Study on Catalyst Performance of Compact Methane Reformer with Nickel Loading

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Abstract. The compact methane reformer has the advantages of small size and high efficiency, making it possible to produce hydrogen on the fuel cell operating site. The development of a reforming catalyst with good selectivity and high stability is of great significance for the industrialization of the reformer. Among them, the nickel content is an important factor affecting the performance and cost of the catalyst. A compact methane reformer experimental platform was designed and built, and Ni/CeO$_2$ catalyst was prepared by equal volume impregnation method. The optimum loading of Ni was determined by experiments to be 10%. The mechanism of the effect of Ni loading on the catalytic performance was studied by XRD and SEM crystal phase analysis.

1. Foreword
In recent years, with the increasing attention paid to energy conservation and environmental protection, designing and developing new energy sources has become an important research project in the domestic and international scientific and technological circles. Among many options, fuel cells have broad application prospects in the transportation industry and distributed energy because of its advantages of high efficiency and cleanliness$^{[1,2]}$. Hydrogen is the main raw material of the fuel cell, which has low density and high risk and is not conducive to transportation and storage. Therefore, using a wide range of sources and low cost of raw materials to produce hydrogen on the fuel cell work site has become an urgent problem to be solved$^{[3,4]}$.

Natural gas (methane generally accounts for more than 98%) plays an important role in China's energy structure, which is low in price and easy to obtain. Using methane to produce hydrogen in the industry has a long history, and the research on production processes and catalysts has been relatively mature. However, the oversized equipment of industrial product is the biggest obstacle of hydrogen production on the fuel cell work site$^{[5]}$. In recent years, the emerging compact methane reformer has the advantages of small size and high efficiency, which makes using methane to produce hydrogen on-site come ture$^{[6]}$.

2. Experimental System and Experimental Scheme

2.1. Compact Methane Reformer Structure
Figure 1 is a schematic diagram of a compact methane reformer. The reformer is connected in parallel by a plurality of units, each unit consisting of a combustion duct and a reforming duct, the two ducts being separated by a thin metal plate. In the combustion pipeline, when methane gas and air flow in the main flow direction, a catalytic combustion reaction occurs in the catalytic layer sprayed on the
surface of the metal plate, and the heat of reaction is transmitted to the catalytic layer of the reforming pipe through the metal plate to supply methane and water vapor. A reforming reaction takes place. The thickness of the metal sheet reaches the order of mm, which effectively increases the heat transfer efficiency and also greatly reduces the size of the reformer.

Figure 1. Schematic diagram of Marine compact methane reformer.

2.2. Experimental System Schematic
The design diagram of the experimental bench is shown in Figure 2. The device is divided into three parts: a feeding device, a methane steam reforming reactor and an analysis device. Methane, N₂ (protective gas) and H₂ are controlled by the mass flow controller and read by the mass flow meter. The water vapor is generated by the water pump and the steam generator. The two raw materials are passed through the three-way valve and all flow into the same pipe. Mix evenly in the subsequent lines. The heat of the methane steam reforming reactor is supplied by a tube furnace which is placed in a constant temperature zone of the tube furnace to maintain a constant reaction temperature. The raw gas flows into the reactor through the preheating line to a temperature close to the reaction to carry out a reforming reaction. The effluent mixed gas is first condensed and dedusted by a pretreatment device, and the remaining reaction products are passed into an online infrared gas component and a calorimeter to analyze the volume fraction of each component, and the results are recorded every second, and the analyzer is connected to a computer for data analysis.

Figure 2. Experimental flow chart.

2.3. Preparation of Catalysts with Different Ni Loadings Using CeO2 as Carrier by Equal Volume Impregnation
According to the Ni loading amount of 6.0wt%~12.0wt% (mass fraction, the same below), the desired Ni(NO₃)₂ was respectively weighed. H₂O was dissolved in n (ml) de ionized water. After being sufficiently dissolved, the Ni(NO₃)₂ solution was immersed on the CeO₂ support and aged at room temperature for 12 hours to produce more uniform crystals. Then, the oil was evaporated in an 80°C oil bath in an evaporator, and the evaporated mixture was dried in a blast drying oven at 120°C for 4 hours. After drying, the sample was ground into a powder and placed in a tube furnace and calcined for 4 hours with the heating rate that was 2°C/min (the same as the calcination rate) was from room temperature to 500°C. Then a Ni/CeO₂ catalyst sample (hereinafter abbreviated as Ni/CeO₂) was prepared.
2.4. Catalyst Characterization Instrument

2.4.1. Scanning Electron Microscope (SEM). The morphology of the catalyst was examined using a scanning electron microscope of the model of SUPRA 55 SAPPHIRE from Carl Zeiss, Germany, with a scan voltage of 3-20 kV.

2.4.2. X-ray Diffraction (XRD) Analysis. The catalyst crystal phase was characterized using an X-ray diffractometer model of D/MAX-Ultima+ by Nippon Ricoh Co., Ltd. with a scanning step size of 0.02° and a scanning range of 10°-90°.

2.5. Experimental Result Evaluation and Analysis Method
The experiment investigated the catalytic performance and working conditions of the catalyst by investigating the conversion rate of CH₄, the amount of H₂ produced, and the ratio of H₂ to CO in the synthesis gas. The calculation formula is as follows:

Methane conversion rate expression:

\[
\text{CH}_4(\%) = \frac{\text{CH}_4(\text{inlet}) - \text{CH}_4(\text{outlet})}{\text{CH}_4(\text{inlet})} \times 100\%
\]

Hydrogen generation rate expression:

\[
\text{H}_2(\%) = \frac{\text{H}_2(\text{outlet})}{\text{CH}_4(\text{inlet}) - \text{CH}_4(\text{outlet})} \times 100\%
\]

The hydrogen production rate is the hydrogen production compared to the methane consumption, which means the hydrogen production corresponding to the methane per unit molar flow. Therefore, when the conversion rate of methane is lowered, the hydrogen production rate remains unchanged, but the actual hydrogen production decreases, mainly due to the decrease in the activity of the catalyst (carbon deposition, poisoning, etc.).

Carbon monoxide selective expression:

\[
\text{CO selectivity}(\%) = \frac{\text{CO}(\text{outlet})}{\text{CO}(\text{inlet}) + \text{CO}_2(\text{outlet})} \times 100\%
\]

3. Experimental Results and Analysis

3.1. Experimental Results of Catalytic Activity of Ni/CeO₂ under Different Ni Loadings
Under the conditions of a reaction temperature of 700°C, a pressure of 1 standard atmosphere, a water-carbon ratio of n (H₂O) / n (CH₄) of 3, and a GHSV of 1000 h⁻¹, the Ni loading is 6% to 12%. Ni/CeO₂ was tested and its catalytic performance is shown in Figure 3. It can be concluded from Figure 3 that when the Ni loading is 6%-10%, the conversion rate of methane increases with the increase of Ni loading, and the hydrogen production rate also increases greatly. When the Ni loading reaches 9%, it is produced. The hydrogen rate reached the highest value of 182.1%, and the methane conversion rate reached 73.6%. When the Ni loading continued to increase, the change of methane conversion rate was no longer obvious, and it decreased at 12%, and the hydrogen production rate also. From the CO selectivity analysis, it can be seen that as the Ni loading increases, the CO selectivity decreases first and then increases, and the minimum value is 22.97% at 9% (23.1% at 10%). At this time, the rate of water vapor reaction is relatively small.

The reasons for affecting Figure 3 are analyzed, mainly Ni content and dispersion. XRD analysis showed that the loading of Ni affected the dispersion of NiO on Ni/CeO₂. At the 6% Ni content, the increase in the loading amount causes the NiO grains to become larger, the active component and the active center to increase, and the methane conversion rate and the hydrogen production rate are greatly increased. However, when the Ni loading reaches 10%, since Ni itself has the property of easy aggregation and easy sintering, the NiO which continues to increase is sintered, and a large amount of
active components cannot uniformly cover the surface of the carrier, but gather in one place. The catalytic activity is decreased. At the same time, it is suspected that an excessive Ni loading will increase the carbon deposition reaction, thereby increasing the selectivity of the reaction to CO, which may affect the activity of the catalyst. Studies have shown that there is an optimum value for the Ni content in the nickel-based catalyst, which allows all active components to be uniformly dispersed at the active sites on the surface of the support, and neither the aggregation phenomenon nor the active center is obtained as much as possible.

Combined with experimental data analysis, comprehensive consideration can be concluded that the most reasonable Ni loading in Ni/CeO$_2$ is 10% under suitable conditions.

![Figure 3. Catalytic properties of catalysts with different Ni loads for methane steam reforming.](image)

3.2. Crystal Phase and Structure of Ni/CeO$_2$ under Different Ni Loadings

3.2.1. XRD Analysis. The results of XRD analysis of each Ni loading amount of Ni/CeO$_2$ can be compared by Figure 4. It can be seen that there are characteristic peaks of NiO at 2, 43.5°, 50.8°, and 75°, and characteristic peaks of CeO$_2$ exist at 2, 3, 3, and 38.5°, and no characteristic peak of Ni is found. It is indicated that the active material Ni is all present in the form of NiO in the Ni/CeO$_2$ catalyst. Longitudinal contrast, as the Ni loading increases from 6% to 10%, it can be seen that the characteristic peak of NiO is gradually becoming stronger, reaching a relative maximum value of 10%. At this time, the characteristic peak is high and sharp, and then the characteristic peak The change in intensity is no longer noticeable even at 43.5°. This is because at the beginning of Ni/CeO$_2$, as the Ni content increases, the grain size of NiO gradually increases, so that the characteristic peak is remarkably enhanced, and the NiO crystal plane of the surface is the most. However, when the Ni loading reaches 10%, the NiO characteristic peak no longer becomes strong and the shape is no longer sharp, and the peak width begins to increase. According to the Scherrer formula: the degree of broadening of the X-ray diffraction band and the grain size of the crystal In inverse proportion, it can be inferred that the continued increase in Ni content may not have a positive effect on the catalytic activity of Ni/CeO$_2$. At the same time, an excessive Ni content tends to cause aggregation of NiO particles, which will seriously affect the catalytic activity of Ni/CeO$_2$.

![Figure 4. XRD patterns of catalysts with different Ni loads.](image)
3.2.2. SEM Analysis. From the results of EDS spectrum in Figure 5, it can be roughly seen that the NiO crystal is uniformly distributed on the surface of the carrier CeO$_2$, and there is an active site on the surface of CeO$_2$, and the content of NiO around it is relatively high around this active site. Figure 6 and Figure 7 show the morphology of the 10% Ni/CeO$_2$ catalyst particles. It can be seen that the surface morphology of the carrier CeO$_2$ is porous, and NiO is a small particle with a size of about 50 nm embedded in the surface of CeO$_2$. It is relatively high, and there is no phenomenon of agglomeration and sintering.

4. Conclusion
CeO$_2$ was used as the carrier in the nickel-based catalyst under the condition of compact methane reformer. The optimum loading of Ni was 10%, the conversion of methane was 73.6%, the hydrogen production rate was 182.1%, and the carbon monoxide selectivity was 23.1%. The catalyst was characterized by XRD and SEM, and the main components, NiO dispersion and surface morphology of the prepared catalyst were obtained.

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