Role of Weakly Adsorbed Water in the Photocatalytic Decomposition of Formic Acid on Pt/TiO₂†

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Photocatalysis is an effective method of oxidizing or decomposing organic contaminants present in low concentrations in the air at room temperature. The rate of photocatalytic decomposition of formic acid on 0.2 % Pt/TiO₂ was studied using transient isothermal reaction and temperature programmed desorption. Formic acid is of interest because it is an intermediate oxidation product of many organics. Transient photocatalytic decomposition shows that water co-adsorbed with formic acid does not significantly affect the rate of decomposition. Water is weakly adsorbed, however, significantly increases the rate. Only hydrogen was formed and any other product such as oxygen or carbon dioxide was not produce when water was injected in the reactor in the dark after photocatalytic decomposition of formic acid. It is inferred that the role of weakly adsorbed water is to replenish the vacant lattice oxygen of TiO₂ surface which are the main reason for the rate decrease.

Key Words: Photocatalytic decomposition, Formic acid, Weakly adsorbed water, Pt/TiO₂.

INTRODUCTION

Heterogeneous photocatalytic oxidation of organic pollutants is a promising process for the treatment of contaminated air. Many organic pollutants in low concentration can be oxidized to CO_2 and H_2O in air at room temperature on TiO_2 under UV irradiation. The UV light excites electrons from the valence band to the conduction band of TiO_2 and hole is produced. The electron-hole pairs can initiate redox reactons with surface species.

A monolayer of formic acid readily decomposed photocatalytically to CO_2 and H_2O on TiO_2 at room temperature in the absence of O_2 in the gas phase[1]. In this reaction, referred to photocatalytic decomposition, water was formed by the reaction between hydrogen and the lattice oxygen of TiO_2 surface[1,2].

Addition of low loadings of Pt to TiO_2 (Pt/TiO₂) increases the rates of photocatalytic decomposition and changes a product distribution[3,4]. When photocatalytic decomposition of formic acid was carried out on Pt/TiO₂, CO_2 and H_2 were produced. In this case, hydrogen atoms transferred to Pt site and combined there to form hydrogen molecules, as is the case of photocatalytic decomposition of acetic acid[5,6].

During the course of our study on the effect of water in the photocatalytic reaction of organic compounds, we observed that weakly adsorbed water dramatically increase the rate of photocatalytic decomposition of formic acid on a Pt/TiO₂ catalyst, but chemisorbed water (strongly adsorbed water) does not show any decomposition. The effect of water on photocatalytic decomposition is of interest because water vapour is usually present in air streams that have low concentrations of volatile organic compounds. Water was found to increase photocatalytic decomposition rate of organic acids[6]. Moggli and Falconer[1] showed that water injected over a TiO_2 doubled photocatalytic oxidation of formic acid, but does not photocatalytic decompo-sition rates. To clarify the relative importance of weakly and strongly adsorbed water, photocatalytic decomposition of formic acid was studied. Formic acid was used because it readily undergoes photocatalytic decomposition and the reaction rate can be directly measured by measuring CO_2 formation since CO_2 is not strongly bound to Pt/TiO₂ at room temperature. Transient reaction experiments were used in this study. A monolayer of formic acid was adsorbed on Pt/TiO₂ and excess organics flushed from the gas phase. The catalyst was then illuminated with UV lights in the absence of gas-phase O_2 and the reaction products were detected by a mass spectrometer. Water was injected by a pulse in the gas phase or adsorbed on the catalyst surface to investigate the weakly or strongly adsorbed water effect, respectively. Species that remained on the surface after photocatalytic decomposition were removed and analyzed using temperature programmed desorption and oxidation.

EXPERIMENTAL

The apparatus used for photocatalytic decomposition, temperature programmed desorption and temperature programmed oxidation was described previously[7]. A Pyrex annular reactor 20 cm high and a 2 cm in diameter was used. The reactor had a 1-mm annular spacing which resulted in high gas flow rates (5 cm/s) over the catalyst to increase mass transfer and to rapidly flushed gas products out of the system. All experiments were conducted with a 100 sccm (standard cm^3/min) flow rate, which was regulated by a mass flow controller. A quartz tube furnace was used to heat the catalyst at a rate of 1 K/s for temperature programmed oxidation and temperature programmed desorption. The 0.2 wt % Pt/TiO$_2$ was prepared using 0.067g H$_2$PtCl$_6$, mixed with 10 g Degussa P-25 TiO$_2$ in 100 mL of 1 M HCl. To this Na$_2$CO$_3$ was added until the pH was about 7-8 and acetic acid (*ca.* 3 mL) was then added until the pH was 4. About 300 mL of water was then added and N$_2$ was bubbled through the solution under an UV lamp for 6 h. This solution was then filtered and washed with H$_2$O. The solid catalyst was dried at 373 K for 24 h. Approximately 25-30 mg of catalyst was coated as a thin layer on the inner side of the annular Pyrex reactor so that all the catalyst was exposed to UV light.

The photocatalytic reaction was initiated by twelve 8-W UV lamps (BLB Korea, type F8T5BLB) equally spaced in a circle about 6 cm from the reactor. Photocatalytic decomposition was carried out by first heating the reactor to 723 K and was maintained for 0.5 h in a 20 % O$_2$ stream to create a reproducible surface. After the reactor was cooled, 2-3 µL of liquid formic acid (Aldrich, 99 %) was injected and evapourated just upstream of the reactor. All gas phase reactants were flushed from the system for about 2 h before photocatalytic decomposition so that the only reactants were on the adsorbed on the catalyst surface. Photocatalytic decomposition was carried out in 100 cm^3/min (STP) of He or Ar flow at room temperature by turning the UV lights on. Reaction was started and stopped by turning the lights on and off, while recording the mass spectrometer signals. A Balzers QS 421 quadrupole mass spectrometer (Balzers TCP015) was used to measure reactor effluent concentrations *versus* time. This mass spectrometer was connected to a computer that recorded multiple mass peaks and the catalyst temperature simultaneously. The mass spectrometer signals were calibrated daily with known volumes of gases injected downstream from the reactor and were corrected for cracking. During photocatalytic decomposition when helium or argon was flowing, a small *m/e* = 32 signal was detected by the mass spectrometer, but this signal did not change when the lights were turned on. Thus, the *m/e* = 32 signal was due to a background signal in the vacuum chamber and the O$_2$ concentration in the feed stream was below the detection limit, which we estimate be 0.3 ppm[8].

The use of dark time allowed for the use of lattice oxygen by the reactions to be investigated as described previously[1,2]. After photocatalytic decomposition, temperature programmed desorption or temperature programmed oxidation was carried out by heating the catalyst to 723 K at a rate of 1 K/s while monitoring the mass signals with the mass spectrometer. The catalyst was then held at 723 K until all mass signals returned to baseline values. Helium or argon (100 sccm) was used for temperature programmed desorption and 20 % O$_2$ was used for temperature programmed oxidation.

RESULTS AND DISCUSSION

Formic acid decomposed photocatalytically to gas-phase CO$_2$ and H$_2$ on Pt/TiO$_2$ in the absence of gas phase oxygen. In the photocatalytic decomposition of HCOOH on TiO$_2$, only CO$_2$ was detected and H$_2$ was not detected in the gas phase[1,2]. Fig. 1 shows the CO$_2$ and H$_2$ formation rate *versus* time for transient photocatalytic decomposition of monolayer of formic acid on Pt/TiO$_2$. Upon UV illumination at 120 s, the rate of CO$_2$ reached a maximum (0.289 µmol/g/s) rapidly. The rate decreased quickly initially and then much more slowly. The rate dropped to 0.036 µmol/g/s after 480 s of photocatalytic decomposition, which is only 12 % of the initial rate. At this point, the coverage of formic acid was 90 %. Interestingly, the initial formation rate of CO$_2$ was larger than that of H$_2$, but became similar to each other as the reaction time increases. Thus, the initial maximum rate of H$_2$ was 0.116 µmol/g/s, which was only 40 % of that of CO$_2$. The amount of H$_2$ produced was only 66 % of that of CO$_2$ for 180 s of reaction and then increased to 76 % for 480 s of the reaction. The difference between the amount of CO$_2$ and H$_2$ was 6.9 and 7.9 µmol/g-cat for 180 s and 480 s, respectively. These differences are due to adsorbed water produced by the reaction of hydrogen and lattice oxygen of TiO$_2$. Water formation was observed on the photocatalytic decomposition of acetic acid on Au/Pt/TiO$_2$ by surface-enhanced IR adsorption spectroscopy *in situ*, as well[4].
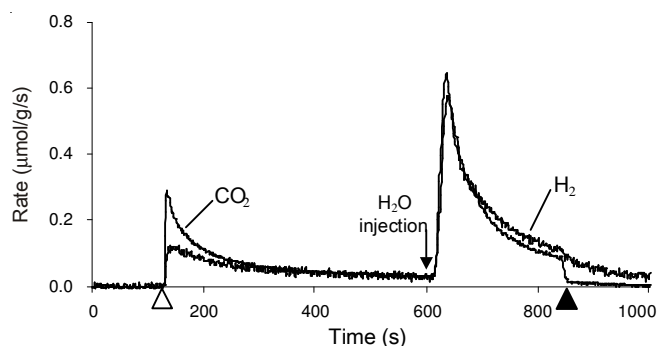

Fig. 1. Formation rate of CO$_2$ and H$_2$ *versus* reaction time during photocatalytic decomposition of a monolayer of formic acid on Pt/TiO$_2$ in He flow. The UV lights were turn on (open triangle) and off (solid triangle). Water (0.1 µL, 220 µmol/g cat) was injected at 600 s as a pulse on the top of the reactor during UV illumination

When water was injected on the top of the reactor during UV illumination, CO$_2$ and H$_2$ formation rate increased dramatically. When 0.1 µL of water (220 µmol/g cat) was injected at 600 s, the rate of CO$_2$ formation was 16 times higher than the rate before water injection, which is corresponding to double of the initial rate. The maximum rate of H$_2$ was slightly higher than that of CO$_2$ in this case. The amount of H$_2$ formed during the reaction from 600 s to 700 s was slightly larger than that of CO$_2$ as well (32.1 *vs.* 30.7 µmol/g cat).

In order to examine the effect of weakly and strongly adsorbed water on the photocatalytic decomposition of HCOOH on Pt/TiO$_2$, two kinds of experiments were carried

out. In the first experiment, only HCOOH was adsorbed initially, whereas in the second experiment, both HCOOH and H_2O were co-adsorbed and then photocatalytic decomposition was carried out. These results are shown in Fig. 2(a) and (b), respectively. In Fig. 2(a), two of 1 mL of HCOOH was injected to saturate the catalyst and the reactor was flushed for 2 h to remove gas-phase HCOOH. The total adsorbed amount of HCOOH was 318 µmol/g. When UV was turned on at 120 s, the initial rate of CO_2 formation was 0.284 µmol/g/s and the rate reduced rapidly. When 88 µmol/g-cat of water was injected at 300 s during UV illumination, the formation rate of CO_2 increased from 0.050 µmol/g/s to 0.305 µmol/g/s. In the second experiment, a mixture of HCOOH and H_2O with mole ratio of 1:4 was used to adsorb HCOOH and H_2O simultaneously on the Pt/TiO_2 surface, because HCOOH is adsorbed more strongly than H_2O on Pt/TiO_2 surface. In Fig. 2(b), 1 µL of the mixture of HCOOH and H_2O was injected to the top of the reactor and the rector was flushed 2 h to remove gas-phase HCOOH and H_2O. The adsorbed amount of HCOOH and H_2O was 253 and 70 µmol/g-cat, respectively. The adsorbed amounts were measured by another experiment, in which photocatalytic oxidation and temperature programmed oxidation were followed after adsorption of the mixture. When UV was on at 120 s, the initial rate of CO_2 formation was 0.239 µmol/g/s. The smaller initial rate in Fig. 2(b) than in 2(a) is due to the lower coverage of HCOOH before the reaction. After 88 µmol/g-cat of water was injected at 300 s, the formation rate of CO_2 was increased from 0.036 µmol/g/s to 0.274 µmol/g/s. The fact that the initial rate of Fig. 2(b) where strongly co-adsorbed water is present is smaller than 2(a) where strongly co-adsorbed water is absent indicates that strongly adsorbed water does not promote the rate of photocatalytic decomposition of HCOOH on Pt/TiO_2. Water effluent from the bottom of

the reactor was detected after water injection, which indicates that weakly adsorbed or gas-phase water is present in the reaction system. In Fig. 2(b), the amount of injected water at 300 s was similar to that of initially adsorbed water. Injected water enhanced the rate of photocatalytic decomposition of HCOOH, whereas initially strongly adsorbed water did not.

To examine the role of water, photocatalytic decomposition of HCOOH was carried out and water was injected to the top of the reactor in the dark after the photocatalytic decomposition. Fig. 3 shows the rates of products as a function of time. UV was turned on at 120 s, turned off at 540 s and then the reactor was maintained for 600 s in the dark. 220 µmol/g-cat of water was injected 30 s after UV was turned off. The amounts of CO_2 and H_2 formation during photocatalytic decomposition of HCOOH before dark time were 38.1 and 30.4 µmol/g-cat, respectively. The difference between the amount of CO_2 and H_2 formed during the photocatalytic decomposition was 7.7 µmol/g-cat. The CO_2 and H_2 formation rates dropped to zero when UV was turned off. Upon water injection in the dark, hydrogen was produced and any other product such as oxygen or CO_2 was not detected in the gas-phase. The maximum rate was 1.6 times higher than that of initial photocatalytic decomposition rate. The H_2 formation was continued for 60 s and the amount of H_2 formed was 6.9 µmol/g-cat, which was comparable to the difference between the amount of CO_2 and H_2 formed during the photocatalytic decomposition. When UV illumination resumed after 600 s in the dark, the CO_2 rate was 7.7 times higher than the value observed before the lights were turned off.

Fig. 3. Effect of water injection during dark time on the photocatalytic decomposition of a monolayer of formic acid on Pt/TiO_2 in He flow. The UV lights were turn on (open triangle) and off (solid triangle). Water (0.1 µL, 220 µmol/g cat) was injected at 570 s as a pulse on the top of the reactor
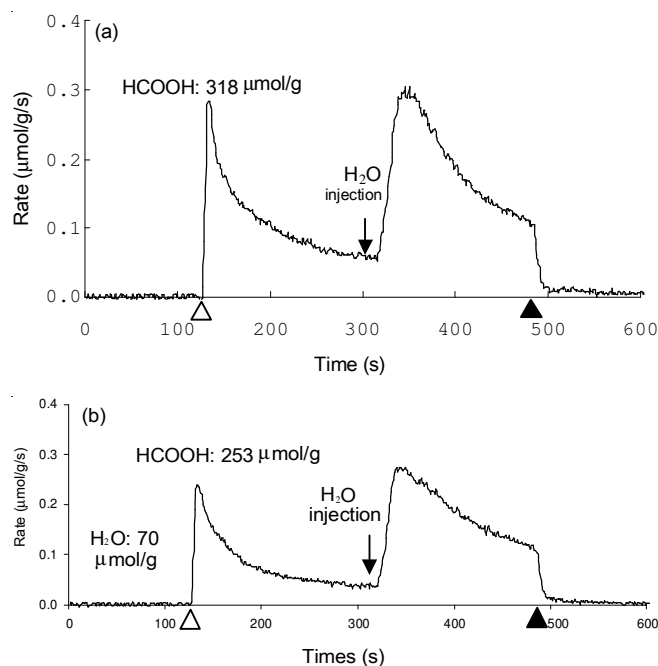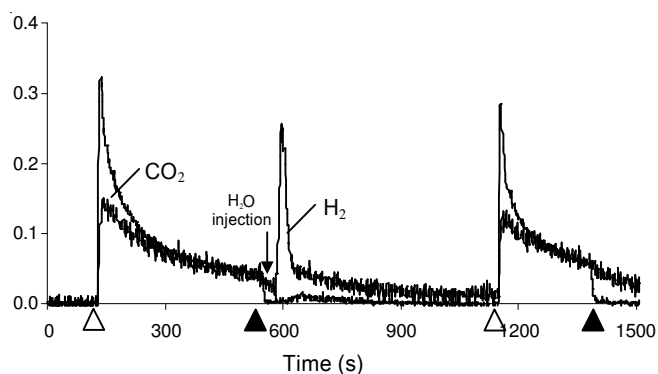

Fig. 2. Effect of weakly and strongly adsorbed water on the photocatalytic decomposition of a monolayer of formic acid on Pt/TiO_2 in He flow. The UV lights were turn on (open triangle) and off (solid triangle). Water (0.04 mL, 88 µmol/g cat) was injected as a pulse on the top of the reactor

As reported[2], lattice oxygen is removed from the TiO_2 surface during photocatalytic decomposition of adsorbed formic acid on TiO_2 and this oxygen vacancies are the main reason for the rate decrease. The CO_2 is detected immediately in the gas phase during transient photocatalytic decomposition, but the water remains adsorbed in the surface as $OH_{(ads)}$ groups.

$$HCOOH_{(ads)} + O_{(lattice)} \rightarrow CO_{2(g)} + H_2O_{(ads)} \qquad (1)$$
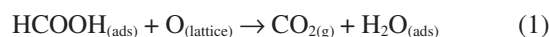
whereas in the case of Pt/TiO_2, CO_2 and H_2 were produced and this reaction does not require oxygen.

$$HCOOH_{(ads)} \rightarrow CO_{2(g)} + H_{2(g)} \qquad (2)$$
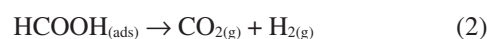
In our catalyst system, 0.2 wt % Pt/TiO_2, both reaction (1) and (2) take place in the initial period. Thus H_2 formation was always less than CO_2 formation. Vacant lattice oxygen plays an important role for hydrogen formation when water was injected. A part of H atoms produces H_2O on TiO_2 surface instead of producing H_2. Then oxygen vacancies are produced and Ti^{4+} is reduced to Ti^{3+}, which reduces the photocatalytic decomposition rate of HCOOH as well. As shown in **Scheme-I**, water reacts with oxygen vacancies to produce H_2 and lattice oxygen is replenished. That's why almost the same amount of CO_2 and H_2 were produced when water was injected during UV illumination. It seems that this reaction is take place by the help of Pt because water did not promote the rate of photocatalytic decomposition of HCOOH on TiO_2 catalyst itself. Yamakata et al. proposed the H_2 formation by H_2O on the methanol oxidation on Pt/TiO_2[9]. We observed the direct formation of H_2 from the reaction of H_2O and lattice oxygen of TiO_2. Abe *et al.*[10] reported on photocatalytic water splitting on Pt/TiO_2 with a Hg arc lamp to produce H_2 in the absence of O_2 production, as well.
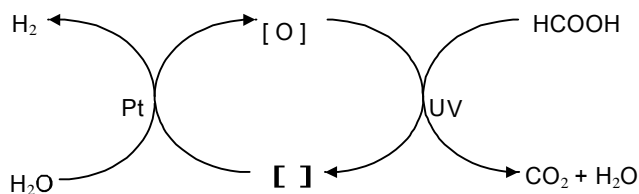
Scheme-I: Proposed reaction scheme for the effect of water in the PCD of formic acid on Pt/TiO_2, where [O] and [ ] represent lattice oxygen and oxygen vacancy on TiO_2 surface, respectively

Hydrogen formation was not observed when water was injected after 5 min when UV was turned off. The vacant lattice oxygen on TiO_2 surface can be replenished by the diffusion from the bulk. An average diffusion rate was measured to be 0.035 µmol O atoms/g-cat/s^2. It seems that the diffusion rate of bulk oxygen enhances in the presence of Pt.

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