

Effects of reaction temperature and water vapor content on the heterogeneous photocatalytic oxidation of ethylene

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Abstract

The photocatalytic degradation of ethylene in airstreams has been studied over the temperature range 30–110 °C using a packed bed reactor containing sol–gel-derived TiO₂ or platinumized TiO₂ particulates. Results of this study indicate that the reactivity of ethylene is greatly enhanced at increased temperatures and that the fraction of ethylene that reacts is stoichiometrically oxidized to CO₂ under all operating conditions. The effect of raising the temperature has been ascribed to decreasing adsorption of water for both types of catalysts, as well as an increase in conventional heterogeneous catalytic reactions occurring on the Pt/TiO₂ catalyst. In addition, platinumizing the TiO₂ photocatalyst and increasing the content of water vapor in the gaseous feed streams both decrease the rate of photocatalytic oxidation of ethylene. The activation energies for the photocatalytic and heterogeneous catalytic oxidation of ethylene were determined to be 13.9–16.0 kJ mol⁻¹ and 82.8 kJ mol⁻¹ respectively.

Keywords: Photocatalysis; Photocatalytic oxidation; Ethylene; Water vapour; Titania; Heterogeneous catalysis

1. Introduction

Purification of groundwater, soils and air polluted by volatile organic compounds (VOCs) is a task that is becoming increasingly important in environmental protection. One promising approach for remediating these systems is to employ semiconductor-mediated photocatalytic oxidation to obtain the complete mineralization (oxidation) of organic contaminants [1–7]. However, most heterogeneous photocatalysis studies have employed aqueous solutions at ambient temperature. Several of these studies have focused on the temperature dependence of the heterogeneous photocatalytic process [8–18]. In general, liquid phase photocatalytic reaction rates were improved by increasing the reaction temperature for temperatures in the range 20–60 °C. Arrhenius behavior has been reported in some cases with activation energies between 10 and 20 kJ mol⁻¹ [9,11,14–16]. These activation energies agree well with those found for OH radical reactions [19].

Studies involving temperature effects on gas phase photocatalytic reactions are far fewer [10,13,18]. The maximum rate for the photocatalytic oxidation of 1-butanol was obtained at 107 °C before it fell off at higher temperatures [13], while the complete mineralization of trichloroethylene (TCE) was obtained by increasing temperature from room temperature to 64 °C and by operating at *W/F* (mass of

catalyst divided by molar flow rate of contaminant) values greater than 6×10^7 g s mol⁻¹ [10]. However, reports also indicate that increasing the reaction temperature decreases the rate of photocatalytic oxidation of propene [18]. It thus appears that the precise role of reaction temperature in photocatalytic reactions requires further study.

Energy utilization in most photocatalytic oxidation processes is inefficient (especially when high power lamps are employed as UV light sources) because all lamps transform electrical energy into heat as well as light. According to the specifications for a 40 W Phillips fluorescent lamp emitting light at a peak of 350 nm, only 21% of the input electrical energy is utilized to produce UV light while 79% of that energy is transformed into heat. The efficiencies with which other types of commercially available UV light sources (e.g. mercury and incandescent) convert electrical energy to light are even lower than for fluorescent lamps. Note that most studies of photocatalytic reactions are conducted at ambient temperature by cooling the reaction apparatus to remove the thermal energy emitted by the lamp. This thermal energy is therefore being wasted rather than being utilized to help drive the oxidation process.

The major aim of the present study is to elucidate further the role of reaction temperature in the gas–solid photocatalytic oxidation of organic compounds. However, determina-

tion of the precise role of reaction temperature in these photocatalytic processes requires a detailed understanding of the mechanism of the photocatalytic reactions. Because of instrumental limitations, a detailed reaction mechanism was not developed in this study. A secondary aim of this study is to illustrate that the total energy, both light and heat, emitted by the light source can be used advantageously to degrade VOCs. In this work, ethylene was chosen as a probe reactant because it is structurally simple, has relatively high reactivity, and is the parent compound of more widespread VOCs of environmental concern (e.g. TCE and tetrachloroethylene). These experiments were conducted at temperatures between 30 and 110 °C. All of these temperatures were achieved by heating the tubular reactor employed in this study with the light source (four 4 W fluorescent UV bulbs), as no other sources of external heat were necessary. In addition to studying the effect of reaction temperature on ethylene photo-oxidation, the influence of water vapor produced during the reaction on the rate of the reaction under steady state conditions was also investigated. More detailed analysis of the kinetics of these reactions was precluded by both the reactor design and the properties of the titania photocatalyst.

2. Experimental methods

2.1. Catalyst preparation

Titanium dioxide aggregates having diameters between 0.5 and 1.4 μm were prepared by a sol-gel technique that involved the controlled hydrolysis of titanium tetraisopropoxide followed by dialysis to $\text{pH} \approx 4$ [20]. Particles were then obtained by evaporation of the solvent, firing to the desired temperature, grinding, and sieving. Full details of this preparation method were presented in an earlier paper [4]. Typical specific surface areas and porosities obtained by Brunauer-Emmett-Teller analysis of N_2 sorption data for these particles were $170 \text{ m}^2 \text{ g}^{-1}$ and 55% respectively when the particles were fired at 300 °C for 4 h. X-ray diffraction analysis indicated that the crystal structure of these particles was primarily anatase (79% anatase, 21% rutile). The primary crystallites that compose the highly aggregated catalyst particles were estimated to have average crystal sizes of ca. 130 Å by using the Scherrer equation to analyze the broadening of the X-ray diffraction peaks.

Platinized titania (Pt/TiO_2) particles were synthesized by impregnating the TiO_2 aggregates prepared as above with an aqueous H_2PtCl_6 solution (8%, Aldrich). The adsorbed H_2PtCl_6 was then directly reduced with a solution of 0.3 M sodium borohydride in 0.01 M NaOH [21]. The Pt/TiO_2 catalyst employed for this study contained 0.3% Pt by weight. Specific surface areas of the platinized titania particles were ca. $160 \text{ m}^2 \text{ g}^{-1}$. Transmission electron micrographs (up to magnifications of 330 000) of these materials do not indicate the presence of individual particles of platinum on the titania particles at this platinum loading (0.3 wt.%). Thus, it appears that the platinum is highly dispersed over the surface of the

titania catalyst. All experiments employed 0.4 g of catalyst. No changes were observed in the physical properties of either the pure TiO_2 or the Pt/TiO_2 catalyst after completing these experiments.

2.2. Apparatus

Photocatalytic oxidation experiments were performed using a fixed-bed tubular reactor operated in a non-circulating mode and interfaced with a Hewlett-Packard 5890 A gas chromatograph [4]. The tubular reactor (a Pyrex tube 11 cm long and 2.4 mm in inner diameter) was surrounded and illuminated by four 4 W fluorescent UV bulbs (GE F4T5-BLB). This particular design was employed because of our interest in demonstrating the complete oxidation of selected VOCs in a gas phase single-pass photoreactor for eventual applications in environmental remediation.

The UV bulbs were used to heat the reactor in all experiments. The reactor and bulbs were placed in an insulated cylindrical glass container (13.5 cm long and 70 mm i.d.) with closed ends. Each end contained a port that allowed an air stream to pass through the container along the outside of the reactor. With the UV bulbs lit, the temperature within the reactor was dependent on the flow rate of the air coolant passing through the container. Reaction temperatures were measured by placing a thermocouple (0.5 mm diameter) in contact with the center of the catalyst bed. The highest temperature attainable in the reactor was ca. 110 °C (with no external air flow). In order to examine the effect of conventional heterogeneous catalytic reactions on the performance of the system, these reactions were conducted under dark conditions. For these experiments, the tubular reactor was covered by aluminum foil to prevent irradiation of the reactor when the UV bulbs were turned on. Temperature variations were less than ± 1 °C in all experiments.

Ethylene (volume ratio of 502 ppm, balance nitrogen, Matheson) and zero air (21% oxygen, balance nitrogen, H_2O less than 5 ppm, total hydrocarbons less than 1 ppm, Liquid Carbonic) were used as received from compressed gas cylinders. In the experiments with high water vapor content, the zero air gas stream was humidified by passage through a water saturator before being mixed with gas from the ethylene cylinder. In these experiments, the water vapor content of the reactant stream was fixed by controlling both the flow rate of the reactant and the temperature of the saturator.

2.3. Product analysis

The product stream from the reactor was allowed to flow continuously to the sampling loop of a chromatographic valve. The gas chromatograph was equipped with a flame ionization detector and a thermal conductivity detector, as well as a Porapak R column to analyze discrete samples of the reactor effluent stream. Concentrations of ethylene were determined by flame ionization detection, while concentrations of CO_2 and H_2O were determined by thermal conductivity detection. The gas chromatograph was calibrated using

known concentrations of reactants and CO_2 . The rate of oxidation at each temperature was measured only after steady state conditions were reached, a process that required no more than 3 h.

During these experiments the only carbon-containing species that were observed were ethylene and carbon dioxide. Mass balance calculations indicated that essentially 100% of the carbon in the feed stream was present in the effluent stream as either carbon dioxide or unreacted ethylene. Thus, it appears that the fraction of ethylene that was converted in the photoreactor was completely oxidized to CO_2 and H_2O . Since intermediate species are expected to form in this reaction, either these species were present in the effluent at low enough concentrations that they were not detected or the rate of oxidation of these intermediates was much higher than their rate of formation.

3. Results and discussion

3.1. Ethylene oxidation over pure TiO_2

Investigations of the photocatalytic oxidation of ethylene to CO_2 and H_2O over a pure TiO_2 catalyst were performed at two different feed concentrations of water vapor and at temperatures from 30 to 110 °C. Fig. 1 shows the per cent conversion of ethylene as a function of reaction temperature under nearly water-free conditions (volume ratio less than 5 ppm) and at a water vapor content of 15 000 ppm. The results indicate that the rate of photocatalytic oxidation of ethylene increased with increasing temperature at both concentrations of water vapor, although operation at higher humidity significantly decreased the rate of photo-oxidation of ethylene. In all cases, the fraction of ethylene that reacted was stoichiometrically oxidized to CO_2 . Since no appreciable oxidation of ethylene over the pure TiO_2 catalyst was observed under dark conditions for the entire temperature

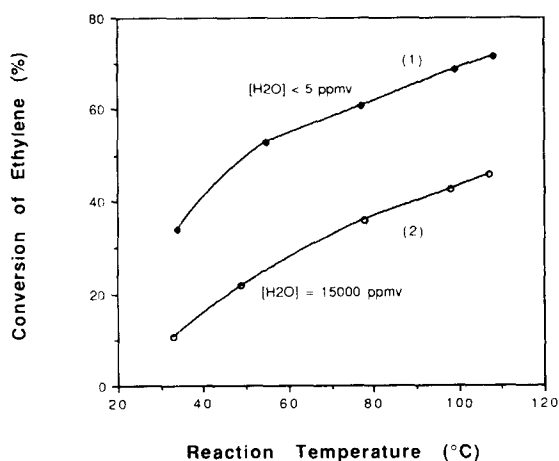


Fig. 1. Effect of reaction temperature on the photocatalytic oxidation of ethylene over a pure TiO_2 catalyst at a volumetric flow rate of 20 ml min^{-1} . Mole fractions of ethylene and oxygen in the feed stream were 2.5×10^{-4} and 0.1 respectively. The mole fraction of water vapor in the feed stream was below 5×10^{-6} for curve 1 and 1.5×10^{-2} for curve 2.

range employed in this study, the temperature effect shown in Fig. 1 could not be ascribed to the heterogeneous catalytic oxidation of ethylene.

In order to clarify the role of reaction temperature in the photocatalytic reactions, the influence of adsorption and desorption of the water produced during the reaction on the conversion of ethylene was examined. Experiments using a water-free reactant feed stream were conducted at 32 and 108 °C in sequence, employing a pure TiO_2 catalyst that had been dried at 110 °C for 20 h before the experiments. The results presented in Fig. 2 demonstrate that when the reaction occurred at 32 °C, the activity decreased dramatically with increasing reaction time. Since no water was detected in the product stream during the first 3 h of operation, presumably all the water formed during this time was completely adsorbed on the catalyst. After about 3 h of operation, a steady state was reached that was characterized by a constant conversion of 40.6% and water appearing in the effluent. Approximately $0.6 \mu\text{mol H}_2\text{O (m}^2 \text{TiO}_2)^{-1}$ (or 36 molecules of water per 100 nm^2 of TiO_2 surface) was adsorbed on the catalyst.

After operation of the reactor at 32 °C for 5 h, the reaction temperature was increased to 108 °C. Dramatic desorption of water that had adsorbed on the catalyst during the previous reaction at 32 °C and a rapid increase in conversion of ethylene were observed as the reactor temperature rose. The new operating temperature was reached within 30 min. Once steady state conditions were achieved, the conversion of ethylene had risen to 70.7% with stoichiometric production of water in the effluent. At both 32 and 108 °C, the ratio $[\text{CO}_2]_{\text{produced}} / [\text{C}_2\text{H}_4]_{\text{converted}}$ was 2, indicating that the fraction of ethylene that reacted was completely oxidized.

The results presented in Fig. 2 suggest that, as ethylene is photo-oxidized to form water, adsorption of this water on the pure TiO_2 catalyst decreased the reactivity of ethylene. If this supposition is true, then the observed increase in activity on

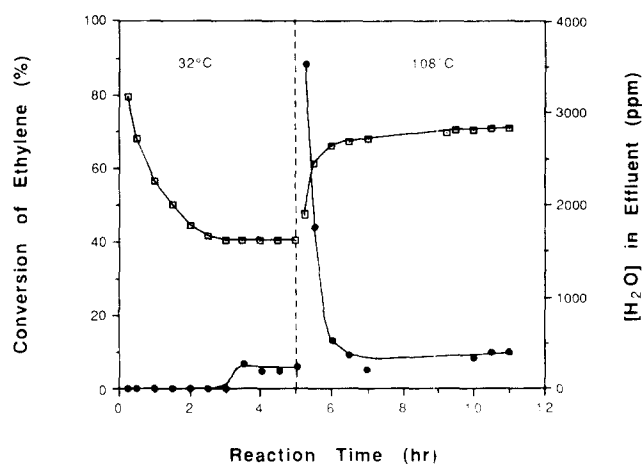


Fig. 2. Effect of adsorption and desorption of water produced during the reaction on the conversion of ethylene (\square) and the concentration of water in the effluent stream (\bullet). Reaction temperature was increased from 32 to 108 °C after 5 h of operation. The TiO_2 catalyst was dried at 110 °C for 20 h before the experiment. Other reaction conditions were the same as for Fig. 1 except that the mole fraction of water vapor was less than 5×10^{-6} .

increasing the reaction temperature to 108 °C would most likely be due to enhanced desorption of water from the catalyst surface at the higher operating temperature. The decrease in activity observed when water was added to the feed stream (Fig. 1) and when water produced during the reaction was adsorbed on the catalyst (Fig. 2) could be ascribed to competition between water and reactants or intermediates for active surface sites.

The influence of the content of water vapor in the feed stream on selected gas–solid photocatalytic oxidation reactions has been examined by some researchers [10,22–24]. According to these reports, it appears that the effect of water vapor depends strongly on the reactant employed and the concentration of water vapor. For the photocatalytic oxidation of TCE, water plays a crucial role in the activity of the TiO₂ catalyst [10,22]. These reports indicated that the presence of water vapor in the reactant stream decreased the initial reaction rates relative to corresponding water-free conditions. However, water vapor was required to maintain photocatalytic activity for extended periods of time. (Note that the complete oxidation of TCE requires that one molecule of water react with each molecule of TCE.) Dibble and Raupp also observed that the rate of TCE oxidation was zero order in water for H₂O mole fractions between 10⁻³ and 5 × 10⁻³. However, water became strongly inhibitory with a negative third-order rate dependence for H₂O mole fractions between 5 × 10⁻³ and 2 × 10⁻² when the TCE mole fraction was 1.89 × 10⁻⁴ [22]. Anderson et al. found that their reaction rates were independent of water vapor concentration for mole fractions of water between 4.2 × 10⁻⁴ and ca. 8.5 × 10⁻³ when operating at 23 °C and between ca. 6 × 10⁻³ and 0.027 at 58 °C. The mole fraction of TCE employed was 3.4 × 10⁻⁴ at both temperatures [10].

In contrast, Ibusuki and Takeuchi [23] reported that the photocatalytic oxidation of toluene (80 ppm in air) on TiO₂ was enhanced by increasing the concentration of water vapor in the system. They also observed that the concentration of CO₂ formed increased linearly with increasing water vapor content between 0% and 60% relative humidity. Moreover, Peral and Ollis [24] found that water vapor feed concentrations of 250–10 000 mg m⁻³ (0.6%–25% relative humidity or ca. 330–13 000 ppm H₂O) inhibited acetone photooxidation but had no influence on the reaction rate of 1-butanol. *m*-xylene oxidation increased with increasing water vapor concentration up to 1000 mg H₂O m⁻³ (ca. 1300 ppm H₂O) and decreased thereafter. These observations were explained in terms of the suppression of hydroxyl radical formation at the catalyst surface and competitive adsorption.

In the present study, water is a product of the reaction and is not required as a reactant. It is also likely that ethylene is less strongly adsorbed onto the TiO₂ surface than water. Thus, at lower reaction temperatures, water that is either present in the feed stream or produced during the reaction may displace surface-adsorbed ethylene, thereby inhibiting photocatalytic oxidation of ethylene. At higher temperatures, the lower coverage of water on the TiO₂ surface may lead to more unoc-

cupied reactive sites (quite possibly hole traps) available for photooxidation of ethylene and/or intermediates.

3.2. Ethylene oxidation over 0.3 wt.% Pt/TiO₂

In a recent publication we reported that the complete oxidation of benzene in air was enhanced by employing a platinumized titania photocatalyst [25]. It appeared that the improved performance of the platinumized catalyst was due to conventional heterogeneous catalytic reactions that occurred on the platinum. In that study, it was possible to obtain the complete oxidation of benzene at relatively high concentrations (ca. 500 ppm) in a single pass through a laboratory-scale reactor operated at temperatures as low as 110 °C. Thus, we were interested in studying the effect of employing a platinumized photocatalyst on the oxidation of ethylene.

The photocatalytic oxidation of ethylene over a 0.3 wt.% Pt/TiO₂ catalyst was compared with the photo-oxidation of ethylene over the pure TiO₂ catalyst over the same temperature range (30–110 °C) but at a higher volumetric flow rate (60 ml min⁻¹ instead of 20 ml min⁻¹) than employed earlier. A dry stream of ethylene was utilized. Data presented in Fig. 3 (curves 1 and 2) indicate that the apparent reactivity of ethylene with Pt/TiO₂ was greatly enhanced over the reactivity of ethylene with pure TiO₂ when the reaction temperature was higher than 60 °C. In fact, 100% conversion of ethylene (and thus complete oxidation) was achieved at temperatures higher than 90 °C. On the contrary, the activity of the Pt/TiO₂ catalyst was slightly less than that of the corresponding pure TiO₂ catalyst at reaction temperatures below 55 °C.

Since much of the improved performance of the platinumized catalyst for the oxidation of benzene could be ascribed to heterogeneous catalytic oxidation [25], a similar investigation was conducted for this study. As shown in Fig. 3 (curve 3), the heterogeneous catalytic oxidation (dark reaction) of ethylene only occurred on the Pt/TiO₂ catalyst at temperatures above 40 °C. As the temperature was increased above

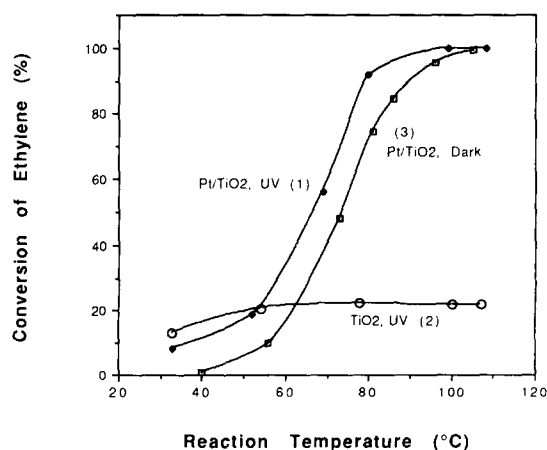


Fig. 3. Effect of platinumization of TiO₂ on the photocatalytic and heterogeneous catalytic oxidation of ethylene at different temperatures with a volumetric flow rate of 60 ml min⁻¹ for all curves. The mole fractions of ethylene, oxygen and water vapor were 3.9 × 10⁻⁴, 4.5 × 10⁻² and below 5 × 10⁻⁶ respectively.

this value, the reaction rate increased dramatically until ca. 100% conversion of ethylene was obtained at 105 °C. However, no appreciable heterogeneous catalytic reaction occurred on TiO₂ at temperatures between 30 and 110 °C, and only photocatalytic oxidation was observed on Pt/TiO₂ at reaction temperatures below 40 °C.

The results described above lead to the following conclusions: (1) platinization greatly improves the conventional heterogeneous catalytic oxidation properties of TiO₂ but has a slightly negative effect on the pure photocatalytic oxidation of ethylene near ambient temperatures; (2) both photocatalytic and heterogeneous catalytic oxidations of ethylene occur on the Pt/TiO₂ catalyst at temperatures higher than 40 °C; (3) the role of increasing reaction temperature is mainly to increase the rate of heterogeneous catalytic oxidation. In fact, conventional heterogeneous catalytic oxidation may become the predominant reaction on an illuminated Pt/TiO₂ surface when the reaction temperature is higher than 60 °C.

The effect of employing platinized TiO₂ catalysts on photocatalytic reactions has been extensively studied [17,26–29]. It was reported that the method of platinization and the amount of platinum loading were important in governing the net effect of platinization [26,27]. In general, enhanced photoactivity was found for Pt/TiO₂ catalysts with low Pt loadings (0.1–1 wt.%). This improved photoactivity has been explained as being due to an enhanced ability to collect photogenerated electrons on the islands of platinum that form at the TiO₂ surface [30]. However, platinization of TiO₂ was also found to decrease its photocatalytic activity for the degradation of hydrocarbons because the presence of the heavy metal led to faster electron–hole recombination [26].

In our study, a 0.3 wt.% Pt/TiO₂ catalyst was employed. A slight decrease in activity for the photocatalytic oxidation of ethylene was observed at reaction temperatures below 55 °C under dry conditions for the platinized catalyst as compared with the pure titania catalyst. The decrease in photoactivity for the platinized catalyst when operating under these conditions may be related to the method employed to prepare the catalyst as well as the reaction conditions. Most photocatalysis studies employ aqueous suspensions of catalyst. These platinized TiO₂ catalysts are often prepared by photodeposition methods [21] using commercially available non-porous TiO₂ powders (e.g. Degussa P25) with relatively low specific surface areas (10–60 m² g⁻¹). In the present study, the Pt/TiO₂ catalyst was prepared by sodium borohydride reduction of chloroplatinic acid that had been previously adsorbed on sol–gel–derived porous TiO₂ particulates characterized by a relatively high specific surface area (170 m² g⁻¹). These experiments also employed gas–solid photocatalytic reaction conditions with a water-free reactant feed stream. Further studies are needed to clarify the effect of utilizing platinized photocatalysts for conducting gas–solid photo-oxidation reactions.

3.3. Activation energies

It has been reported that the photocatalytic decomposition of many organic compounds such as phenol [15,31], chlo-

rophenols [14] and salicylic acid [14] followed first-order kinetics even at high conversions. Apparent first-order rate constants k_{app} for both the photocatalytic and heterogeneous catalytic oxidation of ethylene were calculated according to the following equation at different reaction temperatures:

$$k_{app} = (V/W) \ln[1/(1-X)] \quad (1)$$

where V is the volumetric flow rate of ethylene, W is the mass of catalyst employed, and X is the fractional conversion of ethylene obtained under steady state conditions [32].

According to the Arrhenius equation, k_{app} should increase linearly with $\exp(-1/T)$. In general, these reactions did follow Arrhenius behavior, as shown in Fig. 4. In this figure, $\ln k_{app}$ is plotted against the reciprocal of the absolute temperature for the photocatalytic oxidation of ethylene over the pure TiO₂ catalyst in a water-free stream (curve 1), the same reaction but at a high water vapor content (curve 2), the heterogeneous catalytic oxidation (dark reaction) over the Pt/TiO₂ catalyst in a water-free stream (curve 3), and the oxidation of ethylene over the illuminated Pt/TiO₂ catalyst in a water-free stream (curve 4). Only in the last case was Arrhenius behavior not observed. At lower temperatures (30–45 °C), the slope of this curve was similar to that of the photocatalytic reactions on TiO₂ (shown in curves 1 and 2). At higher temperatures (45–110 °C), the slope was similar to that of the heterogeneous catalytic reaction on Pt/TiO₂ (curve 3). This result indicates that both photocatalytic and heterogeneous catalytic reactions occurred on the illuminated Pt/TiO₂ catalyst, with photocatalytic oxidation being the main reaction at low reaction temperatures and heterogeneous catalytic oxidation dominating at higher temperatures.

Activation energies were obtained from the plots shown in Fig. 4 by the method of least squares. The apparent activation energies for the photocatalytic oxidation of ethylene over the pure TiO₂ catalyst in either water-free or relatively high water vapor content feed streams were 13.9 kJ mol⁻¹ and 16.0 kJ

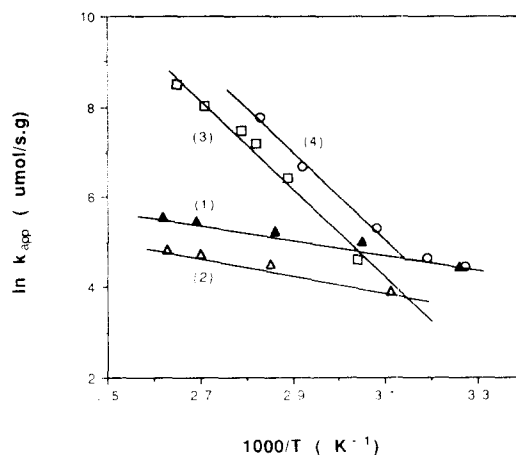


Fig. 4. Arrhenius plots for the oxidation of ethylene: curve 1, TiO₂, UV, [H₂O] < 5 ppm; curve 2, TiO₂, UV, [H₂O] = 1.5 × 10⁴ ppm; curve 3, Pt/TiO₂, dark; curve 4, Pt/TiO₂, UV. The other reaction conditions for curves 1 and 2 were the same as for Fig. 1 and for curves 3 and 4 were the same as for Fig. 3.

mol⁻¹ respectively. These values were in the same range (10–20 kJ mol⁻¹) as those obtained for the photocatalytic reactions of other organic compounds [9,11,14–16]. The activation energy for the heterogeneous catalytic oxidation of ethylene was 82.8 kJ mol⁻¹, which is about 5 times higher than the activation energy required for photocatalytic oxidation.

This difference in activation energies indicates the different reaction mechanisms that can operate in these systems. The heterogeneous catalytic oxidation of ethylene is probably initiated by the dissociative adsorption of one of the reactants on platinum [33]. This step would be characterized by a relatively high activation energy. (Given the relative concentrations of oxygen and ethylene in the reactor, we suspect that the initial step is the dissociation of oxygen on platinum, although we have no experimental evidence to support this hypothesis.) However, the photocatalytic oxidation of ethylene would involve electron transfer processes that are characterized by relatively low activation energies. (Note, however, that the activation energies for photocatalytic oxidation do not include the energy of the UV radiation required to initiate the process by forming electron–hole pairs, which is ca. 300–350 kJ mol⁻¹.)

4. Conclusions

Results of this work indicate that the reaction temperature has a strong influence on the rate of oxidation of ethylene over UV-illuminated TiO₂ or Pt/TiO₂ catalysts in gas phase systems. The notable improvement in activity observed at increased reaction temperatures may be due to an enhanced desorption of water from both types of catalysts at higher operating temperatures. There is also a dramatic increase in the simultaneous heterogeneous catalytic oxidation for the illuminated Pt/TiO₂ catalyst at temperatures in the range 40–110 °C. Activation energies for the photocatalytic and heterogeneous catalytic oxidation of ethylene were determined to be 13.9–16.0 kJ mol⁻¹ and 82.8 kJ mol⁻¹ respectively. The combination of photocatalytic and conventional heterogeneous catalytic reactions over the Pt/TiO₂ catalyst at enhanced temperatures could provide an efficient and practical way to utilize the total energy, both light and heat, emitted by the light source.

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