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Photocatalytic Degradation of Triethylamine on Titanium Oxide Thin Films

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Photooxidation of triethylamine (TEA) in the presence of O_2, N_2, and H_2O over titanium oxide (TiO_2) was investigated using a flat plate reactor. TEA was photocatalytically oxidized to CO_2 and some by-products on TiO_2 thin film catalysts. The intrinsic oxidation rate of the reaction was determined and was dependent on TEA concentration, humidity level, and light intensity. Photocatalytic deactivation was observed in these reactions. Fourier transform infrared (FTIR) and temperature-programmed desorption with a mass spectrometer as a detector (TPD-MS) were used to characterize the surface of the catalyst and study the deactivation mechanism. FTIR and TPD-MS results suggest that accumulation of carboxylic acid species, –N–N=O, and some other carbonaceous species occurred during the reaction. These by-product species or intermediates were chemisorbed on the catalyst surface. They were stable under reaction conditions and might be responsible for deactivation of TiO_2 by either poisoning the active sites directly or blocking the adsorption of TEA on the catalyst surface. © 1999 Academic Press

INTRODUCTION

Degradation of volatile organic compounds (VOCs) by photocatalytic oxidation has been a vigorously investigated subject because of its advantage of being able to completely mineralize VOCs to environmentally benign species (CO_2, H_2O) under mild reaction conditions. Complete destruction of these toxic contaminants that are present in low concentrations in indoor air is of growing interest due to their impact on public health. Nitrogen-containing compounds (components of VOCs) are of concern not only because they pose a public health risk but also because they are well-known poisons of catalysts. While photocatalytic destruction of different hydrocarbons and chlorohydrocarbons has been studied extensively (1–3), not much work has been published with compounds containing nitrogen (4, 5).

Titanium oxide (TiO_2) has been found to be very active in the photooxidation of different organic compounds, including hydrocarbons, aromatics, chlorinated hydrocarbons, aldehydes, and ketones (6–11). DeGussa P25, one of the most active TiO_2 forms, has been widely used in photooxidative studies due to its high activity and commercial availability. P25 powder or thin films coated on substrates have been used in both aqueous and gas phase photocatalytic reactions (12, 13).

Long-term catalytic activity is always desirable in catalysis. Catalyst deactivation and regeneration are very important issues in catalytic reactions. Catalyst design is influenced by such processes. Although catalyst deactivation has been observed in many photocatalytic oxidation reactions, only a few studies of deactivation mechanisms have been carried out.

Blake and Griffin (14) observed slow deactivation in the oxidation of secondary alcohols and suggested that some stable carboxylate species might be responsible for the deactivation. Peral and Ollis (15) studied catalytic oxidation of decamethyltetrasiloxane (DMTS), indole, pyrrole, and dimethylsulfide (DS) using TiO_2 as catalysts and observed reversible deactivation in the oxidation of DS and irreversible deactivation in the case of DMTS, indole, and pyrrole. Silicon, nitrogen, and carbonaceous deposits on the surface in these reactions were detected with Auger electron spectroscopy. Detailed studies of the characterization of surface chemical species and deactivation pathways are desired.

The present work concerns the photodegradation of TiO_2 by triethylamine (TEA) in the gas phase. Triethylamine (TEA) is used widely in industry and can be found in many commercial applications including hair-curing products. TEA has a bad odor and is considered a possible carcinogen. The air tolerance limit of TEA is 0.3 ppm which may be lowered in the near future due to the demand for better indoor air quality. Effects of TEA concentrations, humidity levels, and irradiation intensities on the oxidation rate were examined. Catalyst deactivation was investigated with most of this work being devoted to the characterization of chemical species on the catalyst surface.

EXPERIMENT SECTION

Materials. The P25 TiO_2 powder was purchased from Degussa and used as received. A mixture of 200 ppm TEA

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in nitrogen was obtained from Connecticut Air Gas and diluted to the desired concentration prior to reaction. Ultrahigh purity nitrogen gas (99.998%) and oxygen gas (99.9%) were also obtained from Connecticut Air Gas and used without further purification. Distilled deionized water was used in a bubbler to obtain specified humidity levels.

Preparation of catalysts. The TiO_2 thin film catalysts were prepared using a dip coating method. Ten grams of P25 powder was suspended in water while stirring to make a 200-mL suspension. Precleaned microscope glass slides from Fisher with dimensions of 76 × 18 mm per slide were etched with 2 M NaOH solution for 10 h, rinsed with water, and then neutralized with 0.1 M HCl solutions. The slides were rinsed with distilled deionized water until the rinsing no longer produced AgCl precipitate with $AgNO_3$ solution which indicated that the glass slides were free of Cl^- on the surface. These pretreated glass slides were dipped into the suspension and then taken out. The glass slides were air dried and dipped into the TiO_2 suspension again. The dipping and drying cycles were repeated for eight cycles. The obtained glass slides with TiO_2 loading of about 1 mg/cm^2 were used without further treatment.

Kinetic studies. A flat plate reactor was used for kinetic measurements. The detailed design of the reactor was described elsewhere (16). Four titania-coated glass slides with total UV exposure area of 52 cm^2 were used as catalysts. A 0.7-amp UV black light lamp with peak irradiation at about 352 nm was used as the light source. UV light irradiated the catalysts through a quartz window, which was 2 mm from the catalyst slides. The intensity of the UV irradiation on the surface was 6 mW/cm^2 for all reactions unless mentioned otherwise. All reactants were thoroughly mixed to achieve the desired composition (trace amounts of TEA and H_2O vapor and 10% O_2 and ~90% N_2) before being introduced into the reactor. The total reaction flow rate was 4 L/min. In each experiment, the reactant mixture was passed through the reactor in the dark to equilibrate before the UV light was turned on. The products were analyzed with a gas chromatograph (HP 5890A) and a Brüel & Kjær 1302 multigas monitor. The degree of catalyst degradation from TEA photooxidation was based on the disappearance of TEA.

Characterization of catalysts. The reflectance Fourier-transform infrared (FTIR) experiment was carried out on a Nicolet Magna-IR 750 FTIR spectrometer equipped with a heating unit. A DTGS KBr detector was used. Absorbance in the range of 4000 to 400 cm^{-1} was measured. The catalysts were analyzed before being exposed to the reactants, after equilibration with reactants, and after photodegradation, respectively, using FTIR to determine changes in the surface of the catalysts. The stability of the surface species was also studied with FTIR. After the reflectance spectrum was recorded at ambient temperature, the temperature of the reacted catalyst was increased to 150, 200, 250, and 350°C, respectively, in a nitrogen atmosphere. IR spectra were measured after the catalysts were held at these temperatures for 20 min.

Temperature-programmed desorption (TPD) experiments were also used to study absorbed reaction byproducts or intermediates that remained on the catalyst surface. The reactor used for TPD studies was homemade with a thermocouple inserted as close to the catalyst as possible. The catalyst was scraped from the glass slides coated with TiO_2 thin films and was used as a powder. Twenty-five milligrams of catalyst was used for each TPD analysis. Ultrahigh purity helium was used as the carrier gas at 30 mL/min. In each run of a TPD experiment, the catalyst was purged with helium gas for more than 2 h at room temperature until the baseline was flat to eliminate weakly physiosorbed species and then heated linearly from 30 to 700°C at 10°C/min. The species evolving from the catalysts during TPD were analyzed with a mass spectrometer with a quadrupole ionizing detector (MKS Instrument Inc.).

RESULTS

Catalytic photooxidation of TEA. The influence of water vapor on the photodegradation behavior has been observed in many organic pollutant studies. Trace amounts of water have been shown to greatly enhance the photodegradation of some contaminants (8, 10, 17–19). The effect of water vapor pressure on the photooxidation rate of TEA is shown in Fig. 1. Desorption of the reactants from the surface was observed at the time of illumination; therefore, the reaction data were taken 30 min after the UV light was turned on. At the lowest concentration of water vapor that was used, the oxidation rate was only 0.17 μmol/cm^2 (thin film slide area, also reactor area) -h. While small amounts of moisture increased the oxidation rate to about

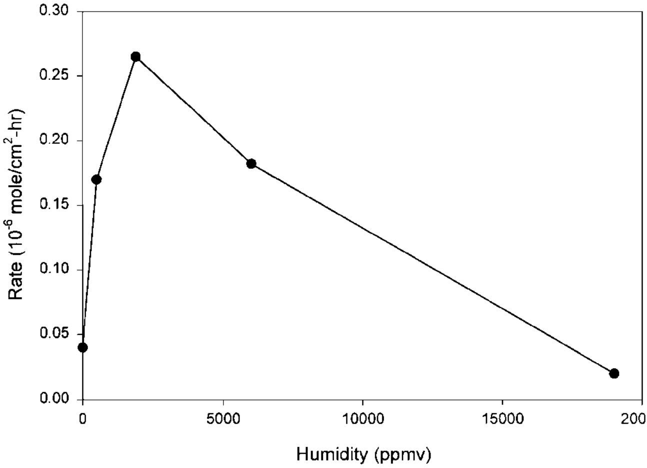

FIG. 1. TEA oxidation rate dependence on humidity level: 10 ppmv TEA, 6.0 mW/cm^2 UV. Reaction rate recorded after reaction for 30 min.

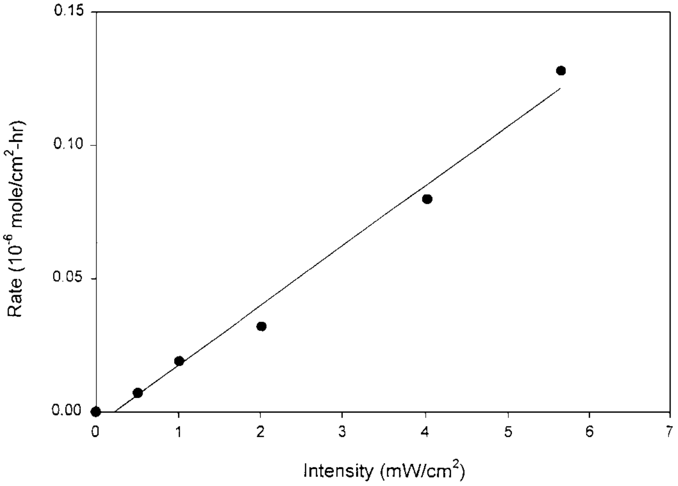

FIG. 2. Oxidation rate dependence on UV intensity: 10 ppm TEA, 6000 ppmv H_2O. Reaction rate recorded after reaction for 30 min.

$0.27\ \mu$mol/cm^2-h, excess moisture played a negative role in the oxidation process. This has been attributed to competitive adsorption of surface active water and VOC molecules (17–19).

Figure 2 shows the dependence of TEA oxidation rate on UV light intensity. The reaction rate increased linearly with UV intensity. According to the literature, at low levels of illumination the rate is first order in intensity because absorption of photons is first order in intensity. The level of illumination at which the rate linearly increases with light intensity is catalyst dependent. Above this level the rate is dependent on the square root of light intensity (20).

Photooxidation profiles for different concentrations of TEA on titanium oxide thin films are shown in Fig. 3. The oxidation rate of TEA decreased with reaction time indicating catalyst deactivation. As the concentration of TEA is increased, the deactivation rate increased. At 20.5 ppmv TEA, the catalyst was almost completely deactivated in 2 h while in the case of 5 ppmv TEA the catalyst still showed some activity after 10 h. The completely deactivated catalysts could not be totally regenerated by oxygen purging with or without the presence of water vapor under UV irradiation overnight. The rate of CO_2 formation and the degree of complete degradation (the ratio of the amount of TEA converted to CO_2 to the total amount of TEA converted) are shown in Fig. 4. As the reaction progressed, both the rate of CO_2 formation and the percentage of complete degradation decreased, indicating that only partial oxidation began to occur as the reaction proceeded and that the degree of oxidation continually decreased with time. No partial oxidation products were detected in the gas phase from GC analysis.

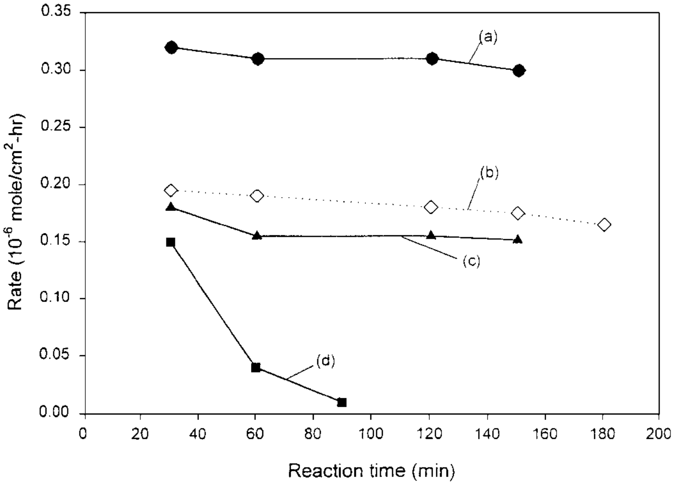

FIG. 3. Oxidation rate dependence on TEA concentration: 6000 ppmv H_2O, 6.0 mW/cm^2 UV. (a) 5.0 ppmv TEA; (b) 10.0 ppmv TEA; (c) 16.3 ppmv TEA; and (d) 20.5 ppmv TEA. Reaction was based on concentration data after the reaction was allowed 30 min to reach steady state.

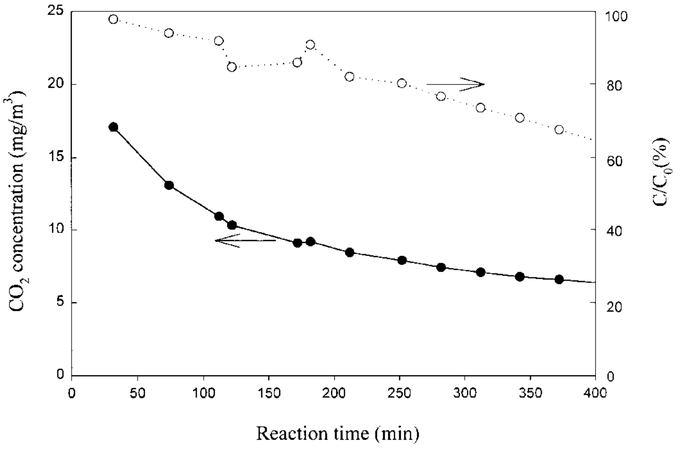

FIG. 4. CO_2 formation rate and degree of complete degradation vs. reaction time: 10 ppmv TEA, 6000 ppmv H_2O, 6.0 mW/cm^2 UV.

FTIR studies. The surfaces of the catalyst under different experimental conditions were analyzed using FTIR as shown in Fig. 5. The catalysts were purged with nitrogen before the FTIR spectra were taken. A distinct sharp peak at ~3641 cm^{-1}, which is attributed to stretching vibrations of surface hydroxyl groups of TiO_2, was observed on the fresh catalyst. Additionally, the fresh catalyst showed a strong peak at 1628 cm^{-1}, which may be due to an O–H deformation vibration. Exposure of the fresh catalyst to TEA vapor for 30 min did not significantly affect surface hydroxyl groups based on IR data. Several new bands in the range of 1400 to 1700 cm^{-1} appeared as seen in Fig. 5b. Several additional peaks also showed up in the range of 2800 to 3000 cm^{-1} corresponding to C–H stretching vibrations of $-CH_2$ and $-CH_3$, indicating that TEA absorbed on the catalyst surface.

After the catalyst was in equilibrium with the reactants, oxidation of TEA was carried out at 5 ppm TEA under UV

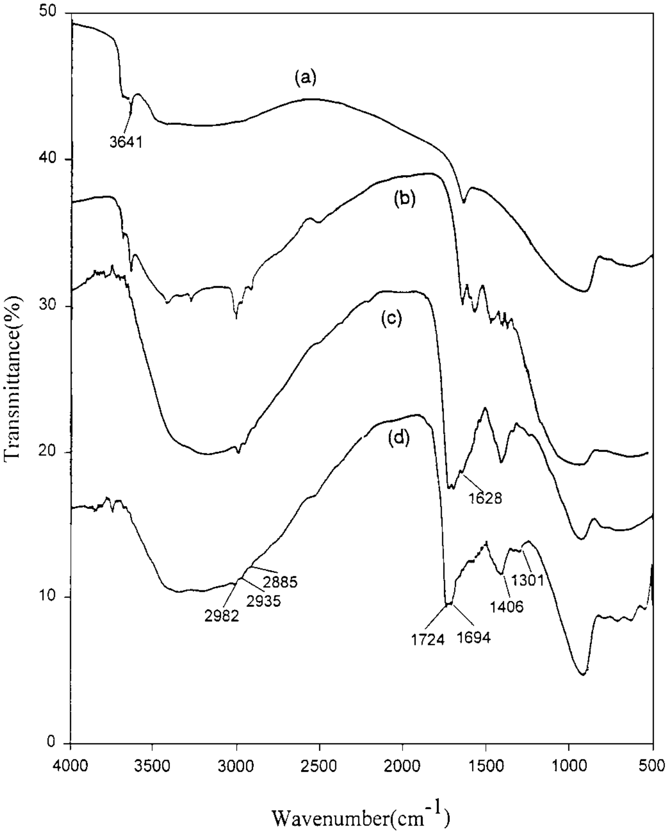

FIG. 5. FTIR spectra of catalysts (a) before exposed to TEA; (b) after saturated with TEA; (c) after deactivation by TEA oxidation; (d) sample (c) resaturated with TEA.

irradiation until the catalyst completely lost activity. The reacted catalyst was examined with FTIR and the spectrum is shown in Figure 5c. The $\nu_{\text{O-H}}$ stretching band at 3641 cm^{-1} disappeared after deactivation indicating that surface hydroxyl groups were completely consumed in the reaction. A new strong doublet at ~1724 and 1694 cm^{-1} superimposed on the broad O–H deformation vibrational band of H_2O was observed, which is assigned to $C=O$ stretching vibrations of –COOH groups. At the same time, several peaks in the range of 3000 to 2500 cm^{-1}, and two peaks at 1406 and 1301 cm^{-1} appeared after deactivation. Peaks at 2982, 2935, and 2885 cm^{-1} are assigned to C–H stretching vibrations of –CH_2 and –CH_3, whereas $\nu_{\text{C-O-H}}$ modes of –COOH may be responsible for the 1406 and 1301 cm^{-1} bands. Weak absorption at 2208 cm^{-1} may be due to $\nu_{\text{N–N=O}}$ (21). These FTIR data suggest that new species are present on the surface of the catalyst. These species could be reaction intermediates and/or products of partial oxidation of TEA that chemisorbed on the surface of the catalyst. Deactivated catalysts show little absorbed TEA on their surfaces even after being exposed to TEA vapor, as shown in Fig. 5d.

More detailed spectra of the changes that occurred on the catalyst surface during reaction are shown in Fig. 6. The spectra of catalysts before and after reaction for 2, 4, 7, and 13 h are displayed. As the reaction progressed, the intensities of the bands at ~1724, 1694, 2208, and 2506 cm^{-1} increased while those of the O–H stretch at 3641 cm^{-1} and bending mode at 1628 cm^{-1} decreased, indicating accumulation of carboxylic acid or carboxylate species accompanied by gradual consumption of surface hydroxyl groups in the first few hours of reaction.

After reaction for 4 h, the surface hydroxyl groups were undetectable by FTIR, and the intensity of the peak at ~1724 cm^{-1} reached a maximum. Further oxidation did not change the intensity of the 1724 cm^{-1} peak, but the intensities of the two peaks at 2506 and 2208 cm^{-1} increased with reaction time, suggesting that another species besides those containing –COOH groups continued to accumulate on the surface after surface hydroxyl groups were consumed.

The FTIR spectra of the deactivated catalyst at different temperatures are presented in Fig. 7. Increasing the temperature from ambient to 200°C led to a decrease in intensity of the broad O–H deformation vibrational band in the range of 1700 to 1400 cm^{-1} due to the loss of H_2O upon heating. Bands at 3000 to 2850, 1724, and 1694 cm^{-1} did not show a significant decrease until 250°C. On the contrary, desorption of H_2O which is responsible for the broad peak in the region of 3000 to 2850 cm^{-1} led to C–H stretching vibrational bands becoming more prominent as the temperature increased. A gradual decrease in intensity of peaks at 1724 and 1694 cm^{-1} after heating the samples to 250°C indicates the slow disappearance of carboxylic acid species.

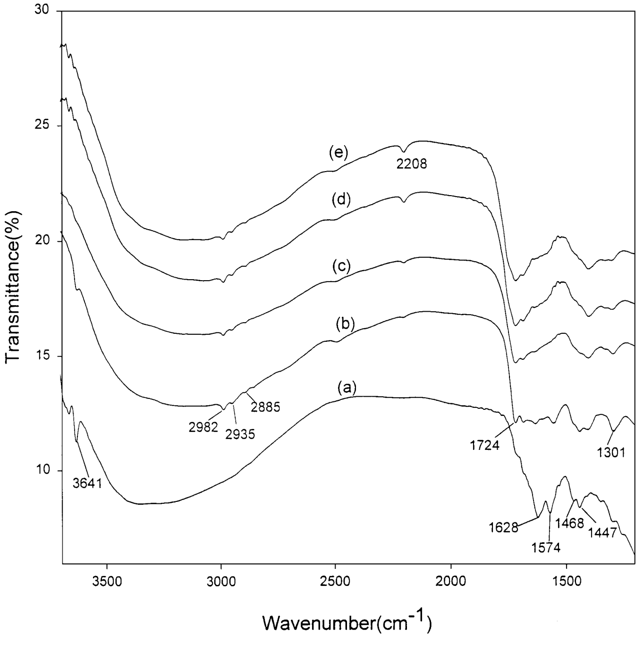

FIG. 6. FTIR spectra of catalyst (a) before TEA oxidation; after TEA oxidation for (b) 2 h; (c) 4 h; (d) 7 h; and (e) 13 h. Reaction condition: 5 ppmv TEA, 6000 ppmv H_2O, and 6.0 mW/cm^2 UV. This reaction condition is also used in Figs. 7–10.

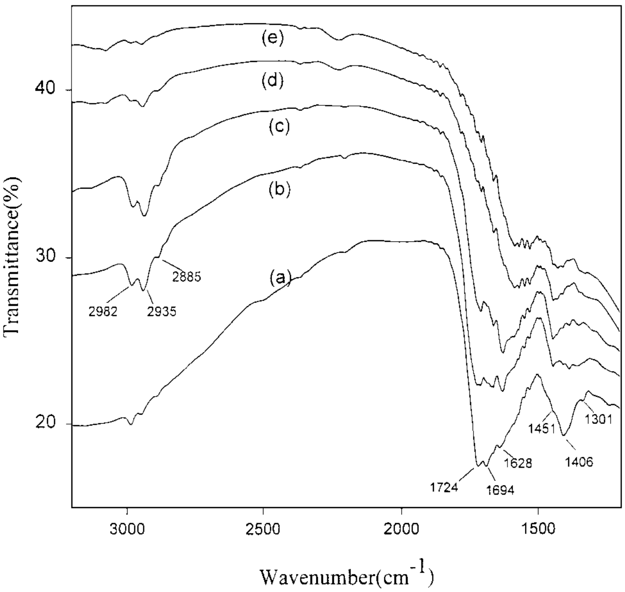

FIG. 7. FTIR spectra of deactivated catalyst after heating to (a) room temperature; (b) 150°C; (c) 200°C; (d) 250°C; and (e) 350°C.

Despite the disappearance of absorbed species, surface hydroxyl groups did not reappear probably due to irreversible surface dehydroxylation at elevated temperatures in N_2 atmospheres.

TPD-mass spectrometry (MS) studies. Although TPD is not a surface analysis technique, combined TPD-mass spectrometry methods have been widely used to study adsorbed species on solid surfaces (22). TPD-MS can yield information on the nature of the adsorption and adsorption strength, can distinguish physisorption and chemisorption, and can be used to determine apparent activation energies of desorption. Mass spectrometry is a very powerful technique for identifying intermediates and products. TPD-MS is quite useful for characterization of catalysts.

The TPD-MS profiles of catalysts after TEA oxidation for 0, 2, 4, 7, and 13 h are shown in Figs. 8, 9, and 10. Although all m/e (mass to charge ratios) were scanned with MS, only the profiles of $m/e = 44$, 30, and 28, which provided information about evolved species, are shown here. The catalyst before the reaction only showed peaks at about 100 and 150°C, which were identified as CO_2. Probably atmospheric CO_2 was physically adsorbed on the TiO_2 surface.

TPD profiles of catalysts after TEA oxidation for 2 h show new peaks at about 240 and 300°C and a small amount of desorption at 450°C, which are assigned to N_2O, CO_2, and CO, respectively. At about 300°C, there are peaks of $m/e = 30$ with much lower intensity in addition to those of $m/e = 44$ and $m/e = 28$. Due to the much lower intensity of $m/e = 30$ peaks compared to those of $m/e = 44$, it is very unlikely that they are due to fragmentation from N_2O. Therefore, we assign these peaks to NO from decomposition of nitrogen-containing carbonaceous species (which also contribute to peaks of $m/e = 44$ and $m/e = 28$) desorbed at this temperature. In addition to CO, CO_2, N_2O, and NO, H_2O was also detected during TPD experiments. It started to be released from the catalyst at ~100°C and was detected until 400°C. Larger quantities of these desorbed species were detected at longer reaction times indicating that these species accumulated on TiO_2. This phenomenon corresponded to a decrease in the oxidation rate. After 7 h, the intensities of the peaks at 250 and 300°C did not increase

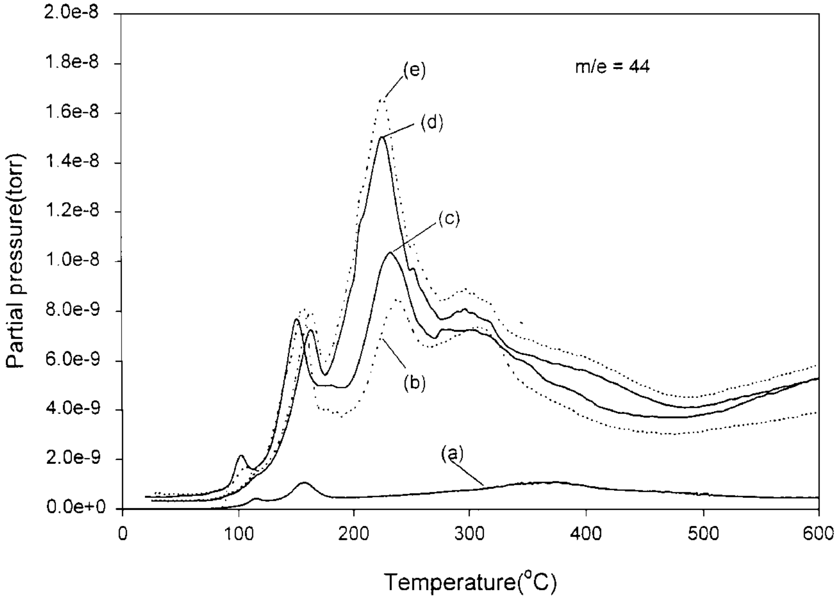

FIG. 8. TPD-MS profiles of catalyst, $m/e = 44$, (a) before TEA oxidation and after TEA oxidation for (b) 2 h; (c) 4 h; (d) 7 h; and (e) 13 h.

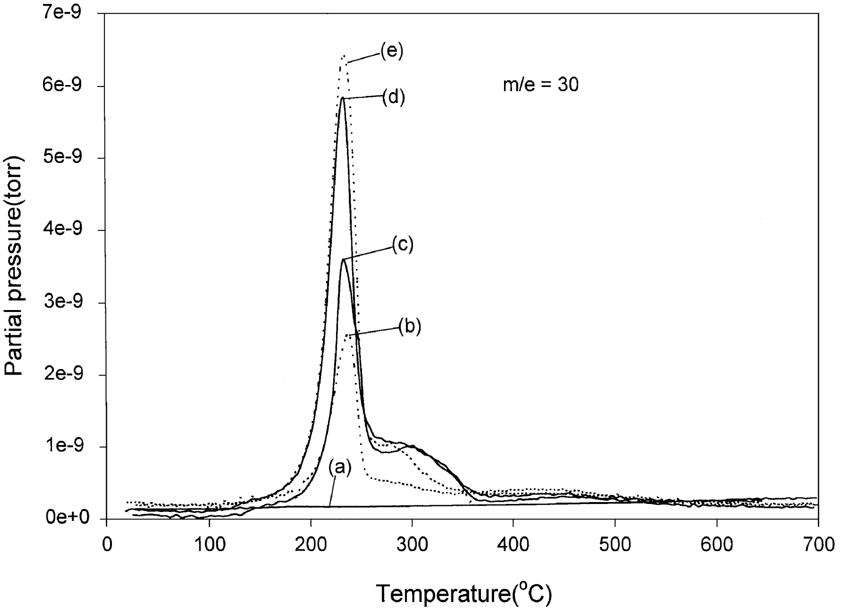

FIG. 9. TPD-MS profiles of catalyst, $m/e = 30$, (a) before TEA oxidation and after TEA oxidation for (b) 2 h; (c) 4 h; (d) 7 h; and (e) 13 h.

significantly with reaction time, but a new and prominent desorption peak due to evolution of CO from the surface appeared at 450°C. These observations are consistent with FTIR results that insignificant amounts of carboxylic acid or carboxylate species were produced after surface hydroxyl groups were consumed. Other carbonaceous species, which strongly bond to the surface, were formed while the catalyst was still partially active for TEA oxidation.

DISCUSSION

Deactivation is a very common phenomenon in photodegradation reactions. Deactivation has been observed in the photodegradation of alcohols, pyridines, aromatic hydrocarbons, silicon, sulfur, or phosphorous containing organic compounds (2, 5, 8, 14). Fast deactivation was observed for TEA oxidation in this study although only a

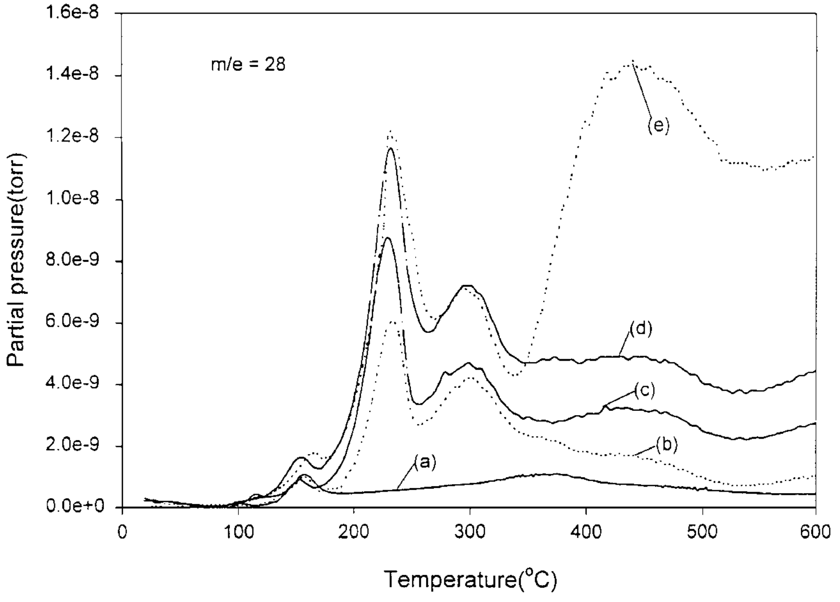

FIG. 10. TPD-MS profiles of catalyst, $m/e = 28$, (a) before TEA oxidation and after TEA oxidation for (b) 2 h; (c) 4 h; (d) 7 h; and (e) 13 h.

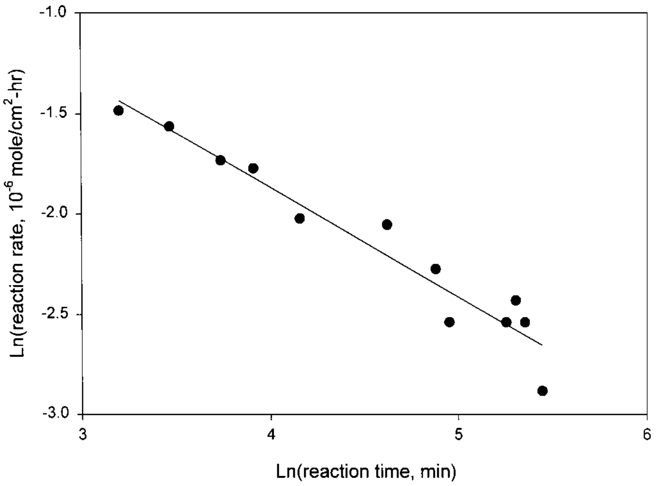

FIG. 11. Ln(reaction rate) vs. ln(reaction time). 10 ppm TEA, 6000 ppmv H_2O.

slight color change on the catalyst was seen after the reaction. A linear correlation is obtained between ln(oxidation rate) and ln(reaction time), suggesting that catalytic activity decreased exponentially with reaction time (Fig. 11). The deactivation was observed almost instantly after the UV light was turned on, and the reaction rate decreased very rapidly, which led to the observation of the strong negative effect of TEA concentration on the reaction rate (Fig. 3). The linear instead of square root relationship between UV intensity and the reaction rate might be also related to the fast deactivation.

Ollis and co-workers used meq (illuminated catalyst surface monolayer equivalents) to study catalyst deactivation for different contaminants (23). Meq was defined as

$$\text{Meq} = \frac{\text{molecules converted}}{\text{(active) catalyst sites}}.$$

Molecules converted can be calculated from the reaction rate and the reaction time, but the number of the active catalyst sites is unknown. A value of 5×10^{14} sites/cm^2 (surface area) adopted from the literature is used for our calculation.

We will calculate meq at a time span of 13 h when the catalyst is close to complete deactivation. The reaction rate for 5 ppmv TEA on 1-cm^2 catalyst thin film area (about 1×10^{-3} g catalyst) is about 0.3×10^{-6} mol/h (Fig. 3). Then, the molecules converted per square centimeter of catalyst thin film area in 13 h will be

$$0.3 \times 10^{-6}\ \text{mol/h} \times 13\,\text{h} \times 6.02 \times 10^{23}\ \text{molecules/mol} = 2.35 \times 10^{18}\ \text{molecules}.$$

Assuming all the thin film catalyst was illuminated, the number of sites per square centimeter of catalyst thin film area will be

$$1 \times 10^{-3}\,\text{g(catalyst)} \times 50\,\text{m}^2\ \text{surface area/g(catalyst)} \times 10^4\,\text{cm}^2/\text{m}^2 \times 5 \times 10^{14}\,\text{sites/cm}^2 = 2.5 \times 10^{17}\ \text{sites}$$

Therefore, the meq for this reaction is 9.4, which is within the range for most catalyst deactivation cases with a single-path flow reactor (23).

Catalyst deactivation during reactions can be due to many different reasons including sintering which results in loss of surface area, poisoning which causes loss of active sites on the surface, and fouling which changes the catalyst surface by blocking pores. Results of many photodegradation reactions over TiO_2 suggest that deactivation is most likely due to reaction residues that remain adsorbed on the catalyst surface (2, 5, 7, 14). In the case of TEA oxidation, several adsorbed species were observed. The observation of $\nu_{C=O}$ and $\nu_{O\text{–}H}$ stetching vibrational bands of –COOH or –COOR groups in the FTIR data and the detection of CO_2 evolving from the surface during TPD experiments suggest that species such as –COOH or –$COOCH_3$ remained on the surface after reaction. TPD studies of acetic acid over TiO_2 conducted by Falconer and co-workers also showed that CO_2 started to evolve from the surface at about 300°C (24).

The FTIR spectra and TPD profiles recorded at different reaction times indicate the accumulation of surface –COOH or –COOR species and gradual consumption of surface hydroxyl groups. According to studies of acetic acid adsorption on anatase TiO_2 conducted by Mathieu and co-workers (25), adsorbed acetic acid neutralizes surface hydroxyl groups. Although we were unable to detect gas phase nitrogen-containing products during the reaction due to detection limits, this reaction is still catalytic according to calculated meq value. Nitrogen-containing species were observed on the surface. These nitrogen species remained on the surface in the form of –N–N=O and were released as N_2O from the surface at about 240°C as indicated in the TPD profiles. Accumulation of these surface species and consumption of surface hydroxyl groups were accompanied by the loss of catalytic activity toward complete oxidation. Ollis and co-workers also suggested that hydroxyl groups were essential for complete oxidative destruction of organic compounds (26).

The mechanism involving hydroxyl groups in this reaction is still not certain. Under UV illumination, electron-hole pairs may be formed in TiO_2. Hydroxyl groups will react with holes to generate hydroxyl radicals which may attack contaminants to form intermediates, such as aldehydes and acetic acids, which can be further oxidized by $O_2\cdot$ or $O\cdot$ to produce CO_2. Pichat and co-workers proposed a reaction pathway for gas phase photooxidation of ammonia to N_2O over TiO_2, as follows (27):

$$(TiO_2) + h\nu \rightarrow p^+ + e^- \qquad [1]$$

$$O^-_{ads} + p^+ \rightarrow O^*_{ads} \qquad [2]$$

$$NH_{3ads} + O^*_{ads} \rightarrow NH_3O^*_{ads} \leftrightarrow NH_2OH_a \qquad [3]$$

$$NH_2OH^*_{ads} \rightarrow NH^*_{ads} + H_2O_{ads} \qquad [4]$$

$$NH^*_{ads} + O_{2ads} \rightarrow HNO_{ads} + O_{ads} \qquad [5]$$

$$HNO_{ads} + HNO_{ads} \rightarrow N_2O_{ads} + H_2O_{ads}. \qquad [6]$$

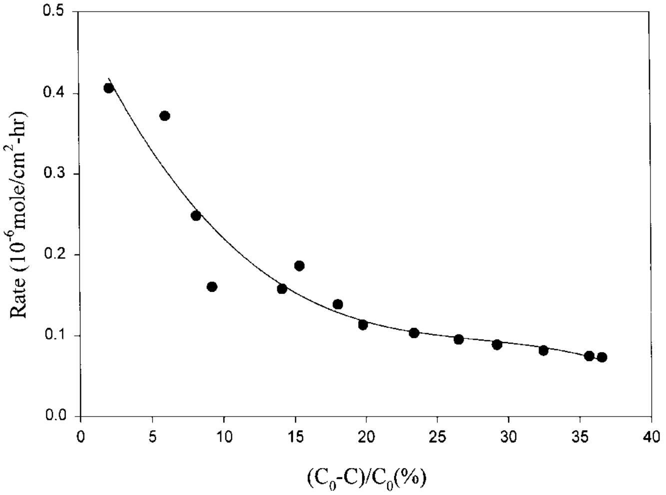

FIG. 12. Correlation of TEA oxidation rate with total amount of surface species. C_0 is the total amount of TEA reacted, and C is the amount of TEA that produces CO_2. 10 ppm TEA, 6000 ppmv H_2O.

Species with asterisks are excited state species. A similar pathway as above might be responsible for the generation of $-N_2O$ species from TEA photooxidation. The mechanism is still under investigation.

The catalyst still showed partial activity toward TEA oxidation even after 4 h after TEA oxidation when surface hydroxyl groups were undetectable by FTIR. We propose that another type of active site may also contribute to the photooxidation of TEA. Further reaction generated other species as indicated by FTIR and TPD results (Figs. 6 and 8–10) with a continued decrease in reaction rate. A correlation of TEA oxidation rate with total amount of surface species, which is the difference between total amount of TEA consumed and the amount converted to CO_2 in terms of carbon content, is shown in Fig. 12. Based on this plot, a deactivation mechanism of initial selective poisoning of more active sites for TEA photooxidation occurs. The more active sites are poisoned by surface carboxylic acid species and $-N-N{=}O$ species while the less active sites are possibly poisoned by other carbonaceous species. These species were stable up to 250°C indicating that they were chemisorbed or bonded to the catalyst surface. Such species may also block the adsorption of TEA on the surface, which is an important step in the reaction.

CONCLUSIONS

Titanium oxide thin films coated on glass slides were active catalysts for the photooxidation of TEA. The oxidation rate was found to be dependent on water vapor pressure, UV intensity, and concentration of TEA. Trace amounts of water greatly enhanced the oxidation of TEA, but excess water played a negative role in the degradation. The overall oxidation rate and the rate for complete oxidation to CO_2 decreased with increasing reaction time. The degree of complete degradation of TEA also decreased due to deactivation of the catalyst. Deactivation was faster at higher concentrations of TEA. The catalyst deactivated exponentially with reaction time.

Several reaction intermediates or partial oxidation products were observed to adsorb on the catalyst surface and deactivate the catalyst by blocking the adsorption of TEA on the surface and/or by poisoning active sites for TEA degradation. These species might be carboxylic acids, carboxylate, $-N-N{=}O$, and other carbonaceous species that can release CO_2 at high temperature. Two different surface carbonaceous species were observed at different degrees of reaction suggesting that there might be more than one type of active site responsible for TEA oxidation and that one type of active site may be more sensitive to deactivation than the other.

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