

Experiment Study of Solar Hydrogen Production by Photo-thermal Driven Steam Methane Reforming with Co/Al₂O₃ Catalyst

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ABSTRACT

Solar-driven steam methane reforming (SMR) is a promising technology for hydrogen production. However, current solar thermochemical and photochemical reactions have different limitations. The former often requires high temperatures to achieve desired yield and neglects the strong activation ability of photons in short-wavelength spectrum, while the latter cannot use solar energy in the long-wavelength spectrum due to catalyst drawbacks, resulting in low solar energy utilization efficiency. To overcome these drawbacks, photo-thermal synergetic catalytic hydrogen production is proposed to achieve higher solar-to-hydrogen efficiency under relatively mild condition. In this work, the photo-thermal synergetic effect of solar hydrogen production from SMR using Co/Al₂O₃ catalyst is experimentally investigated. Results show the H₂ yield by photo-thermochemical reaction (221.7 mmol·h⁻¹·g⁻¹) can be increased by 42.8% at 650°C compared with that of the thermochemical reaction (155.2 mmol·h⁻¹·g⁻¹), and the activation energy of the photo-thermochemical reaction is significantly reduced. The high activity is mainly attributed to photoactivation effect of light in photo-thermochemistry. These findings provide valuable guidance for hydrogen production from steam methane reforming using solar energy.

Keywords: hydrogen production, solar fuel, photo-thermochemical reaction, steam methane reforming

NONMENCLATURE

Abbreviations

SMR	Steam Methane Reforming
PTSMR	Photo-thermochemical Steam Methane Reforming
TSMR	Thermochemical Steam Methane Reforming
WGS	Water Gas Shift

Symbols

F	Molar flow rate
C_i	Concentration ratio of gas i in the outlet gas
Y_{H_2}	Production rate of H ₂
X_{CH_4}	Conversion rate of CH ₄
$Y_{relative}$	Relative H ₂ yield change percentage of PTSMR to TSMR
$X_{relative}$	Relative CH ₄ conversion rate change percentage of PTSMR to TSMR
E_a	Apparent activation energy

1. INTRODUCTION

Hydrogen is a very potential green energy and a substantial chemical feedstock because of its high energy density and the fact that it only produces water after combustion. Steam methane reforming (SMR), the most widely used method for industrial H₂ production, is a strongly endothermic reaction that typically operates at high temperatures (700–1000°C), necessitating huge

energy inputs[1]. Solar energy is the most plentiful renewable energy, as well as the most viable clean energy source for sustainable hydrogen production[2]. Thus, using solar energy to drive SMR can meet its energy demand while lowering greenhouse gas emissions. Thermochemistry and photochemistry are two major routes for directly producing hydrogen using solar energy.

The basic principle of solar thermochemical hydrogen production is to convert solar energy into heat through a collector, then use the solar thermal energy to drive chemical reactions that produce hydrogen. The thermochemical process can utilize the full spectrum solar energy, but suffering exergy loss in the conversion process from light to heat before used by a subsequent endothermic reaction[3]. Moreover, it often operates at relatively high temperature to achieve desired H₂ yield. High temperature not only easily leads to agglomeration and deactivation of the catalyst, affecting long-term operation stability, but also requires expensive high ratio solar concentrators and large mirror fields to convert sunlight into heat.

On the other hand, photochemical process can directly convert ultraviolet and visible light into chemical energy through photocatalyst, as an ideal route for replacing heat with light, which has gained extensive attention[4]. Despite massive research efforts have been paid to photocatalysis, no large-scale applications have been realized so far. The main challenge of all photochemical processes is that the solar energy utilization efficiency stays very low, since it cannot absorb the full spectrum solar energy. The solar-to-hydrogen conversion efficiency of solar photochemical processes is constrained by the weak absorption of sunlight in the visible and infrared regions[5].

It is proposed that photo-thermal catalytic chemistry, which can achieve higher solar-to-hydrogen efficiency and catalytic activity under relatively wild conditions, be used to address the weaknesses of individual thermochemistry and photochemistry. The photo-thermal synergetic strategy combining photon energy and thermal energy in the photo-thermal catalytic chemical system can make better use of the solar spectrum[6]. Therefore, a promising technique to improve industrial hydrogen production is photo-thermal catalytic SMR, which can outperform conventional thermal catalysis while reducing the reaction temperature[7].

Noble metal catalysts often exhibit superior catalytic performance and stability than Ni and Co based catalysts for the photo-thermochemical steam methane

reforming (PTSMR) reaction[5]. There have been several studies to optimize the performance of PTSMR while reducing the amount of noble metal loading, but the cost is still too high to be practical for large scale applications[8]. Both Ni-based and Co-based catalysts have outstanding SMR performance, but the main problem of nickel-based catalysts is their propensity for facile coking and sintering, whereas cobalt-based catalysts have higher carbon deposition resistance[9]. However, Co is susceptible to deactivation by water oxidation[10]. Therefore, maintaining the long-term stability of catalysts is as crucial as high catalytic activity.

In this work, the photo-thermal synergetic effect of solar hydrogen production from SMR is experimentally investigated. As a catalyst for SMR, a stable Co/Al₂O₃ was synthesized by hydrothermal method, and reaction activity of the catalysts was compared under photo-thermochemical and thermochemical conditions. Finally, the roles of the light enhancement reaction is discussed.

2. EXPERIMENT SECTION

2.1 Catalyst preparation

The sample of Co nanoparticles supported on Al₂O₃ nanosheets was prepared according to the following steps. 15.0 g Al(NO₃)₃·9H₂O, 1.15 g Co(NO₃)₂·6H₂O, and 4.2 g CO(NH₂)₂ were dissolved into 50 mL deionized water under magnetic stirring, the molar ratio of Co/(Co+Al) is 0.09. The mixture solution was transferred to a 100 mL Teflon bottle. The Teflon bottle was sealed in stainless autoclave, and heated at 150 °C for 24 h in an electric oven. The resultant precipitate was filtered, washed with deionized water, dried in bake oven at 120 °C for 12 h, and calcined at 500 °C for 8 h in a muffle furnace. The obtained powder was labeled as CoO/Al₂O₃. CoO/Al₂O₃ was put in a quartz tube reactor and pre-reduced by 10 vol% H₂/N₂ with 15 mL·min⁻¹ flow rate at 700 °C for 2 h. The obtained sample was labeled as Co/Al₂O₃.

2.2 Experimental equipment

The experimental apparatus is shown in Fig 1, where a syringe pump was used to control the H₂O flow rate at 8.829 ul/min, mass flowmeters were used to control CH₄ at 6 ml/min and N₂ at 4 ml/min, the molar ratio of water and methane fixed at 2:1. The vaporization tube is long enough to ensure complete vaporization of the water before it contacted with the catalyst. 0.12 g Co/Al₂O₃ was loaded in a quartz tube reactor, and a thermocouple was inserted in the middle of the material to measure the catalyst temperature. The thermochemical methane

steam reforming (TSMR) was powered by the heating furnace, and PTSMR was powered by a 300 W xenon lamp and the heating furnace. The reaction product was collected in gas bags after condensation, and the concentration of the gas was detected by a gas chromatograph.

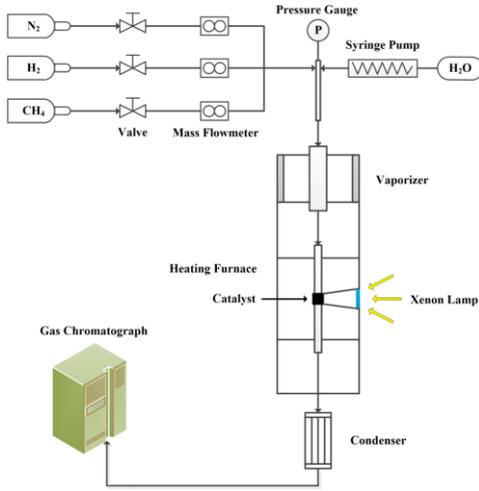
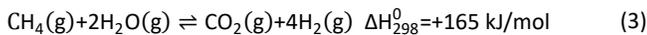
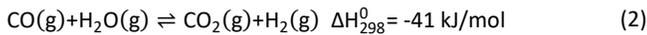
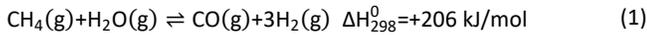


Fig. 1. Experimental equipment

2.3 Catalytic activity test

For SMR process, water steam and methane react at high temperatures (Eq.(1)). During the process, meanwhile, the water gas shift reaction (WGS, Eq.(2)) may take place, which further enhances the production of H₂.



In this work, the production rate of H₂ is obtained by the concentration ratio of H₂ to N₂ in the outlet gas, the outlet CH₄ flow rate can similarly be obtained to know the CH₄ conversion rate:

$$F_{i,\text{out}} = \frac{C_{i,\text{out}} F_{\text{N}_2}}{C_{\text{N}_2}} \quad (4)$$

$$Y_{\text{H}_2} = \frac{F_{\text{H}_2,\text{out}}}{m} \quad (5)$$

$$X_{\text{CH}_4} = \frac{F_{\text{CH}_4,\text{in}} - F_{\text{CH}_4,\text{out}}}{F_{\text{CH}_4,\text{in}}} \quad (6)$$

Where $F_{i,\text{out}}$ represents the flow rate of outlet gas i (H₂ or CH₄); Y_{H_2} represents the production rate of H₂; X_{CH_4} represents the conversion rate of CH₄; C_i and C_{N_2} respectively represents the concentration ratio of gas i and N₂ in the outlet gas; F_{N_2} represents the flow rate of N₂; m is the mass of catalyst placed.

The relative change percentage Y_{relative} is used to compare the H₂ production rate of PTSMR and TSMR,

and the relative change percentage X_{relative} is used to compare the CH₄ conversion rate of PTSMR and TSMR:

$$Y_{\text{relative}} = \frac{Y_{\text{PTSMR,H}_2} - Y_{\text{TSMR,H}_2}}{Y_{\text{TSMR,H}_2}} \quad (7)$$

$$X_{\text{relative}} = \frac{X_{\text{PTSMR,CH}_4} - X_{\text{TSMR,CH}_4}}{X_{\text{TSMR,CH}_4}} \quad (8)$$

Where $Y_{\text{PTSMR,H}_2}$ represents the production rate of H₂ in the PTSMR process; $Y_{\text{TSMR,H}_2}$ represents the production rate of H₂ in the TSMR process; $X_{\text{PTSMR,CH}_4}$ represents the conversion rate of CH₄ in the PTSMR process; $X_{\text{TSMR,CH}_4}$ represents the conversion rate of CH₄ in the TSMR process.

3. RESULTS AND DISCUSSIONS

3.1 Characterization

The reaction activity mainly depends on the composition and microstructure of the catalyst. The Co/Al₂O₃ catalyst after hydrogen reduction in the reactor was tested. The composition of catalyst is characterized by X-ray diffraction (XRD). Fig 2 shows that the catalyst is composed of Al₂O₃ and Co, while the peak of the sample indicates the existence of CoO, which is due to the oxidation of cobalt exposed to air. The catalyst has a Co/(Co+Al) molar ratio of 0.09, and this element proportion is further confirmed by inductively coupled plasma (ICP) test. According to Fig 3, the catalyst is Co nanoparticles supported by Al₂O₃ nanosheets.

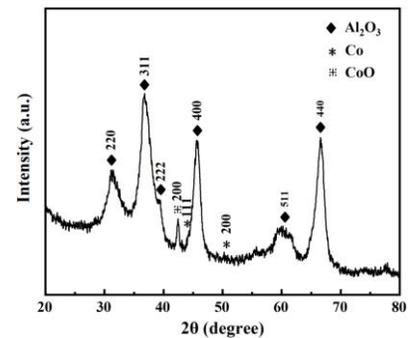


Fig. 2. XRD characterization results of Co/Al₂O₃

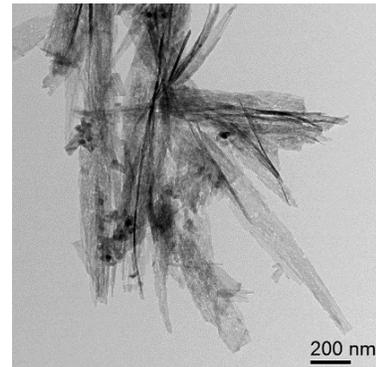


Fig. 3. TEM image of Co/Al₂O₃

3.2 Experimental results of the PTSMR and TSMR

The methane feeding rate $F_{\text{CH}_4, \text{in}}$ is 0.245 mmol/min. The incident light intensity is fixed at 9 kW/m², the catalyst temperature is mainly adjusted by the heating furnace. The temperature is subject to the temperature of the catalyst measured by the thermocouple. In the experiment, the catalyst can maintain almost constant activity for four hours, which demonstrating good photo-thermal durability.

As shown in Fig 4 and Fig 5, irradiation represents PTSMR and dark represents TSMR. Results show that the H₂ yield of PTSMR is significantly higher than that of TSMR at temperatures below 750 °C. Especially at 650 °C, the H₂ yield by photo-thermochemical reaction (221.7 mmol·h⁻¹·g⁻¹) can be increased by 42.87% compared with that of the thermochemical reaction at 660 °C (155.2 mmol·h⁻¹·g⁻¹). Even more surprising, the PTSMR under irradiation can effectively reduce the temperature by 56 °C compared with the TSMR under dark conditions for the same hydrogen production rate (155.2 mmol·h⁻¹·g⁻¹). In Fig 5, the methane conversion rate has the same trend as the H₂ production rate. In addition, at lower temperatures, the photo-thermochemical reaction not only improves the conversion of methane, but also may promote the decomposition of water. In Fig 4 and Fig 5, the relative percentage of H₂ yield enhancement in PTSMR (Y_{relative}) is much larger than that of methane conversion rate (X_{relative}) at 600 °C and 700 °C. Therefore, light further increases the yields of H₂.

While at higher temperatures, the H₂ yield of PTSMR is not much higher than that of TSMR. Since as the temperature increases, the contribution ratio of light and heat has changed. The CH₄ conversion rate of thermochemical reaction has exceeded 93.5% at 750 °C, which indicates that SMR reaction has reached its limit, so the the function of light is weakened and the PTSMR and TSMR become similar.

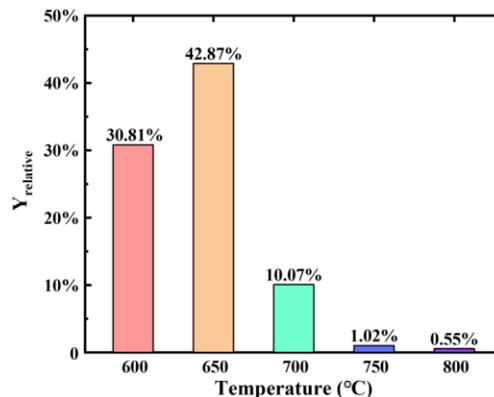
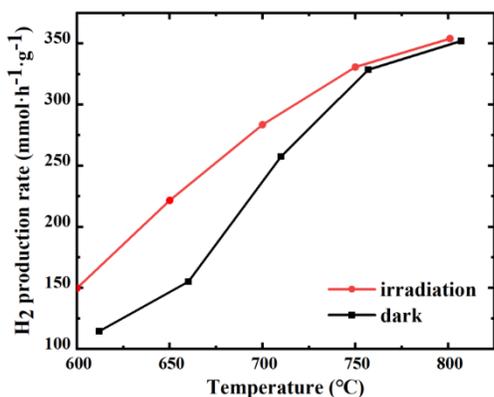


Fig. 4. Y_{H_2} and Y_{relative} varies with temperature

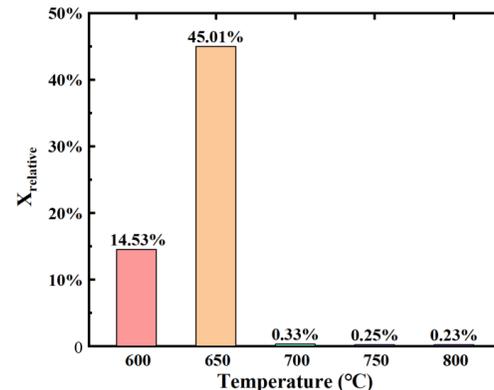
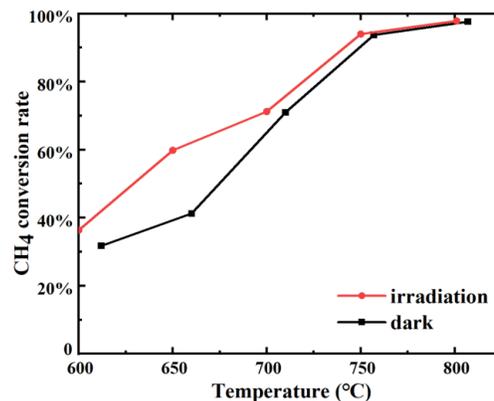


Fig. 5. X_{CH_4} and X_{relative} varies with temperature

3.3 Roles of light

In order to reveal the reasons for the high activity of Co/Al₂O₃ catalyst in PTSMR reaction, the absorption spectrum of the catalyst is tested. In Fig 6, Co/Al₂O₃ has a good absorption in the whole solar spectral region, especially in the visible and infrared regions, which attributed to the strong surface plasmon absorption of Co nanoparticles. There is a sharp band in the 500-700 nm visible region, which is related to the absorption of cobalt spinels (Co₃O₄ and CoAl₂O₄)[11] and the intermetallic charge transfer effect from Co³⁺ to Co²⁺[12]. The strong absorption over the whole spectrum can

reach a high temperature at the catalyst surface through the thermal effect of light.

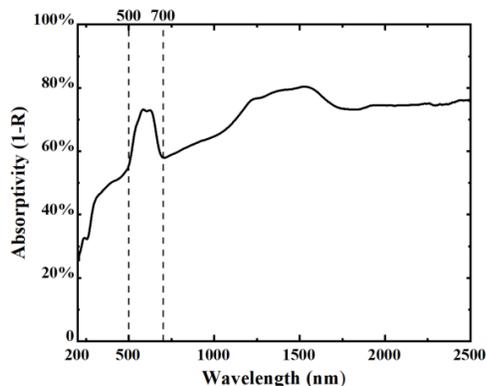


Fig. 6. The absorptivity spectrum of Co/Al₂O₃

Moreover, the photoactivation effect leads to the enhancement of the catalytic activity in the photo-thermochemical reaction. Fig 7 of $\ln(k_{H_2})$ vs $1000/T$ is plotted on the basis of the H₂ production rate values of Co/Al₂O₃ in TSMR and PTSMR reaction, and a fitting curve with strong linear relationship is obtained. The apparent activation energy is calculated from the slope of the fitted curve according to the Arrhenius equation. The apparent activation energy of PTSMR is 40.9 kJ/mol, which is smaller than that of TSMR of 59.0 kJ/mol. Light significantly reduces the activation energy of SMR reaction, thus greatly improving the catalytic activity.

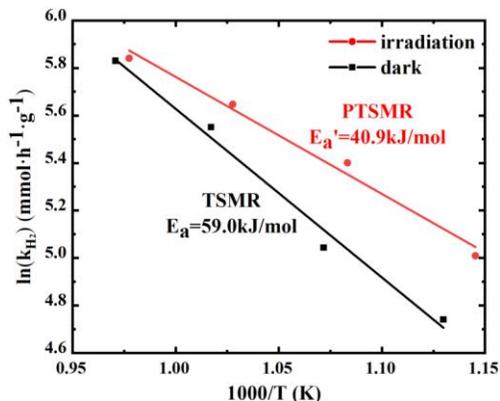


Fig. 7. Apparent activation energy calculation from $\ln(k_{H_2})$ vs $1000/T$ in TSMR and PTSMR

4. CONCLUSIONS

In this work, the thermochemical and photo-thermochemical catalytic activities of Co/Al₂O₃ have been investigated. Results show that light significantly increases the H₂ yield and CH₄ conversion rate at lower temperature. Especially at 650°C, the H₂ production rate of PTSMR (221.7 mmol·h⁻¹·g⁻¹) is 42.8% higher than that of TSMR (155.2 mmol·h⁻¹·g⁻¹). Additionally, the activation energy of the SMR reaction is dramatically lowered by

light irradiation. In terms of kinetics, photo-thermochemical reaction is more favorable than thermochemical reaction in that it can lower the reaction barrier and facilitate the reaction. The elevated activity in PTSMR is mainly attributed to photoactivation effect of light. This work provides an auspicious reference for utilizing solar energy to generate hydrogen from water and methane.

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DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors read and approved the final manuscript.

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