Initial reaction steps in photocatalytic oxidation of aromatics

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Transient reaction at 273 and 300 K was used to study the initial steps in the photocatalytic oxidation (PCO) of benzene, toluene, *p*-xylene, mesitylene, benzyl alcohol, benzaldehyde, and *m*-cresol adsorbed on a thin film of TiO_2 catalyst. Adsorbed aromatics were oxidized by O_2 photocatalytically in the absence of gas-phase aromatics, and the compounds remaining on the surface were characterized by temperature-programmed oxidation and desorption (TPO, TPD). Benzene and methyl benzenes oxidize rapidly at 273 or 300 K to form adsorbed intermediates that are more strongly adsorbed and much less reactive than the original aromatic, which is relatively weakly adsorbed on TiO_2. The catalyst is expected to be covered with these intermediates during steady-state reaction. The rates of PCO of benzene and methyl benzenes to CO_2 are slow relative to complete oxidation of alcohols or chlorinated hydrocarbons. The intermediates do not appear to be alcohols or aldehydes formed by oxidation of a methyl group, nor do they correspond to addition of an hydroxyl to the aromatic ring. Benzyl alcohol oxidizes photocatalytically to benzaldehyde and then to CO_2 and H_2O during PCO, but adsorbed *m*-cresol does not photocatalytically oxidize.

Keywords: transient reaction, photocatalytic oxidation, aromatics, TPD, TPO, intermediates

1. Introduction

Removal or destruction of harmful chemicals that are present in low concentrations in process air streams and indoor air is of growing importance, and heterogeneous photocatalytic oxidation (PCO) is a promising technique for these applications. In PCO, pollutants are oxidized over semiconducting particles (usually TiO_2) illuminated by ultraviolet (UV) or near-UV light. Absorption of photons possessing energy greater than the band gap of the catalyst excites electrons from the valence band into the conduction band. The resulting electron/hole pairs can migrate to the catalyst surface and initiate redox reactions that destroy adsorbed pollutants. Photocatalysis has several advantages over other oxidation processes: (1) high destruction rates at ambient temperature and pressure with low-intensity UV, (2) use of O_2 in air as an oxidant, (3) effective in destroying a broad range of common pollutants, and (4) inexpensive catalyst.

Most gas-phase PCO studies have been carried out under steady-state conditions, and mechanistic information has been inferred from the gas-phase products detected and how they depend on concentrations. Although many pollutants completely oxidize photocatalytically, significant quantities of partially-oxidized products have been observed [1–16]. These products often oxidize much more slowly than the original compound; they can also remain strongly adsorbed and not be detected in the effluent. Their accumulation on the catalyst surface can reduce the catalytic activity [11,17,18], and thus understanding the surface processes and identifying adsorbed species responsible for the slow PCO rates are of interest.

In the current study, transient reaction experiments with mass spectrometric detection were used to investigate PCO of benzene, toluene, *p*-xylene, mesitylene (1,3,5-trimethylbenzene), benzaldehyde, benzyl alcohol, and *m*-cresol adsorbed on TiO_2. Transient PCO was done in O_2/He streams in the absence of gas-phase aromatics using the same procedures described previously for 2-propanol [15]. Transient experiments can provide information about surface processes and reaction mechanisms by separating adsorption, surface reaction, and desorption steps. The absence of gas-phase reactants allows mass balances to determine how much reaction takes place even if gas-phase products do not form. A low concentration of O_2 was used so that O_2 consumption could be measured and included in the mass balance. Toluene PCO was studied most extensively as a representative aromatic and because it is a frequent contaminant of indoor air. Benzene and the other methyl benzenes were used to compare rates to aid in understanding toluene PCO. Photocatalytic oxidations of benzaldehyde, benzyl alcohol, and *m*-cresol were studied because they are possible adsorbed intermediates from the partial oxidation of toluene. After PCO, the UV lights were turned off to stop reaction and the species remaining on the surface were characterized by temperature-programmed oxidation or desorption (TPO, TPD). Surface intermediates that desorb slowly at room temperature can be detected by raising the catalyst temperature in the absence of UV light. The adsorption and oxidation properties of the aromatics were also studied by TPD and TPO.

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During PCO of toluene (80 ppm) in dry air, Ibusuki and Takeuchi [19] detected benzaldehyde (1 ppm) and CO_2 (20 ppm), but toluene reacted much more slowly than propylene and butene. An increase in relative humidity from 0 to 60% resulted in a tenfold increase in CO_2 and a fourfold decrease in benzaldehyde formation. Although benzaldehyde was the only intermediate observed, repeated experiments changed the catalyst color from white to light brown and indicated an accumulation of other intermediates or carbon. In spite of the color change, subsequent experiments produced a constant toluene PCO rate and complete deactivation was not reported. Obee and Brown [20] observed a similar influence of humidity on toluene PCO for feed streams containing less than 10 ppm toluene. The authors also reported an optimal humidity, above which toluene rates dramatically decreased. The optimal humidity was extremely sensitive to the amount of toluene in the feed stream and decreased with toluene concentration. The loss in activity at high humidity was attributed to competitive adsorption between water and toluene. Peral and Ollis [12] also observed that high humidity reduced *m*-xylene PCO rates. Neither study reported the formation of intermediates.

Gratson et al. [21], operating at 50% relative humidity, observed a high conversion of benzene to CO_2 at the onset of PCO, but the rate quickly decreased to a much lower steady-state value. Toluene and xylene behaved similarly, but maintained slightly higher conversions at steady-state. No intermediates were detected. The decrease in the initial rate was attributed to an accumulation of intermediates on the TiO_2 surface, although analyses of used catalysts were not carried out. Jacoby et al. [22] results also suggest that intermediates from benzene PCO accumulate quickly on the catalyst upon UV illumination; carbon dioxide continued to form long after benzene was removed from the feed stream.

More recent studies of toluene PCO [23,24] did not detect gas-phase intermediates in the effluent, but did observe a change in the catalyst color over the course of several experiments. The rate of toluene destruction decreased with time and appeared to correlate with the brown color change. Catalyst deactivation was believed to occur in two stages: an initial rapid decline followed by a more gradual rate reduction. Adsorbed species on a completely-deactivated catalyst were extracted in methanol and analyzed by GC-MS. Several species were present but only benzoic acid was identified. Since initially a deactivated catalyst could be regenerated, but repeated use irreversibly deactivated the catalyst, the type of intermediate appeared to change with time.

In the current study, the initial oxidation of benzene and methyl benzenes is shown to be rapid, and the intermediates that form oxidize at much slower rates. These intermediates are strongly adsorbed and remain on the surface. Their reaction stoichiometry was estimated from O_2 uptake, and the number of oxygen atoms used to form the adsorbed intermediates was small compared to the amount necessary for complete oxidation. Benzaldehyde, benzyl alcohol, and *m*-cresol are shown to be unlikely intermediates in PCO of toluene.

2. Experimental

Transient isothermal reaction and temperature-programmed oxidation and desorption (TPO, TPD) were carried out in an apparatus that was previously described [15]. A thin-film, annular reactor was used to maximize the amount of catalyst that was illuminated during PCO. This photoreactor (fig. 1) consists of two concentric Pyrex cylinders that form an annular region with a 1 mm gap. The outer diameter of the inner cylinder is 2 cm, and the height of each cylinder is 13 cm. The

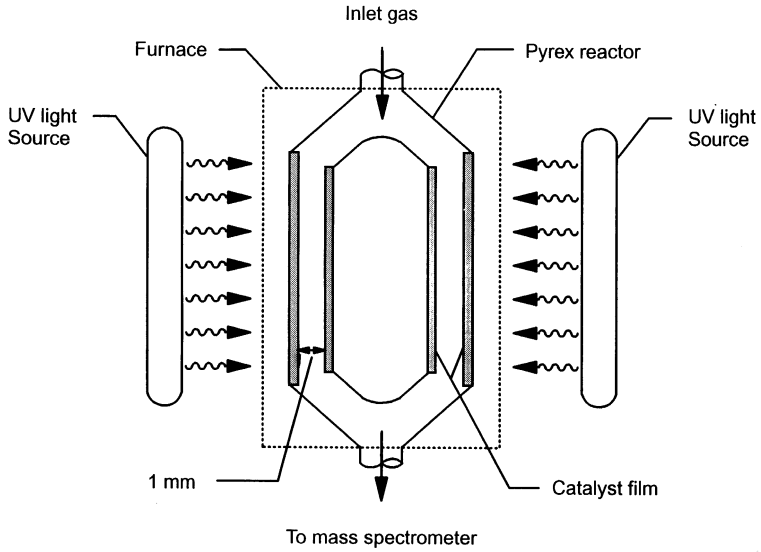

Fig. 1. Schematic of thin-catalytic film, annular reactor for photocatalysis studies.

inner cylinder was evacuated and sealed. An annular photoreactor was used to create a small cross section so that high gas flow rates could be established over the catalyst bed. High flow rates ensured that products desorbing from the catalyst surface were detected quickly. The large diameter of the reactor provided sufficient surface area so that enough catalyst could be deposited on the reactor walls to allow for adequate detection sensitivity by the mass spectrometer.

Degussa P25 titania was used as the catalyst because it consistently provides high PCO activity. This TiO_2 powder consists of non-porous spheres with an average diameter of 30 nm. The specific area is 35–45 m^2/g [25]. Before TiO_2 was deposited onto the reactor walls, the annular region of the photoreactor was washed with a 6 M NaOH solution and rinsed with distilled water. The reactor was then dried and weighed. The NaOH solution roughened the Pyrex surface and increased its ability to hold TiO_2 [26]. Titania was deposited on the photoreactor walls by contacting them with a slurry of TiO_2 in water and then drying the reactor at 373 K. Several slurry applications followed by drying were necessary to deposit an average of 30 mg of TiO_2, which corresponds to a catalyst layer of 0.4 μm average thickness. A TiO_2 thickness of 4.5 μm absorbs 99% of near-UV illumination [27]. Although the catalyst films were not uniform, all the TiO_2 appeared to be illuminated, since TPO after extended PCO detected no unreacted species [15].

The reactor was surrounded by an electric furnace consisting of Kanthal wire wrapped around a quartz cylinder. The wire wrapping was spaced so that the catalyst could be illuminated by six UV lamps (GE F4T5-BLB) positioned evenly around the reactor and furnace at a distance of 2.5 cm from the reactor walls. These 4 W bulbs generate light in the 300–500 nm wave length range (near-UV) with a maximum intensity near 390 nm [28]. A 0.5 mm o.d. chromel–alumel shielded thermocouple was inserted into the annulus so that the tip contacted the catalyst film. Gas flowed continuously over the catalyst at a pressure slightly higher than ambient. Effluent was analyzed immediately downstream from the reactor using a quadrupole mass spectrometer (Balzers, QMA 125) housed in a turbomolecular-pumped, vacuum chamber. A heated, stainless steel capillary diverted some of the effluent into the vacuum chamber for analysis. Computer-controlled data acquisition enabled simultaneous monitoring of selected mass-to-charge ratios, temperature, and elapsed time.

Before each experiment, the catalyst was heated to 723 K in a flowing O_2/He mixture to obtain a reproducible oxide surface. Organics were adsorbed by injecting these liquids into the top of the reactor and allowing them to evaporate into the flowing gas before contacting the catalyst. When benzyl alcohol and *m*-cresol were used, the top of the reactor was heated to speed evaporation, but the catalyst was maintained at 300 K. For benzene and the methylbenzenes (toluene, *p*-xylene and mesitylene), which are weakly adsorbed on the TiO_2 and thus slowly desorb at room temperature, the reactor was cooled to 273 K after adsorption so that both accurate measurements of the amounts adsorbed could be obtained and gas-phase aromatics were not present during PCO. Before the isothermal, transient reaction experiments, the reactor was shielded from the near-UV lights by an aluminum shroud. The lights were then turned on and allowed to warm up for approximately 15 min before removing the shroud. Because the intensity of the lights increased by approximately 5% during the first 10 min of operation, this procedure allowed the lights to reach a constant output before illuminating the catalyst.

Photocatalytic oxidations were carried out at 273 or 300 K for toluene ($C_6H_5CH_3$, Mallinckrodt, 99.9%), benzaldehyde (C_6H_5CHO, Sigma, 99+%), benzyl alcohol ($C_6H_5CH_2OH$ Sigma, 99%), *m*-cresol ($CH_3C_6H_4OH$, Sigma, 99%), benzene (C_6H_6, J.T. Baker, 100%), *p*-xylene ($C_6H_4(CH_3)_2$, Sigma-Aldrich, 99+%), and mesitylene (1,3,5-trimethylbenzene, $C_6H_3(CH_3)_3$, Aldrich 98%). Toluene PCO was carried out for various times in O_2/He mixtures containing either 0.2 or 20% O_2 (100 standard cm^3/min). The other organics were reacted only in 0.2% O_2 for 10 min.

Species that remained adsorbed on the catalyst surface after PCO were analyzed by temperature-programmed oxidation or desorption (TPO, TPD). Temperature-programmed oxidation was also used to study the catalytic decomposition and oxidation of the organics without UV light. During TPO, a 0.2 or 20% O_2/He mixture (100 standard cm^3/min) flowed over the catalyst as the temperature was increased at a constant rate of 1 K/s. During TPD pure He flowed over the catalyst at the same flow rate. The furnace was controlled by a temperature programmer that used feedback from the thermocouple in the reactor. Heating was stopped at 723 K due to difficulties in maintaining a constant heating rate at higher temperatures in the annular reactor and to avoid irreversibly changing the TiO_2 to rutile. Since the rates were not zero at 723 K for benzaldehyde and benzyl alcohol, the reactor was held at 723 K for approximately 20 min until the CO_2 and CO signals dropped to their baseline values.

Desorption rates were obtained from mass spectrometer signals by injecting known quantities of chemicals into the mass spectrometer. These calibrations were carried out in the same gas stream composition as the corresponding experiment. Mass-to-charge ratios unique to desorbed products were monitored whenever possible. Several product signals, however, required correction due to contributions of fragmented ions from other species. Desorption amounts are reported per gram of TiO_2. The catalyst weights were determined by measuring the weights of the reactors before and after depositing TiO_2. Since each reactor weighed 60 g and only approximately 30 mg of TiO_2 were deposited on the reactor walls, pre-

cise catalyst weight measurements were difficult, and this limits the accuracy of the amounts reported.

3. Results

3.1. Temperature-programmed oxidation of aromatics

Benzene and methylbenzenes are relatively weakly bound to TiO_2. The TPO spectra in fig. 2 show that each desorbs starting just above room temperature without decomposing or oxidizing significantly; therefore the same spectra were also obtained during TPD. No gas-phase species other than the original aromatic was observed during TPO or TPD. These aromatics desorbed before TiO_2 reached a sufficiently high temperature to be an oxidation or decomposition catalyst in the absence of near-UV light. Note that the peak temperature increases as the molecular weight increases.

In contrast, the oxygenated aromatics are more strongly bound to the TiO_2 surface, they desorb at higher temperatures, and they undergo reaction during TPO. The parent molecules desorb in broad peaks between 350 and 700 K. Adsorbed benzyl alcohol and benzaldehyde also decompose to CO_2 and CO at temperatures above 650 K.

3.2. Photocatalytic oxidation of benzene, toluene, p-xylene, and mesitylene

Adsorbed benzene, toluene, *p*-xylene, and mesitylene all showed similar PCO behavior. When the catalyst was illuminated at 273 K with UV light in the presence of flowing 0.2% O_2, the O_2 signals immediately dropped, as shown in fig. 3 for mesitylene, but the only products were small amounts of CO_2 (detected after 50–100 s). The rates of O_2 consumption were much greater than the rates of CO_2 formation. In each case, the total amount of CO_2 that formed during 600 s of PCO ($\sim$ 0.6–2.6 μmol/g TiO_2) corresponds to reaction of only $\sim$ 2% of the adsorbed aromatic. The O_2 uptake rate reached a maximum after $\sim$ 30–50 s for the various aromatics and then decayed exponentially. After 600 s the rate of O_2 consumption was 9% of the maximum rate for benzene PCO, and it increased with molecular weight to 22% of the maximum rate for mesitylene PCO. The O_2 signals returned to their initial baseline levels, and the CO_2 desorption rates quickly decreased to zero when the lights were turned off. The amounts of O_2 consumed during the 600 s illumination and the maximum uptake rates are listed in table 1.

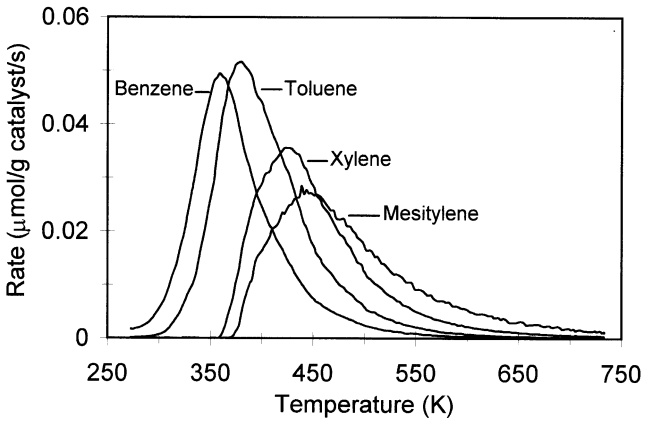

Fig. 2. Temperature-programmed oxidation spectra for benzene, toluene, *p*-xylene, and mesitylene adsorbed on TiO_2.

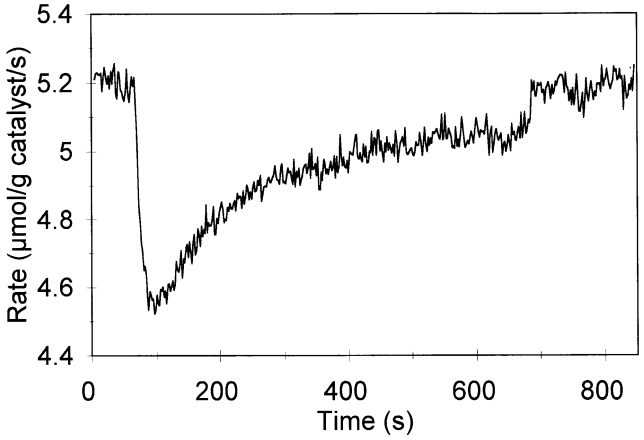

Fig. 3. Change in the O_2 signal for PCO of mesitylene for 130 μmol mesitylene/g TiO_2 adsorbed on TiO_2 at 273 K. The gas flowing over the catalyst was 0.2% O_2 in He.

The TPO and TPD spectra obtained after PCO showed that the O_2 uptake observed during PCO was the result of oxidation of the adsorbed aromatic to an intermediate that remained on the surface at 273 K. The amount of each aromatic that desorbed after PCO was significantly smaller than that observed during TPO or TPD in the absence of UV exposure (table 1). The unreacted aromatics desorbed in the same manner as seen in fig. 2. In addition, H_2O was observed during TPD following PCO whereas none was seen in the absence of UV exposure. Since no other products were seen in significant quantities during TPD, the aromatics apparently were oxidized to H_2O and a strongly-adsorbed intermediate. During TPO in 0.2% O_2, CO_2 and CO formed in addition to H_2O and unreacted aromatic, as shown in fig. 4 for benzene; the spectra for the other aromatics were similar. The CO_2 and CO began forming near 500 K and reached maximum rates at 660–720 K. Water began desorbing at 550–570 K but did not reach a maximum below 723 K. The H_2O spectra are not included in the figures because H_2O formation is limited by desorption, and because calibrations are less accurate for H_2O than the other species. After each TPO, the catalyst was held at 723 K until the H_2O, CO_2, and CO signals decreased to near their baseline levels. The total amounts of species that desorbed during TPO plus while the catalyst was held at 723 K are listed in table 2.

Table 1
Oxygen consumption during PCO at room temperature

Adsorbed aromatic	Amount adsorbed (μmol/g TiO_2)	O_2 consumed in 600 s		Maximum O_2 rate (s^{-1}) $\times 10^3$
		amount adsorbed	amount reacted	amount adsorbed
benzene	34	0.79	0.42	3.8
toluene	75	1.0	0.38	5.1
p-xylene	110	1.3	0.41	5.0
mesitylene	130	1.3	0.36	4.8
benzyl alcohol	270	0.44	–[a]	1.1
benzaldehyde	170	0.48	–[a]	2.3
m-cresol	410	0	–[a]	0

[a] Cannot be measured.

The molecular ratio of O_2 uptake during PCO to reacted aromatic varied between 1.3 and 1.6. The amounts of reacted aromatics were determined by the differences in TPO spectra. Titania is an oxidation catalyst at elevated temperatures in the absence of UV, and thus the CO_2 and CO produced during TPO resulted from catalytic oxidation of the intermediate(s) that had formed during PCO. When TPD instead of TPO was carried out after PCO, only H_2O and unreacted aromatic were observed in significant quantities because oxygen was not available to oxidize the intermediates. The amounts of CO_2 and CO observed during TPO were consistent with the amount of reacted aromatic. A trace amount of benzaldehyde (< 1 μmol/g TiO_2) also desorbed in a peak at 720 K during TPO following PCO of toluene. During TPD following PCO, small amounts of organic products were observed in peaks at 610 and 730 K, but they could not be identified from the cracking fractions because of their small amplitudes. The conversion of toluene to the stable intermediate during PCO was almost identical in 0.2% and 20% O_2, so PCO to form the intermediate appears to be zero order in O_2. A zero-order dependence on O_2 was also observed for PCO of 2-propanol to acetone [15].

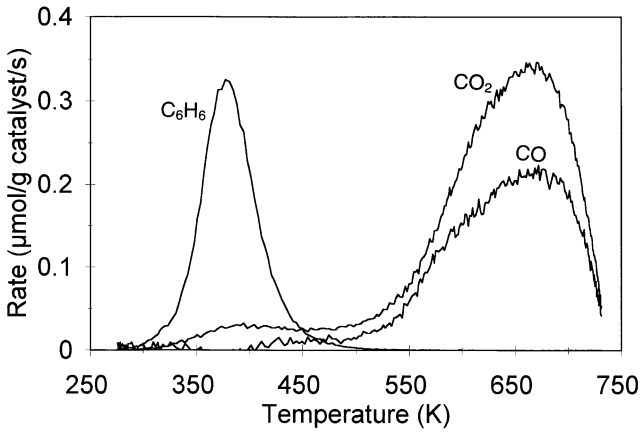

Fig. 4. Temperature-programmed oxidation spectra after PCO of adsorbed benzene for 600 s at 273 K.

A series of toluene PCO experiments was carried out for various illumination times, and TPO in 20% O_2 followed each PCO. The amount of toluene that desorbed during TPO decreased with increased illumination time, and the amounts of CO_2 and CO increased. The differences in the amounts of toluene observed during TPO following PCO and during TPO with no UV exposure were equal to 1/7 of the sum of the CO_2 and CO amounts, as expected from a mass balance. The conversion of toluene during PCO is plotted versus time in fig. 5. Half of the adsorbed toluene reacted within the first 150 s of illumination. The initial reaction rate is first order in toluene; an order of 0.85 in toluene was reported for dilute concentrations (5–190 μmol/ℓ) of toluene in air [29].

3.3. Photocatalytic oxidation of benzaldehyde

Benzaldehyde oxidized to CO_2 during PCO at a much faster rate than benzene and the methylbenzenes oxidized; 26 μmol CO_2/g TiO_2 formed in 600 s of PCO of benzaldehyde. As shown in fig. 6, CO_2 formed as soon as the lights were turned on, quickly reached a maximum rate, and then decreased exponentially. Likewise, O_2 *uptake* increased rapidly, quickly reached a maximum, and then decreased exponentially. When the lights were turned off, the O_2 signal returned to its original level, and CO_2 formation quickly stopped. The TPO spectra after benzaldehyde PCO (fig. 7) show unreacted benzaldehyde with a broad maximum near 510 K, and CO_2 and CO formation above 600 K. Desorption amounts are listed in table 1.

3.4. Photocatalytic oxidation of benzyl alcohol

As shown in fig. 8, adsorbed benzyl alcohol was oxidized photocatalytically at 300 K to benzaldehyde and CO_2. Carbon dioxide formation was delayed relative to benzaldehyde, which had a desorption rate maximum after 250 s. Carbon dioxide formation rate did not reach a maximum during 600 s of illumination. The O_2 uptake (fig. 9) reached a maximum rate after $\sim$ 40 s, but unlike

Table 2
Amounts formed during TPO following photocatalysis for 10 min

Adsorbed aromatic	Amount adsorbed (μmol/g TiO_2)	Desorbed organic	Amount organic desorbed (μmol/g TiO_2)	CO_2 (μmol/g TiO_2)	CO (μmol/g TiO_2)
benzene	34	benzene	13	74	53
toluene	75	toluene	19	240	150
p-xylene	110	*p*-xylene	23	460	220
mesitylene	130	mesitylene	25	660	290
benzyl alcohol	270	benzaldehyde	160	460	170
benzaldehyde	270	benzaldehyde	82	920	410
m-cresol	410	*m*-cresol	190	1100	430

the other organics, it only decreased slightly to a stable rate of 0.2 μmol/(g TiO_2 s), which is much higher than measured during toluene or benzaldehyde PCO. When the lights were turned off, the O_2 signal returned to its original level within 30 s, but the benzaldehyde rate decreased more slowly. The amounts of benzaldehyde and CO_2 that desorbed during PCO were 26 and 4.7 μmol/g TiO_2, respectively.

Benzaldehyde, CO_2, CO and H_2O formed during TPO after PCO of benzyl alcohol (fig. 10). Benzaldehyde desorbed above 350 K in a broad peak that covered almost the entire temperature range. Carbon dioxide and CO formed above 500 K but did not reach maxima by 723 K. The total amounts of desorbed products are listed in table 2.

3.5. Photocatalytic oxidation of m-cresol

When *m*-cresol was adsorbed at 300 K, the TiO_2 turned a faint, but noticeable, yellowish brown. No O_2 was consumed upon UV illumination in 0.2% O_2, and no products desorbed. During TPO after illumination, *m*-cresol desorbed above 500 K in a broad peak centered near 660 K. Carbon oxides formed above 600 K and did not reach maximum rates by 723 K. The amounts desorbed are in table 1. During TPO, the catalyst turned black above $\sim$ 500 K. This color change was subtle at first, but more noticeable by 723 K. Prolonged heating at 723 K in 0.2% O_2 slowly returned the catalyst to its original white. Carbon dioxide and CO formed as the blackened catalyst was held at 723 K, and they did not reach their baseline levels until the catalyst was restored to its original color. Subsequent PCO of other reactants indicated that the catalyst had not been irreversibly altered. Nearly identical TPO spectra and color changes were observed for adsorbed cresol that had not been illuminated, showing that *m*-cresol did not oxidize photocatalytically.

4. Discussion

4.1. Reaction intermediates

Even though significant quantities of gas-phase species do not form during transient PCO of adsorbed aromatics in 0.2% O_2, the O_2 uptake and the TPO and TPD experiments show that the initial step is oxidation of the aromatic to form a stable intermediate. The initial oxidations of benzene, toluene, xylene, and mesitylene are relatively fast, and they form less-reactive intermediates, as indicated by the following:

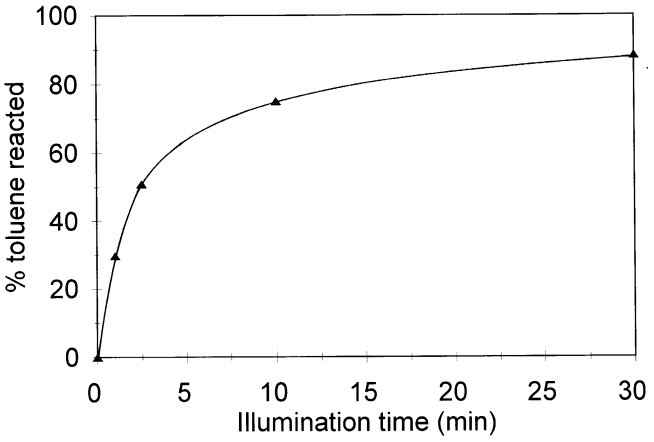

Fig. 5. Percent conversion of toluene during PCO as a function of illumination time.

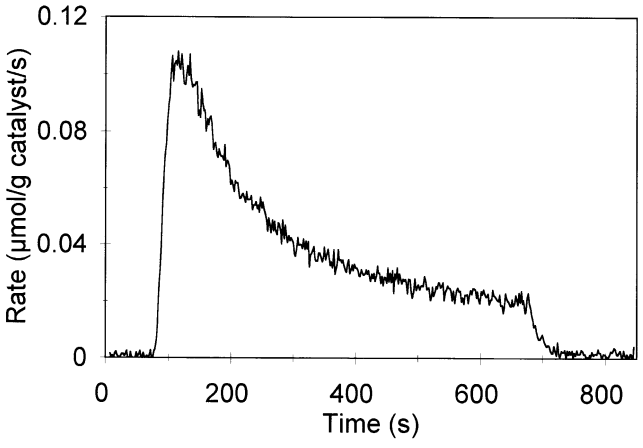

Fig. 6. Formation of CO_2 during PCO of benzaldehyde at room temperature.

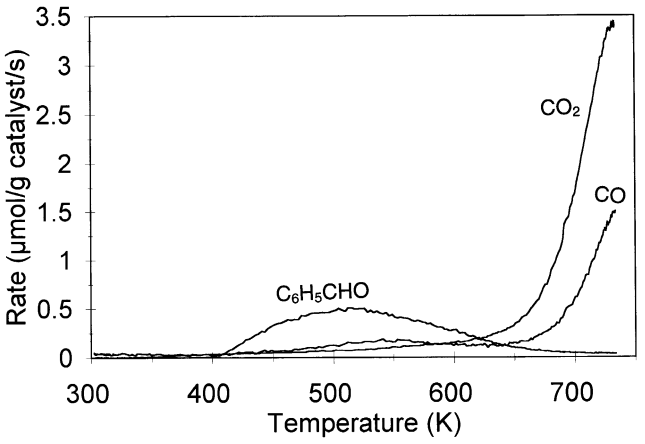

Fig. 7. Temperature-programmed oxidation spectra after PCO of benzaldehyde.

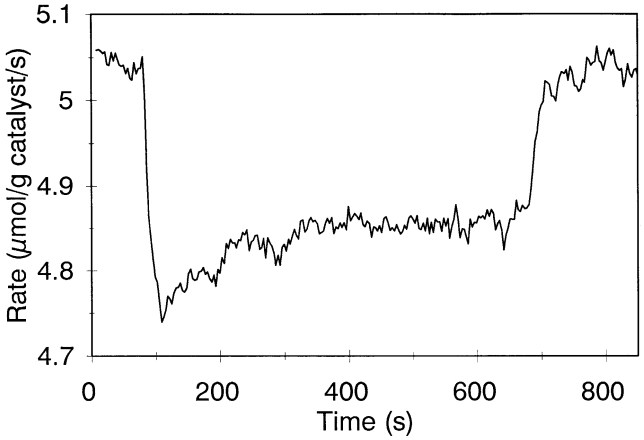

Fig. 9. Change in the O_2 signal for PCO of benzyl alcohol for 270 μmol benzyl alcohol/g TiO_2 adsorbed on the catalyst at 300 K. The gas flowing over the catalyst was 0.2% O_2 in He.

– TPD and TPO both show the amount of aromatic present on the surface decreased significantly after short reaction times.

– Significant O_2 uptake was observed during PCO.

– The amount of H_2O on the surface was higher during TPD after PCO.

– The intermediates that formed during PCO oxidized to CO_2, CO, and H_2O on TiO_2 at elevated temperature in the absence of UV, and the intermediates did not desorb by 723 K in the absence of O_2, whereas the aromatics desorbed at much lower temperatures instead of reacting during TPO.

Water was seen during TPD after PCO, but essentially no gas-phase products formed during PCO. The amount of water seen during TPD is less than expected if the initial oxidation formed a dehydrogenated aromatic and H_2O, both of which remained on the surface during PCO. Thus, the intermediates are likely to be oxygenated aromatics or ring compounds. The intermediates are not adsorbed CO_2 and CO because these species are weakly adsorbed on TiO_2 and desorb at low temperatures [30].

The O_2 uptake is not due to O_2 photo-adsorption, since the amount of O_2 consumed correlated directly with the amount of adsorbed aromatic, and no O_2 was adsorbed during UV illumination without pre-adsorbed organics. After extended PCO, essentially all the aromatics were oxidized to CO_2 and H_2O.

After the exponential decrease in O_2 concentration during the PCO, O_2 consumption leveled off by $\sim$ 450 s, and was relatively constant with higher rates observed for high coverages. The rates of O_2 uptake between 450 and 600 s are 20 to 50 times higher than the rates of CO_2 formation during this time. Thus, the intermediates continued to oxidize but at a slower rate than the original aromatics. At steady-state, a TiO_2 catalyst would be covered almost completely with these intermediates and contain only small amounts of the original aromatics. For example, only one fourth as much toluene adsorbed on a TiO_2 sample that had undergone PCO of adsorbed toluene for 30 min.

The atomic ratios of oxygen consumed during 600 s

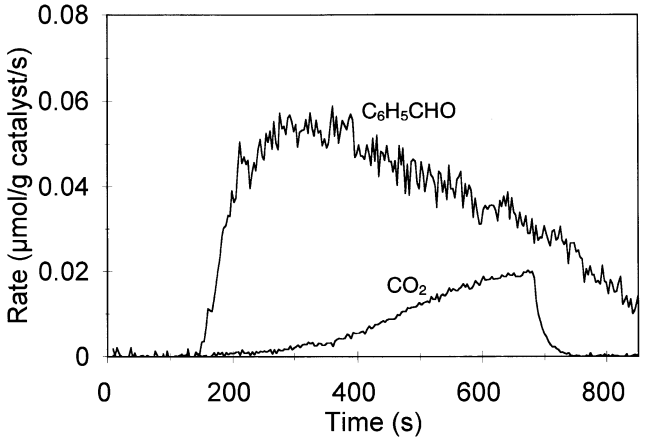

Fig. 8. Products as a function of time during PCO of adsorbed benzyl alcohol at 300 K.

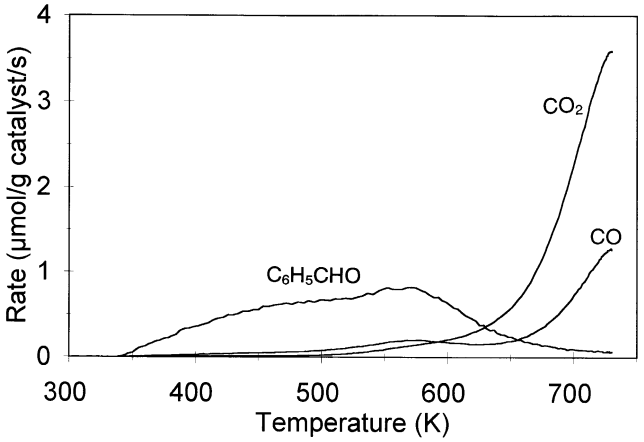

Fig. 10. Temperature-programmed oxidation spectra after PCO of benzyl alcohol.

of PCO to carbon in the *reacted* aromatic (determined from differences in TPO spectra) were between 0.36 and 0.42 for benzene and the methyl benzenes (table 1). These O/C ratios are remarkably similar given the differences in adsorbed aromatics and coverages, and suggest that a similar type intermediate forms for the benzene and methyl benzenes. These ratios are much smaller than needed for complete oxidation (2.5–2.7), and correspond to the reaction of approximately three oxygen atoms for each aromatic molecule. Since the ratios are similar even though the number of methyl groups varied from zero to three, reactions at multiple methyl groups to form the intermediate is unlikely. Some of the oxygen consumed is probably incorporated into the aromatic, and the rest forms water with the hydrogen atoms that are removed.

4.2. Oxygen-containing intermediates

The differences in behavior of the intermediate(s) formed during PCO of toluene and the oxygen-containing aromatics studied indicate that benzaldehyde, benzyl alcohol, and cresol are not likely to be the less-reactive intermediates that form during toluene PCO. Toluene reacts rapidly with O_2, but its intermediates oxidize slowly to CO_2; in contrast, adsorbed benzaldehyde forms CO_2 at a rate that is 10 times faster than toluene forms CO_2. Moreover, when PCO of benzaldehyde is interrupted, unreacted benzaldehyde desorbs during a subsequent TPO, but only very small amounts of benzaldehyde desorb during TPO following toluene PCO. Similarly, benzyl alcohol is not the less-reactive intermediate that forms during toluene PCO since benzyl alcohol reacts (as determined from O_2 uptake) 20–30 times faster than toluene at long times, and benzaldehyde desorbed from the surface *during* PCO. For toluene PCO, no benzaldehyde was detected during PCO.

Cresols form during PCO of toluene in aqueous solution, but they have not been detected during gas-phase PCO. Fujihira et al. [31] suggested cresols form from hydroxyl radical attack on the ring. Hydroxyl radicals are considered to be the reactive species for aqueous PCO [32], but their role in gas-phase PCO is debated. Whereas the intermediates that formed during toluene PCO slowly oxidized to CO_2 and H_2O, adsorbed *m*-cresol did not consume O_2 during UV illumination; no gas-phase products were observed during PCO, and the subsequent TPO was the same as observed without UV illumination. Also, approximately half the adsorbed *m*-cresol desorbed intact, and the catalyst turned black during TPO, but neither cresol nor a color change were observed during TPO after toluene PCO. This color change is probably due to polymerization of *m*-cresol to form polyphenolic compounds. Thus *m*-cresol does not appear to be the intermediate that forms during PCO of toluene.

One possible intermediate of toluene PCO that was not tested was benzoic acid. Its low volatility made evaporation and calibration difficult. Luo and Ollis [24] identified benzoic acid on a deactivated catalyst following repeated toluene PCO experiments. Also, the ratio of oxygen atoms consumed to carbon atoms reacted (7 times the amount of reacted toluene) is 0.38, which is close to that expected value of 0.43 (3/7) for benzoic acid formation from toluene. However, benzoic acid was not detected during PCO nor during TPO or TPD after PCO. Moreover, benzoic acid probably forms through benzyl alcohol and benzaldehyde intermediates. Since these are not the stable intermediates in this study, benzoic acid is probably not present on the catalyst in significant quantities during PCO.

We cannot eliminate the possibility that some of the above oxidized species form during PCO of toluene. They may form during oxidation of the stable intermediate, or they may form in a minor, parallel pathway and be present on the surface in low concentrations. However, they do not appear to be the stable intermediate that forms in the initial stage of toluene PCO.

Another possible stable intermediate, proposed by Ollis [33], is an aromatic peroxide where O_2, perhaps in the form of O_2^- or HO_2 radical [2,3,6,34–36], is inserted between a C–H bond. We observed 20–40% more O_2 consumed than required for peroxides, but peroxides could have formed and some of them reacted further during 10 min of PCO. Also, since some sites on the surface may be more active than others, the intermediates may have reacted further on these sites.

4.3. PCO of benzyl alcohol

Benzaldehyde forms as an intermediate during PCO of benzyl alcohol, since it desorbs during PCO and during subsequent TPO. The O_2 uptake rate was slower for benzyl alcohol than for benzaldehyde for the same surface coverage, so benzyl alcohol initially reacts slower than benzaldehyde. For longer PCO times (> 150 s), however, the O_2 uptake did not decrease as rapidly for benzyl alcohol and was approximately 2–3 times higher than that for benzaldehyde PCO. This suggests that benzyl alcohol or its intermediates react faster than benzaldehyde. Thus, more than one parallel reaction pathway may take place with only part of the alcohol reacting to the aldehyde [37]. Aldehyde formation during PCO of alcohols has been reported for several alcohols [2,4–7,9–12,16]. Some of the weakly adsorbed aldehydes can be displaced into the gas phase by the alcohol or the H_2O product when the surface becomes saturated [2,15]. Benzaldehyde formation was delayed by approximately 70 s after UV illumination is started in fig. 8, presumably

because the catalyst surface was not saturated at the onset of illumination.

5. Conclusions

The first step in photocatalytic oxidation (PCO) of benzene, toluene, *p*-xylene, and mesitylene is fast (half-life of 2.5 min for toluene at 273 K and in 0.2% O_2) and forms less reactive intermediates. The intermediates are much more strongly bound to TiO_2 than the original aromatics, which are relatively weakly bound, and the surface is expected to be covered with these intermediates at steady-state. No gas-phase products form in the first step. The intermediates do not appear to be aldehydes or alcohols formed by reaction with the methyl groups, nor do they appear to have an hydroxyl attached to the ring. On average, approximately three oxygen atoms were consumed per aromatic molecule in this initial step. The intermediates slowly oxidize to CO_2 and H_2O in subsequent steps. Benzyl alcohol oxidizes photocatalytically to benzaldehyde, which eventually forms CO_2, but a parallel path may also exist. Adsorbed *m*-cresol does not undergo PCO on TiO_2.

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