreases the rate of decomposition [7–10]; moreover, it is not easy to irradiate TiO_2 with UV light at a sufficiently high intensity [7]. In addition, inhibition of the reaction in aqueous solutions by the coexisting ions is a serious problem [11].

DNP (2,4–dinitrophenol) is hardly destroyed in conventional wastewater treatment and therefore, there is a pressing need for developing an economical and efficient method for treating wastewaters containing DNP [12,13]. Fortunately, photocatalytic treatment based on TiO_2 can readily decompose nitrophenols [1,14]. For practical application of photocatalysts to purification of water containing DNP, it is necessary to elucidate the decomposition mechanism. We have recently examined DNP decomposition in aqueous TiO_2 suspensions and obtained the following conclusions [15]: (1) the initial rate of decomposition decreases with an increase in the initial DNP concentration, *i.e.*, the reaction is strongly inhibited by DNP; (2) the DNP concentration decreases linearly according to zero-order kinetics over a long duration; and (3) the reaction is inhibited markedly by the product, nitrate ions (NO_3^-). These experimental results were successfully explained using a mathematical model that considered the quick

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aggregation of negatively charged DNP molecules around a positively charged TiO_2 particle [15].

In an aqueous TiO_2-suspension system, however, TiO_2 particles must be separated from the liquid solution after treatment, which is not easy. To solve this problem, studies on immobilized TiO_2 [16–19] have been carried out. Thus, it is useful to clarify how DNP decomposes on immobilized TiO_2.

The objective of the present study is to construct a mathematical model for the photocatalytic decomposition of DNP on TiO_2 immobilized on a glass film and clarify the mechanism. Moreover, the obtained results are compared with those of the aqueous TiO_2-suspension system.

2. Theory

2.1. Formulation of the kinetic expression

The reaction in the TiO_2-suspension system was strongly inhibited by DNP. Nevertheless, DNP was decomposed and its concentration was certainly decreased [15]. TiO_2 has an isoelectric point at pH 6.2, where the TiO_2 surface is positively charged at pH values below 6.2 and negatively charged above this pH [20], leading to changes in the affinity between the TiO_2 surface and coexisting ion species with changes in pH, which in turn remarkably changes the reaction rate [12,13,21].

DNP is a polar organic compound and charged negatively by electron-attracting power of side-chain nitro groups. An aqueous solution prepared by dissolving DNP at around 10 g m^{-3} shows acidic property (about pH 4.5). TiO_2 particles are positively charged in such an acidic solution. Hence, it is predicted that the negatively-charged DNP molecules are rapidly attracted to the surface of positively charged TiO_2 and the TiO_2 surface or its neighborhood is occupied with a DNP aggregate layer. Thus, unlike other reactants, DNP may be decomposed according to unexpected reaction kinetics [15]. Emitted UV light may be interfered with the aggregate layer instantaneously formed in the neighborhood of TiO_2. In addition, the presence of aggregate layers may hinder the formation of hydroxyl radicals and positive holes. These probably appear as reactant inhibition. DNP molecules are supplied from the DNP aggregate layer to the TiO_2 surface, which can shift the photocatalytic decomposition of DNP from first-order to zero-order kinetics even when the DNP concentration is low. A part of the nitrate ion, NO_3^-, formed as a product also stays in the neighborhood of TiO_2, which probably appears as product inhibition. Thus, one cannot neglect the effect of electrostatic field in the photocatalytic decomposition of DNP by TiO_2.

The photocatalytic decomposition of DNP on or near the immobilized TiO_2 is expected to occur in a fashion similar to that of aqueous TiO_2 suspensions. Unlike in the TiO_2-suspension system, however, TiO_2 particles in the immobilized TiO_2 system are usually kept stationary even when a reaction mixture is sufficiently mixed, which may lead to reaction phenomena different from those in the TiO_2-suspension system. In fact, we found the following differences:

(1) The initial rate of DNP decomposition increases with increase in the initial concentrations of DNP.
(2) The NO_3^- ions produced decreases the photocatalytic decomposition of DNP, but its extent is not as large as in the TiO_2-suspension system.
(3) Although there are electrostatic interactions between the DNP molecules and the TiO_2 particles, the extent is not as large as in the TiO_2-suspension system.

At the same time, both the systems had the following similar aspect: although the initial DNP concentration is very low (around 10 g m^{-3}), the DNP concentration decreases almost linearly over a long duration. Thus, the following features must be reflected in the kinetic expression for the immobilized TiO_2 system:

(1) There is no reactant inhibition.
(2) DNP decomposition mostly proceeds according to zero-order kinetics.
(3) There is product inhibition.
(4) There are electrostatic interactions.

The thickness of the immobilized TiO_2 film is about 0.5 μm [22]. In batch-recirculation reaction experiment, moreover, the H_2O_2 concentration in a bulk solution is increased with an increase in the liquid flow rate near the TiO_2 film [8]. These facts indicate that the photocatalytic reaction occurs at the film surface or in its very neighborhood and therefore, the effect of internal diffusion can be neglected. Consequently a mathematical model is constructed on the assumption that the reaction mainly takes place at the surface of the TiO_2 film.

As in the TiO_2-suspension system [15], let us assume that DNP molecules aggregate at high concentration in the vicinity of immobilized TiO_2 because of electrostatic interactions and the DNP molecules in this layer are transferred to the surface of the immobilized TiO_2 and then decomposed. Moreover, the decomposition of DNP is inhibited by the produced NO_3^- ions [15]. These assumptions lead to the following kinetic expression for DNP decomposition:

$$r = -\frac{\mathrm{d}C_\mathrm{b}}{\mathrm{d}t} = \frac{k\,K_\mathrm{H}C_\mathrm{b}}{(e^{\lambda} + K_\mathrm{H}C_\mathrm{b})\left(1 + \frac{C_\mathrm{b0}}{K_\mathrm{ip}}\,\frac{C_\mathrm{b0}-C_\mathrm{b}}{10+C_\mathrm{b0}-C_\mathrm{b}}\right)} \tag{1}$$

with the initial condition

$$C_b = C_{b0} \text{ at } t = 0 \tag{2}$$

where r is the decomposition rate with respect to liquid volume (g m^{-3} min^{-1}), k is the rate constant (g m^{-3} min^{-1}), C_b is the DNP concentration in the bulk liquid (g m^{-3}), K_H is the adsorption equilibrium constant (m^3 g^{-1}), K_ip is the product inhibitor constant (g m^{-3}), and t is the reaction time (min). The subscript b expresses the DNP concentration in the bulk, and the subscript 0 expresses the initial value. In addition, e^{λ} expresses an electrostatic interaction, where λ is the dimensionless surface potential [23,24]. Because TiO_2 and DNP have opposite charges, the λ value in the present system is negative. Under this condition, the DNP concentration on the TiO_2 surface is greater than that in the bulk, which enables us to express zero-order kinetics even when the reactant is at very low concentrations.

As demonstrated later, λ changes with an increase in C_b0. It is difficult, however, to describe the relationship between λ and C_b0 because of the high complexity of the reaction. Considering the trend in the experimental data, we used the following expression as an initial trial:

$$\lambda = -\frac{\kappa_1\kappa_2\ C_\mathrm{b0}}{\exp[-\kappa_3\ C_\mathrm{b0}] + \kappa_2\ C_\mathrm{b0}} \tag{3}$$

where κ_1, κ_2, and κ_3 are the empirical constants, which were determined so that the calculated result for λ agreed with the plotted data. Unfortunately, the numerical solution of Eq. (1) using Eq. (3) did not agree well with the experimental time evolution of C_b. This is probably because λ is proportional not only to C_b0 during DNP decomposition but also to changes with a decrease in C_b. Hence, we partially modify Eq. (3) to obtain:

$$\lambda = -\frac{\kappa_1\kappa_2\ \phi(C_\mathrm{b})}{\exp[-\kappa_3\ \phi(C_\mathrm{b})] + \kappa_2\ \phi(C_\mathrm{b})} \tag{4}$$