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Photocatalysis in microreactors

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Abstract

A photocatalytic microreactor with immobilized titanium dioxide as photocatalyst and illuminated by UV-A light emitting diodes was constructed and tested for the degradation of the model substance 4-chlorophenol. The microreactor consisted of 19 channels with a cross-section of approximately 200 μm × 300 μm. Intrinsic kinetic parameters of the reaction could be determined and mass-transfer limitations for the employed operating conditions could be excluded by calculating appropriate Damköhler numbers. Photonic efficiencies for the degradation of 4-chlorophenol are provided. The illuminated specific surface of the microstructured reactor surpasses that of conventional photocatalytic reactors by a factor of 4–400.

Keywords: Microreactor; Photocatalytic; TiO_2; Kinetics; Mass transfer; UV-A LED

1. Introduction

Today, most research in photocatalysis is still done using a semiconductor catalyst in the form of dispersed powders. For any practical device, however, immobilized catalysts are preferred in order to avoid a costly separation step necessary after the reaction [1,2]. Immobilized systems have the problem that they are difficult to scale and most often have low interfacial surface areas [3]. In this context, microstructured reactors might prove advantageous since they inherently possess large surface-to-volume ratios and thus compensate for the disadvantages associated with the immobilization of the photocatalyst.

During recent years, microreaction technology has developed from a fringe area in catalysis research and reaction engineering into a valuable tool for the chemical industry and many other users who are looking for miniaturized and mobile applications of chemical systems [4,5]. Features unique to microreactors include laminar flow, short molecular diffusion distances, large specific interfacial areas and excellent heat transfer characteristics [6]. For photochemical reactions in particular, microreactors exhibit higher spatial illumination homogeneity and better light penetration through the entire reactor depth in comparison to large-scale reactors [7].

While many papers have been published on heterogeneous catalysis or phase transfer-reactions in microstructured reactors, only few examples for photochemical reactions in microchannels can be found. The few examples in literature include the photochemical coupling of benzophenone to benzopinacol [7], the production of singlet oxygen [8], and the photochemical chlorination of alkylaromates [9]. All of these reactions are carried out without a catalyst. To our knowledge, no photocatalytic reaction has yet been performed in microreactors. In addition, most of the aforementioned references use miniaturized reaction equipment but do not extend this miniaturization to the light source. For example, microscope lamps or 1000 W xenon lamps are used, which—despite obtaining good results—override the advantages associated with the use of miniaturized reaction equipment, such as minimal space and energy requirements.

2. Materials and methods

2.1. Microreactor system

For our investigation, we fabricated a microreaction system in which TiO_2 was deposited as the photocatalyst and which we equipped with a novel type of UV-A light emitting diode (LED). Fig. 1 depicts the employed experimental set-up.

The microstructured device was manufactured from a low temperature co-firing ceramic (LTCC) green body in which 19 microchannels with a cross-section of approximately 300 μm × 200 μm were milled by precision CNC

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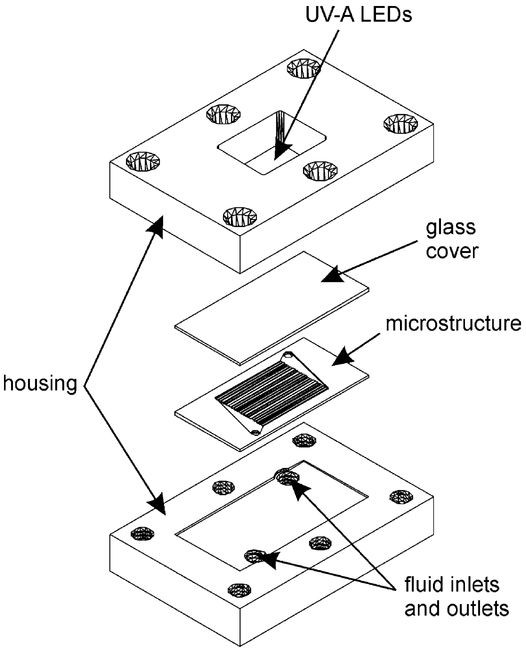

Fig. 1. Microreactor set-up.

machining. The micromachining followed a calcination step in order to obtain the ceramic substrate from the structured green body. This substrate was then subject to the deposition of a titanium film (approximately 5 μm thick) by physical vapor deposition and subsequently to the deposition of the photocatalytic TiO_2 film by anodic spark deposition [10]. Fig. 2 shows a scanning electron micrograph of the cross-section of a typical microreactor channel.

The three different materials (ceramic, titanium and TiO_2) can be clearly distinguished. The photocatalytic TiO_2-layer has a highly porous structure and consists of the two crystal modifications rutile (70%) and anatase (30%) [11]. The specific surface area of the photocatalyst coating has been determined to be on the order of 38 m^2 per deposited gram of TiO_2. Following the deposition of the catalyst, the microstructure was sealed with a glass top using epoxy glue, and mounted in a stainless steel housing. Fluidic connections were made by 1/8 in. PEEK tubing and flangeless fittings (Upchurch Scientific). The reactant flow was driven by a peristaltic pump (Ismatec IPC#4, tubing 0.51 mm i.d.). Illumination was carried out with an array of 11 UV-A LEDs (Toyoda Gosei Ltd., Model E1L5M-3P0A2-01) mounted on a printed circuit board. The peak emission wavelength of the LEDs was 385 nm and the electrical operation conditions were 3.7 V forward voltage and 330 mA forward current (for the 11 LED array). Light intensity of the LED array was measured with an electrical power meter (A.C. Peschel UVM-CP equipped with a UV-A sensor).

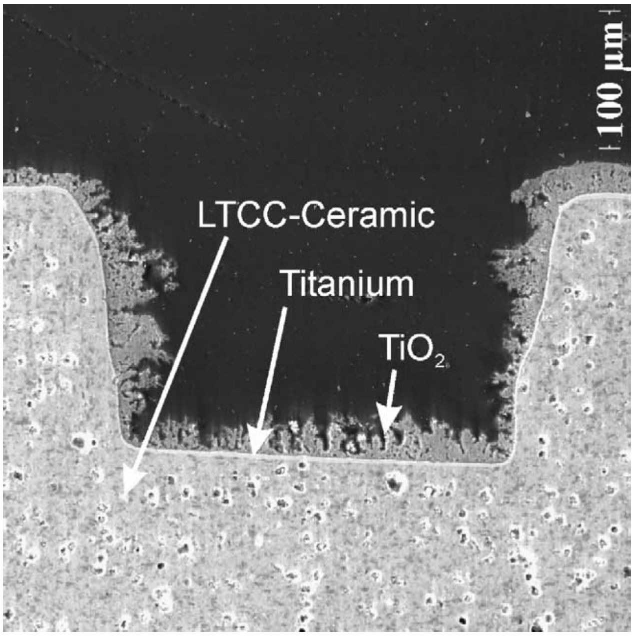

Fig. 2. SEM micrograph of the cross-section of a typical microchannel.

2.2. Degradation of 4-chlorophenol

In order to characterize the photocatalytic performance of the microreactor, the degradation of 4-chlorophenol, a widely employed compound for the testing of photocatalytic systems, was investigated [1]. Solutions of 4-chlorophenol (Merck) were prepared with Milli-Q water and aerated before use. Four different initial concentrations of 4-chlorophenol (0.05, 0.1, 0.25 and 1 mmol l^{-1}) were examined and the photocatalytic degradation was followed by HPLC for five different flow rates under continuous flow operation. Before samples were taken, the solution was passed through the reactor for at least 2 h to ensure that adsorption equilibrium and steady-state conditions had been reached. Chromatograms were registered with standard reversed-phase HPLC using an octyl column (Hypersil WP-300) and the eluent was a mixture of methanol (30%), acetonitrile (10%) and water (60%) containing 1% acetic acid. The flow rate was 1 ml min^{-1} and the detection wavelength was 280 nm. In any kinetic measurement, the initial rate of 4-chlorophenol degradation (R_i) was determined from the initial slope of the individual concentrations versus residence time profiles. The degradation for each initial concentration was measured at least three times and then averaged.

3. Results and discussion

3.1. Degradation kinetics of 4-chlorophenol

The complete photocatalytic degradation of 4-chlorophenol can be summarized as

$$ClC_6H_4OH + 6\tfrac{1}{2}O_2 \xrightarrow{h\nu,TiO_2} 6CO_2 + 2H_2O + HCl \qquad (1)$$

Mills and Wang described 4-chlorocatechol, hydroquinone and benzoquinone to be the major intermediates for the

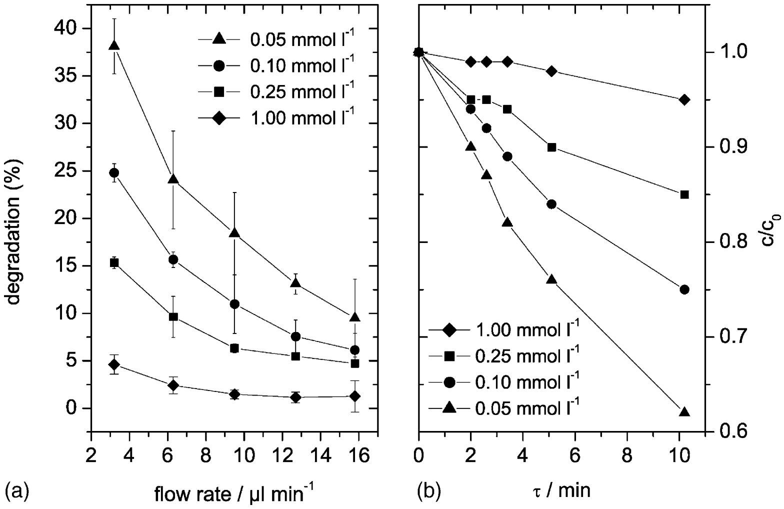

Fig. 3. (a) Degradation of 4-chlorophenol in the photocatalytic microreactor for different flow rates and initial concentrations; (b) data from (a) with flow rates converted to residence times and degradation to dimensionless concentrations.

photocatalytic degradation of 4-chlorophenol [1]. However, in our experiments with the microreactor, we could not detect any of these substances with the employed HPLC method. Fig. 3a depicts the degradation of 4-chlorophenol as a function of initial concentration and flow rate. Higher degradation was observed for lower initial concentrations. Furthermore, degradation decreased with increasing flow rates, which can be explained by the decrease in residence time of the reactants in the microchannels. For kinetic analysis, flow rates were converted to hydrodynamic residence times with $\tau = V/\dot{V}$, where V is the reactor volume and $\dot{V}$ the volumetric flow rate (cf. Fig. 3b). The internal volume of the microreactor (microchannels + inlet and outlet regions) was 0.032 cm^3.

In literature, the photocatalytic degradation of 4-chlorophenol is often described to be governed by Langmuir–Hinshelwood kinetics [12]

$$-\frac{\mathrm{d}[\text{4-CP}]}{\mathrm{d}t} = \frac{k_\mathrm{a} K[\text{4-CP}]}{1 + K[\text{4-CP}]} \qquad (2)$$

where d[4-CP]/dt is the rate of 4-chlorophenol degradation, k_a the apparent reaction rate constant, K the adsorption coefficient of 4-chlorophenol, and [4-CP] the concentration of 4-chlorophenol. Fig. 4 shows a plot of the observed initial reaction rate R_i versus the initial concentrations of 4-chlorophenol. The inset diagram shows the reciprocal R_i versus the reciprocal initial concentration for the data in the main diagram.

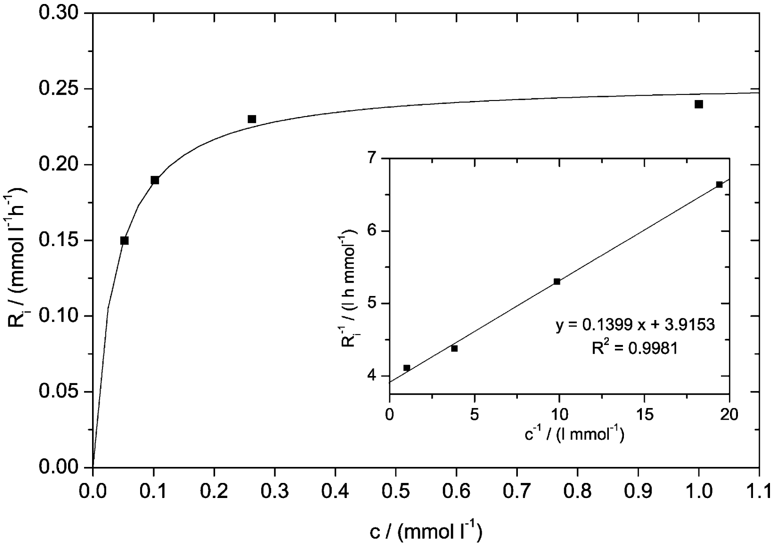

Fig. 4. Observed variation of R_i vs. the initial concentration of 4-chlorophenol measured in the photocatalytic microreactor. The inset diagram shows the double reciprocal plot of the data in the main diagram.

The linearization of Eq. (2) yields a linear relationship with an intercept of k_a^{-1} and a slope of $(k_a K)^{-1}$:

$$-\frac{\mathrm{d}t}{\mathrm{d}[\text{4-CP}]} = \frac{1}{k_a} + \frac{1}{k_a K[\text{4-CP}]} \tag{3}$$

The measured initial reaction rates versus initial concentrations are in good agreement with the Langmuir–Hinshelwood model (solid line in Fig. 4). From the least-squares analysis of the inset diagram in Fig. 4, values of $k_a = 0.26\,\text{mmol}\,\text{l}^{-1}\,\text{h}^{-1}$ and $K = 28\,\text{l}\,\text{mmol}^{-1}$ were found. The k_a value varies strongly with experimental conditions and therefore cannot be compared with data found by other research groups. However, the K value agrees with the results of Mills and Wang who found $K = 1.7\,\text{l}\,\text{mmol}^{-1}$ for wash coats of Degussa P25 TiO_2 [1] and Theurich et al. who found $K = 24\,\text{l}\,\text{mmol}^{-1}$ for suspensions of Sachtleben Hombikat UV 100 [12].

3.2. Influence of mass transfer

For the measured kinetic data to reflect the real intrinsic kinetics of the 4-chlorophenol degradation, a limitation of the overall degradation rate by mass transfer must be excluded. Turchi and Ollis described such mass-transfer limitation for coiled glass-tube reactors [13]. For the special case of microchannel reactors, Commenge et al. developed a criterion, which allows estimating the influence of mass transfer on the kinetic measurement [14]. These authors proved with their calculations that if α, which represents the ratio of the heterogeneous reaction rate at the channel walls to radial diffusion from the channel axis toward the wall, is less than 0.1, then the error in the measured rate constants is less than 3% and can be assumed to reflect the intrinsic kinetics of the investigated reaction. α is frequently referred to as the heterogeneous Damköhler number Da_{II} and is defined for photocatalytic reactions that obey Langmuir–Hinshelwood kinetics as follows [15]:

$$\alpha \equiv Da_{\text{II}} = \frac{k_a}{\beta a/K + \beta a c_b} \tag{4}$$

where k_a is the apparent rate constant, β the mass-transfer coefficient, a the interfacial area per unit volume, K the Langmuir adsorption coefficient and c_b the bulk concentration of the solution. The mass-transfer coefficient can be estimated from Sherwood numbers with $Sh = \beta d_h/D$, where d_h is the hydrodynamic diameter of a microchannel and D the molecular diffusion coefficient. The value of D for 4-chlorophenol is $0.94 \times 10^{-5}\,\text{cm}^2\,\text{s}^{-1}$ [16] and d_h for one microchannel in the used reactor is 240 μm. For typical fluid dynamic conditions in microchannels, such as low flow rates and laminar flow, Sh numbers reach the asymptotic value of 3.66 [17,18]. Hence, mass-transfer coefficients can be calculated with $\beta = 3.66D/d_h$. The interfacial area per unit volume of the photocatalytic TiO_2 film was calculated with the BET surface and a density of TiO_2 of $3.9\,\text{g}\,\text{cm}^{-3}$. Table 1 summarizes the computed Da_{II} numbers for all four initial concentrations of 4-chlorophenol. From these Da_{II} numbers, it becomes obvious that there is no mass-transfer limitation, and therefore the measured kinetic data really reflect the intrinsic kinetics of the photocatalytic reaction in the microreactor.

Table 1
Damköhler numbers Da_{II} and photonic efficiencies ξ for different initial bulk concentrations c_b of 4-chlorophenol

c_b (mmol l^{-1})	Da_{II} number ($\times 10^{-7}$)	Photonic efficiency, ξ (%)
1.0	0.33	0.0262
0.25	1.12	0.0245
0.1	2.43	0.0203
0.05	3.83	0.0162

3.3. Photonic efficiency

The efficiency of a photocatalytic process is difficult to assess. The calculation of quantum yield poses serious difficulties because it implies knowledge of the rate of absorption of ultra-bandgap photons. In the case of photocatalytic reactions, the photonic efficiency ξ represents a more useful term [19]. If monochromatic light is used for illumination of the catalyst, ξ is defined as follows:

$$\xi = \frac{\text{rate of reaction}}{\text{incident monochromatic light intensity}} \tag{5}$$

In our experiment, the incident light intensity from the UV-A LED array measured $1.6\,\text{mW}\,\text{cm}^{-2}$ and the emission wavelength was 385 nm and can be regarded as nearly monochromatic (spectral line half width: 20 nm). Photonic efficiencies were computed for the experimental data represented in Fig. 4 and are summarized in Table 1. Photonic efficiencies must be regarded cautiously. They depend on many experimental parameters, such as catalyst type and reactor geometry, but at least provide some idea of the efficiency of the photocatalytic process. It has been suggested to introduce relative photonic efficiencies [20], however, they are also considered difficult to determine [19] and to compare between research groups. The photonic efficiencies we found for the microreactor experiments are smaller than those reported for kinetic studies in suspensions. Theurich et al. found a photonic efficiency of 0.7% [12] for Sachtleben Hombikat UV 100 and Mills et al. found photonic efficiencies of 1.1% [21,22] for Degussa P25. However, those commercial catalysts are only available as fine powders and therefore are difficult to immobilize as adhesive coats on surfaces. The higher photonic efficiency of the suspended photocatalysts might be attributed to the greater catalytic activity of Sachtleben and Degussa catalysts. This finding clearly indicates that further improvement of the catalytic activity of our immobilized catalyst is required and research in this area is currently under way.

Table 2
Illuminated catalyst surface area per unit of liquid treated inside the reactor κ (adapted from [3])

Photocatalytic reactor	κ ($m^2\,m^{-3}$)
Microreactor	11667
Slurry reactor	2631
External type annular reactor	27
Immersion type with classical lamps	133
Immersion type with new lamps[a]	2667

[a] See [3] for further details.

3.4. *Specific surface area in microreactors*

A property that might contribute favorably to the future use of the microreactors in photocatalysis is their high surface-to-volume ratio. In this context, Ray and Beenackers identified the illuminated specific surface area of a photocatalyst within the reactor that is in contact with the reaction liquid κ as an important design parameter for the construction of photocatalytic reactors [3]. κ for the microreactor was calculated using the following formula:

$$\kappa = \frac{2h + w}{hw} \tag{6}$$

where h is the channel height (200 μm) and w the channel width (300 μm). Note that only the two side walls and the bottom of the channel were covered with photocatalyst, the top was sealed with a glass plate. Table 2 lists typical κ values for different classes of common photocatalytic reactors. It becomes obvious that the κ value for the microreactor surpasses the values for other reactor types due to the large surface-to-volume ratio inherent to any microstructured reactor.

4. Conclusion

In the present investigation, the feasibility of performing photocatalytic reactions in microstructured reactors could be proven. The degradation of 4-chlorophenol was investigated in the microreaction system and kinetic parameters were extracted. Photonic efficiencies for the employed TiO_2 catalyst films are provided. It could be shown, from the calculation of appropriate Damköhler numbers, that the measured kinetic parameters really reflect the intrinsic kinetics because, for the employed experimental conditions, mass-transfer limitations in the microreactor could be excluded. The obtained kinetic parameters agree well with previous findings by other groups. For the microreactor, the specific surface area that is illuminated κ exceeds that of conventional reactor types by a factor of approximately 4–400 depending on the reactor type. Besides the miniaturization of the reaction system itself, we also paid attention to the miniaturization of the illumination source. From recent developments in the optoelectronic industry, it can be expected that smaller and less power-consuming light sources will be available soon, making them suitable for the construction of even smaller and more powerful microreaction devices.

5. Outlook

In principle, the suitability of microreactors for photocatalytic reactions was shown. In order to cope with larger volumetric flow rates, future development of photomicroreactors will have to focus on the numbering-up of these devices. In this context, numbering-up might become an alternative to the otherwise difficult scale-up process of conventional photoreactors. Furthermore, photocatalytic microreactors may find use in small, mobile and low energy-consuming devices for the treatment of odors, exhaust air and waste water.

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