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Transient Studies of 2-Propanol Photocatalytic Oxidation on Titania

Sheldon A. Larson, Jason A. Widegren, and John L. Falconer

Department of Chemical Engineering, University of Colorado, Boulder, Colorado 80309-0424

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Transient reaction techniques were used to study the room-temperature, photocatalytic oxidation (PCO) of 2-propanol on a thin catalyst film of titania (Degussa P25) in an annular reactor. Adsorbed 2-propanol was photocatalytically oxidized in the absence of gas-phase 2-propanol, and the species remaining on the TiO_2 surface were characterized by temperature-programmed desorption (TPD) and oxidation (TPO). Nonphotocatalytic decomposition (TPD) and oxidation (TPO) of 2-propanol and acetone were also studied. The initial PCO of 2-propanol at room temperature rapidly forms acetone and water; water can displace acetone into the gas phase. Adsorbed acetone is subsequently oxidized photocatalytically to CO_2 and H_2O at a slower rate than 2-propanol photocatalytically oxidizes to acetone and it may form a surface intermediate before complete oxidation. Thus, at steady-state, the TiO_2 surface is expected to be covered with H_2O and strongly bound acetone or an intermediate. The surface reaction steps require near-UV light, but desorption does not. Formation of gas-phase acetone and water are desorption limited, but CO_2 and CO formation are reaction limited. The rate of PCO to form acetone is essentially independent of O_2 pressure, and acetone forms at room temperature even in 30 ppm O_2, apparently utilizing lattice oxygen. In contrast, complete oxidation to CO_2 is first order in O_2 at low concentrations and zero order at higher O_2 concentrations. The coverage of photoadsorbed oxygen is low (less than 1 μmol/g TiO_2), and the oxygen is strongly bound to the surface (~200 kJ/mol binding energy). There are no indications that photoadsorbed oxygen was important for PCO; gas phase O_2 is needed to replace lattice oxygen, but this may or may not be photoadsorbed. In the absence of near-UV light, titania is an oxidation catalyst only at much higher temmperatures. Thermal oxidation of 2-propanol also proceeds through acetone formation, but acetone thermally oxidizes faster than 2-propanol. Methanol and ethanol also undergo PCO on TiO_2 at room temperature to form aldehydes, CO_2, and H_2O. © 1995 Academic Press, Inc.

INTRODUCTION

The need to remove organic chemicals that are present in low concentrations in air exhaust streams and in indoor environments requires oxidation catalysts that will operate at low temperatures and with high efficiency. Heterogeneous photocatalysis appears particularly promising for such oxidations because of the proven destruction of a wide range of toxic chemicals in both aqueous phase (1–5) and gas phase (6–24) and because these chemicals can be oxidized with high efficiency. Since photocatalytic oxidation (PCO) in air takes place at room temperature, gas–solid PCO is potentially more energy efficient for organic oxidation than other processes. Moreover, TiO_2 is an inexpensive catalyst.

In heterogeneous PCO, pollutants are oxidized over a semiconducting catalyst (usually TiO_2) illuminated by ultraviolet (UV) or near-UV light. In this paper, we refer to both types of light as UV light. Titania absorbs UV light, which excites electrons from the valence to the conduction band. The resulting electron/hole pairs can migrate to the catalyst surface and initiate redox reactions that destroy pollutants. Many of the previous studies in PCO have focused on aqueous solutions, which require relatively intense levels of UV light to attain reasonable reaction rates (25–30). In contrast, high destruction rates of volatile compounds can be achieved in gas–solid PCO with relatively low light intensities (6–24), and gas–solid PCO is therefore an area of recently renewed interest in remediation and purification technology.

The current study of gas-phase PCO uses 2-propanol as the volatile compound because previous studies have examined both its PCO (6, 7, 25–31) and its bonding to TiO_2 (32–36). The PCO of acetone, a major partial oxidation product of 2-propanol PCO, has also been studied (10, 21). In addition, since alkanes are believed to photocatalytically oxidize through alcohol intermediates (12), understanding the processes in alcohol PCO may increase the knowledge of alkane PCO.

In an early study by Bickley *et al.* (6), PCO of 2-propanol vapor at 300 K was investigated using a unique photoreactor. A powdered rutile catalyst contacted 2-propanol, O_2, and UV light by tumbling inside a rotating container. The 2-propanol quickly reacted to form acetone and H_2O. Acetone was displaced by H_2O and appeared in the gas stream. Adsorbed acetone photocatalytically oxidized at a distinctly slower rate than 2-propanol oxidized to acetone. Most of these studies were done on samples outgassed at

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600 K, and complete oxidation to CO_2 was not observed. Instead, acetone oxidized to a strongly adsorbed intermediate, and the continuation of PCO was observed by O_2 uptake. Carbon dioxide was observed only after PCO on a catalyst that was pretreated by heating in O_2 at 1073 K for 2 h. Rates of O_2 uptake were slower for samples pretreated at 1073 K than those pretreated at 600 K. The authors concluded that this decrease in O_2 uptake rate on samples pretreated at higher temperatures was due to lower concentrations of surface OH groups and that OH groups play a role in the PCO process by increasing O_2 photoadsorption. No reaction occurred in the absence of UV light and only a small amount of acetone formed in the absence of O_2 in the gas stream. In another study, Bickley and Jayanty (7) used TPD to detect products that remained on their rutile surface after PCO of 2-propanol. Acetone, water, formic acid, and a trace quantity of acetic acid were detected.

Isotope studies with oxygen-labeled alcohol and O_2 were carried out to investigate the roles of gas-phase O_2, lattice oxygen, and oxygen originally incorporated in the alcohol (38). The oxygen atoms of the acetone produced from 2-propanol PCO were those originally incorporated in the alcohol. No oxygen exchange between $^{18}O_2$ and the adsorbed organics was detected despite significant uptake of $^{18}O_2$ during reaction.

Most of the previous studies in gas–solid PCO were done at steady-state conditions. Insight into the surface chemical processes was gained mainly by inference from observed gas-phase intermediates and products and the rate dependence on concentrations. An increased understanding of the processes occurring on TiO_2 during PCO is beneficial for improving this technology and for identifying and eliminating undesirable surface processes. Although many organics completely oxidize photocatalytically to form CO_2 and H_2O, several studies (18, 23, 24) observed partial oxidation products. In some cases these intermediates are more toxic and more difficult to photocatalytically oxidize than the original pollutant. Additionally, catalyst deactivation has been reported (10, 19–21, 37) and needs to be studied in more detail.

In the current study, transient reaction experiments with mass spectrometric detection were used to investigate the PCO of 2-propanol. Transient reaction was carried out by adsorbing either 2-propanol or acetone on the TiO_2 surface in the absence of UV light. After the excess gas-phase organic was flushed away, the surface was illuminated by UV light in an O_2/He flow at room temperature, and the gas-phase products were detected by the mass spectrometer. Transient experiments can provide information about surface processes and reaction mechanisms by separating adsorption, surface reaction, and desorption in time, and the effect of UV illumination on each of these steps can be determined. Also eliminating gas-phase organics helps in understanding the role of homogeneous reactions that may be initiated by the catalyst. Because of the high quantum yields of gas–solid photocatalysis, Raupp and Junio (10) suggested that acetone oxidation occurs through a surface-mediated, free-radical chain mechanism.

After surface reaction in O_2/He flow for various times, the UV light was turned off to stop reaction, and the species remaining on the surface were characterized by temperature-programmed desorption (TPD) and oxidation (TPO). Photocatalysis is particularly well suited for such transient studies because the reaction takes place at room temperature and thus surface intermediates and reaction products can remain on the surface. Because the reaction can be interrupted by turning off the lights, it is possible to identify what species are present on the reaction surface after various reaction times. Thus, surface intermediates that may not desorb at room temperature or desorb slowly can be detected by raising the catalyst temperature in the absence of UV light.

These transient experiments were used to study the effect of O_2 concentration, the role of water in the desorption of reaction products, and the effect of 2-propanol surface coverage. Participation of lattice oxygen in PCO was also studied. Because TPD and TPO were used to characterize the species remaining on the surface, TPD and TPO of 2-propanol and acetone were also carried out without UV illumination. The TPO experiments were used to measure 2-propanol and acetone thermal oxidation (non-UV) on TiO_2.

EXPERIMENTAL METHODS

Transient isothermal reaction studies, temperature-programmed desorption, and temperature-programmed oxidation were carried out in an apparatus similar to that

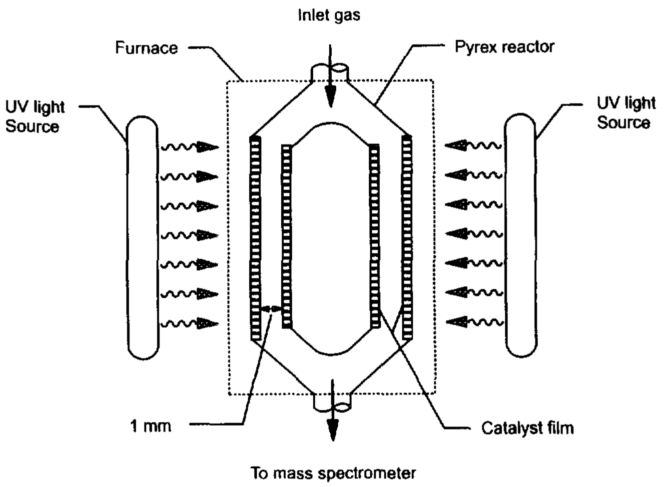

FIG. 1. Schematic of thin-catalyst film, annular photoreactor.

previously described (39, 40). For PCO studies, the conventional packed-bed reactor was replaced by a thin-film, annular reactor to maximize the amount of TiO_2 that was illuminated. The Pyrex reactor, shown in Fig. 1, consists of two concentric cylinders that form an annular region with a 1-mm gap. The cylinders are 13 cm high, and the outer diameter of the inside cylinder is 2 cm. The inner cylinder was evacuated and sealed. An annular reactor was used to create a small cross section so that high gas flow rates could be obtained over the catalyst bed. High flow rates ensured that products desorbing from the surface were detected quickly. The large diameter reactor provided sufficient surface area so that enough TiO_2 could be deposited on the reactor walls to allow reasonable detection sensitivity in the mass spectrometer. The walls of the annulus were coated with powdered TiO_2 by first washing the annular region with a 6 *M* NaOH solution and then rinsing with an aqueous slurry of TiO_2. The NaOH wash roughened the Pyrex surface and increased its ability to hold the TiO_2 (41). The reactor was dried at 373 K and then rinsed a second time with the catalyst slurry. Several photoreactors were prepared following this procedure, which deposited from 30 to 80 mg of TiO_2 on the walls. For 30 mg of TiO_2, the average thickness on the reactor walls was calculated to be 0.4 μm. Although the coating is not uniform, it is sufficiently thin that most of the catalyst is expected to be illuminated by the UV lights that surround the reactor. A TiO_2 thickness of 4.5 μm is needed to absorb 99% of near-UV illumination (21). Since TPO experiments after extended UV illumination detected no 2-propanol (i.e., none of its catalytic decomposition products), all of the TiO_2 appeared to be illuminated in these reactors.

The catalyst used in this study was Degussa P25 titania. This TiO_2 powder consists of nonporous spheres with a diameter of ~30 nm. The specific surface area is 35–45 m^2/g (42). This TiO_2 contains both anatase and rutile phases in approximately a 80:20 ratio, but the microstructure of Degussa P25 is more complex than a physical mixture of anatase and rutile. An amorphous phase is also present, and together with anatase and rutile, these three phases are in intimate contact (42). This catalyst was chosen because it consistently provides high activity and is the most frequently used TiO_2 in photocatalysis.

The photoreactor was surrounded by an electric furnace consisting of Kanthal wire wrapped around a quartz cylinder. The wire wrapping was spaced so that the catalyst could be illuminated by six UV lamps (GE F4T5-BLB) evenly positioned around the reactor and furnace at a distance of 2.5 cm from the photoreactor walls. These 4-W lamps generate light in the 300- to 500-nm wavelength range (near-UV) with a maximum intensity near 390 nm (20). A 0.5-mm-o.d. chromel–alumel, shielded thermocouple was inserted into the annulus so that the tip contacted the catalyst film. Gas flowed continuously over the catalyst at a pressure slightly higher than ambient. Effluent was analyzed immediately downstream of the reactor using a Balzers QMA 125 quadrupole mass spectrometer housed in a turbomolecular-pumped, ultrahigh-vacuum chamber. A heated, stainless-steel, capillary inlet diverted some of the effluent into the vacuum chamber for analysis.

Before each experiment, the catalyst was heated to 723 K in 20% O_2/80% He to obtain a reproducible oxide surface. After the reactor was cooled to room temperature, the gas stream was switched, depending on the experiment, to another O_2/He mixture. Organics were adsorbed at room temperature by injecting these liquids into the top of the reactor and allowing them to evaporate into the flowing gas before contacting the catalyst. For isothermal, transient reaction experiments, the UV lights were covered with an aluminum shroud, then turned on and allowed to warm up for approximately 15 min before the shroud was removed. Because the intensity of the lights increased by approximately 5% during the first 10 min of operation, this procedure allowed the lights to reach constant output. Photocatalytic oxidations were carried out for 2-propanol, acetone, methanol, and ethanol. Both saturation and less-than-saturation coverages were used for acetone and 2-propanol, and the UV-illumination times were also varied. All photocatalytic oxidations were done at room temperature. Computer-controlled data acquisition allowed for simultaneous monitoring of selected mass-to-charge ratios, as well as temperature and elapsed time.

The species present on the surface after isothermal PCO were characterized by temperature-programmed desorption and oxidation. These techniques were also used to study the catalytic decomposition and oxidation of 2-propanol and acetone without UV light. During TPD, an inert gas (He) flowed at 100 standard cm^3/min over the catalyst, whereas an O_2/He mixture was used at the same flow rate during TPO. Unless indicated otherwise, TPO experiments were carried out in a 20% O_2/80% He mixture. For both techniques an organic was adsorbed at room temperature and the catalyst temperature was increased at a constant rate of 1 K/s while the temperature and the amplitudes of multiple mass signals were monitored as functions of time. A temperature programmer coupled with a transformer generated the constant heating rate. Heating was stopped at 723 K due to difficulties in maintaining a linear temperature rate at higher temperatures with this annular reactor and to avoid irreversibly changing the TiO_2 surface.

Desorption rates were obtained from mass spectrometer signals by injecting known quantities of materials into the mass spectrometer. These calibrations were carried out in the same gas stream composition as the corresponding experiment. Mass-to-charge ratios unique to desorbed products were monitored whenever possible. Several signals, however, required correction for contributions of

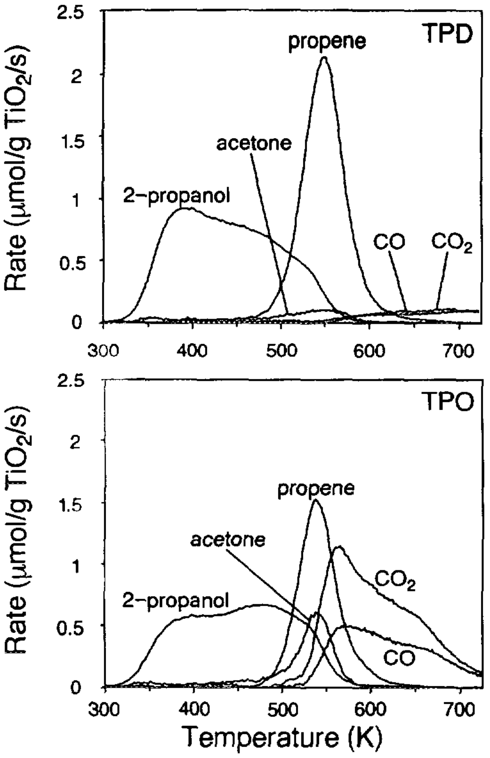

FIG. 2. Temperature-programmed desorption (TPD) and oxidation (TPO) spectra of adsorbed 2-propanol (saturation coverage) on TiO_2. The TPO was performed in 20% O_2.

fragmented ions from other products. For comparison, desorption amounts are reported per gram of TiO_2 catalyst. The catalyst weights were determined by measuring the weight of the reactor before and after depositing the TiO_2. Since each reactor weighed approximately 60 g, and only 30–80 mg of catalyst were deposited on the reactor walls, precise catalyst weight measurement was difficult. Several reactors were used, and some variations in the desorption amounts were observed when comparing results of identical experiments carried out in different reactors. Amounts measured in identical experiments carried out in the same reactor were generally reproducible to within 6%.

RESULTS

TPD and TPO of 2-Propanol

Figure 2 presents TPD and TPO spectra of adsorbed 2-propanol at saturation coverage on TiO_2. During TPD, a significant fraction of 2-propanol desorbed unreacted, starting near 325 K, and most of the remaining 2-propanol dehydrated to propene, which formed in a peak centered at 550 K. A small fraction of the 2-propanol dehydrogenated to form acetone in a peak at 540 K. Small amounts of CO and CO_2 desorbed above 550 K, but the desorption rate maxima were not observed below 723 K. The H_2O spectrum between 300 and 400 K was similar to that of 2-propanol. Above 400 K, the H_2O desorption rate increased to another maximum near 500 K. The H_2O spectra are not presented so that the other curves can be more easily seen. Moreover, H_2O formation is limited by readsorption and H_2O calibrations are less accurate, and thus less information is obtained from their spectra. A carbon material balance, based on the amounts presented in Table 1, shows that 280 μmol 2-propanol/g TiO_2 desorbed or formed gas-phase reaction products.

The TPO spectra of adsorbed 2-propanol, obtained in a 20% O_2/80% He flow stream, are different from the TPD spectra. Less 2-propanol desorbed than during TPD, but the temperature range was the same. Propene and acetone desorbed at the same temperatures as in TPD, but more acetone and less propene formed during TPO. The greatest difference in the spectra is the increased rates of formation of CO and CO_2 during TPO. Both carbon oxides reached rate maxima near 570 K during TPO, whereas no maximum was seen during TPD. The amounts of desorption and reaction products are presented in Table 1.

TABLE 1

Desorption Amounts of Adsorbed 2-Propanol and Acetone on TiO_2 Measured during TPD and TPO

	Desorption amount (μmol/g TiO_2)						
	2-Propanol	Propene	Acetone	CO_2	CO	H_2O	(Total carbon)/3
			Adsorbed 2-propanol				
TPD	120	140	13	16	17	290	280
TPO	100	88	34	140	72	720	290
			Adsorbed acetone				
TPD	—	—	96	78	37	500	130
TPO	—	—	80	220	130	570	200

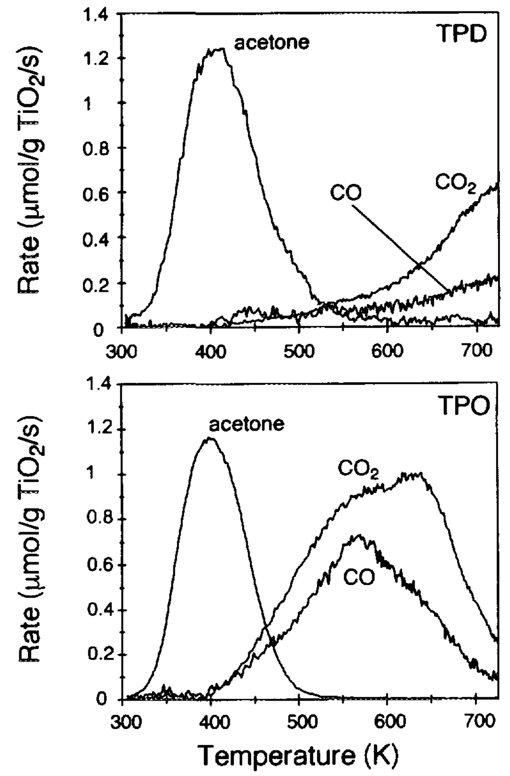

FIG. 3. TPD and TPO spectra of adsorbed acetone (saturation coverage) on TiO_2. The TPO was performed in 20% O_2.

TPD and TPO of Acetone

When acetone was adsorbed to saturation coverage, a significant amount of acetone desorbed intact with a maximum near 425 K during TPD and TPO, as shown in Fig. 3. Because some acetone is weakly adsorbed and slowly desorbs at room temperature, the amount desorbed during TPD or TPO decreases if the sample sits at room temperature for a significant time. During TPD, small amounts of CO and CO_2 desorbed above ~450 K, but their desorptions were also not complete by 723 K, and thus a significant amount of adsorbed species remained on the surface at 723 K. During TPO, the total amount of CO_2 and CO was three times larger than during TPD, as shown in Fig. 3 and Table 1, and thus the amount remaining on the surface after TPO was less than after TPD. Water desorbed, starting near 340 K and continued to 723 K, at which temperature heating was stopped.

The TPD and TPO spectra show that at saturation, 55% of the acetone is bound to the surface sufficiently strongly that it decomposes before it desorbs. At approximately 40% of saturation, 85% of the acetone decomposed or was oxidized during TPO, and the small amount of acetone that desorbed was in a peak at 475 K.

Displacement of Acetone by Water

Studies by Bickley *et al.* (6) and Munuera and Stone (33) concluded that acetone desorption at room temperature during PCO of 2-propanol is due to a displacement process in which 2-propanol and the H_2O product displace the more weakly adsorbed acetone. To study this, acetone was adsorbed to saturation, and then a large excess of water vapor (1850 μmol/g TiO_2) was injected over the catalyst. The first water injection desorbed 16% of the adsorbed acetone, whereas the second and third injections only desorbed an additional 5%. During a subsequent TPO, the acetone, CO_2, and CO signals were all smaller as a result of H_2O injection, but the peak temperatures and peak shapes did not change. Desorption of molecular acetone preferentially decreased, so that only 30% of the remaining acetone desorbed molecularly after H_2O injection.

In an effort to determine whether acetone was adsorbed in more than one type of site on the surface, an interrupted TPO to 523 K was carried out. This temperature was chosen so that mostly molecular acetone was removed from the surface during the interrupted TPO. Afterward, the reactor was cooled to room temperature, and H_2O was injected. Almost no acetone desorbed during several injections of water: a total of 0.5 μmol/g TiO_2 during the first two injections and none during the third. No other species were detected. During the subsequent TPO, the CO_2 and CO spectra were nearly identical to those measured during a normal TPO, although slightly more CO desorbed relative to CO_2. Thus, H_2O was unable to desorb the acetone that resulted in CO_2 and CO formation during TPO.

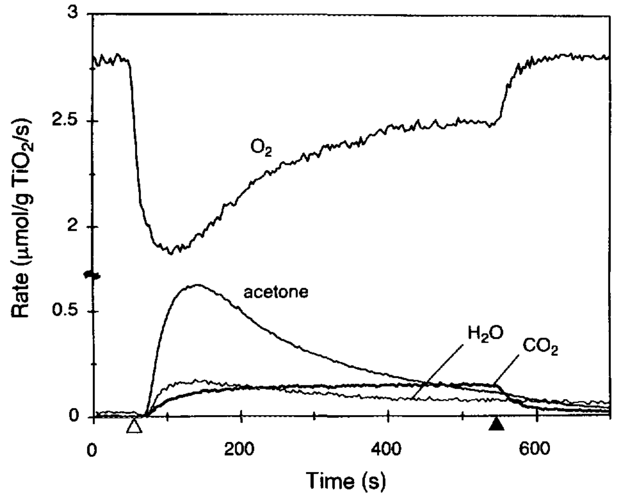

FIG. 4. Product desorption rates and O_2 uptake measured during PCO of adsorbed 2-propanol (saturation coverage) in 0.15% O_2 at 300 K. Triangles along the *x*-axis indicate when UV illumination began (△) and ended (▲).

TABLE 2

Desorption Amounts of Adsorbed 2-Propanol under Various O_2 Concentrations Measured during 10 min of PCO

	Amounts (μmol/g TiO_2)					
O_2 concn (%)	*Acetone*	*CO_2*	*H_2O*	*2-Propanol*	*CO*	*Total C/3*
0.003	40	4	—	—	—	41
0.006	47	6	—	—	—	49
0.15	160	69	64	9	23	200
3	110	280	350	13	16	220
20	110	320	370	14	36	240
40	93	310	410	11	50	220

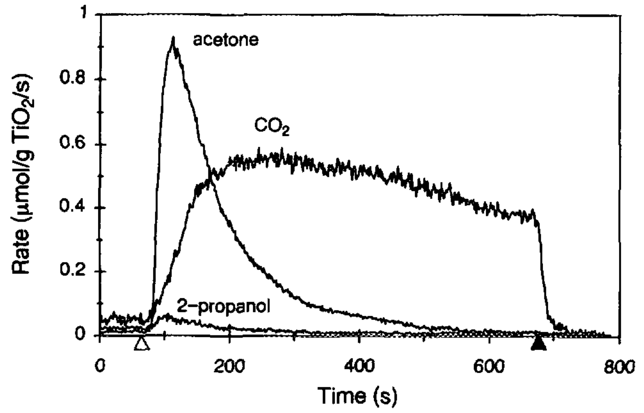

FIG. 5. Product desorption rates measured during PCO of adsorbed 2-propanol (saturation coverage) on TiO_2 in 3% O_2 at 300 K. Triangles along the x-axis indicate when UV illumination began (△) and ended (▲).

Photocatalytic Oxidation of 2-Propanol

Transient isothermal oxidation of adsorbed 2-propanol was carried out at room temperature in a 0.15% O_2/He mixture so that O_2 consumption could be measured. The catalyst was saturated with 2-propanol, and after 2-propanol was removed from the gas phase, the catalyst was illuminated by UV light. As shown in Fig. 4, the O_2 concentration immediately decreased and attained a maximum uptake rate after 60 s of illumination. Acetone, H_2O, CO_2, and small amounts of CO and 2-propanol appeared 20 s after illumination. The small CO and 2-propanol signals are not shown in Fig. 4 for clarity. Acetone, H_2O, and 2-propanol reached maximum desorption rates after 100 s, but CO_2 and CO signals did not reach maxima until 430 s. After 500 s of illumination, the lights were turned off and both CO_2 desorption and O_2 uptake quickly decreased. During the 500 s of illumination, 280 μmol O_2/g TiO_2 were consumed. The amounts of products are listed in Table 2.

Carbon monoxide formation was measured using the mass 28 signal, which was corrected for mass-spectrometer cracking products from CO_2 and acetone. Since the rates of CO_2 and acetone formation in all PCOs of 2-propanol are much higher than that of CO, some or all of the corrected mass 28 signal might arise from fluctuations in the measured cracking fractions. Thus, the amounts of CO formed during PCO may be less than the values reported in Table 2.

Photocatalytic Oxidation Dependence on O_2 Concentration

As shown in Fig. 5, when a higher O_2 concentration (3%) was used, PCO of 2-propanol formed acetone and CO_2 at higher rates. Water and CO also formed at higher rates, but for clarity they are not shown in Fig. 5. The 2-propanol desorption was similar to that observed in 0.15% O_2. For a saturation coverage of 2-propanol, acetone and H_2O formation rates quickly reached maxima (after 40 s) at room temperature. In contrast, CO_2 formation did not reach a maximum rate until approximately 180 s, and CO_2 continued to form at a high rate, whereas the acetone formation rapidly dropped after reaching a maximum. When the UV lights were turned off after 10 min, CO_2 formation rapidly decreased, indicating that CO_2 formation was limited by reaction and not desorption. In contrast, H_2O adsorbs on TiO_2 and has a finite desorption rate at room temperature at high coverages. Thus the H_2O signal decreased slowly when the UV lights were turned off. Table 2 lists desorption amounts.

In 20% O_2, PCO was similar to that in 3% O_2. Acetone desorption was nearly identical to that in Fig. 5. Water desorbed in a manner similar to that of acetone, but the H_2O amplitude was 40% greater than that of acetone, and the H_2O signal did not decrease as rapidly as that of acetone. The maximum CO_2 formation rate was larger than that in 3% O_2, and it was reached sooner (100 s). Photo-

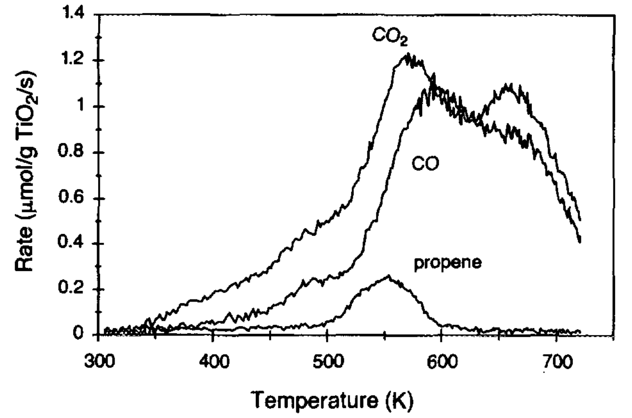

FIG. 6. Temperature-programmed oxidation spectra of TiO_2 after PCO of adsorbed 2-propanol in 3% O_2 at 300 K for 10 min. The TPO was performed in 20% O_2.

TABLE 3

Desorption Amounts from TiO_2 during TPO following 10 min PCO at Various O_2 Concentrations

	Amounts (μmol/g TiO_2)						
O_2 concn (%)	CO_2	CO	Propene	H_2O	2-Propanol	Acetone	Total C/3
0.003	7	110	51	310	36	84	210
0.006	20	240	160	390	26	84	360
0.15	55	98	15	220	—	60	130
3	260	210	24	530	—	—	180
20	270	240	23	440	—	—	190
40	200	190	27	320	—	—	160

catalytic oxidation in 40% O_2 flow was almost identical to that in 20% O_2. The maximum rate of CO_2 desorption was nearly the same as that reached in 20% O_2, but this value was attained after only 70 s. Table 2 summarizes the amounts of products for the various O_2 concentrations.

Figure 6 shows that CO_2, CO, and a small amount of propene formed during TPO (in 20% O_2) after PCO in 3% O_2. Water also formed but is not shown in the figure for clarity. The TPO spectra were similar following PCO in 20 and 40% O_2. In each case H_2O was the dominant product, and H_2O, CO_2, and CO formation continued until heating was stopped at 723 K. The amount of propene was essentially identical for each TPO spectrum, and its maximum was at 550 K. Desorption amounts are listed in Table 3.

Photocatalytic Oxidation of Acetone

Transient isothermal experiments for PCO of acetone in 20% O_2 were carried out after saturating the TiO_2 surface with acetone at 300 K. As shown in Fig. 7, CO_2 was the dominant product, and smaller amounts of CO and acetone formed. No H_2O desorbed during reaction at room temperature. The CO_2 rate increased rapidly upon illumination and reached a maximum at 120 s and then slowly decreased. After 450 s, the UV lights were turned off and CO_2 desorption quickly decreased. The amount of CO_2 desorbed during PCO was 190 μmol/g TiO_2. Acetone desorption gradually reached a maximum and its desorption was almost complete by the time the UV lights were turned off.

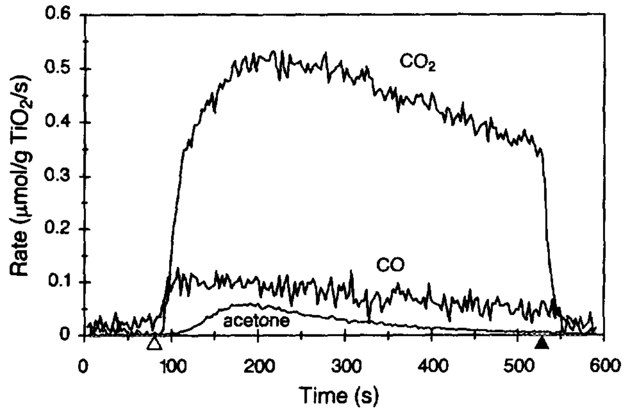

FIG. 7. Product desorption rates measured during PCO of adsorbed acetone (saturation coverage) on TiO_2 in 20% O_2 at 300 K. Triangles along the *x*-axis indicate when UV illumination began (△) and ended (▲).

During TPO following PCO, CO_2 and CO formed in spectra similar to those in Fig. 6. Acetone also desorbed with a maximum at 400 K. The desorption rate maxima for CO, CO_2, and acetone were at 640, 680, and 450 K, respectively. The amounts of CO, CO_2, and acetone were 270, 360, and 22 μmol/g TiO_2, respectively. When the catalyst was illuminated for 20 min, no acetone desorbed during the subsequent TPO.

Photocatalytic Oxidation of 2-Propanol in Low O_2 Concentration

Photocatalytic oxidation of adsorbed 2-propanol was carried out in 0.003% O_2 (30 ppm O_2) to study the reactivity of preadsorbed or lattice oxygen. Before PCO, the catalyst was heated to 723 K in 20% O_2 and then cooled to room temperature in 20% O_2. The O_2 flow was replaced by He flow containing 0.003% O_2 before 2-propanol was adsorbed. Figure 8 shows that acetone and CO_2 formed during UV illumination at 300 K. A small amount of H_2O was also seen. The rate of acetone formation increased rapidly and reached a maximum after 160 s, but the CO_2 rate reached a broad maximum after approximately 250 s. The amounts of acetone and CO_2 desorbed during illumination were 40 and 4 μmol/g TiO_2, respectively. Oxygen uptake rapidly increased when the UV lights were turned on, and its steady-state value probably corresponds to complete O_2 consumption (0 ppm O_2), since it is unlikely that the O_2 concentration would be constant when the rates of acetone and CO_2 formation were changing. A constant O_2

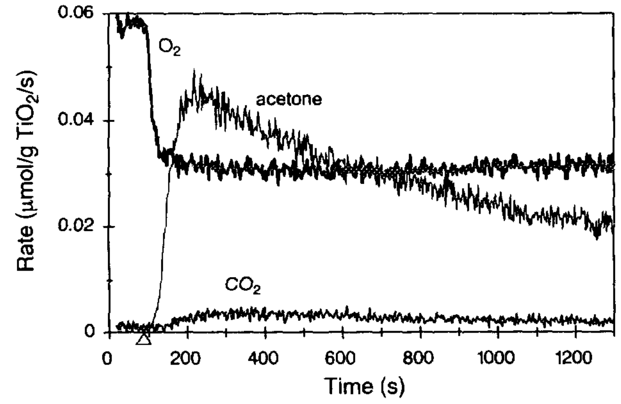

FIG. 8. Product desorption rates measured during PCO of adsorbed 2-propanol (saturation coverage) on TiO_2 in 30 ppm O_2 at 300 K. Triangle along the *x*-axis indicates when UV illumination began.

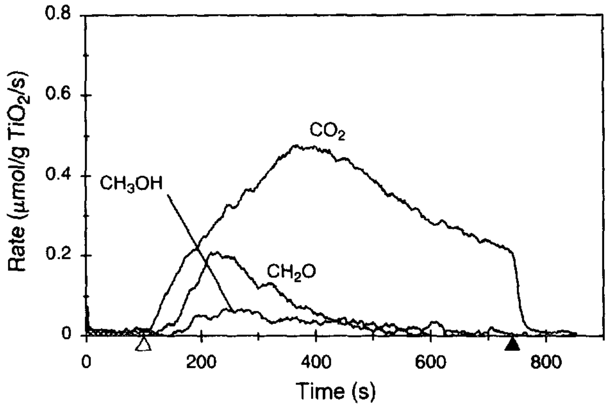

FIG. 9. Product desorption rates measured during PCO of adsorbed methanol (saturation coverage) on TiO_2 in 20% O_2 at 300 K. Triangles along the *x*-axis indicate when UV illumination began (△) and ended (▲).

uptake rate was not observed during 2-propanol PCO in 0.15% O_2 (see Fig. 4). Zero concentration of O_2 was difficult to establish, however, because of the background signal in the vacuum chamber. The O_2 uptake amount was 40 μmol/g TiO_2.

After illumination, the catalyst was heated to 723 K and an additional 84 μmol acetone/g TiO_2 desorbed for a total of 124 μmol acetone/g TiO_2 formed during the first 20 min of illumination. When the experiment was repeated, the rates of product formation were slightly lower than those in Fig. 8, and the total amounts of acetone and CO_2 were reduced to 35 and 3 μmol/g TiO_2, respectively. An additional 86 μmol acetone/g TiO_2 desorbed when the catalyst was heated to 723 K for a total of 121 μmol acetone/g TiO_2 formed in the second PCO. The O_2 uptake was 36 μmol/g TiO_2. No discoloration of the catalyst due to surface reduction was noted during these PCOs at low O_2 concentration, but such color change might be difficult to detect in the thin layers of TiO_2.

Photocatalytic Oxidation of 2-Propanol at Low Coverage

When TiO_2 with a less-than-saturation coverage of 2-propanol was illuminated in O_2, reaction products were detected, but not immediately. For 3% O_2, CO_2 was detected after 163 s, and acetone, H_2O, and CO were detected after 394 s. The TPO spectra obtained after 20 min of UV illumination show that nearly all of the adsorbed 2-propanol reacted during that time, and no acetone was observed. The spectra are similar to those in Fig. 6. When the O_2 concentration was increased to 20 and 40%, the delay times decreased. In 40% O_2, the delay times were 68 s for CO_2 and 127 s for acetone, H_2O, and CO. When the number of UV lights was reduced from six to three, the delay times increased. When the catalyst was saturated with acetone and then 66 μmol 2-propanol/g TiO_2 displaced some of the acetone, the delay time for CO_2 in 20% O_2 was reduced to 16 s and that for acetone and H_2O was 42 s.

Temperature-programmed oxidation carried out after PCO for less-than-saturation coverages showed that even when no acetone was detected at room temperature (i.e., short reaction times or low 2-propanol coverages), acetone had formed and remained on the surface. Acetone desorbs in two maxima, at 390 and 570 K. The low-temperature peak is desorption limited and is due to acetone formed during PCO. The high-temperature peak is reaction limited, and this acetone forms from 2-propanol in a thermal catalytic reaction.

In a series of experiments for various PCO times, the concentration of 2-propanol (as measured by TPO after PCO) steadily decreased with illumination time. The acetone concentration reached a maximum after nearly 300 s of PCO and then decreased. The amount of CO remained essentially constant, but the amount of CO_2 formed during TPO reached a maximum after 600 s of PCO.

When H_2O was introduced into the inlet gas after the onset of UV illumination, but before acetone had appeared in the product stream, acetone formed immediately whether the UV lights were on or off during H_2O introduction. That is, some of the acetone that formed during PCO and remained on the surface was readily displaced by H_2O.

Photocatalytic Oxidation of Methanol and Ethanol

Both methanol and ethanol oxidized photocatalytically at room temperature in 20% O_2 to form partial oxidation products in addition to CO_2 and H_2O. For saturation methanol coverage, CO_2 desorbed almost immediately when the UV lights were turned on, as shown in Fig. 9. After a delay time of 20 s, methanol, formaldehyde, and H_2O desorbed. After 11 min of illumination only CO_2 was ob-

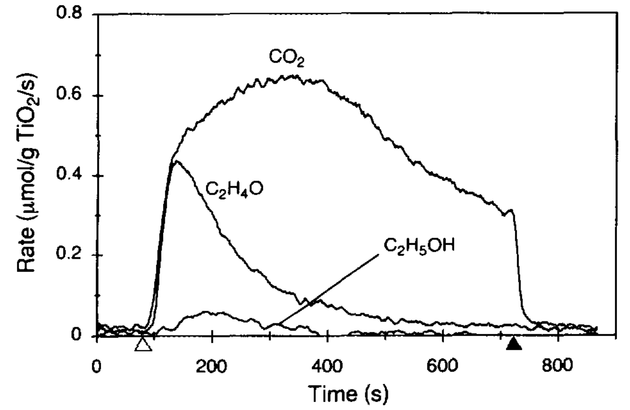

FIG. 10. Product desorption rates measured during PCO of adsorbed ethanol (saturation coverage) on TiO_2 in 20% O_2 at 300 K. Triangles along the x-axis indicate when UV illumination began (△) and ended (▲).

served, and when the UV lights were turned off, the CO_2 signal rapidly decreased. The amounts of CH_3OH, CH_2O, and CO_2 desorbed during 11 min of PCO were 15, 40, and 210 μmol/g TiO_2, respectively. A trace quantity of CO (less than 1% of the CO_2 amount) was also measured.

As shown in Fig. 10, similar behavior was observed for PCO of ethanol under the same conditions. Ethanol, acetaldehyde, CO_2, and H_2O desorbed immediately upon UV illumination. Acetaldehyde reached a maximum desorption rate quickly, but the CO_2 desorption rate did not peak until 250 s. When the UV lights were turned off, the CO_2 signal rapidly decreased. The amounts of C_2H_5OH, CH_3CHO, and CO_2 desorbed during PCO were 11, 80, and 320 μmol/g TiO_2, respectively. The CO was less than 1% of the total amount of CO_2.

Oxygen Photoadsorption

In an effort to study O_2 photoadsorption, a 100-mg sample of TiO_2 was exposed to air and UV light and then placed in a 1-cm-o.d., packed-bed, quartz reactor for TPD analysis. The packed bed was used because the larger diameter of the annular photoreactor and the widely spaced heating wires prevented the reactor from being heated to sufficient temperature to desorb O_2. A total of 0.5 μmol O_2/g TiO_2 desorbed during TPD, starting near 700 K and reaching a maximum at 750 K. On a fresh TiO_2 sample, 0.3 μmol O_2/g TiO_2 desorbed with a similar peak temperature. These experiments were not performed under controlled conditions, but they indicate how strongly oxygen is bound on TiO_2. They also demonstrate why O_2 desorption was not detected during our TPD experiments in the annular photoreactor, which has a temperature maximum of 723 K.

A more controlled TPD experiment was not possible because most of the TiO_2 could not be illuminated in the packed-bed reactor. Instead, efforts to measure O_2 uptake during photoadsorption were performed with a 0.016% O_2/He mixture. The O_2 mass signal was monitored while illuminating the catalyst. No oxygen uptake was detected on an oxidized catalyst, nor was O_2 uptake detected after this catalyst was exposed to H_2O and then illuminated. However, after exposing this catalyst to 2-propanol, the O_2 signal rapidly decreased when the TiO_2 was illuminated and increased when illumination was stopped. In this experiment, an O_2 uptake of 40 μmol/g TiO_2 over 25 min was easily detected. This suggests that an O_2 uptake as small as 1 μmol/g TiO_2 would have been easily detected on surfaces without adsorbed organics, but no uptake was seen.

DISCUSSION

Adsorbed 2-Propanol and Its Decomposition

The TPD spectra of 2-propanol (Fig. 2) closely agree with spectra measured by Kim *et al.* (32) using an atmospheric-pressure flow system. Although these authors observed a low-temperature 2-propanol desorption peak that was not seen in our study, their spectra show 2-propanol peaks at 390 and 500 K that are identical to those shown in Fig. 2. These two 2-propanol desorption peaks indicate two adsorption states on TiO_2: molecularly adsorbed 2-propanol and 2-propoxide (32). Reversibly adsorbed 2-propanol desorbs intact at low temperature. At higher temperature, 2-propoxide recombines with a surface hydroxyl group and 2-propanol desorbs (32). At slightly higher temperature, 2-propoxide dehydroxylates to form propene or dehydrogenates to form acetone. Desorption peaks for propene, acetone, and CO_2 are also at the same temperatures in both studies, and insignificant amounts of H_2 were detected. Although catalyst pretreatment was similar, the TiO_2 catalysts used in these studies have different morphologies. Kim *et al.* (32) used 100% anatase, whereas we used Degussa P25. Bickley *et al.* (42) reported that the individual particles in P25 consist of two types: (1) an amorphous phase together with either anatase or rutile and (2) primarily anatase covered by a thin layer of rutile. Thus the surface layer of P25 may not be mainly anatase. However, the nearly identical TPD spectra suggest that 2-propanol desorption and decomposition are not severely influenced by differences in the surface structure of these two catalysts. Similarities in the spectra also show that the annular reactor yields the same spectra as obtained in packed-bed reactors.

Although propene appears in both TPD and TPO spectra of 2-propanol, no propene forms during TPD or TPO of acetone. This suggests that acetone is not an intermediate for propene formation and acetone formation from 2-propoxide is essentially irreversible.

The 2-propanol saturation coverage per unit surface area on Degussa P25 was 40% greater than that measured gravimetrically in a high-vacuum system by Kim *et al.* (32) on their 100% anatase catalyst. The saturation coverage of 2-propanol on Degussa P25 was calculated as 4.2 molecules/nm^2 from the TPD product amounts listed in Table 1. This value neglects the small amount of 2-propanol that likely desorbs as CO_2 and CO above 723 K (Fig. 2).

Adsorbed Acetone and Its Decomposition

Adsorbed acetone desorbs molecularly at a much lower temperature (Fig. 3) than the acetone formed during 2-propanol dehydrogenation (Fig. 2). The low-temperature acetone peak in Fig. 3 corresponds to a desorption-limited process, whereas the high-temperature acetone peak in Fig. 2 corresponds to a reaction-limited process. Since these processes occur at significantly different temperatures, adsorbed acetone can be distinguished from acetone formed during TPD of 2-propanol. This distinction is useful for interpreting the TPD and TPO spectra obtained after PCO.

Whereas some acetone adsorbed at room temperature is weakly held to the TiO_2 surface, more than half is more strongly adsorbed and decomposes during TPD to CO_2 and CO at elevated temperatures (Fig. 3) or remains on the surface. Most of the species that remain on the surface can be removed by oxidation during TPO to 723 K. Only a fraction of the acetone that desorbs molecularly can be displaced by water at room temperature; the remaining acetone is sufficiently strongly held that it has a peak temperature of 425 K even when a large amount of H_2O is coadsorbed. The more strongly bound acetone either desorbs or decomposes only above room temperature. The species that remain adsorbed after heating an acetone-saturated surface in O_2 to 523 K are not displaced by H_2O at room temperature. The species can be acetone or an intermediate.

The acetone saturation coverage on Degussa P25 calculated using TPD amounts is low since a significant amount of decomposed acetone remains on the TiO_2, as indicated by the high CO_2 and CO desorption rates at 723 K. Also, much more CO_2 and CO were observed during TPO than during TPD, but the amount of molecular acetone was almost identical in each experiment. Thus, TPO provides a better measure of the amount of adsorbed acetone (Table 1). The saturation coverage of acetone on Degussa P25 calculated from TPO data was 3.0 molecules/nm^2, although this value may be low since some acetone is weakly adsorbed on TiO_2.

Thermal Oxidation of 2-Propanol and Acetone

Temperature-programmed oxidation in 20% O_2/80% He of 2-propanol formed the same products as during TPD, but in different amounts. In TPO, considerably more acetone, CO, and CO_2 formed, and the amounts of 2-propanol and propene decreased. Temperatures at which products began desorbing were identical in TPD and TPO. More than twice as much acetone formed during TPO than during TPD; apparently 2-propanol oxidized to acetone on TiO_2 at the same temperature that 2-propanol formed acetone in the absence of gas-phase O_2. The amount of propene decreased by 37% because more 2-propanol oxidized. As in TPD, CO_2 and CO formation during TPO did not begin until after acetone and propene desorption rates became significant. Additionally, the amounts of CO_2 and CO formed during TPD and TPO of 2-propanol and acetone seem to correlate with the amount of desorbed acetone. This suggests that CO_2 and CO form from acetone oxidation. In a previous thermal oxidation study of 2-propanol on TiO_2 (36), FTIR measurements showed that the 2-propoxide species oxidizes to form acetone. Acetone then oxidizes to CO_2 and CO through a surface intermediate (36). Infrared measurements show that propene, which formed by the dehydroxylation of 2-propoxide, is weakly adsorbed on TiO_2, and Nakajim *et al.* concluded that it is not oxidized on TiO_2 (36).

Acetone formed CO_2 and CO at lower temperatures during TPO than TPD, and this demonstrates that TiO_2 is a catalyst for acetone oxidation. Both CO_2 and CO also form faster (at lower temperature) during TPO of acetone than during TPO of 2-propanol. Thus, acetone oxidizes more readily than 2-propanol on TiO_2 to form CO_2 and CO. Since 2-propanol first oxidizes to an acetone intermediate, it follows that acetone oxidizes to CO_2 and CO faster than 2-propanol oxidizes to form acetone. In contrast, 2-propanol is quickly oxidized photocatalytically to acetone, but the subsequent PCO of acetone is markedly slower.

Reaction Steps for Photocatalytic Oxidation of 2-Propanol

Our photocatalytic results for Degussa P25 TiO_2 are in general agreement with the studies reported by Bickley *et al.* (6, 7) on rutile although our rates are significantly faster and CO_2 forms without high-temperature treatment of TiO_2 in our study. Adsorbed 2-propanol undergoes PCO on TiO_2 to form gas-phase acetone, H_2O, and CO_2. A small quantity of CO also appears in the gas phase, but because of the difficulty in correcting for cracking species at mass 28 and the resulting small mass 28 signals, it is possible that no CO formed during 2-propanol PCO. Photocatalytic oxidation of 2-propanol appears to be a series reaction in which 2-propanol is rapidly oxidized to acetone. Some of the weakly bound acetone is displaced into the gas phase by H_2O. The remaining acetone subsequently oxidizes to CO_2, H_2O, and perhaps CO, possibly through a more stable intermediate (6). The steps in the PCO of 2-propanol are discussed in detail in the following sections.

Adsorption

The 2-propanol readily adsorbs on TiO_2 in the absence of UV. Some 2-propanol is reversibly adsorbed since it desorbs during PCO at room temperature and during TPD at low temperatures. The TPO and TPD experiments show that adsorbed 2-propanol does not oxidize or decompose to acetone in the absence of UV light, except at elevated temperatures.

According to several early studies (9, 43, 44), O_2 photoadsorbs on TiO_2 in the presence of UV light. Photoadsorption of O_2 has been measured in several studies. Formenti *et al.* (9) and Gonzalez-Elipe *et al.* (45) reported increases in the O_2^-(ads) EPR signals when TiO_2 was illuminated in the presence of gas-phase O_2 at room temperature. Although the oxygen ion showed a correlation with photocatalytic activity, a quantitative measurement of oxygen surface coverage was not reported.

Previous studies measured the amount of O_2 that photoadsorbed during UV illumination (7, 44) and also TPD of this adsorbed oxygen (7). Bickley and Jayanty (7) heated a rutile sample (BET surface area = 4.2 m^2/g) to 873 K in O_2, rehydroxylated it by exposure to water at room temperature, and then illuminated it with UV for 20 h in O_2. During a subsequent TPD, O_2 desorbed beginning at ~700 K, but heating was stopped by 800 K and the rate of O_2 desorption had not increased much. We also observe O_2 desorption above 700 K. Bickley and Jayanty (7) reported that the saturation coverage of photoadsorbed O_2 was 0.081 molecules/nm^2. From their as-received sample, 0.060 molecules O_2/nm^2 desorbed. The H_2O coverage on the same surface was much higher (2 molecules/nm^2). Boonstra and Mutsaers (44) measured O_2 photoadsorption on several TiO_2 samples by monitoring pressure changes during illumination. They found that the amount of oxygen that photoadsorbed depended on the outgassing temperature. Samples outgassed at high temperature photoadsorbed less oxygen than samples outgassed at low temperature. For example, an anatase (BET surface area = 10.5 m^2/g) sample outgassed at 543 K photoadsorbed 0.010 molecules/nm^2 during 30 min of UV illumination, whereas a sample outgassed at room temperature photoadsorbed 0.063 molecules/nm^2 in the same illumination time.

Our transient studies in low O_2 concentrations did not detect any O_2 photoadsorption on TiO_2 for samples outgassed at 723 K or for samples with adsorbed H_2O. In contrast, when 2-propanol was adsorbed, O_2 uptake from the gas phase onto TiO_2 was readily detected as oxygen participated in PCO and/or replaced lattice oxygen that reacted with the alcohol. Our TPD results show that only a small amount of O_2 (0.008 molecules O_2/nm^2) desorbed following O_2 photoadsorption on an untreated TiO_2 sample illuminated in air and 0.005 molecules O_2/nm^2 desorbed from a sample that was not illuminated. This oxygen is strongly adsorbed (approximately 200 kJ/mol), which indicates that O_2 adsorption is essentially irreversible at room temperature. Results from both types of experiments indicate that the amount of photoadsorbed oxygen is considerably smaller than the saturation coverage of 2-propanol (4.2 molecules/nm^2).

Thus the role of photoadsorbed O_2 has not been well established. The small amounts of photoadsorbed O_2 detected in these studies and the rapid uptake of O_2 observed during reaction indicate that photoadsorbed O_2 may not be the oxidant in PCO. Since lattice oxygen can be involved in the reaction, as described in the next section, it is possible that O_2 adsorbs to replace lattice oxygen depleted by PCO, and the adsorption may not require UV light.

Lattice Oxygen

Several studies reported that PCO of organics can occur without gas-phase O_2. Ait-Ichou *et al.* (31) observed that a small amount of acetone and H_2O formed during initial PCO of 2-propanol with surface lattice oxygen or surface hydroxyl groups. Their catalyst also turned blue, apparently as a result of catalyst reduction by reaction. Djeghri and Teichner (12) also observed a blue TiO_2 catalyst after exposure to methylbutanol and UV light in the absence of O_2. Small amounts of methylbutanol photo-oxidized in the absence of gas-phase oxygen. The rate of this reaction, however, rapidly decreased and reached zero as the TiO_2 became blue. Similarly, Cunningham *et al.* (13) observed limited PCO of methanol and ethanol to aldehydes in the absence of gas-phase O_2, and Walker *et al.* (8) observed PCO of alcohols in the absence of gas phase O_2. These authors suggest that UV light activates lattice oxygen, which then oxidizes alcohols. Gas-phase O_2 replaces reacted lattice oxygen.

Our experiments in 30 ppm O_2 (Fig. 8) also show that lattice oxygen (or strongly adsorbed hydroxyl groups) can participate in PCO of 2-propanol. If all the oxygen required by stoichiometry were supplied by gas-phase O_2, the uptake would be 94 μmol/g TiO_2 for the experiment in Fig. 8. Because of the limited availability of O_2, however, only 54 μmol O_2/g TiO_2 were taken up; the balance of 40 μmol $O_2/gTiO_2$ must have been supplied by the surface. Since the catalyst was heated to 723 K in 20% O_2 prior to PCO, this oxygen is either from the lattice or from hydroxyl groups not removed by heating. The same amount of O_2 (39 μmol/g TiO_2) was supplied by the surface in the repeat experiment; O_2 from the gas phase could have resupplied O_2 in the interval between experiments. The 40 $\mu molO_2$/g TiO_2 corresponds to 1.2 O atoms/nm^2 that are available on the TiO_2 surface for PCO. This amount is several orders of magnitude larger than our measured amount of photoadsorbed oxygen. The total oxygen atom concentration in the TiO_2 surface lattice is estimated to be approximately 12–15 atoms/nm^2, depending on which crystal planes are exposed.

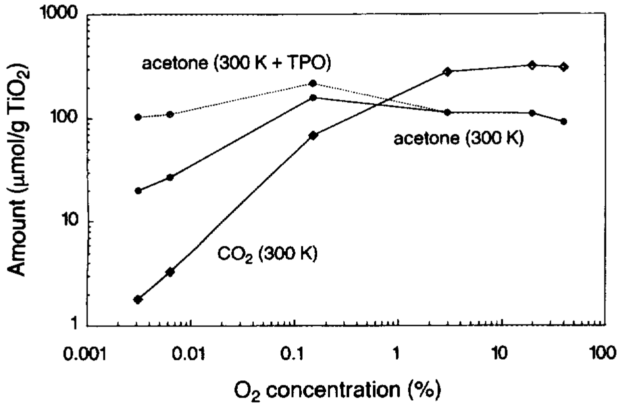

FIG. 11. The amounts of acetone and CO_2 formed during 10 min of room-temperature PCO of adsorbed 2-propanol (saturation coverage) on TiO_2 for 10 min versus O_2 concentration. The dashed line includes the amount of acetone that desorbed from TiO_2 during TPO after PCO.

The charged O_2 species that have been detected in other studies may react with the adsorbed organics or replace reacted lattice oxygen. Walker *et al.* (8) suggested that alkanes require both lattice oxygen and O_2^-(ads) for PCO, but alcohols require only lattice oxygen (O_2^-(ads) is needed to reoxidize the surface). Our results also indicate that photoadsorbed oxygen is not needed to oxidize 2-propanol. Gas-phase O_2 is important for prolonged PCO even if all the reaction is with lattice oxygen, but it is not clear if UV is required for O_2 to adsorb and occupy oxygen vacancies.

Rate Dependence on Oxygen Concentration

Figure 11 shows how the amounts of acetone and CO_2 that desorbed during 10 min of PCO of 2-propanol changed with O_2 concentration. The dashed line at low O_2 concentrations represents the sum of acetone that desorbed during room-temperature PCO plus acetone that desorbed molecularly during the subsequent TPO. For O_2 concentrations above ~3%, the amount of CO_2 is nearly three times the amount of acetone. As the O_2 concentration drops below 1%, however, the amount of acetone does not change much, whereas the amount of CO_2 decreases rapidly. Thus, as the O_2 concentration decreased from 40 to 0.003%, the amount of CO_2 dropped from 310 to 2 μmol/g TiO_2.

Although acetone forms rapidly compared to CO_2, its appearance in the gas phase is due to displacement by H_2O (discussed below), and the method used for Fig. 11 is a reasonable way to estimate the amounts of acetone formed. Some acetone remains on the surface, however. The figure indicates that acetone is essentially zero order in O_2 over a wide concentration range. In contrast, Fig. 11 indicates that CO_2 formation is first order in O_2 at low concentrations and zero order at higher concentrations. Since the rate of CO_2 formation is limited by reaction, other methods can also be used to analyze the data obtained at different O_2 concentrations.

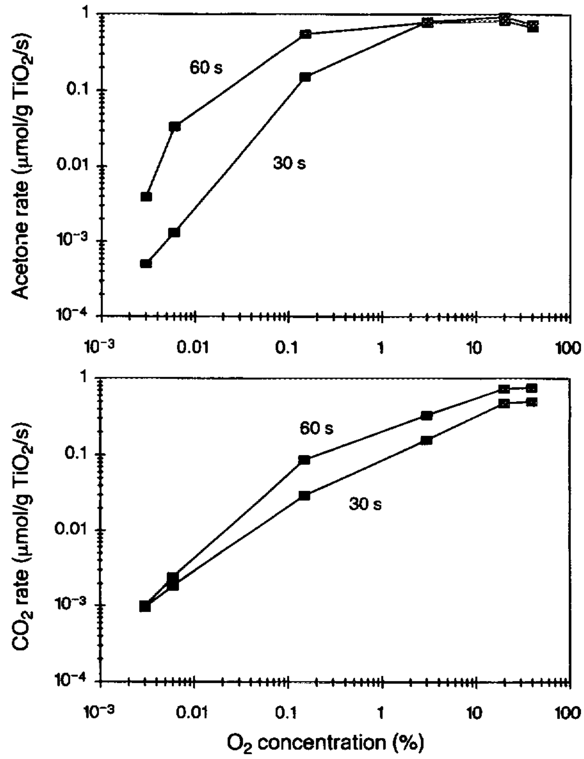

FIG. 12. Rates of acetone and CO_2 formation after 30 and 60 s of reaction for various O_2 concentrations. Adsorbed 2-propanol (saturation coverage) was oxidized photocatalytically at room temperature on TiO_2.

Figure 12 presents a plot of the rate of CO_2 formation versus O_2 concentration. The rates were measured at short reaction times (30 and 60 s) directly from the rate versus time plots. This figure also shows that CO_2 formation is approximately first order (0.87 ± 0.04 order at 30 s and 1.13 ± 0.04 order at 60 s) at low O_2 concentrations and zero order at higher concentrations. The rate of acetone formation in Fig. 12, measured directly from the rate versus time curves, also appears first order in O_2 at low concentrations and zero order at high concentrations. The O_2 concentrations at which acetone formation becomes zero order is much lower than that for CO_2 formation, and the rate measured at 60 s is much higher than that at 30 s for acetone formation, but not for CO_2 formation. The acetone desorption rates used in Fig. 12 are *not* good indications of the reaction rates at these times because acetone also remains on the surface.

Figures 11 and 12 indicate that the PCO of 2-propanol to form acetone is almost zero order in O_2 concentration, even at low O_2 concentrations. Apparently the lattice can supply oxygen during these transient experiments at a sufficient rate that acetone formation is not limited by O_2 availability from the gas phase. In contrast, complete oxidation to CO_2 is first order in O_2 concentration at low concentrations and decreases toward zero order at higher concentrations. Oxidation of acetone to CO_2 and H_2O requires much more O_2 than oxidation of 2-propanol to acetone. Thus, as the O_2 concentration decreases, the rate of acetone formation does not decrease much, but the rate of acetone oxidation to CO_2 and H_2O decreases, so acetone accumulates on the surface or desorbs. These results also show clearly that acetone is an intermediate in the reaction sequence. At 20% O_2, the PCO of 2-propanol to CO_2 is not limited by O_2, indicating that the O_2 adsorption is not a slow step.

Agreement between the dependence of CO_2 formation rate on O_2 concentration observed in our transient studies and that measured for acetone PCO in steady-state experiments suggests that the same processes were measured. Raupp and Junio (10) reported that acetone oxidation to CO_2 is zero order above 15% O_2 and first order at lower O_2 concentrations. Since 2-propanol rapidly forms acetone, the same rate dependence is expected for both 2-propanol and acetone PCO to CO_2. A similar dependence of CO_2 formation on O_2 concentration has been reported for 2-methyl butane PCO (12). In an O_2-rich flow, 40% of the 2-methyl butane completely photo-oxidized to CO_2 and 60% formed acetone. At low O_2 concentrations, nearly all the 2-methyl butane partially oxidized to acetone.

Acetone Formation

Exposure of the catalyst to H_2O during and after PCO demonstrates clearly that the formation of gas-phase acetone is not reaction limited but instead is controlled by the amount of water on the surface. Bickley *et al.* (6) first reported that water displaced acetone from TiO_2 during photocatalysis. As water forms during PCO, it displaces some weakly adsorbed acetone. As shown in the TPD spectra of adsorbed acetone (Fig. 3), the acetone desorption rate in the absence of water is much slower than observed during PCO. Ultraviolet light is not required for acetone desorption and the same displacement by H_2O took place in the absence of UV illumination. Acetone is not photodesorbed and the displacement takes place without UV illumination. Peral and Ollis (21) reported that water inhibits acetone oxidation during photocatalysis at steady state and concluded that H_2O may displace acetone. Raupp and Junio (10) also observed that the PCO rate of acetone decreased at higher H_2O concentrations.

Photocatalytic oxidation of a sufficiently low coverage of 2-propanol results in only CO_2 appearing in the effluent. Acetone and H_2O remain on the TiO_2 surface because their appearance in the gas phase is desorption limited and the coverage does not increase enough for the desorption rates to be significant. Also, as shown by our H_2O injection experiments, not all the adsorbed acetone can be displaced by H_2O.

Surface Intermediates

No partial oxidation product besides acetone (and perhaps CO) desorbed intact either during PCO or during TPO after PCO. Only acetone was displaced during H_2O exposures. During TPO after long PCO times, only CO_2 and CO formed at high temperatures; this formation was similar to that observed for strongly adsorbed acetone. Thus, we cannot determine if a surface intermediate forms during acetone PCO. Bickley and Jayanty (7) reported that trace amounts of formic acid and acetaldehyde desorbed during TPD after 2-propanol photocatalysis. Because of the small amounts of catalyst used in our reactors, trace amounts of such products would probably not have been detected. The intermediate or the strongly adsorbed acetone can be oxidized to CO_2 and H_2O at room temperature or oxidized to CO_2, CO, and H_2O at high temperatures during TPO.

Surface Reaction

In the absence of UV light, acetone forms only from catalytic decomposition of 2-propanol at elevated temperatures. Thus, the surface PCO step that forms acetone from 2-propanol at room temperature requires UV light. Since acetone starts forming almost immediately during PCO and its rate drops to zero while CO_2 is still forming, the acetone formation step is fast relative to complete oxidation to CO_2 and H_2O. Thus, when H_2O was injected into the flowing gas a few seconds after the UV lights were turned on, a large amount of acetone desorbed. As shown by the acetone PCO experiments, CO_2 formation from acetone (and any intermediate that may form from acetone) at room temperature also requires UV light.

As shown in Fig. 4, immediately upon UV illumination, O_2 is consumed, but gas-phase reaction products are only observed after a time lag of 20 s. That is, reaction started immediately, but products were only detected in the gas phase after a delay. Either the acetone that initially forms is strongly bound and subsequent reaction forms more weakly bound acetone, which can be displaced, or the H_2O coverage must increase to a certain value before it can displace acetone. By the time the lights were turned off for the experiment in Fig. 4, 280 μmol O_2/g TiO_2 had been consumed. The amounts of oxygen required to form the products observed during room-temperature reaction are as follows:

acetone:	80 μmol O_2/g TiO_2
CO:	23 μmol O_2/g TiO_2
CO_2:	103 μmol O_2/g TiO_2.

These values were calculated assuming stoichiometric formation of water. A TPO in 0.15% O_2 after reaction indicated that approximately 60 μmol acetone/g TiO_2 were on the surface after reaction. The TPO formed CO and CO_2 from products that remained on the surface (acetone or an intermediate), and this total of 236 μmol O_2/g TiO_2 is a lower limit and is thus consistent with the measured 280 μmol O_2/g TiO_2.

Water and Carbon Dioxide Formation

Water is strongly adsorbed on TiO_2 and accumulates on the surface as reaction proceeds. As its surface coverage increases, the temperature at which H_2O desorbs decreases, and it desorbs at room temperature. Therefore, formation of gas-phase H_2O during PCO is desorption limited, and TPO showed that large amounts of H_2O are present on the surface after PCO. We saw no evidence that H_2O increased the rate of O_2 photoadsorption, as reported by Boonstra and Mutsaers (44), and we saw no evidence that UV increased the rate of H_2O desorption, as reported by Misra (46). In experiments with adsorbed H_2O, the rate of photodesorption from Degussa P25 was below the detection limit of our system, and thus orders of magnitude below the rate of H_2O formation observed during PCO. Thus, H_2O photodesorption does not contribute significantly to the rate of H_2O appearance during PCO.

Carbon dioxide desorbs immediately upon formation because CO_2 is weakly adsorbed on the TiO_2 surface. That is, the rate of appearance of gas-phase CO_2 during PCO is limited by surface reaction. When CO_2 was exposed to TiO_2 at room temperature and TPD was then carried out, neither CO_2 nor CO desorption was detected. Also, the CO_2 formation rate during PCO dropped rapidly when the UV lights were turned off. In contrast, acetone and H_2O adsorb on the surface and their desorption rates depend on their coverages and coverages of other species. Thus, the rates of H_2O and acetone formation changed slowly when the UV lights were turned off.

The rate of CO_2 formation increases with time because CO_2 forms from acetone (and any intermediate that forms from acetone), which starts at zero concentration but forms more rapidly than it is subsequently photocatalytically oxidized to CO_2 and H_2O. Likewise, the formation of CO_2 and CO at high temperature during TPO is not limited by desorption since CO and CO_2 are both weakly bound to the TiO_2 surface.

Gas-Phase Reaction Mechanism

Raupp and Junio (10) suggested that quantum yields greater than one indicate that PCO of acetone occurs through a surface-mediated, OH radical-initiated chain mechanism. Our experiments, in which organics were removed from the gas phase, show directly that adsorbed surface species undergo PCO. A comparison of our rates, normalized per gram of catalyst, would be useful for determining if a gas-phase process takes place in parallel with the surface process. The published rates of acetone oxidation in steady-state studies (10, 21), however, are for reactor systems where only a fraction of the catalyst was exposed to UV light. Thus the amount of catalyst involved in reaction in those studies is unknown.

Photocatalytic Oxidation of Methanol and Ethanol

Both methanol and ethanol readily undergo PCO at room temperature and exhibit many of the same trends seen during 2-propanol PCO. In 20% O_2, aldehydes form as partial oxidation products at room temperature. These aldehydes desorb from the surface and reach maximum rates after short reaction times. The CO_2 rate takes longer to reach a maximum, and its formation continues long after the aldehyde rates have decreased to near-zero values. Thus, rates of methanol and ethanol PCO are similar to that measured for 2-propanol. The TPO carried out after methanol PCO detected CO and H_2O as the main products. Since CH_3OH is expected to decompose to CO and H_2 on TiO_2, the large quantity of CO is likely a result of its decomposition. For C_2H_5OH, CO and CO_2 were similar in amplitude during TPO, as observed following 2-propanol oxidation.

CONCLUSIONS

- An annular photoreactor with a thin film of catalyst provides a system in which transient photocatalytic oxidation studies and TPD/TPO can be carried out to separate adsorption, reaction, and desorption steps.
- Photocatalytic oxidation of adsorbed 2-propanol at room temperature to form acetone is rapid, but subsequent oxidation of acetone to CO_2 and H_2O is slower.
- Strongly bound acetone and possibly other stable surface intermediates form on the TiO_2 surface during PCO, and react only slowly to CO_2 and H_2O. At steady state the surface is expected to be almost covered with these species plus H_2O.
- Surface PCO steps require UV radiation, but desorptions of acetone, CO_2, and H_2O products do not.
- The coverage of photoadsorbed O_2 on TiO_2 is low (0.5 μmol/g TiO_2) in the absence of oxidizable species, and the oxygen is strongly bound (200 kJ/mol). There are no indications that photoadsorbed O_2 is important in PCO.
- Photocatalytic oxidation to form acetone is essentially independent of O_2 concentration above 1% O_2, apparently because lattice oxygen is involved in the reaction, but CO_2 formation is first order in O_2, except at high O_2 concentrations.
- Acetone desorbs during PCO because it is displaced from the surface by H_2O. During steady-state reaction, the degree of partial oxidation to acetone is expected to depend on the concentration of water vapor.
- The thermal decomposition of 2-propanol on Degussa P25 is nearly identical to that on 100% anatase.

- Degussa P25 is a poor thermal oxidation catalyst (no UV light) for 2-propanol, which oxidizes above 525 K. Thus, UV light increase the rate of catalytic oxidation on TiO_2 by orders of magnitude.
- Thermal oxidation of 2-propanol first forms acetone, which oxidizes faster than 2-propanol, so that 2-propanol oxidation to CO_2 and H_2O is limited by the initial oxidation to acetone.
- Methanol, ethanol, and 2-propanol follow similar PCO pathways through aldehyde intermediates.

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