

Systematic experimental study for optimized hydrogen production of Ni/CeO₂ prepared by incipient wetness impregnation technique

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In this present work, different supports (CeO₂/ZrO₂) and different Ni contents based catalysts were prepared by incipient wetness impregnation method and tested in the methane steam reforming (MSR) reaction. The prepared catalysts were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The XRD analysis confirmed the prepared Ni/CeO₂ samples have a pure crystal structure. In the catalytic tests, the effects of reactivity temperature, different support, Ni loading content and the gas hourly space velocity (GHSV) on hydrogen production performance were investigated systematically. The results showed that the optimal reaction conditions for MSR by Ni/CeO₂ catalyst were as follows: 10 wt % Ni/CeO₂, 750 °C, 1500 h⁻¹. The stability test for 12 h at 750 °C indicated that the chosen Ni/CeO₂ catalyst had excellent thermal stability.

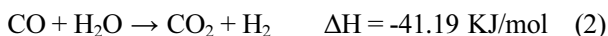
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Introduction

Nowadays, hydrogen is becoming an environmental friendly energy source producing clean energy in an efficient way. Compared with new energy sources such as solar energy and wind energy, hydrogen is a secondary energy source that can be produced in a wide variety of ways, such as photolysis of water, electrolysis of water, and hydrocarbon reforming. The most mature hydrogen production technology is hydrocarbon reforming. Compared with hydrolyzed hydrogen production, hydrocarbon reforming has the characteristics of low cost and high hydrogen production rate.

Methane is widely found in natural gas and biogas in nature. Methane reforming is a widely used method in industries to convert natural gas to H₂ or syngas (H₂+CO) [1-5]. According to different reforming raw materials, it can be divided into partial oxidation of methane [6], carbon dioxide reforming of methane [7, 8] and steam reforming of methane [9, 10]. The methane steam reforming reaction (MSR) is an endothermic reaction and is a fairly mature industrial hydrogen production technology.

The reaction is represented by Eq. (1).



This main reaction occurs at a high temperature, followed by a water gas shift reaction (WGS) which produces CO₂ (eq. (2)).

The methane steam reforming reaction is a complicated process, which may involve multiple reactions. The reaction flows from the surface of the catalyst by water vapor and methane under a high temperature atmosphere. After the catalyst is catalyzed, H₂ and CO are formed. CO₂ will be generated when water is excessive. The reaction is carried out under a certain pressure and high temperature. In such a harsh environment, carbon deposition may occur.

Commonly used noble metal catalysts are Pt, Pd, and Rh. The precious metal catalyst has a certain anti-carbon deposition performance, and has better catalytic performance and stability than the general catalyst. However, it is not widely used due to the expensive price.

It has been reported that noble metal catalysts such as Rh, Ru, Pd and Pt have high activity, stability and carbon deposition resistance [11-13]. Among many traditional metal catalysts, Ni-based catalysts stand out due to their lower cost, good catalytic and higher stability performance at high temperatures [14-16].

The support is one of the essential components of the catalyst. It plays a very important role in the catalyst. One of its basic functions is to support the active component. The support determines the catalytic property of the system. For some specific reactions, besides affecting metal dispersion and providing stability for metal particles, the support can also participate in the reactions [17, 18]. Commonly used supports are γ -

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Al₂O₃, CeO₂, ZrO₂, SiO₂ and others. The support is required to have high mechanical strength, large specific surface area and strong anti-sintering ability. Due to its unique properties, cerium has been widely used in heterogeneous catalysis [19].

Several studies have applied these materials for MSR and concluded that the intermediate metal loadings produce the best catalytic performance [20-22]. A series of nickel catalysts with different metallic contents supported on CeO₂ and ZrO₂ were studied by Dong et al. [20]. They found that nickel loading of 15% wt is optimal. Because it balances the two different catalytic activation points of CH₄ and H₂O. In addition, Roh et al. studied the effect of nickel content on a Ce-ZrO₂/Al₂O₃ support in MSR, and their results showed that with the nickel content of 12% wt., methane has the maximum conversion [21].

In the present study, different supports (CeO₂/ZrO₂) and different Ni contents are used to optimize their composition as catalyst for hydrogen production from the MSR reaction. A series of synthesized catalysts were thoroughly characterized by XRD and SEM. In addition, in order to evaluate the optimal conditions of this process, the influence of the reactivity temperature, different supports, Ni content and the gas hourly space velocity (GHSV) were investigated to achieve a deeper understanding of Ni-based supported catalysts.

Experimental

Samples preparation

To prepare a catalyst using a wet incipient wetness impregnation method, it is first necessary to measure the water absorption of the support. Weigh a certain mass of the support in the beaker which is defined as a, return the analytical balance to zero, add deionized water to the fully immersed carrier with a plastic dropper, measure the mass of deionized water to b, seal the beaker mouth at room temperature. After standing for 12 hours, the deionized water not absorbed by the carrier was filtered off, and the mass was found to be m. Then the support water absorption rate X is:

$$X = (b - m)/a * 100\% \quad (1)$$

Preparation of different wt% Ni loadings catalysts

Ni(NO₃)₃·6H₂O having a corresponding Ni loading amount was weighed into a beaker, and CeO₂ was used as a support. Deionized water was added to Ni(NO₃)₃·6H₂O according to the measured water absorption rate of the support to prepare a precursor solution. After the Ni(NO₃)₃·6H₂O was completely dissolved, the precursor solution and the CeO₂ were immersed, mixed vigorously with a stirrer for 20 min. Standing at room temperature for 12 hours, then the composite was aged at 110 °C for 12 h inside, taken out and ground, and finally calcined at 500 °C for 5 h in a muffle furnace. The Ni loadings

were 6.0 wt%, 8.0 wt%, 10.0 wt% and 12.0 wt% respectively.

Preparation of Ni-based catalysts with different supports

CeO₂ and ZrO₂ were used as carriers to determine the water absorption rate, respectively. Two Ni(NO₃)₃·6H₂O corresponding to 8.0 wt% Ni loading were weighed into different beakers according to the water absorption rate of the support to Ni(NO₃)₃·6H₂O. The deionized water is added to prepare the precursor solution, and the mass of the two beakers is weighed. After the Ni(NO₃)₃·6H₂O is completely dissolved, the precursor solution is impregnated with the two kinds of carriers. A homogeneous mixture of the solution was obtained by stirring with a magnetic stirrer for 20 min. Standing at room temperature for 12 h, then the composite was aged at 110 °C for 12 h. And it was finally calcined at 500 °C for 5 h by using a muffle furnace.

Evaluation of catalytic activity

Test of the catalytic performance of the catalysts was carried out in a fixed bed quartz reactor at atmospheric pressure in the temperature range of 600 °C to 750 °C. The catalyst (2g) was pretreated for 2 hours at 500 °C under hydrogen stream. The reducing mixture gas was a composite of H₂ and Ar (H₂: Ar=1:9, 300 mL/min) and brought in at a ramp rate of 10 °C/min from room temperature to 500 °C.

The schematic diagram of the fixed bed system is shown in Fig. 1. The system consists of three parts: a feeding unit, a methane steam reforming reactor and an analysis part. It is necessary to uniformly fill the catalyst in the middle of the reactor before the reaction. First, a certain amount of quartz sand is added to both ends of the flow channel. The particle size of the quartz sand is close to that of the catalyst particles to avoid the influence of internal diffusion, and then the catalyst sample is poured. The quartz sand not only plays a supporting role, but also helps the gas in the flow channel to be preheated. The outlet gases were detected online by a gas analyzer (Gasboard 3100).

Samples characterization

Powder X-ray diffraction data (XRD) were collected in the Philips X'Pert PRO of PANalytical B.V. with Cu K α radiation ($\lambda = 0.1542$ nm) and a 2θ range of 10-90° to study the crystalline structure of the samples. The morphologies of the synthesized catalysts were studied by scanning electron microscopy (SEM, SUPRA 55 SAPPHIRE).

Samples catalytic evaluation

Conversion of methane (X_{CH_4}) was calculated as follows:

$$X_{CH_4} = \{[(nCH_4)_{in} - (nCH_4)_{out}] / (nCH_4)_{in}\} * 100\%$$

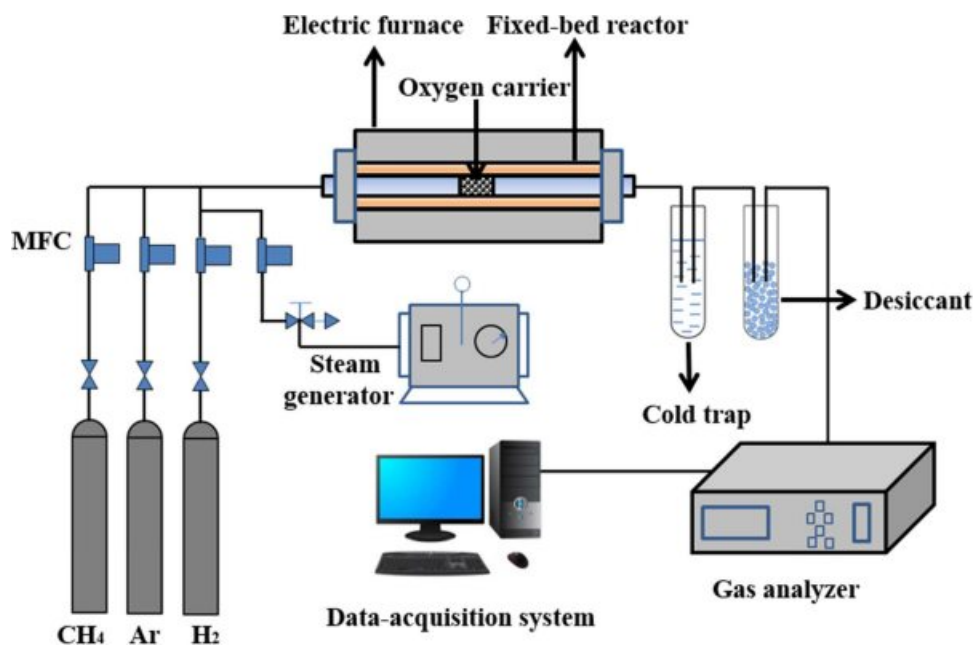


Fig. 1. Schematic diagram of the fixed bed system.

Hydrogen Selectivity (S_{H_2}) to the products was determined as:

$$S_{H_2}(\%) = \frac{(n_{H_2})_{out}}{\{(n_{H_2})_{out} + (n_{CO})_{out} + (n_{CO_2})_{out}\}} * 100\%$$

Hydrogen Yield (Y_{H_2}) was determined as:

$$Y_{H_2} = S_{H_2} * X_{CH_4} * 100\%$$

Results and Discussion

Catalyst characterizations

XRD diffraction result of the Ni/CeO₂ with different Ni loading of 6-12 wt% is displayed in Fig. 2. Compared with standard cards in XRD database, the prepared Ni/CeO₂ samples have a pure crystal structure. The diffraction

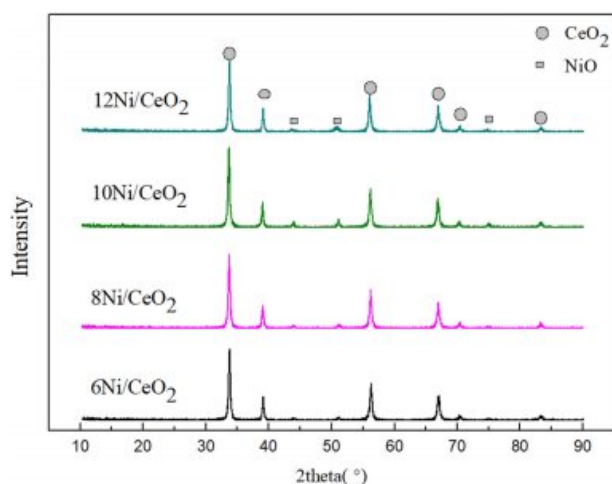


Fig. 2. XRD analysis of the Ni/CeO₂ catalysts.

peaks at $2\theta = 37.4, 43.4$ and 75.6° characterize the cubic NiO phase (JCPDS file no.47-1049) [23, 24]. The diffraction peaks corresponding to CeO₂ at $2\theta = 33.2, 56.6, 67.7,$ and 83.7° are significantly increased.

Fig. 3 shows the morphology of the 10% Ni/CeO₂ catalyst particles. It can be seen that the surface morphology of the carrier CeO₂ is porous, and NiO appears as a small particle with a size of around 50 nm embedded in the CeO₂ surface. The dispersion is relatively high, and no agglomeration and sintering occur.

Catalytic activity

Effect of different supports

Effect of different supports on catalytic activity of Ni-based catalysts was studied in the fixed-bed system.

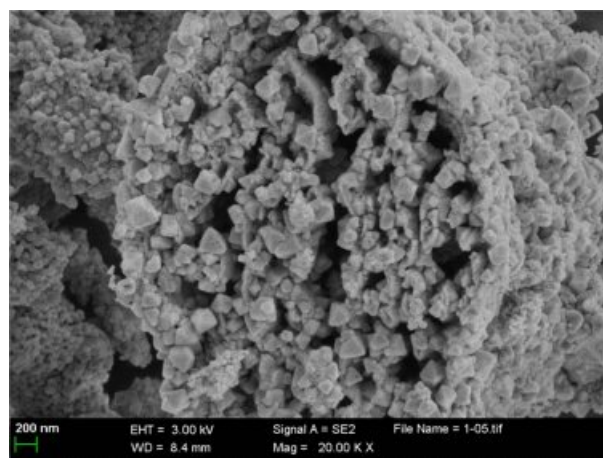


Fig. 3. Results of Ni/CeO₂ scanning electron microscopy with 10%Ni load.

The experimental reaction temperature was 750 °C, the water-carbon ratio $n(\text{H}_2\text{O}):n(\text{CH}_4)$ was 3, and the space velocity was $1,500 \text{ h}^{-1}$. According to Fig. 4, it can be seen that under this condition, the Ni/CeO₂ has a methane conversion rate and a hydrogen yield of 80.9% and 75.6%, respectively. In addition, for the Ni/ZrO₂ catalysts, the CH₄ conversion rate and the H₂ generation rate of the catalyst were 78.6% and 73.8%, respectively. Therefore, the nickel-based catalyst with CeO₂ as a support has better activity regardless of the methane conversion rate or the hydrogen yield. In addition, the hydrogen generation rate is also correlated with the hydrogen selectivity. The results show that the hydrogen selectivity of the catalyst with CeO₂ as the support is 93.4%, and the hydrogen selectivity of the catalyst supported by ZrO₂ is 93.9%. The selectivity will be slightly larger than the former, but the overall difference is small.

Effect of different reaction temperatures

The methane steam reforming reaction is an endothermic reaction and should be carried out in a high temperature atmosphere. A suitable temperature is favorable for the reaction to generate hydrogen and carbon monoxide. When the temperature is too high, it will cause carbon deposition in the methane cracking, and the active component Ni will also be sintered, which will affect the catalytic performance and the high temperature will also threaten the life of the experimental equipment. If the temperature is too low, carbon monoxide will be decomposed to form carbon deposits, which is the main cause of carbon deposition in the catalyst, which in turn affects the catalytic performance. Therefore, the reaction temperature is a very important reaction condition in the MSR reaction.

Fig. 5 demonstrates the comparison of performance of 10% Ni/CeO₂ catalysts at reaction temperatures of 650 °C, 700 °C and 750 °C ($n(\text{H}_2\text{O}):n(\text{CH}_4)=3$, a space velocity of $1,500 \text{ h}^{-1}$).

According to Fig. 5, it is found that the CH₄ conversion

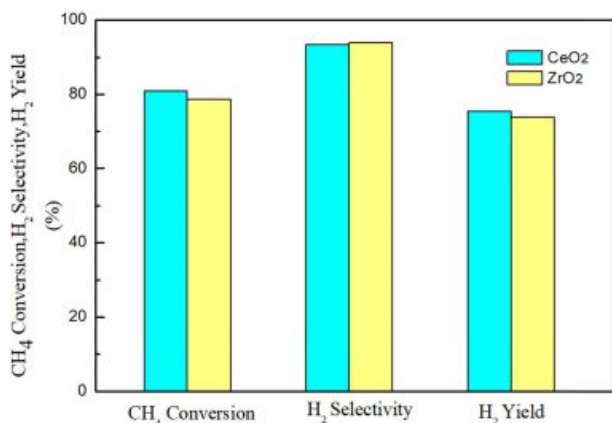


Fig. 4. Comparison of catalytic performance of and ($n(\text{H}_2\text{O}):n(\text{CH}_4)=3$; GHSV = $1,500 \text{ h}^{-1}$; $T = 750 \text{ °C}$).

rate and the H₂ generation rate increase with the increase of temperature. The methane conversion rates are 69.1%, 74.6% and 82.4% at the temperatures of 650 °C, 700 °C and 750 °C, respectively. The CH₄ conversion rate increased by 5.5% when the temperature was raised from 650 °C to 700 °C, and the CH₄ conversion rate increased by 7.8% when the temperature was raised from 700 °C to 750 °C. The rate of increase is more obvious when the temperature is raised from 700 °C to 750 °C. As for the hydrogen generation rate, the corresponding hydrogen generation rates are 45.5%, 59.1%, and 76.1% at the temperatures of 650 °C, 700 °C and 750 °C, respectively. Therefore, 750 °C was selected as the optimal temperature for Ni/CeO₂ catalysts. The reaction temperatures of the following experiments were set to 750 °C.

Effect of loading different amount of active components

Generally, the larger the active component loading at the same mass of the catalysts, the larger the particle

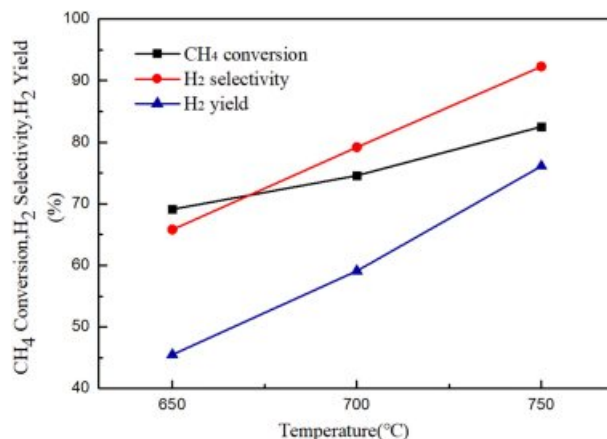


Fig. 5. Methane conversion and H₂ yield at different temperature ($n(\text{H}_2\text{O}):n(\text{CH}_4)=3$, GHSV = $1,500 \text{ h}^{-1}$).

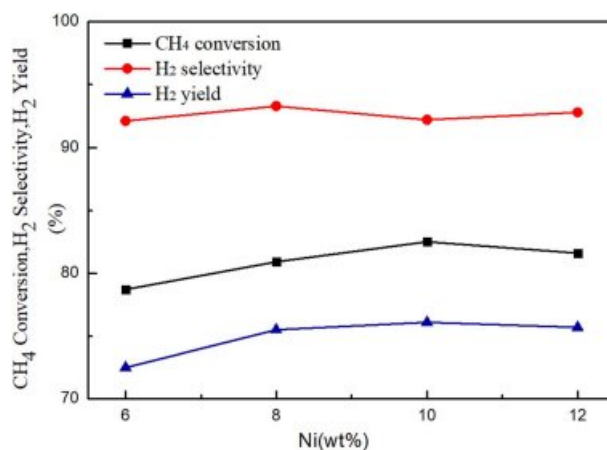


Fig. 6. Methane conversion and H₂ yield/selectivity for different wt % Ni loading ($n(\text{H}_2\text{O}):n(\text{CH}_4)=3$; $T = 750 \text{ °C}$).

diameter of the active component and the corresponding catalytic performance will be better, but when the loading is too large, the active component will aggregate. The active component in this experiment is Ni, which is easy to bring to aggregation and sintering. If the load is too large, it is easy to produce carbon deposits, resulting in a decrease in catalyst performance. Therefore, a suitable Ni loading amount on catalyst plays a crucial role in MSR.

This part mainly investigates the effect of loading of different active components on performance of Ni/CeO₂ with Ni content of 6%, 8%, 10% and 12% respectively (at temperature of 750 °C; n(H₂O): n(CH₄) = 3; and GHSV = 1,500 h⁻¹). Fig. 5 shows the comparison of catalytic capability of 6% Ni/CeO₂, 8% Ni/CeO₂, 10% Ni/CeO₂ and 12% Ni/CeO₂ under the same conditions.

As seen in Fig. 6, the CH₄ conversion rate and H₂ yield are higher at the temperature of 750 °C. The results indicate that the activity increases with the increase of Ni loading from 6% to 10% and the reactivity decreases for the higher loading content of 12% of Ni. The catalysts containing 10% Ni showed the highest CH₄ conversion rate and the H₂ yield among the samples. It can be seen that the CH₄ conversion rate and the H₂ generation rate have a significant increase in the Ni loading from 6% to 10%, which is directly related to the increase of Ni loading, but when the Ni loading is increased from 8% to 10%, the increase rate of hydrogen generation rate in the range is less than 1%. It also can be seen that the hydrogen selectivity decreases from 93.4% to 92.3% when the Ni loading is increased from 8% to 10%. When the Ni loading was continuously increased to 12%, it was found that the CH₄ conversion rate and the H₂ yield were lower than the Ni loading amount of 10%. The reason might be that the catalyst agglomerates to produce agglomerates as the Ni loading becomes larger. The carbon deposition reaction occurs to deteriorate the catalytic performance.

Effect of GHSV

Fig. 7 shows the catalytic performance comparison of methane steam reforming reactions with different GHSV of 1,500 h⁻¹, 2,000 h⁻¹ and 2,500 h⁻¹, respectively. Results show that the CH₄ conversion of methane steam reforming reactions at GHSV of 1,500 h⁻¹, 2,000 h⁻¹ and 2,500 h⁻¹ were 82.5%, 80.2%, and 76.7%, respectively. In addition, the hydrogen yield decreased by 1.9% with the GHSV changed from 1,500 h⁻¹ to 2,000 h⁻¹, while the hydrogen yield decreased by 4.7% from 2,000 h⁻¹ to 2,500 h⁻¹, which is the same as that of the methane conversion. Overall, GHSV of 1,500 h⁻¹ corresponds to the best performance of the catalyst among the conditions.

Stability tests

The methane conversion rate is an important parameter for the stability of the catalyst. An experiment was

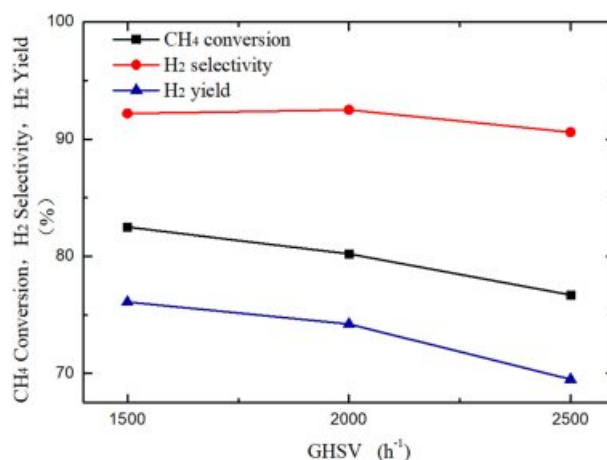


Fig. 7. Effect of GHSV on methane conversion and H₂ yield/selectivity of 10Ni/CeO₂(n(H₂O): n(CH₄) = 3; T = 750 °C).

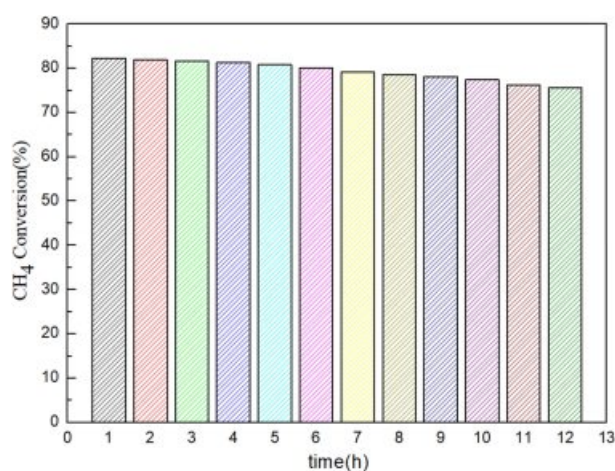


Fig. 8. Stability of catalysts for 10%Ni/CeO₂, Reaction conditions: T = 750 °C, n(H₂O): n(CH₄) = 3, GHSV = 1,500 h⁻¹.

conducted to evaluate the stability of the catalyst at 750 °C for 12 h under flow (10%Ni/CeO₂, n(H₂O): n(CH₄) = 3, and GHSV = 1,500 h⁻¹). The experimental results are shown in Fig. 8. The catalytic activity remained unchanged within 6 h, but the conversion of CH₄ decreased slightly (about 9%). This stability may be related to the small active NiO locations, which are highly uniformly dispersed on the cerium support and have high sintering resistance.

Conclusion

Ni/CeO₂ Nanocrystalline catalysts with different Ni loadings (6, 8, 10, and 12%) were synthesized by a wetness impregnation method for the methane steam reforming (MSR) process. The catalytic performance of Ni/CeO₂ catalyst was studied. XRD results approved the formation of the nanocrystalline of the prepared catalysts. It was shown that the 10 wt% Ni/CeO₂ provided the optimal catalytic activity among the catalysts with

different Ni loadings. The optimal reaction conditions for MSR by Ni/CeO₂ catalyst was as follows: 10 wt %Ni/CeO₂, 750 °C, 1,500 h⁻¹. The stability test for 12 h at 750 °C demonstrated excellent thermal stability of the resulted Ni/CeO₂ catalysts.

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