

Solar-Driven Chemical Looping Methane Dry Reforming on Rh-Doped LaCeO_{3.5} Oxygen Carrier at Mild Temperature

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ABSTRACT

The feasibility of a solar-driven chemical looping dry reforming of methane (DRM) process, which converts solar energy and methane into syngas via a looping material oxygen carrier is investigated experimentally. Thermogravimetric analysis (TGA) experiments were firstly carried out to verify the effect of the Rh-doped LaCeO_{3.5} which were synthesized via modified Pechini method and incipient wetness method and the result shows that Rh greatly improved the reaction kinetics. Photo-TGA experiments were conducted to evaluate the light effect in chemical looping DRM. Under the light condition, the Rh-doped LaCeO_{3.5} shows higher methane conversion, oxygen extraction rate and CO selectivity compared with the undoped one, decreasing the apparent activation energy of the reaction at the same time. Insights obtained from the UV-Vis spectroscopy verified that the surface Rh under the light could promote the activation of surface methane species and increase the light absorbance. Through the integration of solar energy, a high methane to solar fuel conversion efficiency could be achieved. The proposed process has the potential to produce solar fuels at high efficiency with reduced carbon footprint.

Keywords: Methane dry reforming, Photo-enhanced thermochemistry, photothermal synergy, UV-Vis spectroscopy

NONMENCLATURE

Abbreviations

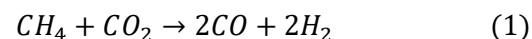
DRM	Dry Reforming of Methane
TGA	Thermogravimetric Analysis
Photo-TGA	Photo-thermogravimetric Analyzer

Symbols

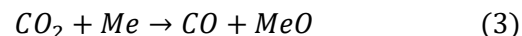
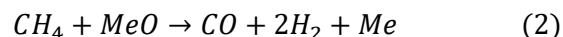
η_{CH_4} Methane cracking rate

1. INTRODUCTION

Dry reforming of methane (DRM) is currently regarded as a novel promising technology for it produce syngas from CO₂ and CH₄ which could limit the green house gas emission [1]:



However, severe carbon deposition and sintering are the main problems of DRM reaction [2]. Meanwhile, the reverse water gas shift reaction (RWGS) is thermodynamic favorable at the DRM reaction temperature (900 °C), which act as another important limitation [3]. The chemical looping DRM using metal oxygen carrier rather than the catalyst to divide the DRM reaction into two steps [4]:



The oxygen carrier is reduced in the reduction step and regenerated in the oxidation step so that it shows good cycle stability compared with the normal catalysts. In this way, the carbon deposition formed in the reduction step would be removed in the oxidation step through the CO₂ atmosphere. On the other hand, the absence of CO₂ in the reduction step prevent it from contacting with the H₂, which suppresses the RWGS reaction thus it is beneficial for obtaining higher syngas selectivity [1].

In our work, we are focusing on the modification of the oxygen carrier, aiming at improving the light reaction

performance. Through efficiently absorbing the solar energy and transforming it into chemical energy, the solar-driven chemical looping DRM could be achieved.

Shafiefarhood et al [5] selected the Rh-promoted $\text{LaCeO}_{3.5}$ to investigate the methane partial oxidation in the thermal condition. Based on this work, we selected the Rh as the promoter doping on the $\text{LaCeO}_{3.5}$ base materials. Rh shows good light absorption performance and could inspire the localized surface plasmonic resonance effect in the UV wavelength under illumination. The reason why the $\text{LaCeO}_{3.5}$ were selected as the oxygen carrier and the base materials of Rh can be described as the following aspects. First, the $\text{LaCeO}_{3.5}$ shows a relatively low equilibrium oxygen pressure which means that it is promising for achieving high CO selectivity [5]. Meanwhile, considering that we are focusing on dividing the thermal and the photo-effect of Rh, it is meaningful to limit the oxygen release performance of the base materials otherwise it could cause a certain amount of interference towards the investigation of Rh.

Our purpose is that distinguishing the contributions between the photo and thermal parts in the energy input during the reaction process, especially illustrating the different effects of Rh in pure heating or light condition. So the essential part of this experiment is to ensure that the reaction could reach the same temperature in both two types of conditions. In this case, the thermal contribution of light could be counteracted and the raising of the reaction performance now is entirely caused by the pure photo effect. Based on this idea, the experiment was conducted on a photo-TGA and detailed discussion were made towards the results.

2. EXPERIMENTAL METHODS

2.1 Synthesis and characterization of the materials

The substrate sample $\text{LaCeO}_{3.5}$ were synthesized via the modified Pechini method and the Rh were doping on the surface via the incipient wetness method (0.5 wt% Rh). Details of the methods could be found elsewhere [6]. Finally, 0.5 g $\text{LaCeO}_{3.5}$ and 0.5 g Rh- $\text{LaCeO}_{3.5}$ were used as the fresh samples.

The powder X-ray diffraction (XRD) pattern was acquired using a Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm) operated at 40 kV and 40 mA. The measurement was taken from $2\theta = 20^\circ$ to 80° . Fig. 1 depicts the XRD patterns and SEM images of the fresh sample.

First, compared with the $\text{LaCeO}_{3.5}$, the XRD results of the promoted sample sustains a rather similar peak positions which only shows a weakening especially on

the low-angle diffraction peak. It can be illustrated that the bulk lattice structure was not changed and the surface loaded amorphous Rh increased. As we know, the surface loaded amorphous Rh has no diffraction peaks. So once the $\text{LaCeO}_{3.5}$ was covered by the amorphous Rh, the peak strength of the crystal phase of Rh-doped $\text{LaCeO}_{3.5}$ would relatively decrease. On the other hand, the SEM images indicate that the doping Rh are in high degrees of dispersion on the surface of $\text{LaCeO}_{3.5}$, which confirms that the Rh changed the surface morphology. The characterization of the samples proved that the Rh were dispersed on the surface rather than the bulk lattice.

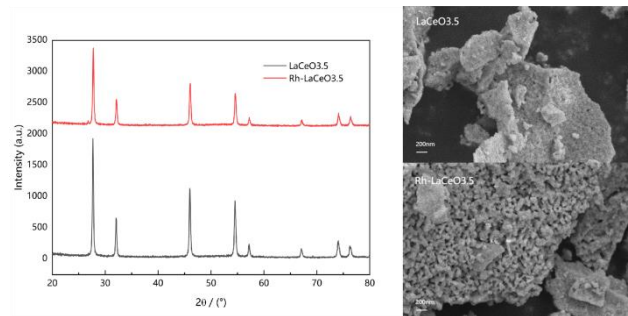


Fig. 1. The XRD patterns and SEM images of the fresh $\text{LaCeO}_{3.5}$ and Rh- $\text{LaCeO}_{3.5}$

The UV-Vis absorbance spectra of the reacted sample were recorded from 300 to 800 nm by Agilent Cary 5000. Details of the UV-Vis spectroscopy could be seen in the results and discussion.

2.2 Experimental Setup

Temperature programmed reduction (TPR) experiments were conducted in a thermogravimetric analyzer (TGA, DTA-60H) to test the performance of sample preparation. At the atmosphere of 10 vol% methane, the temperature was increased from 20 to 1000 °C and kept isothermal for 30 min. More details could be found somewhere else [5].

Solar-driven chemical looping DRM experiments were performed in a Photo-thermogravimetric analyzer (Photo-TGA) with 20 mg sample loading, 40 ml min^{-1} total flow rate and 10 vol% reaction gases (CH_4 for reduction step and CO_2 for oxidation step, balance Ar). A complete cycle contains of 15 min of reduction and 15 min of oxidation, and the reactor was purged with Ar for 7 min after each half cycle. The outlet gas composition was analyzed through a quadrupole mass spectrometer (MS, TILON). A 300 W Xenon lamp (MC-PF300C) was used to simulate the solar light source which the light intensity was fixed to 4.8 W cm^{-2} (20 A). The temperature were setting at 710, 810, 910 °C and the experiments were

performed using unpromoted and promoted sample under or without light.

3. RESULTS AND DISCUSSION

3.1 TGA experiments

3.1.1 CH₄-TPR

Fig. 2 compares the DTG and weight loss data of the promoted and un-promoted samples in the methane TPR experiments. The DTG data describes the differential rate of the change of the weight loss which could be used to analysis the sample reduction temperatures in the methane atmosphere. The initial reduction temperature of Rh-LaCeO_{3.5} decreases into 500 °C while the LaCeO_{3.5} shows no significant turning point until 900 °C. Meanwhile, the overall weight loss increases from 0.5% to around 2%. It was already known that the Rh could promote the methane activation, so that the experiment shows that the surface Rh could efficiently remove the surface oxygen at mild temperature.

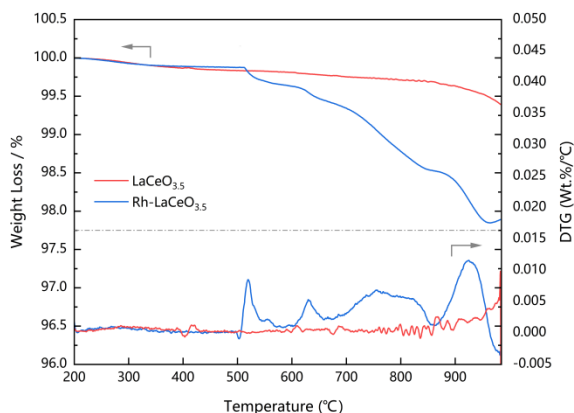


Fig. 2 Weight loss and DTG data of the samples during methane TPR experiments

3.1.2 Kinetics

The reduction half cycle of CL-DRM could be analyzed to verify the kinetic effect of surface Rh. The experiment was conducted on the Photo-TGA without light. As shown in the Fig. 3, the maximum CO gas-production rate increases from 0.3% into 3% after adding the Rh promoter. Just the same as CO, the H₂ maximum gas-production rate of the Rh-LaCeO_{3.5} is also 10 times higher than the un-promoted one. More importantly, the reaction time is shortened from more than 15 min into less than 3 min. We could see that the reaction sustains a stoichiometric ratio of the syn-gas which only product an extremely small amount of CO₂. On the other hand,

the surface Rh shows an obvious kinetic effect which the maximum gas-production rate and the kinetic reaction rate are both improved.

Based on the results of TGA experiments, the thermal effects of surface Rh could be summarized on the two aspects. First, it could reduce the reduction temperature and enhance the oxygen loss capacity of the oxygen carrier. Second, it could facilitate the reaction kinetics and improve the peaking rate of syn-gas-production.

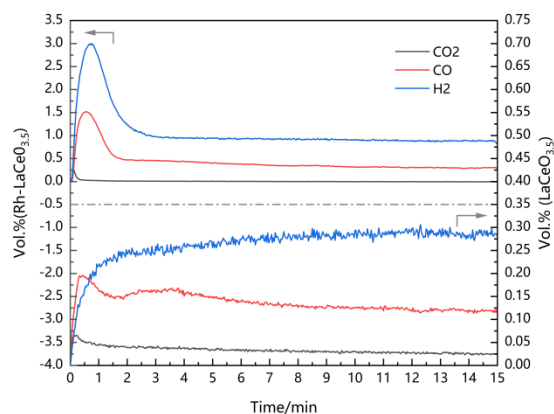


Fig. 3 Outlet gas composition during methane reduction half cycle in 10% methane on Rh- LaCeO_{3.5} and LaCeO_{3.5}

3.2 Photo-TGA experiments

3.2.1 CO Selectivity and CH₄ conversion

We selected the equilibrium section (11-12 min) in the reduction half cycle to evaluate the reaction performance especially in the light condition. As shown in Fig. 4a, the addition of Rh gives rise to the overall CO selectivity into more than 90% which shows a great advantage in DRM reaction. However, the light effect shows a tendency that could be influenced by the changing of the temperature. At 710 °C, the light slightly weaken the selectivity of CO. Moreover, at 910 °C, the light response of Rh decreases. We could see that the light effect of Rh shows the best performance at 810 °C.

For CH₄ conversion rate, the analysis draws a similar conclusion as CO selectivity (Fig. 4b). The addition of Rh shows a non-significant improvement towards methane conversion in relatively low temperature. As the temperature increases, this effect gradually becomes obvious especially at 910 °C. However, in the higher temperature, light cannot act as a promote factor in the reaction process. At mild temperature like 810 °C, the thermal and light performance of Rh both facilitate the conversion of methane which shows a photo-thermal synergistic effect. The results prove that 810 °C is an ideal

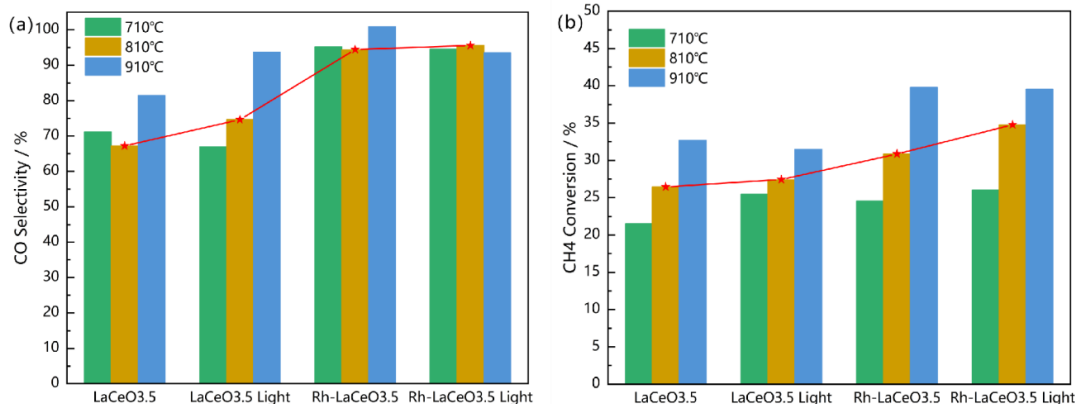


Fig. 4 (a) CO equilibrium selectivity and (b) CH₄ equilibrium conversion rate in 11-12 min during the reduction half cycle

working condition for solar-driven chemical looping DRM which means that simply increasing the temperature does not necessarily promote the synergistic effect of light and heat.

3.2.2 Real-time performance analysis of light reaction

In order to provide deeply insights of the light response of Rh, Fig. 5 gives a comparison of the weight loss and O²⁻ extraction curves of Rh-LaCeO_{3.5}. The first 3 min were chosen to investigate the kinetic stage of the reduction half cycle. As the temperature increases from 710 to 910 °C, the weight loss of the samples without light equally lift from 0.85% into 2.38% with an interval of around 0.75% per 100 °C. Meanwhile, the maximum O²⁻ extraction rate shows the same trends as the changing of the weight loss.

However, comparing with the samples without light at the same temperature, the samples under illumination are not always show a promoting effect especially in high temperature. From 710 to 810 °C, the light on the surface Rh improves the reaction performance. In 910 °C, experiment shows that the weight loss and O²⁻ extraction rate of the light-assisted sample is less than the one without light and this phenomenon is consistent with what we conclude from the CO selectivity and methane conversion at the same high temperature. The light response of Rh might be inhibited when the thermal effect of Rh reaches an optimum condition, which means that there exists an equilibrium temperature point which could balance the thermal and light effect of Rh.

Precisely speaking, 810 °C might not be the accurate position of this point for we cannot set an infinitesimal temperature step size in the actual experiment. Such problems could be solved by computer simulation however it could only act as the auxiliary verification of real experiment.

In conclusion, according to the weight loss and the oxygen extraction rate data, the Rh in light could increase the oxygen removal and the maximum O²⁻ extraction rate, which both depends on a proper temperature.

3.2.3 Activation energy

Derived from the measured CH₄ cracking rate η_{CH_4} and sample temperature, the kinetic parameter values such as the apparent activation energy were determined based on the Arrhenius equation. As shown in Fig. 6, The apparent activation energy of Rh-LaCeO_{3.5} in the dark is 15.15 kJ mol⁻¹, while the Rh-LaCeO_{3.5} under illumination decreases into 12.19 kJ mol⁻¹, demonstrating that the light further improves the effect of surface Rh towards the activation process of the cracking of methane. Though the apparent activation energy of LaCeO_{3.5} decreases a lot under illumination, consider that the samples without Rh shows an extremely low reaction rate whenever adding light or not so that the relative error becomes non-ignorable, thus makes it unmeaningful for our investigation.

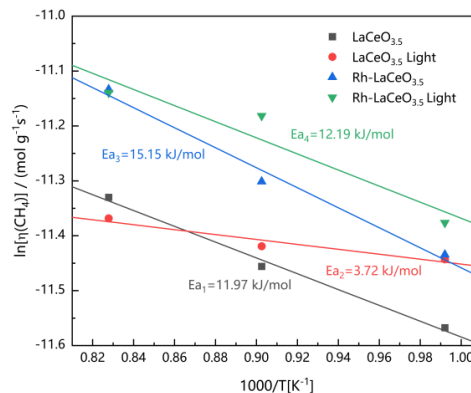


Fig. 6 Arrhenius plots for CH₄ cracking rate η_{CH_4} under direct light illumination and in darkness

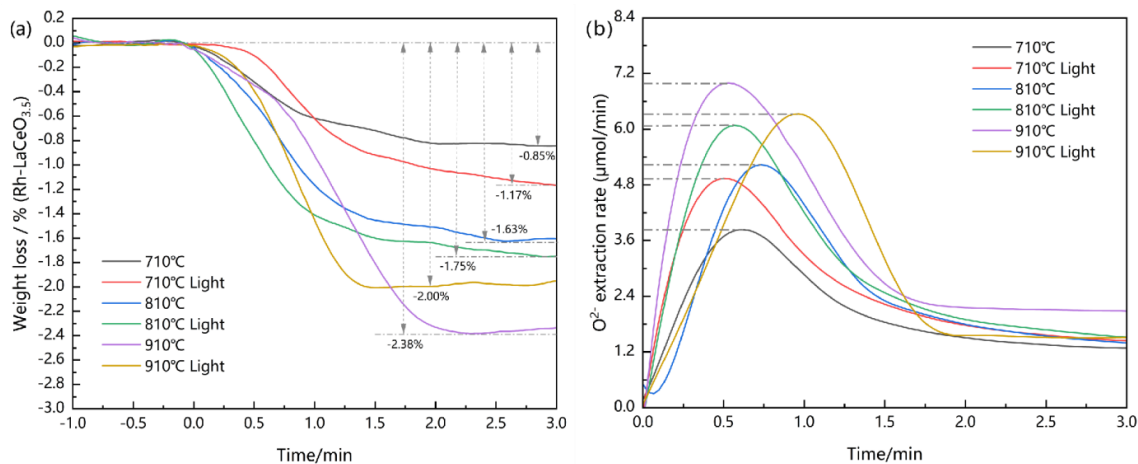


Fig. 5 (a) Weight loss and (b) O²⁻ extraction rate curves of Rh-LaCeO_{3.5} in early 3 min during the reduction half cycle

3.2.4 Characterization of the cycled samples

The UV-Vis and XRD patterns of the reacted samples were shown in Fig. 7. The comparison of the cycled samples could ensure that the heating effect of light were counteracted so that the information of distinguishing the effect of the reaction conducted under light or without light could be gained from the characterization.

As shown in Fig. 7a, the absorption of UVA (320-400 nm) wave increases 5% under light illumination. In visible and near-infrared wavelengths, the absorbance of Rh-LaCeO_{3.5} increases about 20% with light-assisting while the LaCeO_{3.5} basically remains the same.

The XRD patterns (Fig. 7b) give a unique perspective in which through the study of the surface crystal phases to help us understand the mechanism of the light effect. There are two ways resulting in the decreasing of the content of the surface crystal phases. One of them is the addition of Rh which leads to a relatively dropping, and the other one is the possibly coking and sintering after reaction [7]. This could be verified according to the comparison of Fig. 7b and Fig. 1 that the low-angle diffraction peak intensity of the samples decreases after the reaction. Interestingly, through a close comparison of the reacted samples in Fig. 7b, we could find that the light leads to an increase of the content of the surface crystal phases especially for the Rh-doped samples which is opposite from the two ways mentioned above. As a conclusion, the light improves the absorbance of UV-Vis wavelength of Rh-doped samples through the way of facilitating the growth of the surface crystal phases.

4. CONCLUSIONS

This paper aims at investigating the effect of Rh-doped LaCeO_{3.5} oxygen carrier in solar-driven chemical

looping DRM, meanwhile, distinguishing the different contributions towards the photo and thermal effect of the surface Rh of the reaction. The SEM and XRD prove that the rhodium is doping on the surface and the thermal TGA experiments show the thermal effect of surface Rh which could reduce the reduction temperature and facilitate the reaction kinetics. Further, the Photo-thermal TGA experiments indicate that at 810 °C the thermal effect of Rh and the light response of Rh show a synergistic effect which reaches a CO selectivity of more than 90%, meanwhile, the methane conversion and maximum O₂⁻ extraction rates are both increased, and the apparent activation energy is decreased in this condition. Through the comparison of UV-Vis and XRD patterns of the cycled samples, it is indicated that the light on the surface of Rh-LaCeO_{3.5} leads to an increase of the content of the surface crystal phases which could improve the light absorbance of the oxygen carrier. The results provide us with new ideas for the modification of solar-driven chemical looping oxygen carrier that we could base on the photo-thermal synergy to certify the proper temperature of Solar-driven CLDRM rather than the traditional thermodynamic temperature.

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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

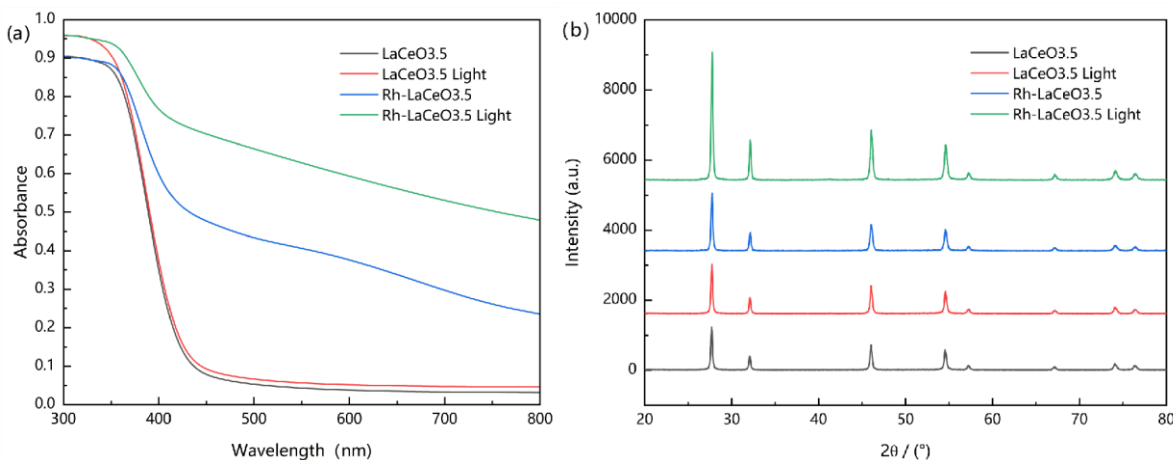


Fig. 7 (a) UV-Vis absorbance spectra and (b) XRD patterns of the cycled samples

paper. All authors read and approved the final manuscript.

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