Photocatalytic Steam Reforming of Methane over Platinum-loaded Semiconductors for Hydrogen Production

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Hydrogen can be photocatalytically produced from methane and water by using platinum-loaded semiconductor photocatalysts. Platinum-loaded lanthanum-doped $NaTaO_3$ ($Pt/NaTaO_3$:La) showed higher photocatalytic activity for this reaction than platinum-loaded TiO_2 did. The apparent quantum yield of this system employing $Pt/NaTaO_3$:La was estimated to be higher than that of photocatalytic water splitting system employing $NiO/NaTaO_3$:La.

Hydrogen is an environmentally benign fuel, and it is well accepted that the hydrogen should be produced from renewable resources and natural energy for the sustainable society in the near future. Methane is not only used as a fuel and a chemical resource, but it also attracts much attention as a hydrogen resource due to the highest H/C value among hydrocarbons, and a system for steam reforming of methane including water–gas shift reaction has been established for hydrogen production.[1] Although methane is converted to CO_2 in the steam reforming of methane, CO_2 could become biomass through photosynthesis and the biomass could be again converted to methane by the aid of biotechnology or biomass technology. Thus, methane is essentially recognized as one of the renewable resources. However, it is known that the steam reforming system is endothermic reaction and requires high temperature, i.e., consuming huge energy.

Photocatalytic system can function even at room temperature by using photoenergy, implying utilization of solar energy, where photoenergy compensates an increase of Gibbs free energy of the reaction system. Thus, up-hill type reaction ($\Delta G > 0$) can proceed even at low temperature. It has been well known that the photocatalytic reactions to produce hydrogen could proceed between water and many kinds of reductants such as alcohols,[2] CO,[3] ethene,[4] and some kinds of carbon-related materials such as active carbon,[4,5] coal, tar sand,[6] and also some kinds of biomass such as sugar, starch, and cellulose.[7] Compared with them, methane, as the most stable hydrocarbon, gives a largely positive Gibbs free energy for this kind of reaction:

$$2H_2O(g) + CH_4 \rightarrow 4H_2 + CO_2, \Delta G_{298K} = 113\,kJ\cdot mol^{-1}. \quad (1)$$

To our knowledge, methane has never been applied to the photocatalytic reaction with water. Here, we studied a new photocatalytic system producing hydrogen from methane and water, i.e., *photocatalytic steam reforming of methane* (PSRM), in a mild condition upon photoirradiation.

TiO_2 (JRC-TIO-8, anatase, $338\,m^2\,g^{-1}$) was supplied from the Catalyst Society of Japan, and Pt/TiO_2 ($335\,m^2\,g^{-1}$) was prepared from the TiO_2 and an aqueous H_2PtCl_6 solution with 50% methanol by photodeposition method. Two samples of lanthanum-doped $NaTaO_3$[8] ($NaTaO_3$:La) were prepared through solid-phase reaction at 1373 K from La_2O_3, Na_2CO_3, and Ta_2O_5 where doping amount of La was 2%; for one sample these start materials were mixed by a conventional mortar, and for another sample they were mechanically mixed well by wet ball-milling using acetone, then both were followed by calcination at 1373 K, referred to as $NaTaO_3$:La(C) and $NaTaO_3$:La(BM), respectively. The former had higher BET specific surface area ($3.6\,m^2\,g^{-1}$, calculated from N_2 adsorption) and smaller average crystallites size (50 nm, calculated from X-ray diffraction) than those of the latter ($1.9\,m^2\,g^{-1}$ and 62 nm, respectively). Pt was loaded on $NaTaO_3$:La by impregnation method using an aqueous nitric acid solution of $Pt(NO_2)_2(NH_3)_2$ followed by calcination in dry air and H_2 reduction at 773 K. NiO was loaded by impregnation method using an aqueous $Ni(NO_3)_2$ solution followed by calcination at 543 K.[8] The semiconductor photocatalysts loading metal or metal oxide are referred to as, e.g., $Pt(x)/TiO_2$ and $NiO(x)/NaTaO_3$:La, where x is the loading amount (wt %) of metal or metal oxide.

Reaction tests were carried out in a fixed-bed flow-type reactor. The catalysts were granulated to the size of 400–600 µm. A thin quartz cell ($60 \times 20 \times 1\,mm^3$) was filled with the photocatalyst sample. As for the $NaTaO_3$:La samples, the sample was diluted by quartz granules to fill the cell. Prior to the photoreaction test, to clean the catalyst surface, the catalyst was photoirradiated by a 300-W Xe lamp in a flow of H_2O vapor (3%) with Ar carrier. H_2O vapor was introduced by bubbling the carrier gas through a saturator containing distilled water. The reaction gas, a mixture of H_2O vapor and CH_4 with Ar carrier, was introduced into the reactor at a flow rate of $50\,mL\cdot min^{-1}$, and the reaction was carried out without heating at atmospheric pressure upon photoirradiation. The temperature of the reactor was raised up to around 348 K by the photoirradiation. The incident light intensity was measured by a photodiode (TOPCON: UD-25, UVR-2) in the range of 230–280-nm wavelength. The outlet gas was analyzed by on-line gas chromatography with a thermal conductivity detector.

Photocatalytic activities of TiO_2 and $Pt(0.1)/TiO_2$ samples were examined in the flow of CH_4 and H_2O vapor. TiO_2 gave only a trace amount of H_2 in the present condition. However, H_2 and CO_2 were obtained as main products on $Pt(0.1)/TiO_2$ (Table 1, Entry 1) with a trace amount of C_2H_6 (0.014 $\mu mol\cdot min^{-1}$) and CO (0.003 $\mu mol\cdot min^{-1}$) as by-products, while no O_2 was detected. The molar ratio of H_2 to CO_2 in the outlet gas was about four, suggesting that the main reaction would be PSRM as shown in eq 1.

During the reaction the color of the catalyst changed to pale

Table 1. Results of the photocatalytic reaction[a]

Entry	Photocatalyst[b]	Production rate[c] /μmol·min^{-1}		Molar ratio of H_2/CO_2
		H_2	CO_2	
1	Pt(0.1)/TiO_2	0.76	0.18	4.2
2	Pt(0.1)/$NaTaO_3$:La(C)	1.5	0.39	3.9
3	$NaTaO_3$:La(C)	0.21	—[d]	—
4	NiO(0.2)/$NaTaO_3$:La(C)	0.18	—[d]	—

[a] Light intensity was 14 mW·cm^{-2} measured in the range of 230–280 nm. The feed gas was a mixture of H_2O (1.5%) and CH_4 (50%) with Ar carrier (total flow rate, 50 mL·min^{-1}). [b] The amount of the catalyst used for filling up the reaction cell was 0.6 g for Entry 1 and 1.0 g for others. [c] The values were obtained at the steady state. [d] <0.1 μmol·min^{-1}.

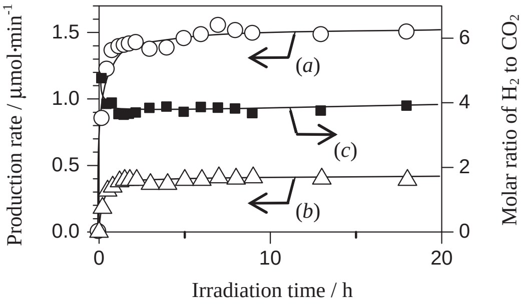

Figure 1. Time course of the production rate of (*a*) H_2 and (*b*) CO_2 on Pt(0.1)/$NaTaO_3$:La(C) upon photoirradiation, and (*c*) that of molar ratio of the produced H_2 to CO_2.

yellow according to the formation of surface organic intermediates. The intermediates were revealed to react with water to produce H_2 and CO_2, and the average composition of them was estimated to be $(CH_2O)_n$. Unfortunately, the H_2 production rate gradually decreased with time as the surface intermediates much accumulated on Pt(0.1)/TiO_2 in the present condition.

When we examined Pt(0.1)/$NaTaO_3$:La(C) sample, much higher photocatalytic performance was found for H_2 production with CO_2 formation from CH_4 and H_2O (Table 1, Entry 2). By-products were hardly observed. As shown in time course upon photoirradiation (Figure 1), after a short induction period,[9] the H_2 production rate became constant and it sustained without deactivation for a long period, at least for 18 h. The molar ratio of H_2 to CO_2 in the outlet gas was almost constant to be four in the steady state. The turnover frequency per surface Pt atom (Pt dispersion was 0.26, calculated from CO adsorption) was estimated to be 68 h^{-1}. This reaction did not proceed in the dark. Without CH_4, H_2 was not produced. These facts indicate that the reaction shown in eq 1 proceeded photocatalytically. The slightly high molar ratio of H_2 to CO_2 in the induction period suggests the formation of the similar surface intermediates. However, no deactivation was observed in this system.

In the present study, the highest H_2 production rate observed was 4.5 μmol·min^{-1} (6.6 mL·h^{-1}), corresponding to 0.6% methane conversion, over Pt(0.03)/$NaTaO_3$:La(BM) upon photoirradiation of maximum intensity (116 mW·cm^{-2}) in the flow of a mixture of 1% H_2O and 10% CH_4. Pt(0.05)/$NaTaO_3$:La(BM) showed higher activity than that of Pt(0.05)/$NaTaO_3$:La(C), suggesting that high crystallinity of semiconductor would be important for the activity in PSRM.

The prepared $NaTaO_3$:La and NiO/$NaTaO_3$:La photocatalysts exhibited high activity for water vapor splitting (0.08 and 0.16 μmol·min^{-1} respectively) as reported.[8] When CH_4 was introduced, the H_2 production rate was accelerated only on the former (Table 1, Entries 3 and 4). On separate experiments using liquid water and bubbling CH_4, only the former produced both H_2 and CO_2, while the latter produced no CO_2. These facts mean that the former was active for both water splitting and PSRM while the latter selectively promoted water splitting even in the presence of methane, suggesting that photocatalyst for PSRM should be designed to activate both methane and water. It seems that $NaTaO_3$:La should be an excellent semiconductor photocatalyst for water activation and Pt would be an effective co-catalyst on $NaTaO_3$:La for methane activation, while NiO co-catalyst on $NaTaO_3$:La would not be suitable for PSRM.

The apparent quantum yield (QY)[10] in the range of 240–270-nm wavelength was estimated for each photocatalytic system under the light with low intensity, 2 mW·cm^{-2}. The QY of the PSRM system employing Pt(0.05)/$NaTaO_3$:La(BM) was estimated to be 30% in this condition. On the other hand, the photocatalytic water splitting system employing NiO(0.2)/$NaTaO_3$:La(BM), one of the best photocatalysts at present, showed lower QY for H_2 production than that of the present PSRM; 13% for water vapor splitting and 20% for liquid water splitting, respectively. Thus, the present PSRM could produce H_2 more efficiently than the water-splitting systems. This would be due to suppression of the reverse reaction of water splitting by predominantly proceeding methane oxidation, and also due to lower ΔG than that for water splitting ($\Delta G_{298K} = 237$ kJ·mol^{-1} for liquid water).

In conclusion, we discovered a new photocatalytic reaction, *photocatalytic steam reforming of methane*, in a flow of methane and water vapor over platinum-loaded semiconductor photocatalysts. This PSRM system can produce H_2 from renewable resources (methane and water) and natural energy (photoenergy such as solar energy). Pt/$NaTaO_3$:La was suggested as a highly active photocatalyst.

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9 It is probably due to the formation of surface intermediates.
10 QY in the range of 240–270 nm was calculated from the results of two photocatalytic runs under the light of $\lambda >$ 240 nm and $\lambda >$ 270 nm: $\text{QY}(\%) = 100 \times (\text{Ne}_1 - \text{Ne}_2)/(\text{Np}_1 - \text{Np}_2)$, where Ne_1 and Ne_2 were the number of reacted electrons and Np_1 and Np_2 were those of incident photons under each condition, respectively; Ne_1 and Ne_2 were determined from the amount of produced H_2 assuming the following reaction: $2H^+ + 2e^- \rightarrow H_2$.