

Concerning the role of oxygen in photocatalytic decomposition of salicylic acid in water

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Abstract

The photocatalyzed oxidation of salicylic acid on pure TiO₂ and ZnO films as well as on TiO₂ films loaded with various amounts of ZnO in N₂O-saturated aqueous solutions has been investigated. It was found that the photoassisted decomposition of salicylic acid did not take place on the irradiated surface of pure TiO₂ and took place on ZnO when N₂O was bubbled through the solution. The deposition of a small amount of ZnO onto the TiO₂ surface was responsible for the appearance of marked photocatalytic activity of material. The information about the electron-scavenger ability of N₂O in interaction with TiO₂ has been obtained by conductivity and photoconductivity measurements. The main conclusion is that the major role of oxygen in photocatalytic oxidation of organic compounds is to be a scavenger for continuous electron removal from photocatalysts.

Keywords: Adsorption; Conductivity; Metal oxides; Photocatalytic decomposition; Salicylic acid

1. Introduction

The application of illuminated semiconductors for the decomposition of organic contaminants in water has been successfully used for a wide variety of compounds [1,2].

The natural oxidant for organic molecules is the oxygen from the air. In a photocatalytic reaction the rate of oxidation by holes has to be balanced by the rate of reduction of electrons. Either the oxidation or the reduction reaction can be the rate-determining step. The results of many experiments have indicated the existence of a larger steady-state concentration of photogenerated bulk electrons compared with the hole concentration [3,4]. Thus electrons can accumulate on the photocatalyst and increase the rate of electron-hole recombination. This causes a decrease in the hole-initiated oxidation of organic molecules. Hence, this excess in photogenerated electron concentration must be removed from the photocatalyst in order to prevent this recombination increase. The molecular oxygen dissolved in solution plays the role of reagent bonding of the photogenerated electrons [5–7]. It was found [3,8] that photocatalytic activity is nearly completely suppressed in the absence of oxygen and the steady-state concentration of oxygen has a profound effect on the rate of photocatalyzed decomposition of organic compounds.

It should be noted that molecular oxygen dissolved in solution takes part also in other stages of this complex process. For example, it was shown by Okamoto et al. [9] that hydroxyl radicals are formed not only via holes but also via hydrogen peroxide (H₂O₂) from O₂⁻. Nevertheless this participation is not critical for the organic photodecomposition as a whole. This is confirmed by the results of Kamat and coworkers [10] and Kim and Anderson [11] which indicate that titanium dioxide (TiO₂) films with an externally applied anodic potential (vs. a saturated calomel electrode) are characterized by a high efficiency in deaerated solutions. For more careful understanding of the role played by dissolved oxygen in photodegradation of organic compounds, another electron scavenger can be employed. The employment of nitrous oxide as a possible scavenger of photogenerated electrons has been investigated recently by Serpone et al. [12]. It was shown that in nitrous-oxide (N₂O)-purged aqueous TiO₂ suspensions there was no effect on the photo-oxidation of phenol. This indicates that N₂O probably does not scavenge electrons from illuminated TiO₂ particles. At the same time, Kamat and Patrick [13] have shown that the trapped electrons on the zinc oxide (ZnO) surface decay faster when the ZnO suspension is saturated with N₂O than in deaerated suspension. The latter indicates the ability of N₂O to act as an electron scavenger in the case of ZnO colloids. It should be noted that the different behaviors of N₂O under the interaction

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with TiO_2 and ZnO has been found in many studies [14–17]. For example, Kudo and Sakata [14] have demonstrated the photodecomposition of N_2O into nitrogen (N_2) and oxygen (O_2) at room temperature on Pt/TiO_2 photocatalyst in the presence of water vapor. No photocatalytic activity was obtained in this study on Pt/SiO_2 and pure TiO_2 , showing that both Pt and TiO_2 were indispensable under these conditions. Cunningham et al. [15] in their work have shown that gaseous N_2O dissociated at room temperature when in contact with the illuminated surface of powdered ZnO . The comparison of these results indicates that photodecomposition of N_2O does not take place on a pure TiO_2 surface but takes place on a pure ZnO surface.

In this paper we investigate the photocatalytic efficiency of pure TiO_2 and ZnO films as well as TiO_2 films loaded with various amounts of ZnO in determining photodegradation of salicylic acid in water when N_2O is bubbled through the solution. Salicylic acid is chosen as a prototype molecule because of its low volatility, suitable solubility in water and well-known spectral characteristics. The effect of N_2O on the electrical conductivity of pure TiO_2 films in the dark and under illumination are also investigated.

2. Experimental section

2.1. Preparation of TiO_2 films

Titanium(IV) oxide films have been coated inside Pyrex tubes by an ultrasonic nebulization and pyrolysis technique [18]. The deposition apparatus was described by Wold and coworkers [19]. The reactor used in this investigation was heated by means of a two-zone mirror furnace (Transtemp Co., Chelsea, MA). Diisopropoxy-titanium-bis(acetylacetonate) was used as a precursor for the preparation of these thin films. It was synthesized according to the method of Yamamoto and Kambara [20]. An alcohol solution of 0.1 M diisopropoxy-titanium-bis(acetylacetonate) was nebulized by a commercial ultrasonic humidifier (Holmes Air) and carried into a Pyrex tube with an inside diameter of 2 cm by oxygen. The Pyrex tube for the deposition of the film was held parallel to the carrier gas flow in the furnace and was rotated by a low speed motor to achieve best uniformity. To obtain a band of film 2 cm wide, the remainder of the tube was masked with an aluminum foil. Typical reaction parameters were as follows: deposition temperature, 450 °C; argon flow rate, 2.8 l min^{-1} ; distance between nozzle and front edge of the film, 7.5 cm. Under such conditions, a film of 350 nm in thickness could be grown in 10 min using 6 ml of precursor solution. All deposited films were post-annealed in a flowing O_2 atmosphere at 450 °C for 20 min.

2.2. Preparation of ZnO films

ZnO films have been coated inside Pyrex tubes by the same ultrasonic nebulization and pyrolysis technique. Zinc 2,4-

pentanedionate (acetylacetonate) was used as a precursor for the preparation of these thin films.

2.3. Thermal decomposition of zinc acetate on TiO_2 films

Zinc acetate was reduced onto titanium(IV) oxide films by thermal decomposition. 30 ml of zinc acetate aqueous solution was added to the Pyrex tube coated inside with transparent TiO_2 film and allowed to soak for 5 min. The concentration of zinc acetate aqueous solution lay in the interval 10^{-3} – 10^{-1} M. After the removal of zinc acetate solution the tube was heated in flowing O_2 at 400 °C for 20 min. The sample obtained by this way was then rinsed with distilled water to remove any excess zinc acetate remaining on the film.

2.4. Measurement of photocatalytic activity

The photocatalytic activities of titanium(IV) oxide films were evaluated by the degradation of salicylic acid. 30 ml of an aqueous 6×10^{-5} M salicylic acid solution were added to a Pyrex tube whose inside surface was coated with a photocatalyst film. The sample to be measured was then irradiated with a 150 W mercury–xenon short arc lamp whose output was passed through a Pyrex filter. The differential absorbance at 296 nm (absorption peak of salicylic acid) was measured using a Perkin-Elmer 552 A spectrophotometer. The change in concentration of salicylic acid of the irradiated sample as a function of time was compared with the reference sample of distilled water.

The photocatalytic activity of these catalysts was measured in the apparatus shown in Fig. 1. N_2O was bubbled through the solution. The measurements of the degradation rates of salicylic acid when different photocatalysts were employed were carried out under identical experimental conditions. The catalyst surface was regenerated each time before activity measurement. After each measurement, the Pyrex tube was filled with distilled water and the film was irradiated by the four commercial fluorescent lamps. The reproducibility of

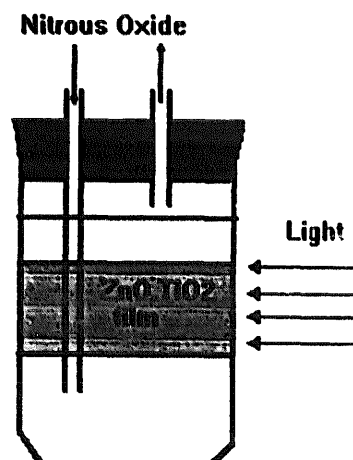


Fig. 1. Photocatalytic cell.

the value of salicylic acid adsorption taking place in the dark when argon was bubbled through the solution was chosen as the criteria for full surface regeneration. In this study, the films were all irradiated for the same time and changes in the concentration of salicylic acid as a function of deposited ZnO amount were compared with the values obtained from the reference sample. H_2O_2 was analyzed spectrometrically using TiOSO_4 as the reagent [21].

2.5. Measurement of TiO_2 conductivity response caused by N_2O adsorption

The titanium(IV) oxide films used for conductivity response measurements were prepared in the same manner as the film for photocatalytic investigations. The only difference was that these films were deposited on $1\text{ cm} \times 1\text{ cm}$ square silica substrates. The films were contacted via gold wires attached with gold paint. Conductance measurements were made by applying between 10^{-7} and 10^{-5} A through the current probes and measuring the voltage drop across the voltage probes using a precision voltmeter. The response to various gases was measured in a special chamber, which could be held at various temperatures. The gaseous atmosphere in the test chamber was switched by means of solenoid valves.

3. Results and discussion

All experiments have been made in the cell shown in Fig. 1. Preliminary measurements were carried out in order to eliminate other possible factors which can be responsible for an observed decrease in the salicylic acid concentration. One such possibility is the adsorption of salicylic acid on the TiO_2 or ZnO/TiO_2 film surface. In order to evaluate this influence, the change in the salicylic acid concentration caused by adsorption was measured. During this process, argon was bubbled through the solution. Irradiation of the catalyst was

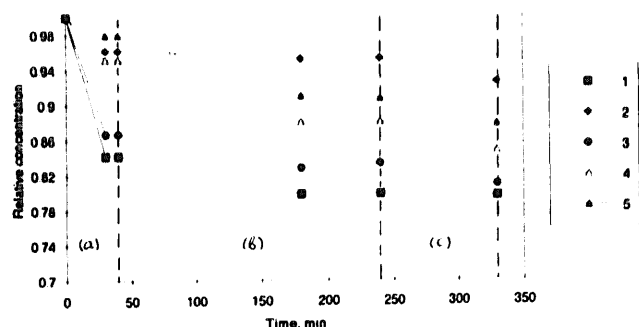


Fig. 2. Dependences of the concentration of salicylic acid on time under different conditions: regions (a), argon bubbling in the dark; regions (b), argon bubbling under the irradiation; regions (c), N_2O bubbling under the irradiation; curve 1, pure TiO_2 ; curve 2, pure ZnO ; curves 3–5, TiO_2 with different amounts of ZnO reduced from aqueous solutions with different concentration of zinc acetate (curve 3, 10^{-3} M; curve 4, 10^{-2} M; curve 5, 10^{-1} M).

carried out only after complete termination of any adsorption-induced change. The initial irradiation of these films under an argon atmosphere was accompanied by a significant apparent decrease in salicylic acid concentration. Additional radiation did not result in a further decrease in the acid concentration. This observed decrease in salicylic acid concentration may arise from photoadsorption. The possibility of photoadsorption in such systems has previously been mentioned by Cunningham and Al-Sayyed [22].

The comparative results of this study can be seen from Fig. 2. Curves 1–5 represent the changes in concentration of salicylic acid with irradiation time for pure TiO_2 and pure ZnO films and for TiO_2 films loaded with various amounts of ZnO . Regions (a) indicate the decrease in concentration of salicylic acid when argon is bubbled into the cell which is kept dark. Regions (b) show the change in acid concentration when argon is bubbled into the cell when illuminated. Region (c) shows the change which occurs when N_2O is bubbled into the solution with the same flow rate, 110 ml min^{-1} . It was shown in [15,16] that N_2O oxide dissociated, under illumination, to produce molecular nitrogen and atomic oxygen on a ZnO surface. It can be seen from region (c), that the photoassisted decomposition of salicylic acid does not take place on an irradiated bare surface of TiO_2 when N_2O is bubbled into the solution. This lack of photoactivity can be correlated with data obtained by Serpone et al. [12] for an aqueous solution of phenol. The deposition of even a small amount of ZnO on a TiO_2 surface is responsible for the appearance of marked photocatalytic activity of the oxide surface. The data plotted in Fig. 2 (regions (c)) indicate there is a marked photocatalytic activity of the ZnO/TiO_2 catalyst towards decomposition of salicylic acid compared with uncoated TiO_2 . The comparative data shown for these films were obtained under similar experimental conditions. Hence, the increase in observed activity must be associated with the role of ZnO on the surface of the TiO_2 film. It should be noted that, when argon is substituted for N_2O at the completion of regions (c), further film irradiation did not give any additional decrease in salicylic acid concentration.

Fig. 3 shows the relative decomposition of salicylic acid as a function of the concentration of the zinc acetate aqueous solution used for depositing ZnO on a TiO_2 surface. It can be seen that the photocatalytic efficiency reached a maximum

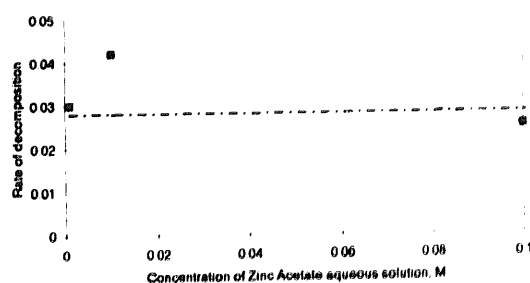


Fig. 3. Rate of photodecomposition of salicylic acid as a function of the concentration of zinc acetate aqueous solution (—); ---, rate of photo-decomposition of salicylic acid on pure ZnO film.

value when a 10^{-2} M zinc acetate aqueous solution was used for the impregnation. Further increase in solution concentration leads to a decrease in the photocatalytic activity of the catalyst toward the degradation of salicylic acid. It should be noted that the TiO_2 photocatalysts impregnated with an aqueous solution of zinc acetate were characterized by an enhanced photocatalytic activity in comparison with the pure ZnO film. This fact can be related to the vectorial transfer of electrons and holes, which takes place in coupled semiconductors possessing different redox energy levels for their corresponding conduction and valence bands [23]. As was shown by Serpone et al. [12], in the ZnO/ TiO_2 combination the electron transfer occurs from the conduction band of light-activated ZnO to the conduction band of light-activated TiO_2 and, conversely, hole transfer can take place from the valence band of TiO_2 to the valence band of ZnO. This efficient charge separation increases the lifetime of the charge carriers and enhances the efficiency of the interfacial charge transfer to adsorbed substrates. Serpone et al. [12] have observed an increase in the photocatalytic activity of the ZnO/ TiO_2 couple in comparison with ZnO suspension toward the degradation of phenol in air-saturated aqueous solution. Identical results have been obtained in our investigation concerning the ZnO/ TiO_2 -assisted photodecomposition of salicylic acid in N_2O -saturated aqueous solution. Thus we can conclude that N_2O scavenges photogenerated electrons in the ZnO and ZnO/ TiO_2 catalysts in a manner similar to chemisorbed molecular oxygen. "Zero" photocatalytic activity of a pure TiO_2 film in such conditions indicates another mechanism of

interaction between N_2O and TiO_2 than that in the $\text{N}_2\text{O}/\text{ZnO}$ system.

To determine the scavenger ability of N_2O in interaction with TiO_2 we investigated the N_2O adsorption-induced response in the resistance of a TiO_2 film. Figs. 4 and 5 show the time-dependent changes in the resistance of a TiO_2 film caused by the interaction with N_2O coming from the gas phase. Fig. 4 shows the resistivity response when the TiO_2 sample has been kept in the dark and Fig. 5 shows this response when the sample has been irradiated by the full light of a Hg-Xe lamp, whose output was passed through a Pyrex filter. It can be seen from these figures that changes in the gaseous atmosphere from chemically neutral nitrogen to N_2O produced upward excursions of the TiO_2 resistance, while the N_2 atmosphere caused the resistance of the film to return to its original value.

Fig. 6 shows the time-dependent change in the TiO_2 film resistance measured for the air- N_2O cycle. It can be seen that in this case the N_2O produced a downward resistance excursion. It should be noted that the steady-state value of the TiO_2 resistance in the N_2O atmosphere was the same in both cycles: N_2 - N_2O and air- N_2O . This fact supports the conclusion about the adsorption-induced character of N_2O -caused resistance change.

Fig. 7 shows the photoconductivity decays in TiO_2 film caused by stopping the illumination in two cases: N_2 and N_2O atmospheres. Upon stopping the illumination the photoconductivity decays faster in the case of a N_2O atmosphere than in N_2 , once more confirming the electron scavenger nature of

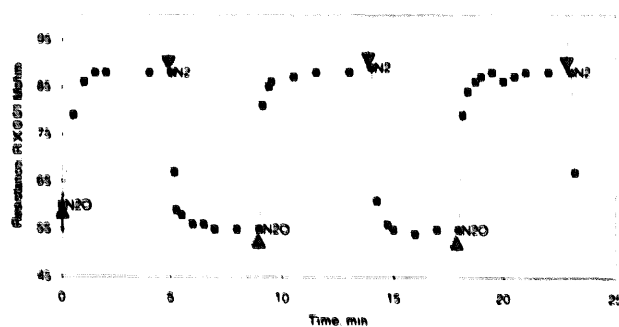


Fig. 4. Resistance vs. time from TiO_2 film measured for sequential N_2 - N_2O cycles.

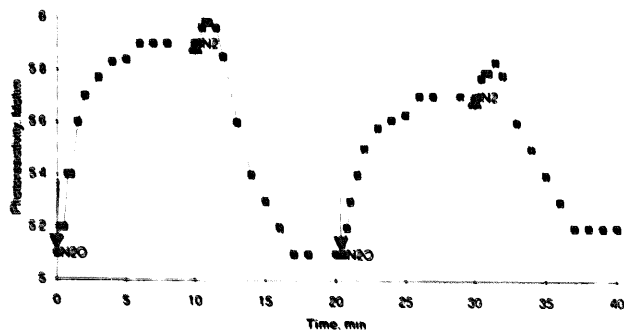


Fig. 5. Photoresistance vs. time for a TiO_2 film measured for sequential N_2 - N_2O cycles.

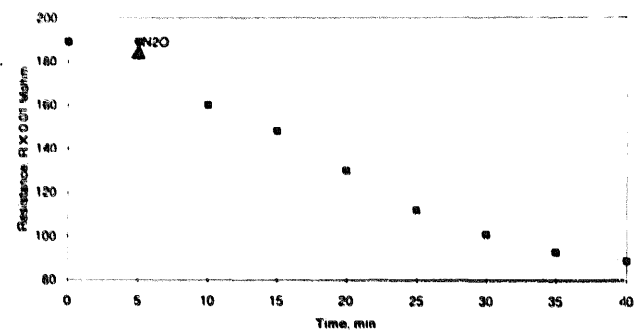


Fig. 6. Resistance vs. time for a TiO_2 film measured for sequential air- N_2O cycle.

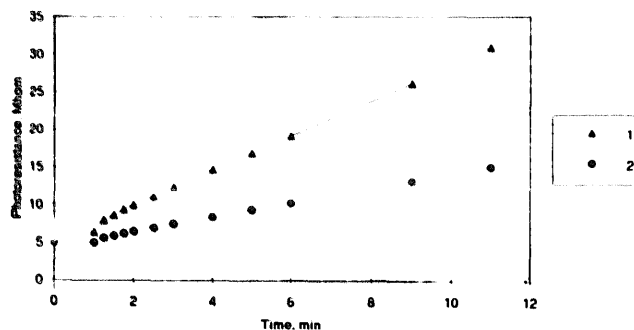
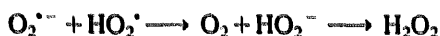


Fig. 7. Photoconductance decay in a TiO_2 film: curve 1, N_2O atmosphere; curve 2, N_2 atmosphere.

N_2O molecules in the $TiO_2-N_2O(g)$ system. Saturation of the gas atmosphere with water vapor did not change the quality character of the phenomenon.

Thus, in both the N_2O-TiO_2 and the N_2O/ZnO systems the N_2O demonstrates the ability to withdraw the photogenerated electrons. The different characters of the N_2O influence on the photo-oxidation of organic compounds in water on ZnO and TiO_2 catalysts can be related to the differences in photodecomposition of N_2O on ZnO and TiO_2 .

Indeed, the photodecomposition of N_2O taking place on a ZnO surface [14–16] leads to the formation of chemisorbed oxygen species, which can participate in the routes usual for air-equilibrated solutions [2,9]. For example,



This dynamical behavior can be responsible for continuous electron removal from an illuminated ZnO surface as takes place in air-saturated solutions.

In the case of TiO_2 , there is no N_2O photodecomposition at room temperature. Thus the first dose of N_2O chemisorbed on the TiO_2 surface in the charged form (N_2O^-) will prevent the further withdrawal of photogenerated electrons. It should be noted, that the formation of N_2O^- anion radicals on the TiO_2 surface under UV irradiation has been investigated by Anpo et al. [17]. This phenomenon could be responsible for the "zero" photocatalytic activity of a TiO_2 slurry or films in N_2O -saturated aqueous solutions. In order to clarify this point, H_2O_2 formation on the illuminated ZnO and TiO_2 surfaces when N_2O was bubbled through the water was measured under typical experimental conditions. It was found that H_2O_2 was produced over illuminated ZnO surface and no H_2O_2 was detected in the case of TiO_2 . These results correspond to the experimental data, obtained by Hoffman and coworkers [24,25], indicating that H_2O_2 is produced on illuminated ZnO and TiO_2 surfaces directly by the reduction of adsorbed dioxygen by conduction band electrons. No H_2O_2 was detected in the absence of oxygen.

Thus on the TiO_2 surface in air-equilibrated aqueous solutions the reactions of superoxide ions removing them from the catalysts surface are very important in the mechanisms of the photocatalytic degradation of organic compounds.

4. Conclusions

The different characters of the photocatalytic action of ZnO and TiO_2 films towards the degradation of salicylic acid in water saturated with N_2O is related to the difference in the photodecomposition of N_2O on ZnO and TiO_2 . Despite the fact that in both systems the N_2O demonstrates the electron

scavenger ability, the photodecomposition of salicylic acid takes place only when the decomposition of N_2O into N_2 and O_2 takes place. We conclude that the reactions of superoxide ions, formed on the TiO_2 surface in air-equilibrated aqueous solutions as well as on the ZnO surface in N_2O -saturated aqueous solutions, removing them from catalysts surface, are very important in photoassisted decomposition of organic compounds.

Acknowledgments

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