MICRO-FLOW REACTION SYSTEMS FOR PHOTOCATALYTIC CARBON DIOXIDE RECYCLING AND HYRDROGEN GENERATION

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ABSTRACT

Microstructured reaction vessels with immobilized photocatalyst thin layer were successfully applied to carbon dioxide recycling and water splitting processes. It was revealed that the yield and selectivity of the reaction can be greatly enhanced under gas-liquid multiphase flow conditions, owing to extraction of reaction products to the gas phase which results in suppression of undesired reverse reaction.

KEYWORDS

photocatalyst, carbon dioxide recycling, hydrogen generation, green synthesis

INTRODUCTION

If we utilize a microreactor with immobilized photocatalytic thin layer on inner walls, its high surface area per unit volume as well as fast rate of mixing, and homogeneous light irradiation through the entire reaction vessel may accelerate photocatalytic reactions effectively. Thus we have applied microreacors with immobilized photocatalyst layer to photocatalytic synthetic reactions [1-4]. In this presentation, we will report our latest results directed toward green and sustainable chemistry.

EXPERIMENT

Microreactors made of Tempax plates with a immobilized photocatalytic TiO_2 layer and a thin film of self-welding fluorinated polymer were employed for preliminary experiments (Fig. 1). For larger production scale experiments, we developed microreaction devices made of duralumin have a reaction zone of 30 mm in width and 60 mm in length. The reaction zone consists of 30-100 parallel grooves and the cross section of the grooves has a rectangular shape of 100-300 μm in depth and width (Fig. 2). The inlet and outlet of the reaction zone have 3D structures to avoid maldistribution of flow and to generate stable multiphase flow. The reaction zone was covered with a quartz or Pyrex plate with immobilized photocatalytic TiO_2 layer, so that the device can be applied to photocatalytic reactions initiated by 365 nm UV-LED (Nichia, 10 W optical power output) irradiation.

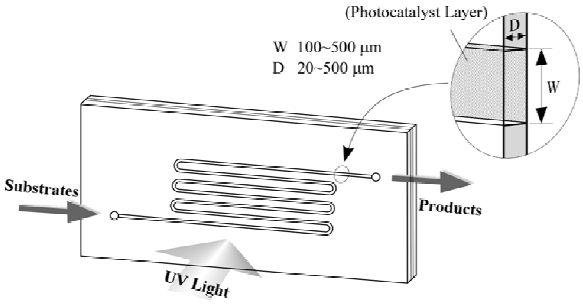

Figure 1. Typical experimental setup for preliminary experiments.

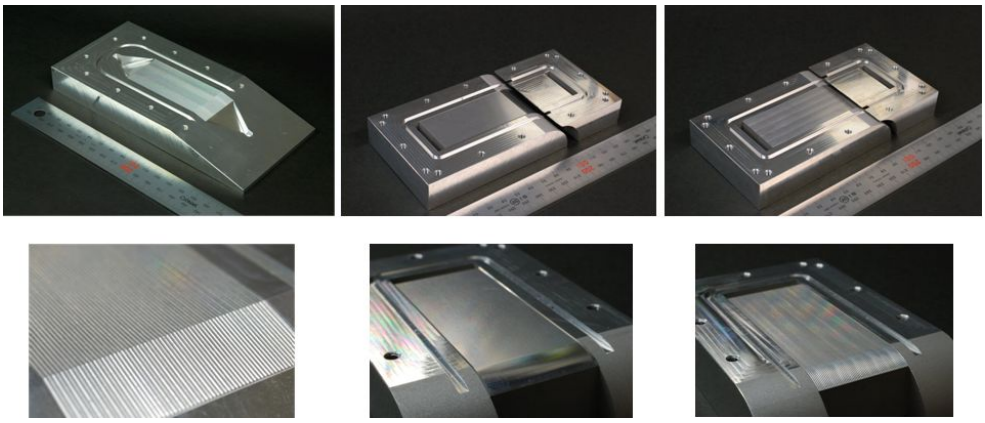

Figure 2. Micro-structured photocatalytic reaction devices for larger scale production.

978-0-9798064-5-2/μTAS 2012/$20©12CBMS-0001

RESULTS AND DISCUSSION

There are many reports on reduction of carbon dioxide by photocatalyst. In particular, reports on reduction of carbon dioxide by water without any sacrificial reagents to produce methanol, formic acid and methane, as indicated in the scheme 1, have been attracted much attention in terms of carbon dioxide utilization for sustainability, even though they showed only significantly low reaction yield. It is inevitable to design a highly efficient reaction system using water as an electron source but without using sacrificial reagents thereby realizing a practical reaction system avoiding environmental load on reactions.

Scheme 1.

$$CO_2 + 2\ H^+ + 2e^- \rightarrow CO + H_2O$$

$$CO_2 + 2\ H^+ + 2e^- \rightarrow HCO_2H$$

$$CO_2 + 4\ H^+ + 4e^- \rightarrow CH_2O + H_2O$$

$$CO_2 + 6\ H^+ + 6e^- \rightarrow CH_3OH + H_2O$$

$$CO_2 + 8\ H^+ + 8e^- \rightarrow CH_4 + H_2O$$

For that purpose, we examined photocatalytic reduction of carbon dioxide in the microreactors. Distilled water saturated with carbon dioxide was loaded into the microreactor then photoirradiated by UV-LEDs under homogeneous laminar flow or gas-liquid multiphase flow conditions. We proved a successful application of the microreactor with high reaction yield which was not shown in conventional methods. Methanol was obtained as a main reaction product. The concentration of methanol reached up to 4.32 mM and the conversion of carbon dioxide saturated in water achieved 12% at maximum in reaction time of 81 seconds. It was revealed that the yield and selectivity of the reaction can be greatly enhanced under gas-liquid multiphase flow conditions (Fig. 3), owing to extraction of produced methanol to the gas phase which results in suppression of undesired reverse reaction.

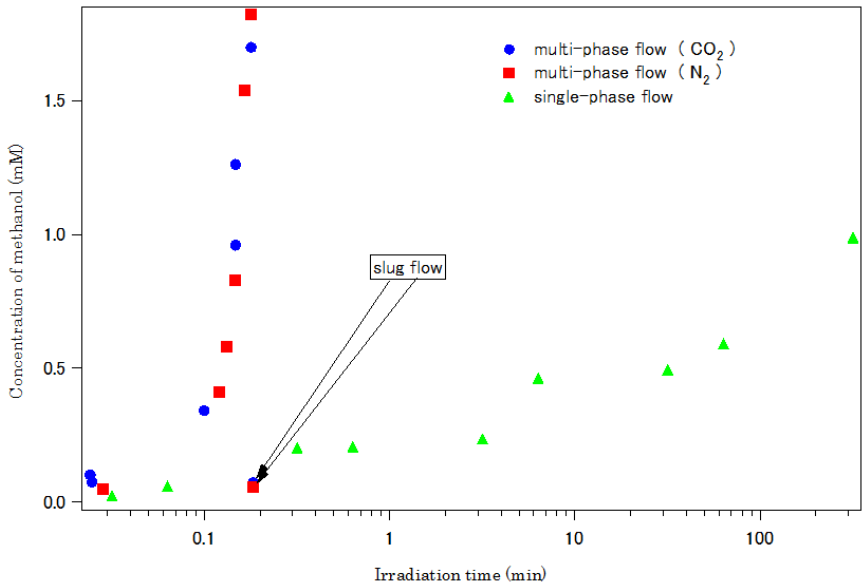

Figure 3. Photocatalytic reduction of CO_2 under multi-phase flow conditions.

The enhancement of the efficiency of water splitting process to yield hydrogen under multi-flow conditions was also successfully examined. The reaction yield dependence on the flow and photocatalyst layer conditions and application of solar active photocatalyst to the reactions will be further discussed to realize the reaction system directed toward green and sustainable chemistry.

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