ELSEVIER

Chemical Engineering Journal 70 (1998) 231–235

Chemical Engineering Journal

Short communication

The influence of the non-irradiated surface area on the kinetics of heterogeneous photocatalytic reaction in a static reactor

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Received 17 October 1997; received in revised form 15 March 1998; accepted 8 May 1998

Abstract

Mathematical modelling, on the basis of the Langmuir–Hinshelwood equation, of a photocatalytic reaction in a static reactor, taking into account in the mass balance the adsorption on the irradiated parts of the catalyst, dark parts of the catalyst and support, reveals that an increase in the surface area of the dark catalyst results in prolonged kinetic curves. If the adsorption on the irradiated and dark parts of the catalyst is ignored in the mass balance, errors can occur in the kinetic parameters calculated from the concentration–time curves. An increase in the surface area of the dark catalyst facilitates the removal of contaminants from the gas or liquid phase to below the threshold permitted concentration (TPC), if TPC corresponds to the surface coverage of the illuminated catalyst with contaminant of higher than 0.37.

Keywords: Modelling; Photocatalytic oxidation; Static reactor; Non-irradiated photocatalyst surface area

1. Introduction

Heterogeneous photocatalysis is now recognized as a method for the oxidative treatment of contaminated water and air [1]. Many studies have been carried out in static reactors in the gas [2–13] and liquid [14–17] phases, the most active photocatalyst being powdered TiO_2. It is common to apply large quantities of TiO_2 powder so as to absorb all the UV light incident on the photocatalyst. Thus, some parts of TiO_2 remain non-irradiated. If the quantity of compound to be oxidized, which is adsorbed on the irradiated and non-irradiated surfaces of the photocatalyst, is comparable with the quantity in the liquid (or gas) phase, the kinetic analysis of the reaction should take into consideration the influence of this adsorption.

Sauer and Ollis [8] were the first to recognize and take into account this influence when analysing the kinetics of acetone disappearance in a monolith reactor.

This study investigates the reaction kinetics in static systems, focusing on the influence of the non-irradiated surface area, and answers three questions.

How does the non-irradiated surface area affect the concentration–time profiles of the oxidized compound?

Is a good fit of the experimental kinetics by the simple Langmuir–Hinshelwood equation a sufficient reason to ignore the influence of the non-irradiated surface area?

What is the optimal non-irradiated surface area of the photocatalyst which can reduce the pollutant concentration to below the threshold permitted concentration as soon as possible?

The last question concerns, for example, indoor air purifiers which can be considered as a static system of perfect stirring. Such purifiers have been developed by Suzuki [13].

This paper does not aim to provide an exact description of all the processes taking place on the photocatalyst surface,e.g., surface diffusion and influence of the adsorbed products. It attempts to show that the simple Langmuir–Hinshelwood equation used traditionally to describe the kinetics of photocatalytic oxidation should be modified when used for static reactors with comparable quantities of substrate in the gas (or liquid) phase and in the adsorbed state.

2. Derivation of equations

It is assumed in the derivation of the equations that the adsorption on the irradiated catalyst, non-irradiated catalyst

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PII S1385-8947(98)00102-8

and support follows a Langmuir isotherm and reaction does not disturb the adsorption equilibrium.

The static system under consideration is composed of a volume V of a perfectly stirred reaction mixture. The photocatalyst in this volume is divided into an irradiated part having S_i adsorption sites and a dark part having S_n adsorption sites. The adsorption constants on these parts are K_i and K_n, respectively. K_i and K_n can have different values because irradiation can heat the surface, and the holes and electrons produced by UV light excitation may change the surface properties as a result of their capture by surface sites. The photocatalyst can be deposited on a support having S_s adsorption sites with adsorption constant K_s. The substrate adsorbed on the irradiated photocatalyst is converted into product with a rate constant k.

Taking into account that the total amount of substrate in the system is distributed between the gas (or liquid) phase and the adsorption sites on the irradiated and non-irradiated catalyst and support, we can derive the following differential equation for the concentration of the substrate in the gas (or liquid) phase

$$\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{-[(kK_iS_ic)/(1+K_ic)]}{V+[(K_iS_i)/(1+K_ic)^2]+[(K_nS_n)/(1+K_nc)^2]+[(K_sS_s)/(1+K_sc)^2]} \tag{1}$$

A detailed derivation of Eq. (1) is given in Appendix A. Integration of this equation gives

$$\begin{aligned} t = {} & -\frac{V}{kK_iS_i}\left[\ln\frac{c}{c_0}+K_i(c-c_0)\right] \\ & -\frac{1}{k}\left(\ln\frac{c}{c_0}-\ln\frac{1+K_ic}{1+K_ic_0}\right)-\frac{K_nS_n}{kK_iS_i}\left[\ln\frac{c}{c_0}\right. \\ & \left.-\ln\frac{1+K_nc}{1+K_nc_0}-\frac{K_i-K_n}{K_n(1+K_nc)}+\frac{K_i-K_n}{K_n(1+K_nc_0)}\right] \\ & -\frac{K_sS_s}{kK_iS_i}\left[\ln\frac{c}{c_0}-\ln\frac{1+K_sc}{1+K_sc_0}-\frac{K_i-K_s}{K_s(1+K_sc)}\right. \\ & \left.+\frac{K_i-K_s}{K_s(1+K_sc_0)}\right] \end{aligned} \tag{2}$$

where c_0 is the concentration of the substrate in the gas (or liquid) phase at adsorption equilibrium and before the start of illumination.

Water is usually present in the gas and liquid phases at the beginning of photocatalytic oxidation, and is produced during this reaction. If there is a negligible change in the water concentration during the reaction, its influence can be taken into account by substitution of $[K_i/(1+K_{H_2O}C_{H_2O})]$, $[K_n/(1+K_{H_2O}C_{H_2O})]$ and $[K_s/(1+K_{H_2O}C_{H_2O})]$ for K_i, K_n and K_s, respectively.

Now, let us consider some particular cases of Eq. (2) which are of practical importance.

(1) All the unsupported photocatalyst in the reactor is illuminated: $S_s=S_n=0$.

$$t=-\frac{V}{kK_iS_i}\left[\ln\frac{c}{c_0}+K_i(c-c_0)\right]-\frac{1}{k}\left(\ln\frac{c}{c_0}-\ln\frac{1+K_ic}{1+K_ic_0}\right) \tag{3}$$

(1.1) The quantity of substrate in the gas (or liquid) phase is much greater than in any adsorbed form: $V \gg [(K_iS_i)/(1+K_ic)]$. This leads to the integrated Langmuir–Hinshelwood equation

$$t=-\frac{V}{kK_iS_i}\ln\frac{c}{c_0}-\frac{V}{kS_i}(c-c_0) \tag{4}$$

(1.1.1) Surface coverage with substrate is high: $K_ic \ll 1$

$$c=c_0-\frac{kS_i}{V}t \tag{5}$$

(1.1.2) Surface coverage with substrate is low: $K_ic_0 \ll 1$

$$c=c_0\exp\left(-\frac{kK_iS_i}{V}t\right) \tag{6}$$

(1.2) The quantity of substrate in the gas (or liquid) phase is much less than in the adsorbed form: $V \ll [(K_iS_i)/(1+K_ic)]$

$$t=-\frac{1}{k}\left(\ln\frac{c}{c_0}-\ln\frac{1+K_ic}{1+K_ic_0}\right) \tag{7}$$

(1.2.1) Surface coverage with substrate is high: $K_ic \gg 1$

$$c=\frac{c_0}{1+kK_ic_0t} \tag{8}$$

(1.2.2) Surface coverage with substrate is low: $K_ic_0 \ll 1$. This situation was probably realized in Ref. [11].

$$c=c_0\exp(-kt) \tag{9}$$

(2) There are non-illuminated parts of the unsupported photocatalyst in the reactor: $S_s=0$

$$\begin{aligned} t= {} & -\frac{V}{kK_iS_i}\left[\ln\frac{c}{c_0}+K_i(c-c_0)\right] \\ & -\frac{1}{k}\left(\ln\frac{c}{c_0}-\ln\frac{1+K_ic}{1+K_ic_0}\right)-\frac{K_nS_n}{kK_iS_i}\left[\ln\frac{c}{c_0}\right. \\ & \left.-\ln\frac{1+K_nc}{1+K_nc_0}-\frac{K_i-K_n}{K_n(1+K_nc)}+\frac{K_i-K_n}{K_n(1+K_nc_0)}\right] \end{aligned} \tag{10}$$

(2.1) The quantity of substrate in the gas (or liquid) phase is much greater than in any adsorbed form: $V \gg [(K_iS_i)/(1+K_ic)+(K_nS_n)/(1+K_nc)]$. Eq. (10) is reduced to Eq. (4) in this case.

(2.2) The quantity of substrate in the gas (or liquid) phase is much less than in any adsorbed form: $V \ll [(K_iS_i)/(1+K_ic)+(K_nS_n)/(1+K_nc)$

$$t=-\frac{1}{k}\left(\ln\frac{c}{c_0}-\ln\frac{1+K_ic}{1+K_ic_0}\right)-\frac{K_nS_n}{kK_iS_i}\left[\ln\frac{c}{c_0}-\ln\frac{1+K_nc}{1+K_nc_0}-\frac{K_i-K_n}{K_n(1+K_nc)}+\frac{K_i-K_n}{K_n(1+K_nc_0)}\right] \quad (11)$$

(2.2.1) Surface coverage with substrate is high: $K_ic \ll 1$, $K_nc \ll 1$

$$c=\frac{c_0}{1+\{(kc_0t)/[(1/K_i)+(S_n/K_nS_i)]\}} \quad (12)$$

(2.2.2) Surface coverage with substrate is low: $K_ic<1$, $K_nc<1$

$$c=c_0\exp\left(-\frac{k}{[1+(K_nS_n)/(K_iS_i)]}t\right) \quad (13)$$

The above equations are applicable to film photocatalysts as well as stirred suspensions. In the last case, irradiated and non-irradiated parts alternate.

During photocatalytic oxidation, intermediate products in the gas (or liquid) phase are often observed. In this case, Eq. (1) can be used for the analysis of the initial rate of oxidation.

3. Results and discussion

The calculations in this paper were made with the following set of parameters, unless otherwise stated: rate constant $k=1$ s^{-1} was taken arbitrarily because its value does not change the shape of the kinetic curves; volume of gas (or liquid) $V=1$ m^3; adsorption constant of irradiated surface $K_i=50$ m^3 mol^{-1}; adsorption constant of non-irradiated surface $K_n=50$ m^3 mol^{-1}; K_i and K_n were taken to be equal as a simplest case; number of adsorption sites on irradiated surface $S_i=1$ mol. Other parameters were varied. This set of parameters allows any transition cases between the limit cases considered in the previous section.

3.1. Effect of non-irradiated surface area on concentration–time curves

Fig. 1 shows the change in concentration–time profiles when the number of sites on the non-irradiated surface increases from 0 to 10 mol (along the arrow). The change in the irradiated surface coverage–time profiles is depicted in the inset. Along each profile, the concentration changes from 2 to 0.02 mol m^{-3} (conversion of concentration: 99%). It can be seen that an increase in the non-irradiated surface area changes the shape of the kinetic curves, making them longer.

The influence of the non-irradiated surface area on the kinetic curves is shown in Fig. 2 for the case when the quantity of oxidized compound in the reactor changes along each profile from an initial value of 10 mol to 0.1 mol (conversion: 99%). The inset in Fig. 2 displays the time profiles of the irradiated surface coverage. The initial concentration of the compound decreases with an increase in the non-irradiated surface area due to adsorption on the non-irradiated surface. The kinetic curves cross each other at the same point only if the initial irradiated surface coverage is high (≥ 0.9). The two curves in Fig. 2 with non-irradiated surface areas of 15 and 20 mol have initial irradiated surface coverages of 0.62 and 0.48 and do not cross the other curves at the same point.

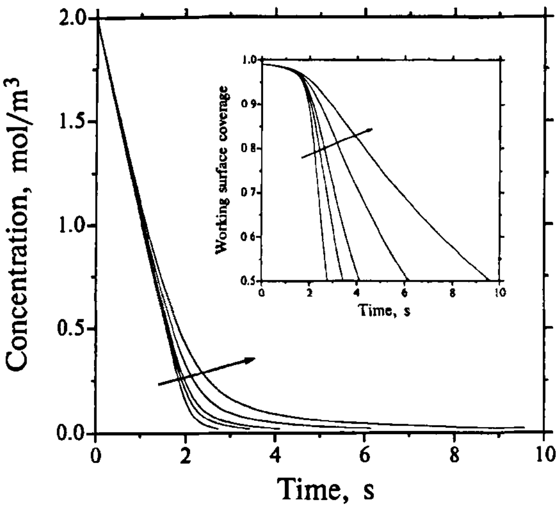

Fig. 1. Influence of non-irradiated surface area on the kinetic curves according to Eq. (10). Initial concentration: 2 mol m^{-3}; final concentration: 0.02 mol/m^3. Non-irradiated surface area along arrows 0, 1, 2, 5 and 10 mol.

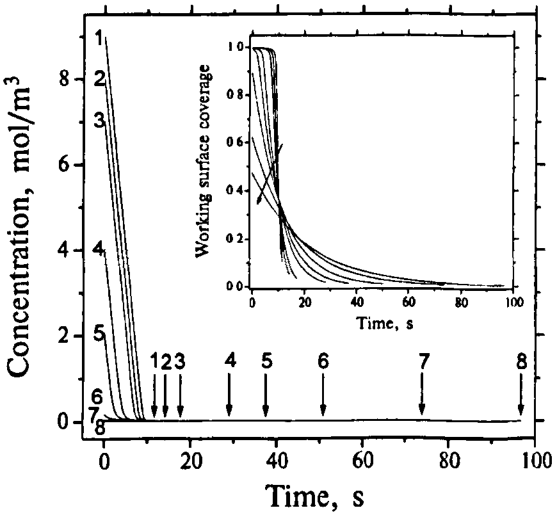

Fig. 2. Influence of non-irradiated surface area on the concentration–time profiles according to Eq. (10). Initial quantity 10 mol, final quantity, 0.1 mol (indicated by arrows). Non-irradiated surface area for curves 1–8: 0, 1, 2, 5, 7, 10, 15 and 20 mol, respectively. Inset shows the time dependence of the catalyst surface coverage. Numbers of curves along the arrow: from 1 to 8.

A consideration of Eq. (10) with the assumptions that the adsorption constants of the irradiated and non-irradiated surfaces are equal, $K_i=K_n$, and the initial quantity of the compound to be oxidized, n_0, is constant and high enough to maintain a high initial surface coverage of the catalyst, $K_ic_0=K_nc_0>>1$, leads to the coordinates of the cross point

$$\Theta_c \approx 1/e \approx 0.368,\ t_c \approx n_0/kS_i$$

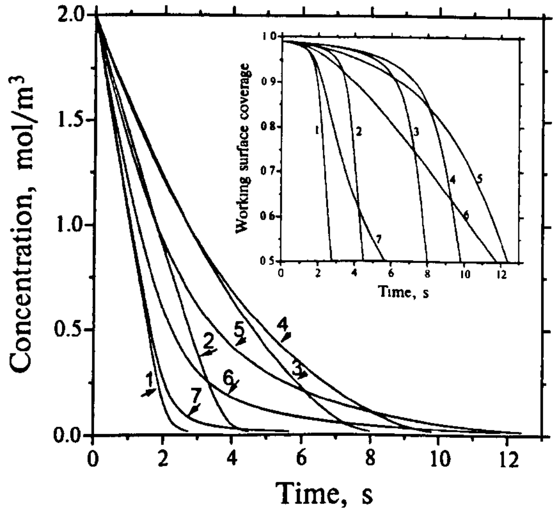

Fig. 3. Effect of the adsorption constant of the support on the kinetic curves according to Eq. (2). Initial concentration: 2 mol m^{-3}; final concentration: 0.02 mol m^{-3}. Non-irradiated surface area: 0 mol. Adsorption constant of support for curves 1–7: 0, 0.1, 0.5, 1, 5, 20 and 200 m^3 mol^{-1}, respectively. Support surface area: 10 mol.

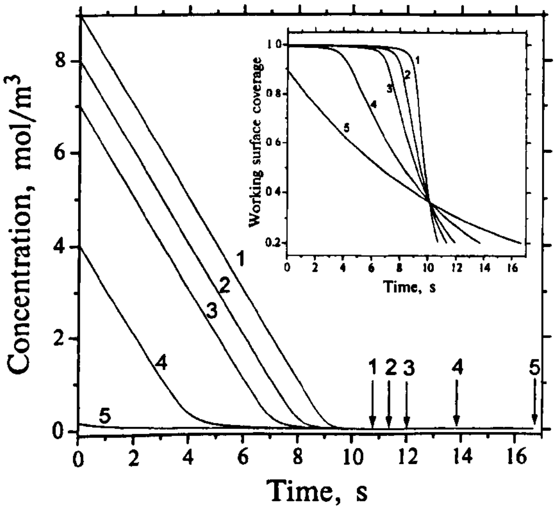

Fig. 4. Influence of the non-irradiated surface area on the time of attainment of TPC according to Eq. (10). Initial quantity 10 mol, final concentration 0.005 mol m^{-3}. Non-irradiated surface area for curves 1–5: 0, 1, 2, 5 and 10 mol^{-1}, respectively. The attainment of the final concentration by the respective curves is indicated by arrows.

where Θ_c is the catalyst coverage at the cross-point and t_c is the time of the cross-point. If $K_n > K_i$, then $\Theta_c < 1/e$, and if $K_n < K_i$, then $\Theta_c > 1/e$, but the common cross-point is retained and changes in t_c are relatively small.

Fig. 3 shows how the variation of the adsorption constant of the support (in the range 0–200 m^3 mol^{-1}) influences the kinetic profiles. Along each of these profiles, the concentration changes from 2 to 0.02 mol m^{-3}. When the adsorption constant is small (0.1–1 m^3 mol^{-1}, curves 2–4), the coverage is also small. Thus, the support functions as if it were an additional volume of the gas (or liquid) phase, because the quantity of adsorbed compound is directly proportional to the concentration in the gas (or liquid) phase, $n_{ads} = S_s K_s c$, as in the case of the volume: $n = Vc$. If K_s is sufficiently large to maintain a high surface coverage (curve 7), the presence of support does not influence the kinetic curve, except for the end part of the curve where the concentration becomes too low to maintain a high support coverage. Curves 5 and 6 represent an intermediate case, with support coverage changing appreciably along each curve.

3.2. Least square fit of the concentration–time profiles by the simple Langmuir–Hinshelwood equation

Experiments in steady state differential reactors have shown that photocatalytic oxidation obeys the Langmuir–Hinshelwood equation [18,19]. This equation has also been applied to describe the reaction kinetics in static reactors [11,20,21] without taking into account the fact that the total quantity of oxidized compound in a static system is distributed between the gas (or liquid) phase and the adsorption sites on the irradiated and non-irradiated surfaces of the photocatalyst. We attempt to show that this approach can lead to incorrect kinetic parameters even if the fit by the Langmuir–Hinshelwood equation is good.

Concentration–time curves were plotted using Eq. (10) with the non-irradiated surface area ranging from 0 to 10 mol. These curves were fitted by the integrated simple Langmuir–Hinshelwood Eq. (4). The kinetic parameters obtained by this least square fit, together with the true kinetic parameters, are displayed in Table 1. It can be seen that the curves are fitted with rather low χ^2, but the fit results in incorrect kinetic parameters.

Table 1
Results of the least square fit of the concentration–time curves according to Eq. (10) by Eq. (4)

S_n (mol)	True values		Least square fit values				
	V/kK_iS_i (s)	V/kS_i (s m^3/mol)	V/kK_iS_i (s)	V/kS_i (s m^3/mol)	Error of V/kK_iS_i	Error of V/kS_i	χ^2
0	0.02	1	0.2848	0.5876	0.0091	0.0258	0.0028
1	0.02	1	0.5602	0.1425	0.0187	0.0525	0.0128
2	0.02	1	0.7711	−0.1609	0.0262	0.0699	0.0213
5	0.02	1	1.409	−1.0691	0.0499	0.1229	0.0612
10	0.02	1	2.715	−3.0012	0.1079	0.2519	0.2584

3.3. Optimal parameters of non-irradiated surface of catalyst for indoor air purification

The optimal non-irradiated surface area of the photocatalyst should allow an indoor air purifier to reduce the pollutant concentration to below the threshold permitted concentration (TPC) in the minimal time. Fig. 4 shows the kinetic curves of photocatalytic oxidation of 10 mol of compound on a photocatalyst having a non-irradiated surface area varying from 0 to 10 mol. Arrows indicate the ends of the concentration–time profiles corresponding to a concentration of 0.005 mol m^{-3}. It can be concluded from these kinetic curves that, if TPC corresponds to an irradiated surface coverage of more than $1/e$, the increase in the non-irradiated surface area accelerates the attainment of TPC. Otherwise, it slows down the attainment of TPC; in this case the non-irradiated surface area should be minimized.

4. Conclusions

(1) An increase in the non-irradiated surface area retards the photocatalytic reaction in a static reactor.

(2) The concentration–time curves of photocatalytic reactions with different non-irradiated surface areas cross each other at a constant point if the initial irradiated surface coverage is more than 0.9.

(3) If the influence of the irradiated and non-irradiated surface area is ignored in the mass balance, significant errors in the kinetic parameters can occur when analysing concentration–time profiles.

(4) The increase in the non-irradiated surface area can speed up the attainment of the TPC if the irradiated surface coverage at TPC is higher than 0.37. Otherwise this increase slows it down.

Appendix A

Derivation of Eq. (1)

The total quantity of substrate in the static system, n, is composed of that in the gas (or liquid) phase and that in the adsorbed state on the irradiated photocatalyst, non-irradiated photocatalyst and support. They are represented by the terms

$$n=cV+\frac{K_iS_ic}{1+K_ic}+\frac{K_nS_nc}{1+K_nc}+\frac{K_sS_sc}{1+K_sc} \qquad \text{(A1)}$$

Differentiation of this equation gives

$$\frac{dn}{dt}=\left[V+\frac{K_iS_i}{(1+K_ic)^2}+\frac{K_nS_n}{(1+K_nc)^2}+\frac{K_sS_s}{(1+K_sc)^2}\right]\frac{dc}{dt} \qquad \text{(A2)}$$

On the other hand, the change in the total amount of the substrate in the system is only due to the reaction:

$$\frac{dn}{dt}=-\frac{kK_iS_ic}{1+K_ic} \qquad \text{(A3)}$$

Combination of Eqs. (A2) and (A3) gives Eq. (1).

Appendix B

Nomenclature

c	Concentration of substrate in the gas (or liquid) phase (mol m^{-3})
c_0	Initial concentration of substrate in the gas (or liquid) phase (mol m^{-3})
K	Adsorption constant (m^3 mol^{-1})
k	Rate constant (s^{-1})
n	Substrate quantity in the system (mol)
n_0	Initial substrate quantity in the system (mol)
S	Number of adsorption sites (mol)
t_c	Cross-point time (s)

Subscripts

i	Irradiated photocatalyst
n	Non-irradiated photocatalyst
s	Support

Greek letters

Θ_c	Photocatalyst coverage at cross point
χ^2	sum of the squares of deviations

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