



## Short communication

Deactivation of SiO<sub>2</sub> supported Ni catalysts by structural change in the direct internal reforming reaction of molten carbonate fuel cell

Won-Jun Jang<sup>a</sup>, Hak-Min Kim<sup>a</sup>, Jae-Oh Shim<sup>a</sup>, Seong-Yeun Yoo<sup>a</sup>, Kyung-Won Jeon<sup>a</sup>,  
Hyun-Suk Na<sup>a</sup>, Yeol-Lim Lee<sup>a</sup>, Da-We Lee<sup>a</sup>, Hyun-Seog Roh<sup>a,\*</sup>, Wang Lai Yoon<sup>b,\*</sup>

<sup>a</sup> Department of Environmental Engineering, Yonsei University, 1 Yonseidae-gil, Wonju, Gangwon 26493, Republic of Korea

<sup>b</sup> Hydrogen Laboratory, Korea Institute of Energy Research (KIER), 512 Gajeong-ro, Yuseong-gu, Daejeon 34129, Republic of Korea

## ARTICLE INFO

## Keywords:

Direct internal reforming (DIR)  
Molten carbonate fuel cell (MCFC)  
SiO<sub>2</sub>  
Deactivation  
Silica hydrate  
K poisoning

## ABSTRACT

A direct internal reforming (DIR) reaction for a molten carbonate fuel cell (MCFC) is carried out using SiO<sub>2</sub> supported catalysts, which are known to be a highly stable in catalytic reactions. The SiO<sub>2</sub> supported Ni catalysts rapidly deactivate in DIR-MCFC. To elucidate the mechanism of the catalyst deactivation, various characteristic analyses (XRD, BET, H<sub>2</sub>-chemisorption, FT-IR, and SEM) of calcined and used catalysts are employed. The co-existence of H<sub>2</sub>O and K causes the formation of the non-active nickel oxide and silica hydrate resulting in the significant decrease of Ni dispersion and BET surface area.

## 1. Introduction

A molten carbonate fuel cell (MCFC) is ultraclean and a suitable solution for stationary power generation [1,2]. In general, a temperature of approximately 650 °C is required for sufficient conductivity within the carbonate electrolyte. Except for the electricity, the heat is additionally produced by an electrochemical reaction. This occurs the internal reforming (IR) associated with close coupling of the endothermic reforming reaction and the exothermic electrochemical reaction within the fuel cell [3,4]. The IR eliminates the need for an external fuel reformer and is practical in high-temperature fuel cells where the steam reforming of methane (SRM) reaction can occur. On the other hand, the IR can be classified by the geometric configuration, defined as the direct internal reforming (DIR) and indirect internal reforming (IIR) [5]. The DIR has advantages with regard to the overall efficiency and CH<sub>4</sub> conversion [6]. The DIR can directly utilize the heat and steam produced from electrochemical reactions [7]. In addition, the conversion of CH<sub>4</sub> is promoted by decreasing H<sub>2</sub> partial pressure due to the consumption of H<sub>2</sub> via electrochemical reactions. However, a disadvantage of the DIR is that the catalyst is deactivated by the deposition of alkali metals resulting from the vaporization of carbonate electrolyte [8]. Therefore, the main issue for DIR-MCFC is to develop an alkali resistant catalyst [9,10].

A DIR-MCFC catalyst requires high loading amounts of Ni (> 50 wt. %) in order to achieve a high CH<sub>4</sub> conversion [11]. Therefore, support materials are important to maintain high Ni dispersion and surface

area. Moreover, the role of the support in DIR-MCFC is highlighted to suppress the deposition of alkali metals on the Ni particle [12,13]. SiO<sub>2</sub> is widely used for the dry reforming of methane reaction due to its high surface area and thermal stability [14]. In addition, SiO<sub>2</sub> has been intensively studied as a shell material for the encapsulation of Ni particles in core-shell catalysts [15–17]. Zhang's group successfully demonstrated that core-shell Ni@SiO<sub>2</sub> catalysts are effective for protecting Ni particles from alkali poisoning in DIR-MCFC [15–17]. However, it has not been determined that these results originated from the unique nature of SiO<sub>2</sub> support or from the physical barrier formed by SiO<sub>2</sub> shell against alkali poisoning.

The purpose of this work is to study the applicability of SiO<sub>2</sub> supported Ni catalysts in DIR-MCFC. The behavior of SiO<sub>2</sub> on calcined and used catalysts has been investigated using XRD, BET, H<sub>2</sub>-chemisorption, FT-IR, and SEM techniques. In addition, we have tried to demonstrate the deactivation mechanism of SiO<sub>2</sub> supported Ni catalysts in the presence of K.

## 2. Experimental

## 2.1. Catalyst preparation

Ni-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> and Ni-MgO-Al<sub>2</sub>O<sub>3</sub> catalysts were prepared using the homogeneous precipitation method [18,19]. NiCl<sub>2</sub>·6H<sub>2</sub>O (98%, Aldrich), MgCl<sub>2</sub>·6H<sub>2</sub>O (99.0%, Aldrich), NaAlO<sub>2</sub> (50–56% Al<sub>2</sub>O<sub>3</sub>, Aldrich), and Na<sub>2</sub>O(SiO<sub>2</sub>)<sub>x</sub>·xH<sub>2</sub>O (26.5% SiO<sub>2</sub>, Aldrich) were used as the

\* Corresponding authors.

E-mail addresses: [hsroh@yonsei.ac.kr](mailto:hsroh@yonsei.ac.kr) (H.-S. Roh), [wlyoon@kier.re.kr](mailto:wlyoon@kier.re.kr) (W.L. Yoon).

precursors.  $\text{Na}_2\text{CO}_3$  (99.5%, Aldrich) was utilized as a precipitation agent. The precipitation was carried out at a temperature of 90 °C and at a pH level of 9. The precipitates were digested at 90 °C for 3 days. The precipitates were filtered on a filter paper (CAT No. 1005-110, Whatman). Then, the solid products were washed several times with distilled water in order to remove impurities. Ni-MgO- $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  and Ni-MgO- $\text{Al}_2\text{O}_3$  catalysts were calcined at 650 °C for 6 h.

$\text{SiO}_2$  supports were prepared by the hydrothermal method using Tetraethylorthosilicate (Marked as TEOS, 98%, Aldrich) and HCl (37%, Aldrich) solution [20]. HCl was dissolved in distilled water. To this solution, TEOS was added drop-wise at 35 °C with constant stirring for 24 h. The mixed aqueous solution was treated for 24 h at 100 °C in a hydrothermal reactor. After the hydrothermal treatment, the products were dried at 100 °C for 24 h in an oven. The dried products were washed several times with distilled water until it reached at a pH of 7.0. The products were dried at 100 °C for 24 h and calcined at 700 °C for 6 h. The commercial fumed  $\text{SiO}_2$  (s5130, Aldrich, Marked as  $\text{SiO}_2$ -C) was also used as a reference. Ni was loaded on the  $\text{SiO}_2$  support by the incipient wetness impregnation method. The catalysts were re-calcined at 650 °C. The loading amount of each catalyst is summarized in Table S1.

## 2.2. Characterization

X-ray diffraction (XRD) was carried out using a Rigaku D/MAX-IIIC diffractometer operated at 40 kV and 100 mA with Ni-filtered Cu-K $\alpha$  radiation. BET surface area and pore volume were measured using nitrogen adsorption at -196 °C with an ASAP 2010 (Micromeritics).  $\text{H}_2$  chemisorption was conducted to measure Ni dispersion using an Autochem 2910 (Micromeritics). The catalysts were reduced at 700 °C for 1 h in a  $\text{H}_2$  flow and then analyzed at 50 °C. The Perkin Elmer FT-IR Spectrometer (Model Spectrum One BV5.0) was used to record the IR spectrum of the catalysts in the range of 4000–400  $\text{cm}^{-1}$ . Scanning electron microscopy (SEM) was carried out using a JEOL Ltd. (Model JSM-7001F) operating at 15 kV.

## 2.3. Catalytic reaction

To see the effects of K on the catalytic performance, an appropriate amount of KOH was impregnated onto the calcined catalysts, followed by calcination at 650 °C for 6 h. The catalytic reaction was carried out in a fixed-bed micro-tubular quartz reactor with an inner diameter of 4 mm at atmospheric pressure. The catalyst charge was 5 mg and  $\text{MgAl}_2\text{O}_4$  was used as the diluent. Before each measurement, the catalyst was pre-reduced in 10%  $\text{H}_2/\text{N}_2$  at 700 °C for 1 h. The gas hourly space velocity (GHSV) of 1,512,000  $\text{h}^{-1}$  at STP was set for the evaluation of the catalysts [21]. The  $\text{CH}_4:\text{H}_2\text{O}:\text{N}_2$  ratio in the feed gas was 1:3:6. The effluent gases from the reactor were chilled, passed through a trap to condense the residual water, and then flowed onto the on-line micro gas chromatograph (Agilent 3000).

## 3. Results and discussion

Fig. 1 illustrates the  $\text{CH}_4$  conversion with time on stream (TOS) over the Ni-MgO- $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  and Ni-MgO- $\text{Al}_2\text{O}_3$  catalysts. In the case of the catalysts without K poisoning (Conventional SRM), the  $\text{CH}_4$  conversions of both catalysts showed similar values of 97% without detectable deactivation and achieved the thermodynamic equilibrium value. When the catalysts were poisoned by K (DIR-MCFC), the Ni-MgO- $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  significantly deactivated with time on stream. The  $\text{CH}_4$  conversion of the Ni-MgO- $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  decreased from 63% to 11% after a 0.5 h reaction. In addition, The Ni catalyst supported on bare  $\text{SiO}_2$  and  $\text{SiO}_2$ -C also showed serious deactivation, as shown in Fig. S1. On the contrary, the Ni-MgO- $\text{Al}_2\text{O}_3$  showed the  $\text{CH}_4$  conversion of 95%, which was only 2% lower than that of the catalyst without K poisoning. Thus, it is expected that the catalyst containing  $\text{SiO}_2$  should have the reason for the

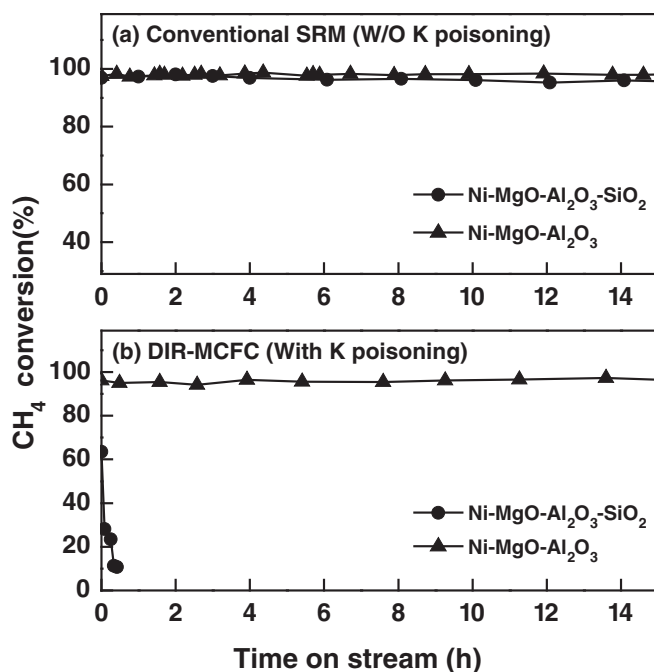


Fig. 1.  $\text{CH}_4$  conversion with time on stream over Ni-MgO- $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  and Ni-MgO- $\text{Al}_2\text{O}_3$  catalysts (Reaction condition:  $T = 650$  °C;  $\text{CH}_4:\text{H}_2\text{O}:\text{N}_2 = 1:3:6$ ;  $\text{GHSV} = 1,512,000$   $\text{h}^{-1}$ ): (a) Conventional SRM (W/O K poisoning), (b) DIR-MCFC (With K poisoning, 4 wt.% K).

deactivation in the DIR-MCFC under the presence of K poisoning.

To understand the reason for deactivation of the Ni-MgO- $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ , the characteristic analysis of calcined and used catalysts was carried out. However, the result of calcined catalyst was similar to that of used catalyst (not shown here) because of the low loading of  $\text{SiO}_2$  (10.5 wt.%). Thus, the Ni catalysts loaded on the bare  $\text{SiO}_2$  and  $\text{SiO}_2$ -C were investigated to verify the behavior of  $\text{SiO}_2$ . Fig. 2 shows the XRD patterns of calcined and used Ni/ $\text{SiO}_2$ , K/Ni/ $\text{SiO}_2$ , and K/Ni/ $\text{SiO}_2$ -C catalysts. All the calcined catalysts only show peaks at 37.3, 43.3, 62.9, 75.4, and 79.4°, which are corresponding to the NiO (JCPDS #47-1049). The characteristic peak of potassium is not observed due to the low loading amount of 4 wt.%. On the other hand, a significant difference is observed over the used catalysts. The diffraction peaks of the Ni/ $\text{SiO}_2$  at 44.5, 51.9, and 76.4° (JCPDS #04-0850) are attributed to the metallic Ni, which is resulted from the pre-reduction prior to the catalytic reaction. This reveals that the Ni/ $\text{SiO}_2$  without K poisoning maintained its active phase for the reforming reaction. On the contrary, the K/Ni/ $\text{SiO}_2$  catalyst shows the diffraction pattern of NiO even though the pre-reduction step. This indicates that the active species of the catalyst (metallic Ni) was oxidized to non-active NiO species due to the K poisoning. In addition, it is interesting to note that the XRD pattern of K/Ni/ $\text{SiO}_2$  shows the peak of crystalline silica hydrate ( $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ , JCPDS #38-0448). This reveals that the  $\text{SiO}_2$  (JCPDS #12-0708) component occurs the sintering in the presence of only  $\text{H}_2\text{O}$ , but it transformed to the crystalline silica hydrate in the co-existence of  $\text{H}_2\text{O}$  and K. The commercial  $\text{SiO}_2$  was also tested as a reference. K and Ni were loaded on the commercial  $\text{SiO}_2$  (Marked as K/Ni/ $\text{SiO}_2$ -C). The same results are also observed on the XRD pattern of the used K/Ni/ $\text{SiO}_2$ -C catalyst.

To identify the various types of bonds on the catalysts, the FT-IR spectra of calcined and used catalysts were investigated. Fig. 3 shows the FT-IR spectra of the calcined and used Ni/ $\text{SiO}_2$ , K/Ni/ $\text{SiO}_2$ , and K/Ni/ $\text{SiO}_2$ -C catalysts. In the case of the Ni/ $\text{SiO}_2$  catalysts without K poisoning, the calcined catalyst shows the same FT-IR spectra with the used catalyst. The absorption peaks at 800 and 1100  $\text{cm}^{-1}$  are assigned to the Si-O-Si symmetric bending and Si-O-Si asymmetric stretching

Download English Version:

<https://daneshyari.com/en/article/4756386>

Download Persian Version:

<https://daneshyari.com/article/4756386>

[Daneshyari.com](https://daneshyari.com)