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Improved catalyst for photocatalytic oxidation of acetaldehyde above room temperature

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Sulfated TiO_2 was more active and deactivated more slowly than Degussa P-25 TiO_2 during PCO of acetaldehyde above 373 K. Thermal catalytic reactions appear to poison both catalysts. Sulfating TiO_2 increased surface area by 60% and increased the number of acetaldehyde adsorption sites by a factor of 1.7.

KEY WORDS: sulfated TiO_2; photocatalytic oxidation; superacid; acetaldehyde; acidity

1. Introduction

The Clean Air Act of 1990 sets limits on the emission of volatile organic compounds (VOCs) from industrial processes. Many waste streams contain VOCs that are dilute in air with the VOC concentration below 1000 ppm [1]. One effective method to destroy dilute concentrations of organic pollutants is heterogeneous photocatalytic oxidation (PCO), which uses a semiconductor catalyst, usually TiO_2, and near-UV radiation to oxidize a wide range of contaminants in both liquid-phase and gas-phase systems [2–9]. During PCO, near-UV irradiation of TiO_2 excites electrons from the valence to the conduction band, leaving holes behind. These electron–hole pairs migrate to the surface where they oxidize adsorbed organics to CO_2 and H_2O.

As with most catalytic processes, improvements in rate, selectivity, and catalyst lifetime are desired to improve the efficiency and expand the applications of PCO. A potentially cost-effective way to improve PCO catalyst performance is to increase the number and strength of surface acid sites since PCO activity has been shown to increase with catalyst surface acidity [10–14]. Sulfated metal oxides are particularly strong acid catalysts [1,15–17]; although they have been classified as superacids, they may not have an acid strength greater than 100% H_2SO_4 [18]. Little work has been done to study the photocatalytic activity of SO_4^{2-}/TiO_2.

Fu *et al.* [16] studied the structure of SO_4^{2-}/TiO_2 and its activity for room-temperature PCO of CH_3Br, C_6H_6, and C_2H_4 in air. For catalysts calcined at 723 K, conversion of CH_3Br over SO_4^{2-}/TiO_2 was 6 times that of TiO_2 that was synthesized in their laboratory. Also, TiO_2 deactivated faster than SO_4^{2-}/TiO_2; after 6 h of PCO, SO_4^{2-}/TiO_2 did not deactivate whereas for TiO_2, conversion decreased from 88 to 20% for C_6H_6 and from 60 to 12% for CH_3Br. For catalysts calcined at 773 K, SO_4^{2-}/TiO_2 was 89.7% anatase and had a surface area 3.6 times that of TiO_2, which was 26.9% anatase. They concluded that the improved rate for SO_4^{2-}/TiO_2 was due to a greater surface area as well as a larger fraction of TiO_2 composed of the anatase phase, which was more active than rutile for PCO.

Previously [19], PCO of heptane, trichloroethylene (TCE), ethanol, acetaldehyde, and toluene were carried out on SO_4^{2-}/TiO_2 and Degussa P-25. At room temperature, SO_4^{2-}/TiO_2 and P-25 oxidized acetaldehyde, trichloroethylene, and heptane at approximately the same rate. Although both catalysts deactivated during acetaldehyde PCO, the origins of deactivation were not studied. This study compares acetaldehyde PCO at and above room temperature on SO_4^{2-}/TiO_2 and P-25 and explores deactivation on both catalysts. In addition, experiments were carried out with TiO_2 that was synthesized by the same method as SO_4^{2-}/TiO_2, but without sulfating, to determine how sulfation affects PCO activity. Hereafter, the three titania-based catalysts will be referred to as SO_4^{2-}/TiO_2 (sulfated TiO_2), P-25 (Degussa P-25 TiO_2), and TiO_2 (TiO_2 prepared by calcining $Ti(OH)_4$ without sulfating).

Photocatalytic oxidation of acetaldehyde is of interest because it is a key indoor air pollutant [20] that is not efficiently oxidized over TiO_2 [7]. The acetaldehyde PCO mechanism has been well-studied at room temperature on P-25 [2,21–24] and a previous study showed that P-25 poisoned rapidly during acetaldehyde PCO above 363 K [8]. Since acetaldehyde forms during PCO of other organics ranging from alkanes to alcohols [2,7,21–27], an effective photocatalyst must oxidize acetaldehyde with minimal deactivation. Although typically carried out at room temperature, PCO using solar energy or high-intensity UV light may operate at elevated temperatures since only a fraction of the output from these sources is in the UV range and the rest heats the catalyst [8,28,29]. Therefore, a practical photocatalyst should be active both at and above room temperature.

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2. Experimental

The transient and temperature-programmed reaction system that was used in this study has been described previously [19]. An annular Pyrex reactor, which was identical to those used in previous studies [21,22,30,31], allowed for high gas flow rates and uniform UV irradiation of the catalyst. Approximately 30 mg of each catalyst was coated in a thin layer (average thickness $< 0.4\ \mu$m) in the annular region of the reactor. During PCO, twelve UV lamps (GE, 8 W) surrounded the reactor to uniformly irradiate the catalyst. These lamps generate light in the 300–500 nm range with a maximum intensity near 360 nm [14]. A furnace made of Ni–Cr wire wrapped around a quartz cylinder surrounded the reactor. The end of a 0.5 mm chromel–alumel, shielded thermocouple contacted the catalyst film to provide feedback to the temperature programmer. A Balzers QMS 200 quadrupole mass spectrometer monitored the reactor effluent directly downstream of the reactor. A 25 μm ID fused silica capillary, which fed directly to the mass spectrometer ionizer, sampled the reactor effluent.

The preparation procedure for SO_4^{2-}/TiO_2 was reported previously [19]. Approximately 30 ml of aqueous H_2SO_4 (0.5 M) was poured over 2 g of powdered $Ti(OH)_4$ followed by drying in air. The sulfate-adsorbed material was then calcined at 723 K in air for 4 h to form SO_4^{2-}/TiO_2. Similarly, a TiO_2 catalyst was prepared by calcining powdered $Ti(OH)_4$ without sulfating. Degussa P-25 is commercially available and was used as received.

Before each isothermal PCO, the reactor was held for 20 min at 723 K in 100 sccm flow of 20% O_2 in He (Praxair, UHP) to create a reproducible surface. For transient PCO at room temperature, two pulses (1400 μmol/g-catalyst each) of acetaldehyde (Aldrich, 99%) were injected upstream of the reactor so that acetaldehyde adsorbed onto the catalyst. Transient PCO was carried out after excess gas-phase acetaldehyde was flushed from the reactor. After a shield was placed between the lights and the reactor, the lights were turned on and allowed to reach a steady output. After 10 min, removing the shields exposed the catalyst to UV irradiation and initiated transient PCO. Isothermal pulse PCO was carried out by injecting four 730 μmol/g-cat pulses of acetaldehyde over a fresh surface with the UV lights on at 298, 373, and 523 K. For all pulse PCOs, acetaldehyde was injected at 1800 s intervals into 100 sccm of 20% O_2 in He flow. Transient and pulse PCO measurements have been shown previously to correlate well with steady-state reaction [19,21–23,30,31].

After transient or pulse PCO for a specified time, the UV lights were switched off and either temperature-programmed desorption (TPD) or oxidation (TPO) was carried out to identify surface species that did not desorb during PCO. Temperature-programmed desorption was carried out in pure He flow. The catalyst was heated at 1 K/s to 723 K and held at this temperature until no products were detected in the gas phase. After cooling the catalyst to room temperature, a subsequent TPO was performed to oxidize species that did not desorb during TPD. The TPO procedure was identical to that of TPD, except the carrier gas was 20% O_2 in He.

3. Results and discussion

3.1. Transient room-temperature PCO

Figure 1 shows transient PCOs of acetaldehyde monolayers on SO_4^{2-}/TiO_2, TiO_2, and P-25 at room temperature.

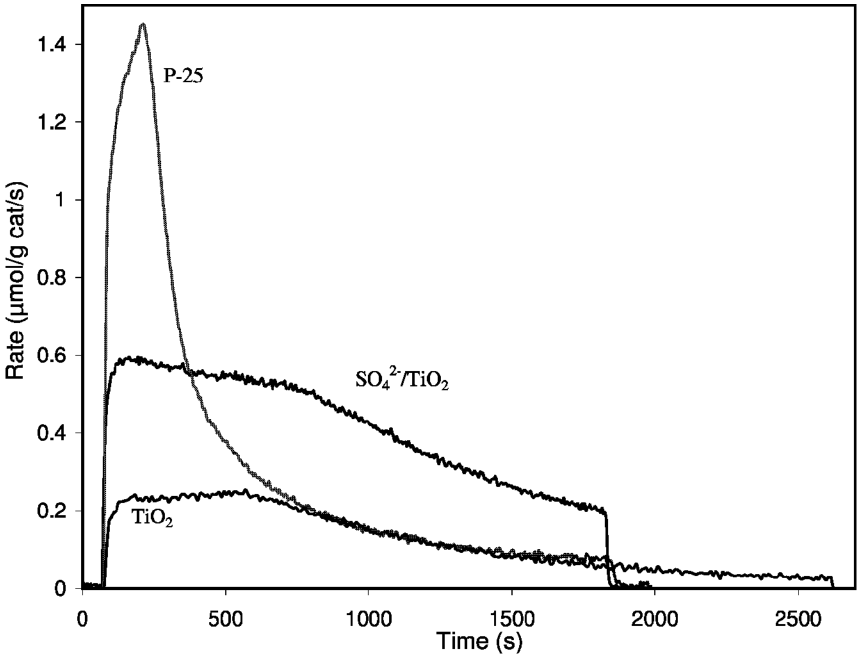

Figure 1. Transient PCOs of acetaldehyde monolayers on P-25, SO_4^{2-}/TiO_2, and TiO_2 in 20% O_2 at room temperature. The UV lights were turned on at 115 s (all catalysts) and off at 1300 s (P-25 and SO_4^{2-}/TiO_2) and 2700 s (TiO_2).

Carbon dioxide was the only product detected in the gas phase and it started forming immediately after UV irradiation of each catalyst at 115 s. After reaching a maximum, the CO_2 formation rate decreased as PCO consumed adsorbed acetaldehyde on each catalyst. When the UV lights were turned off, CO_2 formation rates dropped quickly to zero, indicating that the appearance of CO_2 in the gas phase was limited by surface reaction and not desorption [21,22,30,31].

The amounts of carbon-containing species that remained on the surface after PCO were quantified by TPO so that acetaldehyde coverages could be determined. After PCO, TPO oxidized surface species to CO_2, which desorbed from the surface and was detected by the mass spectrometer. After correcting for stoichiometry, the amounts of CO_2 that formed during PCO and subsequent TPO determined the initial acetaldehyde coverage. At room temperature, saturation coverages of acetaldehyde on SO_4^{2-}/TiO_2, P-25, and TiO_2 were determined to be 540, 400, and 200 μmol/g-cat, respectively. Acetaldehyde coverage that was determined for P-25 agrees well with the value of 370 μmol/g-cat reported by Luo and Falconer [28].

The BET method determined the surface areas of SO_4^{2-}/TiO_2 and TiO_2, both calcined at 723 K, to be 160 and 100 m^2/g, respectively, whereas the surface area of P-25 was approximately 50 m^2/g. Fu *et al.* [16] reported the surface area of SO_4^{2-}/TiO_2, prepared by a sol–gel method and calcined at 773 K, to be 136 m^2/g. For TiO_2, they reported surface areas of 197 and 38 m^2/g for catalysts calcined at 573 and 773 K, respectively.

Figure 1 shows that the maximum CO_2 formation rate during PCO on SO_4^{2-}/TiO_2 was 2.6 times that on TiO_2; also note that acetaldehyde coverage on SO_4^{2-}/TiO_2 was 2.7 times that on TiO_2. This indicates that the sites on SO_4^{2-}/TiO_2 were about as active as those on TiO_2. In addition, CO_2 formation rates on SO_4^{2-}/TiO_2 and TiO_2 (figure 1) have the same shape, suggesting that the active sites on these catalysts were similar. The sites of P-25 were more active than those of SO_4^{2-}/TiO_2 or TiO_2, however.

Figure 2 presents the same data as figure 1, but plotted differently to compare the site activities of the catalysts. For each catalyst, the CO_2 formation rate (μmol/g-cat s) at each point in time was normalized by the amount of carbon that remained adsorbed on the surface (μmol/g-cat). The resulting normalized rate (s^{-1}) was then plotted *versus* the fraction of an acetaldehyde monolayer that had reacted to CO_2. Previous researchers described acetaldehyde PCO using Langmuir–Hinshelwood models that were first order in acetaldehyde concentration [24,25,32]. If acetaldehyde PCO is first order in acetaldehyde coverage and all of the reaction sites are equally active, the CO_2 formation rate should increase initially as intermediates accumulate and thereafter decrease proportionately with coverage, producing a constant normalized CO_2 formation rate in figure 2. Figure 2 shows that the normalized CO_2 formation rates on TiO_2 and SO_4^{2-}/TiO_2 were somewhat constant with coverage; normalized rates after 68% of an acetaldehyde monolayer formed CO_2 were 97 and 85% of the initial normalized rates for SO_4^{2-}/TiO_2 and TiO_2, respectively. This indicates that the CO_2 formation rate decreased at approximately the same rate that acetaldehyde was consumed, which is expected if the PCO sites are all equally active.

Both SO_4^{2-}/TiO_2 and TiO_2 showed small maxima in the CO_2 formation rates after approximately 35% of an acetaldehyde monolayer formed CO_2 and the normalized CO_2 for-

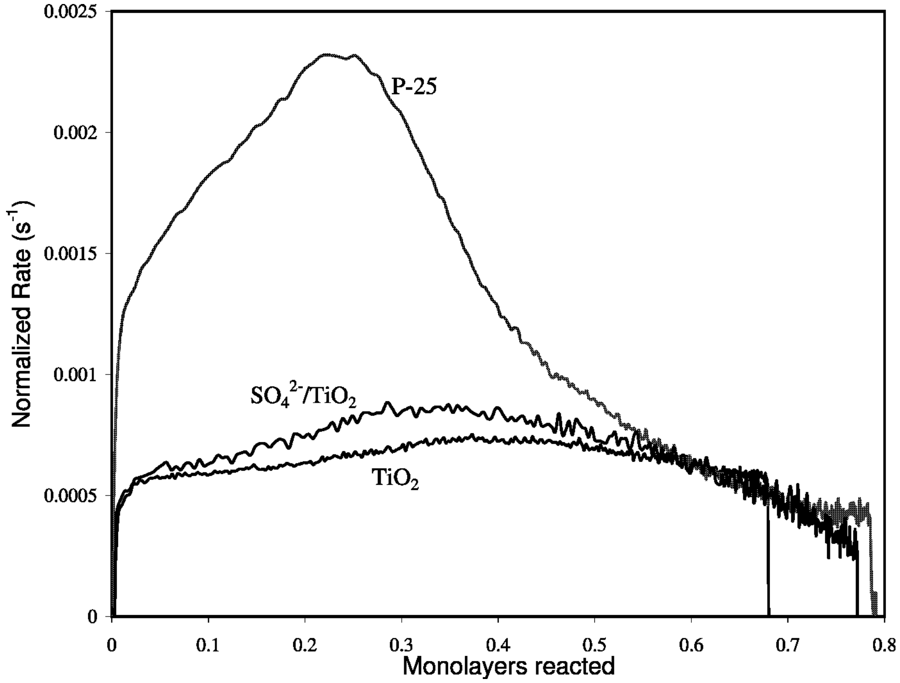

Figure 2. Normalized CO_2 formation rates plotted *versus* the fraction of the initial acetaldehyde monolayer that reacted to CO_2 (one minus fractional coverage) during room-temperature transient PCO in 20% O_2 on P-25, SO_4^{2-}/TiO_2, and TiO_2.

mation rates on SO_4^{2-}/TiO_2 and TiO_2 were comparable at all coverages. Therefore, sulfating TiO_2 did not appear to produce different active sites, but only increased the number of sites that were equally active as those of TiO_2. The increase in the number of active sites upon sulfating was partly due to the 60% increase in surface area.

In contrast to SO_4^{2-}/TiO_2 and TiO_2, the normalized CO_2 formation rate on P-25 (figure 2) increased initially, reaching a maximum after approximately 25% of an acetaldehyde monolayer reacted to CO_2. This initial increase in CO_2 formation rate is not due to delay in detecting gas phase species in the reactor effluent. For transient PCO of other model organics in the same reactor, the maximum CO_2 formation rates quickly reached maxima after approximately 15 s of irradiation; the maximum CO_2 formation rate for acetaldehyde PCO on P-25 occurred after 140 s of UV irradiation. Since acetaldehyde produces CO_2 through acetic acid, formaldehyde, and formic acid intermediates [2,21–24], the increase in CO_2 formation rate may be due to accumulation of these intermediates on the surface.

Figure 2 shows that the CO_2 formation rate on P-25 drops significantly faster than coverage after 25% of an acetaldehyde monolayer formed CO_2. This suggests that the distribution of site activities on P-25 is considerably more broad than on either SO_4^{2-}/TiO_2 or TiO_2. Nimlos *et al.* [25] found that at least two types of active sites for PCO of ethanol and acetaldehyde were required to adequately model PCO on P-25. Similarly, other studies [22,24] proposed that acetaldehyde reacts through at least two pathways, which may be due to different active sites on P-25. Since some of the sites on P-25 appear to be more active than others, P-25 would deactivate more quickly than SO_4^{2-}/TiO_2 if the more active sites are poisoned preferentially.

The rapid decrease in CO_2 formation rate with acetaldehyde coverage on P-25 is not due to a rate-limiting step that is second order in acetaldehyde coverage; a plot of CO_2 formation rate, normalized by dividing the CO_2 rate by the square of acetaldehyde coverage, also showed a dramatic decrease in the normalized rate with decreasing coverage. In addition, the behavior of P-25 during transient PCO does not appear to be due to non-uniform UV irradiation of the P-25 surface. Note that the normalized CO_2 formation rates on SO_4^{2-}/TiO_2 and TiO_2 were approximately constant with coverage, indicating that UV irradiation was essentially uniform. During PCO on P-25, the UV lights and reactor were fixed in the same positions as they were for PCO on SO_4^{2-}/TiO_2 and TiO_2. In addition, the same coating procedure was used for each catalyst and the catalyst films were approximately the same thickness.

3.2. Pulse PCO on P-25

Pulse PCO of acetaldehyde was carried out on P-25, SO_4^{2-}/TiO_2, and TiO_2 to study deactivation and estimate steady-state PCO rates at 298, 373, and 523 K. During pulse PCO, four acetaldehyde injections were spaced approximately 1800 s apart. Carbon dioxide was the only gas phase product detected during pulse PCO and table 1 lists the maximum CO_2 formation rate for each pulse. Repeat experiments determined the reproducibility of the pulse PCO data and table 1 shows the standard deviations on the maximum CO_2 formation rates for each experiment.

Table 1
Maximum CO_2 formation rates (μmol/g-cat s) during pulse PCO of acetaldehyde on SO_4^{2-}/TiO_2, TiO_2, and P-25

	Catalyst								
	P-25			SO_4^{2-}/TiO_2			TiO_2		
Temperature (K)	298	373	523	298	373	523	298	373	523
Acetaldehyde pulse									
1	1.2	1.1	1.5	1.0	0.70	0.66	0.56	0.62	0.28
2	2.2	1.7	1.4	1.6	1.0	0.70	1.1	0.90	0.28
3	2.2	2.0	0.87	1.7	1.7	0.63	1.1	0.90	0.29
4	2.1	1.7	0.44	1.9	2.1	0.57	1.0	1.0	0.25
Standard deviation	0.09	0.05	0.04	0.07	0.07	0.03	0.02	0.08	0.02

Analysis of the acetaldehyde uptake for each pulse indicated that nearly all of the injected acetaldehyde adsorbed and reacted during the first pulse on each catalyst at 298 and 373 K. The amounts of unreacted acetaldehyde in the reactor effluent for subsequent pulses were several orders of magnitude larger than the first pulse, since some adsorption sites were occupied by species from the first pulse. Therefore, CO_2 formation rates for the first pulses at 298 and 373 K were lower than subsequent pulses since the gas phase concentration of acetaldehyde was greater for subsequent pulses. On P-25 at room temperature, the maximum CO_2 formation rate for the second pulse was 1.8 times that of the first acetaldehyde injection. The third and fourth acetaldehyde pulses produced CO_2 at nearly the same rate as the second pulse. Eventually the surface composition should be nearly the same for each pulse since the injections were at regular intervals and the maximum CO_2 formation rates changed less with each successive pulse. Falconer and Magrini-Bair [8] also observed an increasing acetaldehyde PCO rate; they reported that acetaldehyde conversion increased from 9 to 14% during the first 200 min of PCO on P-25 at room temperature.

After four acetaldehyde pulses over P-25 at room temperature, the maximum CO_2 formation rate (table 1) was approximately 1.5 times the maximum CO_2 formation rate during transient PCO (figure 1). During transient PCO, highly active sites might oxidize only one molecule of acetaldehyde whereas during pulse PCO, the same site may oxidize several molecules since gas-phase acetaldehyde replenishes the surface. Also, sites that weakly adsorb acetaldehyde participate in pulse PCO since acetaldehyde on these sites may react before it desorbs. During transient PCO, however, weakly adsorbed acetaldehyde desorbs as gas-phase acetaldehyde is flushed from the reactor in the dark.

Table 1 shows that the maximum CO_2 rates for each pulse at 373 K were lower than those at room temperature on P-25. Figure 3 shows the CO_2 formation rates during pulse PCO of acetaldehyde on P-25, SO_4^{2-}/TiO_2, and TiO_2 at 373 K. The

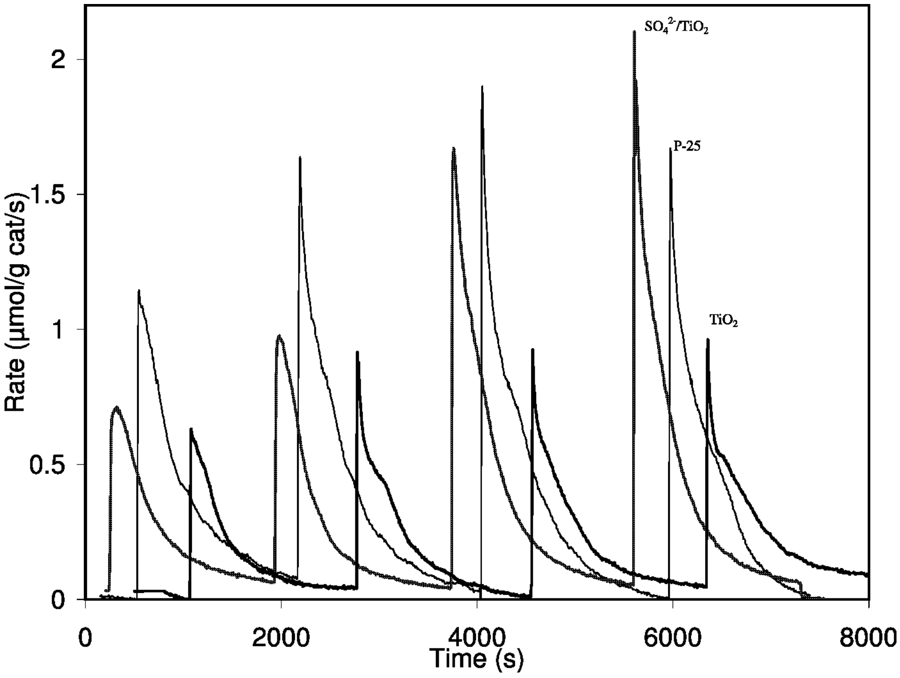

Figure 3. Carbon dioxide formation rates during pulse PCO of acetaldehyde on P-25, SO_4^{2-}/TiO_2, and TiO_2 in 20% O_2 at 373 K.

CO_2 formation rate on P-25 increased during the first three pulses, but then decreased for the fourth acetaldehyde pulse. After four acetaldehyde pulses at 373 K, the maximum CO_2 formation rate was approximately 81% of that at room temperature, suggesting that P-25 may have deactivated during PCO at 373 K. For pulse PCO at 523 K (table 1), P-25 deactivated rapidly; the CO_2 formation rate decreased with each successive pulse so that the maximum CO_2 formation rate for the fourth acetaldehyde injection was only 29% of that for the first pulse. Note that PCO rates at 523 K should be even lower than those listed in table 1 since thermal oxidation contributes to the CO_2 formation rate; CO_2 starts forming at 423 K during acetaldehyde TPO on all catalysts studied.

3.3. Pulse PCO on SO_4^{2-}/TiO_2

At room temperature on SO_4^{2-}/TiO_2, the maximum CO_2 formation rate increased with each successive pulse, reaching 1.9 μmol/g-cat s after four acetaldehyde pulses. This rate is 90% of the maximum CO_2 formation rate on P-25 after four pulses and the CO_2 formation rate on SO_4^{2-}/TiO_2 was still increasing with each pulse whereas the CO_2 rate on P-25 remained relatively constant after the second pulse. This suggests that the steady-state PCO activity of SO_4^{2-}/TiO_2 is comparable to that of P-25 at room temperature.

The similar activities of SO_4^{2-}/TiO_2 and P-25 during pulse PCO contrasts transient PCO, which showed P-25 to be significantly more active than SO_4^{2-}/TiO_2 (figure 1). The similar pulse PCO activities do not appear to be due to acetaldehyde mass transfer limiting the CO_2 formation rate on P-25. Steady-state PCO of acetaldehyde was performed on P-25 to determine if mass transfer limits PCO. During steady-state PCO, UV lights were turned off for several minutes and then back on. If acetaldehyde mass transfer to the surface limits PCO, acetaldehyde would replenish the surface in the dark and the CO_2 formation rate immediately after the dark period would be greater than before the lights were switched off [21]. The CO_2 formation rate was the same before and after the dark period, indicating that acetaldehyde mass transfer to the surface did not limit CO_2 formation during steady-state PCO. For pulse PCO, the gas-phase concentration of acetaldehyde at the time when CO_2 formation reached a maximum rate was more than an order of magnitude greater than that of the steady-state experiment. Therefore, acetaldehyde mass transfer to the surface does not appear to limit pulse PCO on P-25.

Room-temperature pulse PCO rates may be similar on the two catalysts because of site blocking by H_2O, which is a product of acetaldehyde PCO. If some of the highly active sites on P-25 are blocked by adsorbed H_2O, P-25 activity may not be significantly different from that of SO_4^{2-}/TiO_2. Although H_2O also forms on SO_4^{2-}/TiO_2, the site activities on SO_4^{2-}/TiO_2 were nearly uniform so that site blocking by water would affect the PCO rate on SO_4^{2-}/TiO_2 less than P-25. Even with some of the more active sites on P-25 blocked by adsorbed H_2O, CO_2 formation rates during pulse PCO (table 1) were still greater than those of transient PCO (figure 1), since gas-phase acetaldehyde replenished the surface during pulse PCO. Similarly, Muggli *et al.* [21] showed that the steady-state ethanol PCO rate was greater than the maximum rate during transient PCO even though H_2O blocked some of the active sites on P-25 during steady-state PCO.

Photocatalytic oxidation at 373 K (figure 3) was similar to PCO at room temperature on SO_4^{2-}/TiO_2 in that the

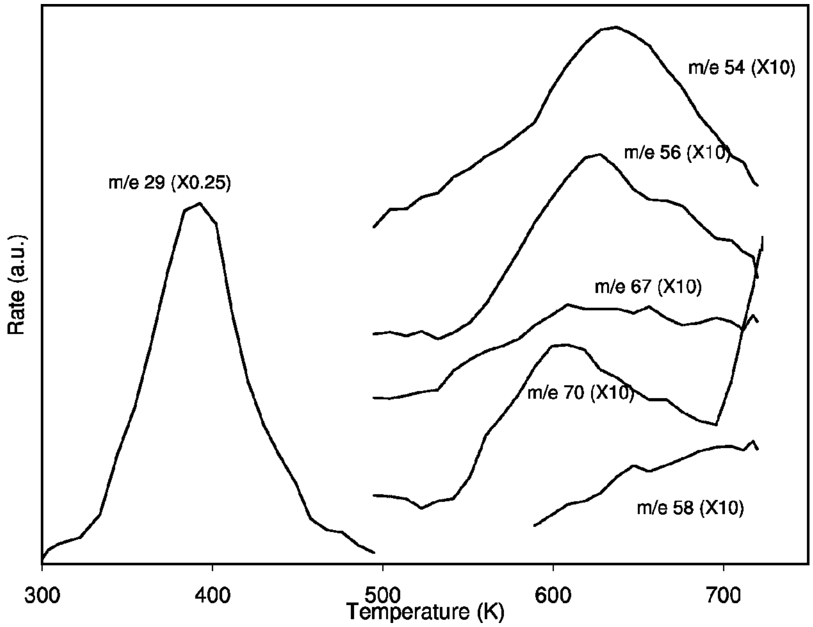

Figure 4. Temperature-programmed desorption to 723 K of an acetaldehyde monolayer on P-25.

maximum CO_2 formation rate increased with each successive pulse. After four pulses, the CO_2 formation rates at 298 and 373 K were comparable, indicating that increasing reaction temperature to 373 K did not deactivate SO_4^{2-}/TiO_2. At 373 K, the maximum CO_2 formation rate after four pulses on SO_4^{2-}/TiO_2 was 1.25 times that on P-25, since P-25 deactivated at elevated temperature. After pulse PCO at 373 K, TPO showed that the amount of carbon on the surface of P-25 (260 μmol/g-cat) was approximately twice that on SO_4^{2-}/TiO_2(125 μmol/g-cat) even though SO_4^{2-}/TiO_2 adsorbs 33% more acetaldehyde at room temperature. Since P-25 deactivated during pulse PCO, the two-fold difference in TPO amounts may be due to a stable species that accumulated faster on P-25 than on SO_4^{2-}/TiO_2. Also, a lower TPO amount for SO_4^{2-}/TiO_2 may be in part due to more acetaldehyde reacting during PCO, since SO_4^{2-}/TiO_2 was more active than P-25 during the fourth acetaldehyde pulse.

After four acetaldehyde pulses on SO_4^{2-}/TiO_2, the maximum CO_2 formation rates at 298 and 373 K were both approximately 3.5 times greater than the rate at 523 K. In addition, the maximum CO_2 formation rate after four acetaldehyde pulses at 523 K was 86% of the initial rate, indicating that SO_4^{2-}/TiO_2 deactivated at elevated temperature. Note that PCO rates at 523 K for all catalysts are lower than the rates in table 1 since thermal catalytic oxidation contributes to CO_2 formation rates.

Comparing pulse PCOs on SO_4^{2-}/TiO_2 and P-25 in table 1 indicates that steady-state PCO rates at room temperature on the two catalysts may be similar, but SO_4^{2-}/TiO_2 deactivates more slowly than P-25 during PCO at elevated temperatures. After four acetaldehyde pulses, the maximum CO_2 formation rate on SO_4^{2-}/TiO_2 was 24 and 30% greater than on P-25 at 373 and 523 K, respectively.

3.4. Pulse PCO on TiO_2

Pulse PCO on TiO_2 was similar to that on SO_4^{2-}/TiO_2; the maximum CO_2 formation rates after four acetaldehyde pulses were comparable at 298 and 373 K, but those at 523 K were approximately one-fourth of these rates and TiO_2 deactivated with each successive pulse at 523 K. The similarity between pulse PCO behavior on SO_4^{2-}/TiO_2 and TiO_2 further indicates that sulfating TiO_2 apparently only increased the number of active sites on TiO_2, without producing any different types of active sites. After four acetaldehyde pulses, the maximum CO_2 formation rate on SO_4^{2-}/TiO_2 was approximately twice that on TiO_2 at each temperature, which is in reasonably good agreement with transient PCO. The CO_2 formation rate during transient PCO was approximately 2.6 times larger on SO_4^{2-}/TiO_2 than on TiO_2.

3.5. TPD of acetaldehyde

Temperature-programmed desorption of acetaldehyde was performed on P-25, SO_4^{2-}/TiO_2, and TiO_2 to determine if similar thermal catalytic reactions occur on the catalysts and to further explore the origins of PCO deactivation at elevated temperature. Figure 4 shows TPD of a monolayer of acetaldehyde on P-25. The mass fragments shown in figure 4 were also detected during acetaldehyde TPD on TiO_2 at approximately the same temperatures. The assignment of species to mass fragments is analogous to previous acetaldehyde TPD studies [28,33,34]. At low temperature, acetaldehyde ($m/e = 29$) desorbed in a peak centered at 400 K and a small desorption peak due to crotonaldehyde ($m/e = 70$) appeared, but it is not shown in figure 4. At higher temperatures, butene ($m/e = 56$), butadiene ($m/e = 54$), and acetone ($m/e = 58$) desorbed. Two high tempera-

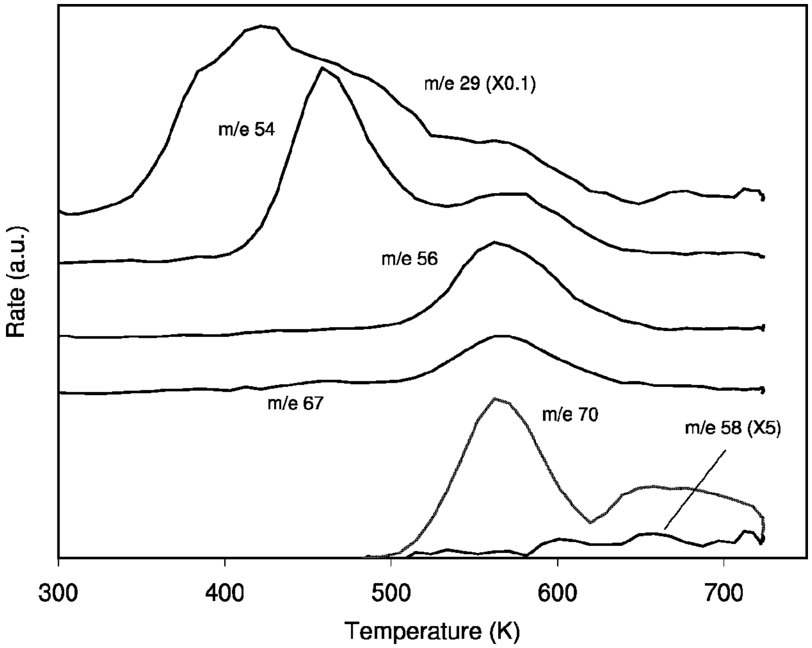

Figure 5. Temperature-programmed desorption to 723 K of an acetaldehyde monolayer on SO_4^{2-}/TiO_2.

ture peaks for $m/e = 70$ were observed, one at 610 K and another peak that was not fully resolved when heating stopped at 723 K. The high temperature $m/e = 70$ signal may be due to crotonaldehyde, as observed on TiO_2(001) by Idriss and Barteau [34] or from pentene as reported by Luo and Falconer [28,33], during TPD on P-25. Although Luo and Falconer [28,33] presented spectra for temperature-programmed hydrogenation (TPH) rather than TPD, they detected the same products at similar temperatures during TPD. Luo and Falconer [28,33] assigned pentene to the high temperature $m/e = 70$ desorption due to a similar $m/e = 55$ signal in the same temperature range. Although not shown in figure 4, a signal at $m/e = 55$ followed the $m/e = 70$ desorption at high temperatures, suggesting that the high temperature $m/e = 70$ desorption was due to pentene. A small peak at $m/e = 67$ is also shown in figure 4, from an unidentified molecule. Our results agree with those reported by Luo and Falconer [28,33] for TPH and TPD on P-25 since they observed the same mass fragments shown in figure 4 at similar temperatures.

Acetaldehyde TPD on SO_4^{2-}/TiO_2 (figure 5) was also similar to TPD on P-25. Acetaldehyde ($m/e = 29$) desorbed in a peak near 400 K, and continued to desorb until the catalyst reached 600 K. Above 500 K, acetaldehyde TPD spectra are remarkably similar for all catalysts. The same mass fragments were detected during TPD on P-25, SO_4^{2-}/TiO_2, and TiO_2, although species desorbed at slightly lower temperatures on SO_4^{2-}/TiO_2. The unique feature of TPD on SO_4^{2-}/TiO_2 was the butadiene ($m/e = 54$) desorption peak at 460 K; butadiene desorbed at significantly higher temperatures on TiO_2 and P-25. Luo and Falconer [28] proposed that butadiene forms on P-25 by dehydroxylation of acetaldehyde dimeric condensation products, the formation of which are catalyzed by both acidic and basic sites. A previous study [19] showed that SO_4^{2-}/TiO_2 had approximately three times as many acid sites as either P-25 or TiO_2 and these sites may be responsible for the low-temperature desorption of butadiene on SO_4^{2-}/TiO_2. Overall, the TPD spectra for P-25, SO_4^{2-}/TiO_2, and TiO_2 indicate that the same reactions occur on these surfaces during TPD.

3.6. Catalyst deactivation

Muggli and Falconer [31] reported that acetaldehyde reacts during TPD to form stable surface species that poison P-25 during PCO. They utilized these reactions to poison the CO_2-producing sites of P-25 and change PCO selectivity. A subsequent study by Falconer and Magrini-Bair [8] reported that P-25 deactivates rapidly during acetaldehyde PCO above 363 K due to thermal catalytic poisoning that takes place in parallel with PCO. They concluded that thermal catalytic decomposition products accumulate on the catalyst surface and deactivate it above 363 K. Luo and Falconer [28] found that acetaldehyde forms trimeric condensation products, higher molecular weight compounds, and coke at relatively low temperatures on P-25. They postulated that these reactions poison P-25 during acetaldehyde PCO.

Similar reactions may have occurred during PCO on SO_4^{2-}/TiO_2 at 523 K because it deactivated, but at a lower rate than did P-25. After PCO of four acetaldehyde pulses at 523 K, the maximum CO_2 formation rate decreased 14% on SO_4^{2-}/TiO_2, compared to a 71% decrease in activity on P-25. The amounts of CO_2 detected during TPO after pulse PCO were 1110 and 1230 μmol/g-cat for P-25 and SO_4^{2-}/TiO_2, respectively. These values are 39 and 14% greater than the amounts of carbon that are contained in the room-temperature saturation coverages of acetaldehyde on

P-25 and SO_4^{2-}/TiO_2, respectively. The large coverages after pulse PCO are most likely due to accumulation of stable surface species that deactivated the catalysts. Pulse PCO at 523 K on TiO_2 was similar to SO_4^{2-}/TiO_2; the maximum CO_2 formation rate after four pulses was approximately 89% of the initial rate and the amount of carbon detected on the surface after PCO was 20% greater than that of an acetaldehyde monolayer at room temperature.

Deactivation during PCO on all catalysts appears to be due to thermal catalytic reactions that poison these surfaces. Experiments were performed to determine if thermal reactions form surface species that react more slowly than acetaldehyde during PCO on P-25 and SO_4^{2-}/TiO_2. Six 1400 μmol-acetaldehyde/g-cat pulses were injected at 600 s intervals over both catalysts in the dark at 373 K in flowing 20% O_2 in He. The catalysts were then cooled to room temperature and transient PCO was carried out.

After acetaldehyde exposure at 373 K, the CO_2 formation rate on P-25 during subsequent room-temperature PCO reached a maximum rate of 0.3 μmol/g-cat s and decreased throughout transient PCO until the lights were switched off. Subsequent TPO oxidized the remaining adsorbed species to CO and CO_2. The total amount of carbon that formed CO and CO_2 during PCO and TPO was 1.2 times the amount of carbon contained in an acetaldehyde monolayer at room temperature. Although the amount of carbon on the surface after acetaldehyde exposure at 373 K was greater than a room-temperature acetaldehyde monolayer, the maximum rate of CO_2 production during transient PCO was only 20% of that for transient PCO of acetaldehyde that was adsorbed at room temperature. The dramatic difference in PCO activity for acetaldehyde exposure at 298 and 373 K indicates that the adsorbed species after acetaldehyde exposure at 373 K reacted more slowly than when acetaldehyde adsorbed at room temperature. The species adsorbed after acetaldehyde exposure at 373 K are most likely the products of thermal catalytic reactions taking place on P-25 at 373 K in the dark.

Similar to P-25, PCO on SO_4^{2-}/TiO_2 formed CO_2 more slowly after acetaldehyde exposure at 373 K than during PCO of an acetaldehyde monolayer that was adsorbed at room temperature. During room-temperature PCO, the CO_2 formation rate reached a maximum of 0.4 μmol/g-cat s and remained there until the lights were turned off after 600 s of irradiation. This maximum CO_2 formation rate is 67% of that for PCO after acetaldehyde exposure at room temperature (figure 1) and the coverage after adsorption at 373 K was 10% greater than at room temperature.

Even though surface species after acetaldehyde adsorption at 373 K oxidized photocatalytically to CO_2 at two-thirds the rate of room temperature acetaldehyde PCO, table 1 shows that pulse PCO rates on SO_4^{2-}/TiO_2 at 298 and 373 K were similar after four acetaldehyde pulses. Note that when SO_4^{2-}/TiO_2 was exposed to acetaldehyde at 373 K in the dark, PCO did not compete with thermal catalytic reactions. During pulse PCO, however, UV irradiated the catalyst as acetaldehyde was injected into the reactor so that PCO oxidized acetaldehyde as it adsorbed. Apparently during pulse PCO on SO_4^{2-}/TiO_2 at 373 K, acetaldehyde PCO formed intermediates more quickly than thermal catalytic reactions produced stable species so that the pulse PCO rate was approximately the same at 298 and 373 K. Previous researchers concluded that at elevated temperatures without UV, acetaldehyde molecules primarily react with each other through aldolization and reductive coupling on different titania catalysts [28,33,34]. During PCO, however, acetaldehyde oxidizes to acetic acid, formaldehyde, and formic acid intermediates on the catalyst surface [2,21–24]. During pulse PCO, these intermediates block acetaldehyde adsorption sites, decreasing acetaldehyde coverage. The lower acetaldehyde coverage should favor PCO since stable species are produced by thermal catalytic reactions between two acetaldehyde molecules whereas acetaldehyde molecules do not react with each other during PCO [2,21–24].

On P-25, however, the CO_2 formation rate during pulse PCO at 373 K was approximately 20% lower than that at 298 K. This decrease in rate was attributed to accumulation of products from thermal catalytic reactions, which poison the surface. Since the PCO activity of P-25 is derived from a fewer number of more active sites than SO_4^{2-}/TiO_2, P-25 would be more susceptible to poisoning if the products of thermal catalytic reactions preferentially block these sites. Also, SO_4^{2-}/TiO_2 oxidized the products of these thermal catalytic reactions more quickly than did P-25; the ratio of transient PCO rate for acetaldehyde exposure at 373 K to the PCO rate after acetaldehyde adsorption at 298 K was 67% for SO_4^{2-}/TiO_2, compared to a value of 20% for P-25. This more than three-fold difference in relative activity indicates that SO_4^{2-}/TiO_2 deactivates less from poisoning by thermal catalytic reactions.

Although stable species formed after acetaldehyde exposure at 373 K, TPO to 723 K regenerated both SO_4^{2-}/TiO_2 and P-25. After pulsing acetaldehyde over each surface at 373 K, TPO to 723 K oxidized surface species to CO and CO_2. After TPO, subsequent room-temperature transient PCOs of acetaldehyde were carried out on both catalysts. Acetaldehyde coverages and CO_2 formation rates during transient PCOs were nearly identical to those of transient acetaldehyde PCOs that were performed prior to acetaldehyde exposure at 373 K.

4. Conclusions

Above 373 K, SO_4^{2-}/TiO_2 was more active than P-25 for PCO of acetaldehyde. More importantly, P-25 deactivated significantly more quickly than did SO_4^{2-}/TiO_2 at elevated temperatures. Since acetaldehyde is a PCO intermediate of other molecules, SO_4^{2-}/TiO_2 may be a superior catalyst for PCO at elevated temperatures. The sites on P-25 were more active than those on SO_4^{2-}/TiO_2 for room temperature PCO of acetaldehyde and they had a broader range of activity than did those on SO_4^{2-}/TiO_2. Thermal catalytic reactions were similar on both P-25 and SO_4^{2-}/TiO_2, but these reactions poisoned P-25 more rapidly during PCO at elevated temperature. Sulfating $Ti(OH)_4$ followed by calcining to form SO_4^{2-}/TiO_2 produced a greater number of active sites than did calcining $Ti(OH)_4$ without sulfating to form TiO_2. The activities of the sites on these two catalysts were remarkably similar, however, suggesting that sulfation did not produce any different active sites for acetaldehyde PCO.

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