Effect of in-situ carbon dioxide sorption on methane reforming by nickel-calcium composite catalyst for hydrogen production

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Abstract. Hydrogen production plays an important role in hydrogen energy development. The steam reforming reaction is an efficiency way for hydrogen production via thermochemical method. But the hydrogen concentration was limited to be about 70% because of thermodynamic equilibrium. In order to avoid equilibrium limiting, the by-product CO\(_2\) removal during reaction was a suitable solution that drives the reaction to the right. In this study, the steam reforming of methane by in-situ CO\(_2\) sorption was investigated. The CaO material was used as CO\(_2\) acceptor because of its high capacity, fast kinetics and generality. The reforming catalysts were prepared by simple physical mixing of the 20 wt.% Ni/Al\(_2\)O\(_3\) catalyst and CaO sorbents. The steam reforming of methane experiments was carried out by a fixed bed reactor. The experimental results indicate that the steam reforming of methane via in-situ CO\(_2\) sorption obviously obtained the H\(_2\) purity above 95% higher than conventional reaction without in-situ CO\(_2\) removal (~72% H\(_2\)). The impurities involving CO and CO\(_2\) during reaction were suppressed below 0.5% before CO\(_2\) sorbent saturation. In this work, the highest H\(_2\) purity and CH\(_4\) conversion were found to be 98.4% and 95% at 873K under steam/carbon ratio of four conditions. The methane steam reforming with high conversion strongly depended on the CO\(_2\) capture performance. The cause was attributed to the equilibrium limiting of reaction overcoming by in-situ CO\(_2\) sorption. It is also found that the product components and methane conversion was insignificantly affected in the range of space velocity from 7200 to 19200 cm\(^3\)/hr/g.

Keywords: hydrogen production, steam reforming, sorption

1. Introduction
Hydrogen is not only an important raw material in chemical industries, but also an ideal energy carrier. Recently, the demand of hydrogen is expected to be continuously increasing because of hydrogen energy development. There are possible ways for hydrogen production such as steam reforming, water electrolysis, ammonia dissociation et al. [1]. In fact, the steam reforming (SR) of methane process have been used for several years, which is a commercial process for hydrogen production. Generally, the SR of methane process consists of endothermic methane-steam reaction and exothermic water gas shift reaction [2]:

\[
\text{Methane-steam reaction: } \quad \text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2 \quad \Delta H_{298K} = +206.3 \text{ kJ/mol} \tag{1}
\]

Water gas shift (WGS) reaction:
\[
\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H_{298K} = -41.1 \text{ kJ/mol} \quad (2)
\]

Overall SR of methane reaction:
\[
\text{CH}_4 + 2\text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 4\text{H}_2 \quad \Delta H_{298K} = +165 \text{ kJ/mol} \quad (3)
\]

According to eq. (3), for complete methane conversion, one mole methane can produce four moles hydrogen. Unfortunately, these disadvantages involving equilibrium limiting, coke formation and low conversion were obviously found in the common SR of methane process. Recently, the promising method called “sorption enhanced process” was desirable for hydrogen production [3]. According to Le Chatelier’s principle, the products during reaction were removed, the equilibrium of reaction can be shifted towards the improvement of hydrogen production. For the SR of methane reaction, the products like as \( \text{CO}_2 \) was available to be captured by the \( \text{CaO} \) materials [4]. The reaction [5] is written by:
\[
\text{CaO} + \text{CO}_2 \leftrightarrow \text{CaCO}_3 \quad \Delta H_{298K} = -178 \text{ kJ/mol} \quad (4)
\]

According to eq. (3) and eq. (4), the “sorption enhanced steam reforming” (SESR) of methane reaction is written by:
\[
\text{CH}_4 + 2\text{H}_2\text{O} + \text{CaO} \leftrightarrow \text{CaCO}_3 + 4\text{H}_2 \quad \Delta H_{298K} = -13 \text{ kJ/mol} \quad (5)
\]

According to eq. (5), the endothermic SR of methane reaction became to be exothermic due to \( \text{CO}_2 \) capture reaction contribution. The energy consumption of methane reaction can be significantly reduced. In order to obtain optimal SESR performance, the fast sorption/desorption kinetics and absence of diffusion limitation were essential for SESR reaction. Recently, the hybrid material comprising reforming catalyst and sorbents have been investigated by previous studies [6–9]. The high mass transfer rate was promising by using the hybrid composites with HTc-like structure (such as Ni-Ca\(_{12}\)Al\(_{14}\)O\(_{33}\)). For the SESR reaction, the \( \text{CO}_2 \) sorbent might be a key material that remarkably affected the mass transfer. Meanwhile, the cost and manufacturing method were also considered necessarily. The objective of this work is to develop the simple physical mixing method for the Ni/Al\(_2\)O\(_3\)/CaO composites catalyst preparation. The \( \text{CaO} \) material was employed to be a \( \text{CO}_2 \) sorbent because of fast sorption/desorption kinetics and low cost. The factors involving the molar ratio of steam to methane (S/C) and space velocity were studied in order to find out the suitable parameters. Additionally, the relationship between \( \text{CO}_2 \) capture capacity and operation factors was also discussed in this work.

2. Experiments

The Ni/Al\(_2\)O\(_3\)/CaO composites (denoted as SESR catalyst) were used to apply the methane reforming reaction in this work. The SESR catalyst was consisted of 20 wt.% Ni/Al\(_2\)O\(_3\) and CaO. The SESR catalyst was prepared by a simple mixture method. The 20 wt.% Ni/Al\(_2\)O\(_3\) powders were well-mixed with Ca(OH)\(_2\) precursor, then granulated to form cylinder shape with 2mm diameter. Finally, the samples were treated at 1023K in order to converse from the Ca(OH)\(_2\) to CaO species. The 80 wt.% CaO sorbent within the SESR catalyst was used.

The schematic diagram of SESR experiments was presented in Figure 1. The fifty grams of SESR catalyst were packed in a tubular reactor with diameter of 3 cm. The catalyst bed length was about 12 cm. Before reaction, the SESR catalysts were pre-treated at 1023K for several hours in a \( \text{H}_2 \) flow, in order to ensure complete reduction for Ni catalyst. All reaction experiments were operated at 873K. The online detector (MRU, Vario plus, resolution 0.01%) was employed to analyze the product components that have been dried by the condenser and the moisture trap.
3. Results and Discussions

The typical SESR of methane profiles were presented in Figure 2. It is clearly found that three behaviours occurred during the reaction. Under initial period (When CO$_2$ sorbent was available), high H$_2$ concentration was obtained during reaction. The by-products such as CO$_2$ and CO can be strongly suppressed. The most of reactant as CH$_4$ was completely reacted with steam. The residue CH$_4$ reactant was determined below 3% in the stream flow. Under the period II, the SESR performance began declining and transferred to the SR stage. Finally, the reaction became the common SR reaction (period III), because CO$_2$ sorbent was exhausted. It is noted that H$_2$ concentration of products under the SESR stage was above 95% higher than that under the SR stage (~70% H$_2$ concentration).

For the period II, it is also found the CO, CO$_2$, and CH$_4$ in a sequence of breakthrough. The results were conformed to eq. (1), eq. (2) and eq. (3). Under the SESR stage, the WGS reaction (eq. (2)) was firstly improved, then followed by the methane-steam reaction (eq. (1)). On the other hand, the WGS reaction efficiency were firstly declined, when CO$_2$ sorbent approached to saturation. The by-products were not availably suppressed.
43% and 66%, respectively. For other S/C ratio conditions, the CH$_4$ conversion of SESR reaction also was higher than that of SR reaction. The CH$_4$ conversion was enhanced about 20-30% via in-situ CO$_2$ sorption enhancement. The result indicates that the equilibrium limiting of SR reaction was an important role to suppress the reaction process. In this work, the maximum CH$_4$ conversion for SESR reaction was obtained to be ~95% under the S/C ratio = 4 and 873K condition.

The effect of space velocity on the CH$_4$ conversion for both SE and SESR reactions was presented in Figure 3(b). Obviously, the CH$_4$ conversion was insignificantly change at a range of space velocity from 7200 to 19200 cm$^3$/g/hr. The CH$_4$ conversions for the SE and SESR reaction kept to be ~60% and ~85%, respectively. The product components, CH$_4$ conversion, CO$_2$ capture capacity under the varied operation conditions were listed in Table 1. The CO$_2$ capture capacities were 35.4 wt.%, 36.6wt.% and 30.8 wt.% at the space velocity of 7200, 12000 and 19200 cm$^3$/g/hr, respectively. The lower capacity of CO$_2$ capture was clearly obtained at the space velocity of 19200 cm$^3$/g/hr. The result reveals the high space velocity was unfavourable for CO$_2$ capture by CaO sorbent.

As shown in Table 1, the H$_2$ concentration strongly depended on the ratio of S/C for SESR reaction. The H$_2$ concentration under different S/C conditions was ranked as S/C=4 > S/C=3 >S/C=2. The CO and CH$_4$ concentration were increased with decreasing the ratio of S/C. Because of CO$_2$ capture reaction by CaO, only ~0.3 wt.% CO$_2$ concentration was found in the product stream. The similar results were also reported by the previous papers [5-6]. Increasing the S/C ratio can improve the reactant conversion leading to the hydrogen yield increase. Moreover, it is also found that similar H$_2$, CO, CO$_2$, CH$_4$ concentrations were produced at the space velocity from 7200 to 19200 cm$^3$/g/hr. The result indicates that the S/C ratio was a significant factor for SESR of methane reaction, compared to the space velocity.

![Figure 3](image_url)

**Figure 3.** Effect of S/C ratio and space velocity on the CH$_4$ conversion for SE and SESR reaction (a) S/C ratio vs. CH$_4$ conversion (12000 cm$^3$/g/hr, 873K), (b) space velocity vs. CH$_4$ conversion (S/C=3, 873K)

| S/C | Space velocity$^a$ (cm$^3$g$^{-1}$hr$^{-1}$) | H$_2$ (%) | CO$_2$ (%) | CO (%) | CH$_4$ (%) | CH$_4$ conversion (%)$^b$ | CH$_4$ conversion (%)$^c$ | CO$_2$ capture capacity (wt.%)$^d$ |
|-----|----------------------------------------|-----------|------------|--------|------------|-------------------------|--------------------------|-------------------------------|
| 2   | 12000                                  | 89.4      | 0.3        | 0.4    | 9.9        | 66                      | 43                       | 33.8                          |
| 3   | 12000                                  | 96.6      | 0.3        | 0.3    | 2.9        | 89                      | 63                       | 36.6                          |
| 4   | 12000                                  | 98.4      | 0.3        | 0.1    | 1.1        | 95                      | 71                       | 33.6                          |
| 3   | 7200                                   | 95.9      | 0.2        | 0.2    | 3.7        | 85                      | 59                       | 35.4                          |
| 3   | 19200                                  | 95.5      | 0.2        | 0.1    | 4.2        | 84                      | 54                       | 30.8                          |

Note: all experiments were performed at 873K.

$^a$: (input flow)/ (Ni catalyst weight without sorbent);

$^b$: CH$_4$ conversion(%) under the SESR stage = (CH$_4$ input - CH$_4$ output)/ CH$_4$ input x 100%;

$^c$: CH$_4$ conversion(%) under the SR stage = (CH$_4$ input - CH$_4$ output)/ CH$_4$ input x 100%;
the data was calculated from the desorption process.

Figure 4 presents the H$_2$ and CO$_2$ product profiles under the varied space velocities. Obviously, the space velocity strongly affected the maintained times of SESR stage. The SESR stage times decreased with increasing the space velocity. The cause was attributed to the available CaO sorbent capacity that would be seen as a constant. For high space velocity condition, more CO$_2$ gases were produced during reaction, the CaO sorbent was fast to approach saturation. Therefore, the SESR stage times under the high space velocity condition was shorter than other low space velocity conditions.

![Figure 4. Effect of space velocity on the H$_2$ and CO$_2$ concentration product profiles for SESR of methane reaction (S/C=3, 873K)](image)

The summary of SESR performance for various SESR catalyst materials was listed in table 2. As shown in table 2, the H$_2$ concentration and CH$_4$ conversion were clearly found to be 80–97% and 80–99%, respectively. The visible differences in H$_2$ concentration and CH$_4$ conversion were obtained even using similar characteristic of catalyst and operating under same conditions. It is suggested that the homogeneity of composite comprising reforming catalyst and sorbent was a major reason. In our work, the H$_2$ concentration from SESR of methane reaction was 97% higher than previous papers [7-12] reported. The results were indirectly demonstrated that the Ni/Al$_2$O$_3$/CaO composites (prepared by our work) was well-mixing by simple physical mixture method, compared to the hybrid synthesis method.

| Reference | Catalyst | T (K) | S/C | H$_2$ (%) | CH$_4$ conversion (%) |
|-----------|----------|-------|-----|-----------|-----------------------|
| In this work | Ni/Al$_2$O$_3$/CaO mixing composites | 873 | 3 | 97 | 89 |
| [7] | NiO–CaO–Ca$_{12}$Al$_{14}$O$_{33}$ hybrid material | 923 | 3.4 | 90 | 80 |
| [8] | Ni-Al-Ca hybrid material | 923 | 4 | 96 | 99 |
| [9] | Ni-Al-Ca hybrid material | 823 | 6 | 94 | 96 |
| [10] | Ni/Al$_2$O$_3$/Li$_4$SiO$_4$ mixing composites | 823 | 3.5 | 93 | 80 |
| [11] | Ni-CaO-mayenite | 923 | 3 | 90 | 96 |
| [12] | NiO–CaO-Ca$_{12}$Al$_{14}$O$_{33}$ mixing composites | 923 | 3 | 80 | 93 |

*: space velocity: 12000 (cm$^3$ g$^{-1}$ hr$^{-1}$)
4. Conclusions
The Ni/Al₂O₃/CaO composite as SESR catalyst was investigated for the SESR of methane reaction. The SESR catalysts were prepared by the Ni/Al₂O₃ catalyst physical mixing the CaO sorbents. The SESR of methane experiments was carried out by a fixed bed reactor. And the different operation factors were discussed in this work.

The experimental results indicate that the SESR of methane by the Ni/Al₂O₃/CaO composite can obtain the product with H₂ concentration above 95%, due to in-situ CO₂ capture by CaO sorbent. Additionally, the CH₄ conversion under the SESR stage was found higher than that under the SR stage. In this work, the highest CH₄ conversion was obtained to be ~95% at 873K and S/C = 4 conditions. Meanwhile, the similar CH₄ conversions were found at a range of space velocity from 7200 to 19200 cm³/g/hr. The result is noted that the S/C ratio was a significant factor for SESR of methane reaction, compared to the space velocity.

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