



Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod



Guidelines for the assessment of the rate law of slurry photocatalytic reactions

G. Camera-Roda^{a,*}, V. Loddo^b, L. Palmisano^b, F. Parrino^b

^a Department of Civil, Chemical, Environmental and Materials Engineering, University of Bologna, via Terracini 28, 40131 Bologna, Italy

^b "Schiavello-Grillone" Photocatalysis Group, Dipartimento di Energia, Ingegneria dell'Informazione e Modelli Matematici – DEIM, University of Palermo (Italy), viale delle Scienze Ed. 6, 90128 Palermo, Italy

ARTICLE INFO

Article history:

Received 16 April 2016

Received in revised form 24 June 2016

Accepted 25 June 2016

Available online xxx

Keywords:

Photocatalysis

Kinetic analysis

Mechanistic kinetic models

Slurry photocatalytic reactors

Langmuir–Hinshelwood kinetics

Formic acid

ABSTRACT

The assessment of the rate law of slurry photocatalytic reactions appears to be a hard task, mainly because in this type of reactions the average rate of reaction, which is experimentally observed in a real reactor, could be very different from the “true” (intrinsic) rate of reaction, which cannot be measured directly. In the present work, it is shown how a proper mathematical model allows the utilization of the differential and/or the integral methods of kinetic analysis. The mathematical model must take into account not only the momentum and the mass balances, but also the radiative transfer equation. However, the discrimination among different proposed kinetic laws remains difficult since these laws usually predict very similar behaviors. In the case of “photodifferential” reactors, kinetic analysis can be carried out considering just the measured average rates of reaction without utilizing the mathematical model. For instance, it is shown that, with a photodifferential reactor, the fitting of the average rate of reaction vs. the substrate concentration gives a satisfactory appraisal not only of the kinetic parameters but also of the average rate of photon absorption. A sufficiently low value of the optical thickness (less than 2.5) is the main requirement to approach the photodifferential condition. Anyway, a strategic choice of the experimentally investigated values of the independent variables (e.g. substrate concentration and irradiance to the reactor) is important for the comprehensiveness of the kinetic analysis.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Kinetic analysis can be employed for two purposes: to obtain the rate equation, which is necessary for the engineering of chemical reactors (design and study of the reactor), or to prove the validity of a proposed kinetic mechanism. If the assumed rate law satisfactorily fits the experimental data, it can be safely used for the engineering of the reactor, especially if its utilization is limited within the experimentally investigated range of values for the intervening independent variables (concentration of the reactants, temperature, etc.), that is without extrapolation. For the validation of a kinetic mechanism, the goodness of fit of the proposed kinetic

model with experimental data remains a necessary condition, but it is not always a sufficient one [1]. This happens for instance when different kinetic mechanisms lead to very similar kinetic equations or to similar predicted behaviors. This is the case of photocatalytic systems. For instance, Turchi and Ollis [2] demonstrated that “many possible mechanisms can give rise to the Langmuir–Hinshelwood rate forms”. Of course, if the form of the rate equation is exactly the same there is no chance of discriminating between different mechanistic models through a validation against data obtained in a real reactor. In this case, other non-kinetic proofs are required. Langmuir-type equations and Quadratic-type rate equations, the two main classes of rate equations presently proposed for photocatalytic systems, are formally different. Nonetheless, the reaction rates predicted by a Langmuir-type equation are so alike to those obtained with a Quadratic-type rate equation that it is difficult to establish which equation gives the best fit of error-affected experimental data [3]. By the way, the development of mechanistic kinetic models able to give a comprehensive description of all the experimentally observed behaviors in photocatalytic systems looks to be a work still in progress with modifications which are constantly proposed and need to be verified [2–23].

Abbreviations: AR, Annular reactor; BLB, Blue light bulb; CFD, Computational Fluid Dynamics; LED, Light emitting diode; LHT, Langmuir Hinshelwood type; MQT, Minero quadratic type; ODE, Ordinary differential equations; PDE, Partial differential equations; PR, Plane reactor; RTE, Radiative transport equation; SE, Simulated experimental; SRPA, Specific rate of photon absorption; UV, Ultra violet; VREA, Volumetric rate of radiant energy absorption.

* Corresponding author.

E-mail address: giovanni.cameraroda@unibo.it (G. Camera-Roda).

<http://dx.doi.org/10.1016/j.cattod.2016.06.050>

0920-5861/© 2016 Elsevier B.V. All rights reserved.

In practice, it is more difficult to assess a mechanistic model than an empirical model, which is sufficient for the engineering of chemical reactors. A mechanistic model, however, can be used for the improvement of the catalytic material or of the process. In fact, a mechanistic model shows “how the system works” [24], thus revealing which are the elementary steps, which should be perfected. This aspect is particularly important for photocatalytic processes, which currently need to arrive at the level of efficiency required by some industrial applications.

In formulating a mechanistic model, the number of adjustable kinetic parameters (the parameters which cannot be evaluated independently) should be kept as low as possible to avoid “overfitting” [25]. This latter phenomenon might have also the consequence of transforming in practice a mechanistic model into an empirical one when the number of parameters is so high, that it becomes difficult to understand whether the goodness of fit is a consequence of the correct identification of the intervening mechanisms or simply of the large degree of freedom. If a better fit is not obtained in spite of the increased complexity and of the increased number of parameters, the validity of the model might be questionable.

Furthermore, photocatalytic processes present some peculiar features, as it is outlined in Table 1, which under many aspects increase the complexity of the system.

It is clear that in photocatalysis the activation of the reaction by the absorption of the photons has the consequence of making necessary the knowledge of the value of the rate of photon absorption, which locally cannot be measured and may vary very much from point to point inside a real photocatalytic reactor. In some respects the photons participate to the reaction as if they were reagents (albeit immaterial reagents) consumed by the reaction [26]. On the other hand, the mole (einstein) is the unit to measure the number of photons and the first step of a photocatalytic event is often presented in the form of a stoichiometric equation: $h\nu + \text{TiO}_2 \rightarrow h^+ + e^-$.

Unfortunately, the law of radiant energy transport leaves little space for the control of the availability of the photons throughout the reactor. The “advection” term which is present in a mass balance equation is absent in the radiative transport equation (RTE), since the photons, unlike the real reactants, cannot be mechanically “mixed”. The geometry and the properties of the illumination system, the geometry of the reactor and the optical thickness are of fundamental importance to obtain a “good” distribution of the radiation inside the reactor. In particular, the optical thickness is a general parameter, which governs the distribution of the light in “participating media” [27,28] and therefore should be considered in the study of any system where photons activate some phenomenon. In a slurry photocatalytic reactor a simple way to modify the value of the optical thickness is to vary the photocatalyst concentration, thus modifying the optical properties of the slurry [29].

The described framework makes kinetic analysis a hard task, which can be to some extent simplified by the use of a “photodifferential” reactor [26,30]. The objective of the present work is to give a survey of the difficulties encountered in the assessment of the rate law of a photocatalytic slurry reaction and to identify some guidelines to resolve these problems. The photocatalytic oxidation of formic acid is here considered as an example to illustrate the proposed procedures.

2. Materials and experimental methods

A slurry of Evonik Aeroxide Degussa P25 titania powders has been used to photocatalytically oxidize formic acid (Fluka) in a laboratory experimental apparatus. This simple organic molecule

is directly mineralized without the formation of intermediate compounds [18,31,32]. The chemicals, the materials and the experimental procedures are the same described in a previous work [30], where all the details can be found. During all the runs, the pH slightly increased from the initial value of 3.5, however without exceeding 4. So, in all the experiments the pH remained well beyond the pH value of the zero charge point for Evonik P25.

The reacting solution flows through an UVA illuminated reactor and is recycled back by a peristaltic pump to the reactor after passing through a stirred tank from where the sample to be analyzed are withdrawn (see Fig. S1 of the supplementary material).

Thanks to the relatively high recirculation rate, the whole system approaches the behavior of a batch apparatus.

Two different types of photocatalytic reactors have been used: a plane reactor (PR) illuminated by UVA LEDs with a narrow emission spectrum showing a peak at 378.5 nm [30] and an annular reactor (AR) illuminated by a linear fluorescent blue lamp (Philips TLD 8W/08 Blacklight Blue lamp) with a narrow emission spectrum showing a peak at 365 nm. The geometry of the reactor and the position of the light source are shown in [30] and in Fig. S2 of the supplementary material for the PR and the AR, respectively.

Table 2 reports the values of the parameters relative to the AR. An analogous table for the PR is presented in [30].

3. Kinetic equation

The rate equation developed by Minero et al. [15,16] has been chosen for the present analysis in the system under investigation and tested against the experimental data obtained at different operative conditions. The choice has been based on the consideration that this equation is probably the one which explicitly takes into account the effect of most of the widely accepted intervening variables (rate of photon absorption, concentration of the substrate, of the oxygen and of the catalyst) with the lowest number of kinetic parameters (only one). The degree of freedom, which is given by the number of kinetic parameters, is an important characteristic of the rate law. A lower number is appreciable since it avoids overfitting, but concurrently the law should be able to reproduce satisfactorily all the essential features of the reaction. The demonstration of the validity of the model, which underpins this kinetic equation, is not the objective of the present work. The aims are instead to understand at which degree it is able to reproduce with only one kinetic parameter some experimental results and to discuss about certain aspects of the kinetic study of photocatalytic slurry systems with the simplicity and the clarity, which follow from the adoption of a one-parameter equation.

The rate equation by Minero et al. [16] can be written in the following form [30], where the dependence on the catalyst concentration disappears if the specific absorption coefficient [34] is constant, as it is usually observed [29].

$$\hat{R} = \eta \times \hat{\phi} = k' C_{\text{ox}} C_s \left(\sqrt{1 + \hat{\phi} \times \frac{2}{k' C_{\text{ox}} C_s}} - 1 \right) \quad (1)$$

where \hat{R} is the reaction rate per unit of photocatalyst mass, $\hat{\phi}$ the specific rate of photon absorption, SRPA, (i.e. the moles of absorbed photons per unit time per unit mass of photocatalyst), η the quantum yield, C_{ox} and C_s the concentrations of the oxygen and of the substrate, respectively. The kinetic equation by Minero et al. (hereafter MQT) belongs to the so called “quadratic-type” class of rate expressions for photocatalytic reactions [3], even though the number of kinetic parameters is just one against the two or more parameters which usually appear in this class of equations.

In view of the fact that the absorption of the photons is the primary step of a photocatalytic event, the volumetric or the specific rate of photon absorption, or some other directly related vari-

Download English Version:

<https://daneshyari.com/en/article/4756981>

Download Persian Version:

<https://daneshyari.com/article/4756981>

[Daneshyari.com](https://daneshyari.com)