Photo-assisted dry reforming of methane over ruthenium loaded strontium titanate

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Abstract: We have investigated the light irradiation effect on dry reforming of methane (DRM). Light harvesting $SrTiO_3$ samples grafted with various contents of Ru catalyst were prepared by photo-deposition method. Although their XRD peaks were all assigned to single phase of cubic perovskite $SrTiO_3$, their optical spectra exhibited the plasmon absorption, indicating the deposition of metallic Ru nanoparticles onto $SrTiO_3$. DRM test was evaluated at 500 °C under UV irradiation and dark condition to investigate the effect of photo-irradiation. The performance of $SrTiO_3$ was highly enhanced by modifying of Ru, and 3 wt% of Ru modified $SrTiO_3$ (Ru3-STO) exhibited the highest activity. UV irradiation promoted higher activity than dark condition, and its CH_4 conversion and CO production were achieved at 72 % and 73 %, respectively.

Keywords: dry reforming of methane (DRM), photo-assisted catalyst, $Ru/SrTiO_3$.

1. Introduction

Methane (CH_4) and carbon dioxide (CO_2) are well-known cogent greenhouse gases. CH_4 has 25 times global warming potential and absorbs heat 200 times higher than CO_2[1]. CH_4 is major component (70- 90%) of natural gas, while CO_2 is highly produced from human activities such as industries and transportations[2]. A strategy for reducing CH_4 and CO_2 gases is to convert them into other more valuable chemicals or fuels[3]. Numerous methods have been developed such as dry reforming of methane (DRM) as the following reaction (1),

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad (1)$$

In this method, both produced gases are known as valuable synthesis gas (syngas), *i. e.* a mixture of carbon monoxide (CO) and hydrogen (H_2). The ratio of produced syngas is 1, which is suitable for producing methanol or other chemicals via Fischer-Tropsch process[2]. Since CH_4 and CO_2 molecules are very stable and difficult to be cracked under moderate condition, high temperature about 1000 ºC is required for conventional DRM. But a high temperature process leads deactivation of catalyst due to carbon deposition, so called coking.

In the present research, we developed a novel catalyst for DRM, which can be used under moderate temperature and assisted by renewal energy such as photons to compensate the required endothermic energy to drive catalyst reaction. We developed Ru nanoparticles modified $SrTiO_3$, in which Ru particles act as DRM catalysts, while $SrTiO_3$ functioned as a catalyst support as well as light harvesting material to provide active charge carriers to assist Ru catalyst.

2. Experimental

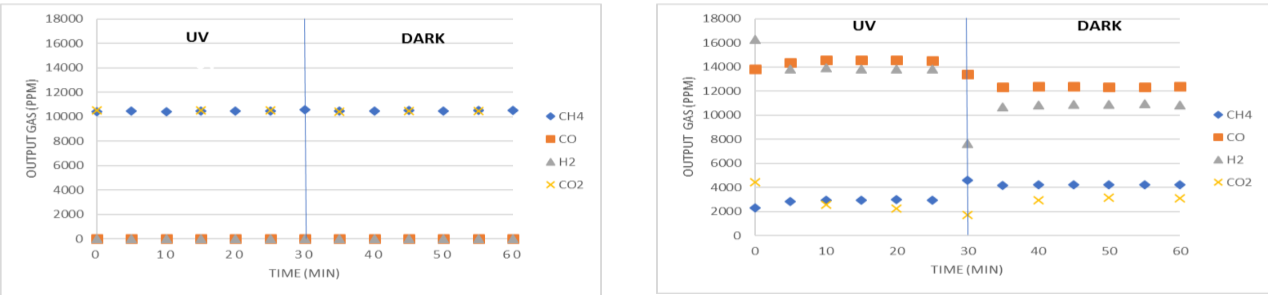
All samples have been prepared by photo-deposition method at room temperature. $SrTiO_3$ nanopowder (Wako Chemicals) was dispersed into aqueous solution containing CH_3OH and $RuCl_3.nH_2O$, then the solution was stirred for 30 min under UV light irradiation. The weight percentage of Ru in aqueous solutions was set at 0, 1, 3, 5 and 7 %, which denoted as Bare STO, Ru1-STO, Ru3-STO, Ru5-STO and

Ru7-STO, respectively. These powders were collected and dried. Then, the samples were characterized by X-ray diffractometer (XRD), diffuse reflectance UV-visible spectrophotometer (DR UV-vis). For DRM reaction, the samples were put into a small ceramic cup in a flow reactor. The composition of feed gas was CH_4/ CO_2 / Ar = 1/ 1/ 98 %, and its flow rate was 10 mL/ min. The DRM reaction was conducted at 500 °C under UV light irradiation and dark condition. The output gases were detected by micro gas chromatograph (Micro-GC) with a TCD detector.

3. Results and discussion

XRD patterns showed that all samples had single phase cubic perovskite and there were no significant pattern change between pristine $SrTiO_3$ and Ru-$SrTiO_3$ samples. The Ru contents and size might be too small to be detected by XRD. In contrast, absorption spectra of Ru containing catalysts exhibited the broad absorption in in the visible region. The absorption became significant by increasing of Ru contents, indicating the successful deposition of metal Ru nanoparticles onto $SrTiO_3$ by photo-reduction method.

Figure 1 shows the change of gas concentrations under DRM reaction for Bare STO (a) and Ru3-STO (b), which was the optimized sample according to the DRM performance. While the bare STO did not exhibit any conversion, Ru3-STO could covert CH_4 and CO_2 into CO and H_2. It is also noteworthy that the UV irradiation significantly improves the DRM activity on Ru3-STO. CH_4 conversion achieved 72 %, while CO generation was 73 % even at 500 °C. Produced amounts of CO and H_2 were almost equivalent, indicating its suppression of coking and water gas shift back reaction. In our system, $SrTiO_3$ acts as light harvester and generates photo-generated electrons and holes. Electrons might be transferred to Ru and reduce CO_2 into CO and O^{2-}, while holes and O^{2-} would drive partial oxidation of CH_4 to produce CO and H_2.



(a) (b)

Figure 1. Catalytic activity of DRM for (a) Bare STO and (b) Ru3-STO at 500 °C. We applied both UV light irradiation and dark condition for each 30 min.

4. Conclusions

We have successfully prepared Ru-STO samples using a simple photo-deposition method. Ru strongly enhanced the catalytic activity of $SrTiO_3$ for DRM at moderate temperature. UV irradiation also improve the activity of catalyst. The optimum Ru content (3 wt%) in the sample gives highest CH_4 and CO_2 conversion. We hope this finding will be useful for our future to produce energy or other more valuable chemicals from green house gases.

References

1. G. Yvon-Durocher, A.P. Allen, D. Bastviken, R. Conrad, C. Gudasz, A. St-Pierre, N. Thanh-Duc, P.A. del Giorgio, Nature, 507 (2014) 488.
2. M. Safariamin, L.H. Tidahy, E. Abi-Aad, S. Siffert, A. Aboukais, Comptes Rendus Chimie, 12 (2009) 748.
3. J. Ashok, S. Kawi, International Journal of Hydrogen Energy, 38 (2013) 13938.