

## Steam Reforming of Biogas on Nickel Fiber Mat Catalysts

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**Abstract**—Nickel fiber mat was investigated as a potential structured catalyst for steam reforming of biogas in the temperature range of 600-700°C. The activity of as-received catalyst was very low owing to the smooth surface of fibers. Pretreatment of the catalyst by oxidation followed by reduction under methane partial oxidation condition significantly improved the catalytic activity, although degradation of the activity was found during the reaction due to oxidation and sintering. This deactivation was retarded by supplying additional hydrogen in the inlet gases or by coating CeO<sub>2</sub> over the catalyst surfaces.

**Key words** : Biogas, Steam reforming, Fiber mat, Nickel catalyst, Degradation

### 1. Introduction

Biogas has emerged as a renewable and low cost source of hydrogen. Therefore there are lots of attempts to successfully utilize this feedstock as a fuel for fuel cells. Biogas consists of mostly methane and carbon dioxide and it is well known that nickel-based catalysts show good activity in CO<sub>2</sub> reforming of CH<sub>4</sub>, although the catalysts are easily deactivated by carbon deposition caused by CH<sub>4</sub> decomposition or Boudouard reaction ( $2CO \rightarrow C + CO_2$ ) [1]. The problem associated with carbon formation could be controlled by modifying the catalysts with promoters [2-3], providing a sufficient amount of steam in the feed gas, or coating layers of protective materials on the catalyst surface.

The main object of this study is to investigate the catalytic behavior of commercial Ni fiber mat in biogas reforming and to enhance the activity and stability of the catalyst. In an attempt to prevent the coke deposition, steam was supplied together with simulated biogas. Moreover, CeO<sub>2</sub> coating was applied to the catalyst surface to improve the resistance toward coking

and oxidation [4-5]. Combined steam and CO<sub>2</sub> reforming of CH<sub>4</sub> also helps control selectivity of product gases easily only by changing the inlet steam/CO<sub>2</sub> ratio [4]. In addition, CeO<sub>2</sub> has been known widely for possessing high concentrations of oxygen vacancies which act as local sources or sinks for oxygen involved in surface reaction [6].

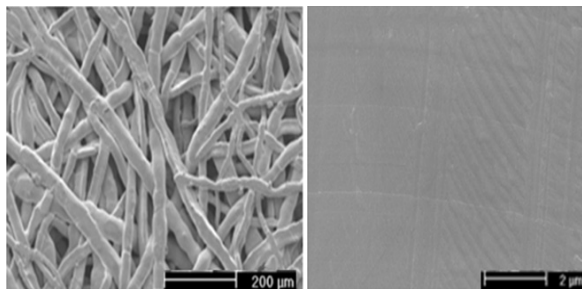
### 2. Experimental

#### 2-1. Catalyst

Commercial Nickel fiber mat (Fiber Tech Co.) of 0.2 mm in thickness was used as a catalyst. According to SEM image, as shown in Fig. 1, the fiber widths were ranged from 50 μm to 70 μm and surface was very smooth. Prior to application, the fiber mat was cleaned by ethanol in sonication for 30 min in order to remove organic materials and participates in the catalyst.

Ceria coating was carried out on the surface of Ni fiber using commercial CeO<sub>2</sub> sol (20% in water, Alfa-AESAR) with particle sizes of 10-20 nm. The coating solution was prepared by mixing the CeO<sub>2</sub> sol and ethanol (99.9%, Hayman) with the weight ratio of 1:2, followed by stirring for 3 hrs. The clean Ni

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**Fig. 1.** SEM image of commercial Ni fiber mat.

fiber mat was coated with  $\text{CeO}_2$  by dip coating at rate of 10 cm/min at room temperature. The dip-coating process was repeated for 3 times with intermediate drying for 15 min at room temperature. After dip-coating, the  $\text{CeO}_2$ -coated fiber mat was dried at  $60^\circ\text{C}$  over night and then heated at a rate of  $2^\circ\text{C}/\text{min}$  to  $300^\circ\text{C}$  under  $\text{N}_2$  flow and maintained at the temperature for 2 hrs.

The catalysts were characterized using conventional methods such as SEM (Phillips FEI XL-30 FEG-ESEM), XRD (Rigaku Minilex II) and XPS (Ulvac-PHI, PHI 5000 Versa Probe).

## 2-2. Reaction

Catalytic reaction was carried out in a reactor with cylindrical stainless steel housing and disk-type catalyst layers. The Ni fiber mat was first cut into circular shape with outer and inner diameters of 50 mm and 8mm, respectively. Then three layers of fiber mats were stacked together while each layer was sandwiched between two Inconel sheets which played as flow paths. All of these layers were fixated by two disk-type stainless steel end plates in the reactor, as was explained in our previous study [7]. Then the reactor was placed in a furnace and heated up to the operating temperature under  $\text{N}_2$  flow with the heating rate of  $5^\circ\text{C}/\text{min}$  before carrying out pretreatment or reforming reactions. A K-type thermocouple was placed at a hole located in the upper end plate at the gas outlet to monitor the reaction temperature. All the reactions were conducted at atmospheric pressure. The simulated biogas with gas composition of 50%  $\text{CH}_4$  and 50%  $\text{CO}_2$  was introduced to the reactor with steam and  $\text{N}_2$  as a

dilute gas. Water was vaporized and mixed with the reactant gas before transporting to the reactor. Typical reforming reaction was carried out at  $600^\circ\text{C}$  with an inlet gas composition of  $\text{CH}_4/\text{CO}_2/\text{steam}/\text{N}_2 = 1/1/1.5/2.5$  under GHSV of 15000 ml/g-h. Composition of the effluent gas was analyzed by gas chromatograph (HP 5890 Series II) equipped with dual TCD detectors using Ar and He as carrier gases after water was removed by a cold trap.  $\text{N}_2$  was used as a reference gas in GC analysis to calculate the amount of product gases and gas conversion.

## 3. Results and Discussion

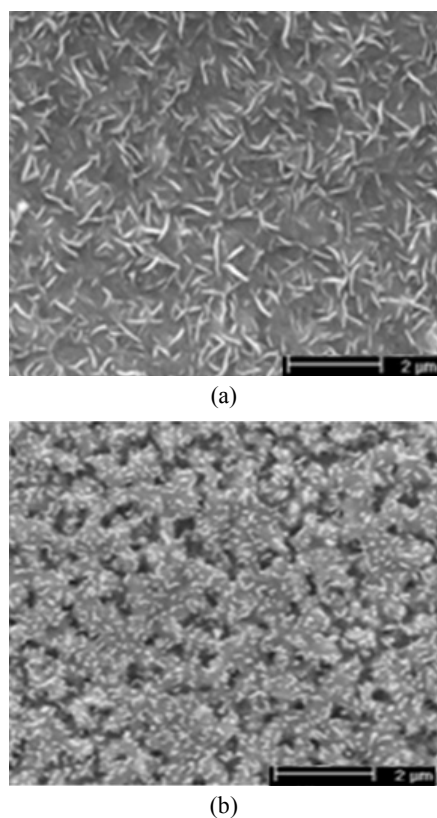
### 3-1. Catalyst activation

Effect of pretreatment condition on catalytic performance of Ni fiber mat was investigated under typical reaction condition at  $600^\circ\text{C}$ . There was no activity detected when the nickel fiber mat was used as it was or reduced by hydrogen. However, after the pretreatment under methane partial oxidation (POX) conditions with a  $\text{CH}_4/\text{air}$  ratio of 1/3 for 30 min at  $700^\circ\text{C}$ , the catalyst began to show reasonable  $\text{CH}_4$  conversion of 26%.

In an attempt to improve catalytic activity, we oxidized the fiber catalysts in air for 24 hrs at  $700^\circ\text{C}$  and then reduced them under  $\text{CH}_4$  in POX condition at the same temperature for 30 min. The oxidation-reduction cycle was previously reported to reconstruct the smooth surface of nickel plate and improve the surface area, thereby promoting its catalytic activity [7]. As expected, by applying this pretreatment process, the initial  $\text{CH}_4$  conversion significantly increased to 50%.

Fig. 2 shows changes in surface morphology of the fiber mat in the pretreatment process. After oxidation, the surface becomes rougher due to the heterogeneous oxide scales in submicron sizes. Then there are plenty of fine grains ranging from nano to submicron sizes deposited on a porous surface after activation under POX condition. It is obvious that the surface appeared to undergo surface reconstruction through oxidation and reduction in POX condition.

Analysis of the activated catalyst by XRD shows only Ni phase while surface analysis by XPS revealed

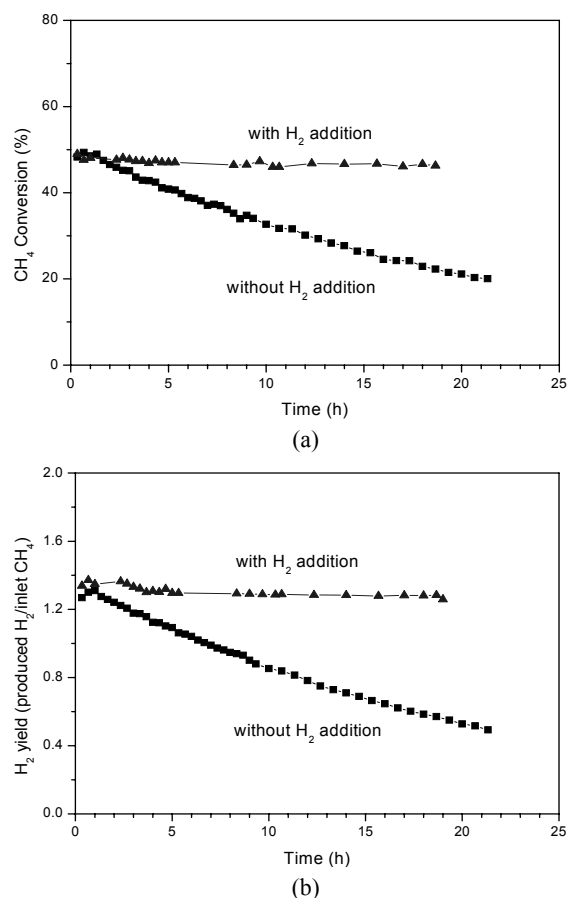


**Fig. 2.** SEM images of Ni fiber mat: (a) after oxidation and (b) after POX treatment.

both  $\text{Ni}^0$  and Ni oxides coexisted after activation process (Figs. 4 & 5). It seems that  $\text{Ni}^0$  produced from the pretreatment process is the active site for steam reforming of biogas, and a number of active sites were increased by oxidation and POX treatment. But further study is needed to clarify the detailed effect of POX treatment on surface activation.

### 3-2. Degradation of catalytic activity and effect of $\text{H}_2$ addition

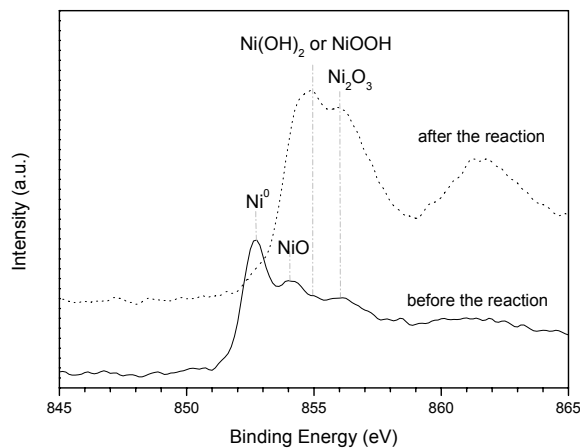
The catalytic performance of metallic Ni fiber mat was monitored for about 20 hrs at  $600^\circ\text{C}$ , and results are presented in Fig. 3. Although the catalytic activity of the Ni fiber mat was significantly improved by the pretreatment process, the produced active surface was not stable under the reforming condition. Without  $\text{H}_2$  addition to the reactant gas,  $\text{CH}_4$  conversion began at 50% and decreased steadily to about 20% in 20 hrs. Likewise,  $\text{H}_2$  yield decreased as methane conversion



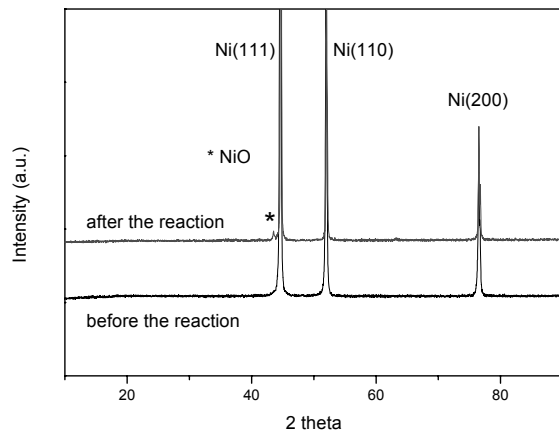
**Fig. 3.** Evolution of (a)  $\text{CH}_4$  conversion and (b)  $\text{H}_2$  yield during biogas steam reforming over Ni fiber mat catalyst at  $600^\circ\text{C}$  with and without addition of  $\text{H}_2$  to the reactant gas.

decreased. When additional  $\text{H}_2$  of 5 vol% in concentration was supplied to the reactant gas, the degradation was suppressed significantly and methane conversion was maintained at 48% for 20 hrs. The carbon balance in all conditions always stayed at 0.99-1.01, indicating that carbon deposition is less likely to account for the degradation of catalytic activity when  $\text{H}_2$  was not supplied.

Fig. 4 shows XPS results of the Ni fiber mat before and after the reaction without  $\text{H}_2$  addition. Based on the relation between binding energy and Ni phases reported previously [8-9], it was found that  $\text{Ni}^0$  was the main phase in the catalyst before the reaction while Ni oxides and hydroxides were predominant phases on the deactivated catalyst. According to the



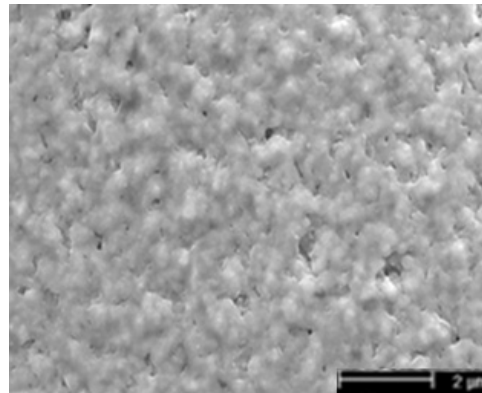
**Fig. 4.** XPS spectra of Ni2p of Ni fiber mat before and after the reaction without addition of H<sub>2</sub> to the reactant gas.



**Fig. 5.** XRD patterns of Ni fiber mat before and after the reaction without addition of H<sub>2</sub> to the reactant gas.

XRD results shown in Fig. 5, NiO peaks were found in the deactivated catalyst.

The existence of Ni oxides and Ni hydroxides on the deactivated catalyst with no obvious evidence about deposition of carbon reveals that oxidation of active Ni<sup>0</sup> sites is one of the main reasons for catalyst deactivation. The oxidation of Ni<sup>0</sup> is due probably to the reaction of Ni with steam in the reactant gas, but more work is needed in the future to investigate the factors governing the oxidation of active Ni<sup>0</sup> sites. Adding hydrogen has been reported to prevent the oxidation of Ni catalysts [10] and to retard the decomposition of CH<sub>4</sub> thus reducing carbon formation [11]. It is



**Fig. 6.** SEM image of the Ni fiber mat after the reaction without addition of H<sub>2</sub> to the reactant gas.

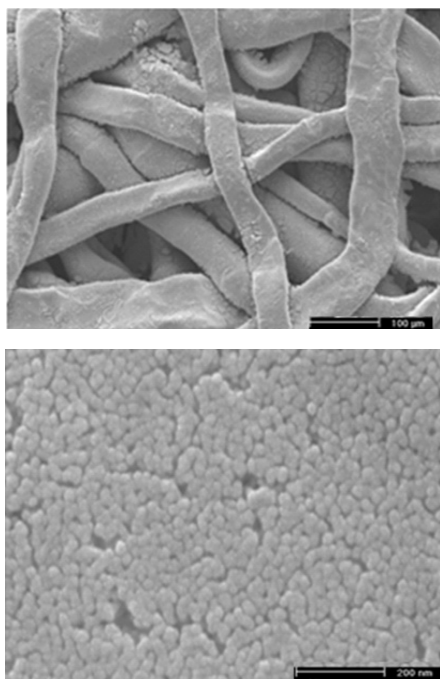
clear from our results that H<sub>2</sub> was able to suppress the oxidation of the Ni fiber mat catalyst during the reaction.

The morphology of deactivated surface by SEM as shown in Fig. 6 indicates that the active surface before the reaction had a tendency to undergo sintering process resulting in the larger grains and disappearance of sub-micron pores. So, it can be concluded that sintering as well as oxidation of active sites attributes to the degradation of catalytic performance of the Ni fiber mat.

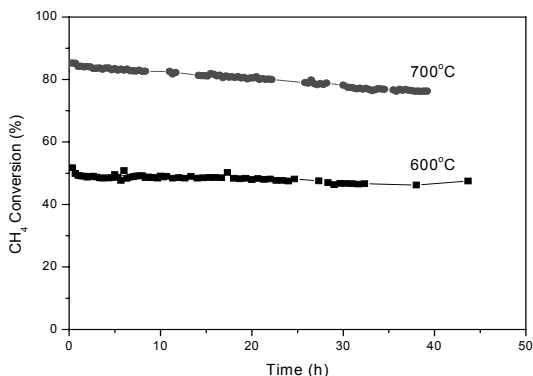
### 3-3. Effect of CeO<sub>2</sub> coating

Fig. 7 shows the surface morphology of CeO<sub>2</sub>-coated Ni fiber mat after heat treatment at 300°C under N<sub>2</sub> flow. Although the coating layer does not cover totally the fiber surface, there are a number of clusters deposited on the surface with CeO<sub>2</sub> particle size approximately as equal as the one in the initial commercial sol. The CeO<sub>2</sub> loading on Ni fiber mat was 8~9 wt%.

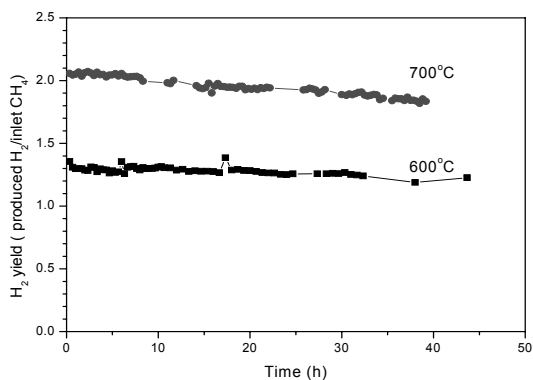
Fig. 8 shows catalytic performance of CeO<sub>2</sub>-coated Ni fiber mat for 40 hrs on stream with the same activation condition used for the metallic Ni fiber mat. Obviously, the addition of CeO<sub>2</sub> inhibited strongly the catalyst degradation which was observed in metallic Ni fiber. The catalytic activity was kept relatively stable at reaction temperature of 600°C while the slow deactivation was found at 700°C.



**Fig. 7.** SEM images of Ni fiber mat coated with CeO<sub>2</sub> after the heat treatment at 300°C.

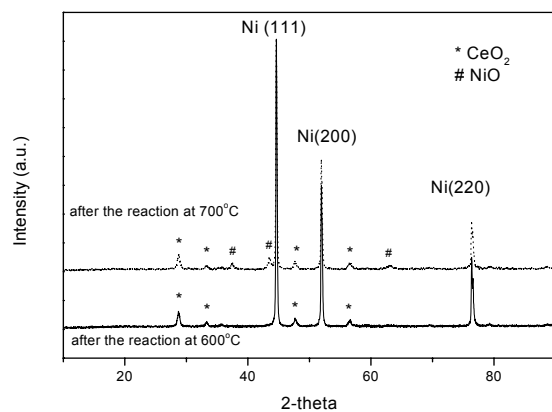


(a)

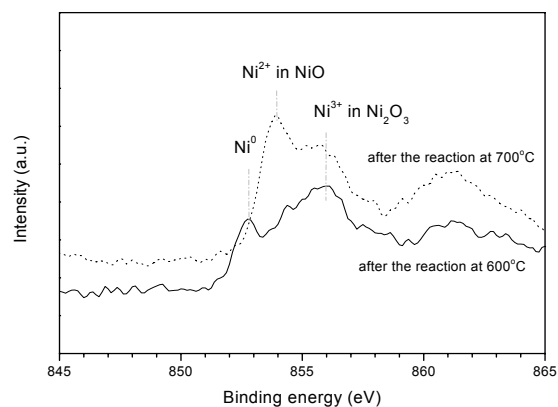


(b)

**Fig. 8.** Evolution of (a) CH<sub>4</sub> conversion and (b) H<sub>2</sub> yield during biogas steam reforming over Ni fiber mat catalyst coated with CeO<sub>2</sub> at 600°C and 700°C.



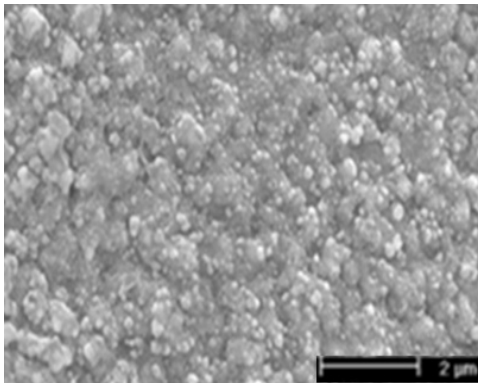
**Fig. 9.** XRD patterns of CeO<sub>2</sub>-coated Ni fiber mat after the reaction at 600°C and 700°C.



**Fig. 10.** XPS spectra of Ni2p of CeO<sub>2</sub>-coated Ni fiber mat after the reaction at 600°C and 700°C.

After the reaction at 600°C for about 40 hrs, NiO peaks were not found in XRD patterns of the catalyst (Fig. 9) as in the case of the pure Ni fiber mat, while XPS data (Fig. 10) shows the existence of both metallic Ni<sup>0</sup> and Ni oxides. However, after the reaction at 700°C, peaks of NiO appear in XRD patterns (Fig. 9) and also Ni oxides become main species on the surface as shown in XPS results (Fig. 10). In addition, the morphology of CeO<sub>2</sub>-coated Ni fiber surface after reaction (Fig. 11) is much different from the initial coated one (Fig. 7).

Comparison of the initial activity of the catalyst with or without CeO<sub>2</sub> coating reveals that the initial activity at reaction temperature of 600°C is quite similar. In addition, CeO<sub>2</sub> apparently helps stabilize the active Ni<sup>0</sup> sites generated by activation process which would



**Fig. 11.** SEM image of CeO<sub>2</sub>-coated Ni fiber mat after 40h-reaction at 600°C.

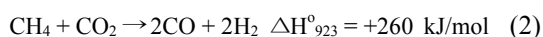
be unstable on the surface without CeO<sub>2</sub> coating or H<sub>2</sub> addition to the reactant gas, as discussed in the previous section. XPS result, however, indicates that oxidation of Ni occurred in the catalyst surface during the reaction at 600°C and the oxidation was accelerated when reaction temperature increased to 700°C leading to degradation of the catalytic performance. Although CeO<sub>2</sub> coating employed in this study did not completely stabilize the catalyst surface, CeO<sub>2</sub> coating significantly increased the catalyst stability at 600°C. We suppose that there are two possible explanations in which the active sites could be protected by CeO<sub>2</sub> coating: (1) CeO<sub>2-x</sub> can easily uptake oxygen species from dissociative adsorption of steam and CO<sub>2</sub> thus decreasing possibility of oxidation of metallic Ni sites; (2) in a close contact with Ni, CeO<sub>2</sub> played as barriers for thermal sintering of active Ni sites [10].

Main reactions which took part in steam reforming of biogas can be described as follows [12]:

Steam reforming of methane:



Dry reforming reaction:



Water gas shift reaction:



CH<sub>4</sub> conversions achieved in this study were 83% at the reaction temperature of 700°C and 48% at 600°C, respectively. According to the equilibrium calculation

assuming no carbon deposition, equilibrium CH<sub>4</sub> conversions are 97% and 71% at 700°C and 600°C, respectively. Concerning the CO<sub>2</sub> conversion, it was nearly zero at 600°C while the conversion increased to 27% at 700°C. Equilibrium CO<sub>2</sub> conversions are 9% and 32% at 600°C and 700°C, respectively. In this study, we fixed the GHSV at 15000 ml/g-h and the reaction is under kinetic limitation. Future work is needed to investigate the effect of GHSV on catalytic performance. Moreover, biogas usually contains impurities such as H<sub>2</sub>S and stability of the catalyst in the presence of impurities requires further investigation.

#### 4. Conclusions

Steam reforming of simulated biogas (CH<sub>4</sub>/CO<sub>2</sub> = 1/1) was investigated over Ni fiber mat catalysts. The results obtained in this study can be summarized as follows:

- (1) The as-received Ni fiber showed no catalytic activity at 600°C under the reforming condition employed in this study. However, the application of consecutive oxidation and reduction under CH<sub>4</sub> partial oxidation condition helped improve significantly the initial activity.
- (2) The activated catalysts were poorly stable during steam reforming reaction thus leading to loss in activity, which is likely attributed to the oxidation and sintering of the active Ni<sup>0</sup> sites.
- (3) Hydrogen addition to the reactant gas could retard efficiently the degradation by preventing the extent of surface oxidation. Moreover, CeO<sub>2</sub> coating can stabilize the active sites by inhibiting oxidation or sintering.

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