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Characterization of Adsorbed Species on TiO_2 after Photocatalytic Oxidation of Toluene

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During the initial step of photocatalytic oxidation (PCO) of toluene on TiO_2 at room temperature, strongly bound intermediates form that are much less reactive than toluene. Temperature-programmed hydrogenation (TPH) is shown to be an effective technique to characterize these intermediates. Titania is a hydrogenation catalyst at elevated temperatures, and the intermediates hydrogenate to benzene and toluene, which are more weakly bound. Platinum was added to TiO_2 to increase the rate of hydrogenation through spillover of hydrogen so that the intermediates were removed at lower temperatures, and the Pt also increased the rate of PCO at room temperature. More than one intermediate may be on the surface, and the intermediates have intact aromatic rings. Similarities in TPH spectra indicate that toluene reacted through benzaldehyde, but benzaldehyde oxidized quickly to some less reactive intermediate. Benzaldehyde adsorbed in more than one form on TiO_2, and these forms had different reactivities during PCO. Benzoic acid is not the less reactive intermediate formed during benzaldehyde PCO. © 2001 Academic Press

Key Words: **photocatalytic oxidation; toluene.**

INTRODUCTION

Heterogeneous photocatalytic oxidation (PCO) is a promising technique for the removal of organic pollutants present in low concentrations in waste gas streams. During PCO, the catalyst absorbs UV light, which excites electrons from the valence band into the conduction band. The resulting electron/hole pairs can then migrate to the surface and initiate redox reactions with adsorbed organics. Though the objective of PCO is complete oxidation, many organics react to form partial oxidation products (1–22). Less reactive, strongly bound compounds form during PCO of BETX (benzene, ethylbenzene, toluene, and xylenes) compounds (7–19). Accumulation of these partial oxidation products can poison the catalyst surface by blocking reaction sites. Toluene, a potential human carcinogen and common air pollutant, was used in this study as a model aromatic to characterize surface intermediates that form during PCO.

Transient reaction of a monolayer of toluene at room temperature was used to measure O_2 consumption and CO_2 formation. The intermediates that form on the surface were characterized by temperature-programmed hydrogenation (TPH) because hydrogenation is expected to saturate the intermediates so that they are more weakly held and desorb. Though H_2 was used for most TPH experiments, some experiments used a D_2 flow to help identify intermediates. Platinum was added to the TiO_2 since it has been reported to increase the rate of PCO (19, 23–27), but also to take advantage of spillover of H atoms onto the TiO_2 to more effectively remove the PCO intermediates from the TiO_2 surface. For Pt loading of 0.2%, less than 0.4% of the TiO_2 surface is covered with Pt, and thus the photocatalytic processes are expected to be similar to those on TiO_2 alone. Fu *et al.* (19) observed that Pt increased both the rate of benzene consumption at 343 K and the ratio of CO_2 produced to benzene consumed.

Most previous studies of gas-phase PCO of BETX compounds on TiO_2 and Pt/TiO_2 have focused on PCO rates rather than on the identification of adsorbed intermediates and surface processes, which are poorly understood (18, 19, 23–31). Ibusuki and Takeughi (8) reported that during PCO of toluene in dry air on TiO_2, a small amount of benzaldehyde formed in addition to CO_2. Larson and Falconer (9) observed that toluene reacts quickly on TiO_2 to form strongly bound intermediates that react more slowly to form CO_2 and H_2O. They observed that the intermediates formed during PCO of toluene reacted differently from benzaldehyde, benzyl alcohol, and *m*-cresol, indicating that these compounds are probably not the intermediates formed during toluene PCO. The less reactive, strongly bound intermediates either thermally decomposed or oxidized during temperature-programmed desorption (TPD) or oxidation (TPO) (9).

Jacoby *et al.* (10) used water to extract adsorbed intermediates from a TiO_2 catalyst following steady-state benzene PCO. Their analysis identified phenol, benzoquinone and/or hydroquinone, and malonic acid as possible intermediates. Since they only reacted several monolayers of toluene, these species may be the primary intermediates.

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D'Hennezel *et al.* (14) observed similar species during a water extraction following humidified benzene PCO on TiO_2.

Recent studies have used extraction and FTIR to study PCO of a continuous flow of toluene on TiO_2 (12–14). These studies found that surface species formed during PCO of unhumidified toluene deactivate the catalyst. Mendez-Roman and Cardona-Martinez (12) observed benzaldehyde and benzoic acid on the surface following toluene PCO and proposed that toluene reacts to form benzaldehyde, which then reacts to benzoic acid, which deactivates the surface. Augugliaro *et al.* (13) detected benzaldehyde, benzene, benzyl alcohol, CO_2, and trace amounts of benzoic acid and phenol during PCO of a continuous flow of toluene on TiO_2 using GC and extraction. The catalyst deactivated after 20 h of PCO of unhumidified toluene. Benzene production was a transient reaction product that appearing during the first 4 h of reaction. Carbon dioxide was always associated with benzene formation and was not detected at later reaction times, when only benzaldehyde was detected in the gas phase. The authors proposed that toluene reacts with adsorbed hydroxyl radicals to form benzaldehyde during the first steps of PCO, and that benzaldehyde then reacts with another hydroxyl radical to form benzoic acid, which decomposes to benzene and CO_2. They proposed that the catalyst deactivated during PCO of unhumidified toluene because surface hydroxyls were consumed (32). In contrast to other studies, they proposed that benzaldehyde was the unreactive intermediate responsible for deactivation during PCO of unhumidified toluene. None of these more recent studies quantified their results; thus, strongly bound intermediates or gas-phase products may have been missed.

Transient reaction techniques are useful for studying PCO because the adsorption, surface reaction, and desorption steps can be separated in time. In the current study, an adsorbed layer of toluene was oxidized in the absence of gas-phase toluene, and less than a monolayer was reacted so that the intermediates detected are more likely to be the result of toluene PCO and not side reactions. Toluene is weakly adsorbed on TiO_2 and desorbs intact at relatively low temperatures (9); thus unreacted toluene can be readily separated from intermediates that are more strongly bound to the surface. Consequently, temperature-programmed experiments are well suited to characterize the intermediates. Photocatalytic oxidation using labeled toluene ($C_6H_5{-}^{13}CH_3$) provided information on the oxidation of ring and methyl carbons on Pt/TiO_2. Benzaldehyde PCO was also studied because it is a possible intermediate during toluene PCO (8, 10, 12–16). The TPH spectra of other proposed intermediates (8, 12, 14) (benzyl alcohol, benzoic acid, and *m*-cresol) were also investigated.

EXPERIMENTAL METHODS

The apparatus used for PCO and the temperature-programmed experiments was described previously (3). A thin-film, annular photoreactor with a 1-mm annular spacing was used to ensure high gas flow rates over the catalyst. This increased mass transfer and rapidly flushed gas-phase products from the reactor. A quartz reactor, which had a porous quartz frit to support the catalyst and allow gas flow, was used for the powdered TiO_2 experiment. The catalysts used were Degussa P25 TiO_2 (75% anatase/25% rutile with a BET surface area of 50 m^2/g) and 0.2% (wt) Pt/TiO_2. Approximately 30 mg of catalyst coated the inside of the Pyrex photoreactor. A cylindrical quartz furnace wrapped with Kanthal wire surrounded the reactor. The heating wire was spaced so that six near-UV lamps (GE F4T5-BLB), positioned evenly around the reactor and approximately 2.5 cm from the catalyst film, could illuminate the catalyst. These 4-W bulbs generate light in the 300–500 nm wavelength range (near-UV) with a maximum intensity at 356 nm (33). The light intensity at the catalyst surface was measured as 0.3 mW/cm^2. A temperature controller used feedback from the thermocouple to maintain a constant heating rate during temperature-programmed experiments. The reactor effluent was analyzed by a quadrupole mass spectrometer (Balzers QMA 125), which was housed in a turbomolecular-pumped vacuum chamber located downstream of the reactor. A heated, stainless steel capillary was used to divert some of the effluent into the vacuum chamber for analysis. Computer-controlled data acquisition simultaneously monitored and recorded selected mass signals, temperature, and elapsed time. The mass spectrometer signals were calibrated by injecting known quantities of gases or liquids into the appropriate gas stream composition, and mass signals were corrected for cracking in the mass spectrometer.

The catalyst was heated to 723 K in a flowing O_2/He mixture before each experiment to obtain a reproducible surface. Organics were injected upstream of the reactor and allowed to evaporate into the flowing gas and adsorb onto the cooled catalyst. Because benzoic acid is solid at room temperature, it was heated to 460 K, and the resulting benzoic acid vapor contacted TiO_2. Because toluene is weakly adsorbed on TiO_2 and slowly desorbs at room temperature, the reactor was cooled to 273 K following toluene adsorption on TiO_2 to ensure that gas-phase toluene was not present during PCO and that accurate measurements of adsorbed and reacted toluene could be made. The reactor was cooled to 253 K for Pt/TiO_2 experiments because toluene desorbed more readily from the Pt/TiO_2 catalyst than from the TiO_2 catalyst. Benzaldehyde PCO was performed at room temperature. For experiments with less than saturation coverage of benzaldehyde, only a fraction of the amount of organic needed for saturation coverage was injected into the flow gas for adsorption. An aluminum shroud shielded the reactor from the near-UV lights at the start of PCO experiments, and the lights warmed up for approximately 15 min before the shroud was removed. The intensity of the lights increased by approximately 5% during the first 10 min of operation, so the warm-up period allowed the lights to reach a constant output before illuminating the catalyst. The PCO was carried out in 0.2% O_2 in He so that the rate of O_2 consumption could be measured.

Species adsorbed on the catalyst surface were analyzed by temperature-programmed oxidation (TPO), temperature-programmed desorption (TPD), and temperature-programmed hydrogenation (TPH). During TPO, a 20% O_2/He mixture (100 standard cm^3/min) flowed over the catalyst surface as the temperature was increased at a constant rate of 1 K/s. During TPD and TPH, pure He and H_2, respectively, flowed over the catalyst at the same rate. Most of the TPH experiments were carried out in 100% H_2 flow to obtain high rates of hydrogenation of the intermediates, but some TPH experiments on TiO_2 used a 5% D_2/He flow (100 standard cm^3/min) and the various deuterated products were detected. Heating was stopped at 723 K because of difficulties in maintaining a constant heating rate at higher temperatures and to avoid irreversible changes in the catalyst at higher temperatures. The catalyst was held at 723 K until all signals returned to their original values. An interrupted TPD to 348 K was performed following toluene PCO but before TPH to remove unreacted toluene so that the amount of unreacted toluene during PCO could be determined, and any toluene formed during TPH could be distinguished from unreacted toluene. Temperature-programmed desorption showed that toluene was much more weakly held than the other species formed, so only toluene desorbed during TPD. During some TPH experiments, the effluent gas flowed through a bed of the polymer resin Tenax TA (from Scientific Instrument Services, total area of 35 m^2/g) adsorbent to trap desorbed organics for headspace analysis with a GC/MS (Hewlett-Packard Model 5890 GC equipped with a HP Model 5791 mass-selective detector). Tenax was used because it has a high affinity for organics but a low affinity for water. The products from several TPHs were collected on the same resin in repeat experiments to obtain higher concentrations for GC/MS analysis.

RESULTS

Photocatalytic Oxidation of Toluene on TiO_2

Toluene is weakly adsorbed on TiO_2, and desorbs intact at relatively low temperatures. Because the toluene desorption rate was finite at 300 K, the catalyst was cooled to 273 K before PCO. As reported by Larson and Falconer (9), when a monolayer of toluene on TiO_2 was illuminated with UV at 273 K, O_2 was immediately consumed. As shown in Fig. 1, the rate of O_2 consumption quickly reached a maximum and then decayed. Carbon dioxide was the only gas-phase species detected during PCO (Fig. 1), and its rate of formation was much slower than the rate of O_2 uptake. Table 1 shows the formation and uptake amounts for PCO. The aromatics reacted and their initial coverages on the catalyst surface are given in Table 1.

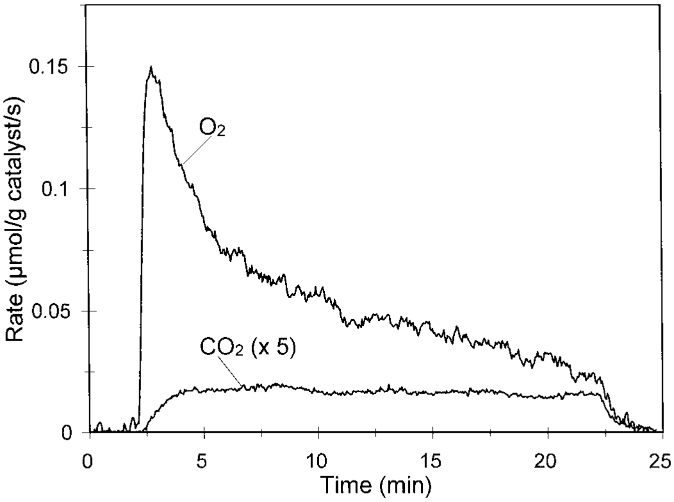

FIG. 1. Oxygen consumption and CO_2 formation during 20-min PCO of toluene adsorbed to saturation coverage on TiO_2 at 273 K.

During TPD of adsorbed toluene when no reaction was performed, toluene desorbed in a single peak with a maximum at 370 K. Saturation coverage of adsorbed toluene at 273 K was determined to be ~80 μmol/g TiO_2. After 20 min of PCO of toluene on TiO_2, only ~22 μmol of unreacted toluene/g of TiO_2, or 27% of the originally adsorbed toluene, desorbed during TPD (Fig. 2). That is, 73% of the toluene monolayer oxidized during 20 min of PCO in the low-intensity light used. Few gas-phase products formed during 20 min of PCO, and the amounts that desorbed during TPD were small, so the rest of the toluene apparently reacted to form surface intermediates that did not desorb by 723 K. Following toluene PCO, a second small toluene peak, with a maximum at 610 K (Fig. 2), desorbed in addition to unreacted toluene. A small amount of benzene also desorbed with two maxima at high temperatures. In addition, CO_2 formed in small quantities over a broad temperature range, and CO desorbed in a high-temperature peak.

TABLE 1

Oxygen Consumed and CO_2 Produced during 20-min PCO

Adsorbed aromatic	Percent saturation coverage	O_2 consumed (μmol/g catalyst)	CO_2 produced (μmol/g catalyst)
		TiO_2	
Toluene	100	68 ± 4	2 ± 0.4
Benzaldehyde	60	38 ± 7	9 ± 2
		Pt/TiO_2	
Toluene	100	135 ± 8	6
Benzaldehyde	60	171	38

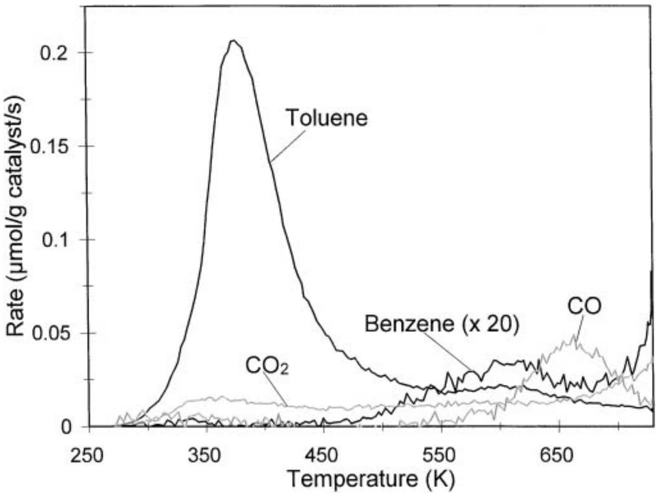

FIG. 2. Temperature-programmed desorption spectra after 20-min PCO of toluene, which was adsorbed to saturation coverage on TiO_2 at 273 K.

The species that were not removed by TPD were oxidized to CO_2 and H_2O during a TPO that followed the TPD. A comparison to the amount of toluene that desorbed during TPD without PCO indicates that the combination of TPD and TPO removed all the adsorbed species. Carbon dioxide formed at temperatures as low as 350 K during TPO; however, most of the surface species remaining after TPD were oxidized to CO_2 at temperatures above 450 K. Temperature-programmed desorption removed only ∼20% of the strongly bound intermediates that formed during PCO. Apparently, TiO_2 is a sufficiently good thermal oxidation catalyst at high temperature that all the intermediates were oxidized during TPO. Tables 2 and 3 show the amount of each desorbing species during TPD and the subsequent TPO for the indicated adsorbed aromatic. The total carbon was calculated by summing the carbon contained in the desorbing species during TPD and TPO.

Temperature-Programmed Hydrogenation of Toluene on TiO_2

Because the intermediates are strongly bound to the surface and do not desorb by 723 K, TPH was used to hydrogenate them; a more hydrogenated species is expected to be more weakly bound to TiO_2. To distinguish products of hydrogenation from the unreacted toluene, an interrupted TPD was first performed to 348 K after PCO to remove unreacted toluene. Toluene had a significant desorption rate at 348 K, and the TiO_2 was held at that temperature until all of the unreacted toluene desorbed. Figure 3 shows the TPH spectra obtained after a 20-min PCO of toluene and an interrupted TPD to remove unreacted toluene. Note that although TPD removed all the unreacted toluene, the largest peak during TPH is toluene, and it forms at much higher temperatures than adsorbed toluene desorbs from TiO_2. In addition to toluene, benzene and a small amount of methylcyclohexane (MCH, not shown for clarity) desorbed during TPH. The reactor effluent was trapped using a bed of Tenax adsorbent for several of these experiments. Subsequent GC/MS headspace analysis of the Tenax confirmed the presence of benzene and toluene. No other organics were detected in identifiable quantities. Neither CO_2 nor CO adsorbs significantly on Tenax and so neither was detected.

TABLE 2

Amounts Desorbed during TPD after 20-min PCO on TiO_2

	Amount desorbed (μmol/g catalyst)						
Adsorbed aromatic	Toluene	Benzene	Benzaldehyde	CO	CO_2	TPO CO_2	Total C
Toluene	25[a]	4		27	12	339	577
Benzaldehyde[b]	4	16	7	12	48	449	682

[a] *Note:* ∼3 μmol/g TiO_2 toluene was from the decomposition of strongly bound intermediates.

[b] Benzaldehyde adsorbed to 60% of saturation coverage.

TABLE 3

Amounts Desorbed during TPD (No PCO) and TPO on TiO_2

	Amount desorbed (μmol/g catalyst)					
Adsorbed aromatic	Toluene	Benzene	CO	CO_2	TPO CO_2	Total C
Toluene	81 ± 8			4		571
Benzaldehyde[a]	3 ± 1	5 ± 2	19 ± 16	16 ± 8	89	175

[a] Benzaldehyde adsorbed to 15% of saturation coverage.

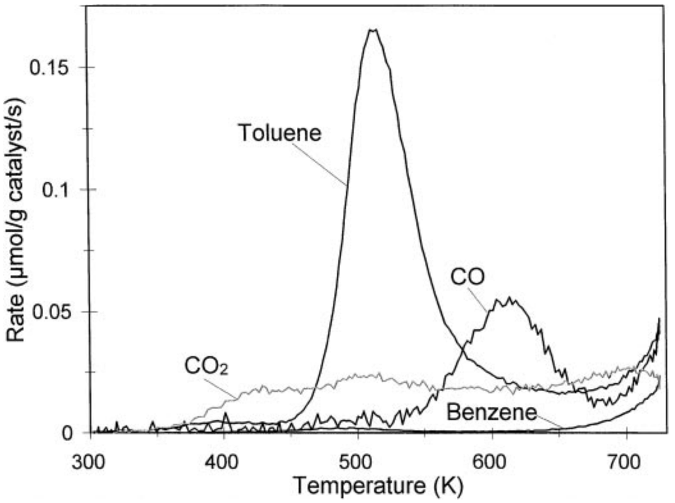

FIG. 3. Temperature-programmed hydrogenation spectra after 20-min PCO of toluene, which was adsorbed to saturation coverage on TiO_2 at 273 K. After PCO, an interrupted TPD to 338 K removed unreacted toluene prior to TPH.

TABLE 4

Amounts Formed during Temperature-Programmed Experiments after 20-min PCO

	Amount desorbed (μmol/g catalyst)								
Adsorbed aromatic	TPD	Toluene	Benzene	TPH MCH	Other organics	CO	CO_2	TPO (CO_2)	Total C
				TiO_2					
Toluene	22 ± 3	29 ± 5	8 ± 2	3 ± 1		20 ± 7	8 ± 2	79 ± 35	533
Benzaldehyde[a]		55	17	1	1	53	9	243	806
				Pt/TiO_2					
Toluene	25 ± 8	25 ± 5	8 ± 1	27 ± 6	20	38	16 ± 3	19 ± 1	695
Benzaldehyde[b]		35	21	10		88	20	20	569

[a] Benzaldehyde adsorbed to 70% of saturation coverage on TiO_2.
[b] Benzaldehyde adsorbed to 30% of saturation coverage on Pt/TiO_2.

The PCO and subsequent temperature-programmed experiment results were reproducible on the same catalyst, even after extensive use of the catalyst. A repeat of the experiment shown in Fig. 3 performed approximately 6 months later showed that the amounts desorbed and reaction rates were approximately the same for PCO and the temperature-programmed experiments.

Table 4 lists the amounts of the desorbing species detected during interrupted TPD, TPH, and the subsequent TPO following reaction of the indicated aromatic. Total carbon was calculated by adding the amount of carbon contained in the desorbing species during interrupted TPD, TPH, and subsequent TPO. Approximately 22 μmol of toluene/g of TiO_2 desorbed during the interrupted TPD. This amount is approximately the same as the amount of unreacted toluene desorbed during a normal TPD following 20-min PCO (Table 2), and this suggests that all the unreacted toluene was removed during interrupted TPD. Although only ~3 μmol of toluene/g of TiO_2 formed at elevated temperatures during TPD from decomposition of strongly bound intermediates following 20-min PCO, 30 μmol of toluene/g of TiO_2 formed during TPH after 20-min PCO and interrupted TPD. Thus, the strongly bound surface species that formed during PCO readily hydrogenated to toluene during TPH. Surface species remaining after TPH were oxidized to CO_2 during TPO. Only 80 μmol of CO_2/g of TiO_2 desorbed during TPO after TPH whereas 339 μmol of CO_2/g of TiO_2 formed during TPO after TPD; therefore, at least 80% of the strongly bound intermediate was hydrogenated to gas-phase products during TPH.

Following TPH, the catalyst had a blue color indicating reduction of TiO_2. The catalyst returned to its white color during the subsequent TPO. Past studies (34–36) have shown that TiO_2 can be reduced in H_2. Two mechanisms for reduction have been proposed:

$$\begin{aligned} &Ti^{4+} + O^{2-} + H_2 \\ &\quad \rightarrow H_2O + V_o + Ti^{3+} + e^- \qquad \Delta H = 183\ \text{kJ/mol} \quad [1] \end{aligned}$$

(34), where V_o represents oxygen vacancies, and

$$TiO_2 + H_2 \rightarrow Ti_3O_5 + H_2O \qquad \Delta H = 8.9\ \text{kJ/mol} \quad [2]$$

(35). Luo and Falconer (36) observed that during TPH of oxidized TiO_2, H_2O from TiO_2 reduction desorbed at 600–620 K, which may indicate that TiO_2 is not reduced until 600 K. A TPO after TPH successfully reoxidized their catalyst.

Photocatalytic Oxidation of Benzaldehyde on TiO_2

Because benzaldehyde has been suggested as the intermediate that forms during toluene PCO on TiO_2 (8, 12–15), the same experiments were carried out for a submonolayer of adsorbed benzaldehyde. A submonolayer was used so that the amounts of desorbing species were similar to the amounts desorbed during TPD and TPH after toluene PCO. Though the amount of benzaldehyde adsorbed corresponds to less than a monolayer, because benzaldehyde is strongly adsorbed the local coverage may not be less than a monolayer. That is, most or all of the benzaldehyde may have adsorbed at the top portion of the reactor rather than being distributed evenly over the entire catalyst surface. Temperature-programmed desorption of benzaldehyde adsorbed to 15% of saturation coverage on TiO_2 was performed. The toluene, benzene, and CO desorption peaks and desorption amounts (Table 3) were similar to those seen during TPD following toluene PCO (Fig. 2). Much of the benzaldehyde did not desorb during TPD, and thus TPO was used to measure the amount of benzaldehyde adsorbed.

Toluene, benzene, CO, CO_2, and unreacted benzaldehyde desorbed during the TPD following 20-min PCO of benzaldehyde at 60% of saturation coverage. The formation of toluene and benzene was similar to the formation of these species during TPD of benzaldehyde without reaction. Carbon monoxide, however, desorbed at a lower temperature during TPD following benzaldehyde PCO, and CO_2 did not form until high temperatures following benzaldehyde PCO, whereas CO_2 formed over a broad temperature range following toluene PCO. Thus, much of the CO and CO_2 formed during TPD after benzaldehyde PCO appears to be from the decomposition of benzaldehyde oxidation products.

Temperature-Programmed Hydrogenation of Benzaldehyde on TiO_2

Though not much benzaldehyde or benzaldehyde decomposition products desorbed during TPD of adsorbed benzaldehyde (20% of saturation coverage), benzaldehyde readily hydrogenated to toluene during TPH, as shown in Fig. 4. Desorption amounts are given in Table 5. In addition to toluene, small amounts of benzene, CO_2, CO, and MCH (not shown for clarity) formed. Toluene formed in two overlapping peaks centered at 550 K and also in a high-temperature peak.

During TPH following benzaldehyde PCO, toluene, benzene, CO, CO_2, and a small amount of benzaldehyde desorbed, as shown in Fig. 5. Desorption amounts are shown in Table 4. Toluene formed in a broad peak at 550 K and a high-temperature peak. The TPH after benzaldehyde PCO is similar to the TPH of adsorbed benzaldehyde, but more CO, CO_2, and high-temperature benzene and toluene formed during TPH after benzaldehyde PCO. All the species formed during TPH after benzaldehyde PCO (Fig. 5) are comparable to the respective species formed during TPH after toluene PCO (Fig. 3).

Temperature-Programmed Hydrogenation of Benzyl Alcohol, Benzoic Acid, and Cresol on TiO_2

During TPH of adsorbed benzyl alcohol, toluene formed in a large peak centered at 525 K and a smaller peak at 725 K. A small amount of benzene also formed, and CO formed in a broad peak. The lower temperature toluene peak was similar to the toluene peak observed during TPH after toluene PCO.

TABLE 5

Amount Formed during TPH and TPO (No PCO)

Adsorbed aromatic	Amount desorbed (μmol/g catalyst) TPH Toluene	Benzene	MCH	CO	CO_2	TPO CO_2	Total C
			TiO_2				
Benzaldehyde[a]	25	5	1	8	2	29	251
			Pt/TiO_2				
Benzyl alcohol	47	1		23	2		>360
m-Cresol	54	2			127		>517
Benzaldehyde[b]	14	2	121	90	13	10	1070

[a] Benzaldehyde adsorbed to 20% of saturation coverage on TiO_2.
[b] Benzaldehyde adsorbed to 55% of saturation coverage on Pt/TiO_2.

Benzoic acid hydrogenated mainly to benzaldehyde at high temperatures. Smaller amounts of toluene and benzene also formed at high temperatures as well as CO_2, CO, and CH_4. The TPH spectra of benzoic acid are significantly different from the TPH spectra after toluene PCO and after benzaldehyde PCO, since not much benzaldehyde desorbed at high temperature after those PCOs.

During TPH of adsorbed *m*-cresol, a small toluene peak formed with a maximum at 520 K, and a large toluene peak formed at 730 K. Both toluene peaks were at the same temperatures as the toluene observed in the TPH following toluene PCO. Carbon monoxide desorbed in a high-temperature peak similar to that observed during TPH after toluene PCO. A small amount of benzene also formed.

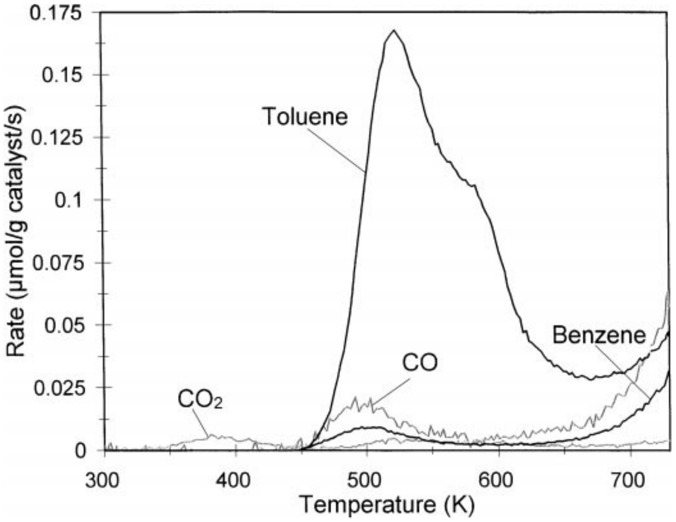

FIG. 4. Temperature-programmed hydrogenation spectra of benzaldehyde, which was adsorbed to 20% of saturation coverage on TiO_2 at 300 K.

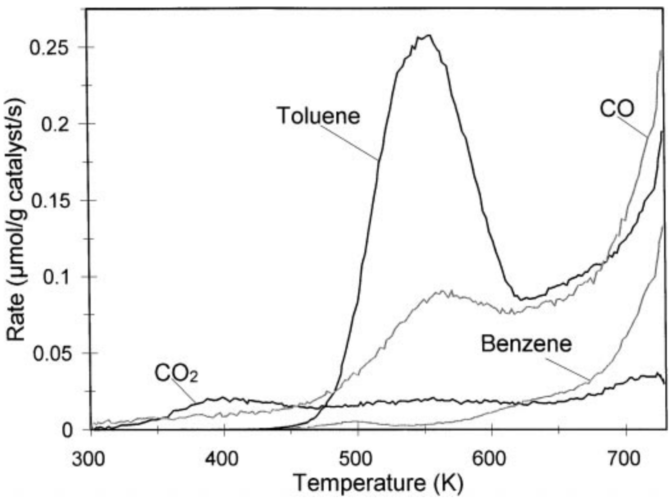

FIG. 5. Temperature-programmed hydrogenation after 20-min PCO of benzaldehyde, which was adsorbed to 70% of saturation coverage on TiO_2 at 300 K.

Temperature-Programmed Hydrogenation with Deuterium on TiO_2

During TPH using 5% D_2, both deuteration of the strongly bound species and deuterium exchange of hydrogen on the adsorbed molecules took place. During a TPH in 5% D_2 of adsorbed toluene when no PCO had been performed, toluene with 0–6 D atoms desorbed, but no MCH formed. Thus, deuterium exchanged with hydrogen on the adsorbed toluene. Figure 6 shows the mass peaks for the deuterated toluene and benzene products that formed during TPH after a 20-min PCO of toluene and an interrupted TPD to remove unreacted toluene. Masses 91, 92, 93, and 94 correspond to deuterated and undeuterated toluene and mass 79 corresponds to benzene with 1 deuterium. The mass spectra indicate that toluene with 0–6 deuterium atoms and benzene with 0–3 deuterium atoms (undeuterated and benzene with 2–3 D not shown) form. Deuterium is added to the strongly bound species by either hydrogenation or exchange. Although 92 amu is the molecular weight of undeuterated toluene, fragmentation in the mass spectrometer results in 91 amu as the main mass detected for undeuterated toluene. Likewise, toluene with 1 D is assumed to be detected at mass 92, and toluene with 2 and 3 D is assumed to appear at masses 93 and 94, respectively. The more highly deuterated benzene and toluene species and undeuterated benzene form in smaller amounts and are not shown in Fig. 6. Because the carrier gas contained only 5% D_2, less toluene formed than formed in the TPH experiment using pure H_2 carrier gas. Experiments with 5% D_2 show that only ∼25% as much toluene and ∼70% as much benzene formed as with pure H_2. In addition, the peaks in Fig. 6 are much broader than those in Fig. 3 and are shifted to higher temperature because of the lower pressure of D_2. Toluene and benzene form at slightly higher temperatures as the amount of deuterium in the molecules increases.

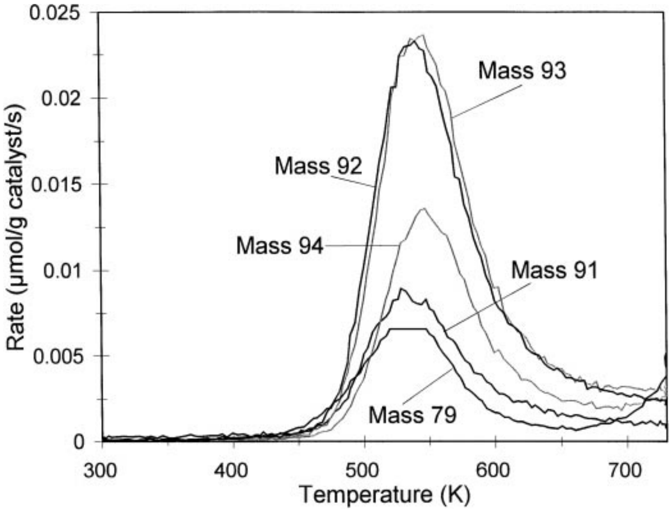

FIG. 6. Temperature-programmed hydrogenation spectra in 5% D_2/He. After 20-min PCO of toluene, which was adsorbed to saturation coverage on TiO_2 at 273 K, an interrupted TPD to 338 K removed unreacted toluene prior to TPH.

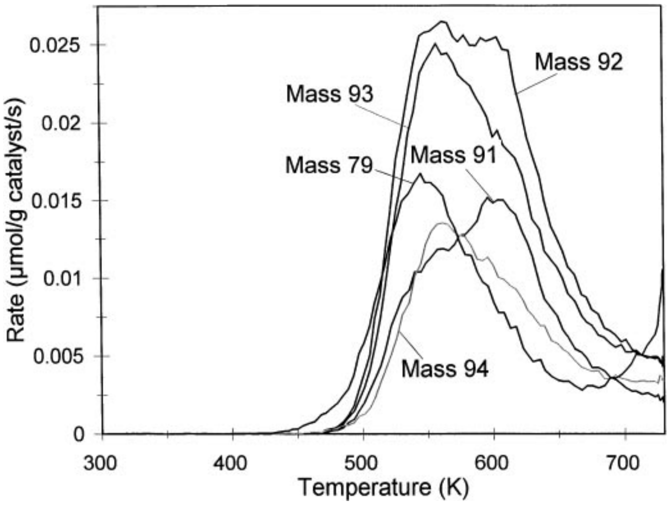

FIG. 7. Temperature-programmed hydrogenation spectra in 5% D_2/He of benzaldehyde, which was adsorbed to 45% of saturation coverage on TiO_2 at 300 K.

For comparison, Fig. 7 shows the TPH of adsorbed benzaldehyde in 5% D_2. The more highly deuterated toluene and benzene products and undeuterated benzene signals are not shown. During TPH of benzaldehyde, two toluene species desorb in overlapping peaks. A more highly deuterated toluene (masses 93 and 94) containing 0–6 D atoms desorbed with a maximum at 555 K, and a less deuterated toluene (masses 91 and 92) containing 0–2 D atoms desorbed with a maximum at 605 K.

Temperature-programmed hydrogenation in 5% D_2 after 20-min benzaldehyde PCO was also performed. The same initial coverage of benzaldehyde was used for the adsorbed benzaldehyde spectra and for the PCO of benzaldehyde. As with the adsorbed benzaldehyde spectra, two toluene peaks formed, but the amount in each peak was significantly different. After PCO, less of both toluene species desorbed, as expected because less benzaldehyde was on the catalyst surface after PCO. More of the less deuterated toluene (higher-temperature toluene peak) desorbed than the more deuterated toluene (lower-temperature toluene peak).

Photocatalytic Oxidation of Toluene on Pt/TiO_2

The PCO of toluene was similar on Pt/TiO_2 to unplatinized TiO_2, but Pt increased the PCO rate. Upon illumination, O_2 was immediately consumed, and a small amount of CO_2 was produced (Fig. 8). Table 1 shows the amount of O_2 consumed and CO_2 produced in 20 min. No other gas-phase products were detected. The maximum O_2 consumption rate on Pt/TiO_2 was approximately twice and the

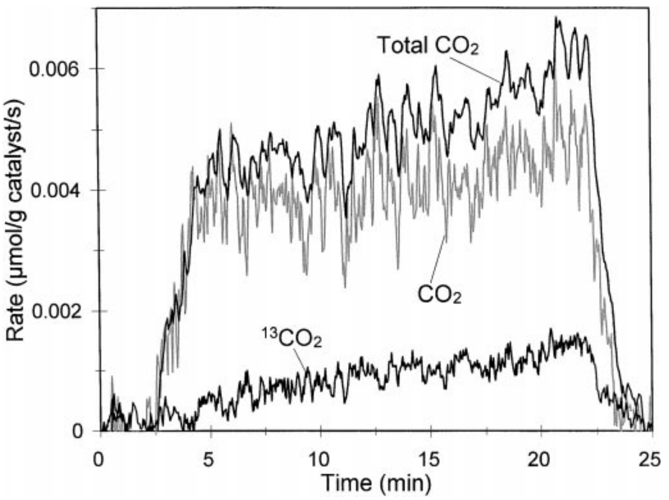

FIG. 8. Carbon dioxide formation during 20-min PCO of toluene (C_6H_5-$^{13}CH_3$) adsorbed to saturation coverage on Pt/TiO_2 at 253 K.

maximum CO_2 production rate on Pt/TiO_2 was approximately 1.5 times the respective rates on unplatinized TiO_2.

When C_6H_5-$^{13}CH_3$ was used during PCO on Pt/TiO_2, CO_2 was produced from both ring carbon ($^{12}CO_2$) and the methyl carbon ($^{13}CO_2$), as shown in Fig. 8. At the beginning of the PCO, $^{12}CO_2$ was preferentially produced, and the $^{12}CO_2/^{13}CO_2$ ratio was 7.5 at 5 min. After 12 min, however, the $^{12}CO_2/^{13}CO_2$ ratio was 3.5, indicating that the methyl C was preferentially oxidized since the $^{12}CO_2/^{13}CO_2$ ratio was less than the stoichiometric ratio of 6.

Temperature-Programmed Hydrogenation of Toluene on Pt/TiO$_2$

The TPH spectra following 20-min PCO of toluene on Pt/TiO_2 and an interrupted TPD are shown in Fig. 9. Methylcyclohexane (MCH) formed in a large peak with a maximum at 410 K and a smaller peak at 575 K. Toluene and benzene formed in two high-temperature peaks, and both CO_2 and CO formed at high temperature. Additionally, ethylene and methane (not shown for clarity) formed during TPH; neither of these species formed during TPH after PCO on TiO_2. Desorption amounts are given in Table 4. Temperature-programmed hydrogenation on Pt/TiO_2 was effective in hydrogenating 95% of the strongly bound intermediates off the surface, so the amount formed during the subsequent TPO was small.

Photocatalytic Oxidation of Benzaldehyde on Pt/TiO$_2$

The PCO of benzaldehyde on Pt/TiO_2 is similar to PCO on TiO_2 (9). Oxygen was immediately consumed (Fig. 10), but the O_2 uptake decayed more rapidly than the O_2 uptake during toluene PCO. Carbon dioxide formed immediately during PCO of benzaldehyde on Pt/TiO_2 and then quickly decayed, and a small amount of benzene was detected during the initial stages (Fig. 10). Benzene production (total of 1 μmol/g catalyst) was negligible after about 8 min. No benzene was detected during toluene PCO on Pt/TiO_2 or benzaldehyde PCO on TiO_2 (9). Oxygen uptake and CO_2 formation amounts are given in Table 1.

Temperature-Programmed Hydrogenation of Benzaldehyde on Pt/TiO$_2$

During TPH of adsorbed benzaldehyde at approximately 55% coverage, benzaldehyde hydrogenated to form mainly MCH in a peak with a maximum at ~450 K. Small amounts of CO, toluene, benzene, and CO_2 also formed during TPH. The amounts desorbed are given in Table 5.

The TPH spectra following 20-min PCO of benzaldehyde at approximately 30% coverage is shown in Fig. 12.

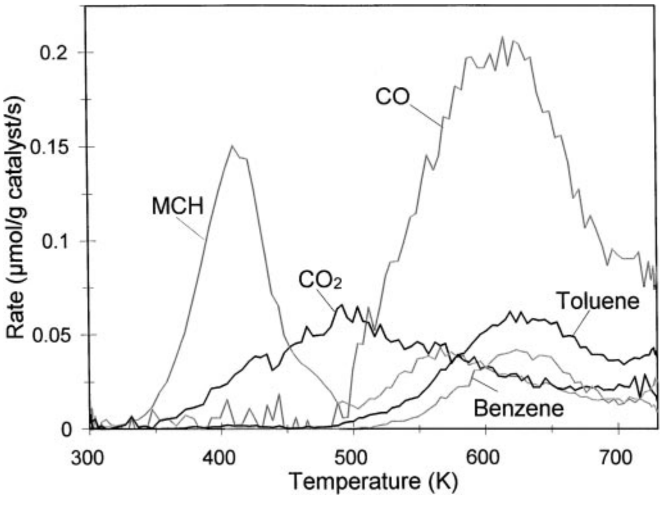

FIG. 9. Temperature-programmed hydrogenation after interrupted TPD and 20-min PCO of toluene, which was adsorbed to saturation coverage at 253 K on Pt/TiO_2.

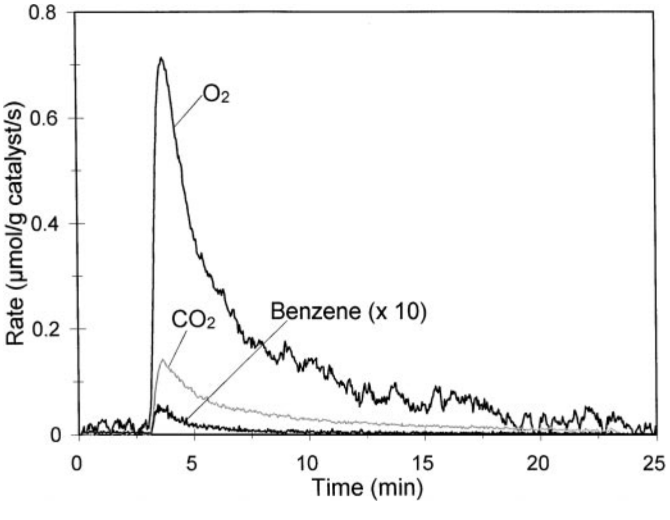

FIG. 10. Oxygen consumption and CO_2 and benzene formation during 20-min PCO of benzaldehyde, which was adsorbed to 60% of saturation coverage at 300 K on Pt/TiO_2.

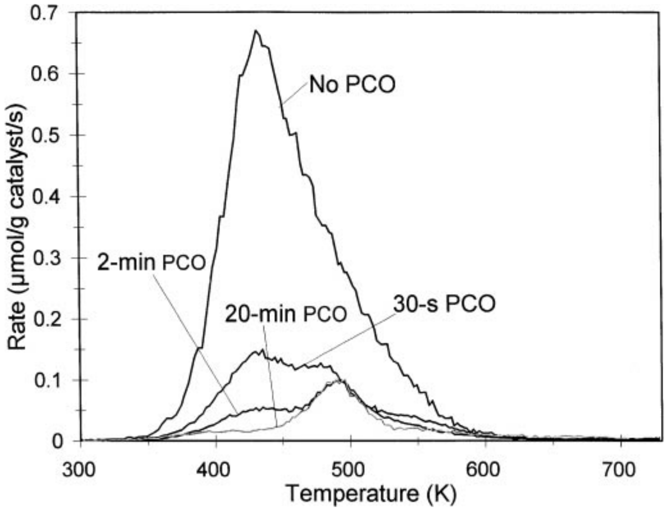

FIG. 11. Methylcyclohexane fomation during TPH of adsorbed benzaldehyde, which was adsorbed to 10–30% coverage at 300 K, and after 30-s, 2-min, and 20-min benzaldehyde PCO.

Although the main hydrogenation product during TPH of adsorbed benzaldehyde was MCH, only a small amount of MCH desorbed during TPH following benzaldehyde PCO. In addition, a significant amount of toluene and benzene formed at high temperatures. Carbon dioxide formed throughout the TPH, and CO was the dominant product and formed in two high-temperature peaks. During TPH following a 10-s PCO of benzaldehyde, methylcyclohexane desorbed in three overlapping peaks with apparent maxima at 420, 480, and 520 K (Fig. 11). Two high-temperature toluene peaks and two benzene peaks were also seen.

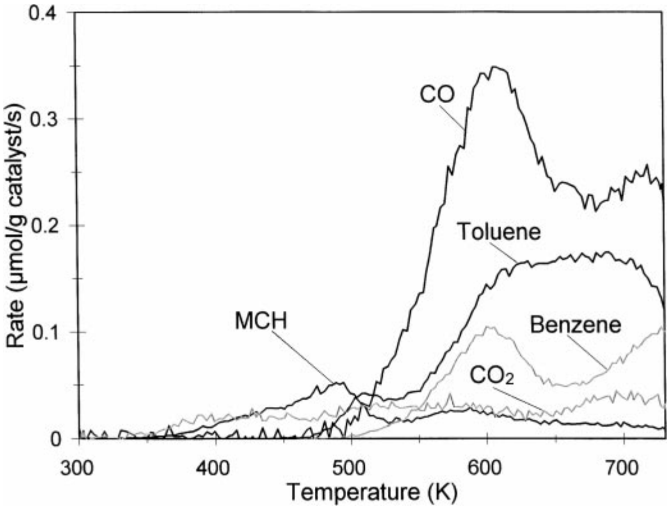

FIG. 12. Temperature-programmed hydrogenation after 20-min PCO of benzaldehyde, which was adsorbed to 30% of saturation coverage at 300 K on Pt/TiO_2.

DISCUSSION

Multiple Forms of Benzaldehyde Adsorption and Different Reactivities

Adsorbed benzaldehyde hydrogenated mainly to MCH, which formed in an asymmetrical peak during TPH on Pt/TiO_2. After only 30 s of PCO, some of the benzaldehyde reacted to surface species that hydrogenate to benzene and toluene at high temperatures. Figure 11 shows the MCH spectra during TPH of adsorbed benzaldehyde and after 30-s, 2-min, and 20-min PCO on Pt/TiO_2. Note that the benzaldehyde coverage differs for the MCH spectra; benzaldehyde was adsorbed to 30% of saturation coverage for TPH of adsorbed benzaldehyde and after 20-min PCO, and benzaldehyde was adsorbed to 10% of saturation coverage for TPH after 30-s and 2-min PCO. The appearance of two distinct MCH peaks after only 30 s of PCO indicates that benzaldehyde adsorbs in more than one form or on more than one type of site. The asymmetrical nature of the MCH peak observed during TPH of adsorbed benzaldehyde is consistent with a large MCH peak at 435 K overlapping a smaller MCH peak at 490 K.

Nagao and Suda (37) concluded that chlorobenzene adsorbs both parallel to the TiO_2 surface through a π-bond interaction and perpendicular to the surface through Cl interaction with surface hydroxyls. Benzaldehyde may also adsorb with its ring both parallel to the surface and perpendicular to the surface through its aldehyde group. Whereas adsorbed benzaldehyde hydrogenated mainly to MCH on Pt/TiO_2, the main hydrogenation products were toluene and benzene on TiO_2. Two overlapping toluene peaks formed during TPH of benzaldehyde on TiO_2 (Fig. 4), and two distinct toluene peaks formed during TPH in 5% D_2 of benzaldehyde on TiO_2 (Fig. 7). The formation of two toluene peaks indicates that benzaldehyde adsorbs in two forms or on two types of reaction sites on TiO_2 catalysts. The lower temperature toluene peak was more highly deuterated than the higher temperature peak. Parallel adsorption of benzaldehyde would provide easier access for exchange and addition of deuterium, resulting in the formation of the more deuterated toluene observed during TPH in 5% D_2. Likewise, deuteration of benzaldehyde adsorbed perpendicular to the surface would be hindered so that this type of benzaldehyde would form the less deuterated toluene.

On Pt/TiO_2, the MCH peaks for both forms of benzaldehyde decreased significantly with PCO; thus, both forms of adsorbed benzaldehyde are reactive. The lower-temperature MCH peak decreased more quickly than the higher-temperature peak, and after 20 min of PCO the lower-temperature peak appeared as a shoulder to the higher-temperature peak (Fig. 11). Therefore, the form of adsorbed benzaldehyde that hydrogenated to the lower-temperature MCH is more reactive than the benzaldehyde that formed the higher-temperature MCH peak. The different forms of benzaldehyde on TiO_2 also react at different rates. The more deuterated toluene decreased faster than the less deuterated toluene with time during benzaldehyde PCO. The benzaldehyde that hydrogenated to the more deuterated toluene oxidized faster.

During benzaldehyde PCO, CO_2 formation almost immediately reached a maximum and then quickly fell (Fig. 10). Thus, a large amount of CO_2 formed as the more reactive benzaldehyde was oxidized, and the CO_2 formation rate decreased as the more reactive benzaldehyde was consumed and oxidation of the less-reactive benzaldehyde became significant. As seen in Fig. 11 after 30 s of PCO, slightly more of the lower-temperature MCH, which corresponds to the more reactive benzaldehyde, formed than the higher-temperature MCH, which corresponds to the less reactive benzaldehyde. After 20 min of PCO, most of the more reactive benzaldehyde had oxidized, but a significant amount of the less reactive benzaldehyde remained on the surface and was hydrogenated to the higher-temperature MCH. Thus, after 20 min, most of the CO_2 formed was from oxidation of the less reactive benzaldehyde, and the CO_2 formation rate was much lower than at the beginning of the PCO.

Intermediates in Toluene PCO

Toluene quickly reacted to form some intermediate, as shown by the immediate O_2 uptake (Fig. 1). This intermediate reacted more slowly to form CO_2 and H_2O. Much less CO_2 formed than O_2 consumed, and since CO_2 adsorption coverage on TiO_2 is low (38), the excess O_2 was incorporated into surface organic species. The PCO of labeled toluene (C_6H_5-$^{13}CH_3$) showed that the ring carbon was oxidized in the initial stages of toluene PCO. At slightly longer reaction times, methyl carbon oxidized preferentially.

The TPH spectra following toluene PCO provide information about the adsorbed intermediates (Figs. 3 and 9). Benzene and toluene are weakly adsorbed on TiO_2 (9) and Pt/TiO_2, so their formation during TPH and toluene PCO is reaction limited. As expected for a fully hydrogenated species, MCH does not significantly adsorb on TiO_2 at room temperature; it is much more weakly bound than toluene, and its appearance during TPH is also reaction limited. The formation of MCH and toluene during TPH suggests that at least one intermediate has a methyl group (or an oxidized methyl group) attached to an aromatic ring. Approximately 60% of the strongly bound surface species on TiO_2 and 75% on Pt/TiO_2 were hydrogenated to toluene and MCH during TPH following 20-min PCO of toluene, so most of the adsorbed intermediates still had an intact aromatic ring with a methyl or oxidized methyl group attached. The complexity of the TPH spectra on TiO_2 and Pt/TiO_2 indicates that more than one intermediate may be on the surface.

Benzaldehyde appears to be an intermediate in toluene PCO, but not the less reactive intermediate responsible for catalyst deactivation. On TiO_2, the toluene that formed during TPH after toluene PCO (Fig. 3) is similar to the lower-temperature toluene peak that formed during TPH of adsorbed benzaldehyde. Likewise, MCH formation on Pt/TiO_2 is similar for TPH of adsorbed benzaldehyde (Fig. 11) and TPH after toluene PCO (Fig. 9). The high-temperature hydrogenation products formed during toluene PCO on Pt/TiO_2 (Fig. 9) did not form during TPH of adsorbed benzaldehyde, but similar high-temperature hydrogenation products form during TPH after benzaldehyde PCO (Fig. 12). The surface species hydrogenated during the TPH after benzaldehyde PCO on TiO_2 (Fig. 5) and Pt/TiO_2 (Fig. 12) appear to be the same surface species on the catalyst surface after toluene PCO (Figs. 3 and 9, respectively). Thus, toluene reacts to form benzaldehyde, which then reacts to form less reactive, strongly bound surface species.

Because toluene adsorbs parallel to the TiO_2 surface, benzaldehyde that is adsorbed parallel to the catalyst surface is expected to form from toluene oxidation. The mass spectra and desorption temperatures of the toluene that formed during TPH in 5% D_2 after toluene PCO (Fig. 6) are comparable to those of the more deuterated toluene that formed at lower temperatures during TPH in 5% D_2 of adsorbed benzaldehyde (Fig. 7). Thus, toluene appears to react predominantly to form benzaldehyde that is adsorbed parallel to the catalyst surface, and little of the toluene forms benzaldehyde that is adsorbed perpendicular to the catalyst surface.

Larson and Falconer (9) concluded that benzaldehyde was not the main intermediate formed during toluene PCO. They found that benzaldehyde reacted to CO_2 at a rate 10 times faster than toluene reacted to CO_2. However, much more benzaldehyde was adsorbed on TiO_2 than toluene in their study, and benzaldehyde PCO was performed at room temperature while toluene PCO was performed at 273 K. In addition, toluene must first react to benzaldehyde; thus, benzaldehyde is expected to react faster than toluene during PCO. They observed that significant amounts of unreacted benzaldehyde desorbed during TPO after benzaldehyde PCO on TiO_2, but only a small amount of benzaldehyde desorbed during TPO after toluene PCO. Our TPH experiments show that benzaldehyde quickly oxidized to less reactive species. Benzaldehyde formed during toluene PCO would also quickly react to less reactive species, and little benzaldehyde would be on the surface during toluene PCO. Thus, the desorption of a small amount of benzaldehyde during TPO after toluene PCO observed by Larson and Falconer (9) is consistent with benzaldehyde as an intermediate in toluene PCO.

Larson and Falconer (9) observed that the PCO of benzyl alcohol was dramatically different from toluene PCO. Benzyl alcohol reacted to form benzaldehyde and CO_2, and more benzaldehyde than CO_2 formed. In addition, CO_2 formation was delayed and did not reach a maximum during

600 s of illumination. Thus, because gas-phase benzaldehyde was not observed during toluene PCO, and because CO_2 formation was higher at longer reaction times, benzyl alcohol does not appear to be an intermediate in toluene PCO. The TPH spectra of benzyl alcohol had similarities to the TPH spectra following toluene PCO (Fig. 3) and the TPH spectra of adsorbed benzaldehyde (Fig. 4). Benzaldehyde probably hydrogenated to benzyl alcohol, which is strongly adsorbed and hydrogenated further to form toluene.

Larson and Falconer (9) also studied the PCO and TPO of cresol since cresols form during PCO of toluene in aqueous solution. Fujihira *et al.* (16) proposed that cresols form from hydroxyl attack on the ring. Hydroxyl radicals are thought to be the reactive species during PCO in the aqueous phase (39), but their role in gas-phase PCO is not well understood. No reaction was detected for adsorbed cresol upon illumination on TiO_2, and subsequent TPO was the same as observed without PCO (9). During TPO of cresol, approximately half of the cresol desorbed intact, and the catalyst turned black. The catalyst color returned to white after extended heating in O_2 at 723 K. Because neither cresol nor a color change was observed during TPO after toluene PCO, cresol does not appear to be an intermediate in toluene PCO.

Benzoic acid has been proposed as the intermediate responsible for catalyst deactivation during PCO of a continuous flow of toluene on TiO_2 (12–14). The authors proposed that benzaldehyde or benzyl alcohol oxidizes to form benzoic acid (12–14). Traces of benzoic acid were detected after toluene PCO using extraction (12–14); however, no mass balance or further analysis of the surface after extraction to confirm that all of the surface species had been removed and identified was reported for any of the studies. Mendez-Roman and Cardona-Martinez (12) also observed benzoic acid on the surface following toluene PCO using FTIR. Augugliaro *et al.* (13) observed that significant amounts of CO_2 and benzene formed during PCO of benzoic acid on anatase. These results suggest that benzoic acid is reactive on TiO_2 and is not the strongly bound intermediate responsible for catalyst deactivation. Because the low volatility of benzoic acid made evaporation and calibration difficult, we did not perform benzoic acid PCO. During TPH of adsorbed benzoic acid, a large amount of benzaldehyde desorbed along with toluene and benzene at high temperatures. Only small amounts of benzaldehyde desorbed after toluene PCO on TiO_2. Thus, though small amounts of benzoic acid may be on the surface during toluene PCO, benzoic acid does not appear to be the less reactive intermediate responsible for catalyst deactivation.

Jacoby *et al.* (10) extracted adsorbed intermediates following PCO of a continuous flow of benzene on TiO_2. Their analysis identified phenol, hydroquinone and/or benzoquinone, and malonic acid as possible intermediates. D'Hennezel *et al.* (14) observed small amounts of hydroxybenzoic acid, hydroxybenzyl alcohol, and hydroxybenzaldehyde following extraction of surface species on TiO_2 after PCO of a continuous flow of toluene. During toluene PCO on several cation-exchanged zeolites, aromatic condensation products formed (40). The amount of these condensation products was dependent on the acidity of the zeolite, and only trace amounts were observed for the less acidic zeolites. No further analysis to determine the reactivity of these species during PCO was performed, but an intermediate similar to the above species observed during extraction may be the less reactive intermediate formed during toluene PCO.

Effect of Pt on Photocatalytic Oxidation

The addition of Pt increased the PCO rate for both toluene and benzaldehyde PCO. Table 6 shows the maximum areal CO_2 formation and O_2 consumption rates on TiO_2 and Pt/TiO_2. The addition of Pt approximately doubled the maximum areal O_2 consumption rates for both toluene and benzaldehyde, but the CO_2 formation rates were only ~1.5 times higher. Thus, Pt increased the initial PCO rate of toluene and benzaldehyde to less reactive intermediates, and it also increased the rate of oxidation of the intermediates to CO_2, but not as much.

Falconer and Magrini-Bair (41) observed that Pt slowed TiO_2 deactivation that resulted during acetaldehyde PCO at high temperatures. They suggested that oxygen spillover from the Pt particles onto the TiO_2 surface oxidized the acetaldehyde reaction products and slowed deactivation. Similarly, oxygen spillover from Pt to TiO_2 may be the reason the toluene and benzaldehyde PCO rates are higher on Pt/TiO_2 than on TiO_2.

In addition to CO_2 formation, a small amount of benzene formed during benzaldehyde PCO on Pt/TiO_2 (Fig. 10). Larson and Falconer (9) did not observe benzene formation during benzaldehyde PCO on TiO_2. The benzaldehyde PCO rate is higher on Pt/TiO_2 than on TiO_2, and only a small amount of benzene formed during PCO. Thus, benzene may have formed during benzaldehyde PCO on TiO_2 without being detected.

TABLE 6

Areal Rates of CO_2 Formation and O_2 Consumption

	Maximum rates × 10^4 (μmol/g catalyst/s)/(μmol/g)			
	TiO_2		Pt/TiO_2	
Adsorbed aromatic	O_2 uptake	CO_2 formation	O_2 uptake	CO_2 formation
Toluene	19	0.5	35	0.65
Benzaldehyde	23	6	47	9

Hydrogenation Reactions on TiO_2

Though TiO_2 is not a typical hydrogenation catalyst, strongly bound surface species were effectively hydrogenated during TPH. Little of the strongly bound surface species desorbed or decomposed during TPD, and thus the information provided by TPD was severely limited. During TPH on TiO_2, however, 80% of the adsorbed intermediates were removed from the surface.

Most studies on TiO_2 in H_2 flow found that TiO_2 is a poor hydrogenation catalyst (42–48). Halliday *et al.* (42) reported that 1,3-butadiene was hydrogenated to butene and some unidentified, strongly bound species; no butane was observed. By replacing H_2 with D_2 in the flow gas, they concluded that self-hydrogenation of 1,3-butadiene formed the butene. In experiments with propadiene in H_2 on TiO_2 (43), they observed that at temperatures below 400 K, isomerization of the propadiene was the main reaction. At higher temperatures, unidentified strongly bound species formed as well as a small amount of propene. They concluded that TiO_2 is not an efficient catalyst for hydrogenation of dienes and alkynes because they react mainly to form strongly bound species that remain on the surface. Propane and isobutane formed propene and isobutene, respectively, when flowed in H_2 over TiO_2 at 750 K (43). About 45% of the isobutane formed strongly bound surface species that did not desorb. Cyclopentane in H_2 flow over TiO_2 resulted in a mixture containing 25% cyclopentane and 25% cyclopentadiene.

Vannice and Poondi (45) saw no hydrogenation of benzaldehyde on TiO_2 (Degussa P25) from 473–723 K. Haffad *et al.* (46), however, observed benzaldehyde hydrogenation on TiO_2 (formed from ex-isopropylate) in both pure He and pure H_2 flow at 573 K. In pure He flow, benzaldehyde converted to toluene and a small amount of benzene. They suggested that the benzaldehyde reacts with surface hydroxyls to form toluene, which desorbs, and a surface benzoate species. A small amount of toluene evolved even after an extended reaction period, suggesting the regeneration of some surface hydroxyl species and the disappearance of surface benzoate species. Haffad *et al.* (46) suggested that benzaldehyde hydrogenation on TiO_2 in H_2 follows the reaction $PhCHO \rightarrow PhCH_2OH \rightarrow PhCH_3 + H_2O$, where Ph is an aromatic ring.

We also observed formation of a small amount of toluene and benzene during TPD at approximately 573 K during TPD of adsorbed benzaldehyde. In their reaction scheme, an adsorbed alkoxy forms toluene by hydrogen transfer and leaves an adsorbed benzoate on the surface, which decomposes to benzene and CO_2. In our study, 3 times as much CO_2 as benzene desorbed during TPD, so although some of the CO_2 may be the result of benzoate decomposition, a significant portion of CO_2 must result from the decomposition of another surface species.

Hydrogenation Reactions on Pt/TiO_2 and Spillover during TPH

For a Pt/TiO_2 catalyst, spillover (49) from the Pt particle to the TiO_2 surface is important in temperature-programmed experiments. During TPH, strongly bound surface species hydrogenate to more weakly bound species that desorb more readily. Because of spillover of H onto the TiO_2 surface, more complete hydrogenation was achieved on Pt/TiO_2, and hydrogenation occurred at lower temperatures.

Ionnides and Verykios (50) explored the interaction of benzene and toluene with Rh dispersed on TiO_2 using TPD and TPH. Their TPD experiments indicated that the aromatics were almost exclusively adsorbed on the support. When Rh/TiO_2 was exposed to H_2 at room temperature, adsorbed benzene readily hydrogenated to cyclohexane, which desorbed at low temperature since it was weakly adsorbed on the surface. On supports without Rh, the aromatic was not hydrogenated in H_2 flow. Thus, Rh provided a site for adsorption and dissociation of H_2, and this spillover hydrogen hydrogenated benzene adsorbed on the support. Toluene exhibited similar behavior in our experiments. Platinum resulted in complete hydrogenation of strongly adsorbed species to MCH at temperatures lower than that at which hydrogenation on TiO_2 occurred.

Vannice and Poondi (45) examined the hydrogenation of a continuous flow of benzaldehyde over reduced Pt/TiO_2 between 333 and 493 K. Benzyl alcohol was the primary product during benzaldehyde hydrogenation, but the amount of toluene and benzene formed increased with higher conversions. Neither cyclohexane nor MCH was detected. In our experiments, in which a monolayer of benzaldehyde was on the surface with no gas-phase benzaldehyde present, no benzyl alcohol was observed, and a significant amount of MCH formed. Vannice and Poondi (45) proposed that benzaldehyde hydrogenated to toluene by the pathway $PhCHO + H_2 \rightarrow PhCH_2OH + H_2 \rightarrow PhCH_3 + H_2O$. Toluene is weakly adsorbed on Pt/TiO_2, and during continuous-flow hydrogenation of benzaldehyde, toluene may be displaced from the surface by gas-phase benzaldehyde before the toluene can hydrogenate to MCH. During TPH of a monolayer of benzaldehyde, toluene was not displaced. In addition, Vannice and Poondi (45) studied benzaldehyde hydrogenation over Pt/TiO_2 catalysts reduced in H_2 flow at 473 and 773 K, and they found that the Pt/TiO_2 catalyst reduced at 773 K was more active for benzaldehyde hydrogenation. In our experiments, the Pt/TiO_2 catalyst was oxidized at the start of TPH, and the catalyst turned a dark blue color characteristic of reduced TiO_2 by the end of the TPH. Differences in the reduction state of the Pt/TiO_2 catalysts may also result in the differences in benzaldehyde hydrogenation observed.

CONCLUSIONS

Temperature-programmed hydrogenation was effective at hydrogenating strongly bound intermediates formed during photocatalytic oxidation (PCO) to more weakly bound species that desorbed during TPH. These strongly bound intermediates did not desorb to a significant extent during TPD. The intermediates formed during toluene PCO have a ring structure with a methyl (or oxidized methyl) group attached. Platinization of TiO_2 increased the toluene PCO rate. Both the ring carbon and the methyl carbon of toluene oxidized during PCO.

Benzaldehyde appears to adsorb in two forms on TiO_2, and these two forms have different reactivities during PCO. Similarities in TPH spectra after benzaldehyde and toluene PCO on both TiO_2 and Pt/TiO_2 indicate that toluene may react through benzaldehyde, which then reacts to form some strongly bound, less reactive intermediate, and this less reactive intermediate does not appear to be benzoic acid. When toluene is oxidized, only one type of adsorbed benzaldehyde forms.

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REFERENCES

1. Walker, A., Formenti, M., Meraiudeau, P., and Teichner, S. J., *J. Catal.* **50**, 237 (1977).
2. Ait-Ichou, I., Formenti, M., Pommier, B., and Teichner, S. J., *J. Catal.* **91**, 293 (1985).
3. Larson, S. A., Widegren, J. A., and Falconer, J. L., *J. Catal.* **157**, 611 (1995).
4. Blake, N. R., and Griffin, G. L., *J. Phys. Chem.* **92**, 5697 (1988).
5. Nimlos, J., Jacoby, W. A., Blake, D. M., and Milne, T. A., *Environ. Sci. Technol.* **27**, 732 (1993).
6. Sopyan, I., Murasawa, S., Hashimoto, K., and Fujishima, A., *Chem. Lett.* **4**, 723 (1994).
7. Peral, J., and Ollis, D. F., *J. Catal.* **136**, 554 (1992).
8. Ibusuki, T., and Takeughi, K., *Atmos. Environ.* **20**, 1711 (1986).
9. Larson, S. A., and Falconer, J. L., *Catal. Lett.* **44**, 57 (1997).
10. Jacoby, W. A., Blake, D. M., Fennell, J. A., Boulter, J. E., Vargo, L. M., George, M. C., and Dolberg, S. K., *J. Air Waste Manage. Assoc.* **46**, 891 (1996).
11. Sitkiewitz, S., and Heller, A., *New J. Chem.* **20**, 233 (1996).
12. Mendez-Roman, R., and Cardona-Martinez, N., *Catal. Today* **40**, 353 (1998).
13. Augugliaro, V., Coluccia, S., Loddo, V., Marchese, L., Martra, G., Palmisano, L., and Schiavello, M., *Appl. Catal. B* **20**, 15 (1999).
14. d'Hennezel, O., Pichat, P., and Ollis, D. F., *J. Photochem. Photobiol. A* **118**, 197 (1998).
15. Fujihira, M., Satoh, Y., and Osa, T., *J. Electroanal. Chem.* **126**, 277 (1981).
16. Fujihira, M., Satoh, Y., and Osa, T., *Nature* **293**, 206 (1981).
17. Lichtin, N. N., and Sadeghi, M., *J. Photochem. Photobiol. A* **113**, 81 (1998).
18. Gratson, D. A., Nimlos, M. R., and Wolfrum, E. J., *in* "Proc. of the 88th Annual Meeting of the Air and Waste Management Assoc.," June 18–23, 1995, San Antonio, TX.
19. Fu, X., Zeltner, W. A., and Anderson, M. A., *Appl. Catal. B* **6**, 209 (1995).
20. Hwang, S.-J., Petucci, C., and Raftery, D., *J. Am. Chem. Soc.* **120**, 4388 (1998).
21. Driessen, M. D., and Grassian, V. H., *J. Phys. Chem.* **102**, 1418 (1998).
22. Fan, J., and Yates, J. T., *J. Am. Chem. Soc.* **118**, 4686 (1996).
23. Fu, X., Clark, L. A., Zeltner, W. A., and Anderson, M. A., *J. Photochem. Photobiol. A* **97**, 181 (1996).
24. Falconer, J. L., and Magrini-Bair, K., *J. Catal.* **179**, 171 (1998).
25. Izumi, I., Fan, F. R. F., and Bard, A. J., *J. Phys. Chem.* **85**, 218 (1981).
26. St. John, M. R., Furgala, A. J., and Sammells, A. F., *J. Phys. Chem.* **87**, 801 (1983).
27. Takahama, K., Sato, T., Yokoyama, M., and Hirao, S., *Nippon Kagaku Kaishi* **7**, 613 (1994).
28. Obee, T. N., *Environ. Sci. Technol.* **30**, 3578 (1996).
29. Blanco, J., Avila, P., Bahamonde, A., Alvarez, E., Sanchez, B., and Romero, M., *Catal. Today* **29**, 437 (1996).
30. Obee, T. N., and Brown, R. T., *Environ. Sci. Technol.* **29**, 1223 (1995).
31. Avila, P., Bahamonde, A., Blanco, J., Sanchez, B., Cardona, A. I., and Romero, M., *Appl. Catal. B* **17**, 75 (1998).
32. Martra, G., Coluccia, S., Marchese, L., Augugliaro, V., Loddo, V., Palmisano, L., and Schiavello, M., *Catal. Today* **53**, 695 (1999).
33. Nimlos, M. R., Wolfrum, E. J., Brewer, M. L., Fennell, J. A., and Bintner, G., *Environ. Sci. Technol.* **30**, 3102 (1996).
34. Haerudin, H., Bertel, S., and Kramer, R., *Faraday Trans.* **94**, 1481 (1998).
35. Matsuda, S., and Kato, A., *Appl. Catal.* **8**, 149 (1983).
36. Luo, S. C., and Falconer, J. L., *Catal. Lett.* **57**, 89 (1999).
37. Nagao, M., and Suda, Y., *Langmuir* **5**, 42 (1989).
38. Luo, S., and Falconer, J. L., *J. Catal.* **185**, 393 (1999).
39. Turchi, C. S., and Ollis, D. F., *J. Catal.* **122**, 178 (1990).
40. Panov, A. G., Larsen, R. G., Totah, N. I., Larsen, S. C., and Grassian, V., *J. Phys. Chem. B* **104**, 5706 (2000).
41. Falconer, J. L., and Magrini-Bair, K., *J. Catal.* **179**, 171 (1998).
42. Halliday, M. M., Kemball, C., and Leach, H. F., *J. Chem. Soc., Faraday Trans. 1* **70**, 1743 (1974).
43. Halliday, M. M., Kemball, C., Leach, H. F., and Scurrell, M. S., *in* "Proceedings, 6th International Congress on Catalysis, London. 1976" (G. C. Bond, P. B. Wells, and F. C. Tompkins, Eds.). The Chemical Society, London, 1977.
44. Kemball, C., *Ann. N.Y. Acad. Sci.* **213**, 90 (1973).
45. Vannice, M. A., and Poondi, D., *J. Catal.* **169**, 166 (1997).
46. Haffad, D., Kameswari, U., Bettahar, M. M., Chambellan, A., and Lavalley, J. C., *J. Catal.* **172**, 85 (1997).
47. Harrison, D. L., Nicholls, D., and Steiner, H., *J. Catal.* **7**, 359 (1967).
48. Dixon, G. M., Nicholls, D., and Steiner, H., *in* "Proceedings, 3rd International Congress on Catalysis, Amsterdam, 1964." Wiley, New Work, 1965.
49. Conner, W. C., Jr., and Falconer, J. L., *Chem. Rev.* **95**, 759 (1995).
50. Ionnides, T., and Verykios, X. E., *J. Catal.* **143**, 175 (1993).