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Aldol condensation of acetaldehyde to form high molecular weight compounds on TiO_2

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Temperature-programmed desorption, hydrogenation, and oxidation are used to show that acetaldehyde undergoes continued aldol condensation beyond crotonaldehyde formation on Degussa P-25 titania to form hexan-2,4-diene-al and higher molecular weight compounds containing conjugated C=C bonds. Aromatic compounds also form, and at higher temperatures coke forms. Degussa P-25 TiO_2 has more sites that catalyze chain propagation reactions beyond formation of C_4 species than do pure anatase or rutile surfaces. These reactions may be responsible for deactivation observed during photocatalytic oxidation of acetaldehyde at elevated temperatures.

Keywords: titania, aldol condensation, aromatics, deactivation, TPH

1. Introduction

Aldehydes, which form during alcohol oxidation or carboxylic acid reduction, play an important role as intermediates in organic reactions. Reactions of aldehydes have been extensively investigated, including Cannizzaro-type reactions to carboxylates plus alcohols by disproportionation [1–3], selective reduction to alcohols [4], selective oxidation to carboxylic acids [5], condensation reaction [1,6–12], and reductive coupling [11–14].

Two aldehyde molecules can react to form C–C bonds through aldol condensation or reductive coupling. With an acid or base catalyst, such as on metal oxide surfaces, two molecules of aldehyde or ketone can combine to form a β-hydroxyl aldehyde or ketone, which is easily dehydrated to form a new aldehyde or ketone with the carbonyl group conjugated with a carbon–carbon double bond [15].

Idriss et al. [1] reported that, when acetaldehyde adsorbs on TiO_2, lattice oxygen acts as a base to abstract a proton from the α position of the aldehyde to form $–CH_2CHO$, a nucleophilic species, which can attack the electrophilic carbonyl group of another aldehyde to form an adsorbed aldol. The aldol then dehydrates to crotonaldehyde. As shown by selectivity and mechanism shifts on oxidized and reduced $TiO_2(001)$ surfaces [11], aldol condensation to crotonaldehyde and crotyl alcohol takes place more readily on oxidized TiO_2, which contains more surface oxide anions. Reduced surfaces facilitate the formation of butene, the product of reductive coupling.

Acetaldehyde reactions on TiO_2 are also of interest since acetaldehyde is an intermediate during photocatalytic oxidation of ethanol on TiO_2 at room temperature [16,17]. Moreover, when acetaldehyde oxidizes photocatalytically on TiO_2 (Degussa P-25) at elevated temperature, the catalyst rapidly deactivates, and the deactivation reaction takes place even in the absence of UV irradiation [18]. Acetaldehyde apparently decomposes or reacts to form surface species at 363 K faster than they can be oxidized photocatalytically. In contrast, at 300 K, these surface species oxidize faster than they form.

Muggli and Falconer [19] used acetaldehyde decomposition at much higher temperature to form species that selectively poisoned TiO_2 for photocatalytic oxidation. During temperature-programmed desorption (TPD) of acetaldehyde on Degussa P-25 TiO_2, they reported that less than 10% of the adsorbed acetaldehyde formed gas-phase products by 723 K; some acetaldehyde desorbed, a small amount of crotonaldehyde formed, and CO and CO_2 formed. Most of the carbon in the original acetaldehyde remained on the surface after TPD. This behavior was not observed on TiO_2 from other sources, and, instead, Idriss et al. [1] and Idriss and Barteau [11] observed that most of the acetaldehyde adsorbed on their TiO_2 formed gas-phase products during TPD. Similarly on oxidized rutile and anatase TiO_2 samples, Rekoske [20] observed that 95% of adsorbed acetaldehyde formed gas-phase products during TPD. Thus, Degussa P-25 exhibits significantly different TPD behavior for acetaldehyde, and it is also one of the best forms of TiO_2 for photocatalytic oxidation of organics.

The objective of the current study is to determine what additional reactions take place on Degussa TiO_2 during TPD and to try to identify the species that form on the surface. Since these species may have multiple carbon–carbon double bonds and be strongly bound to the surface, temperature-programmed hydrogenation (TPH) was used in an attempt to hydrogenate surface species to more weakly bound molecules that desorb. Thus, the idea was to use TPH to remove more surface species than could be removed during TPD. The TPH was carried out above atmospheric pressure to further increase the rate of hydrogenation. Titania is not a good hydrogenation catalyst, but it hydrogenates organics at elevated temperatures [21,22]. Temperature-programmed oxidation (TPO) was used after TPH to determine how much carbon-containing species remained on the surface after TPH and to estimate C/H stoichiometries of surface species; surface species oxidize to CO_2 during TPO even if they are not removed during TPH. The total amount of acetaldehyde originally adsorbed on the TiO_2 was also measured by TPO.

2. Experimental methods

Temperature-programmed desorption (TPD), hydrogenation (TPH), and oxidation (TPO) were performed on Degussa P-25 TiO_2. A packed-bed, tubular reactor (7 mm ID) made of quartz was used with a quartz frit to support the catalyst. About 50 mg of TiO_2 was placed on quartz wool, which was on the reactor frit, and additional quartz wool was also placed on top of the catalyst bed. Temperature was measured with a chromel–alumel thermocouple placed in the center of the catalyst bed. To create a reproducible surface, the catalyst was oxidized in 20% O_2 (balance He) at 723 K for 30 min before each experiment, and the flow was switched to He before the catalyst was cooled to room temperature. The temperature was not increased above 723 K if additional experiments were to be done on the TiO_2 sample, because anatase can undergo a phase change to rutile at higher temperatures. The TiO_2 was saturated with acetaldehyde by injecting excess acetaldehyde gas upstream of the reactor at room temperature in He flow.

The effluent from the reactor was sampled by a Balzers quadrupole mass spectrometer through a capillary. A computer allowed the temperature and multiple mass peaks to be detected simultaneously. A backpressure regulator downstream of the reactor was used to increase the reactor pressure and increase the pressure in the mass spectrometer chamber, and this increased the sensitivity. For TPH, the pressure was maintained at 3 atm, whereas TPO and TPD were carried out at ambient pressure. For all temperature-programmed reactions, the catalyst temperature increased from room temperature to 723 K with a ramp rate of 1 K/s, and the gas flow rate was 100 cm^3/min (STP). For TPH pure H_2 was used, for TPD pure He was used, and for TPO 20% O_2 in He was used.

3. Results and discussion

3.1. TPH of acetaldehyde on TiO_2

The TPH spectra for saturation coverage of acetaldehyde are composed of the same products reported previously by Idriss et al. [1,11] for TPD on several types of TiO_2. As shown in figure 1, both acetaldehyde ($m/e = 29$) and crotonaldehyde ($m/e = 70$) desorb in peaks with maxima around 400 K. Butene ($m/e = 56$) forms with a shoulder at 660 K and a peak that is not complete when heating was stopped at 723 K, and butadiene ($m/e = 54$) forms in two peaks at 550 and 650 K. In addition to these products, which were reported previously for TPD on other TiO_2 samples, a small amount of acetone ($m/e = 58$) forms with a maximum near 700 K, and CO_2 (not shown) also desorbs at this temperature. Water (not shown) desorbs in a wide peak from 400 to 723 K. However, in contrast to results reported by Idriss et al., much of the adsorbed acetaldehyde on Degussa P-25 TiO_2 does not form gas-phase products during TPH. Forty-two percent of the original acetaldehyde remained on the surface in some form after TPH; after TPD about 67% remained, and thus TPH is useful for removing more surface species than TPD. Muggli and Falconer [19] reported that 90% of the acetaldehyde remained on the surface, but we used TPO for both the monolayer of acetaldehyde and after TPD to obtain more accurate measurements. Surface reactions during both TPD and TPH form species that are sufficiently strongly bound that they do not desorb by 723 K, the maximum temperature that could be used without changing the TiO_2 crystal structure.

The products amounts and locations appear to depend on the type of TiO_2 and its pretreatment. Idriss et al. [1,11] reported butene formed at 500–550 K on rutile TiO_2(001), and they also observed two desorption peaks for butadiene at 530 and 620 K from TiO_2 powder (American Instrument Co., anatase, BET surface area 10.3 m^2/g, pretreated in He flow at 800 K for 2 h), but the relative amplitudes of the two peaks were different from those in figure 1. When TPD and TPH of a sample of the American Instruments Co. anatase TiO_2 was run in our system, the results [23] were essentially the same as reported by Idriss et al. Thus,

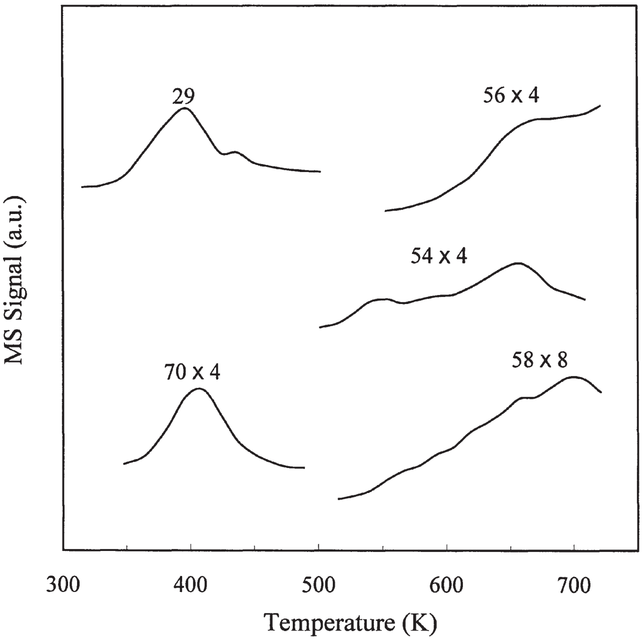

Figure 1. TPH spectra (smaller m/e values) for saturation coverage of acetaldehyde on TiO_2 (Degussa P-25).

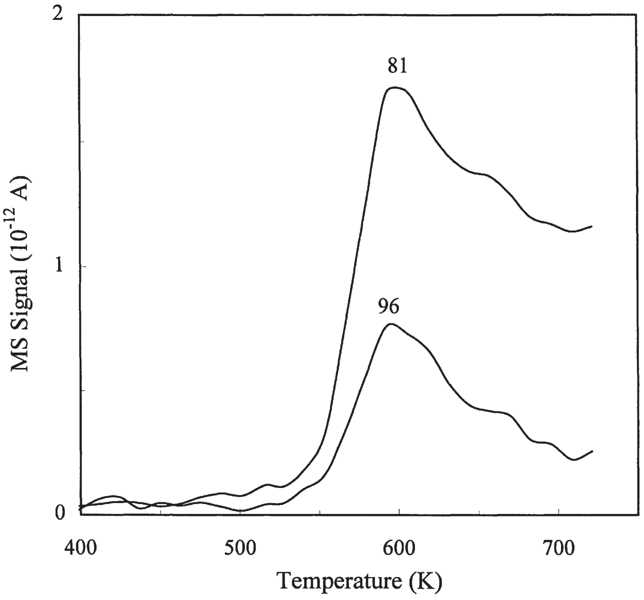

Figure 2. TPH spectra ($m/e = 81$ and 96) for saturation coverage of acetaldehyde on TiO_2 (Degussa P-25).

the differences in the behavior of the TiO_2 samples are not due to different procedures from those used by Idriss et al. The formation of both butene and butadiene on Degussa P-25 might be attributed to its different crystal structure or impurities. Degussa P-25 is a mixture of 75% anatase and 25% rutile and contains residual amounts of SiO_2 and Al_2O_3, and trace amounts of Fe_2O_3 [24]. Simultaneous desorption of acetone and CO_2, though in small amounts, indicates that acetate formed, probably as an O_2 contaminant, which either was introduced by acetaldehyde injection or was left from the TPO gas, oxidized a small amount of the acetaldehyde.

Crotonaldehyde and crotyl alcohol form by aldolization of acetaldehyde, whereas reductive coupling was reported to form butene and butadiene [1,13]. Bimolecular ketonization of acetic acid form acetone. Though no molecules desorbed with more than four carbon atoms in previous TPD studies with acetaldehyde on other types of TiO_2, we detect larger molecules from Degussa P-25 during TPH at 3 atm and during TPD. As shown in figure 2, a product with m/e fragments at 96 and 81 (and smaller peaks at m/e of 67 and 29) desorbs with a maximum near 600 K. The m/e 96 and 81 signals are not from species formed by recombination of smaller fragments in the mass spectrometer since no other compounds had maxima around this temperature. The most reasonable assignment for this species is hexan-2,4-diene-al, $CH_3CH{=}CHCH{=}CHCHO$. This can be synthesized via further aldolization of crotonaldehyde with acetaldehyde:

$$CH_3CH{=}CHCHO + CH_3CHO \rightarrow CH_3CH{=}CHCH{=}CHCHO + H_2O$$

Further aldolization of hexan-2,4-diene-al may form C_8 and higher molecules that are too strongly bound to desorb from TiO_2 by 723 K. Besides the reaction of carbonyl groups, the addition reaction of $-CH_2CHO$ to α–β unsaturated bonds might form branched, long-chain compounds. The formation of these larger molecules on Degussa P-25 would explain why much of the acetaldehyde does not form gas-phase products during TPD. Apparently, Degussa P-25 has more sites that catalyze chain propagation reactions beyond formation of C_4 species. As the temperature increases during TPD or TPH, chain growth is faster than desorption, and this is probably responsible for the catalyst deactivation observed during photocatalytic oxidation of acetaldehyde at 363 K on Degussa P-25 [18]. This oligomerization is also the reaction that selectively poisons the TiO_2 surface at elevated temperature so that partial oxidation products are favored during photocatalytic oxidation at room temperature [19]. The much higher activity of Degussa P-25 for formation of longer chains may be because Degussa P-25 has a higher concentration of acid sites (as measured by pyridine adsorption) and a higher concentration of adsorbed acetaldehyde [23]. More acid sites and more acetaldehyde molecules per nm^2 would both favor these bimolecular reactions.

Table 1
Assignment of fragments.

Fragments	Possible compound
120, 119, 105	Propylbenzene, methylethylbenzene, trimethylbenzene, or acetophenone
106, 105, 91	Ethylbenzene or xylene
92, 91, 77	Toluene
80, 79, 77, 52	Hexatriene or cyclohexadiene
78	Benzene
70, 55	Pentene

As mentioned above, crotonaldehyde forms by attack of a nucleophilic species, $-CH_2CHO$, to a carbonyl carbon of an adsorbed acetaldehyde. The similar reaction of $-CH_2CHO$ with a carbonyl carbon of crotonaldehyde can form hexan-2,4-diene-al. To confirm this, TPH of crotonaldehyde was carried out, and no fragment at $m/e = 96$ was observed; as expected, hexan-2,4-diene-al cannot form from two crotonaldehyde molecules.

In addition to hexan-2,4-diene-al, other molecules larger than crotonaldehyde also form, and mass fragments with m/e up to 134 are detected. The masses and their assignments are listed in table 1. As shown in figure 3, a series of peaks with fragments at m/e of 67, 77, 79, 91, and 105 appear at 550 K, but do not reach their maxima by 723 K. These fragments might represent the following cations: pentadienyl (67), phenyl (77), hexatrienyl or cyclohexadienyl (79), benzyl (91), and phenylethyl or xylenyl (105). These cations suggest that alkylbenzenes and long-chain alkenes form during TPH and desorb. Most of these products desorb as broad peaks that do not reach maxima by 723 K. Since adsorbed benzene or ethylbenzene desorbs with peaks near 450 K [25], formation of these alkylbenzenes during acetaldehyde TPH is reaction-limited. The same mass signals were also seen during

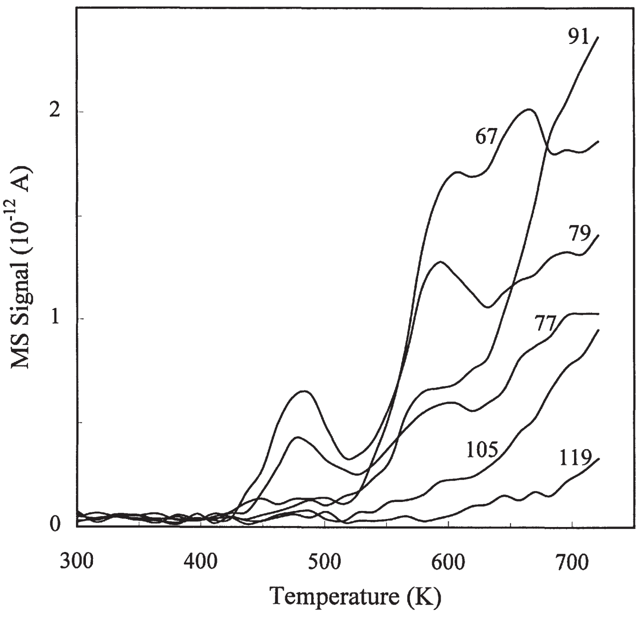

Figure 3. TPH spectra (larger m/e values) for saturation coverage of acetaldehyde on TiO_2 (Degussa P-25).

TPD, but in smaller amounts and likely result from self-hydrogenation. Thus oxygenated or unsaturated surface species may hydrogenate to form these alkylbenzenes and alkenes.

These larger mass fragments do not form by recombination of smaller fragments in the mass spectrometer since they cannot be formed from fragments of butene, butadiene, and acetone, which are the main smaller products in this temperature range. For one TiO_2 sample, TPD was carried out to 850 K, and the alkylbenzene maxima were higher than 800 K, but butene, butadiene, and acetone were not detected at this temperature.

3.2. Stoichiometry

The H/C stoichiometries of adsorbed species were measured from the amounts of CO_2, CO, and H_2O that formed during TPO after various treatments. For a saturation coverage of acetaldehyde at room temperature, TPO yielded a H/C ratio of 1.9 ± 0.1. This is essentially equal to the H/C stoichiometry of 2.0 for acetaldehyde, and suggests that acetaldehyde adsorbed without undergoing significant reaction to gas-phase products at room temperature. It also suggests that TPO can be an effective way to determine the average surface stoichiometry. The H/C value is probably lower than 2.0 because of experimental accuracy, though aldol condensation near room temperature could have formed H_2O [26], which then desorbed.

To determine what species are on the surface after aldol condensation takes place at higher temperatures, TPH was carried out to 500 K for TiO_2 that was saturated with acetaldehyde, and the TiO_2 was then held at 500 K for 30 min before switching the flow to He and cooling the sample to room temperature. Water desorbs in two peaks at 400 and 500 K during TPH, and the H_2O is probably the product of aldolization and dehydration. During the subsequent TPO, the H/C ratio is only 1.1, and this lower value than seen for acetaldehyde is due to H_2O desorption. Since some H_2O from aldolization may remain on the surface after TPH, the H/C ratio of the organic surface species may be lower than 1.1. Thus, the organic surface species after TPH to 500 K have conjugate C=C bonds that form through continued aldolization and dehydration. For crotonaldehyde, the H/C ratio is 1.5, and the ratio decreases to 1.0 as the chain gets sufficiently long. The surface may be composed of a mixture of a coke structure and these surface species with conjugate C=C bonds and H/C ratios of 1.5–1.0.

Temperature-programmed hydrogenation of a saturation coverage of acetaldehyde was carried out to 723 K, and the TiO_2 was held at 723 K for 30 min before switching the flow to He. The subsequent TPO had a H/C ratio of 0.7. Thus, much of the carbon is not removed from the surface by TPH to 723 K, though it is removed by TPO to 723 K. Surface species with H/C ratios from 0.5 to 1.0 are typical of coke, and the aromatic rings seen during TPH are also indicative of the formation of coke-type surface species. The surface species apparently cyclize to aromatic, which further polyaromatize to coke by a carbenium ion mechanism [27]. Thus, as the temperature increases, long-chain species form, including ring compounds.

4. Conclusions

On Degussa P-25 TiO_2, the same products form during TPH of acetaldehyde as reported for other TiO_2 samples: acetaldehyde, crotonaldehyde, butadiene, butene, and acetone. However, more sites are present on Degussa P-25 that catalyze further aldol condensation to form hexan-2,4-diene-al and larger species with conjugate double bonds. In addition, dehydro-cyclization forms aromatics and coke. These surface species with low H/C ratios are probably responsible for TiO_2 deactivation during acetaldehyde photocatalytic oxidation at elevated temperature. The higher concentration (molecules/nm^2) of acetaldehyde on Degussa P-25, compared to anatase TiO_2, and the higher concentration of acid sites may be responsible for higher rate of chain growth on Degussa TiO_2.

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