MULTIPHASE PHOTOCATALYTIC REACTIONS IN A MICROREACTION SYSTEM
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ABSTRACT
A microreaction system with immobilized photocatalyst layer was developed and photocatalytic oxidation and alkylation processes of organic compounds, photocatalytic water-splitting, and photocatalytic reduction of carbon dioxide were examined. These model reactions proceeded quite rapidly with considerably large efficiencies under gas-liquid-solid multiphase flow condition as compared to those in batch reaction systems.

KEYWORDS: Photocatalysis, Multiphase Flow, Carbon Dioxide, Water-Splitting

INTRODUCTION
Since only a small number of studies have been made so far on photochemical reactions conducted in microreactors, we have been developing a microreaction system optimized for photoreactions [1,2]. Especially, we have been investigating photocatalytic oxidation, reduction, and alkylation processes in microreactors [3,4]. One can expect microreactors to exhibit some advantages on photocatalytic reactions, such as higher spatial illumination homogeneity, better light penetration through the entire reactor depth and larger illuminated surface area per unit volume in comparison to large-scale reactors. It was revealed that efficiency and selectivity of some model reactions can be greatly enhanced in comparison to our previous results [2] by utilizing the features unique to microspace, such as gas-liquid-solid multiphase flow.

Though numerous attempts have been made on multiphase catalytic reactions, there are still difficulties on conduction the reactions due to the low reaction yield arising from very low efficiency of interaction and mass transfer between different phases. To produce high interfacial area between the phases, we introduced a sample solution and gas into a microchannel to form gas-liquid-solid multiphase flow. The effect of the multiphase flow on photocatalytic processes will be discussed.

EXPERIMENTAL
Photochemical reaction was carried out in microreactors made of Tempax plates and a thin film of self-welding fluorinated polymer which has a microchannel of 100-500 μm in width, 20-500 μm in depth, and 50-200 mm in length. The inner walls of the microchannel were coated with a photocatalytic TiO2 and metal cocatalyst layer by using sol-gel process. Sample solution and gas were fed into the microreactor with a flow rate between 2 μl/min and 200 μl/min and photoirradiated...
RESULTS AND DISCUSSION

Although Pt-loaded TiO₂ is known to be a highly active photocatalyst, it suspended in pure water does not show photocatalytic activity for water splitting in conventional batch reaction systems probably due to the back reaction on the Pt surface. On the other hand, Pt-loaded TiO₂ immobilized in a microchannel reactor was found to decompose water under gas-liquid-solid multiphase flow condition. Pure water and N₂ buffer gas were introduced into a microchannel and then irradiated with 365-nm UV-LEDs. The yield of H₂ is shown in Fig. 1. The horizontal axis indicates the N₂ gas injection rate while the injection rate of water was kept at a constant value of 2 μL/min. At a lower gas injection rate, micro-bubbles were formed and so-called slug-flow was observed. At a gas injection rate higher than 100 μL/min, a pipe-flow, the gas flowed through the center of the microchannel while the liquid flowed close to the photocatalyst surface, was formed as schematically illustrated in Fig. 2. The yield of H₂ increased as increasing the gas flow rate, namely, as decreasing the thickness of the water layer to 1.3 μm. The fact indicates that undesired back reaction can be suppressed by using the gas-liquid-solid multiphase flow formed in a microchannel.

Photocatalytic reduction of CO₂ was examined by using several sort of metal co-catalyst loaded on the TiO₂ surface. Though it has been known that CO₂ in aqueous solution can be photocatalytically reduced (Scheme 1), only very low reaction yields were reported by using large-scale batch reaction systems. The reaction proceeded very quickly to form methanol as the main product by 6-electron reduction process in our microreaction system. The yield of methanol is more than 1000 times larger than...
that obtained in conventional batch reaction systems and further increased under multiphase-flow condition (Fig. 3).

Scheme 1

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\begin{align*}
\text{CO}_2 + 2 \text{H}^+ + 2\text{e}^- & \rightarrow \text{CO} + \text{H}_2\text{O} \\
\text{CO}_2 + 2 \text{H}^+ + 2\text{e}^- & \rightarrow \text{HCO}_2\text{H} \\
\text{CO}_2 + 4 \text{H}^+ + 4\text{e}^- & \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} \\
\text{CO}_2 + 6 \text{H}^+ + 6\text{e}^- & \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \\
\text{CO}_2 + 8 \text{H}^+ + 8\text{e}^- & \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}
\end{align*}
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The yields of some other model reactions, for instance selective photocatalytic oxidation of organic compounds and alkylation of amines were also increased by using the unique features of microreaction system. Under the multiphase-flow condition, the liquid phase is always saturated with gas even in the end part of the microchannel. In addition, as increasing the gas injection rate, the thickness of the liquid phase decrease. These facts may enhance the reaction efficiency.

CONCLUSIONS

The efficiency of photocatalytic oxidation and alkylation processes, photocatalytic water-splitting, and photocatalytic reduction of carbon dioxide were greatly enhanced by using gas-liquid-solid multiphase flow formed in a photocatalytic microreaction system. The result may arise from very high efficiency of interaction and mass transfer between different phases in the microreaction system.

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