Transient measurements of lattice oxygen in photocatalytic decomposition of formic acid on TiO_2

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In the absence of gas-phase O_2, formic acid extracted lattice oxygen from TiO_2 during photocatalytic decomposition (PCD) at room temperature. The amount of oxygen extracted was determined by interrupting PCD of a monolayer of formic acid after various reaction times and measuring O_2 uptake in the dark. After surface oxygen was depleted by PCD, oxygen diffused from the bulk to replenish the surface oxygen vacancies. The rate of oxygen diffusion to the surface was determined by measuring O_2 uptake after various dark times. A small fraction of the CO_2 that formed during PCD remained on the reduced sites of the TiO_2 surface, but this CO_2 was displaced by O_2 adsorption at room temperature.

Keywords: lattice oxygen, photocatalytic decomposition, formic acid, TiO_2, oxygen diffusion

1. Introduction

Heterogeneous photocatalytic oxidation (PCO) of organic pollutants is a promising process for air decontamination. A wide range of organics in low concentrations in air can be oxidized to CO_2 and H_2O at ambient temperature and pressure on semiconductor photocatalysts under UV illumination. Band gap excitation of semiconductors generates electron–hole pairs that can initiate redox processes.

A monolayer of formic acid readily decomposed photocatalytically on TiO_2 at room temperature to form CO_2 and H_2O without O_2 in gas phase [1]. This reaction, referred to as photocatalytic decomposition (PCD), formed water by extracting lattice oxygen from the TiO_2 surface. At longer reaction times, reaction continued as lattice oxygen diffused from the bulk to the surface, and the reaction became limited by lattice oxygen diffusion. Consequently the reaction rate decreased rapidly with time. However, the PCD rate was much higher after the TiO_2 was held in the dark because lattice oxygen diffused to the surface during the dark time.

In the current study, we measured the amount of oxygen extracted during PCD of formic acid on TiO_2 and the rate of lattice oxygen diffusion. Formic acid was used because it readily undergoes PCD, and its oxidation is of interest since it forms during PCO of other organics, such as ethanol. Transient reaction experiments are well suited to studying a process that depletes lattice oxygen. In these transient experiments, a monolayer of formic acid was adsorbed on oxidized TiO_2 (Degussa P25) and the excess organic was flushed from the gas phase. The catalyst surface

was then exposed to UV illumination in the absence of gas-phase O_2, and the reaction products were detected by a mass spectrometer. The amount of lattice oxygen that was extracted during PCD was measured by injecting O_2 pulses in the dark after PCD for various times. The rate of oxygen diffusion from the bulk was measured by injecting O_2 pulses after a delay time in the dark. The effect of UV intensity on PCD was studied by comparison to a previous study that used lower intensity UV.

2. Experimental

Transient reaction measurements

The apparatus used for photocatalytic decomposition (PCD) and temperature-programmed oxidation (TPO) was described previously [2]. Approximately 30–50 mg of catalyst (Degussa P25 TiO_2, 50 m^2/g surface area) was coated as a thin layer on the inside surfaces of an annular Pyrex reactor so that all the catalyst was exposed to UV light. The annular reactor had a 1 mm annular spacing so that high gas flow rates could be maintained across the catalyst to 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. Twelve 8 W UV lamps (Johnlite, F8T5BlB) surrounded the reactor. This provided a UV intensity of approximately 2.5 mW/cm^2, which is almost an order of magnitude higher than the intensity used in the previous study of formic acid PCD [1].

Transient reaction of formic acid was carried out at room temperature with mass spectrometric detection. Before each experiment the catalyst was held at 723 K for 30 min in

20% O_2 in He and then cooled to room temperature to create a reproducible surface. Two 1 μl pulses of formic acid (Sigma, 99%) saturated the catalyst in the dark at 300 K prior to PCD. 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 carried out in 100 cm^3/min (STP) of He flow by turning the UV lights on at room temperature and observing the products that formed with a Balzers QMG 421C quadrupole mass spectrometer. Reaction was stopped and started by turning the lights off and on. A small $m/e = 32$ signal was detected by the mass spectrometer, but that signal did not change when the lights were turned on. Thus, the m/e 32 signal was due to background gas in the vacuum chamber, and the O_2 concentration in the feed stream was below the detection limit, which we estimate to be 0.3 ppm [3]. For even low concentrations of O_2 in the gas stream, we readily detected a drop in the m/e 32 signal due to photocatalytic oxidation (PCO), and thus the absence of a change in the $m/e = 32$ signal was a good test of the purity of the helium stream.

The mass spectrometer monitored the reactor effluent immediately downstream of the reactor. A computer interfaced to the mass spectrometer recorded the amplitudes of multiple mass peaks simultaneously and the output from a thermocouple in contact with the catalyst. The mass spectrometer was calibrated by injecting known volumes of gases into the flow downstream of the reactor, and signals were corrected for cracking in the mass spectrometer. After PCD, TPO was performed by heating the catalyst at 1 K/s to 723 K in 20% O_2 and holding the catalyst at 723 K until no products were detected. The TPO was used to determine how much formic acid or reaction products and intermediates remained on the surface after PCD.

3. Results and discussion

As reported previously [1], formic acid decomposed photocatalytically to gas-phase CO_2 and adsorbed H_2O in the absence of gas-phase O_2. As shown in figure 1(a), upon UV illumination the rate of CO_2 formation quickly reached a maximum rate and then deceased to 15% of its initial rate after 600 s of PCD. This behavior is similar to that observed previously [1] for lower light intensity (0.3 versus 2.5 mW/cm^2). The CO_2 rate dropped to zero when the lights were turned off. In order for both CO_2 and H_2O to form during formic acid PCD, lattice oxygen must be extracted from the TiO_2 surface. Thus the overall reaction that takes place during UV irradiation of adsorbed formic acid in the absence of gas-phase O_2 appears to be [1]

$$HCOOH_{(ads)} + O_{(lattice)} \rightarrow CO_{2(g)} + H_2O_{(ads)}$$
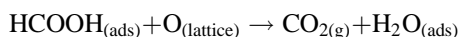
The CO_2 was immediately detected in the gas phase, but water was not seen during PCD and was only detected during a subsequent TPD. When UV illumination resumed
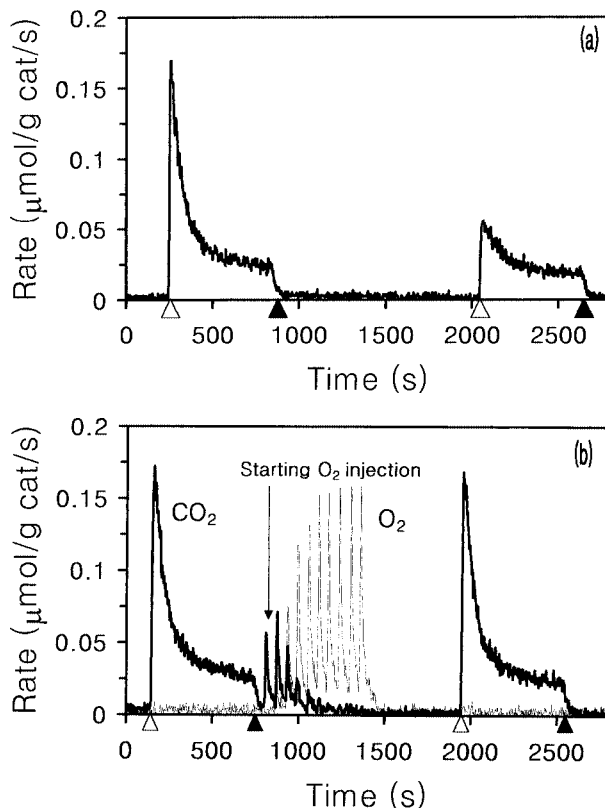

Figure 1. (a) Formation rate of CO_2 during photocatalytic decomposition of a monolayer of formic acid on TiO_2 in He flow. The UV lights were turned on ($\triangle$) and off ($\blacktriangle$) as indicated. (b) Same as (a) but ten pulses of O_2 were injected during the dark time.

after 1200 s in the dark, the CO_2 rate was twice the value observed before the lights were turned off. During the dark time, lattice oxygen diffused to the surface, and thus the rate was higher.

To verify that lattice oxygen was removed from the surface during PCD, the transient reaction experiment was repeated, but ten pulses of 3.3 μmol-O_2/g-catalyst were injected during the dark time. As shown in figure 1(b), the O_2 in the first two pulses was almost completely taken up by the TiO_2 in the dark, so that almost no O_2 was detected in the reactor effluent when these pulses were injected. Less of the subsequent pulses were consumed, and the sizes of the last five pulses were almost identical at the reactor exit. Thus, essentially no O_2 was adsorbed from the last five pulses, and their size served as a calibration to determine the O_2 uptake in the first five pulses.

After all the gas-phase O_2 was swept from the reactor, and the lights were then turned back on, the CO_2 formation rate *was nearly equal to the initial CO_2 rate* of 0.175 μmol/g-cat s. The difference in the rates for figure 1 (a) and (b) after the dark time is due to the difference in available lattice oxygen. For figure 1(a), the dark period was not long enough to replenish all the surface oxygen vacancies by lattice oxygen diffusion from the bulk. Gas-phase oxygen, however, readily replenished the TiO_2 lattice surface oxygen in the dark at room temperature, as reported by others [1,4–6].
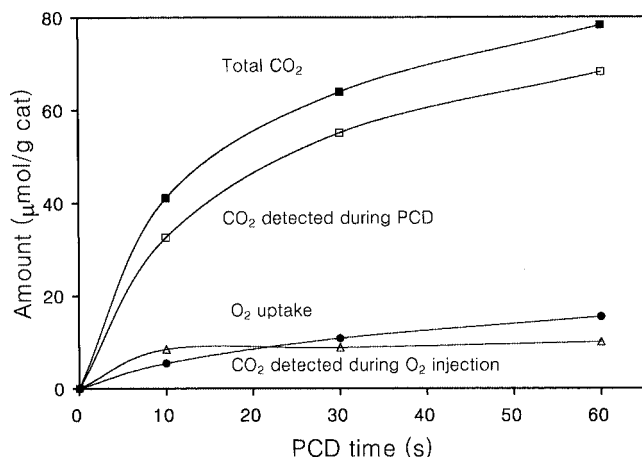
Figure 2. The amount of CO_2 formed during PCD as a function of PCD time, and the amounts of O_2 taken up in the dark and the amount of CO_2 desorbed in the dark.

Interestingly, the first few pulses of O_2 were accompanied by CO_2 evolution from the surface, as shown in figure 1(b). This CO_2 could be from the reaction of a surface intermediate with O_2, or the O_2 could be displacing the CO_2 product that remained on the surface. Since no reaction intermediates were observed when TPD was carried out after PCD or PCO of formic acid, CO_2 probably does not form from an intermediate. Moreover, when $^{18}O_2$ was injected in the dark for the same experiment as in figure 1(b), no ^{18}O-containing CO_2 formed, indicating that gas-phase O_2 was not reacting with an intermediate. Instead, it displaced CO_2 that remained on surface after PCD. Carbon dioxide does not adsorb strongly on TiO_2; when Degussa TiO_2 was exposed to CO_2 at room temperature, only a small amount desorbed during a subsequent TPD [7]. However, the CO_2 coverage increased when the TiO_2 surface was reduced, though the amount adsorbed was still small [7].

In a series of experiments, each starting with a monolayer of formic acid, O_2 uptake was measured after various PCD times, and the amounts of CO_2 detected during PCD and subsequent O_2 injection are plotted in figure 2 versus the PCD time. Both the amount of CO_2 detected during PCD and the O_2 uptake in the dark increased with longer PCD time. The concentration of surface oxygen vacancies is expected to increase with PCD time, at least at shorter times, and thus the amount of O_2 uptake increased with PCD time. The amounts of CO_2 detected during O_2 injection were approximately constant following PCD for 600 s or longer. This CO_2 coverage corresponds to less than 3% of a formic acid monolayer, showing that CO_2 adsorbed only to low coverage, even on reduced TiO_2.

When PCD was carried out for 3600 s, the CO_2 production immediately reached a maximum rate of 0.173 μmol/g-cat s, quickly decreased to 0.03 μmol/g-cat s, and then decreased more slowly to 0.01 μmol/g-cat s. After 3600 s of PCD, 79% of a monolayer of formic acid was still on the surface. A significant amount of lattice oxygen w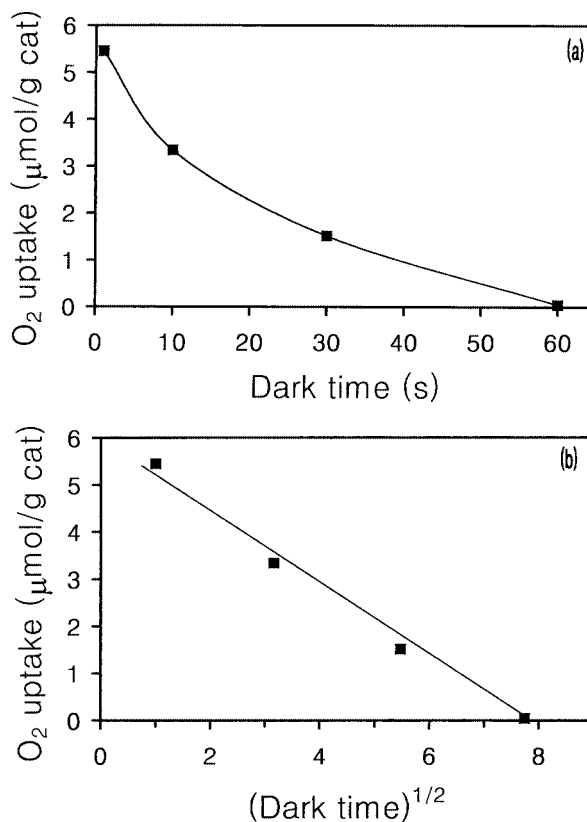as removed from the surface initially, and then reaction continued as oxygen diffused from the bulk to surface, and that diffusion limited the reaction rate.

Figure 3. The amount of O_2 uptake following 10 min of PCD: (a) as a function of dark time and (b) as a function of (dark time)$^{1/2}$.

Because of the reaction stoichiometry, and because lattice oxygen diffuses to the surface during PCD, the amount of O_2 uptake after PCD should be less than half of the total CO_2 formed during PCD. The O_2 replenishes surface lattice oxygen at room temperature. As shown in figure 2, the O_2 uptake is only 20% of the total CO_2 amount. On TiO_2, formic acid adsorbs dissociatively to form formate and a proton [6,8,9], which presumably forms a hydroxyl group. Thus some oxygen vacancies may not form until H_2O forms or H_2O desorbs [8,9].

Figure 3 shows the amount of O_2 uptake versus dark time after PCD. The O_2 uptake was measured in repeat experiments after various dark times following 10 min of PCD. The O_2 uptake decreased with increasing dark time (figure 3(a)), showing that during the dark time the concentration of surface oxygen vacancies decreased. This is expected as lattice oxygen diffuses from the bulk to replenish surface lattice oxygen. The oxygen diffusion rate declines with time, as indicated by the decrease in the absolute value of the slope with time. The lattice oxygen diffusion rate should decrease as the surface becomes oxygenated because of a decrease in the oxygen concentration gradient between the bulk and the surface. As shown in figure 3(b), the O_2 uptake is linear with the square root of dark time, as expected for a diffusion process. Note that the O_2 uptake measurements required a finite time, so the

fit to a linear dependence is good. From this plot, an average oxygen diffusion rate during these experiments was 0.035 μmol O atoms/g-cat s (4×10^9 O at/cm^2 s) throughout the dark time. Rekoske and Barteau [10] reported that the oxygen atom flux from the bulk to the TiO$_2$ surface ranged 0.2–5×10^{11} O at/cm^2 s; the TiO$_2$ was reduced with H$_2$ at 573–773 K. This difference in the two measured values may be ascribed to the difference in temperature and the extent of reduction because higher temperature and higher extent of surface reduction increase oxygen diffusion rates.

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