Light-driven dry reforming of methane using photons as the energy source

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Abstract: a nanocomposite catalyst consisted of metal Rh and $SrTiO_3$, namely Rh#$SrTiO_3$, was synthesized for the first time via a hydrothermal treatment of $SrTiO_3$ nanoparticles in Rh^{3+}-salts solution, followed by UV light illumination in an equimolar mixture of methane (CH_4) and carbon dioxide (CO_2). The Rh#$SrTiO_3$ catalyst efficiently converted the CH_4-CO_2 gas mixture into an equimolar mixture of carbon monoxide (CO) and hydrogen (H_2) under illumination of UV light (Light-driven Dry Reforming of Methane: LDRM). Experimental results showed that the LDRM was promoted over the Rh#$SrTiO_3$ catalyst predominantly via photocatalysis rather than photo-thermal catalysis.

1. Introduction

Dry reforming of CH_4 (DRM) that produces syngas (mixture gases of H_2 and CO) from CH_4 and CO_2 is a promising way to convert natural gas into more valuable chemicals while reducing the emission of green-house gases. The research and development of high-performance DRM catalysts have been accelerated because of the economic- and environmental priority of DRM over the other CH_4 treatments such as steam reforming of CH_4 (SRM). However, the high stability of CH_4 and CO_2 requires high reaction temperatures over 800 ℃ in DRM, which leads to poor fuel efficiencies and short lifetime of the catalyst. There are big challenges to realize DRM catalysts operating at low temperatures without carbon deposition (*i.e.* coking or sooting), which readily occurs at low temperatures and severely inhibits the flow or reactant gases.

Photo-assisted DRM can be a promising method to drive DRM at moderate temperatures without being accompanied by coking or sooting. It is acknowledged that photocatalysts are used for environmental purifications and energy conversions such as water splitting and CO_2 reduction[1, 2]. Both of the water splitting and CO_2 reduction are an up-hill reaction requiring larger gains in free energy (ΔG) than DRM, which suggests a possibility to materialize that promote DRM in moderate conditions under light illumination. However, there have been very few researches on photo-assisted DRM[3], especially those using solely photons as the energy source were very rarely conducted. Herein, we report that a nanocomposite catalyst consisted of metal Rh and $SrTiO_3$ (*i.e.* Rh#$SrTiO_3$) can be synthesized via a facile route and the Rh#$SrTiO_3$ catalyst exhibited amazingly high efficiency toward DRM at moderate temperatures without any external heat. The $SrTiO_3$ component in the Rh#$SrTiO_3$ most probably served as an efficient photon absorber due to the appropriate electronic band structures for both of the desired photoreduction and photooxidation of CO_2 and CH_4, respectively, whereas the Rh component acted as the center of catalysis to drive DRM under light illumination.

2. Method

Rh#$SrTiO_3$ was synthesized by hydrothermal treatment of $SrTiO_3$ powder in $[(CH_3COO)_2Rh]_2 \cdot 2H_2O$ solution, in which the ratio of Rh atom was ranged from 1 to 15 % versus $SrTiO_3$. Then, the prepared samples were put onto a ceramic cup in a flow reactor, which is installed with quartz window for light introduction. CH_4 and CO_2 mixture gas diluted by Ar (CH_4:CO_2:Ar = 1:1:98) was flowed into the reactor. After introducing of gas flow, UV light (300W Hg-Xe lamp) was irradiated onto the sample. Further, to investigate the temperature dependence of activity, the reactor was heated to 500 °C during the light irradiation. Products were analyzed by micro gas chromatography (micro-GC). The crystal structure of Rh#$SrTiO_3$ was identified by XRD.

3. Result and discussion

From the XRD measurement, before DRM structure of the sample was almost the same as the bare $SrTiO_3$, it is noteworthy that our Rh#$SrTiO_3$ became a composite structure, consisting of metal Rh nanoparticles and Rh-doped $SrTiO_3$ under the initial step of DRM reaction. This composite structure plays an key role for efficient DRM reaction and the structure is sustained for long time.

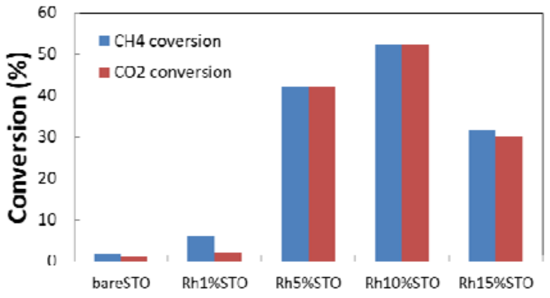

Figure 1. Conversion of CH_4 and CO_2 under UV irradiation.

DRM conversion of each sample was shown in Figure 1. After the light irradiation, the temperature was increased to 135 °C, then maintained at this temperature. Among all samples, 10%Rh#$SrTiO_3$ exhibited the highest activity with more than 50 % conversion of CH_4 and CO_2 by irradiating light. Its products yields of 518 mmol/g_{cat}/h for H_2 and 523 mmol/g_{cat}/h for CO were obtained even under 135 °C. This suggests Rh was acted as cocatalyst for DRM. It's also noteworthy that the products amount and introduced reactants gas ratio was almost 2:1, revealing that our DRM reaction proceed in stoichiometry. Figure 2 shows the temperature dependence of DRM activity (H_2 generation). The reaction without UV irradiation of 10%Rh#$SrTiO_3$ started from 300°C, then the H_2 generation ratio was rapidly increased which is consistent with a typical thermo-catalytic reaction. On the other hand, light irradiated condition also showed increase of activity however the significance of the temperature dependence was much lower than the dark condition. To clarify the contribution of thermal effect, the activation energy (E_a) was calculated from temperature dependence of the reaction velocity. The calculated E_a of our catalyst was less than 10 kJ/mol, which is much lower than the reported activation energy of thermal DRM[5]. These results suggest that the thermal energy for Rh#$SrTiO_3$ under UV irradiation was used for mild activation step such as thermal desorption of products, but Rh#$SrTiO_3$ dominantly converted CH_4 and CO_2 by photocatalytic process rather than thermal process.

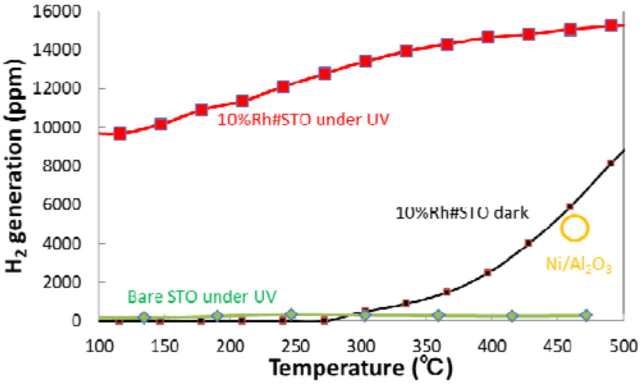

Figure 2. Temperature dependence of the DRM activity.

4. Conclusion

CH_4 and CO_2 were photo-catalytically converted into CO and H_2 in stoichiometry only by irradiating UV onto Rh#$SrTiO_3$. By adding Rh to $SrTiO_3$ the DRM activity was drastically increased and the obtained CO and H_2 yields are much higher than reported values. Our research provides a big impact for efficient conversions of such highly stable molecules to thermal catalytic field.

References

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