



Platinum loaded sodium tantalate photocatalysts prepared by a flux method for photocatalytic steam reforming of methane

Akira Yamamoto^{a,b}, Shota Mizuba^a, Yurina Saeki^a, Hisao Yoshida^{a,b,*}

^a Department of Interdisciplinary Environment, Graduate School of Human and Environmental Studies, Kyoto University, Yoshida Nihonmatsu-cho, Sakyo-ku, Kyoto 606-8501, Japan

^b Elements Strategy Initiative for Catalysts & Batteries (ESICB), Kyoto University, Kyotodaigaku Katsura, Nishikyo-ku, Kyoto 615-8520, Japan

ARTICLE INFO

Article history:

Received 31 August 2015

Received in revised form 17 October 2015

Accepted 20 October 2015

Available online 26 October 2015

Keywords:

Photocatalytic steam reforming of methane

Hydrogen production

Sodium tantalate

Flux method

Molten salt method

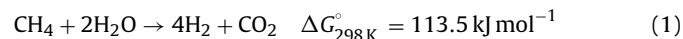
ABSTRACT

Lanthanum-doped sodium tantalate samples (NaTaO₃:La) were prepared by a flux method using a sodium chloride flux with various parameters, such as presence or absence of the flux, solute concentration, hold temperature, and amount of lanthanum doping. SEM images showed cubic and rectangular shapes for the samples prepared by the flux method, somewhat rounded shape for the sample prepared in the absence of the flux, and large particles for the sample without lanthanum doping. Among the parameters, the lanthanum doping and solute concentration much influenced the crystallite size of the NaTaO₃:La samples. Most of these NaTaO₃:La samples loaded with platinum cocatalyst exhibited the photocatalytic activity in the photocatalytic steam reforming of methane around room temperature. Among them, the highest activity was obtained by the Pt/NaTaO₃:La sample prepared by the flux method with moderate solute concentration, enough high hold temperature, and moderate amount of platinum and lanthanum doping. A positive correlation was found between the crystallite size and the photocatalytic activity. When we compared the catalysts having the same crystallite size, the sample prepared by the flux method showed higher photocatalytic activity than the catalyst prepared without the flux. It is suggested that the difference in the shape of particle would be important factor for the photocatalytic activity.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Hydrogen is one of the clean and oncoming energy sources, and its production technology have been developed and investigated by many researchers. As a source of hydrogen, methane is an attractive hydrogen source because of the highest H/C values among hydrocarbons, and it is one of the most abundant natural resource as well as a main component of renewable biogas. Methane can be catalytically converted to hydrogen by steam reforming of methane, which is the practically employed method for the hydrogen production. The overall chemical equation of the steam reforming of methane with successive water-gas shift reaction can be shown in Eq. (1).



This is a highly endergonic reaction; therefore, high temperature, typically more than 1073 K, is necessary to promote the

reaction even in the presence of catalysts. The high temperature operation causes several problems such as the large energy consumption, the irreversible carbon formation, and the necessity of expensive reactor. Thus, lowering the operation temperature has been highly desired in the steam reforming of methane.

Utilization of photocatalysts is expected to be a promising way for the development of the steam reforming of methane at low temperature [1–3]. A reaction between methane and water to form methanol and hydrogen was reported by Taylor et al. over La-doped WO₃ under UV and visible light irradiation [4,5] in an aqueous solution containing methyl viologen dichloride as an electron transfer reagent. Gondal et al. also reported the photocatalytic conversion of methane to methanol in a batch reactor using a visible laser (514 nm) and a WO₃ catalyst [6]. However, these systems might not be suitable for hydrogen production.

On the other hand, our group first reported the photocatalytic steam reforming of methane over heterogeneous photocatalysts using a gas mixture of methane and water around room temperature to produce hydrogen and carbon dioxide directly as shown in Eq. (1), where the photoenergy was added to the system for compensation of the Gibbs free energy change of this reaction [7]. In other words, the utilization of photoenergy enables us to operate

* Corresponding author at: Department of Interdisciplinary Environment, Graduate School of Human and Environmental Studies, Kyoto University, Yoshida Nihonmatsu-cho, Sakyo-ku, Kyoto 606-8501, Japan. Fax: +81 75 753 2988.

E-mail address: yoshida.hisao.2a@kyoto-u.ac.jp (H. Yoshida).

the reaction at low temperatures, which may solve the some problems mentioned above. Platinum-loaded titanium dioxide (Pt/TiO₂) photocatalysts showed the activity at mild temperature under photoirradiation, and gave the stoichiometric ratio of the products (H₂/CO₂ = 4) [7,8]. Various photocatalysts have been developed the photocatalytic steam reforming such as Pt-loaded La-doped NaTaO₃ (Pt/NaTaO₃:La) [7,9], Pt-loaded CaTiO₃ [10,11], Rh-loaded K₂Ti₆O₁₃ [12,13], and Pt-loaded or Rh-loaded β-Ga₂O₃ [14]. It was also found that this photocatalytic reaction could be further promoted at higher temperature; i.e., thermal energy could assist this photocatalytic reaction, which promised further development [15]. However, their photocatalytic activities have been not enough yet, and the further improvement of the photocatalytic activity have been desired for the practical use.

Flux method (molten salt method) is effective for synthesis of high quality crystals (with high crystallinity), and the prepared crystals often have characteristic and uniformed shapes covered with particular flat facets. It is considered that the high crystallinity is an important property for the highly active photocatalyst because crystal defects are believed to function as recombination sites for excited electron and hole pairs. In addition to the crystallinity, the shape of the crystals or the particles is considered to be one of the key factors affecting the photocatalytic activity [16–19]. The crystal facets have been pointed out to help in the separation of photogenerated carriers (electrons and holes), which leads to the high photocatalytic activity [20–22]. The suppression of the recombination is one of the strategies to improve the photocatalytic activity. Up to date, a number of crystals with characteristic shapes were synthesized by flux methods and examined as photocatalysts [23–34].

In the present paper, a flux method was employed to prepare the NaTaO₃:La crystalline samples and the photocatalytic activity was investigated in the photocatalytic steam reforming of methane.

2. Experimental

2.1. Catalyst preparation

Various NaTaO₃:La samples were prepared by a flux method. Solid reagents of Ta₂O₅, Na₂CO₃ (Rare Metallic, 99.99%), La₂O₃ (Kishida, 99.99%), and NaCl (Kishida, 99.5%) were used as purchased. The mixture of Ta₂O₅, Na₂CO₃, La₂O₃, and NaCl was ground in an aluminum mortar for 15 min, where the molar ratio of Na₂CO₃ to Ta₂O₅ was unity. Although it was reported that an excess amount of Na₂CO₃ in the mixture could compensate the volatile sodium and function as a flux [35], in the present study a stoichiometric ratio of Na₂CO₃ was added and NaCl was used as a flux, which can help us to discuss the role of a flux more clearly. The aimed amount of La was 0–5 mol%. The solute concentration of 5–90% is defined in the following equation:

$$\begin{aligned} & \text{Solute concentration } , x (\text{mol}\%) \\ & = \frac{\text{Amount of NaTaO}_3 (\text{mol})}{\text{Amount of NaTaO}_3 (\text{mol}) + \text{Amount of NaCl} (\text{mol})} \times 100 \quad (2) \end{aligned}$$

The mixture was heated in a platinum crucible using an electric furnace with a heating rate of 200 K h⁻¹ to various target temperatures (1073–1473 K, typically 1273 K), successively heated at the same temperature (hold temperature) for 5 h, and then cooled down once to 773 K at a cooling rate 100 K h⁻¹ and then to room temperature without controlling the temperature. The obtained powder was dispersed in hot ion-exchanged water (300 mL, 353 K) and filtrated with suction to separate the powder from the flux. The washing procedure was repeated four times, and dried at 323 K overnight to obtain the NaTaO₃:La sample. These samples are referred to as NaTaO₃:La(x, T, y), where x is the solute concentration defined in

Eq. (2), T is the hold temperature, and y shows the aimed amount of lanthanum doping (mol%), if necessary. On the other hand, a reference sample were prepared without the flux in a solid state reaction method: the starting mixture except for the sodium chloride flux i.e., Ta₂O₅, Na₂CO₃, and La₂O₃, where the solute concentration x corresponded to be 100, was ground well, heated with the same rate of 200 K h⁻¹, maintained at 1273 K for 5 h, and then cooled, followed by washing, in the similar way as mentioned above. This sample is referred to as NaTaO₃:La(100, 1273, 2).

Platinum co-catalyst was loaded onto the prepared NaTaO₃:La samples by an impregnation method. The sample was soaked in an aqueous solution of H₂PtCl₆ (Wako, 99.9%), dried up and calcined at 673 K for 2 h. The sample powder was granulated to the size of 300–600 μm before the photocatalytic activity test. The Pt loaded sample is referred to as Pt(z)/NaTaO₃:La(x, T, y), where z shows the loading amount of Pt (wt%).

2.2. Characterization

X-ray diffraction (XRD) measurement was carried out at room temperature using a Shimadzu Lab X XRD-6000 using Cu Kα radiation (40 kV, 30 mA). The crystallite size was determined by the Scherrer equation using the full width at half maximum (FWHM) of the diffraction line at 2θ = 22.8° in the XRD patterns of NaTaO₃. Scanning electron microscopy (SEM) images were recorded by a JEOL JSM-890. Diffuse reflectance (DR) UV–vis spectrum was recorded on a JASCO V-670 equipped with an integrating sphere covered with BaSO₄ reference. The band gap was estimated from the spectrum according to Tauc plot [36]. The specific surface area was estimated from the amount of N₂ adsorption at 77 K measured using a Quantachrome Monosorb.

2.3. Photocatalytic activity tests

Photocatalytic steam reforming of methane was carried out with a fixed-bed flow reactor as described in our previous studies [7–9]. Shortly, a mixture of the catalyst granules (0.5 g) and quartz sand (1.2 g) was put into a quartz reactor (ca. 50 × 20 × 1 mm³) and the reaction gas of CH₄ (25%) and H₂O (0.75%) with an argon carrier was introduced at a flow rate of 50 mL min⁻¹ without heating at atmospheric pressure. Light irradiation was carried out from a 300 W xenon lamp without using any optical filter, where the light intensity was measured to be 14 mW cm⁻¹ in the range of 245 ± 10 nm. The outlet gas was analyzed by online gas chromatography with a thermal conductivity detector at an interval of ca. 30 min. Since the sensitivity for CO₂ in the argon carrier was low, the experimental error for the values of CO₂ production rate was relatively large.

3. Results and discussion

3.1. Characterization

Fig. 1 shows XRD patterns of the Pt/NaTaO₃:La samples prepared by the flux method at various hold temperatures. A diffraction pattern of Ta₂O₅ (ICSD No. 9112) [37] was observed for the sample heated at 1073 K (Fig. 1a), which indicates that the temperature is not enough to generate the NaTaO₃ phase as desired. At this temperature, Na₂CO₃ would be decomposed to form Na₂O through decarbonation. Considering the melting points of the NaCl flux to be 1074 K [38], the hold temperature and time (1073 K, 5 h) would not be enough for Na₂O to react with the Ta₂O₅ particles. By heating over 1173 K, the clear diffraction lines of the NaTaO₃ phase (ICSD No. 980) [39] appeared without any impurity phase. It was revealed that the higher temperature than 1173 K was necessary to generate the NaTaO₃ crystallites in this method.

Download English Version:

<https://daneshyari.com/en/article/38801>

Download Persian Version:

<https://daneshyari.com/article/38801>

[Daneshyari.com](https://daneshyari.com)