Synthesis of Ni/Al2O3/CaO Composite Catalyst for Hydrogen Production by Steam Reforming of Ethanol

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Abstract. Improving the steam reforming of ethanol by Ni/Al2O3/CaO composite was investigated in this work. The CO2 sorbent plays a key role in the catalytic reaction enhancement. The reforming catalysts were prepared by the as-prepared 10 wt.% Ni/Al2O3 physical mixing with CaO sorbents (from Ca(OH)2 conversion). All reforming experiments were performed under 873K condition. In addition, the suitable parameters of mass ratio of Ni catalyst /CO2 sorbent (20 : 80 w/w) and steam / ethanol molar ratio of five were adjusted in this work. The results indicate that the steam reforming of ethanol via CO2 sorption enhancement obviously produced ~95% H2 greater than common steam reforming of ethanol (~72% H2). Other by-products involving CO2, CO and CH4 can be also obviously suppressed during reaction. For the sorption-enhanced steam reforming, the recyclability of CO2 sorbent is an important issue. The 10 cycles of reaction/regeneration at 873K and 1023K for the steam reforming of ethanol were tested. The results reveal the H2 concentration of products stably keeps above 90% during the cycles test. The performance of CO2 sorbent was insignificant change after 10 cycles. The average capture capacity of CO2 around 17.8 wt.% can be determined during cycles.

1. Introduction

Hydrogen is a good energy carrier with high heat value. Several potential feedstocks involving methane, methanol, ethanol and biomass, have been considered to be applicable to generate hydrogen [1-2]. In fact, the ethanol that is a suitable resource with CO2 neutrality and renewability for hydrogen production can be produced from biomass such as corn, wood waste, municipal solid waste and so on [3]. Typically, the steam reforming (SR) is common method for hydrogen production from ethanol. The major steam reforming of ethanol reaction [3] is as follows:

$$\text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \leftrightarrow 2\text{CO}_2 + 6\text{H}_2$$

(1)

According to eq. (1), one mole ethanol reacts with three moles steam can obtain two moles carbon dioxide and six moles hydrogen. Actually, the reaction is hardly accomplished due to the equilibrium limiting of reaction and the undesired reaction occurrence. However, the undesired products such as CH4, CO, CO2, CH3CHO, coke et al., have been found during the SR of ethanol reaction. These impurities cause to increase the cost intensive purification unit in order to obtain high-purity hydrogen. The coke formation during reaction is other important problem for catalyst efficiency decay. Recently, the sorption-enhanced steam reforming (SESR) reaction has been developed in the past decade by previous papers [3-4]. Based on Le Chatelier’s principle, the CO2 products during reaction were removed, the equilibrium of reaction can be shifted towards the improvement of hydrogen production.
Moreover, the undesired reaction paths can be significantly reduced such as the coke formation. Recently, the other potential sources (such as methane, acetic acid, glycerol, bio-oil et al.) for hydrogen production by SESR technique also have been discussed by studies [5-6].

Indeed, the CO₂ acceptor remarkably affected on the SESR performance. Generally, the CaO material can be seen as a good sorbent, due to its high CO₂ capture capacity, fast sorption/desorption kinetics and low cost [7]. The reaction [3] is written by:

\[
\text{CaO} + \text{CO}_2 \leftrightarrow \text{CaCO}_3
\]  

According to eq.(1) and eq.(2), the SESR of ethanol reaction [3] is written by:

\[
\text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} + 2\text{CaO} \leftrightarrow 2\text{CaCO}_3 + 6\text{H}_2
\]  

Furthermore, the CaO sorbent has a decline problem for continuous carbonation/regeneration cycle [7]. The recyclability of CaO sorbent in practice is a major challenge to keep the SESR performance of Ni/Al₂O₃/CaO composites. In this work, the SESR reaction of ethanol by Ni/Al₂O₃/CaO composites was investigated. The cyclic tests of Ni/Al₂O₃/CaO composites were also performed at between 873K (SESR reaction) and 1023K (regeneration or calcination, CO₂ desorption). The relationship between CO₂ desorbed capacity and product components was discussed in order to understand the CaO sorbent effect on the SR of ethanol reaction.

2. Experiments

2.1 SESR catalyst preparation

The Ni/Al₂O₃/CaO composites were used to be as the SESR catalyst in this work. The bi-functional SESR catalyst was consisted of 10 wt.% Ni/Al₂O₃ and CaO sorbent. Firstly, the 10 wt.% Ni/Al₂O₃ catalyst were prepared by the common impregnation method. The SESR catalyst preparation was shown in Figure 1. The as-prepared 10 wt.% Ni/Al₂O₃ powders were physical mixed with Ca(OH)₂ precursor, then granulated to form cylinder shape with 1mm diameter. Finally, the samples were treated at 1023K in order to converse from the Ca(OH)₂ to CaO species. The proportion of CaO sorbent in the SESR catalyst was adjusted as 80 wt.%. The features of samples were observed and characterized by a field emission scanning electron microscope (Hitachi, S-4800 type, FESEM) and by an X-ray diffraction analyzer with Cu Kα source (XRD, Bruker-D8-ADVANCE), respectively. The porosity of catalyst sample was analyzed by a micromeritics (ASAP 2020). The semi-quantitative metal content was analyzed by an X-ray fluorescence spectrometer (XRF, HORIBA, MESA50).

2.2 Sorption-enhanced steam reforming (SESR) of ethanol experiment

Figure 2 presents the schematic diagram of SESR experiments. The five grams of Ni/CaO samples were packed in a tubular reactor with diameter of 1.27 cm. Prior to experiment, the Ni/CaO samples were activated at 873K for 1hr in a H₂ flow. For the SR experiments, the 40 vol.% ethanol/water solution was used to be the feedstock (the steam/ethanol molar ratio is five). The ethanol solution was pumped at a constant rate of 0.2 ml/min into the evaporator by an HPLC pump, and then the vaporized stream passed through the SESR catalyst bed. The SR reaction was operated at 873K. During the reaction, the online detector (MRU, Vario plus, resolution 0.01%) was used to determine the components of gas products that have been treated by the condenser and the moisture trap.

In this work, the cyclic tests of Ni/Al₂O₃/CaO composites were performed at between 873K (SESR reaction) and 1023K (regeneration). For each cycle, the SESR reaction was terminated when the product of H₂ concentration was determined as below 90%, and then switched to regeneration process. For the regeneration, the Ni/Al₂O₃/CaO composites were treated under a N₂ flowing of 400 ml/min for 1 hr, and then reducing temperature to 873K, started the SESR reaction again.
3. Results and Discussions

Figure 3 shows the FESEM images and element mapping of SESR catalyst. As shown in Figure 3 (a), the smooth surface was found onto the external of cylindrical catalyst. Obviously, the presence of macro-pores can be observed in the interior structure of Ni/Al2O3/CaO composites. It is also found that the grain size range of CaO sorbent was from 100 to 300 nm, as shown in Figure 3 (b). For XRF analysis, the Ni contents of Ni/Al2O3 and SESR catalyst were 7.7 wt.% and 2.4 wt.%, respectively. The CaO content of SESR catalyst was determined as 87 wt.%, consisted with the mixed fraction by catalyst preparation. It is suggested that the well-mixed catalyst/sorbent can obtain a good performance of SESR reaction with highest H2 concentration and lowest CO content [8]. Consequently, the metal distributions have been mapped in order to characterize the homogeneity of SESR catalyst in this work. As shown in Figure 3 (c), the homogeneous distribution of Ni elements was found onto the Al2O3 catalyst supports. Meanwhile, the Ni-Al2O3 well-mixing with CaO sorbent was demonstrated as shown in Figure 3 (d) and (e). Obviously, the several times of Ca elements was found surrounding the Ni element points. It can be assumed that the produced CO2 might be quickly captured during reaction. The cause was attributed to the presence of rich CaO sorbent surround with the activated Ni sites.

For the N2 adsorption/desorption analysis, the BET areas of Ni-Al2O3, CaO sorbent and SESR catalyst were measured as 192.1, 19.6 and 23.2 m²/g, respectively. The total pore volume and average pore size of Ni-Al2O3, CaO sorbent and SESR catalyst were 0.35 cm³/g (7.3 nm), 0.09 cm³/g (17.5 nm), 0.11 cm³/g (11.1 nm), respectively. The N2 adsorption/desorption isotherms of catalyst and CaO sorbent samples were presented in Figure 4. For CaO sorbent, it is clearly obtained that the less N2 adsorbed amount was measured below the relative pressure of 0.9. The result implies that the CaO sorbent exhibits nonporous structure without micro- and meso-pores. Figure.5 shows the XRD patterns of NiAl2O3 catalyst and CaO sorbents. For 10 wt.% NiAl2O3 catalyst, the broad and weak peaks of NiO were found at 37.0° and 43.0°. The result indicates that the tiny Ni metal with nm scale (according to Scherrer equation) distributed onto the surface of supports. The other diffraction peaks at 45.7° and 66.7°, are identified to catalyst supports as Al2O3 crystalline. In this work, the SESR catalyst was
treated at 1023K before reaction, in order to ensure the Ca(OH)$_2$ or CaCO$_3$ conversion to CaO sorbent completely.

![Figure 3](image)

**Figure 3.** FESEM images of (a), (d) SESR catalyst; (c), Ni elements mapping for Ni/Al$_2$O$_3$; (d) Ni elements mapping for SESR catalyst; (e) Ca elements mapping for SESR catalyst

![Figure 4](image)

**Figure 4.** N$_2$ adsorption /desorption isotherms of samples. Square: Ni-Al$_2$O$_3$, circle: SESR catalyst, triangle: CaO sorbent, solid symbol: adsorption data, open symbol: desorption data.

As shown in Figure 5 (b), the major peaks at 32.2°, 37.3°, 53.8° and 64.1°, are identified as CaO compounds. Only, a Ca(OH)$_2$ peak with lower intensity at two theta of 28.6° was found. The crystallize size of CaO was calculated to be 34.1nm by the Scherrer equation. After the SESR of ethanol reaction at 873K, the XRD pattern of SESR catalyst was significantly different (as shown in Figure 5 (c)). It is clearly found that the presence of CaCO$_3$ and Ca(OH)$_2$ substituted for CaO compound. The result demonstrated the carbonation of CaO by CO$_2$ capture during reaction. In addition, the presence of Ca(OH)$_2$ was due to the hydration of CaO with steam. The similar result was presented by previous paper [1]. The SESR catalyst consisted of Ni/Al$_2$O$_3$ and CaO sorbent, was applied on the SR of ethanol reaction for hydrogen production. The gas products (dry basis) of ~95% H$_2$, ~0.5% CO$_2$, ~0.5% CO and ~4% CH$_4$ was obtained during the reaction because of the in-situ CO$_2$ removal. The experimental result indicates the SESR performance strongly depended on the sorbent capacity. When CaO sorbent was saturated by CO$_2$ sorption, the SESR stage would be transferred to the SR stage. The gas products with highest H$_2$ concentration became to the product components of ~72% H$_2$, 20.4% CO$_2$, ~5.3% CO and 1.7% CH$_4$ for common SR. In order to maintain the SESR performance, the regeneration of SESR catalyst was a key issue in practical application. In this work,
the 10 cycles of SESR reaction/regeneration were performed. Figure 6 shows the comparison of products fraction (dry basis) for cyclic SESR of ethanol reaction. The result indicates that the product fractions for the SESR of ethanol reaction were an insignificant change after several cyclic regenerations. The products H₂ fraction of 0.96 for the 1st SESR of ethanol was slightly higher than that of 0.93 for the 10th SESR of ethanol. Moreover, the product fractions of CH₄ and CO gradually increased with increasing cyclic regenerations. The CO₂ desorbed amounts of SESR catalyst for each regeneration process were presented in Figure 7. The similar desorbed amount of CO₂ was found for 10 cycles. The average CO₂ desorbed amounts of SESR catalyst were 17.8 wt.%. For only CaO sorbent part, the average CO₂ desorbed amounts were calculated as 22.3 wt.%. On the other hand, the average conversion from CaO to CaCO₃ was 28.6% for each SESR of ethanol reaction/regeneration cycle.

Figure 5. XRD patterns of (a) Ni/Al₂O₃, (b) SESR catalyst before reaction and (c) SESR catalyst after reaction (CO₂ sorption complete breakthrough)

Figure 6. Comparison of products fraction (dry basis) for cyclic SESR of ethanol reaction. (mole fraction = nᵢ/(n_H₂+n_CH₄+n_CO+n_CO₂), nᵢ (mole) is i species in products)

Figure 7. Comparison of CO₂ desorbed amounts for cyclic SESR catalyst regeneration.

4. Conclusions
In this work, the Ni/Al₂O₃/CaO composite as SESR catalyst was investigated for the SR of ethanol reaction. The SESR catalysts were prepared by the Ni/Al₂O₃ catalyst physical mixing the CaO sorbents. The mass ratio of Ni/Al₂O₃ catalyst and CaO sorbent were 20 wt.% and 80 wt.%, respectively. According to the mapping analysis, the homogeneous distribution of dilute Ni elements was observed on the surface of SESR catalyst. Moreover, the rich Ca elements surrounded the Ni element points.
For the SR of ethanol at 873K, the high H₂ concentration of ~95% was obtained by using Ni/Al₂O₃/CaO composite via CO₂ sorption enhancement. This results strongly demonstrates that Ni/Al₂O₃/CaO composite has well-mixed by simple physical mixture. Indeed, the SESR effect was remarkably affected by the performance of CO₂ capture sorbent. In this work, the 10 cycles of reaction/ regeneration for SESR of ethanol were carried out. The result indicates that the recyclability of SESR catalyst was insignificant change. The average CO₂ desorbed amount of SESR catalyst was 17.8 wt.%. The similar H₂ fraction in products was obtained above 0.9 during the SESR of ethanol cyclic test.

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5. References

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