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A Kinetic Study of the Photocatalytic Degradation of 3-Chlorosalicylic Acid over TiO_2 Membranes Supported on Glass

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The photocatalytic degradation of 3-chlorosalicylic acid to HCl and CO_2 on glass-supported TiO_2 has been investigated in a photoreactor designed to permit both continuous throughput of gaseous and liquid feed streams and frequent exchange of the catalyst. The data for the photodegradation reaction can best be correlated in terms of the rate expression

$$r = kK_1[O_2]K_2[S]/\{(1 + K_1[O_2])(1 + K_2[S])\},$$

where $[O_2]$ and [S] represent the concentrations of oxygen and 3-chlorosalicylic acid, respectively.

INTRODUCTION

In recent years, suspensions of semiconductor particles have been widely employed to catalyze a variety of photochemical reactions. In such work, particular emphasis has been placed on photodegradation reactions involving both inorganic and organic species. Frequently, these studies have focused on species which serve as models of the types of compounds which present severe pollution or waste treatment problems even when they are present at very low concentrations in aqueous solution. For example, Frank and Bard (*1*) have reported that irradiation of an aqueous suspension of a TiO_2 powder brings about the conversion of CN^- and CrO_4^{2-} to CNO^- and Cr^{3+}. Photoirradiation of aqueous solutions of sulfides and sulphites in the presence of CdS leads to production of hydrogen and thiosulfates (*2*, *3*). Moreover, a large number of halogenated organic compounds have been completely oxidized in the presence of TiO_2 particles. Among the compounds studied are dibromoethane (*4*), trichloroethylene (*5*), chloroacetic acids and chlorobenzenes (*6*, *7*), chlorophenols (*8*), benzoic and salicylic acids (*9*, *10*), PCBs (*11*), trichlorophenoxyacetic acid (*12*), chloromethane (*13*), and surfactants (*14*). The susceptibility of such a wide variety of compounds to treatment in this fashion makes photocatalytic degradation a particularly attractive process for both wastewater treatment and water purification.

To date, the vast majority of the investigations in this area have employed suspensions of the semiconducting particles. Fixation of the catalyst on a stationary support would circumvent the need for filtration to recover the catalyst from the reaction mixture. To this end, Serpone *et al.* (*15*) and Matthews (*9*, *10*) have supported TiO_2 on glass beads and glass surfaces, respectively. Both systems proved to be both stable and efficacious catalysts for the photodegradation of dilute solutions of the organic compounds tested.

It is also possible to bring about the photocatalytic oxidation of gaseous hydrocarbons over a bed of TiO_2 particles at room temper-

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ature. For example, in the early 1970s Formenti and his co-workers (*16–18*) studied the photocatalytic oxidation of isobutane and other hydrocarbons over a bed of anatase powder. The research reported in these papers focuses on an alternative approach to preparing a macroscopic TiO_2 catalyst system which can be employed in continuous flow photoreactor systems, namely, attachment of TiO_2 membranes to a glass support structure.

In recent years, several research groups have employed sol–gel techniques to prepare ceramic membranes with interesting permselectivity characteristics. Supported membranes composed of SiO_2, Al_2O_3, and TiO_2 have been investigated to assess their potential for use in ultrafiltration and reverse osmosis. Barringer and Bowen (*19*), Kaiser and Schmidt (*20*), Leenaars and Burggraaf (*21*), and Gieselmann *et al.* (*22*) have all employed somewhat different experimental protocols to prepare such membranes. The variations in these procedures are reflected in both the gross structural characteristics and the microscopic morphologies of the finished membranes. Not only the techniques used in generation of the precursor sol, but also those employed in coating, drying, and calcining the supported membranes have been found to influence the physical and chemical nature of the supported ceramic membrane (*22*). In the present work, we have employed sol–gel techniques in the preparation of TiO_2 ceramic membranes supported on a glass tube for use in a photochemical reactor. This research focuses on the preparation of membranes with desirable photocatalytic properties and on determination of the rate of photodegradation of 3-chlorosalicylic acid over these membranes. This acid is a halogenated aromatic compound which is highly soluble in water. It can be regarded as representative of a wide range of such compounds which are of interest to scientists and engineers concerned with environmental problems.

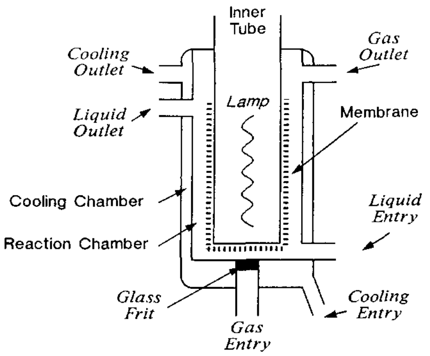

FIG. 1. Schematic diagram of annular photochemical membrane reactor.

EXPERIMENTAL

Apparatus

A schematic diagram of the photochemical reactor is shown in Fig. 1. The reacting fluid flows through an annulus surrounding a medium pressure Hg immersion lamp located at the axis of the cylindrical reactor. The flow of liquid provides both a continuous source of fresh feed and cooling for the lamp. The Pyrex reactor is constructed in a manner such that the inner cylinder of the annulus can be removed and interchanged with other tubes on which different membranes have been coated. The radius and length of the coated region are 2.3 and 20 cm, respectively. The width of the annulus is approximately 3 mm. The reactor can be operated in a continuous mode with respect to the flows of both liquid and gas.

A peristaltic pump (Cole Palmer, Chicago, IL) recirculates the reactant solution between a fluid reservoir and the photochemical reactor. The dissolved oxygen concentration in solution was kept constant during each experiment by bubbling into the reactor a gaseous mixture of N_2 and O_2 in a fixed ratio. To enhance the rate of dissolution of gas in the liquid, the gas entry tube is fitted with a gas frit to enhance the generation of interfacial surface area between the gas and liquid phases. The dissolved oxygen content of the reaction mixture was monitored by a dissolved oxygen probe (Yellow Springs Instrument Model 58, Yellow Springs, OH) placed in the reservoir. The gaseous effluent passes through a trap filled with a solution of $Ba(OH)_2$ and NaOH. This trap permits measurement of the CO_2 produced by reaction. Losses of liquid from the apparatus are minimized by the use of a condenser at the gas outlet.

The pH of the reaction mixture was adjusted as desired by addition of 10^{-3} *N* KOH solution.

The progress of the degradation of 3-chlorosalicylic acid was monitored by measuring the absorbance of the solution at 300 nm. An ion selective electrode was employed to determine the chloride ion concentration. The CO_2 evolved was determined by analysis of the contents of the scrubber.

A 450-W Hg immersion lamp (A.C.E., Vineland, NJ) was employed as the radiation source. The intensity of the radiation employed was measured at 365 nm using a Model 380 radiometer (UDT, Hawthorne, CA). From this measurement and calculations based on the emission spectrum of the lamp and the transmission characteristics of Pyrex, the flux of photons with wavelengths between 300 and 400 nm entering the reactor (i.e., incident on the back surface of the membrane) was determined to be 12 W (3.6×10^{-5} einsteins/s).

Membranes

The starting materials for the preparation of the ceramic membranes were titanium tetraisopropoxide (Aldrich Chemical, Milwaukee, WI) and anhydrous isopropanol (Aldrich). Both were chemically pure grade and were used without further purification.

Water used in reactions was deionized using a Mili-Q Water purification system (Milipore Corp., Bedford, MA).

The colloidal sol was prepared according to a procedure of Anderson *et al.* (*23*). A solution of titanium tetraisopropoxide [$Ti(iso\text{-}OC_3H_7)_4$] in isopropyl alcohol was rapidly mixed with water at room temperature in a well stirred vessel. The hydrolysis reaction was allowed to proceed for 0.5 h.

$$Ti(iso\text{-}OC_3H_7)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4C_3H_7OH.$$

The hydroxide precipitate was peptized with appropriate amounts of HNO_3 to form a highly dispersed, stable colloidal solution. This step involved heating the suspension for ca. 12 h at 80°C.

The exterior surface of the inner glass tube was coated with TiO_2 using the following procedure. The tube was sealed at one end and immersed in the colloidal sol for ca. 30 s. It was then withdrawn at a controlled speed of 16.73 cm/min and dried at room temperature for 1 h. The tube was then calcined in a furnace by heating from 100 to 400°C at a rate of 3°C/min. It was held at the latter temperature for 1 h. This protocol has the effect of depositing one layer of TiO_2 on the external surface of the Pyrex tube. For the experiments reported in this paper, we employed a reactor on which eight layers had been deposited sequentially in this manner. Preliminary experiments involving a study of the effect of membrane thickness on degradation rate indicated that the rate initially increased with an increasing number of layers but reached a plateau for six, seven, and eight layers.

Profilometry measurements indicated that the total thickness of the TiO_2 membrane was 1.3 μm. Although it is impractical to directly assess many of the physical properties of the supported TiO_2 membrane, companion experiments were carried out on unsupported TiO_2 membranes prepared in a similar manner from the same precursor colloidal sol.

To prepare the unsupported membranes, an aliquot of the titania sol was placed in a small flat polystyrene container. The sol was gelled by allowing water to evaporate at room temperature under controlled relative humidity conditions. This gel was then subjected to the same firing conditions as the membrane supported on the wall of the reactor. The average size of the primary particles constituting these unsupported membranes was found to be 8 nm. This value was calculated from the peak width at half-height obtained in X-ray diffraction (XRD) measurements at 25.4°. Said measurements also indicated that the membrane is composed of crystalline particles of anatase. BET measurements indicated a specific surface area of ca. 100 m^2/g and a porosity of ca. 30%. If one uses these values, the length and radius of the coated tube and a tabulated value for the density of anatase, he finds that the total weight of catalyst (TiO_2) in the reactor was $\sim$0.1 g.

Protocol for Kinetic Measurements

Prior to irradiation, the reactant solution was recirculated through the reactor for ca. 20 min. The recirculation rate and the gas flow rates were adjusted as appropriate for the experiment of interest. After the illumination source was switched on, approximately 15 min were required to reach a steady-state operating temperature of 35°C. Consequently, data for the first 15 min of operation were not utilized in determining the mathematical form of the reaction rate expression.

RESULTS AND DISCUSSION

There are a number of variables which can be expected to influence the rate of photodegradation of 3-chlorosalicylic acid. Hence, several experiments were carried out to assess the effects of different process variables on the rate of reaction. Among those variables considered here are the concentrations of 3-chlorosalicylic acid and oxygen, the reaction temperature, and the fluid flow rates. Experiments relevant to each of these variables are discussed in turn.

Studies of the system in the absence of light and in the absence of the TiO_2 membrane indicated that both light and TiO_2 must be present if the photodegradation reaction is to occur.

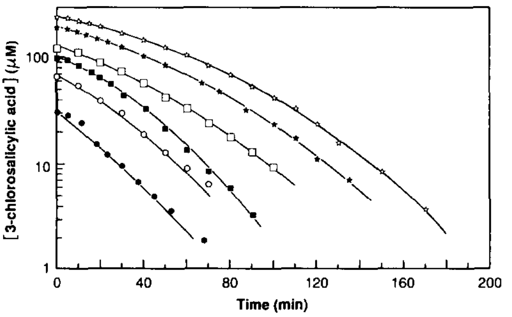

FIG. 2. Test of data for pseudo first-order kinetics–semilogarithmic plot of 3-chlorosalicylic acid (3CSAL) concentration vs time. Dissolved O_2 concentration: 227 μM; gas flow rate: 1000 ml/min; N_2/O_2 ratio = 4/1; liquid recirculation rate: 210 ml/min; total volume of liquid solution: 1000 ml; pH 6; temperature: 35°C.

Analysis for HCl upon termination of the experiment indicated the complete dechlorination of 3-chlorosalicylic acid. More than 98% of the 3-chlorosalicylic acid was converted to chloride ion in the run with the highest initial concentration of reactant (see Fig. 2). While analyses for potential reaction intermediates were not carried out in these experiments, stoichiometric considerations implied by >98% conversion and the quality of the fit of the data to the kinetic model imply that substantive concentrations of intermediates which would interfere with the absorbance measurements are not present.

Production of CO_2 was demonstrated by the precipitation of $BaCO_3$ in the $Ba(OH)_2$ solution used to scrub the effluent gas stream, although quantitative measurements of CO_2 production were not made.

Effects of Species Concentrations on Observed Reaction Rate

1. *3-chlorosalicylic acid.* A series of experiments was conducted in which the only independent variable was the initial concentration of 3-chlorosalicylic acid. The temperature, pH, gas composition, fluid flow rates, and the total volume of the reacting solution were all held constant. Experimental measurements indicated that the dissolved oxygen concentration was the same throughout these experiments. The purpose

TABLE 1

Models Considered in Determining the Functional Dependence of the Reaction Rate on the Concentration of 3-Chlorosalicylic Acid

Model number	Mathematical form of rate expression[a]	Effective number of parameters	Residual sum of squares[b]
	For data obtained at constant C_B		
1	$k_1C_A0.5$	1	0.24
2	k_1C_A	1	0.79
3	$k_1C_A1.5$	1	2.34
4	$k_1C_A^n$	2	0.078
5[c]	$\frac{kK_AC_A}{1 + K_AC_A + K_BC_B}$	2	0.053
6	$\frac{kK_AC_A}{(1 + K_AC_A + K_BC_B)^2}$	2	0.065
	For data obtained with variable C_B		
7	$\frac{kK_AC_AC_B}{1 + K_AC_A + K_BC_B}$	3	0.116
8	$\frac{kK_AK_BC_AC_B}{(1 + K_AC_A + K_BC_B)^2}$	3	0.061
9	$\frac{kK_AK_BC_AC_B}{(1 + K_AC_A)(1 + K_BC_B)}$	3	0.035

[a] A = 3-chlorosalicylic acid; $B = O_2$.

[b] For the data obtained at a constant dissolved oxygen concentration, the residual sum of squares value is based on a fit of all the data for this set of experimental runs. For the data obtained with variable oxygen concentration, the sum of squares is based on the set of experimental data for all runs.

[c] Since C_B is a constant, this rate expression can be rewritten as

$$kK_AC_A/(\kappa + K_AC_A) = (kK_A/\kappa)C_A/[1 + (K_A/\kappa)C_A],$$

where $\kappa = 1 + K_BC_B$. This equation is then essentially a two-parameter equation.

of these experiments was to determine the dependence of the reaction rate on the concentration of 3-chlorosalicylic acid.

In this series of experiments induction periods were observed. However, neither the length of the induction period nor the initial rate could be correlated with the initial concentration of 3-chlorosalicylic acid. Both Sabate *et al.* (*24*) and Matthews (*10*) have discussed this induction period.

Table 1 summarizes the rate expressions which were considered in the analysis of the kinetic data. Both integral and differential methods of data analysis (*25*) were employed in working up the data. Both *n*th-order forms of the rate expression and simple Langmuir–Hinshelwood/Hougen–Watson (LHHW) models have been tested to determine that model which provides the best fit of the data.

Figure 2 contains semilog plots of the data for several different initial concentrations of 3-chlorosalicylic acid. If the data obeyed simple pseudo first-order kinetics, the data for a single run would be expected to fall on a straight line. The departures from linearity indicate that a more complex rate expression is called for. The values of the residual sums of squares found in Table 1 also indicate that simple *n*th-order rate expressions do not provide as accurate a representation of the kinetic data as the LHHW forms. If one forces the data for an individual run to fit the *n*th order form, the best fits are obtained for values of *n* ranging from 0.61 to 0.82. These values again are indicative of the need for use of a more complex mathematical expression to obtain a good fit of the data.

Several research groups (*5*, *10*) have previously used a LHHW model to fit rate data for photocatalytic processes occurring over semiconductors. Models 5–9 in Table 1 are all of this general form. Models 5 and 6 are degenerate forms of models 7 and 8, respectively. These degenerate forms lump the dependence of the reaction rate on oxygen concentration together with the surface reaction rate constant. Models 8 and 9 both correspond to situations where the rate-controlling step is a second-order surface reaction. For model 8 the surface species are both adsorbed on the same type of site. For model 9 the 3-chlorosalicylic acid and O_2 are adsorbed on different types of sites. In all of the models the dependence of the reaction rate on the intensity of the incident radiation is lumped together with the reaction rate constant.

The residual sum of squares analysis based on nonlinear regression (*25*) indicates that the data for constant oxygen concentration are best fit by model 5.

Another approach to assessing the various mathematical forms of the rate expression is to investigate the dependence of the half-life of the reaction on the initial concentration of 3-chlorosalicylic acid. For example, if one considers the degenerate form of model 5 (Table 1), the rate of consumption of 3-chlorosalicylic acid (A) can then be written as

$$\frac{dC_A}{dt} = -\frac{k'C_A}{1 + (K_A/\kappa)C_A}, \qquad (1)$$

where

$$k' = kK_A/\kappa. \qquad (2)$$

Recall that this equation pertains only to those experiments in which the dissolved oxygen-concentration is held constant and that the effects of this concentration are hidden in the parameters k and κ.

Integration gives

$$\int[(1/C_A) + (K_A/\kappa)]dC_A = -\int k'dt \quad (3)$$

or

$$t = \frac{1}{k'}[\ln\left(\frac{C_{AO}}{C_A}\right) + (K_A/\kappa)(C_{AO} - C_A)]. \qquad (4)$$

The half-life ($t_{1/2}$) is defined as the time at which half of the limiting reagent has been consumed. Thus, at a time equal to the half-life, $C_A = C_{AO}/2$ and

$$t_{1/2} = \frac{\ln 2}{k'} + \frac{K_A C_{AO}}{2\kappa k'}. \qquad (5)$$

This equation illustrates a specific application of the generalized fractional-life approach to the analysis of kinetic data (e.g., see Frost and Pearson (*26*) or Laidler (*27*). Ollis *et al.* (*28*) have previously indicated the applicability of Eq. (5) to photocatalytic systems.

Equation (5) indicates that a plot of the experimental half-life versus the initial concentration of 3-chlorosalicylic acid should be linear. Data obtained at a constant concentration of dissolved oxygen are plotted in this fashion in Fig. 3. A least-squares fit of the data indicates that $k' = 0.0517 \pm 0.0057$ min^{-1} and $(K_A/\kappa) = (1.62 \pm 0.19) \times 10^4$ liter/mol. These values compare very favorably with corresponding values of 0.0541 ± 0.0027 min^{-1} and $(1.54 \pm 0.17) \times 10^4$ liter/mol, respectively, determined using nonlinear regression analysis based on all data obtained at the same concentration of dissolved oxygen.

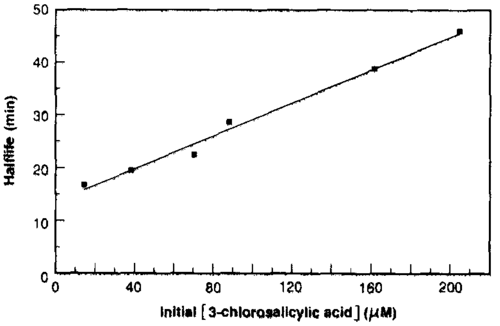

FIG. 3. Dependence of reaction half-life on initial concentration of 3-chlorosalicylic acid. Dissolved O_2 concentration: 227 μM; gas flow rate: 1000 ml/min; N_2/O_2 ratio: 4/1; liquid recirculation rate: 210 ml/min; total volume of liquid solution: 1000 ml; pH 6; temperature: 35°C.

2. *Dissolved oxygen.* In order to evaluate the effects of the dissolved oxygen concentration on the rate of the photodegradation reaction, a series of experiments was performed in which the N_2/O_2 ratio in the gas feed stream was varied. Since the solubilities of these gases obey Henry's Law, these variations have the effect of varying both the gas phase partial pressure of oxygen and the concentration of oxygen dissolved in the aqueous phase. It should be noted that no degradation was observed when pure N_2 was used as the feed gas. Data obtained in these experiments were used to test models 7–9 in Table 1. The residual sum of squares analysis indicates that the best fit of the data is obtained when model 9 is employed. The conclusion that the best model is the two-site model in which the two sites differ in character is consistent with mechanisms proposed by other investigators (*29, 30*).

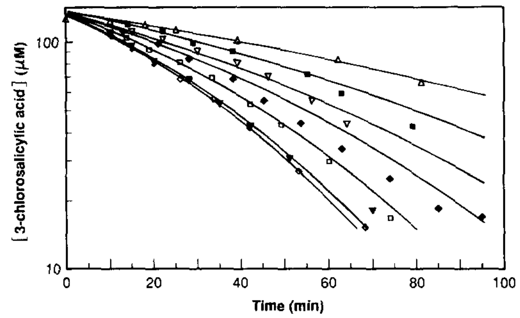

FIG. 4. Concentration versus time plots for test of Model 9. Gas flow rate: 1000 ml/min; liquid recirculation rate: 210 ml/min; total volume of liquid solution: 1250 ml; pH 6; temperature: 35°C. Dissolved oxygen concentrations (μM): ◇-1134; ▼-906; □-422; ◆-227; ▽-159; ■-109; △-64.

This result is consistent with our earlier conclusion that model 5 provides the best fit of the data when the oxygen concentration is held constant.

Based on a study of the photoassisted oxidation reactions of 2-methyl-2-butyl alcohol and isobutane over TiO_2, Pruden Childs and Ollis (*31*) reported that their kinetic data were best fit by a two-site model in which all sites are equivalent. Hence, responses to the question of which type of Langmuir–Hinshelwood/Hougen–Watson model best fits experimental kinetic data for the photoassisted oxidation of organic species dissolved in aqueous solution must be viewed from the perspective of the specific organic compounds involved.

Figures 2 and 4 indicate the fit of the data to model 9 for runs in which both different initial 3-chlorosalicylic acid concentrations and different dissolved oxygen levels were employed. Note that the model provides a very accurate representation of the data. Table 2 contains a summary of the parameter estimates determined by nonlinear regression for model 9 (*25*).

3. *Chloride ion.* The addition of NaCl to the initial reactant mixture to produce a solution which is 250 μ*M* in chloride had no effect on the degradation process. Hence, at the level studied, this product of the reaction does not have an inhibitory effect.

Deactivation Effects

After performing the various experiments described above, an additional experiment was performed in which the reaction conditions were the same as those prevailing during the first experiment using the same TiO_2 membrane. The observed rate of the photocatalytic degradation reaction was the same as that observed during the first experiment. Hence, no significant deactivation of the membrane occurred over a total elapsed time of 60 days despite exposure to a variety of experimental conditions. During this period the membrane was subjected to irradiation for a total of approximately 70 h.

Mass Transfer Effects

A persistent problem in the analysis of kinetic data obtained from systems employing heterogeneous catalysts is that of elucidating the influence of diffusional and other mass transfer processes on the observed reaction rate. In the present instance, this problem is of particular concern in light of an analysis by Turchi and Ollis (*32*) of data reported by Matthews (*9*) for the photocatalytic oxidation of salicylic acid over a TiO_2 film coated on the wall of a coiled glass tube reactor. Some debate persists (*33*) as to the precise magnitude of these effects, but agreement exists that in Matthews' system mass transport processes influenced the observed reaction rate. While the apparatus and chemical system studied by Matthews (*9*) both differed from those employed in the present work, they are sufficiently similar

TABLE 2

Best Estimates of Parameters for Model 9

$$r = \frac{kK_AK_BC_AC_B}{(1 + K_AC_A)(1 + K_BC_B)}$$

at 35°C

$k = (5.44 \pm 0.61) \times 10^{-6}$ mol/l min.

$K_A = (0.0150 \pm 0.0028) \times 10^{6}$ liter/mol.

$K_B = (7.1 \pm 1.2) \times 10^{3}$ liter/mol.

that a discussion of potential mass transport limitations in our system is warranted here.

In order to address the question of whether the reaction rates observed in our system were affected by mass transfer processes, we employed a combination of experimental measurements and a theoretical analysis. The issue of mass transfer between the bulk liquid and the external surface of the catalyst membrane was investigated by varying the flow rates of both the gas and liquid streams. No significant differences in the degradation rate were observed when the gas flow rate was varied between 500 and 1500 ml(STP)/min or when the liquid recirculation rate was varied between 130 and 300 ml/min. All kinetic data reported in this paper were obtained at flow rates in the middle of these ranges. Physical limitations on the equipment prevented us from exploring wider ranges of flow rates. For the aqueous phase, Reynolds numbers (based on the hydraulic diameter) corresponding to these flow rates are of the order of 50. This value would nominally correspond to a laminar flow regime. However, the flow of the gas introduces a high degree of turbulence in this system, thereby facilitating mass transfer processes. It is unlikely that mass transfer of reactants or products between the bulk fluids and the external surface of the catalytic membrane is rate controlling in our system. The rate of the photocatalytic reaction is sufficiently slow and the external mass transfer processes sufficiently rapid that no significant differences in species concentrations develop across the fluid boundary layer at the membrane surface.

The question of whether or not diffusional processes within the pore structure of the TiO_2 membrane influence the observed reaction rate was addressed in analytical terms using a limiting condition order-of-magnitude analysis. The rate expression which provides the best fit of the data (model 9 or its degenerate form, model 5) is of the general Hougen–Watson form. If, as a limiting condition, the rate expression is reduced to a pseudo first-order form in which the dissolved oxygen concentration is regarded as a constant, one can use the classic straight cylindrical pore model to estimate a value of the effectiveness factor for this catalytic system.

Implicit in this model is the assumption that the catalytic activity is uniformly distributed along the length of the catalyst pore. In the case of the photocatalytic membrane which is illuminated from the backside, the intensity of the radiation decreases exponentially with distance from the source according to the Beer–Lambert Law. Hence, the conventional analysis is not strictly applicable to the present system. Nonetheless, it does provide a useful basis for order of magnitude calculations. Some of the discrepancies between the physical world and the mathematical model will be ameliorated in employing the observed kinetic parameters which incorporate the radiation intensity as a factor, thereby effectively averaging the radiation intensity over the structure of the catalyst.

Experimental measurements of the pore size distribution for an unsupported membrane indicated that the average pore radius is ca. 20 Å, a value which is consistent with calculations based on the void volume per gram and the BET specific surface area (*34*). This unsupported membrane was prepared from the same sol and subjected to drying and firing conditions comparable to those for the TiO_2 membrane deposited on the wall of our reactor. Profilometry measurements on our reactor indicated a membrane thickness (average pore length) of 1.3 μm. Using the methods described by Reid *et al.* (*35*), we estimated the diffusivity of 3-chlorosalicylic acid to be ca. 0.86×10^{-5} cm^2/s at 308°K. The slopes of the curves in Fig. 2 correspond to apparent pseudo first-order rate constants in the range from 0.025 to 0.042 min^{-1}.

An analysis based on these values indicates that the effectiveness factor for the membrane catalyst is ca. 0.96. Thus, the system is operating in a regime where intraparticle diffusion effects are beginning to become significant, i.e., the reaction rate is limited to some extent by the rate at which 3-chlorosalicylic acid molecules can diffuse into the pores of the catalyst. This fact implies that in future work it may be appropriate to modify the experimental protocol used to prepare the catalyst so as to reduce such constraints, especially if one desires to consider operation at higher temperatures. Nonetheless, the preliminary results reported in this paper clearly demonstrate the technical feasibility of using this approach to bring about the photocatalytic degradation of organic materials present at low concentrations in aqueous solution.

Quantum Yield

The apparent primary quantum yield (APQY) of this reaction can be viewed as the ratio of the number of molecules of 3-chlorosalicylic reacting to the number of photons with wavelengths in the range 300–400 nm incident on the reacting system.

$$\text{APQY} = 100\left[\frac{\text{rate of degradation reaction}}{\text{rate of supply of photons}}\right]. \tag{6}$$

The rate at which photons are supplied is referenced to the photon flux arriving at the TiO_2 membrane. Since the rate of the photocatalytic reaction depends on the concentrations of both 3-chlorosalicylic acid and oxygen, the apparent quantum yield also depends on these variables. However, for present purposes it is sufficient to note that when the feed gas was pure oxygen and the concentration of 3-chlorosalicylic acid in the liquid phase was 100 μM, the apparent quantum yield was 0.12%. As earlier workers have noted (e.g., see Formenti *et al.* (*16–18*)) the true quantum yield (based on the number of photons absorbed by the TiO_2 catalyst) cannot be easily determined when a solid catalyst is placed in the path of the radiation.

Mechanism

When TiO_2 is employed as a photocatalytic material in the form of a membrane, its chemical properties are expected to be the same as when it is employed in powder form. Consequently, the molecular phenomena responsible for the reaction mechanism should be identical in both instances. Several research groups (*10, 12, 29, 30*) have indicated that the initial steps in the photocatalytic reaction can be presented as

$$TiO_2 \xrightarrow{h\nu} e^- + h^+ \tag{7}$$

$$h^+ + H_2O \rightarrow \cdot OH + H^+ \tag{8}$$

$$e^- + O_2 \rightarrow \cdot O_2^- \xrightarrow{H^+} HO_2\cdot \tag{9}$$

$$2HO_2\cdot \rightarrow O_2 + H_2O_2 \tag{10}$$

$$H_2O_2 + \cdot O_2^- \rightarrow \cdot OH + OH^- + O_2 \tag{11}$$

Repeated attacks of $\cdot OH$ and $HO_2\cdot$ free radicals on the aromatic ring can lead to the formation of free chlorine atoms via a chain transfer reaction. These chlorine atoms can then scavenge electrons to yield chloride ions

$$Cl\cdot + e^- \rightarrow Cl^- \tag{12}$$

The fact that the rate of degradation of 3-chlorosalicylic acid is markedly affected by the concentration of dissolved oxygen suggests that the reduction reaction shown in Eq. (9) must play an important role in governing the observed reaction rate. This situation suggests that it would be appropriate to alter the surface characteristics of the membrane in a manner that would decrease the rate of the electron-hole pair recombination reaction. Chemical doping might provide such an improvement in the electronic properties of the membrane. Such modifications would presumably enhance the activity of the catalyst and the efficacy with which the photodegradation reactions could be accomplished. Experiments in this direction are in progress in our laboratory.

CONCLUSIONS

TiO_2 membranes supported on glass are able to function as catalysts for the photodegradation of chlorinated aromatic compounds. The reactor configuration employed in the present study permits one to obtain highly reproducible kinetic data for these reactions.

Degradation of 3-chlorosalicylic acid to HCl and CO_2 is consistent with a rate law of the general Langmuir–Hinshelwood/Hougen–Watson form corresponding to a rate-limiting step which involves two adsorbed species, 3-chlorosalicylic acid, and oxygen. The rate was not influenced by the concentrations of other species.

No significant deactivation of the catalyst was noted.

It is suggested that since oxygen acts as a scavenger of electrons formed by the absorption of a photon, the activity of the catalyst could be enhanced by doping the TiO_2 with species which facilitate the electron transfer step.

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