

Experimental study of solar-enhanced photo-thermochemical CO₂ reforming of CH₄ for syngas production

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ABSTRACT

The use of solar energy to produce solar fuels, such as CO and H₂, by the reforming reaction between CH₄ and CO₂ is a promising technology to alleviate the global warming effect caused by CO₂. The carbon dioxide reforming of methane (CRM) reaction is an endothermic reaction, and can only be carried out at a high temperature. The photo-thermochemical CRM method is studied, in which solar energy is directly concentrated on Ni/CeO₂ catalyst to reduce the CRM reaction temperature. XRD and SEM are used to characterize the composition and morphology of Ni/CeO₂ catalyst. And the synergetic effects of light and heat in photo-thermochemical reactions are investigated. The results show that photo-thermochemical reactions have higher CH₄ conversion and production rate of H₂ than thermochemical reactions at the same temperature. It is found that photo-generated carriers play an important role in improving CRM performance. These findings provide a promising way to consume CO₂ and achieve the goal of carbon neutrality.

Keywords: photo-thermochemical reaction, CO₂ reforming of CH₄, CO₂ consumption, solar fuels

NOMENCLATURE

Abbreviations

| | |
|-------|----------------------------------------------------------|
| CRM | Carbon dioxide Reforming of Methane |
| PTCRM | Photo-thermochemical Carbon dioxide Reforming of Methane |
| TCRM | Thermochemical Carbon dioxide Reforming of Methane |

Symbols

| | |
|----------------------------|--------------------------------------------------------|
| X_{CH_4} | Conversion of CH ₄ |
| α_{relative} | Relative conversion change percentage of PTCRM to TCRM |
| F_{out} | Flow rate of produced gas |
| F_{in} | Flow rate of feeding gas |
| Y | Proportion of a gas in the total gas |

1. INTRODUCTION

The widespread use of fossil fuels has caused a large number of greenhouse gas emissions, such as CO₂ (carbon dioxide) and CH₄ (methane)^[1]. For example, the concentration of CO₂ in the atmosphere has increased from 0.028% in 1750^[2] to 0.041% in 2019. China plans to reach the peak of carbon dioxide emissions in 2030 and achieve carbon neutrality in 2060. This goal makes it urgent to consume CO₂. It is a promising way to convert CO₂ into other useful products, such as H₂ and CO.

CH₄ has many times the heat absorption capacity of CO₂ and is another greenhouse gas that needs attention^[3]. The CO₂ reforming of CH₄ (CRM) is an ideal way because that it can consume the two gases to generate H₂ and CO for further utilization^[4]. However, CRM is more difficult to occur than other CH₄ reforming reactions, such as partial oxidation of methane or steam reforming of methane. From the thermodynamic equilibrium of different CH₄ reforming ways, the conversion of CH₄ in CRM is the lowest and it requires

higher temperature^[5]. The low CH₄ conversion and high temperature in traditional CRM reaction hinder its large-scale applications in industry. The use of solar energy is a potential way to enhance CRM reaction and reduce the reaction temperature. Meanwhile, solar energy is stored as chemical energy available at any time.

At present, there are several ways to use solar energy, such as photocatalysis, solar thermochemistry and solar photo-thermochemistry. The photocatalysis has been studied intensively since Fujishima and Honda^[6] discovered the photo-electrochemical effect of TiO₂ in the process of water splitting. Additionally, photocatalytic CRM also attracts increasing attention. But most semiconductors can only be activated by ultraviolet(UV) light, which accounts for only 5-7% of solar energy^[7]. This will cause a lot of solar energy loss. On the other hand, the solar thermochemical reaction is a promising method for fuel production and solar energy storage^[8-10], but it suffers from exergy loss in conversion from sunlight to heat. The photo-thermochemical reaction can avoid these two defects by using UV and visible light in the photocatalytic route, and infrared light in the thermochemical route. The photo-thermochemical approach is a prospective alternative to CRM.

The supported noble metal catalysts and Fe-, Co-, Ni-based catalysts are mainly used for CRM^[11]. Noble metal catalysts show the best catalytic performance and stability, but they are not suitable for large-scale applications because of the high cost. Due to the low cost and high catalytic activity, Ni-based catalysts are more promising for the industry. However, Ni-based catalysts suffer from inactivation after long-term use as a result of carbon deposition and the sintering of nickel nanoparticles^[12]. Ceria-based oxide consists of Ce⁴⁺ and Ce³⁺, which can absorb and release oxygen vacancies. Pan et al. proved that light illumination on CeO₂ can prevent carbon deposition by increasing Ce³⁺ concentration^[13]. Thus, CeO₂ is a suitable carrier for Ni-based catalysts.

In this work, a nanoscale Ni/CeO₂ is synthesized by a simple method as the catalyst of photo-thermochemical carbon dioxide reforming of methane (PTCRM) and thermochemical carbon dioxide reforming of methane (TCRM). The synergistic effect of light and temperatures in PTCRM is studied and the performance is compared with TCRM. The influences of light on CH₄ conversion are studied. The production rates of H₂ in PTCRM and TCRM are discussed at a representative

condition. The stability of the catalyst is also investigated.

2. EXPERIMENT

2.1 Preparation of Ni/CeO₂

15.47g Ce(NO₃)₃·6H₂O and 4.144g Ni(NO₃)₂·6H₂O are dissolved into 20 mL de-ionized water with stirring. 6.865g C₆H₈O₇·H₂O is dissolved into 50 mL de-ionized water with stirring. The C₆H₈O₇·H₂O solution is dripped into Ce(NO₃)₃·6H₂O and Ni(NO₃)₂·6H₂O solution with stirring. The mixed solution is put in an oil bath at 60 °C for 3h, then dried in a bake oven at 80 °C for 24h, and ground to obtain powder. 2.5g powder is heated to 400 °C in a muffle furnace at a heating rate of 1.5 °C/min and kept at the temperature for 4h. Then the powder is heated from 400 °C to 700 °C at a heating rate of 10 °C/min and kept for 2 h. NiO/CeO₂ is obtained.

The resulting NiO/CeO₂ is ground in a mortar, 0.4 g of the powder is placed in a quartz tube reactor with a square piece in the middle of the tube. Before reaction, the NiO/CeO₂ should be reduced to Ni/CeO₂ by 10% H₂/N₂ mixed gases at 700 °C for 2h.

2.2 Experimental equipment

As shown in Fig. 1, the mass flow rates of CH₄, CO₂, N₂, and H₂ are controlled by mass flowmeters. A gas stream of CH₄(3mL/min), CO₂(3.3mL/min), and N₂(4ml/min) is fed to the reactor with the mass of the catalyst fixed at 0.4g. A 300W Xenon lamp with a condenser is used as a light source. The composition of the produced gas is analyzed by gas chromatography (GC), with N₂ as an internal standard gas.

The energy is provided by the heating furnace in TCRM experiments, and both the heating furnace and Xenon lamp in PTCRM experiments. The temperature of the catalyst is measured by a quartz casing-wrapped thermocouple inserted in the middle of the catalyst.

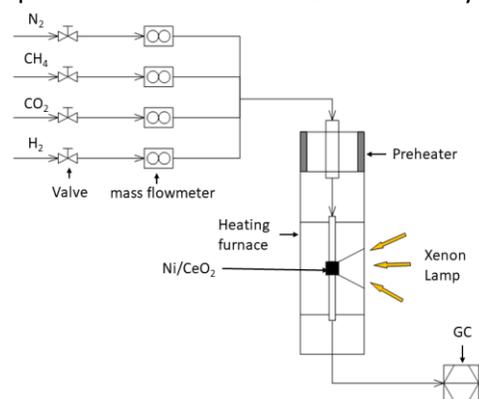


Fig. 1 Experimental equipment

3. RESULTS AND DISCUSSION

3.1 Characterization

The composition and morphology of the catalyst are very important for the performance of CRM reaction. Considering that the surface of Ni/CeO₂ is oxidized in air, the composition of the unreduced NiO/CeO₂ is analyzed by X-ray diffraction (XRD). The result in Fig. 2 shows that the catalyst consists of CeO₂ and NiO compared the peaks with reference patterns. The morphology of Ni/CeO₂ is simply observed by Scanning electron microscope (SEM). The result in Fig. 3 indicates that Ni/CeO₂ catalysts used in experiments are nanoscale and the nanoparticles agglomerate together at the micron level.

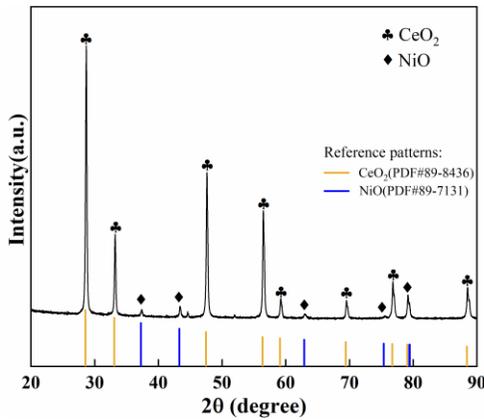


Fig. 2 XRD result of NiO/CeO₂

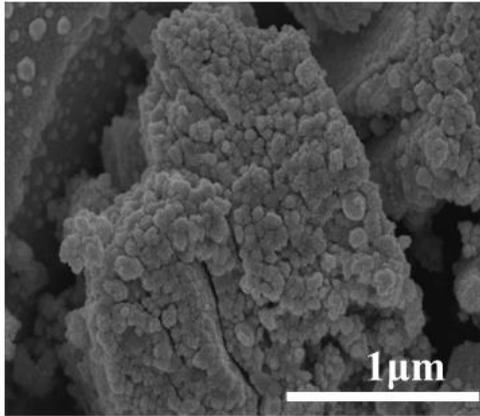


Fig. 3 SEM result of Ni/CeO₂

3.2 Photo-thermochemical activity tests

The reaction processes in CRM reaction are listed as Eqs. (1)-(4).



Eq. (1) is the main and target reaction which consumes CH₄ and CO₂ to produce syngas. It has the highest enthalpy, so high temperature is beneficial to the reaction. Eq. (2) is reverse water-gas shift (RWGS) which would consume H₂ and increase the CO fraction in production. Eq. (3) is a methane cracking reaction which generates carbon deposited on the catalyst, and it is the main reason for catalyst deactivation due to carbon deposition. Eq. (4) can reduce the negative effect of carbon deposition, so many researchers give a slightly higher CO₂ flow rate.

In this work, a wide temperature range is studied in both TCRM and PTCRM conditions. A constant light intensity of 12.89 kW/m² is used in PTCRM condition. The CH₄ conversion (Eq. (6)) and the relative change percentage of the conversion between TCRM and PTCRM (Eq. (7)) are calculated by following equations.

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

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

$$\alpha_{\text{relative,CH}_4} = \frac{X_{\text{CH}_4,\text{PTCRM}} - X_{\text{CH}_4,\text{TCRM}}}{X_{\text{CH}_4,\text{TCRM}}} \times 100\% \quad (7)$$

where F_{out} is the flow rate of produced gas; F_{in} is the flow rate of feeding gas; Y is the proportion of a gas in the total gas; X_{CH_4} is the conversion of CH₄; $\alpha_{\text{relative,CH}_4}$ is the relative change percentage of CH₄ conversion between PTCRM and TCRM.

3.2.1 The influence of temperature on CH₄ conversion with a constant light intensity

The CH₄ conversion in TCRM and PTCRM and relative change percentage are shown in Figs. 4 and 5, respectively. In Fig. 4, the conversion increases significantly with rising temperature because CRM is an endothermic reaction that favors high temperatures. In addition, PTCRM has a higher CH₄ conversion compared with TCRM at the same temperatures below 700 °C. This may be because the catalyst possesses photoelectric response under light irradiation, which will accelerate

the CRM reaction. The photocurrent of Ni/CeO₂ is further tested in Section 3.3.

Another phenomenon is that the enhancement from the constant light becomes weaker with the increase of temperature, which is expressed by $\alpha_{\text{relative,CH}_4}$ in Fig. 5. The CH₄ conversion in PTCRM is even slightly lower than TCRM at a temperature of 700 °C. This phenomenon may be due to the change of the contribution ratio of light and heat with the increase of temperature when light intensity is constant. On one hand, the reaction rate varies exponentially with temperature and the contribution proportion of light decreases with the increase of temperature. On the other hand, due to the surface irradiation, the temperature of the catalyst surface is higher than that of the inside, so the enhancement of light can't make up for the negative impact of the low temperature inside the catalyst.

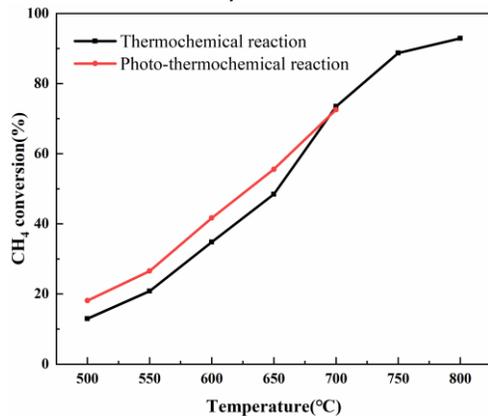


Fig. 4 CH₄ conversion under TCRM and PTCRM conditions

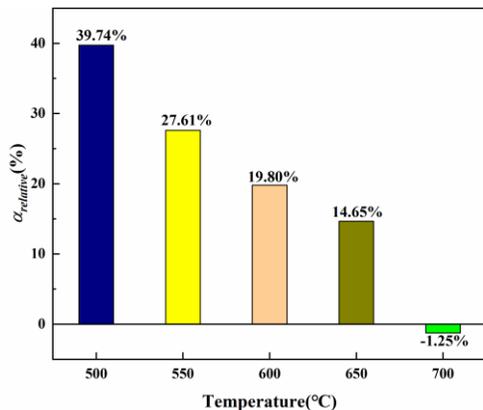


Fig. 5 Relative change of CH₄ conversion between TCRM and PTCRM

3.2.2 The influence of light on H₂ production at a constant temperature

The reaction temperature of 650 °C is chosen as a representative temperature to investigate the H₂ production rate under TCRM and PTCRM conditions, and the results are shown in Fig. 6. The solid lines are data tested in 160 min and the dotted lines are average H₂ production rates. It is observed that light irradiation has a positive effect on H₂ production, which corresponds to the increase in CH₄ conversion. Besides that, the production rate of H₂ remains unchanged during the 160 min test, so the Ni/CeO₂ catalyst is stable when used in the CRM reaction.

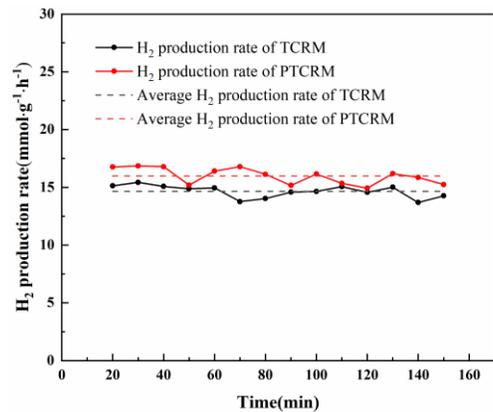


Fig. 6 H₂ production rate under TCRM and PTCRM at 650 °C

3.3 Photoelectric effect of Ni/CeO₂

When exposed to light, the photocurrent in Ni/CeO₂ catalyst is the reason for performance improvement^[14]. An electrochemical workstation is used to verify the existence of photocurrent. The photocurrent is measured under the conditions of illumination and non-illumination, the result is shown in Fig. 7. It is obvious that a stable photocurrent is generated when the catalyst is irradiated by light. And the photocurrent would disappear when the light is cut off. Therefore, the photocurrent is generated by light irradiation, and it can promote the performance of PTCRM reaction.

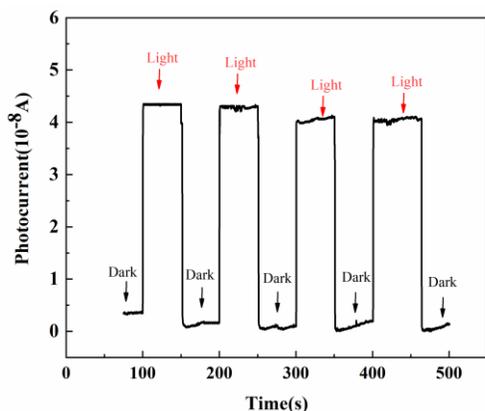


Fig. 7 Photocurrent of Ni/CeO₂ catalyst

4. CONCLUSION

In this work, a solar-enhanced photo-thermochemical CO₂ reforming of CH₄ is proposed by investigating the synergetic effect of solar light and heat. We have prepared a nanoscale Ni/CeO₂ catalyst and characterized the catalyst by XRD and SEM. Compared with TCRM, PTCRM shows higher CH₄ conversion and H₂ production rate at temperatures below 700 °C. With the rising temperature, the improvement decreases due to the decrease in the contribution ratio of light. The photo-electric effect in Ni/CeO₂ is detected, which results in the enhancement of PTCRM. The significant improvement of PTCRM indicates that it may be a potential approach for industrial CRM and better utilization of solar energy.

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