



## Deactivation characteristics of Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst for cyclic regeneration in a portable steam reformer

Sungchul Lee<sup>a,\*</sup>, Gayatri Keskar<sup>b</sup>, Changchang Liu<sup>b</sup>, William R. Schwartz<sup>b</sup>, Charles S. McEnally<sup>b</sup>, Ju-Yong Kim<sup>a</sup>, Lisa D. Pfefferle<sup>b</sup>, Gary L. Haller<sup>b</sup>

<sup>a</sup> Energy Laboratory, Corporate R&D Center, Samsung SDI Co., Ltd, 428-5, Gongse-dong, Giheung-gu, Yongin-si, Gyeonggi-do 446-577, Republic of Korea

<sup>b</sup> Department of Chemical and Environmental Engineering, Yale University, P.O. Box 208286, New Haven, CT 06520, USA

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### ABSTRACT

The requirements of process parameters, e.g. air pump flow rate and operational pressure are restricted by confined space and limit the performance of portable steam propane reformer. This makes it difficult to operate a catalyst in the portable reformer under mild operation conditions. Hence, the catalyst can be rapidly deactivated. The deactivation behavior of Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst was investigated for coke deposition and active metal sintering. Coke formation by the propane pyrolysis was predominantly responsible for deactivation at low reaction temperature. Coke formation can be thermodynamically reduced by elevating the temperature and hence the steam reformer was operated at high temperature to inhibit coke formation. Although the Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst made small amounts of coke at high temperature, it was deactivated by the encapsulated carbon on active metal during long term operation. Because a compact air pump for catalyst regeneration was available during the shut-down procedure of our portable fuel cell system, the catalysts could be regenerated by coke oxidation. The cyclic oxidation was useful for long term operation. The properties of the used catalyst and the coke were investigated by XRD, NEXAFS, XANES-TPO, TGA and TEM. The Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst in our portable reformer showed stable activity for steam propane reforming in cyclic oxidation operation for 500 h.

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### 1. Introduction

Polymer electrolyte fuel cell (PEFC) systems are good candidates to commercialize because of their various applications, such as a portable power system for outdoor activity and off-grid power supply system. These applications require fuel accessibility, high energy density of fuel and robust system control. Hydrocarbon-based fuels, such as liquefied petroleum gas (LPG), gasoline, diesel, and alcohol can be used as fuel sources for a portable fuel cell system [1–5]. Commercial propane is readily available (at any gas station or supermarket in the Republic of Korea) and is widely used for outdoor applications. Because LPG can be easily vaporized at room temperature, the fuel feeding of LPG is effective and easily controlled in a fuel cell system.

The portable steam reformer requires the availability of various components: (1) the flow rates and operational pressure of the air pump are restricted due to the limited available space and electric power for the compact system, (2) the steam reformers used for this application should have a wide operating range compared to industrial plants, making it easier to select the optimal

operating parameters, (3) the catalysts may be regenerated without additional equipment, e.g., switching regenerator, (4) the reformer requires some electric power, which comes from the integrated battery in the system, to start, shut down and regenerate the catalysts and it is important to minimize additional power consumption of the integrated battery, and (5) although mild regeneration procedures improve the stability against to catalyst sintering, air oxidation is a reasonable technique for the regeneration of catalysts in the portable fuel cell system.

Nickel based catalysts, i.e. Ni/Al<sub>2</sub>O<sub>3</sub>, Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and Ni-Mg/Al<sub>2</sub>O<sub>3</sub> are remarkably active for steam reforming of light hydrocarbons at low temperature [6–11]. However, coke formation and the active metal sintering are expected to cause deactivation of Ni catalysts. The methods of preventing catalytic deactivation by coke deposition are coke minimization control and regeneration of deactivated catalyst. The first approach is coke minimization that controls the number of active sites in an ensemble and prevents the formation of metal carbide by the addition of secondary metals [12–16]. The second approach to prevent catalytic deactivation by coke build up is regenerative removal of the coke formed on the catalytic surface during steam reforming. Typically in industry, O<sub>2</sub> or air is used to oxidize coke in the regenerator [17]. During the regeneration step, a hot spot may form in the catalyst bed, and a part of the catalyst may be sintered. To minimize catalyst

\* Corresponding author. Tel.: +82 31 288 4878.

E-mail addresses: [scat.lee@samsung.com](mailto:scat.lee@samsung.com), [sc673.lee@gmail.com](mailto:sc673.lee@gmail.com) (S. Lee).

sintering, coke removal by different gasifying agents, such as O<sub>2</sub>, air, CO<sub>2</sub>, H<sub>2</sub> and N<sub>2</sub>, have been studied [18]. The performance of the gasifying agents decreases in the order O<sub>2</sub> > air > CO<sub>2</sub> > H<sub>2</sub> > N<sub>2</sub>. This literature, which suggested that the efficient coupling of air oxidation ( $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ ,  $\Delta H^\circ = -394.5 \text{ kJ/mol}$ ) and reverse Boudouard reaction ( $C_{(s)} + CO_{2(g)} \rightarrow 2CO_{(g)}$ ,  $\Delta H^\circ = 175.2 \text{ kJ/mol}$ ), led to better regenerative operation for reducing catalyst sintering. During start-up and shut-down operation of the residential fuel cell system, the catalyst beds are purged by steam for safety reasons [19]. Steam feeding without any fuel can deactivate the Ni based catalyst, because the steam quickly oxidizes the Ni metal. Li et al. have reported improvement in the thermal stability of Ni/Mg(Al)O catalyst by the addition of small amounts of precious metals. The metallic Ni particles are re-dispersed on the catalyst surface, resulting in high and stable activity [20].

Comparing Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts with Ni/Al<sub>2</sub>O<sub>3</sub> catalysts used for steam reforming, we know that Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst exhibits OSC, a function necessary for oxidation of surface carbons and hydrocarbons. In this study, steam reforming reactions of Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst were carried out at different reaction temperatures (500, 600, 700 and 800 °C). After reaction for 5 h, the Ni metal particle size and amount of coke were measured using various characterization methods. The Ni metal particle sizes after oxidation were measured to study the stability of regeneration (where reaction and regeneration temperatures were the same). Finally, we investigated both steady-state operation and cyclic oxidation operation of Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst for 500 h. The relationship between the high temperature stability and the properties of Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst were studied during the steam reforming reaction.

## 2. Experimental

### 2.1. Preparation of catalysts

Two kinds of catalysts, powder and monolith samples, were prepared. The CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support with a nominal Al/Ce molar ratio of 13.5 was prepared by physically mixing gamma aluminum oxide (γ-Al<sub>2</sub>O<sub>3</sub>, Alfa Aesar) and cerium oxide (CeO<sub>2</sub>, Aldrich) in water. Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst was prepared by impregnation (Ni/Ce/Al molar ratio = 0.08/0.06/0.86, surface area = 120.7 m<sup>2</sup>/g, and pore volume = 0.34 cm<sup>3</sup>/g). Nickel (II) nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Aldrich) was used as the metal source. The Ni solution was prepared by dissolving nickel(II) nitrate hexahydrate in 150 ml of water and the CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support was suspended in 100 ml of water. Each solution was stirred for 1 h. The Ni solution was added to the suspended CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> solution, and then the final mixture was refluxed at the boiling temperature for 40 h. After refluxing, the sample was evaporated and dried at 100 °C in a vacuum oven. For the monolith catalyst, the refluxed slurry was coated on cordierite (600 cpsi) and dried at 100 °C in a vacuum oven. The dried samples were finely ground and calcined under flowing air at 540 °C for 6 h.

### 2.2. Characterization

The properties of the Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst were characterized by X-ray diffraction (XRD, Bruker, AXS D8Focus diffractometer), and transmission electron microscopy (TEM, TECNAI TF20 FEG TEM/STEM). To determine the Ni oxidation state and local atomic structures, in situ and ex-situ X-ray absorption measurements were performed at the Ni K edge (8333 eV) using the Si(111) monochromator crystal at X18B beamline at the National Synchrotron Light Source, Brookhaven National Laboratory. One hundred mg of each sample were pressed into a self-supporting wafer and placed in a

stainless steel cell equipped with beryllium (0.5 mm thick, Aldrich) windows, gas inlet and outlet, liquid nitrogen cooling line, and heating elements allowing the in situ controlled atmosphere treatments up to 750 °C. To investigate the effect of oxidation temperature, each sample was oxidized at 750 °C by flowing 10% O<sub>2</sub>/He for 30 min to 1 h and quenched to room temperature using liquid nitrogen. X-ray absorption near edge structure (XANES) spectra were collected during sample oxidation with a 5 min interval between the scans [21–23].

A temperature programmed oxidation (TPO) technique was used to characterize the oxidized samples by mass spectrometry. Approximately 50 mg of each sample was loaded into a quartz cell. Prior to each TPO run, the sample cell was purged by ultra zero grade air at room temperature, and the baseline was monitored until stable. After baseline stabilization, the sample cell was heated at a rate of 10 °C/min and held for 1 h at 800 °C to ensure complete metal and coke oxidation.

Thermal gravimetric analysis (TGA) was used to determine the amount of coke formed. TGA data were collected in a Setaram Setsys 1750 instrument under air flow. Samples were heated to 150 °C in pure argon for 1 h to dehydrate before initiating the temperature program. The initial weight change of the sample was measured between 150 and 1000 °C, when heated at 10 °C/min for two successive ramps. The second ramp was used as a baseline correction for the first.

### 2.3. Steam reforming reaction

Propane steam reforming reaction was carried out in a fixed bed reactor (16 mm-ID × 600 mm-high). The powder catalyst (500 mg) was loaded for the catalytic activity study, and the monolith sample (16 mm-OD × 100 mm-high) was loaded the long term activity studies. The flow rates of reactants (C<sub>3</sub>H<sub>8</sub> and air) and internal standard (N<sub>2</sub>) gases were controlled by using a mass flow controller (MFC). A syringe pump was used to feed water in to the system. The powder and the monolith catalysts operated at a space velocity of 36000 ml/g-cat h and 7200 h<sup>-1</sup> respectively. Gas compositions were measured by a real-time gas analyzer after removing the water from the reformate gas. The real-time gas analyzer (Rosemount) was equipped with a non-dispersive infrared detector for CO, CO<sub>2</sub> and CH<sub>4</sub> and a thermal conductivity detector for H<sub>2</sub>. The flow rate of the dried reformate gas was measured by wet gas meter (Shinagawa). For reaction-oxidation cycles, every cycle was composed of a propane steam reforming for 10 h and an air oxidation (air flow rate = 400 ml/min) at the same reaction temperature for 10 min.

## 3. Results and discussion

### 3.1. Characterization of Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst after propane steam reforming

Nickel supported on CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts were evaluated for propane steam reforming. Cerium oxide exhibits the OSC function, which can oxidize surface carbon and propane. For Ni/Al<sub>2</sub>O<sub>3</sub> catalyst, the formation of carbon filaments caused Ni particles to detach from the support thus leading to catalytic deactivation. However, we believe that Ni particles on CeO<sub>2</sub> promoted catalyst remained on the Al<sub>2</sub>O<sub>3</sub> support due to the strong interaction of Ni with the support. The activity of Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst was studied by temperature programmed reaction (heating rate = 5 °C/min) with a constant steam/carbon ratio (S/C = 3), propane flow rate (30 ml/min) and reaction pressure (1 atm). Fig. 1 reveals the results of temperature programmed propane steam reforming on the Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst. The H<sub>2</sub> and CO concentrations gradually

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