Photocatalytic Reduction in Microreactors

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Photocatalytic reduction of benzaldehyde and nitrotoluene in microspace was investigated by using a microreactor with immobilized titanium dioxide. Advantages of a photocatalytic microreaction system which has a remarkably large surface-to-volume ratio have been examined.

During the last decade, microreaction system has developed using the features unique to microspace such as short molecular diffusion distance, excellent heat-transfer characteristics, laminar flow, and large surface-to-volume ratio.[1–4] Microreaction systems are successfully examined especially in analytical chemistry and biochemistry applications.[5,6] Though we can expect microreactors to exhibit higher spatial illumination homogeneity and better light penetration through the entire reactor depth in comparison to large-scale reactors, there are only several reports on photoreactions in microreactors.[7–12] Thus, we are investigating applications of microreactors on organic photoreactions. In this report, we will describe photocatalytic reduction in a microfabricated reactor.

A photocatalytic reaction can take place on an irradiated surface. Most research on the reaction is carried out using dispersed powders in conventional batch reactors. A costly 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. A microfabricated reactor with immobilized photocatalyst has a large surface-to-volume ratio and may have some advantages over conventional batch reactors on the reaction.

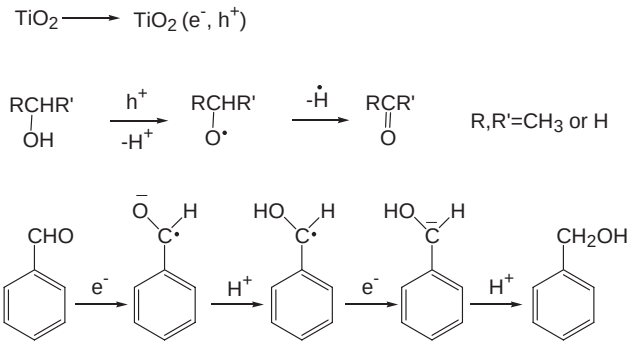
Titanium dioxide (TiO_2), particularly in the anatase form, is the most widely used photocatalyst due to its chemical stability. Photoexcited TiO_2 oxidizes a reactant that donates an electron to TiO_2 while it reduces a reactant that receives an electron. Photoxidations of organic compounds using TiO_2 as a photocatalyst have been fruitfully investigated and there are some reports on the photoreduction process on the TiO_2 surface. Li and co-workers[13,14] reported photoreduction of aldehydes to their corresponding alcohols and nitro compounds to their corresponding amino compounds by using conventional batch reactors. In this investigation, we have examined photocatalytic reduction of benzaldehyde and nitrotoluene as a model reaction in microreactors to prove its advantages on the organic 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. We employed UV light emitting diodes (UV-LEDs) for the excitation light source of photocatalyst. 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. So an array of 365 nm UV-LEDs (Nichia NSHU590B, Optical Power Output: 1.4 mW) was employed for the excitation of a photocatalytic microreactor.

Photoreduction was carried out with a microreactor made of quartz which has a microchannel of 500 μm width, 100 μm depth, and 40 mm length. The bottom and side walls of the microchannel were coated with a photocatalytic TiO_2 layer. 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 area per unit of liquid of the microreactor is calculated to be $1.4 \times 10^4\ m^2\ m^{-3}$ without taking into account of the roughness of the TiO_2 surface. The value is much larger than the typical illuminated specific surface area of photocatalyst of conventional batch reactors.[14] Alcohol solutions of benzaldehyde or nitrotoluene saturated with nitrogen were introduced to the microreactor with a syringe pump and irradiated with UV-LEDs. All experiments were carried out at room temperature.

The photoreduction of benzaldehyde was examined in three alcohol media, methanol, ethanol, and 2-propanol. The reaction yields benzyl alcohol and a ketone corresponding to the alcohol media. The reaction mechanism can be expressed as shown in Scheme 1.[15] The excited state of TiO_2 is denoted as TiO_2 (e^-, h^+). The electron in the conduction band 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 benzaldehyde.

Photoreduction efficiencies of 1.0×10^{-4} M benzaldehyde are summarized in Table 1. It indicates that the photoreduction proceeds very rapidly in the microreactor and ethanol offers the highest efficiency of the reaction. The efficiency is slightly lower in methanol and the lowest when 2-propanol is employed as a solvent. Irradiation of benzaldehyde in ethanol purged with oxygen does not yield any detectable benzyl alcohol.



Scheme 1. Photoreduction of benzaldehyde.

Table 1. Photoreduction of benzaldehyde in photocatalytic microreactor excited with 365 nm UV-LED

Solvent[a]	Irradiation Time/s	Yield/%	
		Benzaldehyde	Benzyl alcohol
Ethanol (a)	0	100	0
Ethanol (a)	5	100	0.2
Ethanol (a)	10	99	1
Ethanol (a)	20	97	2.9
Ethanol (a)	30	96	4.6
Ethanol (a)	60	90	10.7
Methanol (a)	20	98	2.5
2-Propanol (a)	20	99	0.8
Ethanol (b)	20	100	0

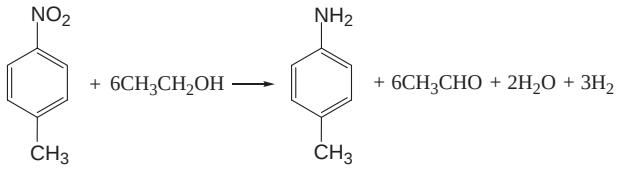
[a]Purged with (a) nitrogen and (b) oxygen during photoirradiation.

By assuming that the reaction proceeds in accordance with the mechanism proposed in Scheme 1, we can interpret the results as follows. 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 benzyl alcohol. An alcohols having lower pK_a tends to provides more protons and alkoxy radicals. The pK_a value 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. Our observations are thus consistent with the reaction mechanism proposed in Scheme 1. 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.[13] Thus, we further examined photoreduction of nitro compounds in the photocatalytic microreactor. Table 2 and Scheme 2 indicate the reduction of 1.0×10^{-4} M of *p*-nitrotoluene in ethanol saturated with nitrogen as a function of irradiation time of 365 nm UV-LED. Reduction increased with increasing the residence time and reaches 45.7% at a residence time of 60 s. Photoirradiation of the solution purged with oxygen did not yield any detectable *p*-toluidine. Similar to the mechanism for the photoreduction of benzaldehyde, the photoreduction of *p*-nitrotoluene must be coupled with the oxidation of ethanol. The higher reduction efficiency is related to the lower reduction potential of the nitro group and the reduction is estimated to proceed via a hydroxylamine intermediate. Further experiments with other multifunctional compounds are under progress.

In conclusion, we have developed an photocatalytic microreactor for reduction of organic compounds. The reactions proceeded within 60 s to yield 10.7% of benzyl alcohol from benzaldehyde and 45.7% of *p*-toluidine from *p*-nitrotoluene by the excitation of 365 nm UV-LED. Optimization of excitation wavelength and photon density, design of the microreactor, flow rate and irradiation time are under progress for the establishment of the photocatalytic microreaction system.

Table 2. Photoreduction of nitrotoluene in photocatalytic microreactor excited with 365 nm UV-LED

Irradiation time/s	Yield/%	
	p-Nitrotoluene	*p*-Toluidine
0	100	0
10	68.3	8.3
20	55.5	18.0
40	33.8	31.3
60	32.7	45.7



Scheme 2. Photoreduction of nitrotoluene.

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