Improvement of the stability of a ZrO\textsubscript{2}-modified Ni–nano-CaO sorption complex catalyst for ReSER hydrogen production

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A Ni–nano-CaO sorption complex catalyst was modified with ZrO\textsubscript{2} to improve its stability for use in hydrogen production from steam methane reforming (SMR). Nano-ZrO\textsubscript{2} was introduced into a support containing nano-CaCO\textsubscript{3} and Al\textsubscript{2}O\textsubscript{3}. The sorption complex catalyst, ZrO\textsubscript{2}–Ni–nano-CaO, was prepared by infusing Ni into the ZrO\textsubscript{2}–nano-CaO support, followed by calcination. The catalyst was evaluated with a bench-scale fixed bed reactor under the following reaction conditions: a temperature of 600 °C, a steam–carbon mole ratio of 4:1, a gas hourly space velocity of 1800 h\textsuperscript{-1}, and a regeneration temperature of 800 °C. The reaction was performed under an atmosphere of nitrogen. The ZrO\textsubscript{2}-modified sorption complex catalyst could achieve 20 cyclic runs of ReSER hydrogen production, while the sorption complex catalyst without the ZrO\textsubscript{2} modification rapidly deactivated after three cyclic runs. Brunauer–Emmer–Teller analysis showed that the catalyst surface area of the new catalyst had increased. Furthermore, the addition of ZrO\textsubscript{2} could prevent the formation of NiAl\textsubscript{2}O\textsubscript{4} in the sorption complex catalyst, which we believe to be the main cause of the improvement in the catalyst stability.

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1. Introduction

Hydrogen plays an important role in the petroleum refining and chemical engineering industries, as well as its potential in a future hydrogen-economy. The current commercial production of hydrogen requires fossil fuels as feed material. Specifically, about 70% of the world’s commercial hydrogen is produced by the steam methane reforming (SMR) method. The sorption-enhanced reforming process (SERP) is a developing technique for hydrogen production that is based on the SMR method. Advantages of the SERP technique include a shorter process time, a decrease in the reforming reaction temperature, and an increase in energy efficiency. Since its initial discovery, this method has become an area of intense interest [1–3].

Studies on the SERP technique focus on the development of high temperature, over 600 °C, CO\textsubscript{2} adsorbents. These adsorbents are used to capture the CO\textsubscript{2} released from the reforming reaction by mixing the CO\textsubscript{2} with a Ni-based reforming catalyst [4–6]. More exactly, the CaO-based CO\textsubscript{2} adsorbent is the reactive adsorbent, and then reaction of this adsorbent in capturing CO\textsubscript{2} at high temperatures has been widely studied [7–15]. In our previous study, we proposed a new process that we refer to as reactive sorption-enhanced reforming (ReSER), which uses nano-CaO as the CaO-based CO\textsubscript{2} adsorbent [16–19]. A significant feature of the ReSER process is the rapid reaction of nano-CaO with CO\textsubscript{2}, and achieves the high conversion of CaO in short time. This reaction occurs quickly and results in a rapid reforming reaction for hydrogen production. We also proposed the preparation of a sorption complex catalyst wherein the catalyst contained both nano-CaO and Ni as the adsorbent and catalyst components, respectively. The sorption complex catalyst can be used in dual fluid-bed reactors to meet the
requirements of the CaO carbonation and the CaCO₃ calcination processes for ReSER hydrogen production. This catalyst can also circumvent the differences between the density of the CaO-based CO₂ adsorbent and the Ni catalyst during the operation.

Satrio et al. [20,21] studied a core-shell Ni–CaO sorption complex catalyst that was prepared from a drum. Approximately 94–96% (v/v) hydrogen was obtained using this sorption complex catalyst, under temperatures of 520–650 °C at atmospheric pressure on a bench-scale fixed bed reactor. We also used an extrusion method to make the sorption complex catalyst and obtained 95% (v/v) hydrogen when evaluating it on a fixed bed [22]. However, in general the study of the sorption complex catalyst is still in its infancy, and to date no research has yet been reported on the stability of the complex catalyst.

ZrO₂ has outstanding properties in oxygen ion delivery and a high chemical stability. It has been successfully used in the modification and improvement of the lifetime of Ni catalysts in the SMR reaction [23–26], and a number of studies on the ZrO₂–Ni–CaO catalyst system have been reported [27–33]. For instance, Seo used CaO to render the Ni–ZrO₂ catalyst more stable for a methane CO₂ reforming reaction [27]. Bellido et al. studied the function of CaO on a ZrO₂ support for an ethanol synthesis of methyl-carbonate from propylene carbonate [30,31], and these results revealed that the addition of CaO could improve anti-carbonation properties and extend the lifetime of the catalyst.

In this study, a nano-CaO catalyst, which has properties different from those in the aforementioned studies, was introduced in the sorption complex catalyst in the reaction of CaO with CO₂. The nano-CaO content was above 30 wt%. The ZrO₂-modified Ni–CaO sorption catalytic complex and its potential to improve the stability of the catalyst during ReSER hydrogen production were examined. The reactive relationship of CaO, NiO, and ZrO₂ in the catalyst was also studied.

2. Materials and methods

2.1. Reagents and instruments

Nano-CaCO₃ (>95 % purity, Hu Zhou Ling Hua Ltd., China), with a particle size of 70 nm, was used as the nano-CaO-based adsorbent precursor. ZrOCl₂·8H₂O (99% purity, Sinopharm Chemical Reagent Co. Ltd.) was used as the ZrO₂ precursor. Ni(NO₃)₂·6H₂O (98% purity, Shanghai HengXin Chemical Reagent Co., Ltd.) was used as the Ni source.

The Brunauer–Emmet–Teller (BET) surface area and the Barrett–Joyner–Halenda (BJH) desorption average pore diameter of the catalyst were measured using nitrogen physisorption at liquid N₂ temperatures with a Micromeritics BELSORP-mini II (BEL Japan, Inc.). The crystalline phases of the prepared adsorbent were determined using an X-ray diffractometer (XRD, D/MAX-RA, Rigaku, Japan). The reducibility of the catalysts were tested using a TP-5000 III for the temperature programmed reduction (TPR) process (Tianjin Xianquan Industry and Trade Development Co., Ltd.). The adsorption tube was filled with 50 mg of catalyst and placed under a gas feed of 5% H₂ in N₂. With a heating rate of 10 K/min, the temperature was increased from 373–1073 K. Morphology was investigated using transmission electron microscopy (TEM, JEM-1230, JEOL, Japan) and scanning electron microscopy (SEM, S-4800, HITACHI, Japan). The sorption capacities of the catalysts were measured through thermogravimetric analysis (TGA, Pyris 1, PerkinElmer).

2.2. Preparation of the sorption complex catalyst

2.2.1. Preparation of the ZrO₂-modified Ni–CaO sorption complex catalyst

To prepare the ZrO₂–CaO–Ni sorption catalyst, a solution of aqueous ammonia (25 wt%) was added into a zirconium oxychloride solution at 0.1 M to form a Zr(OH)₄ gel. Zr(OH)₄ gel was filtered and washed with deionized water until no Cl⁻ ion remained. The collected Zr(OH)₄ gel was then mixed with nano-CaCO₃ powder and aluminum gel additives. The mixed slurry was dried and pressed into a cylinder with a diameter of approximately 2 mm. The catalyst was then calcinated at 550 °C for 2–5 h to form the ZrO₂–CaCO₃ support. A 0.2 M Ni(NO₃)₂ solution was then prepared and infused into the ZrO₂–CaCO₃ support under an atmospheric of air; the resulting Ni content was 15 wt%. The catalyst was dried at 100–150 °C and calcinated at 500–800 °C to form a ZrO₂-modified Ni–CaO sorption complex catalyst, hence referred to as "cat-1."

2.2.2. Preparation of the Ni–CaO sorption complex catalyst

The preparation process for this catalyst is identical to that described above in Section 2.2.1, with the exception that the Zr(OH)₄ gel was not added. This Ni–CaO sorption complex catalyst is hence referred to as "cat-2."

2.3. Evaluation of ReSER hydrogen production

Evaluation of the sorption complex catalysts, cat-1 and cat-2, in the ReSER process was completed using the sequence shown in Fig. 1. A fixed bed reactor, created from a stainless steel tube with a size of φ 500 mm × 15 mm, was used in these reactions. The reactor bed was filled with 5 g (particle size 1 mm) sorption complex catalyst. GC analysis was used to analyze the components of the produced gas. Methane conversion and hydrogen concentration were defined by Eq. (1) where

\[
X_{\text{CH}_4} = \frac{F_{\text{out}} - F_{\text{out}1} \times y_{\text{CH}_4}}{F_{\text{CH}_4}} \times 100\% (1)
\]

\[
X_{\text{CH}_4} (\%) \text{ is the conversion of methane; } F_{\text{CH}_4} (\text{ml/min}) \text{ is the flow rate of methane; } F_{\text{out}} (\text{ml/min}) \text{ is the effluent flow rate of the product gas; and } y_{\text{CH}_4} (\%) \text{ is the methane content.}
\]

The catalyst was reduced at the temperature of the reforming reaction before it was used in the reforming reaction with H₂. The operating conditions were as follows: a temperature of 600 °C, a steam–carbon mole ratio of 4:1, a gas hourly space velocity of 1800 h⁻¹, a regeneration temperature of 800 °C, and an atmosphere of nitrogen at atmospheric pressure. Multiple reactions and regeneration runs were conducted to evaluate the stability of the sorption complex catalyst. For each reaction and regeneration cyclic run, the reaction was going on until the time showed H₂ content decreased to an equilibrium.
content without CO₂ capture. Similarly, the regeneration was going on until the time showed full CaCO₃ decomposition without CO₂ released.

3. Results and discussions

3.1. Evaluation of the ReSER hydrogen production

As shown in Fig. 1, methane from the cylinder mixed with the steam and entered the reactor from the top. According to the test conditions eliminating inner and outer diffusion [22], the evaluation conditions were set with the weight of the catalyst and feed flow at 0.167 g min/mL of methane. The other operation conditions include a temperature of 600 °C, a mole ratio of steam to water of 4:1, and a regeneration temperature of 800 °C under atmospheric pressure. The first cat-1 ReSER test result is shown in Fig. 2. The maximum hydrogen content was 97.3% (v/v) in the section of the reactive sorption-enhanced reforming. The calculated conversion of methane was 93.7%.

Similarly, the results of the first sorption complex catalyst, cat-2, in the ReSER test are shown in Fig. 3. The maximum hydrogen content produced from the sorption-enhanced reforming is 96.8% (v/v), and the calculated conversion ratio of methane is 93.4%. In this case, however, the catalyst activity decreased sharply within 10 min of the decay of the CO₂ sorption capacity.

Twenty runs of the ReSER hydrogen production for cat-1 were carried out under the same operating conditions. The results are shown in Fig. 4. The hydrogen content produced in the reactive sorption-enhanced reforming reaction section by cat-1 was over 95% (v/v), and the methane conversion ratio was over 90% for each run. The maximum hydrogen content was 97.3% (v/v), and the methane conversion ratio was 93.7%. The hydrogen contents of the three runs were 96.8% (v/v), 95.1% (v/v), and 90.3% (v/v), respectively. The cat-1 catalyst showed an improvement in stability. After 20 runs, cat-1 was named cat-1-used and cat-2, after three runs, was named as cat-2-used. We used a thermogravimetric analyzer (TGA) to analyze the sorption capacity in an attempt to understand the observed differences in catalyst deactivation. The sorption capacities of cat-1-used and cat-2-used were measured at 2.11 and 3.09 kmol/kg, respectively. Two used sorption catalytic complex were found to have enough CO₂ sorption capacity to enhance the reforming reaction. The deactivation of cat-2 was mainly attributed to the catalytic components rather than to
3.2. Reasons for stability improvement

The deactivation of SMR catalysts is normally attributed to the coke. Three grams of cat-1-used and cat-2-used samples were placed in an oven and heated, in air, to 300 °C to burn the coke. After 1 h of heating, the cat-1-used and cat-2-used samples were weighed, and the lost weights were regarded as the coke. The results showed that the coke contained in cat-1-used and cat-2-used were 0.6 and 1.0%, respectively. We also use thermal gravity detective temperature analysis (TG–DTA) to test the coke content. The coke content can be calculated by dividing the catalyst weight decrease after burning by the original catalyst weight. This result showed that the coke content is 0.77%. According to the principle that the coke content should be over 10% to deactivate catalyst, which is a higher percentage than we saw in either catalyst sample, we concluded that catalyst deactivation was not being caused by coke formation. A detailed analysis using TEM, XRD, BET, and TPR was performed for the sorption complex catalysts cat-1, cat-2, cat-1-used, and cat-2-used to determine and illustrate the reasons for the different stabilities of the catalysts.

3.2.1. TEM test results

The prepared Zr(OH)₄ gel was analyzed by TEM (Fig. 5). The particle size of Zr(OH)₄ was lower than 10 nm, which was much smaller than the nano-CaCO₃ particle size. Hence, Zr(OH)₄ could be attached to the surface of the nano-CaCO₃ particle. Fig. 6 shows the TEM image of the ZrO₂–CaCO₃ support. The cubic shape of the nano-CaCO₃ particle and the flocules on its surface were clearly seen as ZrO₂ particles. ZrO₂ was formed by heating and dehydrating Zr(OH)₄ at 550 °C. The cat-1 TEM image is shown in Fig. 7. For the sorption complex catalyst, not only are the cubic shapes of the nano-CaCO₃ particles and the flocules seen, but also the dark points. These dark points were NiO crystals that were distributed on the surface of the nano-CaCO₃ particles. The size of the NiO crystal was found to be approximately 10–20 nm. Similarly, the cat-2 TEM image was measured (Fig. 8). There was no
flocculent ZrO$_2$ on the nano-CaCO$_3$ particle surface of cat-2, as compared to that of cat-1.

The cat-1-used TEM image is shown in Fig. 9. The cat-2-used TEM image is likewise shown in Fig. 10. Fig. 9 shows that the nano-CaCO$_3$ particles retained their cubic shapes, and that there were a number of pore channels in the nanoparticle. These channels might be formed through multiple carbonations and calcinations. Alternatively, Fig. 10 shows that there were no pore channels in cat-2-used, which we assume is because only three runs were tested for the ReSER hydrogen production. Furthermore, the NiO crystal size of cat-1-used increased compared to cat-1. Similar results were reflected in Fig. 10 for cat-2-used. To determine the NiO crystal size precisely, the NiO crystal size before and after deactivation was measured using XRD, and the NiO crystal size was calculated using the Scherrer equation.

3.2.2. XRD test results

The analytical results of the XRD test are shown in Fig. 11. In these data, cat-1 and cat-2 were found to contain only NiO crystal. No Ni existed in the catalyst before the reduction. Alternatively, cat-1-used contained a large amount of active Ni crystal, while cat-2-used had only a few. An additional important outcome of the XRD test was that while there was no spinel (Ni$_2$AlO$_4$) present in the cat-1-used sample, a spinel was found in the cat-2-used sample. Therefore, ZrO$_2$ could protect the formation of a spinel in the sorption catalytic complex and thus improve the catalyst stability under the same operating conditions.

The crystallite sizes of NiO and Ni in both the fresh and the spent catalysts were calculated using the Scherrer equation (Table 1). Table 1 summarizes the NiO and Ni crystallite sizes of both cat-1 and cat-2. The crystal size of NiO (17.68 nm) in cat-1 was a little larger than that of cat-2 (12.12 nm). The crystal sizes of both NiO and Ni were found to increase after several reaction cycles in the two catalysts. The ZrO$_2$-modified sorption complex catalyst was not useful in limiting the growth of the Ni crystal. The Ni crystal size continued to increase during the ReSER process.
3.2.3. BET test results

Table 2 summarizes the surface area, pore volume, and pore size data obtained from the BET test on cat-1 and cat-2. From these data, cat-1 clearly has a higher surface area when compared to cat-2; the surface area of fresh cat-1 (69.5 m²/g) was twice that of cat-2 (30.8 m²/g). According to our previous results, the crystallite size of ZrO₂ was about 10 nm, much smaller than that of nano-CaCO₃. When Zr(OH)₄ was calcinated at 823 K, Zr(OH)₄ was dehydrated to form ZrO₂ and release water molecules. The emersion of these water molecules formed pores and increased the surface area. The cat-1 and cat-2 surface areas decreased after several ReSER reaction cycles. However, cat-1 maintained a surface area of 37.7 m²/g after 20 cycles, while that of cat-2 decreased to 18.1 m²/g after only three cycles. Therefore, the increase in the surface area was found to be the main factor contributing to high catalyst stability. Meanwhile, a decrease in the surface area of the catalyst predominantly accounted for the catalyst’s deactivation.

3.2.4. TPR test results

Fig. 12 shows the TPR results of cat-1 and cat-2, with curve ‘a’ representing cat-1 and curve ‘b’ representing cat-2, respectively. NiO/Al₂O₃ has several known and distinct peaks [27]. The TPR patterns of cat-2 also showed three distinct peaks. The first peak maximum at 329.8 °C was attributed to the reduction of free NiO species, and the second peak maximum at 649.8 °C could be assigned to the existing NiAl₂O₄ species, which could be formed by NiO and Al₂O₃ [17]. Cat-1 contained only two distinct peaks; the first peak, which was lower than that of cat-2, appeared at 279.8 °C and was attributed to the reduction of free NiO species. The second peak appeared at 556.8 °C and was attributed to the NiO₂ species. The existence of ZrO₂ in the CaCO₃-Al₂O₃ layer prevented NiO and Al₂O₃ from interacting and forming NiAl₂O₄, which could reduce the catalyst activity. TPR analysis was also completed on the used cat-1 and cat-2. The NiAl₂O₄ species could not be found in the cat-1-used sample; however, the NiAl₂O₄ species was found to exist in the cat-2-used sample.

4. Conclusion

Investigation of a ZrO₂-modified Ni-nano-CaO sorption complex catalyst showed the encouraging result that 20 ReSER cyclic runs could be achieved when, which is a significant improvement when compared to the Ni-nano-CaO sorption complex catalyst without ZrO₂, which produces only 3 cyclic runs. The preparation of the 10 nm Zr(OH)₄ gel is used as the precursor of the ZrO₂, which modifies the Ni-nano-CaO sorption complex catalyst, is significant. It can efficiently increase the surface area of the catalyst by the decomposition of Zr(OH)₄. ZrO₂ between NiO and Al₂O₃ can prevent the formation of NiAl₂O₄ as well as subsequently increase the stability of the ZrO₂-Ni-CaO catalyst system in the ReSER process. The addition of ZrO₂ can significantly extend catalyst lifetime.
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