

# Catalyst Design to Change Selectivity of Photocatalytic Oxidation

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Different selectivities for photocatalytic oxidation (PCO) of ethanol were observed for two types of adsorption sites on TiO<sub>2</sub>, and this identification led to the design of a photocatalyst with enhanced selectivity to acetaldehyde, a partial oxidation product. Transient photocatalytic oxidation (PCO), steady-state reaction, temperature-programmed desorption (TPD), temperature-programmed oxidation, and isotope labeling were combined to determine the reactivity of the different adsorption sites. During PCO, weakly bound ethanol preferentially formed gas-phase acetaldehyde, whereas strongly bound ethanol (which decomposes during TPD) primarily produced CO<sub>2</sub>. Weakly bound ethanol appears to adsorb on sites that are not available for acetaldehyde adsorption. This information, combined with the fact that acetaldehyde decomposes to a strongly bound intermediate during TPD, led to the design of a catalyst that was modified with acetaldehyde TPD products, which were stable during PCO. The TPD products of acetaldehyde preferentially poison the sites where ethanol is strongly bound so that selectivity to acetaldehyde increased during ethanol PCO. Higher selectivity was seen during both transient and steady state experiments, and at 54–60% conversion the ratio of partial to complete oxidation on the poisoned catalyst was five times that on fresh TiO<sub>2</sub>. © 1998 Academic Press

## INTRODUCTION

Heterogeneous photocatalytic oxidation (PCO) of low concentration of organics with air has the potential to be an effective means of reducing the concentrations of pollutants. Organics can be oxidized to CO<sub>2</sub> and H<sub>2</sub>O at room temperature on TiO<sub>2</sub> catalysts in the presence of UV or near-UV illumination. The UV light excites electrons from the valence to the conduction band of the semiconductor catalyst, leaving holes behind. The electron–hole pairs can initiate redox reactions with surface species.

The main advantages of PCO are that the reaction is reasonably fast at room temperature and a wide range of organics can be oxidized. A disadvantage, however, is that significant quantities of partial oxidation products can form under some conditions and in certain cases the partial oxidation products are less reactive and more toxic (1). However, if partial oxidation products can be made with high

selectivity, then PCO may have the potential to be used for preparation of some specialty partial oxidation products (2–8).

Partial oxidation using photocatalysis has been studied previously. Formenti *et al.* (9) photocatalytically oxidized paraffins on anatase TiO<sub>2</sub> in a differential reactor. At low conversion of isobutane (3.2%), the selectivity to acetone was approximately 75%. Under similar conditions, isobutylene and propane were also found to produce acetone but with lower selectivities. Normal butane produced butanone with a selectivity of 30% and only complete oxidation products were observed for ethane, propene, 1-butene, and 2-butene. These experiments were run at high organic concentrations (37.5%).

Wada *et al.* (3) used a MoO<sub>3</sub>/SiO<sub>2</sub> catalyst to photocatalytically oxidize ethane to acetaldehyde and formaldehyde at temperatures above 463 K. The reaction products were acetaldehyde, formaldehyde, ethanol, ethene (trace), and small amounts of CO and CO<sub>2</sub>. They observed an increased yield of aldehyde products with an increase in the ethane feed rate. Increasing the oxygen feed rate improved aldehyde yield for a 75-W mercury lamp but had no effect when illuminating the catalyst with a 200-W lamp. The greatest yields of acetaldehyde and formaldehyde were obtained at 493 K and 0.4% conversion of ethane. The yield of acetaldehyde increased quickly above 400 K and reached a maximum between 475 and 500 K. The yield of formaldehyde, however, continued to increase with temperature over the range of temperatures studied.

In the current study, ethanol was used as a model compound to study PCO because it forms partial oxidation products (1, 10–13) and it is a pollutant from industrial processes such as breweries and bakeries. Nimlos *et al.* (10) detected significant amounts of acetaldehyde and formaldehyde, and smaller amounts of acetic acid in the gas-phase during PCO of ethanol in a recirculating batch reactor. Sauer and Ollis (1) observed acetaldehyde and formaldehyde as partial oxidation products of ethanol PCO. In previous studies (11, 12), we detected acetaldehyde during transient PCO of a monolayer of ethanol.

Acetaldehyde is typically produced by thermal cracking of ethane to ethene, followed by catalytic oxidation via the Wacker process, which is relatively costly and

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energy-intensive. During photocatalytic oxidation, ethane has been reported to produce acetaldehyde (3). Thus, a complete photocatalytic pathway for the oxidation of paraffins to aldehydes exists. Also, the partial oxidation of ethanol has been proposed as an attractive alternative to produce acetaldehyde (5–8).

The objective of this work was to use temperature-programmed desorption (TPD) and transient PCO to determine the reactivity of molecules adsorbed in different forms on titania in order to obtain a better understanding of the basic processes that take place during PCO. The result of this understanding allowed us to design a titania catalyst with higher selectivity for partial oxidation of ethanol to acetaldehyde. Our previous TPD and transient PCO experiments (11, 12) appeared to indicate that weakly and strongly held ethanol react at different rates. That is, when transient reaction of a partial monolayer of ethanol was carried out in the absence of gas phase ethanol, selectivity to complete oxidation was high. In contrast, at saturation coverage, a large fraction of the ethanol formed gas-phase acetaldehyde. Thus, weakly adsorbed ethanol, which is more plentiful at saturation coverage, appeared to favor partial oxidation products, whereas more strongly adsorbed ethanol had a high selectivity for complete oxidation. However, at low coverages the potential for readsorption and further oxidation of partial oxidation products is greater than at saturated coverage, and thus a direct measure of the selectivities is desired.

Kim and Barteau (14) performed TPD of ethanol in both a flow reactor system and under UHV conditions. They concluded that ethanol adsorbs both molecularly and dissociatively at room temperature on anatase  $\text{TiO}_2$  powder. Desorption of the molecularly adsorbed ethanol was observed at 350 K in the flow reactor, whereas ethoxide recombination resulted in ethanol desorption at 390–400 K. At higher temperatures, ethene and acetaldehyde were the main decomposition products.

Iwasawa (15) postulated that weakly bound molecules, existing only in the presence of gas-phase molecules, change the selectivity and enhance the reactivity of strongly bound species. The dehydrogenation of ethanol to acetaldehyde on a  $\text{SiO}_2$ -supported niobium monomer catalyst was used as a model system. Iwasawa observed that ethanol dehydration to ethene above 600 K predominated during TPD of a monolayer of adsorbed ethanol. Dehydrogenation to acetaldehyde and  $\text{H}_2$  was favored when the reaction was carried out at 523 K in the presence of gas-phase ethanol. However, if acetaldehyde and  $\text{H}_2$  were desorption-limited, the results can also be explained by their displacement by gas-phase ethanol during the reaction at 523 K.

Oyama (16) studied the catalytic oxidation of ethane on vanadium oxide supported on silica. He concluded that partial and complete oxidation products resulted from two types of adsorption sites, similar to the conclusions of Kung

and Kung (17) on the oxidation of butenes on ferrite catalysts. Oyama suggested that ethane reacted to acetaldehyde and ethene through intermediates bound to surface oxygen, whereas complete oxidation resulted from metal-bound intermediates.

We attempted to decrease the fraction of adsorbed ethanol that was strongly adsorbed on  $\text{TiO}_2$  (during TPD this ethanol dehydrated or dehydrogenated) to produce a photocatalyst with higher selectivity for partial oxidation products. We have observed that acetaldehyde is strongly adsorbed on  $\text{TiO}_2$  (11), and only 10% of the monolayer desorbed or decomposed to gas-phase products during TPD to 723 K. Furthermore, PCO of coadsorbed acetaldehyde and ethanol indicated that acetaldehyde may not adsorb onto the sites where weakly bound ethanol adsorbs. Thus, TPD of acetaldehyde to 723 K was used in an attempt to preferentially poison the sites that strongly adsorb ethanol, and TPD of  $^{13}\text{C}$ -ethanol was used to verify that the adsorption sites had changed.

The effect of poisoning on the selectivity was studied in both transient and continuous flow (quasi steady state) experiments. In the transient experiments, the ethanol had both carbons labeled with carbon-13 so that the reaction products detected during PCO could be distinguished from any products that formed from the  $^{12}\text{C}_2$ -acetaldehyde that was used to poison the surface. In the steady state experiments,  $^{12}\text{C}_2$ -ethanol was used. The adsorption sites were also studied by transient PCO of a monolayer of coadsorbed  $^{13}\text{C}_2$ -ethanol and  $^{12}\text{C}_2$ -acetaldehyde.

The selective PCO of ethanol to acetaldehyde was significantly increased by poisoning the surface so that a larger fraction of the adsorbed ethanol was more weakly bound. This indicates that the weakly adsorbed ethanol, presumably molecularly adsorbed, preferentially forms partial oxidation products or that the acetaldehyde formed on these sites can more readily desorb before it is completely oxidized. The ethanol that is held sufficiently strongly that it dehydrates or dehydrogenates during TPD preferentially oxidized completely to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  during PCO. This poisoning process is not optimized, but indicates the potential for modifying the catalyst properties to change selectivity based on an understanding of the adsorption and reaction properties determined by transient measurements.

## EXPERIMENTAL METHODS

The apparatus used for PCO, TPD, and temperature-programmed oxidation (TPO) was described previously (18). Degussa P-25  $\text{TiO}_2$  powder was coated as a thin layer (average thickness  $<0.5 \mu\text{m}$ ) on the inside of an annular Pyrex reactor so that essentially all the  $\text{TiO}_2$  was exposed to UV light for PCO. The annular spacing was 1 mm so that high gas flow rates could be maintained across the catalyst to minimize mass transfer effects and rapidly flush

gas-phase products from the reactor. The outside diameter of the reactor was 2 cm and the reactor was 13-cm high so that sufficient catalyst mass was present to allow detection of reaction products by the mass spectrometer. The photocatalytic reactor was surrounded by a quartz furnace with heating wires for TPD, and the furnace was surrounded by six UV lamps (GE, 4 W). The maximum light intensity was near 360 nm (10). The tip of a chromel-alumel thermocouple (0.5-mm diameter) contacted the side of the reactor wall to record temperature during TPD and to provide feedback to the temperature programmer.

Before each experiment, the reactor was heated in 3% O<sub>2</sub> in He to 723 K, in order to create a reproducible surface, and then cooled to room temperature. The sites that adsorbed ethanol more strongly were poisoned by injecting three pulses of 1 mL each of acetaldehyde in He flow over the catalyst at 373 K. After the acetaldehyde was flushed from the gas phase, the catalyst temperature was ramped to 723 K to decompose the adsorbed acetaldehyde.

For transient PCO or TPD, the organic of interest was injected immediately upstream of the reactor and allowed to evaporate and adsorb onto the catalyst surface at room temperature. Ethanol and acetaldehyde were coadsorbed by injecting an approximately equimolar gaseous mixture. Photocatalytic oxidation and TPD were performed for ethanol (Midwest Grain, 200 proof), <sup>13</sup>C<sub>2</sub>-ethanol (CH<sub>3</sub> <sup>13</sup>CH<sub>2</sub>OH, Isotec, 99+%), and acetaldehyde (Aldrich, 99.5+%). All transient PCOs were carried out at room temperature in 0.2% O<sub>2</sub> after any excess organic was flushed from the gas phase. For transient PCO, ethanol with both carbons labeled with <sup>13</sup>C was used so that the gas phase species from the ethanol could be distinguished from species that might form from the carbeneous layer that resulted from acetaldehyde decomposition. This isotope labeling also allows us to determine if any exchange took place between ethanol and the adsorbed species.

Temperature-programmed desorption was carried out by heating the catalyst in He at a constant rate of 1 K/s to 723 K. The catalyst was held at this temperature until no desorption products were detected in the gas phase. For transient PCO, metal shields were placed between the reactor and the UV lights before the lights were switched on. When the lights reached a steady-state output, reaction was initiated by removing the shields. During coadsorption experiments, TPO was performed after PCO by heating the catalyst at 1 K/s in 0.2% O<sub>2</sub> flow to obtain an accurate measure of the amounts of each carbon isotope. A Balzers QMA 125 quadrupole mass spectrometer monitored the reactor effluent immediately downstream of the reactor. The mass spectrometer was interfaced to a computer so that multiple mass peaks could be recorded simultaneously during PCO and TPD. The mass spectrometer signals were calibrated frequently by injecting known volumes of gases or liquids into the flow stream downstream of the reactor, and signals

were corrected for cracking in the mass spectrometer. Calibration of the <sup>13</sup>C species was accomplished by injecting the corresponding <sup>12</sup>C species into the mass spectrometer. Although water is a reaction product, its signal is not plotted in the figures because its calibration is less accurate and because water appearance in the gas phase is limited by desorption from the TiO<sub>2</sub> surface so that the water signal does not provide kinetic information.

Continuous flow reaction studies were performed in the same system with a 20% O<sub>2</sub> in He stream. Either approximately 70 or 1000 ppm of ethanol was introduced into the system via a gas bubbler. After the ethanol, O<sub>2</sub>, and He gas mixture reached steady state in the dark, the shields were removed from the UV lights and the gas phase products detected by a mass spectrometer.

## RESULTS AND DISCUSSION

### Temperature-Programmed Desorption

Figure 1 shows the TPD spectra of ethanol from fresh TiO<sub>2</sub>. As has been reported previously (11), approximately 60% of the ethanol desorbed in two broad peaks at 450 and 650 K. The remaining ethanol either dehydrated to ethylene in a peak at 660 K, dehydrogenated to acetaldehyde at 650 K, or decomposed to CO in a peak at 660 K. The dehydration pathway was favored over the dehydrogenation pathway by a ratio of 1.8 to 1. Approximately 5% of the adsorbed ethanol remained on the catalyst surface after TPD and was oxidized during a subsequent TPO.

During ethanol TPD on the {011}-faceted TiO<sub>2</sub>(001) surface, Kim and Barteau (20) detected ethanol, acetaldehyde, and ethylene at similar temperatures. However, they observed less dehydrogenation to acetaldehyde and did not detect any CO. On anatase powder, Kim *et al.* (21)

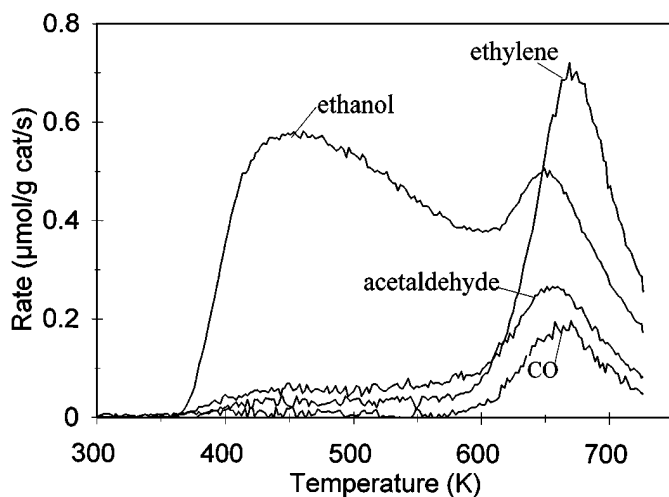


FIG. 1. Temperature-programmed desorption of ethanol from fresh TiO<sub>2</sub>.

reported that 61.8% of the ethanol desorbed, and acetaldehyde (9.4%), ethylene (8.8%), diethyl ether (6.5%), and water (4.7%) were detected along with other minor products.

In contrast to ethanol, acetaldehyde and its decomposition products were sufficiently strongly bound to the surface that less than 10% of the monolayer formed gas phase products during TPD, and the species remaining on the surface turned the catalyst brown at 723 K. As reported previously (11), acetaldehyde desorbed with a maximum at 400 K and a shoulder at 655 K. High temperature CO and CO<sub>2</sub> were detected and their desorptions were incomplete when heating was stopped at 723 K. A small crotonaldehyde desorption peak was observed near 400 K. During the subsequent TPO, the species that remained on the surface were oxidized to CO<sub>2</sub>, and the total amount of carbon agreed well with the value obtained during TPO of acetaldehyde. Also, the amount of H<sub>2</sub>O detected during TPO was small compared to the amount of CO<sub>2</sub>, indicating that the surface species that resulted from acetaldehyde decomposition has a high carbon-to-hydrogen ratio.

Idriss *et al.* (22) investigated the selectivity and mechanism shifts during acetaldehyde TPD on TiO<sub>2</sub>(001). They observed that the main reaction pathway changed from reductive coupling to aldol condensation as the surface was oxidized by annealing. For the TiO<sub>2</sub>(001) surface annealed at 750 K, the TPD products were: acetaldehyde (30%), ethanol (36%), butene (1%), crotonaldehyde (19%), and crotyl alcohol (14%). Although we checked for all of these products, no ethanol or butene and only acetaldehyde and small amounts of crotonaldehyde were detected. In addition, the TPO performed after TPD clearly indicates that acetaldehyde mainly decomposes on Degussa titania to a stable species that does not desorb during TPD.

The TPD spectra of ethanol changed significantly when the catalyst was poisoned with the TPD products of acetaldehyde, as described in the experimental methods section. A TPO experiment carried out after acetaldehyde TPD shows that 540  $\mu\text{mol/g}$  catalyst of carbon were deposited on the surface during acetaldehyde TPD, corresponding to 82% of an acetaldehyde monolayer. Figure 2 shows that the amount of ethanol that desorbed intact from the poisoned surface was 44% of that on a fresh surface, but the amount of ethanol that dehydrated or dehydrogenated during TPD was only 19% of that on a fresh surface. That is, the more strongly bound ethanol was preferentially poisoned by the carbon deposit.

#### Transient PCO on Fresh TiO<sub>2</sub>

As reported previously (11, 12), transient PCO of a monolayer of ethanol on fresh TiO<sub>2</sub> (Fig. 3) produced acetaldehyde, CO<sub>2</sub>, water, and a small amount of ethanol. Ethanol is probably displaced from the surface by the water product. Approximately 15% of the ethanol monolayer

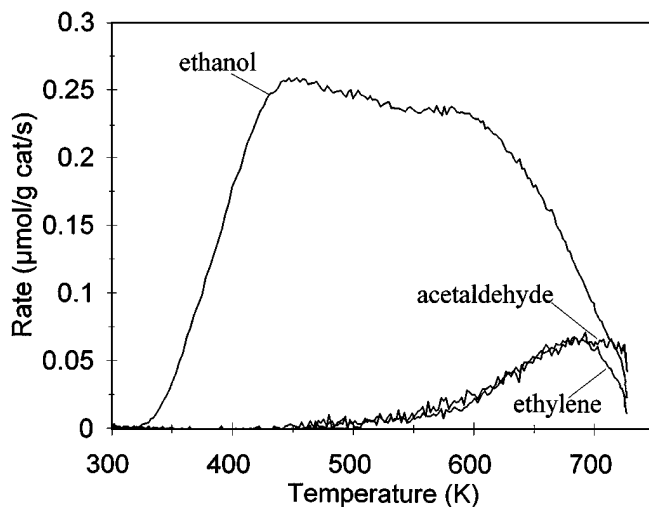


FIG. 2. Temperature-programmed desorption of ethanol from poisoned TiO<sub>2</sub>.

was rapidly oxidized photocatalytically to form gas-phase acetaldehyde. The remaining ethanol oxidized more slowly to CO<sub>2</sub> and H<sub>2</sub>O, and CO<sub>2</sub> production continued until the UV lights were turned off. The immediate maximum in the rate of acetaldehyde desorption indicates that ethanol oxidation to acetaldehyde is fast and most likely does not react through a stable intermediate. Note that although not much acetaldehyde desorbs from TiO<sub>2</sub> at room temperature or at elevated temperature during TPD, it readily desorbs during PCO of ethanol. The amount of acetaldehyde that desorbs during PCO of ethanol is approximately four times that which desorbs during acetaldehyde TPD, even though more acetaldehyde is on the surface at the start of the TPD.

During transient PCO of a monolayer of acetaldehyde, the amount of acetaldehyde that desorbed was less than

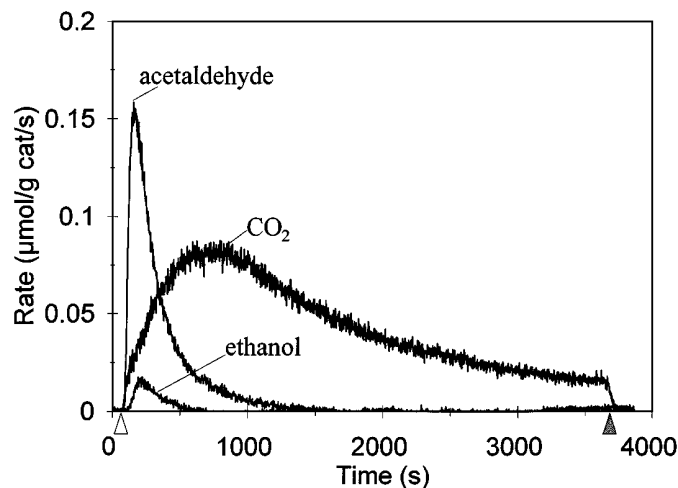


FIG. 3. Transient PCO of a monolayer of ethanol on fresh TiO<sub>2</sub> in 0.2% O<sub>2</sub>. The triangles indicate when the UV lights were turned on and off.

5% of that which desorbed during transient PCO of a monolayer of ethanol (11). Apparently, the weakly adsorbed ethanol photocatalytically oxidizes to acetaldehyde on a site that does not adsorb acetaldehyde, even though a monolayer of acetaldehyde contained more molecules ( $330 \mu\text{mol/g}$  catalyst) than a monolayer of ethanol ( $280 \mu\text{mol/g}$  catalyst) (11). At less-than-saturation coverage, ethanol did not produce any gas-phase acetaldehyde during transient PCO (12). Either the gas-phase acetaldehyde readsorbed and was oxidized, or none of the ethanol was weakly adsorbed.

#### PCO of Coadsorbed Ethanol and Acetaldehyde

Figure 4 shows the PCO after a gaseous mixture of  $^{13}\text{C}_2$ -ethanol ( $^{13}\text{CH}_3^{13}\text{CH}_2\text{OH}$ ) and  $^{12}\text{C}_2$ -acetaldehyde were coadsorbed. Interestingly, 85% of the gas-phase acetaldehyde was produced from PCO of ethanol. The amounts of each carbon isotope from PCO and the subsequent TPO indicated that the initial monolayer was 55% acetaldehyde. In repeat experiments, ethanol and acetaldehyde were adsorbed sequentially; PCO of ethanol produced the majority of the gas phase acetaldehyde, however, regardless of the order of adsorption. The oxidation rate of  $^{13}\text{C}_2$ -ethanol to  $^{13}\text{CO}_2$  was greater than the acetaldehyde oxidation rate to  $^{12}\text{CO}_2$  until later stages of the reaction. The amount of ethanol and acetaldehyde on the surface before PCO, approximately  $370 \mu\text{mol/g}$  catalyst, is greater than the amount in a monolayer of either ethanol ( $280 \mu\text{mol/g}$  catalyst) or acetaldehyde ( $330 \mu\text{mol/g}$  catalyst), and further indicates that some of the ethanol and acetaldehyde adsorb on different sites.

The rates of  $^{12}\text{CO}_2$  and  $^{13}\text{CO}_2$  formation were approximately constant after 150 to 400 s of PCO, respectively.

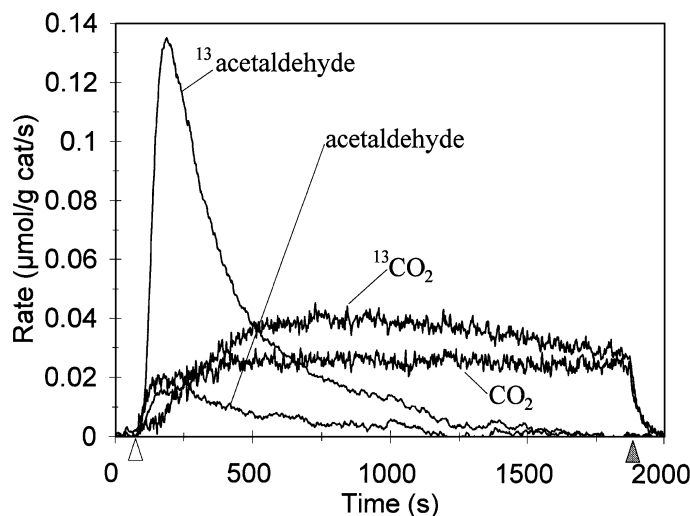


FIG. 4. Transient PCO of a monolayer of coadsorbed  $^{13}\text{C}_2$ -ethanol and acetaldehyde in 0.2%  $\text{O}_2$  on fresh  $\text{TiO}_2$ . The triangles indicate when the UV lights were turned on and off.

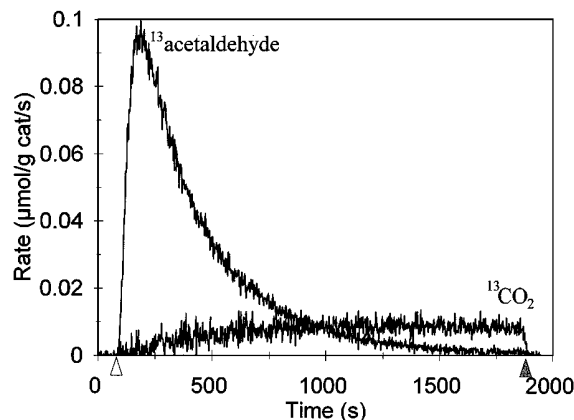


FIG. 5. Transient PCO of a monolayer of  $^{13}\text{C}_2$ -ethanol on poisoned  $\text{TiO}_2$  in 0.2%  $\text{O}_2$  in He. The triangles indicate when the UV lights were turned on and off.

Moreover, when the lights were switched off after 1800 s of PCO, the rate of  $^{13}\text{CO}_2$  formation was approximately equal to the rate of  $^{12}\text{CO}_2$  formation even though the amount of  $^{12}\text{C}$ -species on the surface was nearly twice that of  $^{13}\text{C}$ -species (since more  $^{13}\text{C}$ -containing products desorbed during PCO). Ethanol may preferentially adsorb on more reactive sites to give a higher PCO rate, even though ethanol reacts through an acetaldehyde intermediate (11). Additionally, previous results (11) show that the behavior of acetaldehyde PCO is complex and the rate of  $\text{CO}_2$  formation decreases with increasing acetaldehyde coverage.

#### Transient PCO on a Poisoned Surface

Figure 5 shows that for a transient PCO on the poisoned surface, the product distribution was significantly different from that on a fresh titania surface. For 1800 s of PCO, the amounts of acetaldehyde and  $\text{CO}_2$  were 80 and 11% of those on a fresh surface, respectively. Also, no  $^{12}\text{CO}_2$  formed during PCO; i.e., the carbon-containing species deposited from acetaldehyde decomposition was not oxidized. After 1800 s of PCO on the poisoned surface, approximately half of the monolayer reacted to gas-phase products and the selectivity to acetaldehyde was 85%, compared to 35% selectivity on fresh  $\text{TiO}_2$ . This experiment was repeated twice using different photoreactors with similar results. Clearly, the thermal decomposition products of acetaldehyde decrease the rate of complete oxidation more than the rate of partial oxidation during PCO of ethanol by preferentially poisoning the sites that produce  $\text{CO}_2$ .

A poisoning procedure using the PCO product of mesitylene was also investigated, since this adsorbed species was not very reactive. However, the rates of both acetaldehyde and  $\text{CO}_2$  formation were lower than those on fresh  $\text{TiO}_2$  during ethanol PCO and no enhancement in selectivity was observed. This indicates that the acetaldehyde poisoning is selective and the increase in partial oxidation selectivity is not merely a coverage effect.

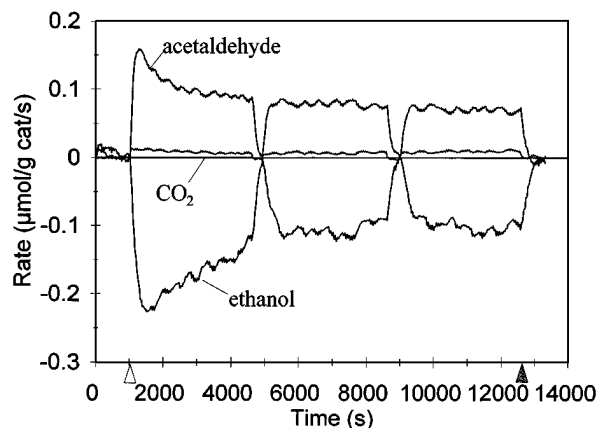


FIG. 6. Flow experiment for PCO of ethanol (1000 ppm) on poisoned  $\text{TiO}_2$  in 20%  $\text{O}_2$  in He.

### Continuous Flow Reaction

The reaction rates and product selectivities were measured for the fresh and poisoned catalysts under quasi steady-state conditions with gas-phase ethanol present for comparison to the transient experiments. An example of the startup behavior for the poisoned catalyst is shown in Fig. 6. Note that the initial rate of acetaldehyde production was twice that of the steady-state value. Similarly, the rate of ethanol uptake was greater during the initial stages of the reaction whereas the rate of  $\text{CO}_2$  formation remained constant throughout the PCO. This behavior may be the result of competitive adsorption between water (and possibly other intermediates) and ethanol. Initially, ethanol occupies all the sites where it can weakly adsorb and the initial rate of acetaldehyde production is at a maximum. Water produced by PCO may block some sites where ethanol weakly adsorbs and reduce the rate of acetaldehyde production. Since  $\text{CO}_2$  forms on sites to which ethanol adsorbs strongly, water may not block ethanol adsorption on these sites and thus the rate of  $\text{CO}_2$  formation is constant.

Table 1 lists the gas hourly space velocities (GHSV), rates, conversions, and selectivities after at least 3 h of PCO on fresh and poisoned  $\text{TiO}_2$  at two ethanol concentrations, which correspond to high and low conversions. For

1000 ppm ethanol, poisoning decreased the rate of acetaldehyde production by approximately 70%, whereas the  $\text{CO}_2$  rate decreased by 88%.

At a lower ethanol concentration and higher conversion, the effect of poisoning is more dramatic. For 70 ppm ethanol, poisoning decreased the rate of acetaldehyde production by 33% whereas the rate of  $\text{CO}_2$  formation decreased by 87%. This means that the ratio of the rates of acetaldehyde to  $\text{CO}_2$  formation on the poisoned surface was five times that on fresh  $\text{TiO}_2$ . The greater selectivity difference between the poisoned and fresh catalysts at higher conversions might be expected (23). Higher ethanol concentration (and lower conversion) results in more weakly held ethanol on the surface and thus more acetaldehyde. At lower ethanol concentration on fresh  $\text{TiO}_2$ , a larger fraction of the adsorbed ethanol is strongly held and any gas-phase acetaldehyde that is produced may readsorb on the catalyst to be further oxidized to  $\text{CO}_2$ . On the poisoned catalyst, however, fewer sites are available for readsorption. Thus, less acetaldehyde intermediate oxidizes even at higher conversions. Similarly, when the reactant feed rate was increased, Wada *et al.* (3) observed an increase in the selectivity of partial oxidation products, possibly due to an increase in the amount of weakly bound species.

### Adsorption Sites on $\text{TiO}_2$

The difference in the number of molecules in a monolayer of ethanol ( $280 \mu\text{mol/g catalyst}$ ) and acetaldehyde ( $330 \mu\text{mol/g catalyst}$ ) indicates that some sites are available for adsorption of acetaldehyde but not ethanol. In contrast, PCO of coadsorbed ethanol and acetaldehyde shows that some sites (at least  $50 \mu\text{mol/g catalyst}$ ) adsorb ethanol but not acetaldehyde. Furthermore, experiments have shown that acetaldehyde and ethanol can displace each other to a certain extent, indicating that some sites are shared by both. Temperature-programmed desorption on the poisoned  $\text{TiO}_2$  surface indicates that the sites that weakly adsorb ethanol preferentially produce acetaldehyde during PCO.

Ethanol adsorbs both molecularly and as an ethoxide at room temperature on  $\text{TiO}_2$  (14, 24–29). Additionally,

TABLE 1  
Continuous Flow of Ethanol PCO

Catalyst	Ethanol concentration (ppm)	GHSV ( $\text{h}^{-1}$ )	Conversion (%)	Acetaldehyde selectivity (%)	Rate of formation $\times 10^3$ ( $\mu\text{mol/g catalyst/s}$ )	
					Acetaldehyde	$\text{CO}_2$
Poisoned	63	$5.8 \times 10^5$	54	88	40	11
	1000	$7.8 \times 10^5$	5	94	80	10
Fresh	70	$1.6 \times 10^6$	60	58	60	85
	950	$1.6 \times 10^6$	8	87	270	80

different bonding sites (single titanium atom or bridge two titanium atoms) for ethoxides have been proposed (29–31). Kim and Barteau (14) concluded that ethanol adsorbs both molecularly and dissociatively at room temperature on anatase TiO<sub>2</sub> powder. The molecularly adsorbed ethanol, possibly hydrogen bonded to the surface, may be the weakly bound ethanol observed in our experiments. The absence of a hydrogen atom available for hydrogen bonding in acetaldehyde may explain why acetaldehyde does not adsorb onto these sites.

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