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SOLAR SYNGAS PRODUCTION VIA CHEMICAL-LOOPING CYCLE FROM REDOX CYCLING OF NIO IN A HONEYCOMB REACTOR

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ABSTRACT

Solar energy driven hydrogen production has gradually become a hotspot in the study of solar energy utilization. Chemical-looping cycle provide a possibility to produce hydrogen under a lower temperature and atmospheric pressure. Here, a honeycomb reactor is proposed to make the hydrogen production process is carried out at 600 °C. Experiments are performed via an endothermic NiO reduction reaction with methane. NiO is made into porous honeycomb chambers, realizing the integration of OC and reactor. The performances of hydrogen production are experimentally examined at the methane flow rate of 300-600 ml/min. The results show that the increasing of methane inlet flow rate of the reaction can make the hydrogen production is gradually advanced. But there is an optimal value, once the flow rate is excessive, it will have an inhibitory effect on the hydrogen production. Also, methane always maintains a high conversion rate as long as the oxygen content of OC is not deficient. Additionally, 15 cycles reaction are performed. The chemical-looping cycle hydrogen production process in the honeycomb reactor is proved to be extremely stable.

Keywords: hydrogen production, chemical-looping cycle, solar energy, honeycomb reactor.

NOMENCLATURE

Abbreviations	
OC	Oxygen Carrier
Symbols	
m_i	Mass of Species i
M_O	Molar Mass of Oxygen
n_i	Mole Amounts of Species i
r_0	Oxygen Transfer Rate
u_i	Moles Consumed Per Unit Time of Species i
X	Fractional Oxidation
α_i	Number of Oxygens Required Per Mole of Species i
η	Conversion Rate of Methane

1. INTRODUCTION

Due to many problems caused by traditional energy, renewable energy has gradually become a hotspot in the field of energy research. As the most abundant renewable energy on earth surface, solar has some issues including decentralization and discontinuity[1]. Concentrated solar thermochemistry is an effective way to overcome these difficulties, which converts solar energy into the chemical energy of CO or H_2 and stores it [2]. Direct solar thermal decomposition of water to H_2 usually need an extremely high temperature requirement of more than 2200 °C [3]. The excessive temperature not only has the large number of thermal radiation losses, but also present a challenge to the reactor materials [4]. To reduce reaction temperature of hydrogen production process, an alternative approach is to employ hydrocarbon materials as reactant [5, 6]. Methane steam reforming is another way to produce H2, which is carried out over Ni-based catalyst at no less than a temperature of 800 °C and a pressure of 14 atm [7]. The limitation of working conditions restricts the combination with concentrated solar energy. A promising way to produce hydrogen using concentrated solar energy is the chemical-looping cycles [8].

The schematic diagram of solar syngas production via chemical-looping cycle from redox cycling of NiO is

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displayed in Figure. 1. During the chemical-looping cycles, a variety of metal oxides have been tested as the oxygen carriers (OC) [9]. Among the rest, nickel oxide is considered as a dramatic OC material for chemical-looping cycles, due to it exhibits a lower reaction temperature with methane and good catalytic effect of its reduction products on the reaction of methane and stream[10], which could improve the performance of hydrogen production. The reduction reaction is highly endothermic, so solar energy could be employed to meet the requirement as input. Nickel oxide, as the partial oxidant of methane, needs to react with air to regenerate after losing oxygen. The reaction could release a large amount of heat at high temperature of 1200 °C steadily and continuously [11].

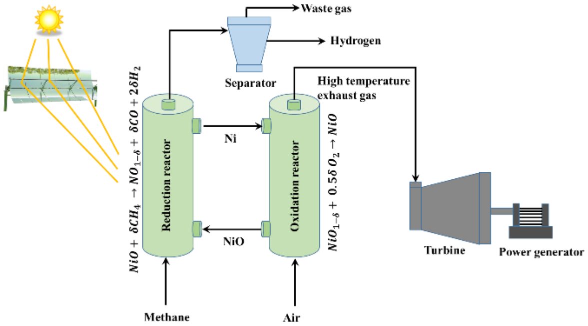

Figure 1 Schematic diagram of solar syngas production via chemical-looping cycle from redox cycling of NiO

The endothermic reaction of NiO with CH_4 producing H_2 is represented as:

$$NiO + \delta CH_4 \rightarrow NO_{1-\delta} + \delta CO + 2\delta H_2 \quad (1)$$

NiO could be regenerated by direct reaction with air:

$$NiO_{1-\delta} + 0.5\delta\, O_2 \rightarrow NiO \quad (2)$$

During the endothermic reaction stage, other possible side reactions may occur and affect the reaction products:

$$4NiO + \delta CH_4 \rightarrow 4NiO_{1-\delta} + \delta CO_2 + 2\delta H_2O \quad (3)$$

$$H_2O + CH_4 \rightarrow CO + 3H_2 \quad (4)$$

$$H_2O + CO \rightarrow CO_2 + H_2 \quad (5)$$

$$CH_4 \rightarrow C + 2H_2 \quad (6)$$

$$H_2O + C \rightarrow CO + H_2 \quad (7)$$

In our previous work, a novel honeycomb fixed-bed reactor for chemical-looping cycles was constructed [11, 12]. In this reactor, OC was integrated into the honeycomb chamber, which could improve the reaction rate and the conversion of the reactants [11]. In previous experiments, it was found that the water vapor generated by the reduction reaction was locked in the honeycomb reactor structure and could not be discharged at the same time with other gases. As shown in Eq. (4) and (5), water vapor can promote the methane chemical-looping hydrogen production. Based on this, the performances of chemical-looping cycles hydrogen production under different conditions are analyzed.

2. EXPERIMENTAL SECTION

2.1 *Experimental materials*

The active component of OC is NiO, with Al_2O_3 doped into the iron oxide as an inert support material. The preparation and processing of honeycomb oxygen carriers have been described in our previous literature. NiO/Al_2O_3 powders could be obtained by the coprecipitation method. Then the reactor and OC can be integrated by molding the powder into a honeycomb structure [11, 12].

The oxygen carrier is regarded as not only the solid reactant but also the composition material of the honeycomb chamber. The configuration diagram for the honeycomb fixed-bed reactor is shown in Figure. 2. As shown, the oxygen carriers and support materials are made into a cylindrical monolithic block with a series of axial microchannels. In this way, the integration of the oxygen carrier and reaction chamber is achieved.

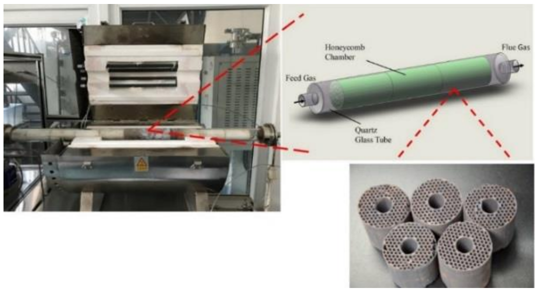

Figure 2 The configuration diagram for the honeycomb fixed-bed reactor and the honeycomb OC

2.2 *Experimental method*

The solar energy is collected by the parabolic concentrator and transferred to the reactor through the heat-conducting oil to provide the heat required for the endothermic reaction. During the endothermic, methane is introduced into the honeycomb reactor at 300-600 ml/min, and the reaction temperature is maintained at 600 °C. During the OC regeneration stage, air is fed at 1200 °C. The processes are all controlled an integrated controller and operated at an atmospheric pressure.

The experimental data is analyzed based on the composition of gas at the reactor outlet, which is collected and detected by gas chromatography.

During the partial oxidation of methane, oxygen is released from the lattice of NiO and it is recovered in the form CO, CO_2 and H_2O. The oxygen transfer rate is calculated by:

$$r_0 = M_O \times (\alpha_{CO} \times u_{CO} + \alpha_{H_2O} \times u_{H_2O} + \alpha_{CO_2} \times u_{CO_2}) \qquad (8)$$

where M_O is the molar mass of oxygen, α_{CO} and α_{H_2} are the number of oxygens required per mole of CO and H2 to convert from reactant to product, u_{CO} and u_{H_2} are the moles consumed per unit time of CO and H_2.

Fractional oxidation is a nondimensional indicator the indicates the conversion of OC and it is defined as:

$$X = \frac{m_{ox} - m}{m_{ox} - m_{red}} \qquad (9)$$

where m is the instantaneous mass of the oxygen carrier, and m_{ox} and m_{red} represent the mass of the oxygen carrier in a completely oxidized and reduced state, respectively.

The conversion rate of methane is an important index to measure the reaction performance, which could be calculated by:

$$\eta = \frac{n_{CO} + n_{CO_2} + n_C}{n_{CO} + n_{CO_2} + n_C + n_{CH_4}} \qquad (9)$$

Where the n_i is the mole amounts of species i.

3. RESULT AND DISCUSSION

The influence of inlet methane flow rate on hydrogen production is studied. Figure. 3 shows that the concentration of gas components at the reactor outlet under four inlet methane flows during the reaction process. In the initial phase of the reaction, regardless of the flow rate, the product is primarily CO_2. This is due to the fact that the methane is rapidly and completely oxidized by the oxygen carrier at a higher oxygen content stage. With the increase of methane in the reactor, a stable reducing atmosphere is formed, and the hydrogen content at the outlet gradually increased and stabilized. As the flow rate increase gradually, the mutation time of hydrogen production is gradually advanced. In the meantime, methane conversion is not particularly affected. It is indicated that the increase of flow rate can effectively inhibit the complete oxidation of methane at the initial stage of reaction without reducing the methane conversion. It could be seen that the yield of hydrogen is very high even higher than the theoretical value calculated by Eq. (3). The similar results have been found in fluidized bed reactors[13]. But the reduction reaction is carried out at 800 °C. It points to the formation of carbon deposition as the reason for the export concentration showing this phenomenon. Also, the reaction Eq. (3) dominates the early stage, and a lot of H_2O is generated, which is locked in the reactor due to the honeycomb structure. This result is provided by the phenomenon that during the oxidation reaction process after the reduction reaction, some water is carried out of the outlet pipe by high-speed air (3000 ml/min) without any water input. The water remaining in the reactor reformates with methane and carbon deposition under the catalysis of Ni, as shown in Eq. (4) and (7). The water-gas shift reaction (Eq. (5)) is enhanced as well. Therefore, the amount of hydrogen produced is increased.

Compared with methane steam reforming for hydrogen production, chemical-looping cycle hydrogen production partially oxidized methane by means of OC, which effectively reduces the temperature of hydrogen production and enables the process to be carried out under atmospheric pressure. Compared with the conventional chemical-looping reforming for hydrogen production, the using of honeycomb reactor make it to be realized that the hydrogen production could be carried out at a lower temperature with the same outlet hydrogen concentration. This is due to the honeycomb structure providing better turbulence, enhanced gas-solid contact and diffusion of the gas in the body of OC, resulting in improving the performance of the reactions. And the ability of the honeycomb chamber to hold water allows CH_4 and CO to react with H_2O, increasing the hydrogen production.

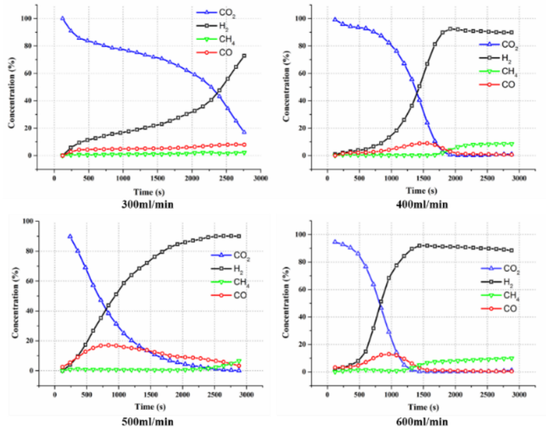

Figure 3 Effect of CH_4 flow rate on measured outlet gas components during the reduction of nickel oxide

The effect of OC fractional oxidation on methane conversion rate is shown in Figure. 4(a). in the area with the fractional oxidation greater than 0.2, the fact that methane can be almost completely transformed would be affected by the change of flow rate. As the oxygen content of the carrier decreased further, the methane conversion rate began to decrease gradually. The higher the flow rate is, the higher the fractional oxidation of the change starting position is. The reason could be explained as follows: the lower the oxygen content in OC, the farther away the remaining oxygen-containing lattice is from the gas-solid contact surface. The amount of methane that can be oxidized by lattice oxygen is very limited, so it is difficult for a large amount of methane to participate in the reaction, causing the methane conversion rate to plummet. It can give a guidance about the reduction reaction. A high OC utilization efficiency and a high methane conversion could be obtained with an appropriate end stage. The effect of OC fractional oxidation on exportation hydrogen concentration in Figure. 4(b). The lower the oxygen content of OC, the better the partial oxidation effect of methane, and the higher the hydrogen production. It is noted that, as the flow rate increase from 300 ml/min to 500 ml/min, a gradual advance toward higher hydrogen production. But, when the flow rate is further increased to 600 ml/min, the hydrogen production process is limited, resulting in a decrease in the proportion of hydrogen exported. It means that, simply increasing the methane flow rate cannot guarantee the continuous improvement of the hydrogen production, and there is an optimal value for the hydrogen concentration to the optimal level. It could be also seen that when the flow rate is 600 ml/min, the experimental points are relatively sparse in the region with high fractional oxidation at the same time interval. This indicates that too high methane flow rate will lead to too fast oxygen loss rate of OC in the stage dominated by reaction Eq. (3), which will lead to a rapid decrease of fractional oxidation. This may be the primary cause that leads to excessive flow to restrict the effect of hydrogen production.

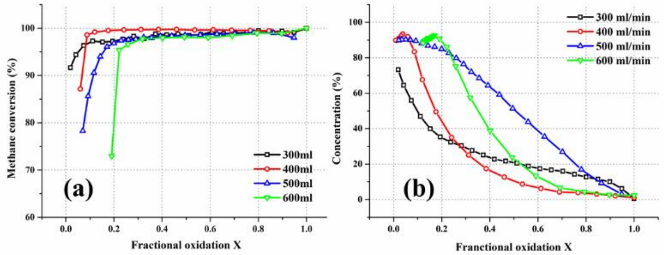

Figure 4 Effect of OC fractional oxidation on methane conversion rate (a) and exportation H_2 concentration (b)

High cyclic stability is an essential requirement for the application of the chemical-looping cycles. Figure. 5 illustrates the stability of OC and chemical-looping cycles hydrogen production process for 15 cycles. The circulation experiments are carried out under the condition of 600 ^{o}C and 300 ml/min. Throughout the circulation process, OC keeps almost complete conversion and the reaction performance is hardly affected. In the meantime, the conversion rate of methane, the yield of hydrogen and the oxygen transfer rate of OC are almost brought into correspondence in each cycle reaction. All these result show that the chemical-looping hydrogen production process of honeycomb NiO/Al_2O_3 has excellent stability. The proposed honeycomb chamber is formed by OC, which allows OC to be uniformly distributed in the honeycomb chamber. And the structure plays an important role in improving the stability.

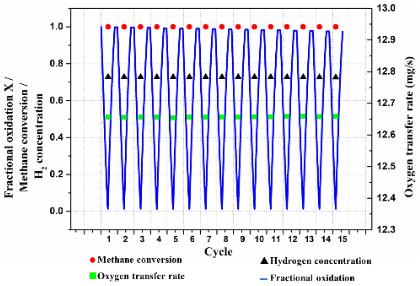

Figure 5 Cyclic stability of methane conversion, hydrogen yield, oxygen transfer rate and fractional oxidation during the chemical-looping cycle hydrogen production process

4. CONCLUSIONS

In this work, the performance analysis and cyclic stability analysis of chemical-looping cycle hydrogen production are carried out using a honeycomb fixed-bed reactor. NiO/Al_2O_3 is selected as the material of OC, which is not only the supporting material of the honeycomb reactor, but also the reactant used to partially oxidize methane. The experiments are carried out at the reduction temperature of 600 ^{o}C, the oxidation temperature of 1200 ^{o}C and the methane flow rate of 300-600 ml/min. The results show that the using of honeycomb reactor could reduce the reaction temperature of chemical-looping hydrogen production process and make it come true that the process is carried out at atmospheric pressure with a high hydrogen yield. The increasing of methane inlet flow rate of the reaction can make the hydrogen production is gradually advanced. But when the flow rate increase to a certain value, if it continues to grow, too high methane flow rate will lead to too fast oxygen loss rate of OC. This may lead to restrict the hydrogen production. Under the condition of sufficient oxygen content of OC, the conversion rate of methane is maintained above 95%. Additionally, the results of repeated cycle experiments show that the chemical-looping cycle hydrogen production process using honeycomb reactor has excellent cyclic stability. The honeycomb reactor would be expected to offer a new possibility to make the concentrated solar energy driven chemical-looping cycle hydrogen production under a lower temperature and better stability to be realized.

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REFERENCE

[1] Chuayboon S, Abanades S, Rodat S. Syngas production via solar-driven chemical looping methane reforming from redox cycling of ceria porous foam in a volumetric solar reactor. Chemical Engineering Journal. 2019;356:756-70.

[2] Steinfeld A. Solar thermochemical production of hydrogen––a review. Solar energy. 2005;78:603-15.

[3] Agrafiotis C, Roeb M, Sattler C. A review on solar thermal syngas production via redox pair-based water/carbon dioxide splitting thermochemical cycles. Renewable and Sustainable Energy Reviews. 2015;42:254-85.

[4] Abanades S, Charvin P, Flamant G, Neveu P. Screening of water-splitting thermochemical cycles potentially attractive for hydrogen production by concentrated solar energy. Energy. 2006;31:2805-22.

[5] Brkic M, Koepf E, Meier A. Solar carbothermal reduction of aerosolized ZnO particles under vacuum: Modeling, experimentation, and characterization of a drop-tube reactor. Chemical Engineering Journal. 2017;313:435-49.

[6] Leve̊que Gl, Abanades Sp. Thermodynamic and kinetic study of the carbothermal reduction of SnO2 for solar thermochemical fuel generation. Energy & Fuels. 2013;28:1396-405.

[7] Barelli L, Bidini G, Gallorini F, Servili S. Hydrogen production through sorption-enhanced steam methane reforming and membrane technology: a review. Energy. 2008;33:554-70.

[8] Marxer D, Furler P, Takacs M, Steinfeld A. Solar thermochemical splitting of CO 2 into separate streams of CO and O 2 with high selectivity, stability, conversion, and efficiency. Energy & Environmental Science. 2017;10:1142-9.

[9] Adanez J, Abad A, Garcia-Labiano F, Gayan P, de Diego LF. Progress in Chemical-Looping Combustion and Reforming technologies. Progress in Energy and Combustion Science. 2012;38:215-82.

[10] Luis F, Ortiz M, García-Labiano F, Adánez J, Abad A, Gayán P. Hydrogen production by chemical-looping reforming in a circulating fluidized bed reactor using Ni-based oxygen carriers. Journal of Power Sources. 2009;192:27-34.

[11] Zhang H, Hong H, Jiang Q, Deng Yn, Jin H, Kang Q. Development of a chemical-looping combustion reactor having porous honeycomb chamber and experimental validation by using NiO/NiAl 2 O 4. Appl Energy. 2018;211:259-68.

[12] Zhang H, Liu X, Hong H, Jin H. Characteristics of a 10 kW honeycomb reactor for natural gas fueled chemical-looping combustion. Appl Energy. 2018;213:285-92.

[13] Chiron F-X, Patience GS, Rifflart S. Hydrogen production through chemical looping using NiO/NiAl2O4 as oxygen carrier. Chem Eng Sci. 2011;66:6324-30.