

Role of Lattice Oxygen in Photocatalytic Oxidation on TiO₂

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In the presence of low-intensity UV lights, lattice oxygen is extracted from the TiO₂ surface at room temperature by adsorbed formic acid. Transient photocatalytic oxidation (PCO) and decomposition (PCD) of formic acid to CO₂ and H₂O were combined with interrupted reaction and temperature-programmed desorption to directly show that lattice oxygen is the oxidizing species during PCD, whereas adsorbed oxygen oxidizes organics during PCO. The rates of lattice oxygen extraction and diffusion of lattice oxygen from the TiO₂ bulk to the surface to replenish the extracted oxygen were measured. The initial rate of decomposition (oxidation) of formic acid in the absence of gas-phase O₂ is one-seventh the rate in 3% O₂. Lattice oxygen vacancies are readily replenished by O₂ in the dark at room temperature, but H₂O does not re-oxidize them, even during UV exposure. Surface diffusion of formic acid to active sites does not limit photocatalytic reaction. Lattice oxygen extraction causes slow deactivation of TiO₂. © 2000 Academic Press

INTRODUCTION

Heterogeneous photocatalytic oxidation (PCO) has potential applications for the complete oxidation of organic pollutants in dilute systems. A wide range of organics can be oxidized to CO₂ and H₂O at room temperature on TiO₂ catalysts in the presence of UV or near-UV illumination. The UV light excites electrons from the valence to the conduction band of the semiconductor catalyst, leaving holes behind. The electron-hole pairs can initiate redox reactions with surface species.

To clarify the relative importance of adsorbed and lattice oxygen during PCO, photocatalytic reaction of formic acid was studied in the absence of gas-phase O₂. This reaction will be referred to as photocatalytic decomposition (PCD) to distinguish it from PCO, which takes place when gas-phase O₂ is present. Formic acid was used as a model reactant because it readily undergoes both PCD and PCO. Furthermore, the reaction rate can be directly measured since formic acid produces CO₂ during both PCD and PCO without forming any long-lived intermediates. Since CO₂

is not strongly bound to TiO₂ at room temperature (1), its appearance in the gas phase during transient reaction is an accurate measure of its rate of formation. In addition, formic acid oxidation is of interest since it is a volatile organic compound (VOC), and it is formed during PCO of other organics, such as ethanol (1–3).

Photocatalytic Decomposition

Sclafani *et al.* (4) studied PCD and PCO of gas-phase acetic acid on several semiconductor and insulator metal oxides. During PCD on TiO₂, acetic acid formed CH₄, CO₂, and smaller amounts of ethane. For PCD over the two types of TiO₂ catalysts they studied, the steady-state CO₂:CH₄ ratios were 1.7 and 20.6, and the rate of ethane formation was more than an order of magnitude lower than the rates of CH₄ and CO₂ formation. Acetic acid should produce a combination of products with a C–H–O ratio of 1:2:1; the C–H–O ratios for the products during PCD were 1:1.5:1.3 and 1:0.2:1.9 for their two TiO₂ catalysts. Similar results were reported for the other semiconductors they studied; the products contained proportionately more oxygen and less hydrogen than the reactant. Although the reactions were at steady state, the additional oxygen in the products may be from the lattice since only 2–17% of an acetic acid monolayer reacted on the TiO₂ catalysts, based on the acetic acid monolayer coverage on Degussa P-25 TiO₂ (1). Alternatively, an O₂ impurity would produce CO₂ and H₂O. Water may have formed but it was not detectable in their experiments; its formation would lower the amount of H in the gas-phase products.

Nosaka *et al.* (5) used ESR to detect methyl radicals during PCD of acetic acid in water on TiO₂. The authors proposed that a photo-induced hole reacts with acetic acid to produce CO₂, •CH₃, and H⁺. They reasoned that the methyl radicals should predominantly form CH₄. Chemseddine and Boehm (6) also observed CO₂ formation during PCD of aqueous acetic acid and chloroacetic acids on TiO₂. Kim and Anderson (7) studied the photocatalytic and photoelectrocatalytic degradation of aqueous formic acid. They found that removal of oxygen decreased the photocatalytic degradation of formic acid, but the photoelectrocatalytic rate decreased only slightly.

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Lattice Oxygen

Lo *et al.* (8) used AES, EELS, UPS, LEED, and TPD to study the adsorption of O₂ and H₂O on oxidized and reduced TiO₂. They concluded that Ti³⁺ species were generated by UV illumination at room temperature in the absence of both O₂ and organics. Gas-phase O₂ reoxidized the TiO₂ at room temperature. Similarly, exposure to water reduced the number of Ti³⁺ sites, but these sites were regenerated upon UV illumination, even with H₂O still adsorbed. Since no Ti³⁺ was produced during 1 h of UV illumination at higher temperatures (323–473 K), they concluded that, at 323–473 K, oxygen diffused from the TiO₂ bulk to oxidize the surface as fast as it was reduced. A high-intensity mercury lamp was required to reduce their TiO₂ at room temperature; 20–60 min of illumination by a lower intensity UV source did *not* reduce TiO₂. For our experiments, the low-intensity black lights are not expected to reduce the surface in the absence of adsorbed organics.

Gopel *et al.* (9) studied the interaction of O₂ with TiO₂(110) defects created by annealing in vacuum at 900 K or by Ar⁺ sputtering. The Ar⁺ sputtering produced a variety of defects whereas annealing produced only oxygen vacancies. The concentration of oxygen vacancies decreased upon exposure to O₂ at 300 K. Similarly, Pan *et al.* (10) determined that annealing TiO₂(110) at 1000 K created a slightly oxygen-deficient surface that was reoxidized by O₂ but not H₂O at room temperature. However, the highly oxygen-deficient Ar⁺-sputtered surface could not be fully oxidized by O₂ at room temperature. Water slightly reoxidized the Ar⁺-sputtered surface, although not as much as O₂.

Gravelle *et al.* (11) studied the photocatalytic activity of reduced anatase and rutile TiO₂. They concluded that reduction produced two types of Ti³⁺ ions in the lattice. The first type was created from moderate reduction and exhibited low reactivity to oxygen at 77 K; the other was produced during more severe reduction. The TiO₂ was reduced by pretreatment at 573–773 K in vacuum, with CO, or with H₂. In addition, TiO₂ was reduced by room-temperature UV illumination under vacuum for 12 h or in the presence of isobutane for 10–180 min. Exposure of reduced TiO₂ to O₂ at room temperature eliminated Ti³⁺ sites. Adsorbed O₂ produced O₂⁻ in the dark on reduced TiO₂, but UV was required to produce O₂⁻ on fully oxygenated TiO₂. They observed a decrease in the O₂⁻ surface concentration when the catalyst was exposed to isobutane and UV illumination. No reaction took place between isobutane and O₂⁻ in the dark.

Larson *et al.* (12) studied the role of lattice oxygen during PCO of 2-propanol in a low O₂ concentration (30 ppm). Their mass balance indicated that oxygen from the lattice participated in PCO. They estimated that 1.2 oxygen atoms/nm² were available for PCO; some of this oxygen could have diffused from the bulk. Gas-phase oxygen was

necessary for prolonged PCO of 2-propanol, but they concluded that O₂ does not photoadsorb.

Previously (13, 14), we showed that adsorbed acetic acid decomposes photocatalytically on TiO₂ at room temperature through two pathways. In a path that does not require lattice oxygen, the α -carbon in acetic acid forms CO₂ and the methyl group produces methane. In a second reaction pathway that extracts oxygen from the TiO₂ lattice, the α -carbon forms CO₂ and two methyl groups form ethane. Lattice oxygen that was extracted during PCD was replenished either by adding gas-phase O₂ or by waiting in an inert atmosphere for lattice oxygen to diffuse from the bulk to the surface.

In the current study, we utilized PCD to better understand the role of lattice oxygen during PCO. A monolayer of formic acid was adsorbed on oxidized TiO₂, and any excess organic was flushed from the gas phase. The surface coverage of formic acid was known at all times since no other organic intermediates form on the surface when formic acid oxidizes or decomposes (1). The TiO₂ surface was then exposed to UV illumination in the absence of gas-phase O₂, and the reaction products were detected by a mass spectrometer. Since gas-phase O₂ was not available to replenish the surface during PCD, the rates of lattice oxygen extraction and diffusion of lattice oxygen from the bulk to the surface could be measured. The possibility that surface diffusion of formic acid affects the reaction rate during these transient experiments was investigated to ensure that lattice oxygen diffusion was limiting the rate.

During PCO, O₂ either adsorbs on the TiO₂ surface or replaces lattice oxygen that was removed by reaction. Since the concentration of adsorbed oxygen on TiO₂ has been difficult to measure, the role of adsorbed oxygen in PCO has been difficult to determine. Thus, PCD was used to study the reactivity of lattice oxygen. The objective of this study is to better understand the surface processes involved in PCD and how they relate to PCO. Interrupted PCDs for various periods of dark time provided insight into the role of lattice oxygen. Different procedures (heating and injections of oxygen, formic acid, or water) were performed during the dark period after PCD to provide information on the roles of lattice oxygen, water, and formic acid surface diffusion and to verify that lattice oxygen was extracted during PCD.

EXPERIMENTAL METHODS

The apparatus used for PCD, PCO, temperature-programmed desorption (TPD), and temperature-programmed oxidation (TPO) was described previously (12). Approximately 30 mg of Degussa P-25 TiO₂ catalyst was coated as a thin layer (average thickness, <0.5 μ m) on the inside of an annular Pyrex reactor so that all the TiO₂ was exposed to UV light for PCO. The annular reactor had a 1-mm annular spacing so that high gas flow rates could be maintained

across the catalyst to minimize mass-transfer effects and rapidly flush gas-phase products from the reactor. The outside diameter of the reactor was 2 cm and the reactor was 13-cm high so that sufficient catalyst mass was present to allow detection of reaction products by the mass spectrometer. Six UV lamps (GE, 4 W) surrounded the photocatalytic reactor, and the light intensity at the catalyst surface, measured with a radiometer, was approximately 0.3 mW/cm^2 . The maximum light intensity was near 360 nm (3).

Before each experiment the reactor was held at 723 K for 30 min in approximately 20% O_2 in He and then cooled to room temperature to create a reproducible surface. Two $1\text{-}\mu\text{L}$ pulses of formic acid (Sigma, 99%) saturated the catalyst in the dark at 300 K prior to PCD or PCO, and all experiments started with the surface saturated. After exposure to HCOOH , the reactor was flushed for 2 h to remove gas-phase HCOOH , so that only reaction of the adsorbed monolayer was studied. Photocatalytic decomposition was studied by illuminating the TiO_2 in $100 \text{ cm}^3/\text{min}$ STP of He flow, and PCO was carried out in 3% O_2 flow. Metal shields were placed between the reactor and the UV lights at the start of the experiments, and the shields were removed after the lights attained a steady-state output to illuminate the catalyst and initiate transient reaction at room temperature.

A Balzers QMA 125 quadrupole mass spectrometer monitored the reactor effluent concentration immediately downstream of the reactor as a function of time. The mass spectrometer was interfaced to a computer to record multiple mass peaks simultaneously. The mass spectrometer signals were calibrated by injecting known volumes of gases into the flow stream downstream of the reactor, and the signals were corrected for cracking in the mass spectrometer. After PCO or PCD, TPD or TPO was performed by heating the catalyst at 1 K/s to 723 K and holding at this temperature until no desorption products were detected. A He flow gas was used for TPD whereas a 20% O_2 in He gas mixture was used for TPO.

To understand the roles of lattice oxygen and surface diffusion of formic acid, the lights were turned off for varying lengths of time, thereby interrupting PCD or PCO, and the effect of the periods of dark time on the subsequent rate of CO_2 formation was measured when the lights were turned back on. In addition, for some experiments, pulses of either O_2 (560 or $170 \mu\text{mol/g catalyst}$) or formic acid ($430 \mu\text{mol/g catalyst}$) were exposed to the catalyst in the dark after PCD. To determine the effect of formic acid coverage and surface diffusion on the rate of PCD, a pulse of formic acid ($90 \mu\text{mol/g catalyst}$) was also injected with the lights on during PCD. Pulses of water ($180 \mu\text{mol/g catalyst}$) were injected in the dark and during UV illumination to investigate the role of water during PCD. The effect of lattice oxygen diffusion from the bulk was further investigated by raising the catalyst temperature to 400 K in the dark after PCD.

RESULTS

Photocatalytic Decomposition of Formic Acid

At elevated temperatures and in the absence of O_2 and UV irradiation, formic acid primarily dehydrates on TiO_2 to form CO and H_2O ; a small amount of CO_2 also forms (1). In contrast, formic acid photocatalytically decomposes to gas-phase CO_2 and adsorbed H_2O in the absence of gas-phase O_2 . Figure 1 shows the CO_2 formation rate versus time for transient PCD of a monolayer of formic acid. Upon UV illumination, the CO_2 formation rate quickly reached a maximum and then rapidly decreased. After 2200 s of PCD, the rate was approximately $0.008 \mu\text{mol/g catalyst/s}$, which is 8% of the initial rate. However, 91% of the formic acid monolayer remained on the surface. *The rate of CO_2 formation decreased much faster than the surface coverage of formic acid decreased.* Note also that the rate decrease has at least two time constants: the rate dropped rapidly initially and then much more slowly and could not be adequately fit by one exponential.

When the lights were turned back on after the TiO_2 had been in the dark for 3600 s, the rate of CO_2 formation was 10 times higher than the rate when the lights were turned off (Fig. 1), and the rate again quickly dropped to approximately $0.008 \mu\text{mol/g catalyst/s}$. As shown in Fig. 1, subsequent periods of dark and light times showed similar behaviors; the CO_2 production rate increased after each period of dark time and it approached a value of approximately $0.008 \mu\text{mol/g catalyst/s}$ during extended illumination. As the length of the dark time increased, the increase in the rate of CO_2 formation was larger when the lights were turned on. The PCD rates and their behaviors with time were reproducible. When three PCDs, each with a fresh monolayer of formic acid, were carried out, the CO_2 formation rates

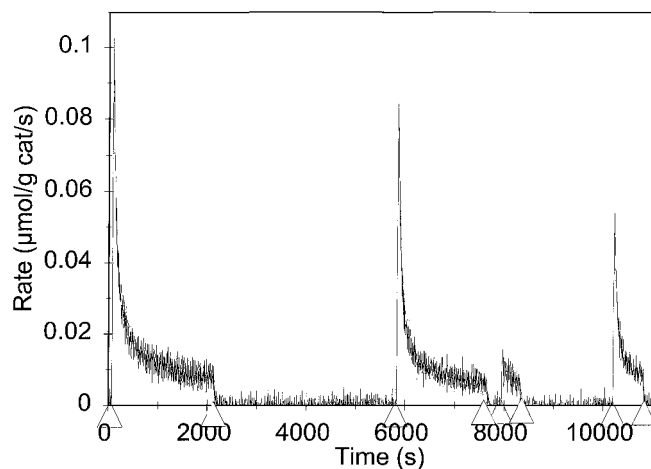
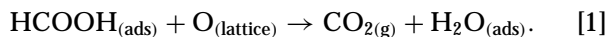


FIG. 1. Formation rate of CO_2 during photocatalytic decomposition of a monolayer of formic acid on TiO_2 in He flow. The UV lights were turned on (open triangles) and off (solid triangles) as indicated.

versus time plots coincided within the noise level of the CO₂ signal.

Since the rate of CO₂ formation quickly dropped to zero when the lights were turned off, as shown in Fig. 1, and since CO₂ does not adsorb to a significant extent on TiO₂ (1), the appearance of CO₂ in the gas phase is reaction limited. No other gas-phase products, such as H₂ or H₂O, were detected during PCD, but H₂O is not expected to desorb from TiO₂ at room temperature because it adsorbs much more strongly than CO₂. When TPD was carried out after the lights were turned off, however, water started desorbing at 380 K. During TPD in the absence of PCD, a monolayer of formic acid dehydrated to form CO and H₂O starting at 400 K (1) and CO₂ formed at high temperatures. Since CO does not adsorb on TiO₂ (1), CO formation during TPD is reaction limited, and thus water from dehydration does not form until 400 K. Therefore, the H₂O that formed from 380 to 400 K was *not* from catalytic dehydration of formic acid, but instead is a product of PCD. The amount of water that desorbed between 380 and 400 K was estimated to be 80% of the amount of CO₂ that formed during the PCD that was carried out prior to the TPD. No other intermediates or products were detected during the TPD to 723 K after PCD. For CO₂ and H₂O to form from formic acid during PCD, a source of oxygen is necessary. Since no O₂ was in the gas phase, lattice oxygen must be the source. Thus, the reaction that takes place during UV irradiation of a monolayer of formic acid in the absence of gas-phase O₂ appears to be



The CO₂ is immediately detected in the gas phase during transient PCD, but the water remains adsorbed on the surface and is only detected during the subsequent TPD. Several experiments described below were carried out to verify that lattice oxygen is involved in the PCD of formic acid.

The increase in the rate of CO₂ formation after a period of dark time is consistent with lattice oxygen oxidizing the adsorbed formic acid. During the dark period, when lattice oxygen was not being depleted by PCD, it diffused from the bulk to replace the surface lattice oxygen that had been consumed when the lights were on. Adsorption of an O₂ impurity from the gas phase does not appear to be responsible for the higher rates after the dark periods since the O₂ signal in the mass spectrometer did not decrease when the lights were turned on.

Photocatalytic Oxidation of Formic Acid

When 3% O₂ was in the gas phase, CO₂ formation from PCO of formic acid showed different behavior from that in Fig. 1. As shown in Fig. 2, upon UV illumination the rate of CO₂ formation during PCO quickly reached an initial rate that was 7 times higher (0.72 μmol/g catalyst/s) than the ini-

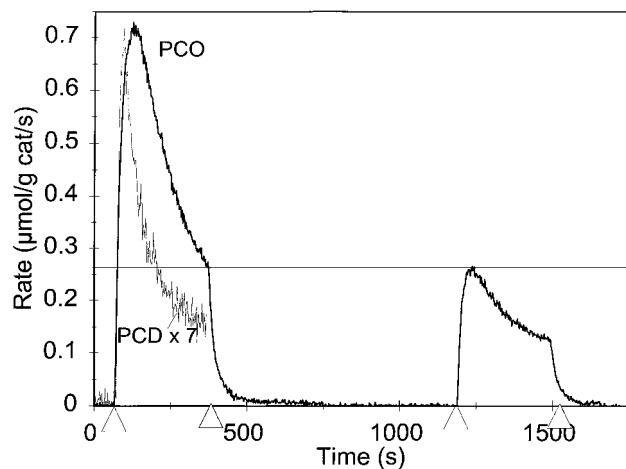


FIG. 2. Formation rate of CO₂ during photocatalytic oxidation of a monolayer of formic acid on TiO₂ in 3% O₂ in He flow. The UV lights were turned off for 3600 s and then back on. The CO₂ formation rate in He from Fig. 1 is included for comparison.

tial rate during PCD. Moreover, the rate of CO₂ formation decreased more slowly with time to 0.26 μmol/g catalyst/s after 300 s. This rate was approximately 36% of the initial rate, whereas the formic acid coverage was 64% of a monolayer. The CO₂ rate dropped much faster during PCD; after 300 s, the rate was approximately 20% of the initial rate and the formic acid coverage was 96% of a monolayer. The CO₂ formation rate from Fig. 1 is included in Fig. 2 to show that the PCD rate decreases substantially faster than the PCO rate, indicating that gas-phase O₂ is required to maintain a sustained photocatalytic rate.

When the lights were turned off, the rate of CO₂ formation dropped relatively rapidly. After the catalyst was held in the dark for 3600 s and then the lights were turned back on, the CO₂ formation rate during PCO was *identical to that measured just before the lights were turned off*. This result is in sharp contrast to that obtained when O₂ was absent from the gas phase during PCD (Fig. 1). This suggests that the source of oxygen for PCD is lattice oxygen because it was depleted during UV illumination, whereas the oxygen source for PCO (adsorbed and/or lattice oxygen) was not depleted.

Photocatalytic Decomposition with O₂ and Formic Acid Injections in the Dark

Experiments were performed to explore the roles of adsorbed O₂ and investigate the diffusion of lattice oxygen from the bulk to the surface. When 1200 s of PCD was followed by 3600 s of a period of dark time, the CO₂ rate during PCD after the dark period was 82% of the initial rate, and the formic acid coverage was 93% of a monolayer. When this experiment was repeated but the catalyst was exposed to a pulse of formic acid during the 3600-s dark period, the

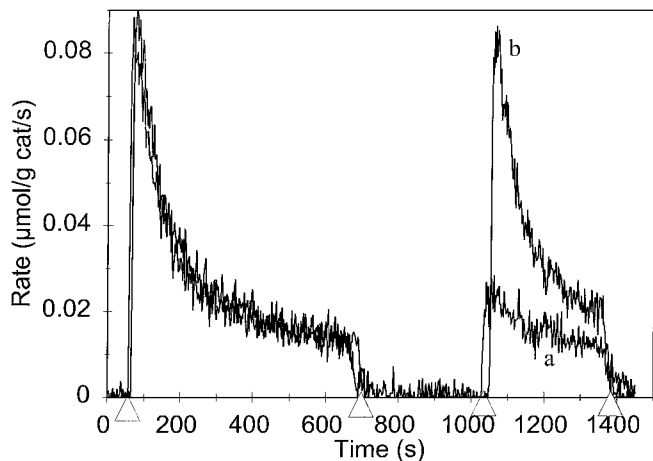


FIG. 3. Formation rates of CO_2 during photocatalytic decomposition of a monolayer of formic acid on TiO_2 in He flow. (a) The TiO_2 was held in the dark for 420 s; (b) a pulse of O_2 was injected over the TiO_2 during the 420-s period of dark time.

PCD rate was the same as the initial rate. That is, 3600 s was a sufficient period of dark time to replenish the lattice oxygen that had been depleted during 1200 s of PCD. The only reason the PCD rate was lower than the initial rate after the 3600-s dark period was because the surface was not saturated with formic acid. Indeed, when PCD was followed by a 9600-s dark period, the subsequent PCD rate was the same as that after a 3600-s dark period. When O_2 instead of formic acid was pulsed over the catalyst during a 3600-s dark period after 1200 s of PCD, the rate of CO_2 formation was the same when the lights were turned on as that measured without O_2 injection. That is, the TiO_2 surface was completely oxidized by diffusion of lattice oxygen during the 3600 s in the dark.

Since lattice oxygen appears to diffuse in 3600 s to completely re-oxidize the surface oxygen vacancies created by PCD, experiments were carried out for shorter periods of dark times. For curve a in Fig. 3, a monolayer of formic acid was photocatalytically decomposed for 600 s. The initial rate is less than that in Fig. 1 because the catalyst deactivated during weeks of experimentation. The UV lights were turned off for 350 s, and when they were turned back on, the rate of CO_2 production had increased from 0.015 to 0.025 $\mu\text{mol/g catalyst/s}$. When the experiment was repeated but a 170 μmol of $\text{O}_2/\text{g catalyst}$ pulse was injected in the dark, the results were quite different. All the O_2 was swept from the reactor during the 350-s dark period. As shown in curve b in Fig. 3, when the lights were turned back on, the CO_2 formation rate was 0.085 $\mu\text{mol/g catalyst/s}$, which is nearly equal to the initial CO_2 rate of 0.09 $\mu\text{mol/g catalyst}$. Apparently surface lattice oxygen that was depleted during PCD was replenished in the dark by gas-phase O_2 so that when UV illumination resumed, the rate of CO_2 formation of curve b was much greater than that of curve a.

Photocatalytic Decomposition with Heating during Dark Time

The rate that lattice oxygen diffuses from the bulk to replenish the reduced TiO_2 surface should increase at higher temperatures since oxygen diffusion in TiO_2 is activated (8). Figure 4 shows two interrupted PCDs, each for a monolayer of formic acid; 600 s of illumination was followed by a 420-s dark period. For curve a the catalyst was kept at room temperature for the 420-s dark period; the rate after the dark period was 0.02 $\mu\text{mol/g catalyst/s}$. For curve b the catalyst was heated to 400 K and quickly cooled to room temperature during the 420-s dark period. When UV illumination resumed, the rate of CO_2 formation was 0.033 $\mu\text{mol/g catalyst/s}$, which is 1.6 times the rate without heating. The increased rate after heating the TiO_2 in the dark further suggests that lattice oxygen diffusion from the bulk to the surface limits the rate of PCD at longer times. The higher lattice oxygen concentration at the surface after the catalyst was heated in the dark caused the rate of CO_2 formation to be higher when the lights were turned on.

Photocatalytic Reactions with H_2O Injections

The effect of water on PCD and PCO was investigated by injecting pulses of water (180 μmol of $\text{H}_2\text{O}/\text{g catalyst}$) both in the dark and during UV illumination. The water did not displace any formic acid. Figure 5 shows interrupted PCO of a monolayer of formic acid. Water was injected during the 420-s dark period and again during UV illumination after a total time of 1600 s. After water was injected in the dark, the CO_2 rate during PCO was 1.8 times the rate measured before the lights were turned off. As shown in Fig. 2, during PCO in 3% O_2 , the CO_2 formation rate did not change after a period of dark time. When water was

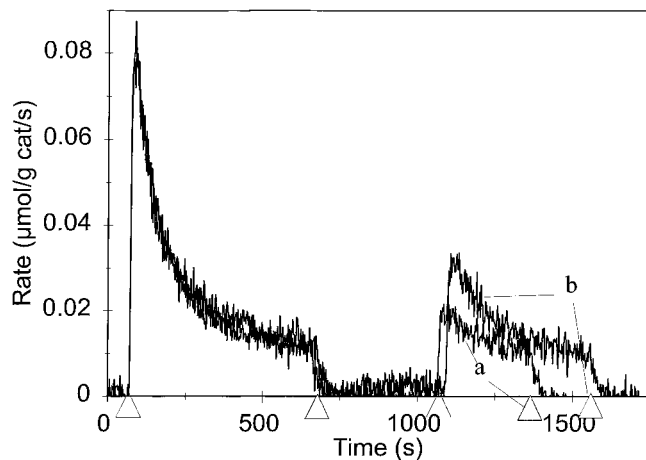


FIG. 4. Formation rates of CO_2 during photocatalytic decomposition of a monolayer of formic acid on TiO_2 in He flow. During the 420-s period of dark time, the TiO_2 was (a) held at room temperature, (b) heated to 400 K, and then cooled to room temperature.

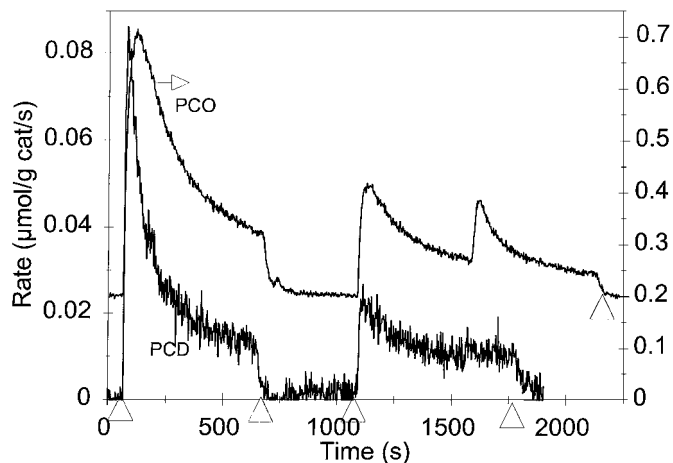


FIG. 5. Formation rates of CO₂ during photocatalytic decomposition (He flow) and oxidation (3% O₂ flow) of a monolayer of formic acid on TiO₂. The lights were turned off as indicated. Water was injected after 700 s (in the dark) and 1600 s (with the UV lights on).

injected *during* PCO, the CO₂ formation rate was 2.4 times the rate before injection, as seen in Fig. 5. Water injections increased PCO rates by similar amounts whether it was injected in the dark or during PCO. In contrast, water did *not* affect the CO₂ formation rate during PCD. Figure 5 shows that, after water injection in the dark, the subsequent CO₂ rate during PCD was the same as that observed for a 420-s dark period without water injection. Furthermore, a subsequent water injection during UV illumination (at 1600 s) did not change the CO₂ rate. This suggests that water does not oxidize reduced TiO₂, either in the dark or under UV illumination, similar to the conclusions reached by Pan *et al.* (10). Note in Fig. 5 that UV illumination was stopped after 1800 s for PCD but after 2200 s for PCO.

DISCUSSION

Absence of Gas-Phase O₂ during PCD

Several measurements showed that the concentration of gas-phase O₂ was sufficiently small during PCD experiments so that the PCD rates were not affected. A small *m/e* 32 signal was detected by the mass spectrometer when helium was flowing during PCD, *but this signal did not change when the UV lights were turned on*. Photocatalytic oxidation is a sensitive method for detecting O₂ in a gas stream since changes in the O₂ signal were readily detected when low concentrations of O₂ flowed over organic-covered TiO₂ and UV lights were turned on (1, 12, 15, 16). Thus, the small *m/e* 32 signal was due to a background signal in the mass spectrometer vacuum chamber, rather than to an O₂ impurity in the helium stream.

For the experiment in Fig. 1, the amplitude of the O₂ signal was estimated to correspond to an O₂ concentration of less than 0.3 ppm. For the flow rates used, during the

first 5800 s of PCD and dark time, less than 3.2 μmol of O₂/g catalyst would have adsorbed for a 0.3 ppm impurity, but 16.5 μmol of O₂/g catalyst were required if gas-phase O₂ supplied the oxygen for the 2200 s of reaction. Furthermore, a 2.2 ppm O₂ impurity would be required to produce CO₂ at the rate observed for longer PCD times (approximately 0.008 μmol/g catalyst/s); this level of O₂ impurity would be readily detected by the mass spectrometer.

When the catalyst was heated in the dark after PCD (Fig. 4), the CO₂ production rate was greater during subsequent UV illumination than when the catalyst was held at room temperature in the dark. This experiment also shows that a small O₂ impurity was *not* responsible for reoxidization of the surface because heating the catalyst should not increase the O₂ impurity concentration.

The effect of water on PCO has not been explained at the present time. Figure 5 was included, however, to show that PCD and PCO oxidize organics by different mechanisms. Furthermore, the striking difference in the effect of water on PCD and PCO provides additional evidence that the increase in the rate of PCD following a period of dark time is not because of a small O₂ impurity in the helium. If such an impurity were present, PCD should behave like PCO in low O₂ concentrations and H₂O should increase the rate of CO₂ formation, but it did not.

Surface Diffusion of Formic Acid

One possible explanation for the increased rate after the dark time in Fig. 1 is that formic acid reacts first on the most active sites on TiO₂, and the reaction slows as these sites are depleted of formic acid. During the period of dark time the formic acid that remains on the surface could then diffuse to these active sites, and thus the rate would be higher when the lights are turned back on. Since no rate increase was seen after the period of dark time for PCO in Fig. 2, however, the PCO rate does not appear to be limited by formic acid diffusion. Formic acid is expected to surface diffuse at the same rate during PCO and PCD, and since PCD is slower than PCO, PCD is apparently not limited by formic acid diffusion.

An additional experiment was done to determine whether most of reaction takes place on a small number of highly active sites. After 1200 s of PCD of a monolayer of formic acid, 90 μmol of HCOOH/g catalyst were injected upstream of the reactor with the lights on. The injected formic acid is expected to adsorb on active sites that were empty after 1200 s of PCD. This injection increased the rate of CO₂ production from 0.01 to 0.03 μmol/g catalyst/s, indicating the PCD rate dependence on formic acid concentration is greater than 1. A portion of the increase in rate may be because some sites are more active for formic acid PCD, or because a small amount of O₂ was dissolved in the formic acid. However, the rate after the formic acid injection was less than 30% of the initial CO₂ production

rate, which further shows that PCD is not limited by surface diffusion of formic acid to active sites.

Roles of Adsorbed and Lattice Oxygen during UV Illumination

When UV light illuminates TiO₂ in the absence of gas-phase O₂, adsorbed formic acid extracts oxygen from the lattice to form CO₂ and H₂O, and the reduced surface is replenished by diffusion of lattice oxygen from the bulk. Indeed, Fig. 4 shows that heating the catalyst in the dark increased the rate of lattice oxygen diffusion from the bulk so that a higher lattice oxygen concentration at the surface increased the rate of CO₂ formation when the lights were turned on.

In Fig. 3, the difference in the rates for curves a and b after the period of dark time is due to the difference in available lattice oxygen at the surface. For curve a, the dark period of 350 s was too short to replenish all the depleted surface lattice oxygen by diffusion of lattice oxygen from the bulk. A pulse of gas-phase oxygen (curve b), however, readily replenished the surface lattice oxygen *in the dark at room temperature*, as reported by others (8–11). These results show that the increase in the CO₂ production rate after a dark period is due to replenishment of surface lattice oxygen. They also show that UV light is not required for gas-phase O₂ to oxidize the reduced TiO₂ surface. Since a pulse of O₂ (curve b, Fig. 3) increases the rate significantly more than a pulse of formic acid (discussed above), the availability of surface lattice oxygen limits CO₂ formation during PCD.

For the PCO shown in Fig. 2, the CO₂ formation rate did *not* increase after the period of dark time. Since the period of dark time would have allowed any depleted oxygen to be replenished by gas-phase O₂, neither lattice nor adsorbed oxygen are depleted during PCO in 3% O₂, presumably because O₂ adsorbs as fast as it reacts. If UV light were required for O₂ to adsorb, however, then the period of dark time would not have allowed depleted oxygen to be replenished. Significant photoadsorption of O₂ appears unlikely since Larson *et al.* (12) did not detect any O₂ photoadsorption when fresh TiO₂ was illuminated in 30 ppm O₂ flow. They concluded that the amount of photoadsorbed O₂ was less than 1 μmol/g catalyst.

To further show the difference between the roles of lattice and adsorbed oxygen, PCO was carried out in 3 ppm O₂. Immediately upon UV illumination, the CO₂ rate reached a maximum of 0.08 μmol/g catalyst/s and the O₂ signal dropped to the background level. Due to deactivation of the catalyst, this initial rate is lower than that in Fig. 1, but it is comparable to that measured during PCD for the catalyst at this stage in its deactivation. After 1200 s of PCO, the CO₂ formation rate was 0.016 μmol/g catalyst/s, even though only approximately 0.011 μmol of O atoms/g catalyst/s was supplied from the gas phase. The O₂ conversion remained

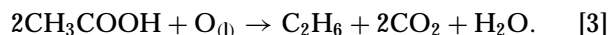
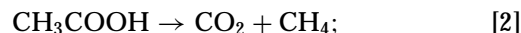
at 100% for 1200 s of PCO *and for an additional 1000 s after PCO was stopped*. This corresponds to an uptake of 24 μmol O atoms/g catalyst during PCO and the following 1000-s dark period. This oxygen uptake agrees well with the 26 μmol/g of catalyst of CO₂ that formed during PCO. These results show that both lattice oxygen and O₂(g) were consumed during PCO at this low O₂ concentration, and the lattice oxygen was then replenished by gas-phase O₂ in the dark. The gas-phase O₂ increased the CO₂ formation rate above that seen during PCD. After 1200 s of PCO in 3 ppm O₂, the CO₂ formation rate was 0.016 μmol/g catalyst/s, which is 60% greater than the rate after 1200 s of PCD.

The first step in PCO may be similar to that of PCD since the surface was fully oxygenated and saturated with formic acid at the start of both transient experiments. However, the substantially higher rate of PCO in 3% O₂ indicates that although lattice oxygen may react during PCO, the dominant reaction is with adsorbed oxygen.

When O₂ was injected during a 3600-s period of dark time after PCD, it did not increase the rate because 3600 s was long enough for lattice oxygen to diffuse to the surface, and either the O₂ injection or the lattice oxygen diffusion replenished the surface lattice oxygen. This experiment also indicates, however, that either the adsorbed oxygen coverage was low after the gas-phase O₂ was removed or adsorbed oxygen does not participate in PCD. The O₂ injection should have replenished any adsorbed oxygen consumed during the initial PCD, whereas the period of dark time is only expected to replenish lattice oxygen.

Comparison between Acetic Acid and Formic Acid PCD

As reported previously (13, 14), in the absence of gas-phase O₂, acetic acid decomposes by parallel pathways during transient experiments to form CH₄, C₂H₆, CO₂, and H₂O:



Note that Reaction [2] does not require lattice oxygen whereas Reaction [3] does. Reaction [3] is the analogous reaction to that reported here for PCD of formic acid. For acetic acid PCD, CH₄ is presumably produced either by recombination of CH₃(_{ads}) with H(_{ads}) or through a reaction between CH₃(_{ads}) and surface hydroxyls or water. In contrast, during PCD of formic acid, no evidence of H₂ was observed. Hydrogen atoms might form, but might not be able to recombine at a measurable rate on TiO₂.

CONCLUSIONS

Formic acid photocatalytically decomposes at room temperature to CO₂ and H₂O on TiO₂ without gas-phase

O₂ by extracting oxygen from the lattice (HCOOH_(ads) + O_(lattice) → CO_{2(g)} + H₂O_(ads)). As the surface lattice oxygen was depleted, lattice oxygen diffusion from the bulk limits the PCD rate. Bulk oxygen diffuses to an oxygen-deficient surface at approximately 0.008 μmol/g catalyst/s (10⁻⁴ atoms/nm²/s). During PCO in excess O₂, the surface is fully oxygenated, and the rate of PCO is much faster than the rate of PCD, so adsorbed oxygen appears to play a major role in PCO. Gas-phase O₂ replenishes reduced TiO₂ in the dark, but H₂O does not re-oxidize TiO₂, even during UV illumination. Surface diffusion of formic acid to active sites does not limit either PCD or PCO. Continued PCD deactivated the TiO₂ catalyst.

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