JOURNAL OF CATALYSIS **180,** 111–122 (1998)
ARTICLE NO. CA982276

Identification of Adsorbed Species during Steady-State Photocatalytic Oxidation of Ethanol on TiO_2

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Received February 20, 1998; revised August 31, 1998; accepted September 2, 1998

The identification and concentrations of species on a TiO_2 surface during photocatalytic oxidation (PCO) of ethanol were determined by combining transient and steady-state PCO with temperature-programmed desorption (TPD) and oxidation (TPO). Ethanol and its partial oxidation intermediates (acetaldehyde, acetic acid, formaldehyde, and formic acid) are on the catalyst surface, and their concentrations depend on the ethanol, O_2, and water feed concentrations. The rate of PCO was greater initially than at steady state for all experimental conditions, and this initial deactivation may be due in part to the accumulation of acetaldehyde on the surface. Weakly bound ethanol preferentially forms acetaldehyde whereas the more strongly bound ethoxide species preferentially produces CO_2. Increasing the gas-phase ethanol concentration produces more of the weakly bound ethanol and therefore a greater rate of acetaldehyde production. Increasing the O_2 concentration from 0.2 to 20% only increased the steady-state rate of reaction by 50% and did not change the selectivity. Although ethanol and water compete for sites, adding 0.5% water (13% relative humidity) to the feed stream did not change either the rate or selectivity and only marginally increased the amount of adsorbed water.

INTRODUCTION

Heterogeneous photocatalytic oxidation (PCO) has potential applications for the complete oxidation of organic pollutants in dilute systems. A wide range of organics can be oxidized to CO_2 and H_2O at room temperature on TiO_2 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. Though recent studies have shown that PCO can oxidize a number of gas-phase organic compounds (1–25), the reaction mechanisms are poorly understood and the intermediates, particularly if they do not leave the catalyst, are often not identified.

The objective of this study is to identify adsorbed species present *during steady-state PCO* and how they change with reaction conditions and reaction times. Temperature-programmed desorption (TPD) was combined with temperature-programmed oxidation (TPO) to identify surface species and their concentrations. Ethanol was used as a model reactant because it is a pollutant from industrial processes such as breweries and bakeries. In addition, ethanol forms several reaction intermediates and its reaction mechanism has been studied (1–5). Gas-phase ethanol, O_2, and water concentrations were varied to determine their effect on PCO rates, selectivities, and surface compositions.

Previously, we used TPD and TPO to show that intermediates cover a large fraction of the surface during transient PCO (1, 2) and their concentrations initially increase with reaction time. Since the gas phase did not supply additional ethanol to the surface during transient PCO, the surface composition is expected to be different during steady-state PCO. Identifying adsorbed species *at steady state* will improve our understanding of catalytic reactions and help verify proposed reaction mechanisms and identify deactivation processes. Comparing the adsorbed species at steady state to the intermediates determined by transient PCO might also identify unreactive poisons.

For most catalytic systems, identifying the adsorbed species during steady-state reaction is difficult. Photocatalytic oxidation is uniquely suited for identification of adsorbed species *under reaction conditions*, however, because it takes place at room temperature. Thus, the surface composition should not change much as reaction stops because:

- the desorption rates of intermediates are low at room temperature;
- turning off the UV lights stops reaction quickly so the surface composition does not have much time to change;
- the surface is saturated and the concentration of organic reactant is low in the gas phase so that the amount of additional reactant exposed to the surface during shutdown is small.

Thus, species detected during a subsequent TPD are more likely to represent the steady-state surface composition

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0021-9517/98 $25.00

than when a typical catalytic reaction is stopped by lowering the temperature. However, intermediates with high reactivity will have low surface concentrations, may react before TPD, and may not be detected.

Since the previous transient PCO experiments (1, 2) were done in 0.2% O_2, a few transient PCO reactions were carried out in 20% O_2 so that transient and steady-state experiments could be compared. Transient techniques are useful for studying PCO because turning off the UV light after various reaction times (to stop PCO) and performing TPD can follow the buildup and consumption of intermediates on the catalyst surface. An added advantage of transient PCO is that only a monolayer or submonolayer of organic is reacted, so that the surface species detected during TPD are more likely to be intermediates and not spectator species accumulating on the surface from side reactions.

The intermediates identified during transient PCO were acetaldehyde, acetic acid, formaldehyde, and formic acid (2). Transient studies showed that ethanol forms acetaldehyde, which either desorbs or oxidizes through at least two parallel pathways, only one of which involves acetic acid. In 0.2% O_2, approximately 15% of a monolayer of ethanol formed gas-phase acetaldehyde, and 25% reacted on the surface through the pathway acetaldehyde $\rightarrow$ acetic acid $\rightarrow$ formaldehyde + CO_2 $\rightarrow$ formate $\rightarrow$ CO_2. The remaining 60% oxidized more slowly through a pathway that did not contain acetic acid as an intermediate: acetaldehyde $\rightarrow$ formate + formaldehyde $\rightarrow$ formate + CO_2 $\rightarrow$ CO_2.

The same intermediates were also identified in batch reactor studies of ethanol PCO (4, 5, 14). Nimlos *et al.* (5) identified acetaldehyde, acetic acid, formaldehyde, and formic acid as intermediates. Sauer and Ollis (4) proposed that ethanol reacts to acetaldehyde, which then forms CO_2 both directly and through a formaldehyde intermediate. To provide closure on their carbon mass balance, they proposed that acetic acid and formic acid desorbed from the illuminated portions of the catalyst and reversibly collected on the dark TiO_2. The authors stated that acetic acid and formic acid react quickly on illuminated TiO_2 and therefore are present only in low concentrations for a fully illuminated reactor. Our transient experiments indicate, however, that acetic acid and formic acid can be present at high concentrations (1, 2). Similarly, Vorontsov *et al.* (14) only identified acetaldehyde and CO_2 for PCO of ethanol in a batch reactor and they proposed a two-step mechanism: ethanol $\rightarrow$ acetaldehyde $\rightarrow$ CO_2. An increase in the initial charge of ethanol inhibited the acetaldehyde oxidation rate; this inhibition was attributed to acetaldehyde displacement by ethanol.

Kennedy and Datye (26) studied the photothermal catalytic oxidation of ethanol on TiO_2 using a thin-film annular reactor at steady state. During PCO on TiO_2 between 323 and 473 K, acetaldehyde, CO_2, and minor amounts of formaldehyde were detected in the gas phase. They reported 80% selectivity to acetaldehyde during PCO at 373 K and 6400 ppm ethanol. Falconer and Magrini-Bair (27) investigated steady-state PCO of acetaldehyde (60 ppm) from 297 to 473 K in 15.5% O_2. The catalyst was stable during PCO at room temperature on TiO_2 but deactivated rapidly at elevated temperatures, due to thermal decomposition of acetaldehyde.

In the majority of these steady-state studies, most intermediates did not desorb during room-temperature PCO and thus could not be identified. For reaction of many monolayers during steady-state reaction, one potential problem with using TPD to identify surface intermediates, however, is the possibility of detecting species from minor side reactions. In this study, however, surface intermediates identified by TPD after steady-state PCO are compared to those determined previously by transient PCO of a monolayer (2). Therefore, the amounts of the reaction intermediates and any accumulated poisons could be determined. In these studies, all the surface species except oxygen were observed. No O_2 desorbed from TiO_2 and thus we were unable to determine the surface concentration of O_2 or the species that formed from O_2 before they oxidized ethanol. Note also that conversions were large at low ethanol concentrations, and in those cases the surface compositions measured by TPD are an average value across the reactor length.

EXPERIMENTAL METHODS

The apparatus used for PCO and TPD was described previously (28). Approximately 30 mg of Degussa P-25 TiO_2 catalyst was coated as a thin layer (average thickness <0.5 μm) on the inside of an annular Pyrex reactor so that all the TiO_2 was exposed to UV light for PCO. For an annular reactor with a 1-mm annular spacing, 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. A quartz furnace with heating wires for TPD surrounded the photocatalytic reactor, and six UV lamps (GE, 4 W) surrounded the furnace. The light intensity at the catalyst surface, measured with a radiometer, was approximately 0.3 mW/cm^2. The maximum light intensity was near 356 nm. 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 steady-state and transient experiments, heating the reactor for 30 min in approximately 20% O_2 in He to 723 K and then cooling to room temperature created a reproducible surface. Metal shields were placed between the reactor and the UV lights, which were turned on until they reached a steady-state output. A Balzers QMA 125 quadrupole mass spectrometer monitored the reactor effluent immediately downstream of the reactor. The mass spectrometer, which was interfaced to a computer, recorded multiple mass peaks simultaneously during PCO, TPD, and TPO. 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.

For steady-state PCO, a He/O_2/ethanol gaseous mixture flowed across the catalyst at 200 cm^3/min at standard conditions (GHSV, *based on the catalyst volume*, of 1.6×10^6 h^{-1}). To add ethanol to the gas phase, He flowed through an ethanol bubbler at 273 K, and this stream mixed with a O_2/He flow. Water vapor was added to the feed stream in some experiments by passing a portion of the dry carrier gas through a water bubbler at room temperature and recombining this stream with the feed downstream of the ethanol bubbler. When the partial pressure of ethanol reached steady state, as measured by the mass spectrometer, reaction was initiated by removing the shields from the UV lights. To correct for any baseline drift of the mass spectrometer during PCO, the UV lights were switched off at regular intervals for 6 min and then turned back on. Since the rate of acetaldehyde production temporarily increased after this dark time, this procedure also provided additional information about the reaction process. The difference between ethanol consumed and products formed was at most 9% of the ethanol consumed. After hours of PCO at room temperature, the UV lights were turned off and the flow gas was immediately switched to pure He. After the mass spectrometer signals stabilized, the catalyst was heated to 723 K in He (100 cm^3/min at standard conditions) at a constant rate of 1 K/s to obtain TPD spectra. A TPO in 20% O_2 in He then oxidized any remaining species that did not desorb or decompose to gas-phase products during TPD. Typically, at least two replicates of steady-state experiments were performed for each set of experimental conditions to determine reproducibility.

Transient reaction experiments used ^{13}C-labeled ethanol ($CH_3{}^{13}CH_2OH$), which was injected immediately upstream of the reactor and allowed to evaporate and adsorb onto the catalyst surface at room temperature in 20% O_2 flow. After excess ethanol was flushed from the gas phase, a transient PCO was initiated in 20% O_2 by removing the shields from the UV lights. After PCO at room temperature for a time period on the order of tens of minutes, TPD was carried out. At the end of the temperature programming, the catalyst was held at 723 K until no desorption products were detected. Plots of rates versus time were generated using frequent calibrations of the gas-phase products by injecting known quantities into the mass spectrometer. To calibrate the ^{13}C species, the corresponding ^{12}C species was used.

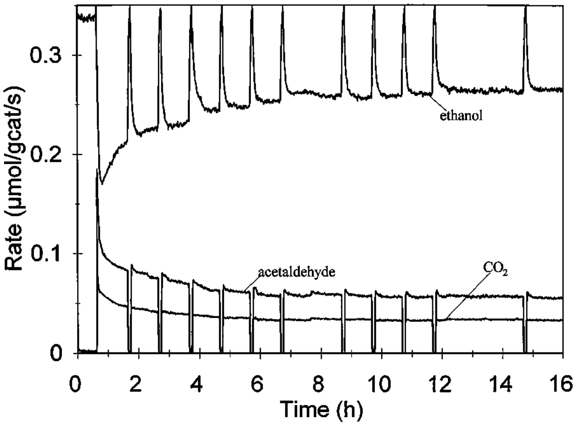

FIG. 1. PCO of 100 ppm ethanol in 0.2% O_2 in He flow without water.

RESULTS

Steady-State PCO at Low Ethanol Concentration in 0.2% O_2

The rates of ethanol consumption and acetaldehyde and CO_2 production are plotted versus time in Fig. 1 for PCO of 100 ppm ethanol in 0.2% O_2 flow. The rates of acetaldehyde and CO_2 formation quickly reached maxima upon UV illumination (Table 1), rapidly decreased, and then more slowly decayed to near steady-state values (after approximately 7 h of illumination). Between 7 and 16 h of PCO, the rates decreased more slowly, at approximately a linear rate, which was calculated as a percentage of the rate at 7 h (Table 2). Table 3 lists the conversions, selectivities, and rates. After 16 h of PCO, 22 monolayer equivalents of ethanol had reacted to acetaldehyde and CO_2. Immediately after the 6-min dark period, the rate of acetaldehyde production was slightly greater than before the lights were turned off, whereas the rate of CO_2 production was not enhanced after the dark time.

TABLE 1

Initial Rates of Acetaldehyde and CO_2 Formation during Steady-State PCO

Concentrations			Initial rates (μmol/g/s)	
Ethanol (ppm)	O_2 (%)	Water (%)	Acetaldehyde	CO_2
0	0.2	0	0.18	0.09[a]
100	0.2	0	0.19	0.08
0	20	0	0.55	0.85[a]
100	20	0	0.54	0.17
1000	20	0	0.8	0.18
100	20	0.5	0.27	0.15
1000	20	0.5	0.8	0.18

[a] Maximum CO_2 rate from transient PCO.

TABLE 2

Deactivation Rates of Acetaldehyde and CO_2 Formation during Steady-State PCO

Concentrations			Deactivation rates (%/h)	
Ethanol (ppm)	O_2 (%)	Water (%)	Acetaldehyde	CO_2
100	0.2	0	0.5	0.2
100	20	0	1.8	3.0
100	20	0.5	1.3	1.5
1000	20	0	1.5	0.8
1000	20	0.5	1.2	0.5

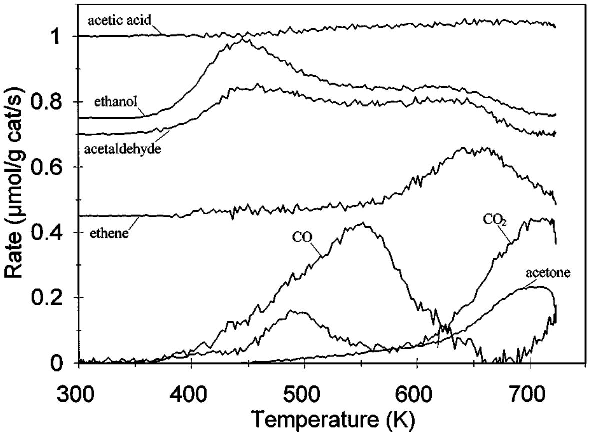

FIG. 2. TPD spectra after PCO of ethanol in 0.2% O_2 in He flow without water.

Figure 2 shows TPD spectra obtained after 16 h of PCO of ethanol (100 ppm) in 0.2% O_2 flow. Ethanol, acetaldehyde, ethene, acetic acid, acetone, CO, CO_2, and water desorbed from the TiO_2 surface during TPD. Note that no O_2 desorbed, and the water desorption is not shown in Fig. 2 for clarity. Ethene and acetaldehyde formed from dehydration and dehydrogenation of ethanol, respectively, as shown by TPD of a monolayer of ethanol (2). Similarly, acetone formed by bimolecular ketonization of acetic acid, as has been reported (2, 29). The CO_2 formed from decomposition of acetaldehyde, formic acid, and bimolecular ketonization of acetic acid. The CO formed from decomposition of formic acid and formaldehyde, as has been observed previously (2). Neither CO nor CO_2 adsorbs significantly on TiO_2 at room temperature (2).

The total amount of carbon in the desorbed species from TPD and subsequent TPO (Table 4) is similar to the amounts of carbon detected during TPO (2) of saturated coverages of ethanol (560 μmol carbon/g catalyst), acetaldehyde (660 μmol carbon/g catalyst), and acetic acid (820 μmol carbon/g catalyst). The amount of carbon in a monolayer of formic acid (350 μmol carbon/g catalyst) is significantly less than for the other species since it has only one carbon. Therefore, the surface appears to be saturated during steady-state PCO. Note that after the UV lights were turned off, less than 0.4% of a monolayer of ethanol was exposed to the surface. Thus the surface is not saturated as a result of how PCO was stopped.

In addition to the carbon-containing species, a significant amount of water is adsorbed on the surface so that the total molecular coverage after steady-state reaction is larger than that for adsorption of any of the organics on a fresh surface. Figure 3 shows water desorption spectra for this steady-state experiment and for the TPD experiments for the various reaction conditions. Because water is so strongly bound, desorption is not complete by 725 K, and Fig. 3 shows desorption during the temperature ramp and while the TiO_2 was held at 725 K. Each curve in Fig. 3 is an average of four to six curves; the signals were almost identical in repeat experiments and averaging reduced the noise. The 90% confidence limits on the areas under the curves ranged from ±1 to ±14%.

Table 4 shows the surface composition determined from TPD and TPO after 1, 3, and 16 h of PCO, along with 90% confidence limits. The amount of adsorbed ethanol decreased with increasing reaction time and the amount of acetic acid on the surface increased. The amount of formaldehyde/formic acid decreased slightly as PCO continued, and the amount of adsorbed water did not change.

TABLE 3

Conversion, Rates, and Selectivities during PCO of Ethanol

Concentrations					Rates (μmol/g/s)		
Ethanol (ppm)	O_2 (%)	Water (%)	Conversion (%)	Selectivity of acetaldehyde (%)	Ethanol	Acetaldehyde	CO_2
100	0.2	0	22	76	0.08	0.06	0.04
100	20	0	30	75	0.11	0.09	0.06
1000	20	0	8	87	0.30	0.27	0.08
100	20	0.5	35	77	0.13	0.10	0.06
1000	20	0.5	8	88	0.28	0.23	0.06

TABLE 4

Amounts of Adsorbed Species after Steady-State Reaction

PCO time (h)	Concentrations			Amounts of species on surface from TPD (μmol/g)			CO_2 from TPO (μmol/g)	Total carbon (μmol/g)
	Ethanol (ppm)	O_2 (%)	Water (%)	C_2H_5OH	C_2H_3OOH	HCOOH/HCHO		
1	100	0.2	0	183	64	28	85	628
3	100	0.2	0	132 ± 9	89 ± 25	20 ± 13	100 ± 13	605 ± 64
16	100	0.2	0	126	112	12	161	707 ± 36
1	100	20	0	138 ± 19	87 ± 4	87 ± 5	67 ± 21	673 ± 22
14	100	20	0	100 ± 15	79 ± 12	55 ± 3	106 ± 55	624 ± 43
1	1000	20	0	196 ± 12	156 ± 13	18 ± 2	102 ± 41	847 ± 51
14	1000	20	0	200 ± 21	77 ± 18	45 ± 4	149 ± 40	824 ± 73
18	100	20	0.5	44 ± 4	38 ± 10	33 ± 1	82 ± 21	335 ± 38
16	1000	20	0.5	119 ± 13	102 ± 31	24 ± 6	101 ± 22	643 ± 65

Note. The numbers after the ± indicate 90% confidence limits.

The amount of a strongly bound intermediate that did not desorb during TPD but formed CO_2 during TPO increased with PCO time. A carbon-containing species that does not desorb during TPD should form CO_2 during the subsequent TPO. This species is most likely acetaldehyde, however, since it is an intermediate in ethanol PCO and as shown previously (2), 90% of a monolayer of acetaldehyde does not desorb during TPD, but acetaldehyde and the species that form from its decomposition during TPD can be oxidized to CO_2 during TPO. Some ethanol and acetic acid may also contribute to CO_2 formed during TPO after TPD, but only a few percent of a monolayer of ethanol, acetic acid, formaldehyde, and formic acid do not form gas-phase products during TPD (2). Therefore, the exact amount of adsorbed acetaldehyde could not be determined. The adsorbed intermediates that formed during PCO were acetic acid, formaldehyde/formic acid, and acetaldehyde.

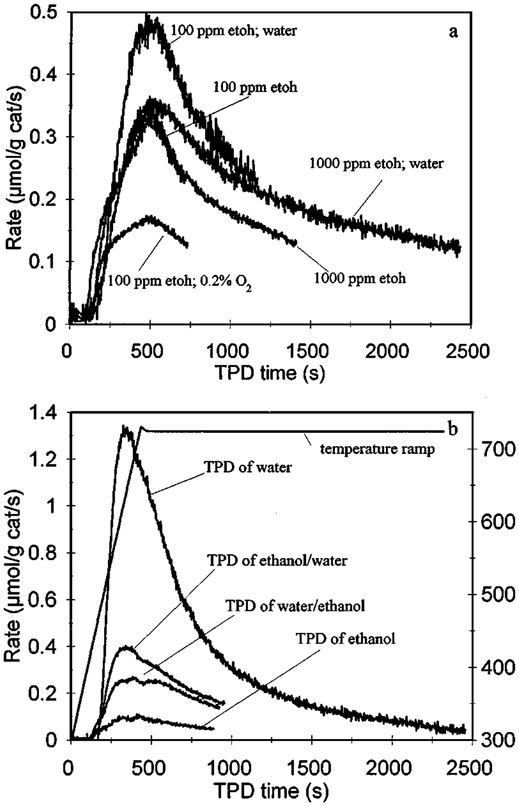

FIG. 3. (a) Water desorption rates during TPD after PCO under various conditions. (b) Water desorption rates during TPD of water and coadsorbed water and ethanol, and ethanol desorption rate.

Steady-State PCO at Low Ethanol Concentration in 20% O_2

The behavior during PCO of ethanol (100 ppm) in 20% O_2 was similar to that shown in Fig. 1 except the rates of both acetaldehyde and CO_2 were approximately 50% greater. That is, a nearly 100-fold increase in the O_2 concentration only increased the rates by 50%. The rates of acetaldehyde and CO_2 formation quickly reached maxima upon UV illumination, rapidly decreased, and then more slowly decayed to near steady-state values after approximately 4 h of illumination. The long-term deactivation rates are reported as percentages of the rates after 4 h of illumination in Table 2.

After the 6-min dark period, the rate of acetaldehyde production was 35–48% greater than before the lights were turned off, but the dark period did not change the rate of CO_2 evolution. The subsequent TPD had products and peak temperatures similar to those in Fig. 2, but with different amounts (Table 3). Approximately 32 monolayer equivalents of ethanol had reacted after 14 h of PCO, and the surface composition is shown in Table 4. As the PCO time increased from 1 to 14 h, the amount of adsorbed ethanol decreased by 28%, acetic acid decreased by 9%, and formaldehyde/formic acid decreased by 37%. The amount of adsorbed water was the same after 1 and 14 h of PCO and was 1.8 times the amount of adsorbed water during PCO at 0.2% O_2 (Fig. 3). The amount of CO_2 that formed during

TPO increased 58%. The total amount of carbon in surface species was nearly constant between 1 and 14 h of PCO, as shown in Table 4.

PCO at High Ethanol Concentration and 20% Oxygen

The acetaldehyde and CO_2 formation rates at 1000 ppm ethanol were 2.7 and 1.3 times those at 100 ppm ethanol, respectively. Photocatalytic oxidation of 1000 ppm ethanol in 20% O_2 also had high initial rates for formation of acetaldehyde and CO_2, similar to those in Fig. 1. When the catalyst was first exposed to UV light, the rate of acetaldehyde formation was 4 times the rate of CO_2 formation (Table 1), and both rates rapidly decreased in the first hour of reaction. The acetaldehyde rate decreased faster, to less than one-third of its initial value, whereas the CO_2 rate decreased to half its initial value. The rates decreased more slowly after 8 h of PCO and this long-term deactivation is reported in Table 2 as a percentage of the rates at 8 h.

In contrast to the results obtained with 100 ppm ethanol, when the lights were turned back on after checking the baseline, the rates of acetaldehyde and CO_2 were the same as before the lights were turned off. After 14 h of PCO, 73 monolayer equivalents of ethanol had reacted and the surface composition is shown in Table 4. Both the amounts of adsorbed ethanol and water were not significantly different after 1 and 14 h of PCO, whereas acetic acid coverage decreased by 51%, the formaldehyde/formic acid coverage increased by 150%, and the amount of CO_2 formed during TPO increased by 46%. The total amounts of carbon in surface species and adsorbed water did not change between 1 and 14 h of PCO. Furthermore, the water TPD signal (Fig. 3) was the same as that for PCO at 100 ppm ethanol and 20% O_2. Comparison of the ethanol TPD signals after PCO in 100 and 1000 ppm ethanol (Fig. 4) shows that more weakly bound ethanol is on the surface during PCO at 1000 ppm.

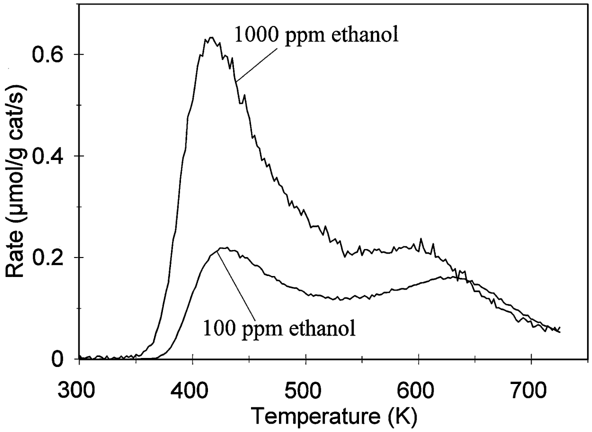

FIG. 4. Ethanol desorption during TPD after PCO (20% O_2) in 100 and 1000 ppm ethanol.

PCO of Ethanol in 20% Oxygen and Water

The rates and selectivities during PCO at both 100 and 1000 ppm ethanol in the presence of water vapor (13% relative humidity) were similar to those obtained for PCO without water. The initial rates of acetaldehyde and CO_2 formation were greater than those after 16 h of PCO at 100 and 1000 ppm. Between 8 and 16 h of PCO at 100 ppm, the acetaldehyde and CO_2 rates decreased more slowly and are reported as percentages of the rates at 8 h in Table 2. During PCO at 1000 ppm ethanol, the long-term deactivation rates were based on the rates after 7 h of illumination. Immediately after the 6-min dark period during PCO at 100 ppm, the rate of acetaldehyde formation was approximately 24% greater than before the lights were turned off, but it decreased to the steady-state value after 4 min of PCO. In contrast, under dry conditions the rate of acetaldehyde production increased by 35–48% after the dark period and took 16 min to reach the steady-state value.

The same products were on the surface after PCO in the presence of water as those detected under dry conditions, but the total coverages of adsorbed organics were lower. For 100 ppm ethanol, the organic coverage under humid conditions was 54% of that under dry conditions (Table 4). At 1000 ppm, it was 78% of the coverage under dry conditions. For 100 ppm ethanol, water in the feed decreased the amount of adsorbed ethanol by 56%, acetic acid by 52%, and formaldehyde/formic acid by 40%. Similarly for 1000 ppm ethanol, water in the feed decreased the amount of adsorbed ethanol by 40% and the formaldehyde/formic acid by 47%. The amount of acetic acid increased by 32%, although the variability in this amount was large and therefore the acetic acid coverage may not be significantly different under the two conditions. The amount of CO_2 formed during TPO decreased by 23 and 32% during PCO under humid conditions at 100 and 1000 ppm ethanol, respectively.

The amount of adsorbed water during PCO at 100 ppm ethanol and 20% O_2 was 40% greater under humid conditions. For PCO at 1000 ppm ethanol, humidifying the feed increased the amount of adsorbed water less (Fig. 3), although the amounts could not be directly compared since the curves have different shapes and water desorption was not complete when the TPD was stopped.

The addition of 0.5% water to the feed did not change the initial acetaldehyde formation rate in 1000 ppm ethanol (Table 1), but in 100 ppm ethanol, the rate decreased by 50%. For PCO in 0.5% water and 100 ppm ethanol, the initial rate of acetaldehyde formation increased sharply, decreased *below* its steady-state rate, and then increased more slowly to 0.13 μmol/g catalyst after 30 min of PCO. For all other experiments, however, the rate of acetaldehyde formation increased sharply upon UV illumination and then decayed to its steady-state value.

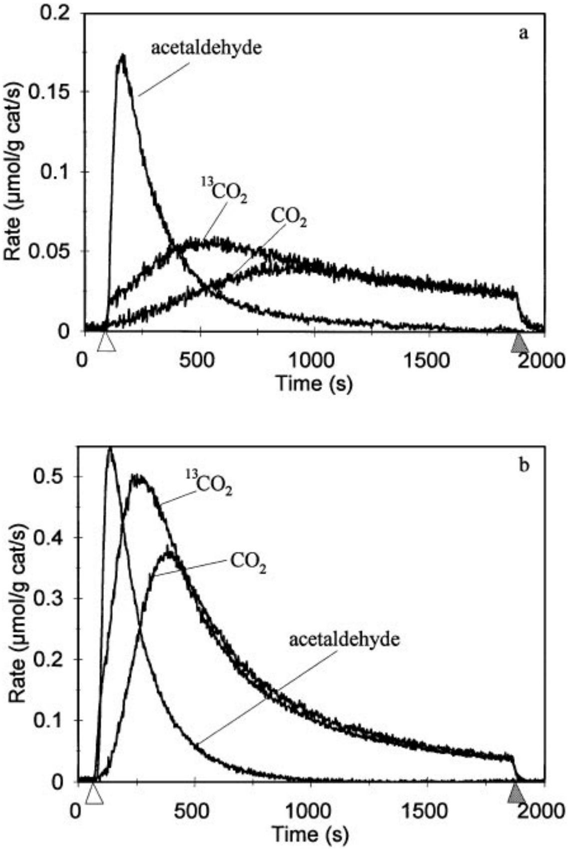

FIG. 5. Transient PCO of a monolayer of ^{13}C-ethanol ($CH_3{}^{13}CH_2OH$) in (a) 0.2% O_2 and (b) 20% O_2.

Transient PCO of Ethanol in 0.2% and 20% Oxygen

Figures 5a and 5b show transient PCO of a monolayer of 1-^{13}C-ethanol ($CH_3{}^{13}CH_2OH$) in 0.2 and 20% O_2 in He flow, respectively. The results in Fig. 5a were reported previously (2) but are included here for comparison. Acetaldehyde and smaller amounts of ethanol (not shown) desorbed quickly after illumination, and initially $^{13}CO_2$ formed faster than $^{12}CO_2$. The rate of $^{13}CO_2$ formation reached a maximum after 600 s of illumination, whereas $^{12}CO_2$ formation did not reach a maximum rate until after 1000 s. The $^{13}CO_2$ and $^{12}CO_2$ formation rates were equal after 1500 s of illumination and both quickly decreased to zero when the UV lights were switched off. For 20% O_2 (Fig. 5b), the initial rate of acetaldehyde formation was 2.8 times higher, and the maximum rate of CO_2 production was 9 times the maximum rate in 0.2% O_2. Initially, the α-carbon reacted to $^{13}CO_2$ faster than the β-carbon formed $^{12}CO_2$. Since the reaction rate was greater in 20% O_2 flow than in 0.2% O_2, the $^{13}CO_2$ and $^{12}CO_2$ formation rates reached maxima earlier because the ethanol monolayer was consumed faster.

Transient PCOs of ethanol with coadsorbed water in 0.2% O_2 are shown in Figs. 6a and 7a. For Fig. 6a, water was adsorbed first and then the catalyst was exposed to two pulses of ethanol (560 μmol/g catalyst). Note that both the acetaldehyde and CO_2 rates of formation are nearly identical to the transient PCO of a monolayer of ethanol (Fig. 5a). To determine the effect of water on ethanol adsorption, the adsorption procedure was repeated and a TPD (Fig. 6b) instead of a PCO was performed. Figure 6b shows that 58% of the ethanol desorbed in two broad peaks, 11% dehydrogenated to acetaldehyde, 23% dehydrated to ethene, and 7% decomposed to CO during TPD. The coverage of ethanol was approximately 255 μmol/g catalyst, which is 9% lower than an ethanol monolayer (280 μmol/g catalyst).

Transient PCO of coadsorbed ethanol and water was also investigated by first adsorbing a monolayer of ethanol and then injecting two pulses of water (560 μmol/g catalyst). Figure 7a shows that the amount of acetaldehyde formed during PCO is approximately one-third that in Fig. 6a. In addition, the rate of CO_2 formation is greater and reaches a maximum sooner (after 400 s of illumination) than when water was adsorbed first. The greater maximum rate of CO_2 formation is surprising because water reduced the ethanol coverage to 180 μmol/g catalyst. The lower ethanol coverage may be the reason that the maximum rate of CO_2

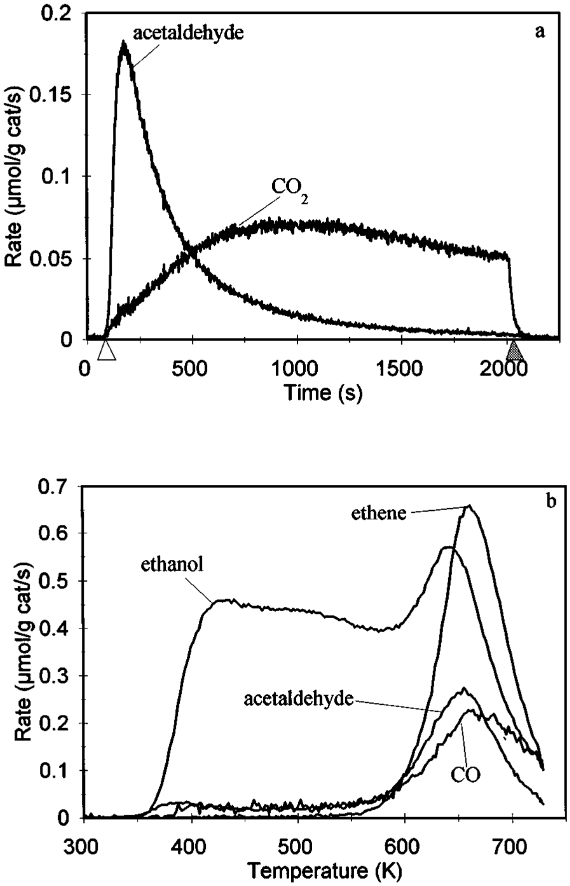

FIG. 6. (a) Transient PCO and (b) TPD spectra of coadsorbed water and ethanol in 0.2% O_2 (water adsorbed first).

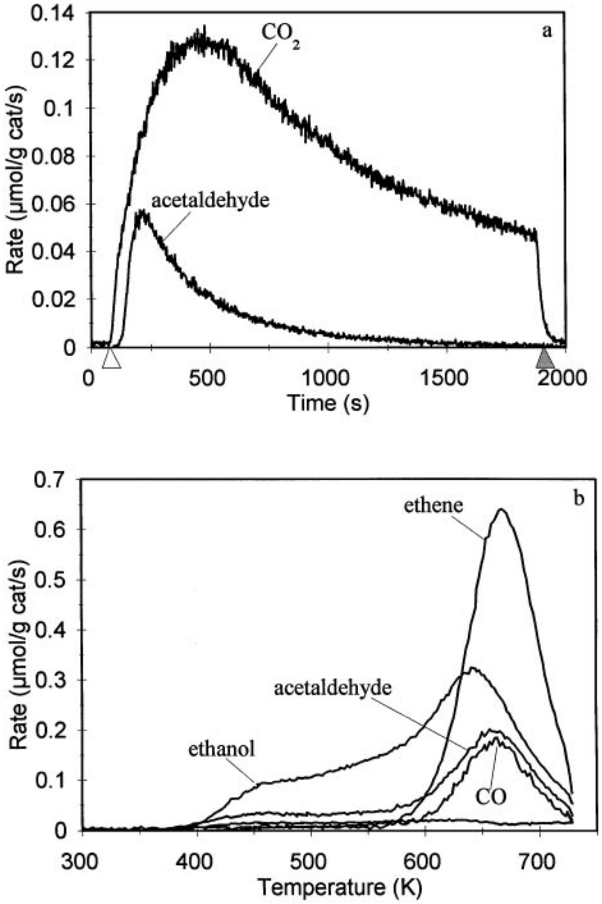

FIG. 7. (a) Transient PCO and (b) TPD spectra of coadsorbed ethanol and water in 0.2% O_2 (ethanol adsorbed first).

formation occurs earlier. When TPD was performed after the adsorption procedure was repeated (Fig. 7b), the same products desorbed at similar peak temperatures as Fig. 6b. However, the amount of weakly bound ethanol that desorbed near 425 K was approximately one-fourth that in Fig. 6b. The amount of more strongly bound ethanol that dehydrogenated, dehydrated, or decomposed during TPD was approximately 87% of that in Fig. 6b. Note that even though less weakly and strongly bound ethanol is on the surface, the CO_2 rate is greater when ethanol is adsorbed before water. The water desorption signals from the TPDs in Figs. 6b and 7b are shown in Fig. 3b. Approximately 40 μmol/g catalyst more water desorbed when ethanol was adsorbed first, and water desorption was not complete when the TPD was stopped. Figure 3b includes water desorption during TPDs of both water and ethanol for comparison.

DISCUSSION

The species on the TiO_2 surface during steady-state PCO (ethanol, acetaldehyde, acetic acid, formaldehyde, formic acid, and water) are the same as those identified during transient PCO (2). Another species, which does not desorb during TPD, may also be on the surface since the subsequent TPO produced a significant amount of CO_2. However, a large fraction of this CO_2 is likely due to oxidation of acetaldehyde and the reaction products it forms *during TPD*; when TPD is carried out for a monolayer of acetaldehyde, most of it reacts to form surface species that do not desorb (2).

The PCO does not appear limited by oxygen mass transfer because increasing the O_2 concentration a factor of 100 only increased the steady-state rate by approximately 50%. Likewise, if ethanol mass transfer were limiting, the adsorbed ethanol concentration would be low, but as shown in Table 4, significant amounts of ethanol are on the catalyst during PCO at each condition. Furthermore, increasing the ethanol concentration by a factor of 10 only increased the rate of CO_2 production by 33%.

Effect of Ethanol Concentration

The rate of CO_2 formation in 20% O_2 (dry) was 33% greater at 1000 ppm than at 100 ppm ethanol, and correspondingly the amounts of intermediates and more strongly bound ethanol (much of which formed ethylene and acetaldehyde during TPD) were 28% greater. The acetaldehyde rate nearly tripled and the TPD spectra (Fig. 4) after PCO show that the amount of weakly bound ethanol (desorption peak at 425 K) at 1000 ppm was 2.9 times that at 100 ppm. As shown previously (3), the sites to which ethanol weakly adsorbs preferentially produce acetaldehyde, and the sites that form strong bonds with ethanol preferentially produce CO_2. Raising the gas-phase ethanol concentration increases the amount of weakly bound ethanol and therefore increases the rate of acetaldehyde production. Although Sauer and Ollis (4) proposed a one-site Langmuir–Hinshelwood model, Nimlos *et al.* (5) required a two-site model to fit their data. Additionally, higher ethanol concentrations should displace adsorbed acetaldehyde into the gas phase faster. Kennedy and Datye (26) reported selectivity to acetaldehyde increased with ethanol concentration during photothermal catalytic oxidation at 373 K on Pt/TiO_2. Similarly, Vorontsov (13) *et al.* observed selectivity to acetaldehyde increased with ethanol concentration in a batch reactor study on TiO_2. Increasing the ethanol concentration from 100 to 1000 ppm in the presence of 0.5% water yielded results similar to dry conditions; more weakly bound ethanol increased the rate of acetaldehyde formation by approximately 2.3 times, whereas the CO_2 rate remained the same. Increasing the ethanol concentration produced 1.9 and 2.7 times as much adsorbed ethanol during PCO under dry and wet conditions, respectively. Increasing the ethanol concentration did not change the water surface coverage under dry conditions but decreased it during PCO in the humidified feed.

Effect of Water

Water, when its feed concentration was 50 times that of ethanol, only decreased the surface coverage of organics by 46%, and when the water was only 5 times the ethanol feed concentration, the surface coverage of organics was lower by 22%. Thus, water, even though it strongly adsorbs on the surface, only displaces a fraction of the adsorbed organics. In both cases, however, water did not change the rates of acetaldehyde and CO_2 formation, even though it lowered the surface coverages of organics.

This surprising result shows that simple Langmuir–Hinshelwood models proposed previously (4, 5) do not fully explain the role of water in PCO. Sauer and Ollis (4) performed PCO of ethanol under humid conditions, but did not include water in their model presumably because its surface concentration was assumed constant. Nimlos *et al.* (5) used adsorption experiments carried out under dry conditions to derive constants for their PCO model. Our results show, however, that a significant amount of water is adsorbed on the catalyst surface during PCO and it reduces the number of sites available for adsorption.

Although competition for sites between ethanol and water reduced the organic coverages, water did not change the rate or selectivity of PCO. Figures 6a and 6b show that ethanol displaces adsorbed water and Fig. 7b shows that water preferentially displaces weakly adsorbed ethanol. Since the weakly adsorbed ethanol preferentially produces acetaldehyde, the competition between ethanol and water during steady-state PCO for these sites should reduce the rate of acetaldehyde formation. As shown previously (1), however, water also displaces acetaldehyde which adsorbs more strongly than the acetaldehyde formed from weakly adsorbed ethanol, and this should increase acetaldehyde formation. These competing processes appear to compensate in the presence of water so that the selectivity does not change significantly. Acetaldehyde displacement by water might be expected to reduce the rate of CO_2 formation, but since adsorbed acetaldehyde also reduces the PCO rate, its removal may compensate for the lower organic coverage.

For gas-phase PCO of 1% 1-butanol on TiO_2, Blake and Griffin (6) observed that 1% water in the gas phase did not change the PCO rate. Peral and Ollis (30) reported that the PCO activity of acetone, 1-butanol, and *m*-xylene changed with water concentration. Addition of 5% water to the feed decreased the rate of acetone PCO but did not influence the rate of 1-butanol PCO. The conversion of *m*-xylene increased with the addition of trace amounts of water but higher concentrations inhibited the reaction. The authors explained these results by competitive adsorption between the organic reactant and water. Since acetone weakly adsorbs on TiO_2, water displaces it, but 1-butanol adsorbs more strongly and thus is not displaced as readily.

The difference in amounts of adsorbed ethanol and water with adsorption order (Figs. 3b, 6b, and 7b) indicates that ethanol is more effective at displacing water than water is at displacing ethanol. When water was adsorbed first, nearly a monolayer of ethanol adsorbed even though all the water was not displaced. This indicates that water adsorbs on sites where ethanol cannot. Additionally, on a water-saturated surface, each adsorbed ethanol molecule displaced more than one water molecule on average.

The long-term deactivation rates decreased when water was added to the feed during PCO at both 100 and 1000 ppm ethanol. The deactivation rates for acetaldehyde formation decreased by 36 and 33% when water was present during PCO at 100 and 1000 ppm, respectively. Similarly, the deactivation rates for CO_2 formation decreased by 63 and 52%. Water may displace acetaldehyde and other strongly bound poisons that accumulate on the surface. As shown previously (1), water can displace a fraction of an adsorbed monolayer of acetaldehyde. This acetaldehyde may be more strongly bound to the surface than acetaldehyde formed from weakly bound ethanol. Adsorbed acetaldehyde reduces PCO activity (3), and water may displace it from the surface and thus reduce deactivation. Blake and Griffin (6) observed a similar reduction in photocatalytic activity by aldehydes. They proposed a rate expression for 1-butanol PCO that is negative order in 1-butanal since adding 1-butanal to the feed inhibited the reaction rate of the alcohol.

Less acetaldehyde was on the surface during PCO with gas-phase water, since less CO_2 formed during TPO (Table 4), and the overall coverage of organics was lower when water was present. Only ethanol and its PCO intermediates desorbed during TPD, but a strongly adsorbed poison could also be on the surface. Water reduced the CO_2 deactivation rate more than the acetaldehyde deactivation rate, which suggests that the poison accumulates on the sites to which ethanol strongly adsorbs.

Effect of Dark Time on PCO

During PCO of 100 ppm ethanol, the rate of acetaldehyde production increased (above its previous value in UV light) after the 6-min dark period. After the lights were switched off for 6 min and then back on during *transient* PCO, acetaldehyde and CO_2 were oxidized at the same rate as before the lights were switched off. Therefore gas-phase ethanol, which competes for sites with water produced during steady-state PCO, causes the enhancement in the acetaldehyde rate after the dark period. When the lights are switched off, water production stops and gas-phase ethanol displaces weakly adsorbed water, as can be seen in Fig. 7b. The experiments in Figs. 6 and 7 show that ethanol and water can displace each other. Since the sites that weakly adsorb ethanol preferentially produce acetaldehyde, and the concentration of ethanol on these sites increases during the dark time, the rate of acetaldehyde is greater immediately after UV illumination resumes. After several minutes, the rate of acetaldehyde formation decays to its steady-state value as the competition with water for adsorption sites resumes. Addition of 0.5% water to the feed stream decreased the enhancement of the acetaldehyde rate after the dark period. Ethanol competes with water for sites when the lights are off and therefore less ethanol builds up on the weakly bound sites. Even though the rate that PCO produces water is much smaller than the rate water flows to the reactor for 0.5% water, Fig. 3 shows that adding water to the feed during PCO at 100 ppm ethanol (water/ethanol ratio = 50) only increased the amount of adsorbed water by 40%.

The increase in acetaldehyde formation rate is greater in 20% O_2 than 0.2% O_2, presumably because PCO is faster and more adsorbed water is produced at the higher O_2 concentration. The acetaldehyde rate did not increase after the dark period during PCO at 1000 ppm ethanol, since water does not compete for sites as effectively at this higher ethanol concentration, as seen in Fig. 3. At both 100 and 1000 ppm ethanol, the rate of CO_2 remained constant when the lights were turned on after baseline correction. Apparently, the dark time did not significantly increase the amount of strongly bound ethanol, which preferentially produces CO_2.

Effect of Oxygen Concentration

For PCO of 100 ppm ethanol, increasing the O_2 concentration from 0.2 to 20% increased both the acetaldehyde and CO_2 rates by only 50%. Similarly, Blake and Griffin (6) reported no change in reaction rate when the O_2 concentration increased from 2 to 22%. Increasing the O_2 concentration increased the amount of adsorbed water by approximately 80% and decreased the coverage of organics by 12% (Table 4) at steady state. Since the rate is greater in 20% O_2, more water is produced and occupies more surface sites (Fig. 3). The amount of adsorbed ethanol decreased by 21%, presumably due the increased competition for sites with water. The amount of adsorbed water during steady-state PCO in 20% O_2 (Fig. 3a) was similar to that of coadsorbed ethanol and water (Fig. 3b). Adsorbed acetic acid coverage decreased by 29%, but formaldehyde/formic acid coverage *increased* by a factor of 3.6.

Previous transient reaction studies (2) determined two pathways during PCO, and they are shown in Fig. 8. Note that these pathways do not represent elementary steps, but indicate the surface intermediates that have been detected. Only one of the pathways involves acetic acid. The change in surface composition with O_2 concentration suggests that the higher oxygen concentration favors one pathway in the mechanism. One possibility is that increasing the O_2 concentration increases the rate of the acetaldehyde → formaldehyde + formic acid step since more formaldehyde/formic acid and less acetic acid are on the surface. Conversely, the rate of acetic acid oxidation may increase with O_2 concentration more than the oxidation rate of formaldehyde/formic acid and therefore acetic acid coverage would be lower in 20% O_2. Acetic acid is probably not displaced by water since it was not detected in the gas phase during PCO.

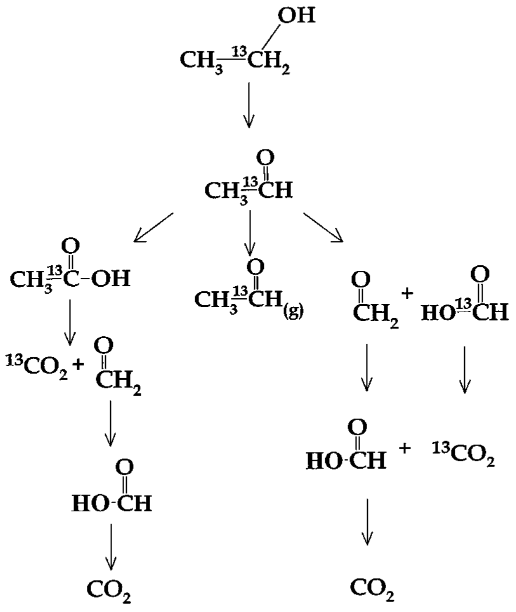

FIG. 8. Mechanism of the PCO of ethanol.

Initial PCO Rates

For PCO at each condition, the initial rates of acetaldehyde and CO_2 production (Table 1) were significantly greater than their steady-state values. This initial deactivation could be caused by the accumulation of an inactive species, such as acetaldehyde, on the surface. Adsorbed acetaldehyde, which may be 15–25% of the organic surface carbon, may be responsible for deactivation since it decreases the rate of PCO (2, 3). Alternatively, intermediates may occupy some of the sites to which ethanol weakly adsorbs, decreasing the rate of acetaldehyde production as PCO continues. Extraction of lattice oxygen may cause the greater initial rates, but the acetaldehyde and CO_2 rates should then be greater after the 6-min dark period for PCO in both 100 and 1000 ppm ethanol, since lattice oxygen should be replenished during the dark period.

For PCO in 20% O_2, the initial rates of CO_2 production are similar for all ethanol and water concentrations (Table 1). This indicates that all the sites that preferentially produce CO_2 are initially occupied during PCO under all conditions studied. The initial rate of acetaldehyde production is the same for PCO with and without water in 1000 ppm, since water does not effectively compete with ethanol for sites at low water/ethanol ratios. Apparently, ethanol occupies all the acetaldehyde-producing sites initially during PCO in 1000 ppm with and without water. For PCO in 100 ppm, however, the initial rate of acetaldehyde production is 50% lower when 0.5% water is present in the gas phase. At the higher water/ethanol ratio water competes more effectively for the sites that preferentially produce acetaldehyde and lowers the rate. In addition, the initial rate of acetaldehyde production is greater at the higher ethanol concentration, as is expected since there is more weakly adsorbed ethanol under these conditions.

Comparison of Transient and Steady-State PCO

Although transient reaction techniques are ideal for mechanistic studies, one must be careful when extrapolating transient results to steady state. As shown in Fig. 5, increasing the oxygen concentration from 0.2 to 20% during transient measurements increases the rate of CO_2 formation more than the rate of acetaldehyde production. However, the steady-state selectivity does not change when the O_2 concentration increased. During transient PCO, only a monolayer of organic reacts and a highly active site may only catalyze reaction of one molecule. At steady state, however, gas-phase reactants replenish the same site and therefore can significantly change the overall selectivity.

The initial rates of acetaldehyde production during transient PCO (Fig. 5) were the same as those in the flow system with 100 ppm ethanol for both 0.2% (Fig. 1) and 20% O_2. Apparently, the amount of weakly adsorbed ethanol did not significantly increase when 100 ppm ethanol was added to the gas phase. During PCO at 1000 ppm ethanol, the initial rate of acetaldehyde production was approximately 45% greater than during transient PCO and the rate decayed more slowly. Apparently higher ethanol concentrations produce more weakly adsorbed ethanol. The longer decay in the initial acetaldehyde rate at 1000 ppm ethanol suggests that some acetaldehyde-producing sites are highly active initially but not at steady state.

The maximum rate of CO_2 production during transient PCO is 3.7 times greater than the initial CO_2 rate in 20% O_2 and 1000 ppm ethanol. During transient PCO in 20% O_2, approximately one-third of the ethanol monolayer reacted to acetaldehyde and CO_2 before the maximum CO_2 rate was reached. When gas-phase ethanol is present, the surface is saturated throughout the reaction. The greater maximum CO_2 production rate during transient PCO may be the result of more sites available for O_2 adsorption at lower coverage. In 0.2% O_2, however, the initial and maximum rates of acetaldehyde and CO_2 production are nearly the same during transient PCO and for 100 ppm ethanol in feed.

Figure 7 shows that reducing the amount of weakly adsorbed ethanol reduces acetaldehyde production during PCO. Furthermore, the maximum rate of CO_2 production increases, even though less ethanol is on the surface. Since acetaldehyde reduces PCO activity, decreasing its amount should increase activity. Furthermore, lower ethanol coverages may produce more sites for oxygen adsorption and therefore a greater CO_2 rate.

CONCLUSIONS

The combination of steady-state PCO followed by TPD identified surface species *and their concentrations* under or near reaction conditions. Ethanol and its intermediates (acetaldehyde, acetic acid, formaldehyde, formic acid, and water) are all on the titania catalyst at steady state. The surface is saturated under all PCO conditions. A surface species that does not desorb during TPD was detected and is likely acetaldehyde. The catalyst deactivated during PCO for all experimental conditions and this deactivation may in part be due to the accumulation of acetaldehyde on the surface. Higher ethanol concentration increases the amount of weakly adsorbed ethanol, which preferentially produces acetaldehyde during PCO. More strongly bound ethanol preferentially produces CO_2. Although water competes with ethanol for sites, increasing the gas-phase concentration only marginally increases the amount of adsorbed water.

ACKNOWLEDGMENTS

Acknowledgment is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. We also gratefully acknowledge support by the National Science Foundation, Grant CTS-9714403. K.H.L. acknowledges support from the NSF-REU Grant EEC-9531361.

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