Chemical Engineering Journal 135S (2008) S303–S308

Chemical Engineering Journal

www.elsevier.com/locate/cej

Photocatalytic reactions in microreactors

Yoshihisa Matsushita [a,*], Nobuko Ohba [b], Shinji Kumada [b],
Kosaku Sakeda [b], Tadashi Suzuki [b], Teijiro Ichimura [b]

[a] Department of Chemistry, Tokyo Institute of Technology, 2-12-1 Ohokayama, Meguro, Tokyo 152-8551, Japan
[b] Department of Chemistry and Materials Science, Tokyo Institute of Technology, 2-12-1 Ohokayama, Meguro, Tokyo 152-8551, Japan

Abstract

A photocatalytic microreactor with immobilized TiO_2 layer was developed and the processes of degradation and reduction of organic compounds, and amine *N*-alkylation in microspace were examined. These model reactions proceeded very rapidly with considerably large photonic efficiencies. In contrast to the result in a batch reactor, we successfully observed *N*-alkylation reaction of benzylamine by using the microreactor with immobilized Pt-free TiO_2 as well as TiO_2/Pt. These results suggest the feasibility of a catalytic microreaction system on organic photoreactions.

Keywords: Microreactor; Photocatalyst; Alkylation; UV-LED

1. Introduction

Recently, much attention has been paid to chemical reactions in microreactors using the features unique to microspace such as short molecular diffusion distance and fast mixing, extremely effective heat exchange, laminar flow, and large surface-to-volume ratio [1–5]. Although microreaction systems are successfully examined in the wide range of applications of organic chemistry, surprisingly small number of studies have so far made on applications of microreactors to photoreactions [6–15]. Microreactors can be expected to exhibit some distinct properties on photoreactions, such as higher spatial illumination homogeneity and better light penetration through the entire reactor depth in comparison to large-scale reactors. Therefore we are studying organic photoreactions in microreactors [16,17] (Fig. 1).

Since a photocatalytic reaction takes place on a photoirradiated catalyst surface, a microreactor which has a large surface-to-volume ratio may prove its advantages on the reaction. Study of light-induced electron-transfer reactions on semiconductor catalyst has become one of the most attractive research areas in photochemistry. Wide varieties of organic reactions were successfully examined by using semiconductor photocatalyst [18]. Most research on the reaction is carried out using dispersed powders in conventional batch reactors. A separation step of the powders is required after the reaction. Though systems with immobilized catalyst can avoid the step, they tend to have low interfacial surface areas. Thus we have developed a photocatalytic microreaction system. In this report, we will describe the study on the photocatalytic degradation and reduction of organic compounds, and amine *N*-alkylation processes in a microreactor with immobilized photocatalyst.

2. Experimental

Photoreaction was carried out with microreactors made of quartz which has a straight microchannel of 500 μm width, 10–500 μm depth, and 50 mm length. The bottom and side walls of the microchannel were coated with a photocatalytic TiO_2 layer in anatase form by using the sol–gel process. The microchannel was made by micromilling and the surface of the bottom wall was left in rough conditions. The fact increases the surface-to-volume ratio of the photocatalyst layer and enhances mass transport to the direction perpendicular to the flow by formation of turbulence (Fig. 2a and b). Particles of Pt were loaded on the TiO_2 layer for the study of photocatalytic *N*-alkylation of amines by using a photodeposition method [19].

It has been widely accepted that the illuminated specific surface area of photocatalyst within a reactor is the most important design parameter of photocatalytic reactors. The illuminated specific surface areas per unit of liquid of the microreactor with a microchannel of 100, 300, 500, and 1000 μm depth were calculated to be 1.4×10^4, 7.3×10^3, 6.0×10^3, and 4.0×10^3 m^2/m^3, respectively, without taking into account of roughness of the

---

* Corresponding author. Tel.: +81 35734 2765; fax: +81 35734 2765.
E-mail address: matsushita.y.aa@m.titech.ac.jp (Y. Matsushita).

1385-8947/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2007.07.045

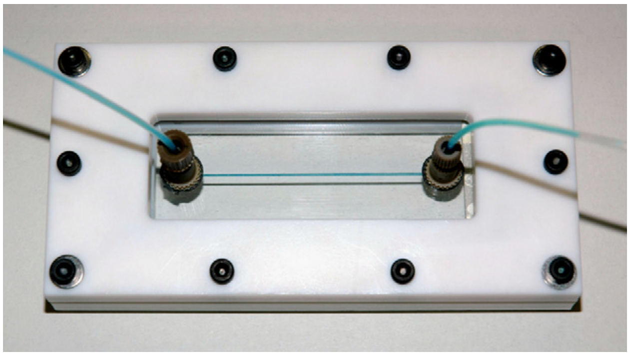


Fig. 1. Photograph of the photocatalytic microreactor. The microchannel was filled with aqueous solution of methylene blue for the purpose of clarity.

photocatalyst surface. Thus the microreactors with immobilized photocatalyst have much larger values of illuminated specific surface area of photocatalyst than typical conventional batch reactors [20].

The microchannel was covered with a quartz plate and sample solutions were introduced into the microreactor with a syringe pump. The microreactor was irradiated by a XeCl excimer laser (308 nm, 2 Hz, 15 ns pulse duration), a OPO laser excited with the third harmonic of a Nd^{3+}:YAG laser (5 Hz, 15 ns pulse duration), or UV light emitting diodes (UV-LEDs, 365, 385 nm).

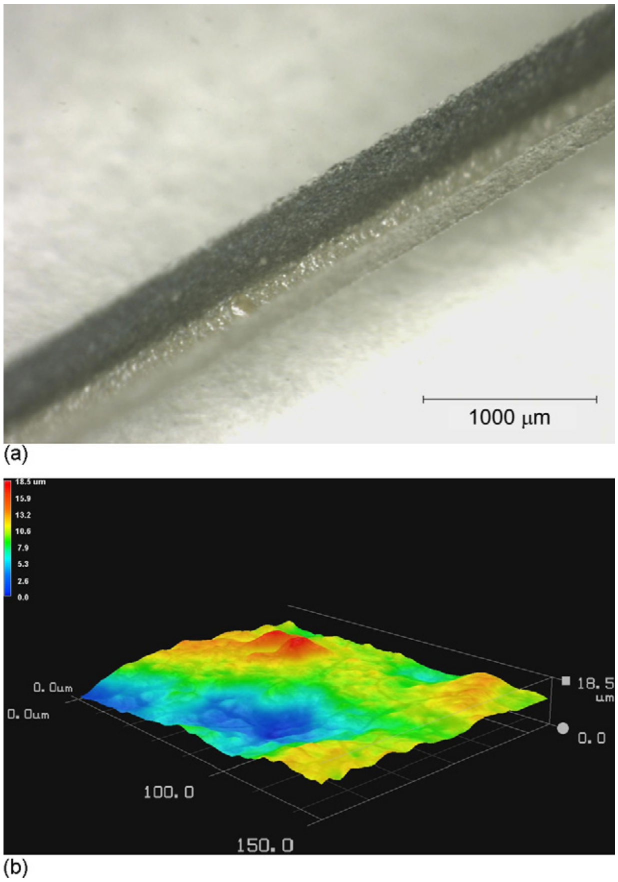


Fig. 2. (a) Optical micrograph of a microchannel and (b) contour map of a bottom wall of a microchannel.

3. Results and discussion

3.1. Photodegradation of organic compounds

Photoexcited TiO_2 oxidizes a reactant that donates an electron to TiO_2 while it reduces a reactant that receives an electron. Photodegradation of organic compounds in aqueous solutions have been fruitfully investigated by using TiO_2 as a photocatalyst. In the first place, we examined photodegradation of pollutants of the environment such as chlorophenols, bisphenol A, and dimethylformamide (DMF) in a microreactor of 100 μm depth as a model reaction to probe the feasibility of microreactor on photocatalytic reactions. To appear the advantages of the miniaturized reaction vessel, a light source of minimal space and lower photon cost is suitable for the microreaction system. Thus we employed UV-LEDs as well as lasers for the excitation light source of photocatalyst.

As can be seen in Fig. 3, the photodegradation reaction took place quite quickly. The degradation of organic compounds in a photocatalytic microreactor excited with 385-nm UV-LED has been reported by Gorges et al. [9]. Considering from the band gap energy and the absorption spectrum of TiO_2, we can expect higher reaction efficiencies with a light source of higher photon energy. Therefore we examined the excitation wavelength dependence of photocatalytic degradation by using a tunable OPO laser. Fig. 4 shows an action spectrum of degradation of DMF in the photocatalytic microreactor. The result indicates that the reaction efficiency should be very sensitive to the excitation wavelength. It was confirmed that higher reaction efficiencies would be achieved as increasing the excitation photon energy in the wavelength region of 400–340 nm.

To further examine the advantages of UV-LED as excitation light source of a photocatalytic microreaction system, photonic efficiencies of photodegradation were also examined by using several different light sources. To assess the efficiency of a photochemical reaction process, we often use the quantum yield which is defined with the ratio of number of reaction product

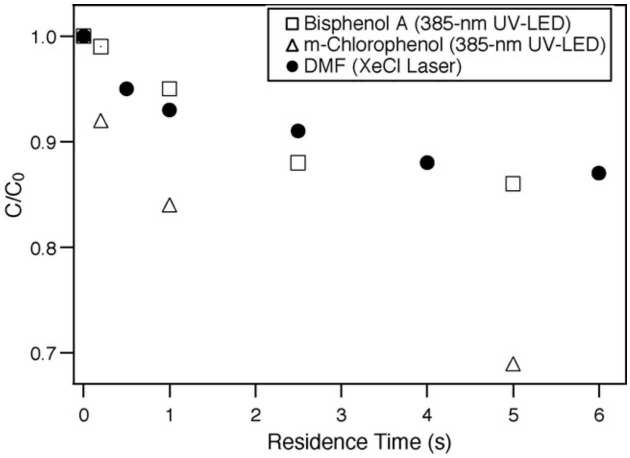


Fig. 3. Photocatalytic degradation of bisphenol A, *m*-chlorophenol, and DMF in aqueous solutions excited with UV-LEDs and a XeCl laser. The concentrations of substrate normalized with the initial concentration (5.2×10^{-4} M) were plotted against residence time.

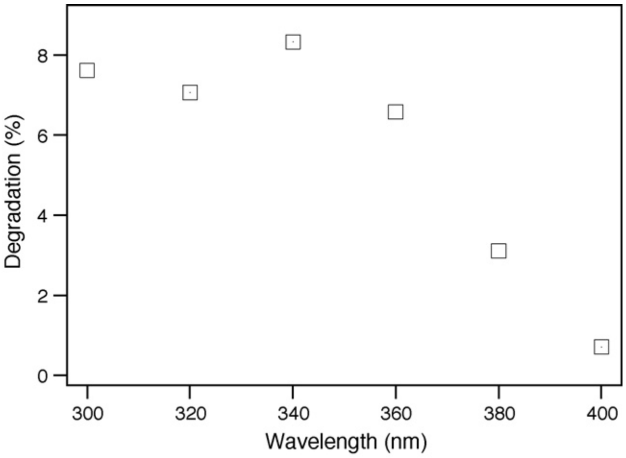


Fig. 4. Action spectrum of photocatalytic degradation of DMF (5.2×10^{-4} M). A photocatalytic microreactor of 100 μm depth was excited with a tunable OPO laser.

molecules to number of absorbed photons:

$$\phi = \frac{\text{number of reaction product molecules}}{\text{number of absorbed photons}} \qquad (1)$$

On the other hand, the calculation of quantum yield on a photocatalytic process poses serious problems since particles of photocatalyst will absorb, scatter, and transmit incident light. A more useful term is the photonic efficiency, ξ, which is defined as the number of reaction product molecules divided by the number of photons of monochromatic light incident inside the window of a reaction vessel [21].

$$\xi = \frac{\text{number of reaction product molecules}}{\text{number of incident monochromatic photons}} \qquad (2)$$

Table 1 summarizes photonic efficiencies of photocatalytic degradation of DMF in the microreactor of 100 μm depth excited with a XeCl laser, a tunable OPO laser, and UV-LEDs. Among these light sources, 365-nm UV-LEDs exhibited a considerably large photonic efficiency. Thus an array of 365-nm UV-LEDs (Nichia NSHU590B, Optical Power Output: 1.4 mW, 7 LEDs/Array) was employed as an excitation light source for the photocatalytic reactions described in the following section.

The photonic efficiencies obtained by XeCl and OPO laser excitation were considerably lower than the case of UV-LED excitation. One possible explanation of the lower photonic efficiencies is that adsorption of the substrate is rate limiting and higher density of photons within the short pulse duration is not used efficiently for the reaction. Assuming that this adsorption can be described by the Langmuir–Hinshelwood equation, one can obtain a linear relationship with the reciprocal values of initial reaction rate and initial concentration [18]:

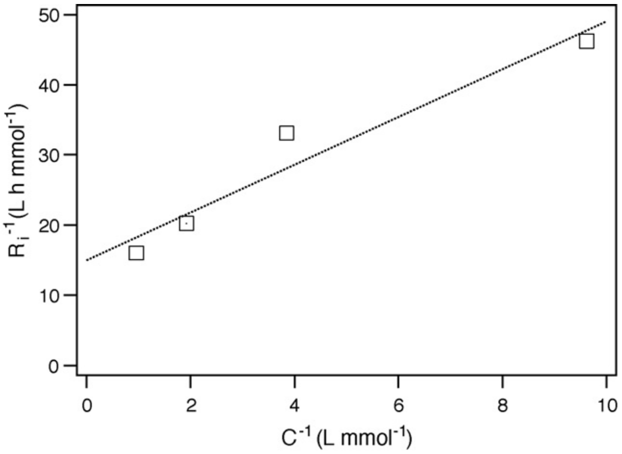


Fig. 5. Plot of the inverse of the initial reaction rate of DMF photodegradation as a function of the reciprocal value of the initial concentration.

$$-\frac{1}{R_\mathrm{i}} = \frac{1}{k_a} + \frac{1}{(k_a K[C_0])} \qquad (3)$$

where R_i is the initial reaction rate of photodegradation, k_a the apparent reaction rate constant, K the adsorption coefficient of substrate on the photocatalyst surface, and $[C_0]$ is the initial concentration of the substrate. The double reciprocal plot for DMF photodegradation yields a straight line, indicating that the reaction process governed by the Langmuir–Hinshelwood kinetics (Fig. 5). The adsorption coefficient, K, was calculated to be 4.6×10^3 L mol^{-1} from the slope and the intercept of the line.

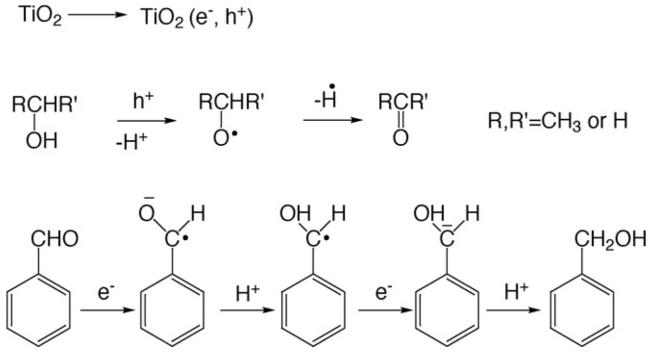
3.2. Photocatalytic reduction in microreactors

As compared with the extensive studies of photocatalytic oxidation process of organic compounds in aqueous solutions and in the gas phase, there are rather small number of reports on the photocatalytic reduction process in organic solvents by using conventional batch reactors [22,23].

We have studied photocatalytic reduction of benzaldehyde in alcohol solvent (Scheme 1) as a model reaction in microreactors to prove its advantages on organic photocatalytic reactions [17]. The photoreduction was examined in three alcohol media, methanol, ethanol, and 2-propanol. The reaction yields benzylalcohol and ketone corresponding to the alcohol media. The photoreduction proceeded very rapidly in the microreactor and

Table 1
Photonic efficiencies of photocatalytic degradation of DMF (5.2×10^{-4} M) in the microreactor of 100 μm depth

Light source	Wavelength (nm)	Incident light intensity	Photonic efficiency (%)
Excimer laser	308	0.36 mJ/pulse	0.034
OPO laser	400	0.15 mJ/pulse	0.0019
OPO laser	380	0.15 mJ/pulse	0.0092
OPO laser	360	0.090 mJ/pulse	0.084
UV-LED	385	0.30 mW	0.010
UV-LED	365	0.67 mW	0.28



Scheme 1. Photocatalytic reduction of benzaldehyde.

ethanol offers the highest efficiency of the reaction to yield 10.7% of benzylalcohol within the irradiation time of 60 s. The efficiency is slightly lower in methanol and the lowest when 2-propanol is employed as a solvent.

The photoreduction is selective for several multifunctional compounds. It has been known that the nitro group is reduced more readily than the aldehyde group when *p*-nitrobenzaldehyde is employed as a substrate in a batch reactor [23]. Thus we further examined photoreduction of nitro compounds in the photocatalytic microreactor. Photoreduction was carried out with alcohol solutions of *p*-nitroacetophenone saturated with nitrogen or oxygen (Scheme 2). Sample solutions were introduced into a microreactor of 100 μm depth and irradiated with an array of 365-nm UV-LEDs. Fig. 6 indicates the reduction of 1.0×10^{-4} M of *p*-nitroacetophenone in ethanol saturated with nitrogen as a function of irradiation time. Reduction increased with increasing the irradiation time and reaches 92.5% at the irradiation time of 120 s. The photonic efficiency of the photoreduction was calculated to be 0.69%. Photoirradiation of the solution purged with oxygen did not yield any detectable *p*-aminoacetophenone.

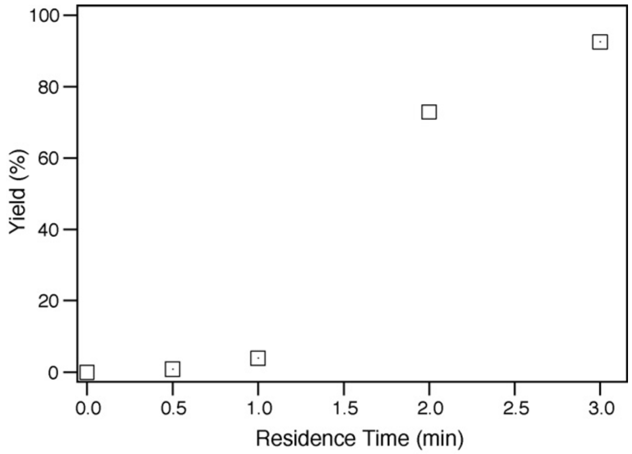
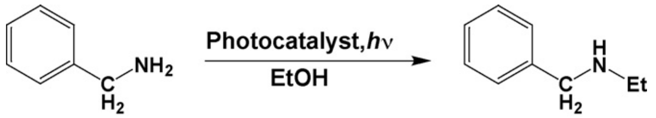


Fig. 6. Photocatalytic reduction of *p*-nitoroacetophenone (1.0×10^{-4} M) to yield *p*-aminoacetophenone in the photocatalytic microreactor excited with 365-nm UV-LEDs.

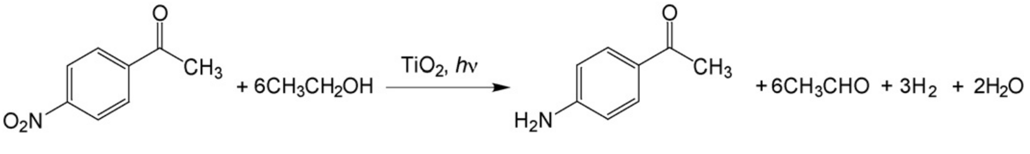


Scheme 3. Ethylation of benzylamine on photocatalyst surface.

The mechanism of the photoreduction of benzaldehyde and *p*-nitoroacetophenone can be interpreted as follows. The photoreduction must be coupled with the oxidation of alcohol. The electron in the conduction band of the excited state of TiO_2 is available for transference and the electron hole in the valence bond is open for donation. The electron hole can oxidize an alcohol to give a corresponding carbonyl compound while the reduction is initiated by an electron transfer from TiO_2 to substrate. Under oxygen-saturated conditions, the electrons in the conduction band of the excited TiO_2 are captured by oxygen. Thus the photoirradiation does not give any detectable *p*-aminoacetophenone. An alcohols having lower pK_a tends to provides more protons and alkoxy radicals. The pK_a values is the lowest for methanol and the highest for 2-propanol among the three alcohols. Therefore the lowest concentrations of the protons and alkoxy anions are available for the protonation and electron hole quenching in 2-propanol. Although methanol has the lowest pK_a value, the reaction intermediate, the methoxy radical is kinetically much less stable. For the reasons given above, the photoreduction carried out in ethanol is most efficient. The higher reduction efficiency of *p*-aminoacetophenone is related to the lower reduction potential of the nitro group and the reduction is estimated to proceed via a hydroxylamine intermediate. As can be seen in Fig. 6, the reaction yield does not increase linearly with the increasing of the residence time. Further experiments to probe the reaction intermediate and reaction kinetics by laser spectroscopy are under progress.

3.3. Amie N-alkylation process

Most of the researches on microreaction systems revolve around two questions: How can we improve the reaction yield and selectivity by using microspace? Can we find a reaction which occurs only in the microspace? In our knowledge, there are not so many reports which well addressed the second question. Here we will describe our results on photocatalytic *N*-alkylation of amines (Scheme 3) which may be one of the answers of the second question.



Scheme 2. Photocatalytic reduction of *p*-nitroacetophenone.

Observed photocatalytic processes of *N*-alkylation of aromatic amines by alcoholic solvents in microreactors were considerably different from those in conventional batch reactors. It has been known that *N*-alkylation of aromatic amines occurred by UV irradiation of Pt loaded TiO_2 (TiO_2/Pt) suspended in a variety of alcohols. Ohtani et al. [24] studied *N*-alkylation process of amines by irradiation 400-W high-pressure mercury of TiO_2/Pt. They reported that *N*-alkylation of benzylamine occurred with the yield up to 84.4% by 4 h irradiation and aniline was *N*-alkylated with 8.1% yield by 20 h irradiation in ethanol solvent. They also reported that *N*-alkylation of amines could not be observed by irradiation of Pt-free TiO_2.

The *N*-alkylation of benzylamine and aniline was studied in the photocatalytic microreactors of 300 μm depth excited with 365-nm UV-LEDs. The reaction proceeded very rapidly in the photocatalytic microreactor with immobilized TiO_2/Pt. The *N*-alkylation in ethanol proceeded within only 150 s to yield 85% of *N*-ethylbenzylamine from benzylamine and 34% of *N*-ethylaniline from aniline. The photonic efficiency of the *N*-alkylation of benzylamine was calculated to be 0.35%. In contrast to the result in batch reactors, we also successfully observed *N*-alkylation reaction of aromatic amines by using the microreactor with immobilized Pt-free TiO_2 as well as TiO_2/Pt. The *N*-alkylation in ethanol proceeded within only 150 s to yield 43% of *N*-ethylbenzylamine with Pt-free TiO_2 (Fig. 7).

The reaction mechanism can be interpreted in terms of dehydrogenation of alcohol. The dehydrogenation of ethanol occurs on the surface of photocatalyst to form acetoaldehyde and H_2. Substrate benzylamine is *N*-ethylated by condensation of photoproduct carbonyl with benzylamine. The reduction of the resulting intermediate by H_2 occurs to yield the *N*-ethylbenzylamine.

Photoexcited TiO_2 oxidizes a reactant that donates an electron to TiO_2 while it reduces a reactant that receives an electron. It has been known that depositing Pt on TiO_2 enhances the photocatalytic activity by serving as an electron sink and consequent slowing charge recombination. Since the electron-hole recombination within the photocatalyst is in competition with the reaction process, the reaction efficiencies must be strongly affected by the surface-to-volume ratio of a photocatalytic reactor. In fact, we obtained an experimental result indicating that the yield of *N*-alkylation was considerably increased as increasing the surface-to-volume ratio of the microchannel [25]. Thus the photoreaction can proceed so rapidly in the microreactor which has a remarkably large surface-to-volume ratio and the *N*-alkylation of benzylamine may be observed even in the microreactor without Pt co-catalyst.

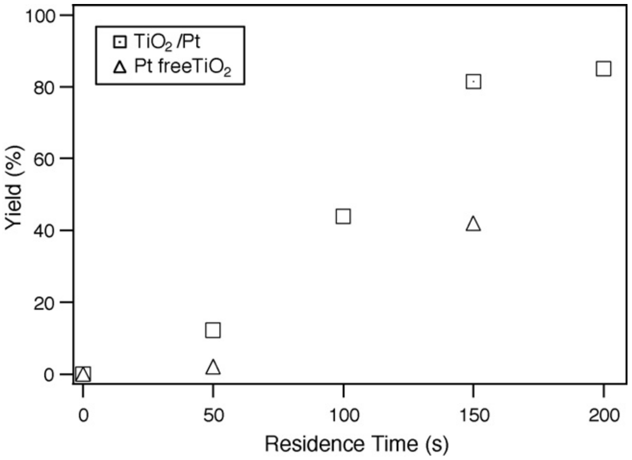


Fig. 7. Photocatalytic *N*-ethlylation of benzylamine (1.0×10^{-3} M) in the microreactors of 300 μm depth with immobilized TiO_2/Pt and Pt-free TiO_2 excited with 365-nm UV-LEDs.

4. Conclusion

In conclusion, we have developed a photocatalytic microreactor and examined the feasibility of the photocatalytic microreaction system on organic photoreactions. Photocatalytic degradation, reduction, and amine *N*-alkylation processes were investigated. These model reactions proceeded very rapidly with considerably large photonic efficiencies. In contrast to the result in a batch reactor, we successfully observed *N*-alkylation reaction of benzylamine by using the microreactor with immobilized Pt-free TiO_2 as well as TiO_2/Pt. Since the electron-hole recombination within the photocatalyst is in competition with the reaction process, the reaction efficiencies must be strongly affected by the surface-to-volume ratio of a photocatalytic reactor. Further experiments for the direct observation of reaction intermediate by laser spectroscopy are under progress to elucidate detailed reaction kinetics and to establish the photocatalytic microreaction system.

Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research (No. 16550134) from the Ministry of Education, Culture, Sports and Technology of Japan. We are grateful to Mitsui Engineering and Shipbuilding and Co. Ltd. in support of this work.

References

[1] W. Ehrfeld, V. Hessel, H. Lowe, Microreactors, Wiley-VCH, Weinheim, 2000.
[2] C. Wiles, P. Watts, S.J. Haswell, E. Pombo-villar, Lab. Chip 1 (2001) 100.
[3] N. Aoki, S. Hasebe, K. Mae, Chem. Eng. J. 101 (2004) 323.
[4] J. Yoshida, A. Nagaki, T. Iwasaki, S. Suga, Chem. Eng. Technol. 28 (2005) 259.
[5] K. Sato, A. Hibara, M. Tokeshi, H. Hisamoto, T. Kitamori, Anal. Sci. 19 (2003) 15.
[6] K. Yamashita, Y. Yamaguchi, M. Miyazaki, H. Nakamura, H. Shimizu, H. Maeda, Anal. Biochem. 332 (2004) 274.
[7] H. Lu, M.A. Shumidt, K.F. Jensen, Lab. Chip 1 (2001) 22.
[8] K. Ueno, F. Kitagawa, N. Kitamura, Lab. Chip 4 (2002) 231.
[9] R. Gorges, S. Meyer, G. Kreisel, J. Photochem. Photobiol. A 167 (2004) 95.
[10] H. Nakamura, X. Li, H. Wang, M. Uehara, M. Miyazaki, H. Shimizu, H. Maeda, Chem. Eng. J. 101 (2004) 261.
[11] T. Fukuyama, Y. Hino, N. Kamata, I. Ryu, Chem. Lett. 33 (2004) 1430.
[12] H. Maeda, H. Mukae, K. Mizuno, Chem. Lett. 34 (2005) 66.
[13] G. Takei, T. Kitamori, H.-B. Kim, Catal. Commun. 6 (2005) 357.
[14] S. Teekateerawej, J. Nishino, Y. Nosaka, J. Appl. Electrochem. 35 (2005) 693.

[15] K. Jähnisch, U. Dingerdissen, Chem. Eng. Technol. 28 (2005) 426.
[16] T. Ichimura, Y. Matsushita, K. Sakeda, T. Suzuki, Photoreactions, in: T.R. Dietrich (Ed.), Microchemical Engineering in Practice, Blackwell Publishing, in press.
[17] Y. Matsushita, S. Kumada, K. Wakabayashi, K. Sakeda, T. Ichimura, Chem. Lett. 35 (2006) 410.
[18] A. Mills, S. Le Hunte, J. Photochem. Photobiol. A 108 (1997) 1.
[19] J. Lee, H. Park, W. Choi, Environ. Sci. Technol. 36 (2002) 5462.
[20] A.K. Ray, A.A.C.M. Beenackers, AIChE J. 44 (1998) 477.
[21] J. Theurich, M. Linder, D.W. Bahnemann, Langmuir 12 (1996) 6368.
[22] C. Joyce-Pruden, S. Pross, J.K. Kreisel, Y. Li, J. Org. Chem. 57 (1992) 5087.
[23] F. Mahadavi, T.C. Bruton, Y. Li, J. Org. Chem. 58 (1993) 744.
[24] B. Ohtani, H. Osaki, S. Nishimoto, T. Kagiya, J. Am. Chem. Soc. 108 (1986) 308.
[25] Y. Matsushita, N. Ohba, S. Kumada, K. Sakeda, T. Suzuki, T. Ichimura, Catal. Commun., submitted for publication.