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Photocatalytic degradation of ethylene over thin films of titania supported on glass rings

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Abstract

Volatile organic compounds present in air at low concentrations can be oxidized to carbon dioxide and water when exposed to thin films of titania irradiated with near UV light. Borosilicate glass rings were coated with a titania-sol generated by controlled hydrolysis of titanium isopropoxide. A reactant stream containing either 48.99 or 1055 ppm of ethylene was fed continuously to a tubular reactor packed with the coated glass rings and surrounded by blacklight blue fluorescent bulbs. The effluent was analyzed by gas chromatography. Titania supported on glass rings exhibited higher photocatalytic activity than unsupported titania pellets. Preliminary kinetic studies of photocatalytic oxidation of ethylene suggest that the reaction rate can best be described using a Langmuir-Hinshelwood-Hougen-Watson rate expression. ©1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

In recent years, heterogeneous photocatalysis has received wide interest as a promising technique for remediating environmental pollution via both liquid phase and gas phase reactions. Photocatalysis provides a number of attractive features [1]. First, this process involves the actual destruction of organic contaminants rather than merely transfer of a contaminant from one phase to another, e.g., from a gas or liquid phase to a solid phase in a process such as adsorption on activated carbon, or from a liquid phase to a gas phase in the case of air stripping of volatile contaminants. By employing photocatalysis, one can achieve complete oxidation of a wide variety of organic pollutants to carbon dioxide and water in a reactor operating near ambient temperature. Moreover, utilization of solar energy to initiate photocatalytic oxidation reactions over TiO_2 is possible [2–5].

In the past, most research on the heterogeneous photocatalytic oxidation of environmental contaminants has focused on the use of TiO_2 photocatalysts for purification of water [6–8]. However, photocatalytic oxidation in the gas phase has recently attracted more interest. The reason for the increasing interest is that the rates of photocatalytic oxidation of some organic compounds (e.g. trichloroethylene) are reported to be orders of magnitude higher in the gas phase than in the liquid phase at similar temperatures and levels of irradiation [9]. The observed high reaction rates have led to an interest in applications involving not only the purification of air but also the purification of contami-

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nated soils and water via processes that combine photocatalytic oxidation in the gas phase with air stripping of volatile compounds [1].

Nevertheless, the efficiency of photocatalytic processes in the gas phase needs to be improved. To date, photocatalytic studies have usually employed various photocatalysts in the form of powders or pellets [6–8]. However, the vast majority of these studies have involved titania-based materials. Recent experiments in our laboratory show that the extinction coefficient of titania film is about $10^{-3}\,\mathrm{nm}^{-1}$ at a wavelength of 360 nm when the angle of incidence of the light on the film is 90°. Most of the incident radiation is absorbed in a film that is only a few microns thick. Therefore, a major problem associated with using unsupported photocatalysts in a photoreactor is that a large amount of catalyst is needed, but only the thin exterior layer of the typical unsupported photocatalyst actually absorbs UV light. Consequently, only a small fraction of the solid is active with respect to its capability to bring about photodegradation reactions. Possible solutions to this problem involve utilization of a thin layer of titania coated on a variety of supports, e.g., glass rings, aluminum sheets, etc., in novel reactor configurations.

The purposes of this paper are to present a procedure for fabrication of a photocatalyst system consisting of titanium dioxide supported on glass rings and to assess the photocatalytic activity of the catalyst for oxidation of ethylene present at low concentrations in air. A preliminary analysis of kinetic data for this photodegradation reaction is also presented.

2. Experimental

2.1. Preparation of catalysts

The active component of the photocatalysts, namely titanium dioxide, is prepared by a sol-gel method [10]. Titanium tetraisopropoxide (417 ml) (Aldrich Chemical, Milwaukee, WI) is hydrolyzed in 5000 ml of water to which 36.1 ml of concentrated nitric acid (Aldrich Chemical, Milwaukee, WI) has been previously added. Precipitation occurs immediately. The suspension is peptized in order to obtain a clear sol. The sol is then dialyzed for 3–4 days using a sol to water ratio of 1 : 10 until a final pH of 3.5 is reached. The support is a borosilicate glass ring, which has an outer diameter of 6 mm, a wall thickness of 1 mm, and a length of 6 mm. The glass rings are submerged in the titania-sol and then withdrawn at a constant speed of 22 cm/min. The rings are then dried at 100°C for 2 h and subsequently fired at 350°C for 3 h. The coating procedure can be repeated as many times as necessary to obtain the desired number of layers of titania.

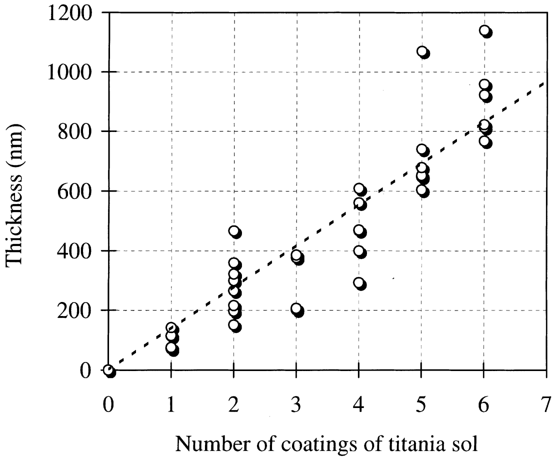

Fig. 1. Dependence of the thickness of the titania film on the number of coatings of titania-sol applied to the glass rings. The dotted line represents the best fit straight line obtained from a regression analysis.

Although direct assessments of some physical properties of the catalyst, e.g., its specific surface area, porosity, and crystal structure, are not feasible for this supported catalyst, estimates of these properties can be obtained by using unsupported titania particles as a surrogate for the supported titania film. For a catalyst fired at 350°C for 3 h, typical values of the specific surface area and porosity, as obtained from a BET analysis of nitrogen adsorption data for the catalyst, are $150\,\mathrm{m}^2/\mathrm{g}$ and 47%, respectively [11]. X-ray diffractometry (XRD) of a corresponding unsupported titania powder that was fired at 300°C indicated that the crystal structure of the particle is primarily anatase (89% anatase and 11% rutile) [12]. The thickness of the titania film supported on the glass rings was measured by scanning electron microscopy. Fig. 1 shows the data for the thickness of the film as a function of the number of coats of the titania-sol applied.

Linear regression analysis was employed to fit the data to a straight line (see the dotted line in Fig. 1). The fact that the straight line fits the data reasonably well suggests a linear relationship between the film thickness and the number of coats of titania applied. The slope of the line (which represents the thickness of one layer of the titania film) is 130 nm.

2.2. Experimental apparatus

A tubular photoreactor was employed for the photocatalytic degradation experiments. The reactor is a borosilicate glass column obtained from Ace Glass (Vineland, NJ). The reactor has an inner diameter of 1.5 cm and an effective length of 25 cm. The glass rings coated with titania (see Section 2.1) are used to randomly pack the borosilicate glass column. The reactor is placed along the axis of an acrylic vessel. The vessel is 28 cm long and 12.7 cm in diameter. The ultraviolet light sources are eight Wyco blacklight blue fluorescent bulbs (8 watts) obtained from Bulb Direct (Pittsford, NY). The light intensity emitted from the bulbs was 5.2 mW/cm^2. These bulbs are located 3.8 cm away from the reactor and are evenly spaced around the axis of the reactor.

The reactor module is also equipped with several inlets at both ends of the column through which cooling air flows in order to facilitate maintaining a constant temperature during the experiment. The cooling air flows in the annulus between the borosilicate column and the acrylic vessel. To monitor the temperature, a fiberoptic thermometer (Luxtron, Model 3000, Santa Clara, CA) is used. Fiberoptic temperature probes (Luxtron, Model MAM-10) are placed at both ends and at the midpoint of the glass reactor.

Ethylene was employed as the reactant to be oxidized. Compressed gas cylinders containing ethylene at concentrations of 48.99 ppmv and 1055 ppmv were obtained from Scott Specialty Gases (Plumsteadville, PA). The balance of the cylinder contents was hydrocarbon-free air containing less than 0.1 ppmv total hydrocarbon. The flow rates of the gases from the cylinders are controlled by Omega FMA-113 mass flow controllers (Omega Engineering, Stamford, CT). The feed gases either go directly to the photoreactor (if no addition of water is required) or go through a sparger to become saturated with water vapor prior to going to the photoreactor. After passing through the reactor, the effluent gas stream is sampled via a 250 μl sampling loop connected to a gas chromatograph. The gas chromatograph is a Hewlett-Packard G1800A GCD system equipped with an electron ionizing detector. The column used in the gas chromatograph is a 30 m × 0.32 mm GasPro Gas Separator Column (Alltech Associates, Deerfield, IL). The volumetric flow rate of the gas in the system is measured using a bubble flow meter.

3. Results

3.1. Effect of number of coats of TiO_2 on the conversion of ethylene

Photocatalytic oxidation of ethylene was employed as a model reaction to compare the photocatalytic activities of two types of titania catalysts. The photocatalysts of primary interest were glass rings on which different numbers of layers of the titania film (one, two, or three) had been deposited. For these experiments, the reactant stream contained 48.99 ppmv of ethylene in air. A reactant gas feed rate of 50 ml/min was divided into two streams: one stream (30 ml/min) flowed through the water saturator to become saturated with water at room temperature while the other stream (20 ml/min) bypassed the saturator. This division of the feed stream results in the feed to the reactor having a relative humidity level of approximately 60%, once the two streams are recombined prior to entering the reactor. This humidity level corresponds to a gas phase mole percentage of water vapor of 1.8. The reactor is filled with approximately the same number of rings, regardless of the number of titania coats applied to the glass supports. The temperature of the reactor is controlled by the use of cooling air. In the absence of cooling air, the temperature of the reactor is about 90–110°C. This temperature decreases to 30–40°C when cooling air is employed. The results involving unsupported titania pellets were obtained by Fu et al. [13]. The titania pellets employed in Fu's experiment were prepared by the sol-gel method and consist solely of titanium dioxide.

The results of the activity measurements for several photocatalysts are presented in Table 1. In every case,

Table 1
Conversion of ethylene over various photocatalysts

Catalyst	Number of coats of titania	W/F ratio[a] (g s/mol)	Conversion of ethylene (%)	
			Without cooling (T ∼90–110°C)	With cooling (T ∼30–40°C)
TiO_2[b]	1	2.5×10^6	72.5	14.8
TiO_2[b]	2	5.0×10^6	88.3	23.3
TiO_2[b]	3	7.5×10^6	86.3	24.3
TiO_2 pellets[c]	none	1.2×10^8	45.7	10.7

[a] W/F ratio represents the ratio of the weight of catalyst (W) to the molar flow rate of reactant (F).

[b] Initial concentration of ethylene = 48.99 ppmv, concentration of water vapor = 1.8% (v/v).

[c] The activity data were obtained from Fu et al. [13].

the results show higher conversions of ethylene at the higher temperature. Higher conversion of ethylene was also achieved when the catalysts supported on glass rings were employed, rather than the unsupported titania pellets. The increases in the photocatalytic activity of the supported titania were more significant at the higher temperature. Note that the W/F ratios for the experiments with the supported catalyst were at least one order of magnitude lower than that for the experiment with the unsupported catalyst pellets.

Comparison of the photocatalytic activities of glass rings coated with one layer of titania with those coated with two layers indicates that greater degradation of ethylene occurs in the latter system. However, the activities of the glass rings on which three layers of titania were deposited are similar to those of the glass rings with two layers of titania, despite the presence of a greater amount of catalyst in the former case. There are several possible explanations of these results. One explanation is that ultraviolet light cannot penetrate the entire depth of three layers of titania; therefore, only a portion of the three-layer catalyst is active. Another possible explanation is that the surface reaction rate is so rapid that the reactant is depleted before reaching the innermost layer of the titania film. However, our previous experience with thin-film TiO_2 catalysts indicates that the first explanation is much more likely.

3.2. *Preliminary kinetic studies of photocatalytic oxidation of ethylene*

Preliminary kinetic studies were performed for the photocatalytic oxidation of ethylene. Ethylene in air at an initial concentration of 1055 ppmv was employed for these experiments. Glass rings which were coated with titania were packed in the photoreactor. The total amount of titania in the reactor is approximately 8.8 mg. To control the temperature of the reaction, cooling air was employed. In these experiments, the temperature in the reactor varied from 45 to 50°C along the length of the reactor. The flow rate of the feed stream was varied from ca. 10 to 90 ml/min in order to obtain data in the form of a plot of conversion versus the ratio of the weight of catalyst to the flow rate of reactant (W/F) (see Fig. 2).

The kinetic data were fit to a number of power law rate expressions (1/2 order, first order, and 3/2 order) and to a Langmuir-Hinshelwood-Hougen-Watson (LHHW) rate expression. After linearization of the appropriate integrated form of the plug flow reactor design equation, linear regression analyses of the data were carried out. The analysis for the 3/2 order rate equation did not provide a meaningful fit of the data. Hence this rate expression was eliminated from further consideration. Subsequently, parameters obtained from the regression analyses of the three remaining models were used to evaluate the predicted conversion as a function of W/F. Inspection of the differences between the predicted conversions and the experimental values indicated that the LHHW rate expression provides the best fit of the data. The form of this LHHW model is shown below

$$r = \frac{k\,K\,C}{1 + K\,C} \tag{1}$$

where r is the reaction rate (mol/g s), k is the reaction rate constant (mol/g s), K is the adsorption equilibrium constant (l/mol), and C is the concentration of ethylene (mol/l).

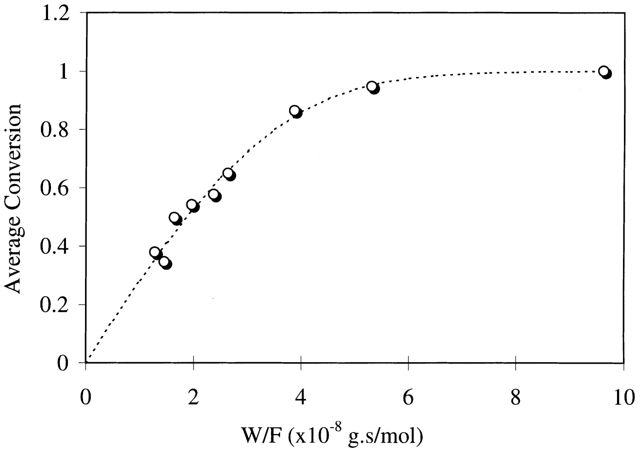

Fig. 2. Plot of average conversion versus the ratio of the weight of catalyst (W) to the molar flow rate of ethylene (F). The dotted line represents the predicted conversion obtained using the Langmuir-Hinshelwood-Hougen-Watson rate expression with values of 4.27×10^{-9} mol/g s and 4.95×10^{4} l/mol for k and K, respectively.

Table 2
Parameters from regression analyses of various linearized Langmuir-Hinshelwood-Hougen-Watson rate expressions

Linearized form	k (mol/g s)	K (l/mol)
$\frac{WC_o/F}{\ln(C/C_o)} = -\frac{1}{kK} - \frac{1}{k} \cdot \frac{(C - C_o)}{\ln(C/C_o)}$	3.59×10^{-9}	8.18×10^{4}
$\frac{WC_o/F}{(C - C_o)} = -\frac{1}{k} - \frac{1}{kK} \cdot \frac{\ln(C/C_o)}{(C - C_o)}$	4.27×10^{-9}	4.95×10^{4}
$\frac{(C - C_o)}{WC_o/F} = -\frac{1}{K} \cdot \frac{\ln(C/C_o)}{\tau} - k$	4.00×10^{-9}	5.82×10^{4}

Substitution of this rate expression into the design equation for a plug flow reactor [14] gives

$$\frac{W}{F} = \frac{1}{k\,K\,C_o} \ln\left(\frac{C_o}{C}\right) + \frac{1}{k}\left(\frac{C_o - C}{C_o}\right) \tag{2}$$

where C_o is the inlet concentration of ethylene (mol/l).

Since one can rewrite Eq. (2) in a variety of forms, three different sets of kinetic parameters were obtained from linear regression analyses of the three different linearized forms of the integrated LHHW rate expression (see Table 2). The values of the reaction rate constant range from 3.59×10^{-9} to 4.27×10^{-9} mol/g s and the value of adsorption equilibrium constant lies between 4.95×10^{4} and 8.18×10^{4} l/mol. The dotted line in Fig. 2 represents the conversions predicted by the LHHW model, using values of 4.27×10^{-9} mol/g s and 4.95×10^{4} l/mol for k and K, respectively. The model appears to provide a very good fit of the data. The other sets of LHHW parameters provide similar fits of the data.

4. Conclusions

At both high and low temperatures, titania supported on borosilicate glass rings exhibits higher photocatalytic activity for the oxidation of ethylene than unsupported titania pellets. Glass rings on which two layers of titania had been deposited have a higher activity than those on which only one layer of titania had been deposited. This result is a consequence of the greater amount of catalyst available in the reactor. However, glass rings on which three layers of titania were present were characterized by a photocatalytic activity similar to that obtained from glass rings on which two layers had been deposited. One explanation for this result is that the ultraviolet radiation may not be able to penetrate the entire depth of the titania film, thereby rendering part of the film inactive.

A preliminary kinetic analysis of data for the photocatalytic oxidation of ethylene indicates that a two-parameter Langmuir-Hinshelwood-Hougen-Watson model can be used to describe the experimental data.

References

[1] X. Fu, W.A. Zeltner, M.A. Anderson in: P.V. Kamat, D. Meisel (Eds.), Semiconductor Nanoclusters: Physical, Chemical, and Catalytic Aspects, Elsevier, Amsterdam, 1996, p. 445.
[2] R.W. Matthews, Solar Energy 38 (1987) 405.
[3] D. Bahnemann, D. Bockelmann, R. Goslich, M. Hilgendorff, D. Weichgrebe, in: D.F. Ollis, H. Al-Ekabi (Eds.), Photocatalytic Purification and Treatment of Water and Air, Elsevier, Amsterdam, 1993, p. 301.
[4] J.E. Pacheco, M. Mehos, C. Turchi, H. Link, in: D.F. Ollis, H. Al-Ekabi (Eds.) Photocatalytic Purification and Treatment of Water and Air, Elsevier, Amsterdam, 1993, p. 547.
[5] F.W. Wilkins, D.M. Blake, Chem. Eng. Prog. 90 (1994) 41.
[6] D.M. Blake, Bibliography of Work on the Photocatalytic Removal of Hazardous Compounds from Water and Air, NREL/TP-430-6084, National Renewable Energy Laboratory, 1994.
[7] D.M. Blake, Bibliography of Work on the Photocatalytic Removal of Hazardous Compounds from Water and Air Update Number 1 to June 1995, NREL/TP-473-20300, National Renewable Energy Laboratory, 1995.
[8] D.M. Blake, Bibliography of Work on the Photocatalytic Removal of Hazardous Compounds from Water and Air Update Number 2 to October 1996, NREL/TP-430-22197, National Renewable Energy Laboratory, 1996.
[9] N.N. Lichtin, M. Avudaithai, Environ. Sci. Technol. 30 (1996) 2014.
[10] Q. Xu, M.A. Anderson, J. Mater. Res. 6 (1991) 1073.
[11] X. Fu, L.A. Clark, Q. Yang, M.A. Anderson, Environ. Sci. Technol. 30 (1996) 647.
[12] X. Fu, W.A. Zeltner, M.A. Anderson, Appl. Catal. B: Environ. 6 (1995) 209.
[13] X. Fu, L.A. Clark, W.A. Zeltner, M.A. Anderson, J. Photochem. Photobiol. A: Chem. 97 (1996) 181.
[14] C.G. Hill, Jr., An Introduction to Chemical Engineering Kinetics & Reactor Design, Wiley, New York, 1977, p. 263.