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Catalytic and Photocatalytic Oxidation of Ethylene on Titania-Based Thin-Films

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The effect of reaction temperature on the catalytic and photocatalytic oxidation of ethylene on unplatinized and platinized versions of a TiO_2/ZrO_2 mixed-oxide thin-film catalyst is presented in this study. Ethylene conversion data collected using a recirculating tubular reactor are analyzed using a half order model of reaction kinetics. When operated in the presence of UV, both catalysts exhibit significant (95% confidence) increases in the reaction rate constant at 70 °C compared to 30 °C—no difference is observed between unplatinized and platinized versions at these two temperatures. However, only the platinized catalyst performs better at 107 °C compared to its performance at 70 °C. Also, at 107 °C in the presence of UV, the reaction rate constant obtained for the platinized catalyst is a factor of 2 larger than that obtained using the unplatinized catalyst. Catalytic reaction rate constants for the platinized catalyst were 1 (107 °C) to 2 (70 °C) orders of magnitude lower than corresponding photocatalytic reaction rate constants. Comparisons between the thin-film catalysts studied here and a previously reported particulate catalyst show a fundamental difference in photocatalytic behavior, mainly due to insufficient utilization of the internal bulk of the particulate catalyst.

Introduction

The removal of ethylene (C_2H_4, a plant hormone that promotes the ripening of fruits and vegetables and accelerates the aging of flowers) on titania-based materials has previously been reported by a number of researchers (*1*−*5*). The effects of temperature (*2*−*5*), water vapor concentration (*2*−*4*), and ethylene concentration (*3, 4*) have been presented in these studies. In addition, Fu et al. (*1*) reported enhanced photocatalytic performance of mixed-metal oxide (TiO_2/SiO_2 and TiO_2/ZrO_2) particles compared to pure titania for degrading ethylene. Fu et al. (*2*) also reported enhanced degradation of ethylene at elevated temperatures through the addition of platinum to pure titania particles. The increased reactivity was attributed to an increase in conventional heterogeneous (nonphoto) catalytic reactions occurring on the Pt/TiO_2 catalyst.

In this study, the effect of reaction temperature on the catalytic and photocatalytic oxidation of ethylene on unplatinized and platinized mixed-oxide TiO_2/ZrO_2 *thin-films* was examined. Coating a thin film of catalyst onto a support allows for more efficient distribution of light and can decrease the hydrodynamic pressure drop problems encountered when using unsupported particulate catalysts. Thin-film photocatalytic reactors have been previously reported for oxidation of various compounds in both the liquid (*6*−*8*) and gas phase (*9*−*13*). In this study, ethylene conversion data collected under dry conditions using a multipass, recirculating tubular reactor were analyzed using a half order model of reaction kinetics. Calculated reaction rate constants were then used to compare the behavior of the two catalyst formulations under different reaction conditions. The results obtained with supported thin-films were compared to previously reported results using similarly prepared particulate forms of the catalyst (*2*).

Experimental Section

Catalyst Preparation and Characterization. The mixed-oxide catalyst material used in this study was prepared using a sol−gel processing approach (*1*) in which titania and zirconia sols were prepared separately prior to combining (*13*). Three layers of active catalyst material were deposited onto borosilicate glass cylinders or “rings” (4 mm o.d. × 3 mm i.d. × 12 mm long) that were prerinsed with high purity water. The glass rings were prepared by cutting thin-wall glass tubing (Kimble Glass, Deerfield, IL) to the required length. After applying each layer, the rings were dried in air at 100 °C for 1 h. The coated rings were then fired in air in a furnace at 350 °C for 3 h using a 3 °C per minute ramp rate. Physical properties of this catalyst can be estimated from measurements on the unsupported particulates. Fu et al. (*1*) have reported the specific surface area and porosity of similarly prepared TiO_2/ZrO_2 particulates as 250 $m^2\ g^{-1}$ and 55%, respectively.

Platinization was achieved by impregnating rings coated as above with an aqueous chloroplatinic acid solution (8 wt % H_2PtCl_6, Aldrich, Milwaukee, WI) (*2*, *14*). The adsorbed H_2PtCl_6 was subsequently reduced with a solution of 0.1 M sodium borohydride ($NaBH_4$, Aldrich, Milwaukee, WI) in 0.01 M sodium hydroxide. Transmission electron micrographs (up to 3.3×10^5 magnification) of similarly prepared particulates do not indicate the presence of individual platinum particles on the titania catalyst at a platinum loading level of 0.3 wt % (*2*, *14*). Rather, it is likely that the platinum is uniformly dispersed over the surface of the catalyst. The platinized rings employed in this study did not exhibit any noticeable dark color; however, a faint dark color was observed with rings that were nominally loaded with five times the amount of platinum as those employed herein.

To determine the mass of catalyst employed in this study, an ammonium sulfate [$(NH_4)_2SO_4$, Fisher Scientific, Pittsburgh, PA]/sulfuric acid (H_2SO_4) digestion procedure was employed (*15*−*17*). For each sample, 4 g $(NH_4)_2SO_4$ was added to 10 mL of hot concentrated H_2SO_4. After the $(NH_4)_2SO_4$ completely dissolved in the H_2SO_4, five catalyst-coated glass rings were added to the solution. The samples were covered and carefully boiled for 1 h. After removing the glass rings from the solution, appropriate dilutions were performed to result in a 1% acid solution. Visual inspection of the digested rings suggests that the digestion process completely removed all of the catalyst coating. Elemental analyses (Ti, Zr, and Pt) were subsequently performed using inductively coupled plasma−mass spectrometry (ICP-MS) at the Soil and Plant Analysis Laboratory at the University of Wisconsin−Madison. The average total mass of catalyst deposited on each ring was determined to be 0.12 mg, with an average composition by weight of 10% zirconia and 1.4% platinum (platinized version only), with the balance titania.

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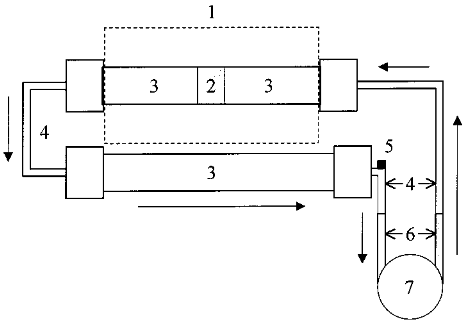

FIGURE 1. Experimental set up. 1—temperature controlled chamber with four UV light sources; 2—illuminated section of glass tube (photocatalytic experiments only) randomly packed with eight catalyst-coated glass rings; 3—nonilluminated sections of glass tube (not packed with catalyst-coated glass rings); 4—stainless steel tubing; 5—sampling port (septum); 6—Viton pump tubing; 7—peristaltic pump.

Reactor Apparatus. The catalytic and photocatalytic oxidation experiments employed a recycling loop as shown in Figure 1. The recycling loop consisted of a 27 mL (1.5 cm i.d. × 15 cm long) glass tube that held eight catalyst-coated glass rings packed randomly in the center, a 30 mL (1.5 cm i.d. × 17 cm long) empty glass tube, a sampling port (septum), stainless steel tubing, and a peristaltic pump with Viton (Cole Palmer, Vernon Hills, IL) pump tubing. For all experiments, the total mass of catalyst (W) was 1.0 mg, and the total void volume of the empty loop, the "reservoir" (V_{res}), was 72.5 mL. By suitable adjustment of a cooling air stream and/or a heat tape, the average reactor air temperature (measured by placing a J-type thermocouple in a glass insert located at the center of the packed bed) was maintained at average temperatures of 30 °C, 70 °C, or 107 °C (± 2 °C).

For the photocatalytic experiments, four 4 W fluorescent light bulbs (F4T5BL, WIKO Brand, Bulb Direct Co., Pittsford, NY) were symmetrically spaced at a radius of 2.5 cm from the axial centerline of the reactor. These bulbs produce a strong peak centered at ca. 365–370 nm and provided an average measured light irradiance of 3.1 mW cm^{-2}. Light irradiance levels were measured at the center of the reactor housing (after removal of the catalyst-containing glass tube) using a light meter (Model IL 1400 with Super-Slim probe in the 250–400 nm wavelength range, International Light, Newburyport, MA) and were obtained by rotating the light probe at 45 degree increments and averaging the individual measurements (individual values ranged from 2.8 to 3.4 mW cm^{-2}, with 6.2% relative standard deviation, $n = 10$). Based on separate (unpublished) studies with ethylene using multiple reactor geometries, it appears that the catalyst does not absorb all of the UV radiation present in this reactor. In addition, it has previously been shown that a thin-film loading of 0.3–0.5 mg cm^{-2} of Degussa P-25 titania was required for complete absorption of UV radiation at 5.3 mW cm^{-2} (*18*). In the experiments reported here, the catalyst loading was approximately 1 order of magnitude below this level.

Prior to performing any degradation studies, leak-free operation and tubing compatibility were verified by introducing ethylene into the recycling loop at room temperature with the UV lights turned off and monitoring the concentration over extended time periods. In experiments with other analytes, the effect of sample withdrawal (250 μL per sample, see below) on analyte concentration was shown to be minimal with the recycling loop employed in this study. After removal of 15 samples from the recycling loop maintained at room temperature and with the UV lights turned off, the measured decrease in analyte concentration was only ca. 4%. In future studies, the effect of sample removal may be decreased even further by removal of a minimum number of samples and/or removal of smaller sample volumes (e.g., 100 μL) from the recycling loop.

At the beginning of an experiment, the UV lights were energized (photocatalytic experiments only), the pump was started, the reactor temperature was allowed to reach the set temperature, the recycling loop was broken between the pump outlet and the inlet of the reactor, and the loop was flushed with room air for 10–15 min. Next, a gas sampling bag filled with ethylene at a concentration of 4.3×10^{-5} mol L^{-1} (1055 ppm) with the balance ultra zero air (<0.1 ppm total hydrocarbons, <5 ppm water vapor, AGA Specialty Gas, Cleveland, OH) was connected at the reactor inlet, and the ethylene mixture was pumped through the reactor. [Although such a high ethylene concentration is not indicative of most horticultural applications (with the possible exception of apple storage and banana ripening facilities), it was necessary to allow for a sufficient number of samples to be obtained for all experiments. In addition, these reaction conditions were chosen to allow comparison to work performed by Fu et al. (*2*)]. After 3 min, the gas sampling bag was detached, the loop was closed, and sampling was initiated. The recirculating flow rate maintained by the pump was 200 mL min^{-1}, except where otherwise noted. Gas samples (250 μL) were withdrawn from the recycling loop at regular intervals by inserting a gastight syringe through the sampling port. Values of initial ethylene concentration (C_{A0}) ranged between 2.9×10^{-5} mol L^{-1} and 4.1×10^{-5} mol L^{-1}.

Gas Chromatography. The reactor contents were analyzed using a Hewlett-Packard 5890 Series II gas chromatograph (GC). The column effluent was routed through a thermal conductivity detector (TCD) and flame ionization detector (FID) connected in series—since measurement of thermal conductivity is a nondestructive detection technique, both detectors produced a response from a single sample. The FID (maintained at 300 °C) was used to monitor the concentration of ethylene, while the TCD (maintained at 200 °C) was used to monitor the concentration of carbon dioxide produced during oxidation of ethylene. The concentration of water vapor, also a product of the reaction, was not monitored during the experiments. Helium flowing at 30 mL min^{-1} was used as the carrier gas. A 250 μL injection was performed using a gastight syringe. The GC column was a Porapak R packed column (6 feet long × 1/8 in. o.d., 80/100 mesh, Alltech Associates, Deerfield, IL) that was maintained at 40 °C for 4 min.

Kinetics. To allow estimation of kinetic rate constants, the concentration of ethylene (C_A, in units of mol L^{-1}) was measured over time. The data generated were then fit using a general power law model (including powers of 0, 0.5, 1, 1.5, and 2) and a Langmuir–Hinshelwood–Hougen–Watson (LHHW) model of reaction kinetics. The half order model and LHHW model both provided adequate fits to the data; however, the half order model provided a slightly better fit in all cases. A linearized form of the half order kinetic model can be given as

$$C_A^{\ 1/2} = C_{A0}^{\ 1/2} - k\frac{Wt}{2V_{\mathrm{res}}} \tag{1}$$

where k is the reaction rate constant (in units of $mol^{1/2}$ $L^{1/2}$ g^{-1} s^{-1}), W is the catalyst mass (in units of g), t is time (in units of s), and V_{res} is the reservoir volume (in units of L)—see Hill (*19*) for a detailed discussion of kinetic modeling. The reaction rate constant can be determined by performing a least-squares regression analysis of $C_A^{1/2}$ versus t, where the reaction rate constant is the negative slope multiplied by $2V_{res}/W$.

Results and Discussion

Effect of Temperature with Unplatinized TiO_2/ZrO_2 Thin-Films. The degradation of ethylene was measured over time

TABLE 1. Half Order Reaction Rate Constants (in units of $mol^{1/2}$ $L^{1/2}$ g^{-1} s^{-1}) for Thin-Films

catalyst	30 °C	70 °C	107 °C
unplatinized[a]	1.80×10^{-4}	3.22×10^{-4}	3.34×10^{-4} [b]
platinized[a]	1.67×10^{-4}	3.35×10^{-4}	6.62×10^{-4}
platinized[c]	[d]	4.03×10^{-6}	3.60×10^{-5}

[a] Photocatalytic oxidation (with UV irradiation). [b] Average of four separate experiments (relative standard deviation = 1.4%). Includes one replicate with a recirculating volumetric flow rate of 100 mL min^{-1} (not significantly different at 95% confidence from replicates performed at 200 mL min^{-1}, the flow rate used for all other experiments reported in this study). See text for individual values. [c] Catalytic oxidation (without UV irradiation). [d] Ethylene degradation not observed.

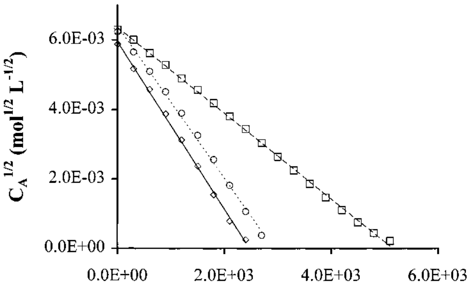

FIGURE 2. Fit of the ethylene conversion data obtained with photocatalysis at 30 °C (□), 70 °C (○), and 107 °C (◇) with an unplatinized TiO_2/ZrO_2 thin-film catalyst to a 1/2 order kinetic model.

at three different temperatures (30 °C, 70 °C, and 107 °C) in an initially dry (<5 ppm water vapor) feed stream with an unplatinized TiO_2/ZrO_2 thin-film catalyst (10 wt % zirconia) in the presence of UV light. A linearized half order model was used to calculate a kinetic rate constant at each temperature, as listed in Table 1. Reaction rate constants were determined by performing least-squares regression analyses, as shown in Figure 2.

To assess the reproducibility of the experimental procedure and to explore the possibility of any mass transfer limitations from the bulk flow to the catalyst surface at the recirculating flow rate used in this study (200 mL min^{-1}), the reaction rate constant at 107 °C was calculated from multiple experiments. Three experiments were performed at a flow rate of 200 mL min^{-1}, while one was performed at 100 mL min^{-1}. The individual rate constants were 3.40×10^{-4}, 3.31×10^{-4}, 3.30×10^{-4}, and 3.37×10^{-4} (flow rate = 100 mL min^{-1}) $mol^{1/2}$ $L^{1/2}$ g^{-1} s^{-1}. The reaction rate constant measured at 100 mL min^{-1} was not significantly different from the three reaction rate constants measured at 200 mL min^{-1} (average = 3.34×10^{-4}, 95% confidence interval = 1.3×10^{-5} $mol^{1/2}$ $L^{1/2}$ g^{-1} s^{-1}). Although not a rigorous experimental investigation, this result suggests that mass transfer limitations were not present at 200 mL min^{-1}. The average reaction rate constant at 107 °C using all four experiments was 3.34×10^{-4} $mol^{1/2}$ $L^{1/2}$ g^{-1} s^{-1}, with a relative standard deviation of 1.4%.

Rigorous statistical analyses were performed to determine whether the difference in reaction rate constants (i.e., the difference in slopes) at the three temperatures is statistically significant—see Draper and Smith (*20*) for a complete discussion of the significance of slopes. Confidence intervals (that provide lower and upper limits within which the true value is contained) were calculated for each of the reaction rate constants to evaluate significance. The reaction rate constant calculated at 30 °C (95% confidence interval (CI): 1.77×10^{-4} to 1.83×10^{-4} $mol^{1/2}$ $L^{1/2}$ g^{-1} s^{-1}) is significantly lower than the reaction rate constants calculated at 70 °C (95% CI: 3.07×10^{-4} to 3.37×10^{-4} $mol^{1/2}$ $L^{1/2}$ g^{-1} s^{-1}) and 107 °C (95% CI: 3.28×10^{-4} to 3.51×10^{-4} $mol^{1/2}$ $L^{1/2}$ g^{-1} s^{-1}); however, the reaction rate constant calculated at 70 °C is not significantly different from the reaction rate constant calculated at 107 °C. Thus, with the unplatinized catalyst, increasing the reaction temperature from 70 °C to 107 °C does not appear to have a significant effect on the reaction rate constant. The same phenomenon was also recently observed with the photocatalytic oxidation of acetone vapor on TiO_2/ZrO_2 thin-films (*13*).

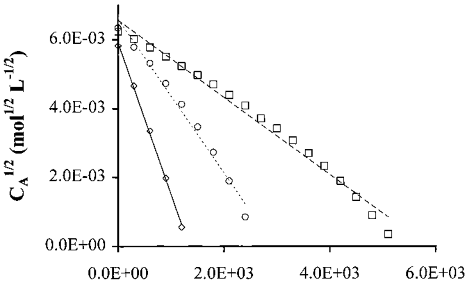

FIGURE 3. Fit of the ethylene conversion data obtained with photocatalysis at 30 °C (□), 70 °C (○), and 107 °C (◇) with a platinized TiO_2/ZrO_2 thin-film catalyst to a 1/2 order kinetic model.

Using GC/TCD, the production of carbon dioxide was monitored to calculate a mass balance based on the following reaction:

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \qquad (2)$$

The average number of moles of carbon dioxide produced per mol of ethylene degraded (mineralization ratio) was 1.9 at 30 °C, 1.9 at 70 °C, and 2.0 at 107 °C, indicating that the ethylene was completely mineralized to carbon dioxide and water. In addition, no other peaks were detected with the GC/FID during periods of photocatalytic oxidation.

Effect of Temperature with Platinized TiO_2/ZrO_2 Thin-Films. The degradation of ethylene was also measured over time in an initially dry feed stream at three different temperatures (30 °C, 70 °C, and 107 °C) with a platinized TiO_2/ZrO_2 thin-film catalyst (10 wt % zirconia and 1.4 wt % platinum) in the presence of UV light. A linearized half order model was again used to calculate a kinetic rate constant at each temperature, as listed in Table 1. Reaction rate constants were determined by performing least-squares regression analyses, as shown in Figure 3. As with the unplatinized catalyst, the reaction rate constant calculated at 30 °C is significantly lower (95% CI: 1.56×10^{-4} to 1.77×10^{-4} $mol^{1/2}$ $L^{1/2}$ g^{-1} s^{-1}) than the reaction rate constants calculated at 70 °C (95% CI: 2.96×10^{-4} to 3.75×10^{-4} $mol^{1/2}$ $L^{1/2}$ g^{-1} s^{-1}) and 107 °C (95% CI: 6.21×10^{-4} to 7.02×10^{-4} $mol^{1/2}$ $L^{1/2}$ g^{-1} s^{-1}). However, in contrast to the unplatinized catalyst, the reaction rate constant calculated at 70 °C is also significantly lower than the reaction rate constant calculated at 107 °C. In fact, the reaction rate constant at 107 °C is nearly double the reaction rate constant at 70 °C.

Comparisons can also be made between the unplatinized and platinized catalyst at each temperature. At 30 °C and 70 °C, the reaction rate constants calculated using the unplatinized catalyst are not significantly different from the reaction rate constants calculated using the platinized catalyst. However, at 107 °C, the platinized catalyst provides a significant increase (a factor of 2) in the reaction rate constant compared to the unplatinized catalyst.

The improved photocatalytic activity of platinized catalyst materials at relatively low platinum loadings (0.1–1 wt %, similar to that employed herein) has previously been observed, and explanations have been proposed (*2, 14, 21*). The general mechanism for the process of photocatalysis involves the illumination of a semiconductor catalyst surface with light of energy greater than the semiconductor band gap, resulting in the promotion of electrons from the valence band to the conduction band. This leaves behind positive holes in the valence band. It is possible that the electrons and holes will simply recombine (i.e., return of excited electrons to the valence band), effectively decreasing the rate of the photocatalytic process. Alternatively, the electrons can be scavenged by an oxidant (typically molecular oxygen), and the positive holes can be scavenged by oxidizable compounds (e.g., water vapor to form reactive hydroxyl radicals and/or possible direct oxidation of hydrocarbons, although this latter possibility is somewhat controversial), thus enabling overall reactions to occur. [Note that even though the ethylene/air mixture that is introduced to the reaction system is dry, some water is physisorbed to the thin film catalyst at the start of all experiments. In addition, water vapor is generated during the oxidation of ethylene, as shown in eq 2.] It has been theorized that the improved photocatalytic performance observed with platinized catalyst materials in aqueous systems can be attributed to an enhanced ability to collect photogenerated electrons on the islands of platinum that form at the catalyst surface, thereby resulting in a more efficient reduction of oxygen as compared to unplatinized catalyst materials (*2*, *14*, *21*, *22*). In addition, it has been reported that molecular oxygen undergoes dissociative adsorption on platinum metal (*14*, *23*). Although the actual mechanism is not known, the presence of these highly reactive dissociated species, especially at higher temperatures, coupled with the more efficient utilization of photogenerated electrons may explain the observed enhancement in reaction rate constant with the platinized thin-films at 107 °C but not at 30 °C or 70 °C.

The effect of conventional heterogeneous catalysis alone (i.e., with the UV lights turned off) was also examined at each of the three temperatures (30 °C, 70 °C, and 107 °C) with the platinized TiO_2/ZrO_2 thin-film catalyst used above. As before, a linearized half order model was used to calculate kinetic rate constants at 70 °C and 107 °C—conventional catalysis was not observed at 30 °C (see Table 1). Catalytic reaction rate constants calculated with the platinized catalyst were 1 (107 °C) to 2 (70 °C) orders of magnitude lower than corresponding photocatalytic reaction rate constants (both are significant at a 95% confidence level). It is evident that, although conventional catalysis occurs to some degree at temperatures above 30 °C, the addition of UV light greatly enhances the oxidation of ethylene to carbon dioxide and water.

As with the unplatinized photocatalytic experiments, the production of carbon dioxide using the platinized catalyst was monitored using GC/TCD. The average mineralization ratio was 1.9 at 30 °C, 1.9 at 70 °C, and 2.0 at 107 °C.

Comparison to Particulates. Similar experiments were previously performed by Fu et al. (*2*) using unplatinized (TiO_2) and platinized (0.3 wt % platinum, balance TiO_2) *particulate* catalysts. These data were collected using a single pass (i.e., noncirculating) fixed-bed tubular reactor (Pyrex, 2.4 mm inner diameter, 11 cm length) that was packed with 0.4 g of catalyst particles. Ethylene at an initial concentration of 1.59×10^{-5} mol L^{-1} was passed through the reactor at a volumetric flow rate (F_V) of 1×10^{-3} L s^{-1} (60 mL min^{-1}). As with the experiments performed in this study, the water vapor concentration was also less than 5 ppm. The geometric configuration of the reactor and the four 4 W fluorescent light bulbs (F4T5BLB, GE Brand, Bulb Direct, Pittsford, NY) employed by Fu et al. (*2*) was similar to that employed in this study. Light irradiance measured for that system [1.65×10^{-7} einsteins s^{-1} or 5.9 mW cm^{-2} (*1*, *24*)] was about a factor of 2 greater than that employed here.

TABLE 2. Half Order Reaction Rate Constants (in units of $mol^{1/2}$ $L^{1/2}$ g^{-1} s^{-1}) for Particulates[a]

catalyst	30 °C	70 °C	107 °C
unplatinized[b]	1.34×10^{-6}	2.56×10^{-6}	2.56×10^{-6}
platinized[b]	8.14×10^{-7}	6.71×10^{-6}	1.99×10^{-5} [c]
platinized[d]	[e]	4.49×10^{-6}	1.99×10^{-5} [c]

[a] Calculated from data presented in ref *2*. [b] Photocatalytic oxidation (with UV irradiation). [c] Calculated from a fractional conversion of 1.0 (i.e., 100% degradation of ethylene). Hence, reaction rate constant may be underestimated. [d] Catalytic oxidation (without UV irradiation). [e] Ethylene degradation not observed.

For comparison, half order reaction rate constants can be calculated at each of the temperatures studied herein using the data presented by Fu et al. (*2*). Rate constants can be calculated using reported fractional conversion (f_A) values according to the following equation

$$k = \frac{2 F_V C_{A0}^{\ 1/2}}{W}(1 - \sqrt{1 - f_A}) \tag{3}$$

where fractional conversion is calculated as

$$f_A = 1 - \frac{C_A}{C_{A0}} \tag{4}$$

The half order reaction rate constants for photocatalytic and catalytic oxidation of ethylene using unplatinized and platinized particulates are provided in Table 2. A number of similarities and differences can be observed between the thin-film and particulate systems. First, the photocatalytic reaction rate constants calculated using unplatinized and platinized particulates follow a similar pattern as described above with thin-films. With the unplatinized catalyst, an increase in reaction rate constant is observed between 30 °C and 70 °C; however, no difference is observed between 70 °C and 107 °C. With the platinized catalyst, increased reaction rate constants are observed at both 70 °C and then again at 107 °C. The behavior differs somewhat in that the rate constants observed with the platinized particulates are slightly lower at 30 °C and slightly higher at 70 °C as compared to the unplatinized particulates. With the thin-films, no difference is observed between unplatinized and platinized versions at these two temperatures. With the platinized catalyst, no catalytic oxidation was observed with either the particulates or thin films at 30 °C.

A major difference between the two systems is that the photocatalytic reaction rate constants calculated with the thin-films are about 2 orders of magnitude higher than the corresponding reaction rate constants calculated with particulates. Actually, the observed differences in reaction rates between thin-films and particulates might be even greater if measured with equivalent levels of light irradiance, since the UV radiation is not completely utilized in the reactor apparatus used here. In addition, note that the level of water vapor, the other major factor controlling the reaction rate constant in these systems, is similar (less than 5 ppm initially) in both studies. A likely explanation for this result is that the UV light incident on the outside of the particle bed is quickly absorbed by the catalyst. Therefore, only a small percentage of particulate catalyst is actually photoactivated. In contrast, the UV light is better distributed and more efficiently utilized in the thin-film system, resulting in photoactivation of a much larger percentage of the catalyst. This would explain the larger reaction rate constants listed in Table 1 for the thin-films.

If this proposed explanation is true, the reaction rate constants calculated with conventional catalysis alone should be nearly equivalent between particulates and thin-films since the internal bulk of the particulate catalyst is accessible to both heat and reactants. As shown in Tables 1 and 2, the catalytic reaction rate constants calculated with thin-films and particulates are relatively similar. The rate constants at 70 °C are within 10%, and the rate constants at 107 °C are within a factor of 2 (thin-films > particulates). The particulate catalytic reaction rate constant at 107 °C may be slightly underestimated since it is calculated based on a fractional conversion of 1.0.

For purposes of illustration, it is possible to calculate reaction rate constants using the data presented by Fu et al. (*2*) that are adjusted to account only for the particulate catalyst mass that is *illuminated*. The most meaningful comparison of this type is for the unplatinized samples where photocatalysis is the only process occurring—the platinized versions include both photocatalytic as well as catalytic effects. Assuming *spherical* particles with an average diameter of 1 mm (reported range: 0.5−1.4 mm), illumination of the entire outer surface of each particle (a reasonable assumption considering that the size of the particles is on the same order as the inner diameter of the reactor, 2.4 mm), and a UV penetration depth ranging between 1.0 and 4.5 μm [a 1 μm penetration depth is obtained from data obtained in our laboratory using TiO_2 thin films (*25*), and 4.5 μm is obtained from the literature for Degussa P25 particles (*26*)], a semiquantitative estimate for the percentage of catalyst that is actually illuminated can be set between 0.3 and 1.3%. This estimate is obtained by subtracting the volume of a sphere with a diameter of 1 mm (representing the total catalyst particle volume) from the volume of a sphere with a diameter of either 0.9955 or 0.9990 mm (representing the portion of the catalyst particle volume that is not activated by UV light) and dividing this difference by the total catalyst particle volume. Dividing the unplatinized particulate reaction rate constants listed in Table 2 by 0.003 and by 0.013 (to account only for the portion of catalyst that is illuminated assuming a penetration depth of 1.0 and 4.5 μm, respectively) yields corrected values that bound the unplatinized thin-film reaction rate constants measured in this study, as listed in Table 1. More specifically, the corrected unplatinized particulate reaction rate constants range between 1.0×10^{-4} and 4.5×10^{-4} $mol^{1/2}\ L^{1/2}\ g^{-1}\ s^{-1}$ at 30 °C and between 2.0×10^{-4} and 8.5×10^{-4} $mol^{1/2}\ L^{1/2}\ g^{-1}\ s^{-1}$ at 70 °C and 107 °C. This is excellent agreement considering the above-mentioned assumptions and the less than rigorous estimation method employed for this comparison.

The difference between thin-films and particulates with regard to light distribution affects one of the major conclusions drawn by Fu et al. (*2*): that "the role of increasing reaction temperatures is mainly to increase the rate of heterogeneous catalytic oxidation". It was stated that at temperatures above 60 °C, "conventional heterogeneous catalytic oxidation may become the predominant reaction on an illuminated Pt/TiO_2 surface". This conclusion was reached because at relatively high temperatures (i.e., above 70 °C), the rates of reaction with platinized particulates are very similar with and without the use of the UV lights (i.e., the effect of photocatalysis is observed to be very small). However, as mentioned, a likely cause is that the majority of the particulates is not efficiently illuminated. As shown in the present study, when the catalyst is efficiently illuminated, as with the thin-films, heterogeneous catalytic oxidation plays a much smaller role in the overall reaction (at the temperatures investigated in this study).

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