

Solar hydrogen production under combined solar light and thermal effect at mid-and-low temperature –experimental and thermodynamic analysis

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ABSTRACT

The efficient use of solar energy to produce hydrogen by thermochemical and photochemical reactions is quite challenging and promising. Solar thermochemical processes can make use of full spectrum sunlight but ignore the energy quality differences between spectrums, while photochemical processes can convert light into chemical energy but use part of the solar spectrum. To explore the possibility of combining solar light and heat, an experimental study of photo-thermochemical methanol steam reforming reaction is conducted in a fixed bed reactor. Photochemical and thermochemical reactions are carried out simultaneously on Cu/ZnO/Al₂O₃ catalyst. Compared to thermochemical reactions (TRs), the photo-thermochemical reaction (PTR) shows an increased conversion rate, especially at low temperature. At 188°C, the PTR improves the yield of hydrogen by 32.9%. According to the characterization results, the photo-generated electrons contribute to the enhancement of the PTR. The mechanism for the increased conversion rate is further discussed from the thermodynamics perspective. These findings provide a reference for future integrated use of light and heat at mid-and-low temperatures.

Keywords: photo-thermochemical reaction, methanol steam reforming, photo-generated electron, hydrogen production

NONMENCLATURE

Abbreviations

TR Thermochemical reaction

PTR	Photo-thermochemical reaction
<i>Symbols</i>	
$n_{\text{CH}_3\text{OH}}$	the mole amount of methanol
n_{H_2}	the mole amount of hydrogen
ν_{H_2}	the stoichiometric coefficient of hydrogen
Y_{H_2}	yield of product X
Y_{relative}	relative change percentage
$Y_{\text{H}_2,\text{pt}}$	hydrogen yield of PTR
$Y_{\text{H}_2,\text{t}}$	hydrogen yield of TR
ΔG	Gibbs free energy change
ΔH	enthalpy change
ΔS	entropy change
W	electric work generated by light
$\Delta G'$	Gibbs free energy in PTR reaction

1. INTRODUCTION

Global warming caused by greenhouse gases especially CO₂, poses a challenge to the world. Using a carbon-free energy, like hydrogen etc., is attractive. Many technologies have been researched for hydrogen production by solar energy, such as solar thermochemical water splitting cycles [1], solar photochemical water splitting [2], solar photoelectrochemical water splitting [3] and so on. The thermochemical processes can utilize solar energy in the full spectrum. The photochemical and photoelectrochemical processes can directly convert ultraviolet and visible light into chemical energy. There

are still a number of problems that need to be addressed before these technologies can be taken out of laboratory scale. In solar thermochemical processes, light of all spectrum is directly converted into heat before use, leading to the exergy loss in the light-to-heat process. The two-step solar thermochemical water splitting cycles also suffer from various engineering problems caused by high temperatures ($>1000^{\circ}\text{C}$)[4]. For photochemical and photoelectrochemical water splitting technologies, only part of the solar spectrum can be used well. For example, the widely used TiO_2 catalyst[5] can only use the ultraviolet light in the solar spectrum, with visible and ultraviolet light being wasted. Developing a technology which can combine the advantage and avoid the disadvantages of photochemical and thermochemical processes is quite significant.

Solar methanol steam reforming is a promising hydrogen production method. The reaction is an endothermic one, in which solar energy is transferred to chemical energy. The reaction temperature ($150\text{-}300^{\circ}\text{C}$) is mild and easy to realize. $\text{Cu/ZnO/Al}_2\text{O}_3$ catalyst [6] is widely used as thermocatalyst in this reaction. Material with existence of Cu/ZnO can also be used as photocatalyst[7]. Therefore, the $\text{Cu/ZnO/Al}_2\text{O}_3$ has the potential to be used as a catalyst combining the effects of light and heat.

In this work, a hydrogen production method is proposed by combining photochemical and thermochemical reactions. An experimental photo-thermochemical methanol steam reforming reaction with $\text{Cu/ZnO/Al}_2\text{O}_3$ as a catalyst is carried out on a fixed bed reactor. The characterization of the catalyst provides a basis for the reaction mechanism. Finally, the light enhancement mechanism based on the second law of thermodynamic is discussed.

2. EXPERIMENTAL SECTION

The process flowchart of the experiment apparatus is shown in Fig. 1. The methanol solution is pre-prepared with the molar ratio of water and methanol fixed at 1:1. A syringe is used to ensure the accuracy of flow. High purity nitrogen is used as the internal standard gas. The reactants are vaporized and preheated at the reaction temperature before touching the catalyst. In thermochemical experiments, the temperature of the catalyst is maintained by a heating furnace. While in the photo-chemical case, light from the Xenon lamp and heat from the heating furnace are energy sources. The quartz reactor filled with catalyst is 13mm long, 13mm wide and 3mm thick. A thermocouple is inserted in the middle of

the reactor to monitor temperature. The reactant mixture is cooled and separated in the condenser after the reaction. The gas products are collected in a collection bag. A gas chromatograph (GC-2014) with thermal conductivity detection is used to test the gas concentration and composition. Argon was used as the carrier gas. In order to ensure the accuracy and stability of measurements, each test point was stabilized for approximately 2 hours and measured for 4-5 times.

$\text{Cu/ZnO/Al}_2\text{O}_3$ catalyst is used in this experiment. Before the experiment, the catalyst is activated in the 0.5-10% H_2/N_2 mixture atmosphere with temperature gradually increased from 180°C to 240°C . The total process lasts for approximately 12h.

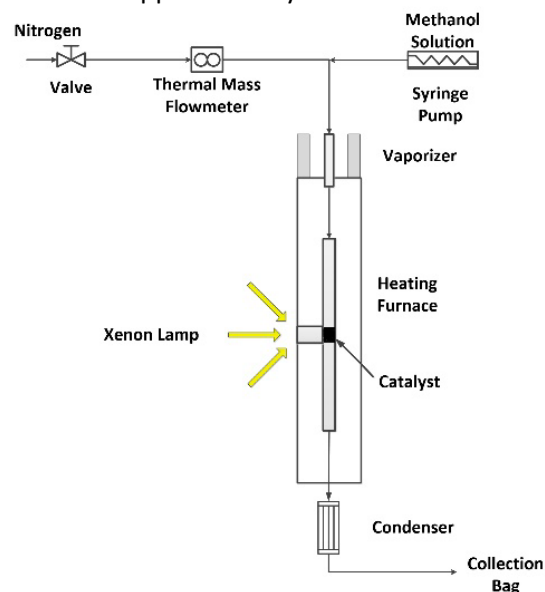


Fig. 1. Flowchart of the experiment apparatus

3. RESULTS AND DISCUSSION

3.1 Characterization of the $\text{Cu/Zn/Al}_2\text{O}_3$ catalyst

The reaction activity depends mainly on the microstructure and composition of the catalyst. The composition of catalyst is measured by the X-ray diffraction(XRD). The catalyst before filled into quartz reactor (unreduced) and after experiment(used) are all tested. According to Fig. 2, the peaks of the samples indicate the existence of CuO and ZnO . The peaks of Al_2O_3 can't be found because Al_2O_3 is highly dispersed. After the catalyst was used in the reaction, Cu can be detected because CuO is reduced into Cu before the reaction process. The specific surface area based on BET theory is $95.32\text{ m}^2/\text{g}$. The N_2 adsorption and desorption isotherm curve is shown in Fig. 3. The shape of adsorption desorption curve indicates that the catalyst is

mesoporous material and the cylindrical gaps exist in the catalyst.

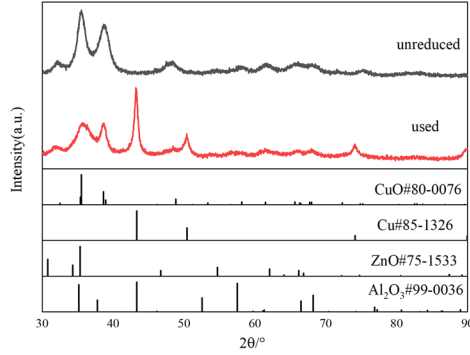


Fig. 2. XRD results of the Cu/ZnO/Al₂O₃ catalyst before (unreduced) and after reaction (used)

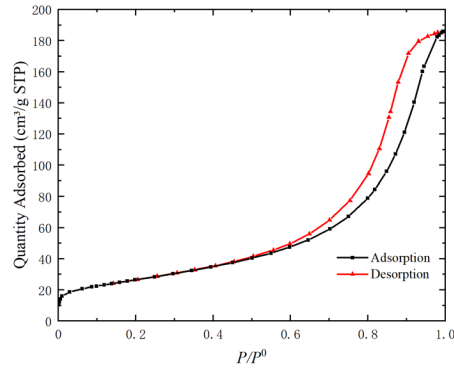
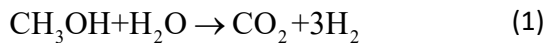


Fig. 3. N₂ adsorption and desorption isotherm curve of the CuO/ZnO/Al₂O₃

3.2 Experimental results of the TR and PTR

In the experiment section, the methanol steam reforming reaction happens in the reaction system:



The catalyst activity is mainly measured by yield.

$$Y_{\text{H}_2} = \frac{n_{\text{H}_2} / \nu_{\text{H}_2}}{n_{\text{CH}_3\text{OH}}} \quad (3)$$

where Y_{H_2} is the hydrogen yield; $n_{\text{CH}_3\text{OH}}$ represents the mole amount of methanol into the reactor, n_{H_2} is the mole amount of hydrogen produced in the reaction; ν_{H_2} is the stoichiometric coefficient of H₂ equal to 3 according to Eq.(1).

The relative change percentage Y_{relative} is used to compare PTR and TR:

$$Y_{\text{relative}} = \frac{Y_{\text{H}_2,\text{pt}} - Y_{\text{H}_2,\text{t}}}{Y_{\text{H}_2,\text{t}}} \quad (6)$$

where $Y_{\text{H}_2,\text{pt}}$ is the hydrogen yield of the PTR, and $Y_{\text{H}_2,\text{t}}$ is the hydrogen yield of the TR.

3.2.1 The influence of temperature at fixed light intensity on H₂ yield

The mass of the catalyst remains constant (0.590g) throughout the experiment. The methanol solution feeding rate is 3 ul/min, which is controlled by a syringe pump. When the incident light intensity is fixed at 9kW/m², the catalyst temperature is mainly adjusted by a heating furnace.

As shown by the black line in Fig. 4, the hydrogen yield increases rapidly in the temperature range between 180°C and 240°C, which is influenced by the kinetics. At above 240°C, the rate increases slowly at 260°C, and decreases at 280°C. The decrease is mainly due to the side reaction. With the incident light intensity fixed at 9kW/m², the hydrogen yield shows the same trend as shown by the red dots in Fig. 4. Differently, the inflection point moves left at 240°C instead of 260°C in the TR. To make a better comparison, the relative change percentage is used in Fig. 5. Y_{relative} decreases with temperature. At 188°C, the value of Y_{relative} reaches 32.9%. The reasons might stem from the enhancement of indirect recombination of photo-generated carriers with the increasing temperature. Once the carriers recombine, the energy of light will change into heat. With the increasing temperature, the PTR and TR becomes similar.

3.2.2 The photo-electric response test on CuO/ZnO/Al₂O₃ catalyst

To further study the reaction mechanism, the electrochemical workstation is used to test the photo-electric response. In Fig. 6, the catalyst shows a stable response to the light stimulation. The photo-generated electron possibly account for the enhancement of PTR compared to TR.

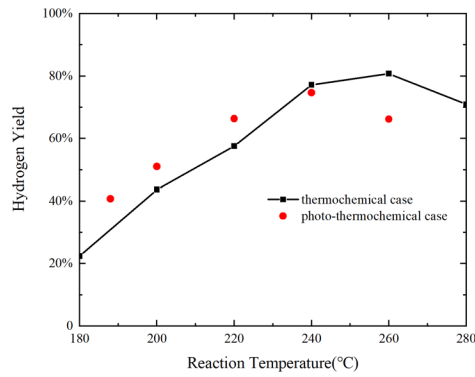


Fig. 4. Y_{H_2} varies with temperature

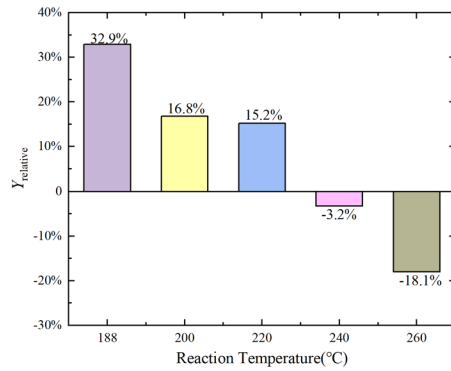


Fig. 5. $Y_{relative}$ varies with temperature

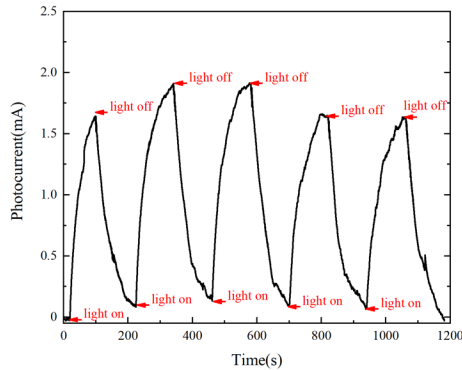


Fig. 6. Photo-electric response of catalyst to light

3.3 Proposed enhancement mechanism

From the perspective of the second law of thermodynamics, the driving force of the TR is written as:

$$\Delta G = \Delta H - T\Delta S \quad (7)$$

where ΔG , ΔH and ΔS are the Gibbs free energy change, enthalpy change and entropy change of a single

reaction, respectively. A reaction can only take place when

$$\Delta G \leq 0 \quad (8)$$

For the methanol steam reforming reaction and methanol decomposition reaction, ΔG of the TR and PTR varies with temperature, as shown in Fig. 7. Reaction 1 and 2 are easy to happen at a higher temperature. At a low temperature ($<150^\circ\text{C}$), ΔG of reaction 2 approaches 0, and the side reaction can hardly take place.

As tested in section 3.2.2, with the addition of light to the catalyst surface, the photo-generated electron has been produced, thus changing the reaction equilibrium.

The driving force in the PTR is:

$$\Delta G' = \Delta G - W \quad (9)$$

where W is the electric work generated by the light with the photo-generated electron, acting as a energy carrier. The changed Gibbs free energy is shown as a red dotted line in Fig. 7. As more electric is added to reaction system, the reaction can occur more easily (see Fig. 4 for more details).

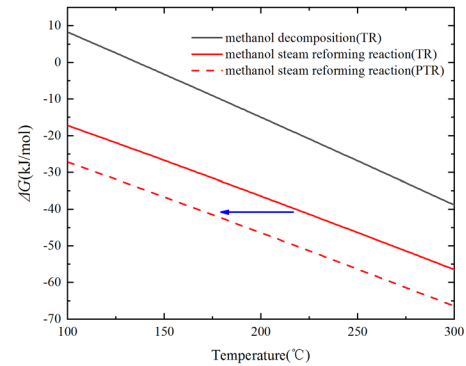


Fig. 7. ΔG of the TR (reaction 1, red solid line and reaction 2, black solid line) and PTR (reaction 1, red dotted line) varies with temperature

4. CONCLUSION

In this study, a hydrogen production method is proposed by combining the effect of solar light and heat and using $\text{Cu/ZnO/Al}_2\text{O}_3$ catalyst. The main conclusions are listed as follows:

- 1) The PTR can achieve higher hydrogen yield rate compared to the TR, especially at temperatures below 240°C . The PTR improves the conversion rate of methanol by 32.9% at 188°C .

- 2) The photo-electric response is detected in the catalyst, accounting for the photo-thermochemical phenomenon.
- 3) The performance improvement mechanism of the PTR is discovered. The photo-thermochemical processes can enhance the driving force of the chemical reaction compared to thermochemical processes.

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