JOURNAL OF CATALYSIS **179,** 171–178 (1998)
ARTICLE NO. CA982215

Photocatalytic and Thermal Catalytic Oxidation of Acetaldehyde on Pt/TiO_2

John L. Falconer*,[1] and Kimberley A. Magrini-Bair†

*Department of Chemical Engineering, University of Colorado, Boulder, Colorado 80309-0424; †National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401

Received January 9, 1998; revised July 8, 1998; accepted July 10, 1998

Low concentrations of acetaldehyde in air (60 ppm) were oxidized over TiO_2 (Degussa P25) and 0.5% Pt/TiO_2 catalysts from 24 to 200°C by photocatalytic and thermal catalytic reactions. On Pt/TiO_2, the contribution by photocatalytic oxidation (PCO) is a maximum at 140°C, where conversion is 2.8 times that at 24°C. Titania without Pt deactivates rapidly during PCO at elevated temperature due to a thermal catalytic reaction that takes place in parallel with PCO, but the addition of Pt dramatically slows deactivation. Apparently, Pt supplies spillover oxygen onto the TiO_2, and the oxygen oxidizes the acetaldehyde decomposition products in a dark reaction. Deactivated TiO_2 without Pt was regenerated by PCO at room temperature. Seven distinct reactions (photocatalytic and thermal catalytic) are identified on Pt/TiO_2.

INTRODUCTION

Heterogeneous photocatalytic oxidation (PCO) uses the combination of a catalyst and UV or near-UV illumination to catalyze oxidation reactions. One potential application is oxidation of organic pollutants in air or water. Photocatalytic oxidation has numerous advantages over other treatment methods because reaction takes place at room temperature, only low intensity UV lights are needed, and organics at low concentrations can be oxidized. Moreover, the TiO_2 catalyst is inexpensive. During PCO, UV light excites electrons from the valence to the conduction band of the semiconductor catalyst and leaves holes behind. The electron–hole pairs initiate redox reactions with surface species.

Although PCO is effective at room temperature, the catalyst temperature may be higher in solar energy applications since the sun supplies both UV and IR. Also, as pointed out by Fu *et al.* (1), only a percentage of the energy from high intensity UV lights is in the UV range (21% for a 40-W bulb), and the rest provides heat. Thus, since TiO_2 catalysts may be operated above room temperature, PCO rates at elevated temperature are of interest. If the temperature is sufficiently high, the addition of a noble metal like Pt can cause a parallel thermal catalytic reaction. In addition, a synergistic effect may be present so that the reaction rate at a higher temperature is larger than a linear combination of PCO and thermal catalytic oxidation.

In previous studies of PCO on TiO_2, the effect of temperature on conversion appears to depend on the organic molecule being oxidized and the experimental conditions. Pichat *et al.* (2) reported that conversion during PCO of propene decreased as temperature increased. At 455 K, a light intensity 20 times as high as that used at 320 K still yielded a lower conversion. In contrast, Obee and Brown (3) reported that the rate of toluene (0.17 ppm) PCO increased with temperature from 24 to 57°C at high humidity, but at low humidity higher temperature had no effect. For 1,3-butadiene, the PCO rate increased more at high humidity, and for formaldehyde the rate decreased. Blake and Griffin (4) reported that conversion for photodecomposition of 1-butanol increased with temperature from 298 to 378 K. The rate was three times faster at 378 than at 298 K and had a maximum at 380 K. Similarly, Kennedy and Datye (5) observed a maximum at 373 K for the rate of ethanol PCO on TiO_2. Obee and Hay (6) observed that the PCO rate of ethylene on TiO_2 increased with temperature ($E_{act} = 3.4$ kcal/mol), and all rates dropped as the humidity increased. Anderson *et al.* (7) reported that the rate of PCO of 500 ppm trichloroethylene (TCE) on TiO_2 was independent of temperature, but selectivity to CO_2 was significantly higher as the temperature increased above 45°C.

Fu *et al.* (8) studied PCO of benzene (491 ppm) over TiO_2 from 70 to 140°C. Titania was an oxidation catalyst in the dark at elevated temperature, and the dependence of benzene conversion on temperature in the presence of UV was attributed to this thermal oxidation reaction on TiO_2. Only a fraction of their catalyst was exposed to UV light, and thus much more catalyst was available for thermal catalytic oxidation than PCO. Only a fraction of the reacted benzene formed CO_2, but a large amount of catalyst area was available for adsorption of intermediates because their flow rate was 0.007 monolayer equivalents per hour. Fu *et al.* (8) also studied PCO of benzene over Pt/TiO_2 from 70 to

---

[1] Corresponding author. E-mail: john.falconer@colorado.edu.

0021-9517/98 $25.00

140°C. Platinum increased both benzene conversion and selectivity to CO_2 (8). At 70°C, Pt increased the rate more than a factor of 2. By 130°C, conversion was 100% in the dark, so any synergistic effect of Pt on PCO at elevated temperature could not be detected.

In contrast to benzene PCO, Fu *et al.* (1) found that 0.3% Pt slightly decreased the PCO rate of ethylene (500 ppm) compared to TiO_2 alone. Raising the temperature desorbed water, which competed effectively for sites with the weakly adsorbed ethylene, and increased the thermal catalytic reaction rate. On TiO_2 alone, raising the temperature increased the conversion in the presence of UV for some flow rates; no dark reaction was seen between 30 and 110°C. For Pt/TiO_2, the conversion increased significantly, from 9 to 100% as the temperature increased from 32 to 90°C. Thus, Pt/TiO_2 was more active than TiO_2 above 55°C, but the dark reaction was responsible for all the increase on Pt/TiO_2.

Ait-Ichou *et al.* (9) found that Pt increased photohydrogenation rates of gas-phase C_3H_4, C_3H_6, and C_4H_8 on TiO_2 by as much as a factor of 14 at room temperature under dry conditions. Under humid conditions, the rates of C_3H_4 and C_3H_6 hydrogenation increased a factor of 2.2–2.7. In contrast, the photohydrogenation of C_3H_6 on TiO_2 was an order of magnitude slower when dry than when wet. In addition, different products formed when Pt was present. Titania can dehydrogenate alcohols in the presence of UV irradiation (10), but H_2 production is limited because TiO_2 is reduced. Platinum, however, makes TiO_2 a photocatalyst for this reaction; they concluded that Pt removed electrons from the support and provided a site for H atom recombination. In contrast, Linsebigler *et al.* (11) found that PCO of CO on TiO_2 was not enhanced at 105 K by the addition of Pt. They concluded that electron trapping in the Pt particles either does not occur or is ineffective in enhancing the PCO rate. Thus, the effect of Pt appears to depend on the molecule being oxidized.

Datye *et al.* (5, 12) observed that Pt increased the rate of ethanol PCO, and they observed a significant photothermal synergistic effect. The overall conversion on illuminated Pt/TiO_2 was much greater than the sum of conversions for PCO on TiO_2 plus thermal catalytic reaction on Pt. Both acetaldehyde and CO_2 were formed faster on Pt/TiO_2 at all temperatures, and the selectivity to CO_2 was higher. The synergistic effect depended on how the catalysts were prepared. For catalysts prepared by photoreduction, the enhanced rate was attributed to an electronic effect below 373 K. At higher temperatures, the synergistic effect was attributed to the interaction of photo and thermal catalytic oxidations. They also saw the synergistic effect for a mixture of TiO_2 and Pt/SiO_2 but only above 373 K, and they concluded the synergism was related to gas-phase transport of acetaldehyde from TiO_2 to Pt.

In the current study, acetaldehyde was used as a model pollutant since it is a contaminant in indoor air, and it forms as a partial oxidation product during ethanol PCO. Acetaldehyde at low concentration was oxidized on TiO_2 and Pt/TiO_2 as a function of temperature. Acetaldehyde might be expected to behave differently from many organics because it desorbs slowly from TiO_2; instead, it reacts to form stable surface species when TiO_2 is heated (13, 14). Raising the temperature of TiO_2 (Degussa P-25) to 450°C desorbs less than 10% of a monolayer of acetaldehyde. Thus, as the reaction temperature increases, reaction on TiO_2 to form surface species is expected to compete with PCO, and Pt should affect this reaction.

The objective of the current study is to determine how Pt and elevated temperatures affect PCO of acetaldehyde at low concentrations. Low intensity UV irradiation, small amounts of catalyst, and high gas flow rates were used so that conversions did not reach 100% at the highest temperatures (200°C). These conditions allowed us to determine the change in rate due to UV irradiation at high temperature, where conversions were 100% in many previous studies. Relatively high conversion was necessary at 200°C, however, in order to measure conversions at room temperature at the same flow rates. These low conversions are clearly not those desired for pollution treatment, but they allow the rates to be compared and the differences between PCO and thermal catalytic oxidation to be distinguished.

A relatively thin layer of catalyst was used so that most of the catalyst was active for PCO, and thermal catalytic reaction did not obscure PCO. The UV light intensity decreases with distance into TiO_2 and only penetrates about 4 μm, so most of the PCO takes place in the top part of a 4-μm layer. In contrast, essentially all the Pt/TiO_2 should be active for thermal catalytic oxidation if mass transfer is not limiting. The other advantage of using a thin layer is that the catalyst sees many monolayer equivalents of acetaldehyde. This thin layer allows steady state to be obtained quickly for low acetaldehyde concentrations, and it allows deactivation to be studied. Since the relative contributions of PCO and thermal catalyst oxidation depend on catalyst thickness, comparisons between studies must be made with care.

Photocatalytic oxidation of acetaldehyde has been studied previously on TiO_2 but only at room temperature, and it has not been studied on Pt/TiO_2. Sopyan *et al.* (15, 16) reported that at low concentrations, PCO on TiO_2 was first order in acetaldehyde. At high concentrations and low light intensity, mostly acetic acid formed, but at low concentrations, CO_2 was the primary product. A quantum yield of 19% was obtained at high concentrations of acetaldehyde, and quantum yields were greater than 100% at low UV intensities (0.4 mW/cm^2). In a batch reactor, Sauer and Ollis (17) detected small amounts of formaldehyde during acetaldehyde PCO, but mostly CO_2 formed. Nimlos *et al.* (18) observed formaldehyde as a significant product of acetaldehyde PCO, and they detected small levels of acetic acid and even smaller amounts of methyl formate. They could not determine if formic acid formed. In contrast, Muggli *et al.* (13) studied acetaldehyde PCO at room temperature with transient methods and only observed CO_2 in the gas phase; formic acid, formaldehyde, and acetic acid formed on the surface but were only removed by raising the temperature. Also, both raising the temperature and adding Pt to TiO_2 are expected to increase the selectivity to complete oxidation, as observed for other organics (5, 7, 8). In addition, Kennedy and Datye (5) studied ethanol PCO on TiO_2 and Pt/TiO_2 in a flow system, and because ethanol reacts through an acetaldehyde intermediate, they had significant concentrations of acetaldehyde in their system. However, besides CO_2 and acetaldehyde, the only product they observed was formaldehyde, which comprised less than 1.5% of the total conversion. Similarly, Muggli *et al.* (14) studied PCO of ethanol on TiO_2 at room temperature and only observed acetaldehyde and CO_2 products; the acetaldehyde did not form other gas-phase intermediates. Since these studies were under similar conditions to the current study, although the study by Kennedy and Datye was at higher concentrations, CO_2 is expected to be the dominant product in our system. Thus, we measured the conversion of acetaldehyde and did not try to detect reaction products. The addition of water in high concentrations to the feed might be expected to displace intermediates from the surface. The different concentrations of water used in these previous studies might be expected to result in different product distributions.

Water was not added to our feed stream so that the surface processes were less complicated and so that subsequent studies could determine the effect of humidity. However, as shown in studies for ethanol PCO, where the concentration of surface species were measured (14), a significant fraction of the surface at steady state is covered with water, even when the feed is dry. For a low concentration of ethanol, increasing the water feed from 0 to 5000 ppm only doubled the surface concentration of water. Thus, even when water is not added to the feed, the water product adsorbs sufficiently strongly on the surface so that the surface processes are expected to be similar under dry and wet conditions.

EXPERIMENTAL METHODS

Reaction System

The cylindrical photoreactor was stainless steel and used in a downflow mode. The catalyst was deposited onto a quartz disk, which was illuminated through a quartz window located at the top of the reactor. The quartz disk, whose diameter was 3.8 cm, was centered on a 2-micron-grade, 3-mm thick, stainless steel frit, which was 5 cm in diameter. Feed gas entered the photoreactor radially through four, equally spaced, 1.5-mm tubes. Flow was then forced downward across the catalyst, through the exposed frit area, and out the reactor through a single 3-mm tube. Lines leading into and out from the reactor were either Teflon® or stainless steel. The reactor was located in a GC oven with a hole cut in top for the UV light. Approximately 50 cm of each of the four 3-mm inlet tubes were in the oven to preheat the feed gas. A flexible probe, type K, grounded thermocouple was inserted into the photoreactor so that its tip was in contact with the catalyst surface.

A portion of the outlet stream was pumped to a dual-column, portable gas chromatograph (Microsensor Technology, Inc., model P200) for analysis. This system is capable of detecting parts per million concentration of acetaldehyde, and it can detect water, but not CO_2. Feed streams consisting of 60 ppm acetaldehyde were produced by mixing synthetic air (20% O_2/80% N_2) with gas stream from a premixed tank (Scott Specialty Gas) that contained 250-ppm acetaldehyde (balance N_2). Mass flow controllers were used to produce a total flow rate of 440 cm^3/min for Pt/TiO_2 and 220 cm^3/min for TiO_2. The gas streams have an O_2 concentration of 15.5%.

Ultraviolet Light Source

The low-intensity UV light source was a 6-W black light (Vilber-Lournat T-6L) mounted in a Cole Palmer holder. The UV intensity was measured by a UVP digital UVX radiometer at the catalyst surface, which was approximately 10 cm from the light source, as 0.08–0.10 mW/cm^2. Because the light bulb was changed, the UV light intensity was approximately 10% higher for experiments on TiO_2.

Reaction Conditions

The gas hourly space velocity (GHSV) was $6.2 \times 10^6\ h^{-1}$ for all runs on Pt/TiO_2. For TiO_2, the GHSV was half this value. Note that the GHSV was calculated using the catalyst volume, which was estimated from the catalyst weight. Residence time in a photocatalytic reactor is often not a useful measure since only a thin layer of catalyst is involved in the reaction, and thus GHSV based on the volume of the reactor (approximately 75 cm^3) was not used. For Pt/TiO_2, the flow rate corresponds to 0.2 monolayer equivalents of acetaldehyde/min. Since the catalyst was deposited as a thin layer on a nonporous quartz disk and feed was introduced radially through four inlets, the flow pattern was not like that of a plug flow reactor (PFR). Instead, turbulence appeared to cause the reactor to behave like a continuous stirred tank reactor (CSTR), and the results below support this conclusion. Reaction was run at temperatures from 24 to 200°C. After an initial period of 1–2 h in the dark at the beginning of each day to allow adsorption to come to steady state, the temperature was raised to various values, and the conversion measured in the presence and absence of UV irradiation. Steady state was typically reached in 30 min or less for Pt/TiO_2 after the temperature was changed or after the light was turned on or off at a given temperature.

The feed gas was dry, and for most conditions, the water concentration measured by the GC was less than a few parts per million. For some of the earlier experiments during the day, the water concentration was a few hundred parts per million, but conversion was not affected.

Catalyst Preparation

Particulate TiO_2 (Degussa P-25) was platinized with a photodeposition technique first described by Krauetler and Bard (19). The TiO_2 particles (5 g) were suspended in a solution of 0.001 *M* H_2PtCl_6 (Aldrich Chemicals, 48% Pt) in 0.1 *N* HCl. This solution was brought to pH 7 with concentrated Na_2CO_3, then acidified to pH 4 with glacial acetic acid. The catalyst-containing solution was then purged with nitrogen, sealed, and illuminated with a 1000-W Xe-Hg arc lamp (ORC Corporation, Model XM-1000) for 6 h. The platinized TiO_2 was filtered and rinsed with deionized water until the filtrate reached pH 7. The catalyst was then removed from the filter and heated at 110°C for 12 h to remove water. The dried material, which contained about 0.5 wt% Pt as determined by atomic absorption, was ground and sonicated in 50 ml of 2-propanol. Unmodified TiO_2 was also sonicated in 50 ml of isopropanol. The Pt/TiO_2 and the TiO_2 were coated onto a quartz disk from an isopropanol slurry with an atomizer spray bottle and then dried at 110°C. No other pretreatment was used to remove more strongly bound water or propanol, and PCO was carried out on the catalyst after drying. Experiments were also carried out after the catalysts had sat in room air for several days; this did not appear to affect the catalyst activity. The catalyst weights were 16.2–19.0 mg, which corresponds to thicknesses of 3.7–4.3 μm.

RESULTS

Thermal and Photocatalytic Oxidation on Titania

Titania without Pt was run at half the space velocity used for Pt/TiO_2 because the conversions were lower on TiO_2 than on Pt/TiO_2 at elevated temperatures; the lower space velocity yielded higher conversions and thus more sensitivity. Conversion dropped significantly with time at higher temperatures for TiO_2, indicating deactivation, and thus steady-state conversions were not measured over the temperature range. When a fresh TiO_2 catalyst was used (after pretreatment at 110°C in air), conversion at 24°C was only 9% initially, but increased to around 14% after an additional 200 min in acetaldehyde flow with the UV light on. Since a monolayer of acetaldehyde is 330 μmol/g TiO_2 (13), the TiO_2 was exposed to 20 monolayer equivalents of acetaldehyde in 200 min. Since acetaldehyde adsorbs strongly on TiO_2, the slow approach to steady state is not related to time needed to saturate the surface, but it may be related to other species (such as isopropanol used for depositing the catalyst layer) that remained on the catalyst surface after pretreatment at 110°C. The catalyst was then stable for 360 min, with the conversion increasing to 15%. Thus, at room temperature, TiO_2 is a relatively stable catalyst for acetaldehyde PCO. During more than 10 h of acetaldehyde exposure at 24°C, the catalyst converted 8.5 monolayer equivalents of acetaldehyde without deactivation.

TABLE 1

Conversion on TiO_2 Catalysts

Temperature (°C)	Percentage conversion (%)	Deactivation observations
25	16	Steady state
60	20	Steady state
90	$23 \rightarrow 3.5$	Continuous deactivation (half life: 35 min)
25	$5 \rightarrow 13.5$	Continuous increase in activity (steady state not reached in 100 min)

Note. Experiments were carried out in the order presented.

Table 1 shows how conversion changed with temperature for the TiO_2 catalyst after the long reaction time at 24°C. Conversion was higher at 60°C, and the catalyst appeared to be stable. At 90°C conversion initially increased to 23.5% but then decreased approximately exponentially with a half-life of 35 min. The conversion appeared to stabilize at 3.5% at 90°C. The catalyst had no activity in the dark at 90°C. When the catalyst temperature was decreased to 30°C in UV light, conversion was only 5% but steadily increased with time.

After this TiO_2 sample had regained its full activity at 25°C, it was exposed to acetaldehyde *in the dark* at 90°C to determine whether deactivation was due to a thermal or a photocatalyzed reaction. After an initial desorption of acetaldehyde, some consumption of acetaldehyde was observed (maximum of 2.5%), but this dropped to zero after about 40 min at 90°C. When this catalyst was exposed to UV light at 90°C, acetaldehyde conversion was only 2%. That is, the catalyst was poisoned at 90°C in the dark at least as fast as in UV light. When the catalyst temperature was lowered to 30°C, conversion due to PCO increased with time.

On another TiO_2 sample, conversion was 10.7% at 25°C, and when the temperature was increased to 110°C, conversion dropped to 1%; deactivation was faster at 110°C than at 90°C. The TiO_2 was active in the dark at higher temperatures. At 185°C, conversion was 6.7% in the dark and only 7.4% with UV lights. Thus, the PCO contribution to conversion at 185°C was less than 1%. After measurements were made at 185°C, however, the TiO_2 had deactivated and PCO conversion was less than 1% when the catalyst was cooled to 60°C.

Thermal and Photocatalytic Oxidation on Pt/TiO$_2$

When a Pt/TiO$_2$ catalyst sample was first exposed to UV lights in acetaldehyde flow, an initial high activity was observed but it decreased rapidly in 10 min and then stabilized. A similar high initial activity has also been observed for ethanol PCO on TiO$_2$ (14). The initial high activity could be because the surface is initially covered with a monolayer of reactant, but at longer reaction times much of the surface is covered with reaction intermediates. This catalyst sample was then used for several days for PCO and thermal catalytic oxidation at a range of temperatures and as various changes (flow rates, light intensity, percentage of water in feed) were made in the system. During this time, more than 70 monolayer equivalents of acetaldehyde reacted, and some deactivation may have taken place, but conversions were constant at a given condition. A series of measurements were then made of conversions versus temperature, as shown in Fig. 1, and no deactivation was evident during these measurements. The lower solid line is the conversion of acetaldehyde in the dark. Platinum is a thermal catalyst for acetaldehyde oxidation with a measurable conversion above 100°C at the flow rate used, and the conversion increased approximately exponentially with the temperature. The upper solid line in Fig. 1 is the conversion with the lights on and shows that Pt/TiO$_2$ is an effective photocatalyst up to at least 200°C.

The conversions in Fig. 1 were obtained over several days and in a random order. That is, the temperature was increased and decreased several times to measure conversion over the temperature range. Some PCO conversions were measured before the dark experiments and some afterwards. The lines through the data points are best-fit fifth- and sixth-order polynomials. The smooth lines through the data points indicate that the rates are reproducible, and in contrast to the results obtained for TiO$_2$, the Pt/TiO$_2$ catalyst did not deactivate for the time scale of these experiments. More than 45 monolayer equivalents of acetaldehyde reacted to generate the results in Fig. 1. The dashed line in Fig. 1 is the difference between the two curves and corresponds to the PCO enhancement in rate over thermal catalysis.

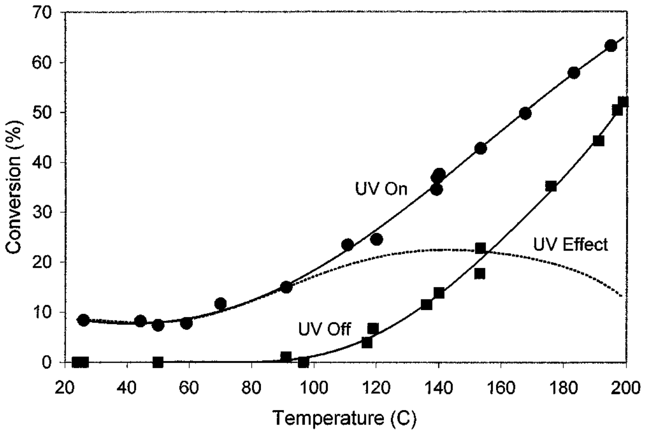

FIG. 1. Conversion of acetaldehyde versus temperature for 0.5% Pt/TiO$_2$. Feed concentration of acetaldehyde is 60 ppm and O$_2$ concentration is 15.5%. The GHSV, based on the volume of catalyst, is $6.2 \times 10^6\ h^{-1}$. The UV effect is the difference between the curves with UV on and UV off. The UV intensity at the surface is 0.08–0.10 mW/cm^2.

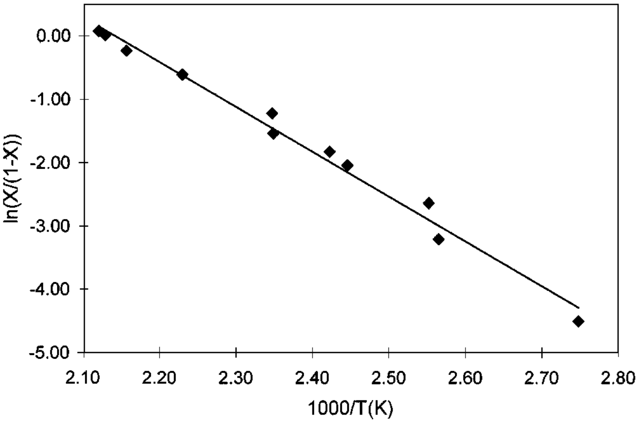

FIG. 2. Ln$[X/(1-X)]$ versus inverse temperature, where X is conversion, for thermal catalytic oxidation of acetaldehyde on 0.5% Pt/TiO$_2$. The reaction was assumed to be first order in acetaldehyde, and the reactor was modeled as a CSTR.

In a separate experiment, acetaldehyde was exposed to a fresh Pt/TiO$_2$ sample at 25°C for several hours, and then reacted photocatalytically at elevated temperature. The conversion initially decreased by 5% in the first 3 h as the temperature dropped from 98 to 93°C and was then almost constant for 22 h at 93°C while almost 60 monolayer equivalents of acetaldehyde reacted. Thus, any deactivation on Pt/TiO$_2$ was much slower than on TiO$_2$.

Because the conversion for the thermal reaction increased smoothly with temperature, it was used to estimate an activation energy. As mentioned in the Experimental Methods section, the reactor was modeled as a CSTR. The thermal catalytic reaction was assumed to be first order in acetaldehyde, and since the O$_2$ concentration was essentially unchanged by reaction, the O$_2$ dependence was not important. A plot of $\ln[X/(1-X)]$ versus inverse temperature, where X is conversion, should be a straight line for a first-order reaction in a CSTR. As shown in Fig. 2, the fit was quite good. The corresponding plot for a first-order reaction in a PFR did not yield a straight line. The activation energy calculated from the slope in Fig. 2 is 14.1 ± 2 kcal/mol.

If PCO and the thermal catalytic oxidation are assumed to take place in parallel, then the difference between total conversion (with UV lights on) and conversion in the dark is an approximate measure of the conversion due to PCO. Note, however, that at the higher temperatures less acetaldehyde is available to react by PCO because some of it reacts by thermal catalytic oxidation, and vice versa, less acetaldehyde is available for the thermal catalytic oxidation. Because the reactor was not run as a differential reactor at the higher temperature, the conversions are not additive. However, as a first approximation, the difference (UV effect curve in Fig. 1) is an indication of the conversion due to UV irradiation. The PCO rate increased above 60°C, and the maximum conversion due to PCO was near 140°C; it is almost three times the conversion measured at room temperature. Although the PCO contribution to total conversion decreases above 140°C, the UV effect at 200°C is larger than at room temperature. The decrease in the UV effect at higher temperatures is partially due to the reactor not being differential and, thus, conversions not being additive. However, other effects may also cause the UV effect to decrease at high temperatures.

A turnover frequency (TOF) of $3 \times 10^{-4}\ \mathrm{s}^{-1}$ was estimated at 24 and 60°C for PCO on Pt/TiO_2 using a surface coverage of acetaldehyde of 330 μmol/g TiO_2 (13). Although this TOF is not large, the feed concentration is lower than for most typical catalytic processes, and the TOF would be expected to be higher at higher concentrations of acetaldehyde since PCO on TiO_2 was reported to be first order in acetaldehyde (15, 16). This TOF corresponds to a reaction rate of 0.002 μmol/m^2/s. The conversions were different for TiO_2 and Pt/TiO_2 at 25°C, but so were the flow rates, so that the rate constant for Pt/TiO_2 was only 15% higher than that for TiO_2.

DISCUSSION

Parallel Reactions

The *overall* parallel reactions that take place on TiO_2 and Pt/TiO_2 and some of their relative activation energies are shown in Table 2. The catalyst is indicated for each reaction, but note that in reaction 3, Pt is the catalyst that oxidizes the poison, which is on the TiO_2 surface. All reactions have positive activation energies. Seven reactions compete in parallel on Pt/TiO_2, and their relative contributions to the complete oxidation of acetaldehyde change with temperature. The activation energy was measured only for reaction 1, but for some reactions, activation energies could be compared. The justifications for each of these reactions are presented in the following subsections. The reaction mechanisms and the sequences of reactions that take place on the surface to yield these overall reactions were not studied. Previous studies of PCO of acetaldehyde on TiO_2 (13, 15–18) detected acetic acid, formic acid, and formaldehyde as surface intermediates, and one study observed methyl formate in low concentrations (18). Based on previous studies, as described in the Introduction, CO_2 and H_2O are the only products that are expected to form in significant amounts under our conditions (see Table 2).

TABLE 2

Reaction + Catalyst		Activation energy
Dark reactions		
$CH_3CHO \xrightarrow{Pt} CO_2 + H_2O$	(1)	$E_1 = 14.1$ kcal/mol
$CH_3CHO \xrightarrow{TiO_2}$ poison	(2)	$E_2 > E_6$
poison $\xrightarrow{Pt} CO_2 + H_2O$	(3)	E_3
$CH_3CHO \xrightarrow{TiO_2} CO_2 + H_2O$	(4)	E_4
UV-Catalyzed reactions		
$CH_3CHO \xrightarrow{TiO_2} CO_2 + H_2O$	(5)	E_5
poison $\xrightarrow{TiO_2} CO_2 + H_2O$	(6)	E_6
$CH_3CHO \xrightarrow{Pt, TiO_2} CO_2 + H_2O$	(7)	E_7

Thermal Catalytic Oxidation of Acetaldehyde on Pt

As shown by the lower curve in Fig. 1, acetaldehyde oxidizes on Pt by thermal catalytic oxidation (reaction 1) in parallel with the PCO reactions, and above about 150°C thermal catalytic oxidation is the dominant reaction on the Pt/TiO_2 catalyst. Note, however, that essentially all the Pt is active for the thermal catalytic oxidation, but not all the TiO_2 sees the full intensity of the UV light, and thus not all the TiO_2 is equally active for PCO. Thus, if a thinner layer of catalyst were used, thermal catalytic oxidation would not contribute as much to the total conversion and would not be the dominant reaction until higher temperatures. In contrast, the thermal catalytic reaction would be responsible for more of the conversion at lower temperatures for a thicker layer of catalyst.

Acetaldehyde Decomposition on TiO_2

Since acetaldehyde deactivates TiO_2 rapidly in the dark at 90°C, acetaldehyde must decompose or react on TiO_2 at elevated temperature to form a surface poison (reaction 2). Acetaldehyde decomposes slow enough at room temperature, however, that TiO_2 did not deactivate during 10 h of PCO at 25°C. The activation energy for acetaldehyde decomposition on TiO_2 (E_2) is larger than that for PCO of the decomposition products (E_6) since the TiO_2 catalyst is poisoned at elevated temperatures in the absence of Pt; i.e., the rate of acetaldehyde decomposition increases faster than the PCO rate of the poison on TiO_2. During TPD, acetaldehyde decomposes or reacts on TiO_2 before it desorbs, and less than 10% of a monolayer desorbs or forms gas phase species by 450°C (13). Gas-phase CO_2 from acetaldehyde decomposition was only seen starting at 225°C during TPD, but dimerization and polymerization may take place at lower temperatures. Idriss and Barteau (20) reported that acetaldehyde formed crotonaldehyde by aldol condensation. Perhaps aldol condensation also makes longer chain molecules on the TiO_2 surface and these molecules act as poisons for PCO.

Oxidation of Catalyst Poison by Pt

Acetaldehyde should also decompose on the TiO_2 surface of Pt/TiO_2 by reaction 2 since Pt covers such a small fraction of the surface. However, deactivation was much slower on Pt/TiO_2 than on TiO_2 at all temperatures, with or without UV illumination. In addition, the PCO rate was not lower on the Pt/TiO_2 catalyst when the reaction was first run in the dark at elevated temperatures. When the same experiment was done for TiO_2, significant deactivation was seen. Thus, Pt catalyzes oxidation of the poison that forms in reaction 2; reaction 3 takes place *in the dark* to remove the poison faster than it forms. Reaction 3 probably involves O_2 or oxygen atoms that spill over from the Pt to the TiO_2 surface. Platinum is known to catalyze oxidation of carbonaceous species on oxide supports in the dark (21). At elevated temperatures, reaction 3 is faster than PCO of the poison on TiO_2 (reaction 6), since TiO_2 deactivates much faster in the absence of Pt.

Thermal Catalytic Oxidation of Acetaldehyde on TiO_2

At elevated temperatures, acetaldehyde is also oxidized by TiO_2 in the dark (reaction 4), but the rate is slower than reaction 1. The conversion for the dark reaction on Pt/TiO_2 (reaction 1) at 185°C was about 13 times that on TiO_2. At room temperature, the rate of reaction 4 was much slower than PCO on TiO_2, but at elevated temperature PCO was poisoned more, so mainly thermal catalytic oxidation was observed on TiO_2 at high temperatures.

Photocatalytic Oxidation on TiO_2

As has been reported previously (13, 15–18), acetaldehyde is oxidized photocatalytically on TiO_2 (reaction 5) at room temperature, and the rate increases with temperatures from 25 to 90°C. Thus, reaction 5 is activated. However, the rate of reaction 2 also increases with temperature, and the decomposition products accumulate on the TiO_2 surface and deactivate it. Thus, an activation energy could not be obtained for reaction 5, since rates could not be measured on an unpoisoned catalyst surface above 60°C.

Photocatalytic Oxidation of Catalyst Poison on TiO_2

The products of acetaldehyde decomposition can be removed from the TiO_2 surface in UV light (reaction 6), since TiO_2 that was deactivated at 90°C (either in the dark or in UV) could be regenerated to its original activity by PCO at room temperature. This process does not require Pt. Thus at room temperature the poison is removed faster than it forms; reaction 6 is faster than reaction 2. In contrast, at 90°C and higher, reaction 2 is faster because it has a higher activation energy ($E_2 > E_6$).

Photocatalytic Oxidation on Pt/TiO_2

Reaction 7 assumes that both Pt and TiO_2 are involved in PCO. The Pt may increase the O_2 concentration on the TiO_2 surface and thus accelerate PCO. Since PCO does not have a strong dependence on O_2 concentration for 15.5% O_2, this seems unlikely. Since the rate of PCO of acetaldehyde on TiO_2 increases with temperature at low temperatures, it may also increase at higher temperatures, but the TiO_2 is poisoned at high temperatures so that an unpoisoned rate could not be measured on TiO_2. If that is the case, then the only role of Pt could be to remove the acetaldehyde decomposition products in a dark reaction. That is, reaction 7 may not take place, although the study by Kennedy and Datye (5) showed that Pt enhanced PCO of ethanol on TiO_2. Our data are consistent with this conclusion since the rate of PCO increases faster than the thermal catalytic reaction. Because acetaldehyde deactivates TiO_2 so rapidly, we could not measure the PCO rate on TiO_2 at elevated temperatures. Based on the temperature dependence reported for PCO of other reactants on TiO_2, we do not expect that the conversion would change as much on TiO_2 as we observe for Pt/TiO_2.

Thus, Pt has a dramatic effect on the high temperature PCO of acetaldehyde, but the UV effect starts decreasing above 140°C. For organics such as toluene, TCE, and C_2H_4, desorption would be expected to significantly decrease coverage at 200°C. Acetaldehyde does not have a significant desorption rate at 200°C (13), although perhaps it can be displaced by water more readily at elevated temperatures. The decreased UV effect at high temperatures may be an artifact of the experiments because the reactor is not differential and less reactant is available for PCO, as discussed above. Also, at elevated temperatures, the steady-state surface coverage of the poison may be higher, so less TiO_2 is available for PCO. That is, E_2 could be greater than E_3 so that the rates of reactions 2 and 3 are comparable at higher temperatures.

Note that the amount of catalyst affects how much more active Pt/TiO_2 is than TiO_2. When the amount of catalyst is increased above a certain thickness, most of the additional catalyst will not see the UV light and, thus, will not be involved in the PCO. The additional Pt/TiO_2 can be involved in the thermal catalytic reaction, however, and thus the rate will be higher for a thicker Pt/TiO_2 layer but not for a thicker TiO_2 layer. In addition, the difference between the light and dark reactions on Pt/TiO_2 (the UV effect in Fig. 1) is strongly dependent on how much catalyst was used, and thus, comparisons between studies need to be done carefully.

Catalyst Deactivation

At room temperature, TiO_2 is an effective catalyst for PCO of acetaldehyde. Because of acetaldehyde decomposition or reaction on its surface; however, TiO_2 does not appear to be an effective catalyst *at elevated temperatures* for

PCO of acetaldehyde. Acetaldehyde decomposes to form stable surface species faster than they can be oxidized at 90°C, but at 25–60°C, the acetaldehyde decomposition rate is slower, and the catalyst is stable. In contrast, Pt/TiO_2 is an effective thermal oxidation and PCO catalyst at elevated temperature. The conversions in Fig. 1 were measured over several days by both increasing and decreasing the temperature, and steady state was usually obtained in approximately 30 min. Note that the results for both PCO and thermal catalytic oxidation fall on smooth curves. No evidence was obtained for deactivation of Pt/TiO_2 although more than 45 monolayer equivalents of acetaldehyde reacted during the experiments used to generate Fig. 1. In addition, more than 70 monolayer equivalents of acetaldehyde reacted before these experiments were carried out. Fu *et al.* (8) also reported differences in accumulation on the surface for PCO of benzene on TiO_2 and 0.1% Pt/TiO_2. They observed a yellow color on TiO_2 after reaction but no color change for Pt/TiO_2. Thus, even a low loading of Pt may be sufficient to slow deactivation significantly.

Sauer and Ollis (22) reported that almost all TiO_2 catalysts deactivate in flow reactors when more than a monolayer equivalent of contaminant is converted. We did not see significant deactivation for TiO_2 at room temperature when eight monolayer equivalents had reacted. The TiO_2 catalyst without Pt rapidly deactivated at high temperature so that when the temperature was lowered, the TiO_2 was completely inactive (within detection limits) at room temperature. Less than one monolayer equivalent reacted over the TiO_2 catalyst at elevated temperatures before it was significantly deactivated for PCO at room temperature.

On Pt/TiO_2, however, the platinum plays an important role in minimizing catalyst deactivation at elevated temperatures, and Pt may also decrease deactivation at room temperature, but a much longer experiment is necessary to determine this. For the data in Fig. 1, 45 monolayer equivalents of acetaldehyde reacted without evidence of deactivation. When another Pt/TiO_2 catalyst was run for 24 h at 90°C, 66 monolayer equivalents of acetaldehyde were converted, and the conversion only dropped a few percentage points during this time. Note that the calculation of the monolayer equivalents reacted is based on all the catalyst being exposed to UV light. Since some catalyst does not see UV or sees much less light, more monolayer equivalents reacted on the top part of the catalyst layer.

CONCLUSIONS

Titania is an effective catalyst for photocatalytic oxidation (PCO) of low concentrations of acetaldehyde at room temperature but *not* at elevated temperature. Although the rate of PCO on TiO_2 appears to increase with temperature, acetaldehyde decomposes in a dark reaction on TiO_2 at elevated temperature and the decomposition products rapidly deactivate the catalyst. These decomposition products can be oxidized by PCO at room temperature to reverse the deactivation. The addition of Pt, even in low concentrations, to TiO_2 has three beneficial effects on acetaldehyde PCO:

- Deactivation is slowed dramatically due to spillover of oxygen from the Pt, and oxidation of the acetaldehyde decomposition products is significantly faster than acetaldehyde decomposition, even in the dark.
- Acetaldehyde oxidizes on Pt in a thermal catalytic reaction in parallel with PCO.
- The PCO rate is higher at elevated temperature, and the rate has a maximum at 140°C. This increased rate may be due to Pt or the same PCO rate might occur on TiO_2 alone if the catalyst did not rapidly deactivate.

ACKNOWLEDGMENTS

J.L.F. gratefully acknowledges support by the National Renewable Energy Laboratory (Contract AXE-7-17070-01) and the University of Colorado Council on Research and Creative Work. We also thank Dr. Ed Wolfrum and Dr. Greg Glatzmeier for their experimental assistance.

REFERENCES

1. Fu, X. F., Clark, L. A., Zeltner, W. A., and Anderson, M. A., *J. Photochem. Photobiol.* **97**, 181 (1996).
2. Pichat, P., Herrman, J. M., Disdler, J., and Mozzanega, M.-N., *J. Phys. Chem.* **83**, 3122 (1979).
3. Obee, T. N., and Brown, R. T., *Environ. Sci. Technol.* **29**, 1223 (1995).
4. Blake, N. R., and Griffin, G. L., *J. Phys. Chem.* **92**, 5697 (1988).
5. Kennedy, J. C., III, and Datye, A. K., *J. Catal.*, in press.
6. Obee, T. N., and Hay, S. O., *Environ. Sci. Technol.* **31**, 2034 (1997).
7. Anderson, M. A., Yamazaki-Nishida, S., and Cervera-March, S., "Photocatalytic Purification and Treatment of Water and Air" (D. F. Ollis and H. Al-Ekabi, Eds.), p. 405. Elsevier, Amsterdam, 1993.
8. Fu, X. F., Zeltner, W. A., and Anderson, M. A., *Appl. Catal. B* **6**, 209 (1995).
9. Ait-Ichou, I., Formenti, M., Pommier, B., and Teichner, S. J., *J. Catal.* **91**, 293 (1985).
10. Pichat, P., Herrmann, J.-M., Disdier, J., Courbon, H., and Mossanega, M.-N., *Nouv. J. Chim.* **5**, 627 (1981).
11. Linsebigler, A., Rusu, C., and Yates, J. T., Jr., *J. Am. Chem. Soc.* **118**, 5284 (1996).
12. Datye, A. K., Kennedy, J. C., III, Barela, M., and Prairie, M. R., Abstract, *in* "Proceedings, of 3rd International Conference on TiO_2 Photocatalytic Purification and Treatment of Water and Air, Orlando, FL, Sept. 23–26, 1997," p. 77.
13. Muggli, D. S., McCue, J. T., and Falconer, J. L., *J. Catal.* **173**, 470 (1998).
14. Muggli, D. S., Lowery, K., and Falconer, J. L., *J. Catal.*, submitted.
15. Sopyan, I., Murasawa, S., Hashimoto, K., and Fujishima, A., *Chem. Lett.*, 729 (1994).
16. Sopyan, I., Watanabe, M., Murasawa, S., Hashimto, K., and Fujishima, A., *J. Photochem. Photobio. A: Chem.* **98**, 79 (1996).
17. Sauer, J. L., and Ollis, D. F., *J. Catal.* **158**, 570 (1996).
18. Nimlos, M. R., Wolfrum, E. J., Brewer, M. L., Fennell, J. A., and Bintner, G., *Environ. Sci. Technol.* **30**, 3102 (1996).
19. Krauetler, B., and Bard, A. J., *J. Am. Chem. Soc.* **100**, 4317 (1978).
20. Idriss, H., and Barteau, M. A., *Catal. Lett.* **40**, 147 (1996).
21. Conner, W. C., Jr., and Falconer, J. L., *Chem. Rev.* **95**, 759 (1995).
22. Sauer, J. L., and Ollis, D. F., *J. Catal.* **163**, 215 (1996).