



# Reforming activity and carbon deposition on cermet catalysts for fuel electrodes of solid oxide fuel cells

Koichi Eguchi\*, Kentaro Tanaka, Toshiaki Matsui, Ryuji Kikuchi

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

## ARTICLE INFO

### Article history:

Available online 23 February 2009

### Keywords:

Solid oxide fuel cells  
Anode  
Cermet  
Carbon deposition  
Steam reforming

## ABSTRACT

The activities of cermet catalysts composed of Ni and oxides for steam reforming of methane were investigated for internal reforming of solid oxide fuel cells. For all catalysts studied, the reaction attained almost equilibrium above 500 °C at the space velocity of 20,000 l kg<sup>-1</sup> h<sup>-1</sup>. The kinetic-controlled reaction and difference in activity among the catalysts were observable at S.V. = 60,000 l kg<sup>-1</sup> h<sup>-1</sup>. The reforming activity was higher for Ni-YSZ (YSZ: yttria-stabilized zirconia) than Ni-ScSZ (ScSZ: scandia-stabilized zirconia), whereas the highest activity was attained on Ni/Al<sub>2</sub>O<sub>3</sub>. However, the catalyst performance was degraded with carbon deposition in the course of the reaction. The tolerance to carbon deposition and, therefore, the life of the catalyst was significantly affected by the oxide material in the cermet. The carbon deposition was most rapid on Ni/Al<sub>2</sub>O<sub>3</sub>. The high loading of Ni also facilitated the deposition on the Ni-YSZ and Ni-ScSZ catalysts. It is noted that the carbon deposition rate was significantly smaller for Ni-ScSZ than the case of the Ni-YSZ.

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## 1. Introduction

Internal reforming of hydrocarbons for solid oxide fuel cells (SOFCs) is attracting in deriving high conversion efficiency and simplified generation system. High temperature operation of the fuel cells enables reforming in the cell chamber, which contributes to the efficient transfer of heat generated from the fuel cells for internal reforming. Hydrocarbons are internally reformed to hydrogen and carbon monoxide fuels directly on the fuel electrode. The fuel electrode catalysts are generally Ni-oxide composites for attaining high activity for reforming and electrochemical oxidation of fuel, and serving as current collector. Extremely high content of Ni is accepted to ensure continuous electric path in the anode layer. The catalytic reforming activities of such cermet catalysts were not investigated in detail, though the catalytic behavior of finely dispersed Ni catalyst on alumina-based support for reformer has been thoroughly investigated. Carbon deposition, being the main cause of the anode deactivation, should be analyzed for the stable operation of internal reforming cells. Chain growth reaction of carbonaceous species leads to plugging in the pores of the anode layer. The cermet catalysts are requested to be tolerant to carbon deposition formed by decomposition of hydrocarbon fuel. It has been known that the electronic interaction of support oxide

significantly affects the activity and tolerance to carbon deposition for conventional reforming catalysts [1–6]. The ease of carbon deposition on the electrode was dependent on the cermet material and steam to carbon ratio (S/C ratio) [7–12]. For the heavier hydrocarbons with C–C bond, carbon deposition is facilitated as compared with methane [13–16]. On the other hand, higher hydrocarbons will be preferable from the view point of fuel economy. Commercial reforming catalysts based on Ni/Al<sub>2</sub>O<sub>3</sub> are added with an alkaline earth metal component which is known to be effective to suppress carbon deposition [17–20]. Ni-YSZ (yttria-stabilized zirconia) cermet has been most popularly employed as a fuel electrode for SOFCs. Ni-ScSZ (scandia-stabilized zirconia) cermet has been reported as effective in suppressing carbon deposition in dry operation with methane [11,21]. Then, we aimed to evaluate the catalytic activity and stability of these cermets for internal steam reforming of hydrocarbons. In the present study, methane and propane were supplied as hydrocarbons. The electrode cermets used were Ni-YSZ and Ni-ScSZ, and the obtained results were compared to those of catalysts prepared by the impregnation method.

## 2. Experimental

### 2.1. Preparation of materials

Fuel electrode cermets examined here were Ni-YSZ and Ni-ScSZ, which were simply prepared by mechanical mixing of NiO

\* Corresponding author. Tel.: +81 75 383 2519; fax: +81 75 383 2520.  
E-mail address: [eguchi@sci.kyoto-u.ac.jp](mailto:eguchi@sci.kyoto-u.ac.jp) (K. Eguchi).

**Table 1**  
Ni content and calcination temperature for each catalyst.

Catalyst	Ni content	Calcination temperature
Ni-YSZ	10, 20, 50, 80 vol.%	1000 °C
Ni-ScSZ	10, 20, 50, 80 vol.%	1000 °C
Ni/Al <sub>2</sub> O <sub>3</sub>	5 vol.%	850 °C
Ni/YSZ	20 vol.%	1000 °C

and oxide materials. Commercial yttria-stabilized zirconia, YSZ and scandia-stabilized zirconia, ScSZ powders from Tosoh (TZ8Y, 8 mol% Y<sub>2</sub>O<sub>3</sub>) and Daiichi Kigenso Kagaku Kogyo (10 mol% Sc<sub>2</sub>O<sub>3</sub>), respectively, were used. The Ni-based cermetes were prepared by mixing of NiO (Wako Chemical) and stabilized zirconia powders. The volumetric ratios of the cermet source are summarized in Table 1. These oxide mixtures were ball milled for 24 h and heated in air at 1000 °C for 5 h with the heating and cooling ramp rate of 200 °C h<sup>-1</sup>. The resultant catalyst prepared by mechanical mixing is denoted as Ni-oxide catalyst by using a dash.

Some Ni/YSZ and Ni/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by the impregnation process, which are hereafter denoted as Ni/oxide by using slash. The oxide powder of YSZ or  $\gamma$ -alumina (BET surface area: 147 m<sup>2</sup> g<sup>-1</sup>, Sumitomo Chemical) was immersed in the Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O solution at 80 °C, and then the solution was evaporated to dryness. After dried powder was obtained, Ni/YSZ and Ni/Al<sub>2</sub>O<sub>3</sub> catalysts were heated in air at 1000 and 850 °C, respectively, for 5 h.

## 2.2. Gravimetric analysis of carbon deposition

The amount of deposited carbon on the Ni-based cermet was estimated by heating the sample in air by combustion of carbon. Ni-based cermet was mounted on a Pt basket of a thermogravimetric analyzer (Shimadzu, TGA-50). The samples were heated in air at a heating rate of 10 °C min<sup>-1</sup> up to 1000 °C. The weight of the catalyst decreased on heating in air when deposited carbon was burned off from the catalyst. The catalysts used here for the evaluation of carbon deposition were Ni-YSZ and Ni-ScSZ.

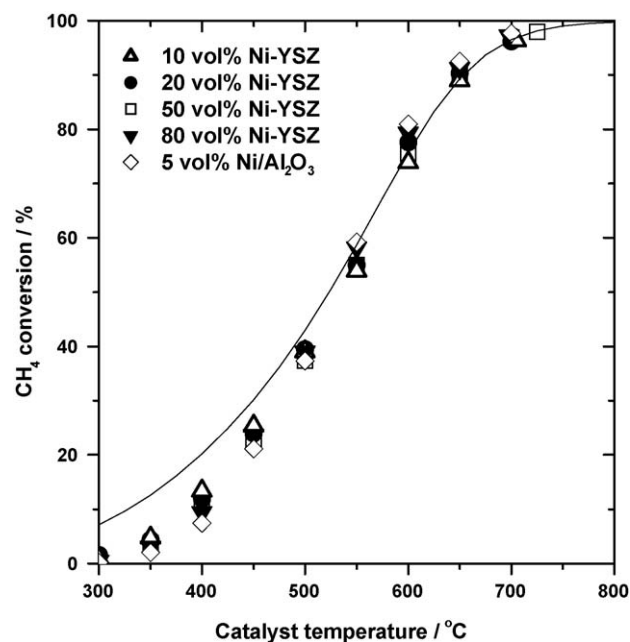
## 2.3. Catalyst characterization

Temperature programmed reduction (TPR) was conducted using CHEMBET-3000. The catalyst sample (25 mg) was reduced in 5% H<sub>2</sub>/Ar at a flow rate of 30 ml min<sup>-1</sup> (25 °C, 1 atm) with a heating rate of 10 °C min<sup>-1</sup>. Specific surface area of catalysts was determined by the conventional BET method with N<sub>2</sub> adsorption using a Shimadzu Gemini 2375 instrument. The microstructure of the catalysts was observed by scanning electron microscope (SEM, Shimadzu SSX-550).

## 2.4. Catalytic activity evaluation

The catalytic activity for steam reforming of methane and propane was measured using a conventional fixed bed flow reactor under atmospheric pressure. Prior to the evaluation of catalysts, the reduction of the catalyst was carried out at 800 °C for 2 h in 10% H<sub>2</sub>/N<sub>2</sub>. Gaseous mixture of hydrocarbon and nitrogen was fed to the steam evaporator. Then, the reactant gas was supplied to the catalyst bed at designed reaction temperatures through mass flow controllers. The reaction temperature was varied in the range of 300–800 °C.

Compositions of influent and effluent gas were analyzed by on-line gas chromatographs equipped with FID (Shimadzu, GC-8A) and TCD (VARIAN, CP-4900). The steam in the feed and reformat was trapped by a condenser at ca. 3 °C before the gas analysis.



**Fig. 1.** Temperature dependence of CH<sub>4</sub> conversion over Ni-YSZ and Ni/Al<sub>2</sub>O<sub>3</sub>. Reaction conditions: CH<sub>4</sub> 10%, H<sub>2</sub>O 15%, N<sub>2</sub> 75%; S.V. = 20,000 l kg<sup>-1</sup> h<sup>-1</sup>. The solid line shows the equilibrium conversion.

## 3. Results and discussion

### 3.1. Activity of cermet for steam reforming of methane

Nickel-YSZ cermet has been employed as the most standard fuel electrode material suitable for internal reforming of SOFCs. The activity for the steam reforming of methane over Ni-YSZ catalysts has been evaluated as a function of temperature and space velocity. Two space velocities were employed to clarify the difference in activity among the catalysts with different composition ratios. It was clear from Fig. 1 that at the low space velocity condition of 20,000 l kg<sup>-1</sup> h<sup>-1</sup> the activities of the catalysts were in the similar level. The solid line in the figure is the calculated conversion from the thermodynamic equilibrium. The activity increased with an increase in reaction temperature, in line with the rise in the equilibrium conversion. The activity reached the equilibrium level above 500 °C. This means that at higher temperatures the equilibrium was already achieved at the front zone of the catalyst bed. This level of space velocity is close to that employed generally for the catalytic reformer. However, the reaction on the fuel electrode layer corresponds to the higher velocity conditions, since the flowing fuel only pass the outermost layer of the anode.

To clarify the difference among the catalysts in such a circumstance, the steam reforming of methane was carried out at higher space velocity of 60,000 l kg<sup>-1</sup> h<sup>-1</sup> as shown in Fig. 2. The activities of the catalysts were different from each other as they scattered below the equilibrium line. The activity increased with increasing content of Ni up to 50 vol.%, though the activity was lowered for 80 vol.% Ni sample than that of 50 vol.% Ni because of the agglomeration of Ni and reduced surface area for the higher Ni content of 80 vol.%. The highest activity was attained by Ni/Al<sub>2</sub>O<sub>3</sub> catalyst supported by impregnation because of the effective dispersion of Ni on large surface of alumina as compared to Ni-YSZ cermet. The Ni-YSZ cermet activity was lower than that of Ni/Al<sub>2</sub>O<sub>3</sub>.

The dependences of the activities on the composition are summarized for Ni-YSZ and Ni-ScSZ cermet catalysts at two

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