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

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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^{-1} h^{-1}. The kinetic-controlled reaction and difference in activity among the catalysts were observable at S.V. = 60,000 l kg^{-1} h^{-1}. 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_2O_3. 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_2O_3. 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.

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_2O_3 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

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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_2O_3	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_2O_3) and Daiichi Kigenso Kagaku Kogyo (10 mol% Sc_2O_3), respectively, were used. The Ni-based cermets 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^{-1}. The resultant catalyst prepared by mechanical mixing is denoted as Ni–oxide catalyst by using a dash.

Some Ni/YSZ and Ni/Al_2O_3 catalysts were prepared by the impregnation process, which are hereafter denoted as Ni/oxide by using slash. The oxide powder of YSZ or γ-alumina (BET surface area: 147 $m^2\,g^{-1}$, Sumitomo Chemical) was immersed in the $Ni(NO_3)_2{\cdot}6H_2O$ solution at 80 °C, and then the solution was evaporated to dryness. After dried powder was obtained, Ni/YSZ and Ni/Al_2O_3 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 thermo-gravimetric analyzer (Shimadzu, TGA-50). The samples were heated in air at a heating rate of 10 °C min^{-1} 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_2/Ar at a flow rate of 30 ml min^{-1} (25 °C, 1 atm) with a heating rate of 10 °C min^{-1}. Specific surface area of catalysts was determined by the conventional BET method with N_2 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_2/N_2. 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 reformate was trapped by a condenser at ca. 3 °C before the gas analysis.

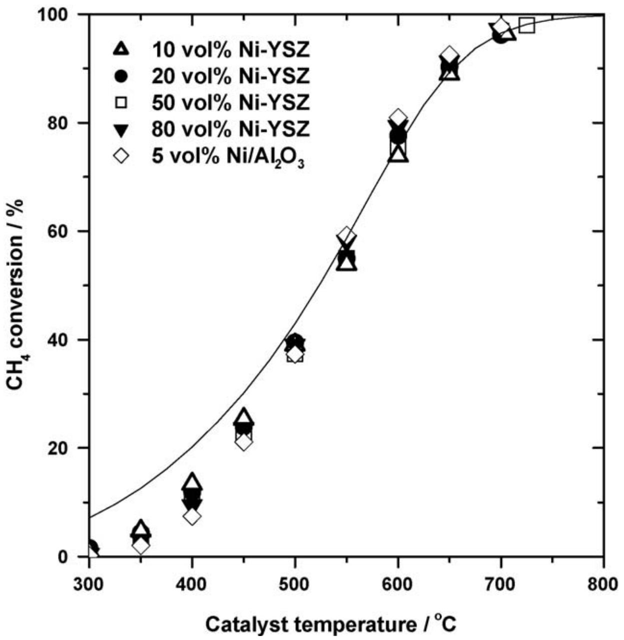

Fig. 1. Temperature dependence of CH_4 conversion over Ni–YSZ and Ni/Al_2O_3. Reaction conditions: CH_4 10%, H_2O 15%, N_2 75%; S.V. = 20,000 l kg^{-1} h^{-1}. The solid line shows the equilibrium conversion.

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^{-1} h^{-1} 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^{-1} h^{-1} 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_2O_3 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_2O_3.

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

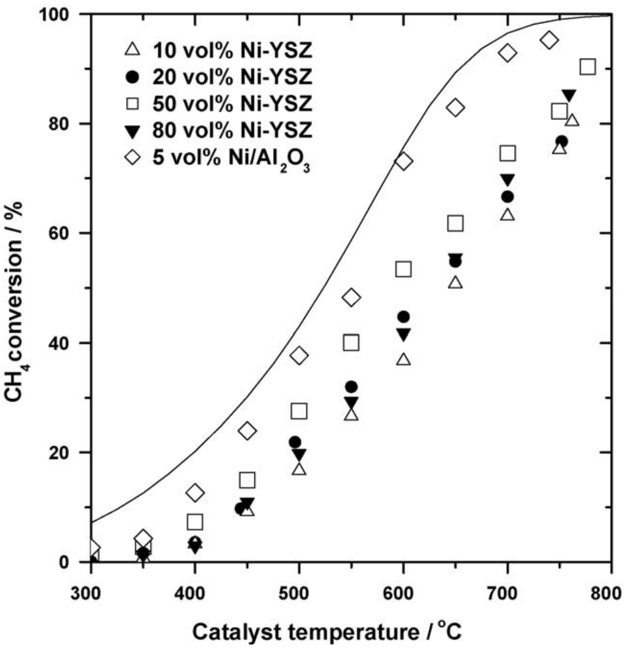

Fig. 2. Temperature dependence of CH_4 conversion over Ni–YSZ and Ni/Al_2O_3. Reaction conditions: CH_4 10%, H_2O 15%, N_2 75%; S.V. = 60,000 l kg^{-1} h^{-1}. The solid line shows the equilibrium conversion.

different temperatures (Fig. 3). The activity of Ni–ScSZ was slightly lower than the series of Ni–YSZ cermet samples at every composition as shown in Fig. 3. As in the case of Ni–YSZ, the activities of the Ni–ScSZ cermet catalysts went through a maximum at the composition of 50 vol.% Ni for the reaction at 500 and 700 °C. The activity rise in low Ni content region corresponds to the evolution of the active site with increasing active species Ni, whereas the decrease with Ni abundance is ascribed to agglomeration of metal and decrease in active surface. The surface area of the cermets decreased with increasing amount of Ni because of the ease of sintering for metallic Ni as summarized in Table 2.

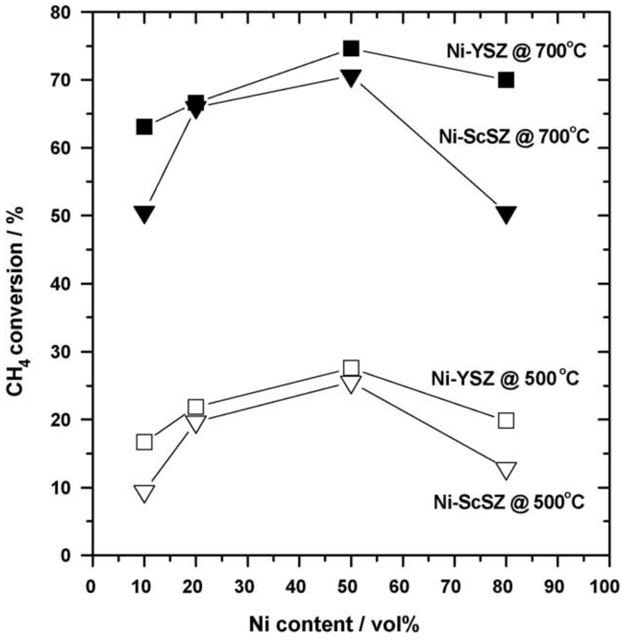

Fig. 3. CH_4 conversion as a function of nickel content in Ni–YSZ and Ni–ScSZ at 500 and 700 °C. Reaction conditions: CH_4 10%, H_2O 15%, N_2 75%; S.V. = 60,000 l kg^{-1} h^{-1}.

Table 2
BET surface area and the fraction of low-temperature peak in TPR profile.

Ni content/vol.%	BET surface area/ m^2 g^{-1}		Fraction of low-temperature peak in overall reduction amount/%	
	Ni–YSZ	Ni–ScSZ	Ni–YSZ	Ni–ScSZ
10	4.6	3.4	63.0	42.3
20	4.0	2.9	51.0	42.3
50	3.6	2.0	46.1	31.1
80	2.6	2.0	37.9	30.0

Temperature programmed reduction profiles of catalysts are shown in Fig. 4. The reduction of nickel oxide in the cermet proceeded as two step peaks in the TPR profile. The reaction was initiated at *ca.* 350 °C forming a reduction peak at *ca.* 420–470 °C. After passing through the minimum, the reduction rate again increased from *ca.* 500 °C forming a broad hydrogen consumption around 650 °C. The integrated amount of H_2 consumption for the sum of the two reduction peaks agreed well with that expected from the bulk reduction of NiO to metallic Ni. Thus, this two step reduction corresponds to the stoichiometric reduction of bulk nickel oxide. The two step reduction behavior has been reported [9,22,23]: the peak at lower temperature was ascribed to the reduction of NiO free from the influence of support, whereas the peak at higher temperature was correspondent to the reduction of NiO with strong interaction with support. Then, the fraction of low-temperature peak in overall reduction amount was calculated, and it was revealed that its fraction was always larger for the case of Ni–YSZ than that of Ni–ScSZ (Table 2). Therefore, the difference in the interaction between Ni and oxide leads to the difference in the distribution of surface Ni species. This factor should strongly affect the catalytic activity for methane steam reforming as is observed in Fig. 3.

3.2. Degradation of activity by carbon deposition

The important part of this study is to clarify the carbon deposition behavior for the catalyst. The deposition of carbon leads to detrimental destruction of the anode microstructure and cell performance during internal reforming mode of operation.

The time courses of the reaction over Ni–YSZ and Ni–ScSZ at steam to carbon ratio of 0.9 (S/C = 0.9) at 700 °C are shown in Fig. 5. Decreases in reactivity of the catalyst can be ascribed to deactivation with the deposition of carbon with an elapse of time. The reaction condition, i.e., the S/C ratio, was set within the carbon

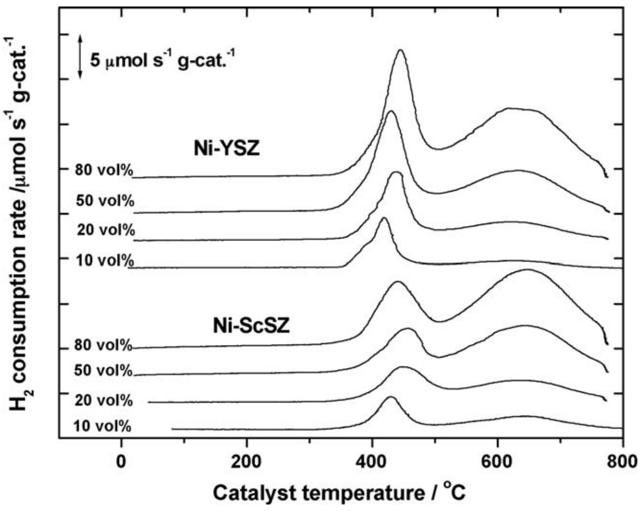

Fig. 4. TPR profiles of Ni–YSZ and Ni–ScSZ. Measurements were conducted at a heating rate of 10 °C min^{-1} in 5% H_2/Ar.

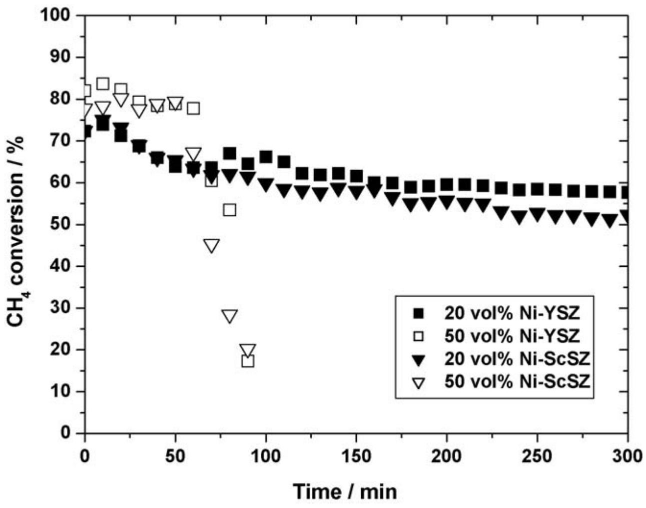

Fig. 5. CH_4 conversion as a function of time on stream over Ni–YSZ and Ni–ScSZ at 700 °C. Reaction conditions: CH_4 10%, H_2O 9%, N_2 81%; S.V. = 20,000 l kg^{-1} h^{-1}.

deposition region expected from the equilibrium. At 700 °C boundary S/C ratio for the deposition of carbon is S/C ratio of 1.1; thus, the carbon deposition is expected for the reaction. As the carbon deposition proceeded, the methane conversion degraded gradually. The degradation of the activity depends on the accumulated deposition amount of carbon. The degradation was accelerated for the sample with higher content of Ni. The activity on 50 vol.% Ni–YSZ decreased suddenly after 70 min of operation. The degradation behavior was also observed for the case of Ni–ScSZ cermet. The heavy Ni content of 50 vol.% again gave rise to the rapid degradation with carbon deposition. This result suggests the problem of the cermet used for the fuel electrode of SOFCs. The volumetric percentage of Ni generally used for the fuel electrode is around 50% to ensure the electric path in the electrode layer. The high composition of Ni, on the other hand, easily gives rise to the deactivation through carbon deposition.

Although the degradation rates for Ni–YSZ and Ni–ScSZ were almost the same for the case of 20 vol.% Ni in the short term observation, the carbon deposition difference was continuously monitored for the longer period for 10 and 20 vol.% Ni systems. The behavior in the extended period is shown in Fig. 6 in addition to the degradation curve for the Ni/Al_2O_3 catalysts. The durability tests were conducted at S/C = 0.6 for 5 h. The difference in the degradation was obvious among the cermets. The initial activity was the highest for the Ni/Al_2O_3 catalyst, but the degradation was extremely rapid on this catalyst. This implies that the active component has been well dispersed on the large surface of alumina. However, the active center also serves as the facilitated deposition site for carbon. The degradation of 20 vol.% Ni samples was slower than the case of the 10 vol.% samples for both Ni–YSZ and Ni–ScSZ. Though the composition dependence of deposition rate should be investigated in detail, there may be an optimal composition range to avoid carbon deposition. The degradation rate of Ni–YSZ was obviously faster than the case of Ni–ScSZ. The CH_4 conversion was stabilized for the long period for Ni–ScSZ cermet, whereas the activity abruptly dropped for 20 vol.% Ni–YSZ after 600 min of operation.

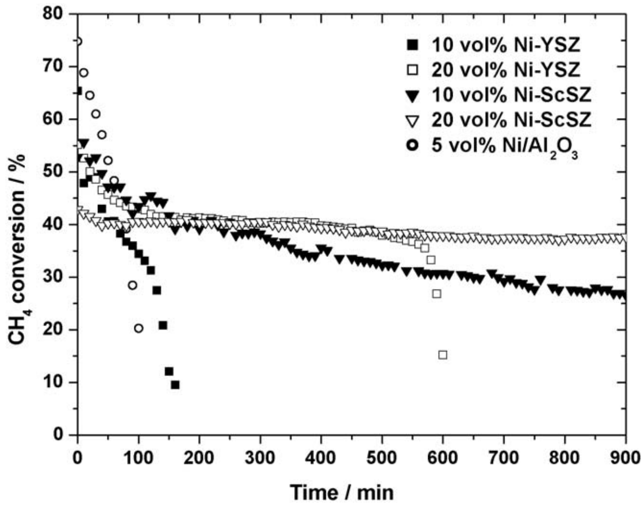

Fig. 6. CH_4 conversion as a function of time on stream over Ni–YSZ, Ni–ScSZ and Ni/Al_2O_3 at 700 °C. Reaction conditions: CH_4 10%, H_2O 6%, N_2 84%; S.V. = 20,000 l kg^{-1} h^{-1}.

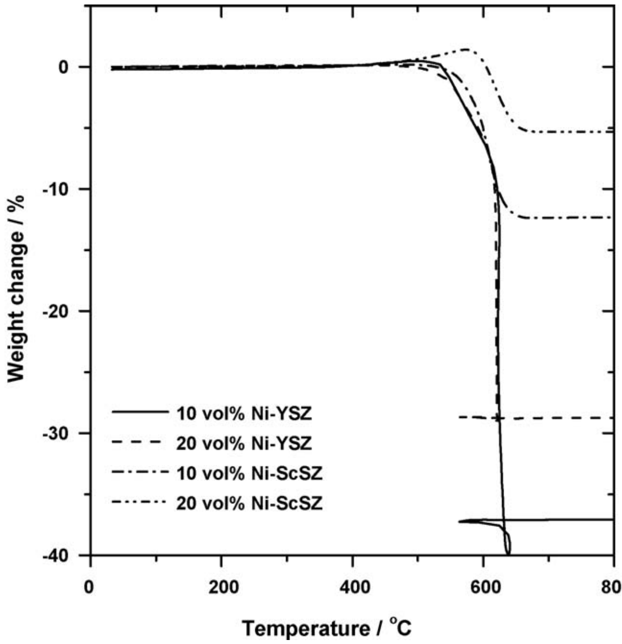

Fig. 7. TG profiles of Ni–YSZ and Ni–ScSZ in air at a heating rate of 10 °C min^{-1}. Measurements were conducted after steam reforming reaction at S/C = 0.6.

3.3. Gravimetric analysis of deposited carbon

The deposited carbon on cermet can be removed by Ni-catalyzed oxidation reaction with steam and/or oxygen. The deposited amount was then estimated from the weight loss during the course of heating in air. The time course of the weight change is shown in Fig. 7. The sample was exposed to the gaseous mixture of methane and steam at S/C = 0.6 for 5 h, and then transferred to the gravimetric analyzer. The sample weight was stable up to 400 °C, then slight weight gain initiated due to the oxidation of Ni to NiO. This weight increase disturbs the estimation of the amount of deposited carbon. But the Ni oxidation accompanies smaller weight change than carbon deposition which can be subtracted from the amount of bulk Ni. Then, the curve was followed by the sharp and sudden decrease in the weight at *ca.* 600 °C. The decrease was ascribed to the gasification through carbon oxidation. In the case of Ni–YSZ cermet, it was difficult to stabilize the temperature after the rapid burning of a large amount of carbon due to heat unbalance. The low-temperature shift at the end of the weight decrease was caused by unbalanced heat through sudden stop of the oxidation. The weight decrease upon carbon removal was largest for the case of 10 vol.% Ni–YSZ; the smaller weight decrease

Table 3
Weight loss and carbon deposition measured by TG analysis.

Catalyst[a]	Weight loss/%	Deposited carbon ratio (g-carbon/g-cat. × 100)/%
10 vol.% Ni–YSZ	37.2	39.6
20 vol.% Ni–YSZ	28.8	33.4
10 vol.% Ni–ScSZ	12.5	15.8
20 vol.% Ni–ScSZ	5.5	11.7

[a] The catalysts were exposed to the gaseous mixture of methane and steam at S/C = 0.6 for 5 h prior to the thermo-gravimetric analysis.

due to less amount of deposited carbon was estimated for the case of Ni–ScSZ cermet as summarized in Table 3.

As the carbon number in the fuel increases, carbon deposition might be facilitated even with supply of a large amount of steam. By supply of methane with sufficient steam, carbon deposition can be avoided. This is not the case for other hydrocarbons. Propane was supplied to the cermet for gravimetric measurement of deposited carbon. The deposition rate was significantly larger with the supply of C_3H_8 than the case of CH_4 at 700 °C, and was too rapid to describe in a figure. The observation at 600 °C was easier due to slower deposition rate. The time courses of the reaction over 20 vol.% Ni–YSZ and 20 vol.% Ni–ScSZ at S/C = 0.3 are shown in Fig. 8. A gradual decrease of the propane conversion on Ni–YSZ was observed after 500 min from the start of the reaction which is caused by the deposition of carbon. On the other hand, the conversion on the Ni–ScSZ cermet was stable up to 700 min of operation. It confirms the facilitated deposition of carbon for the Ni–YSZ than Ni–ScSZ.

3.4. Effect of preparation procedure on carbon deposition behavior

Scanning electron micrograph of (a) NiO–YSZ prepared by mechanical mixing and (b) NiO/YSZ prepared by impregnation are shown in Fig. 9. The microstructures of the oxide mixtures were not largely different from the other. The microstructure of impregnated NiO/YSZ was slightly more porous than that of mechanically mixed NiO–YSZ. Both of them became porous after reduction at elevated temperatures because of the phase change into metallic Ni.

The effect of preparation procedure for the cermet on the catalytic activity for reforming was investigated for the Ni–YSZ cermet prepared by the mechanical mixing and the Ni/YSZ cermet by impregnation. The time courses of the reaction over the cermets at S/C = 0.6 are shown in Fig. 10. The initial activity of the impregnated Ni/YSZ for the methane steam reforming was higher than the case of mechanically mixed Ni–YSZ when they were

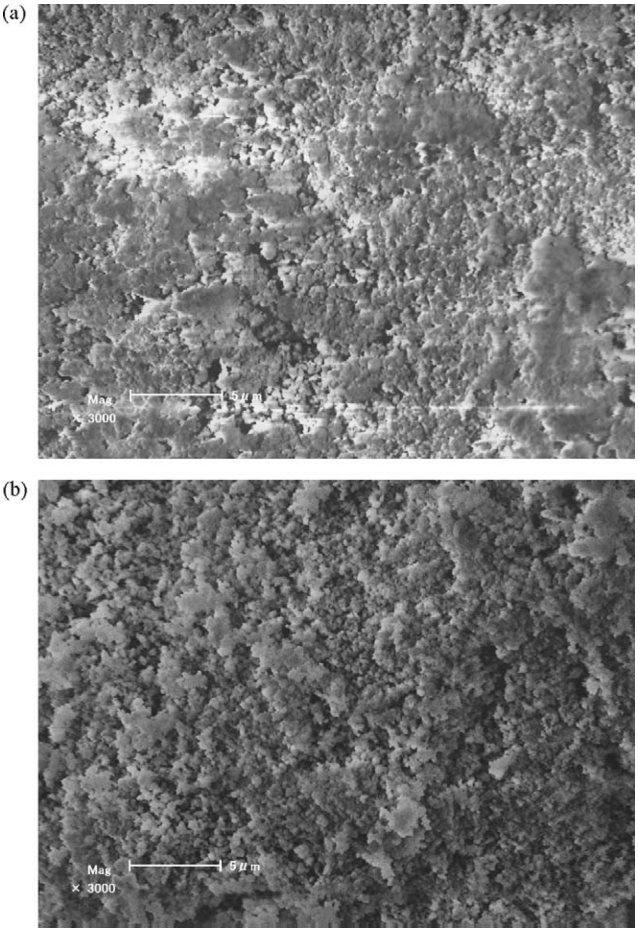

Fig. 9. SEM images of (a) NiO–YSZ prepared by mechanical mixing and (b) NiO/YSZ prepared by impregnation.

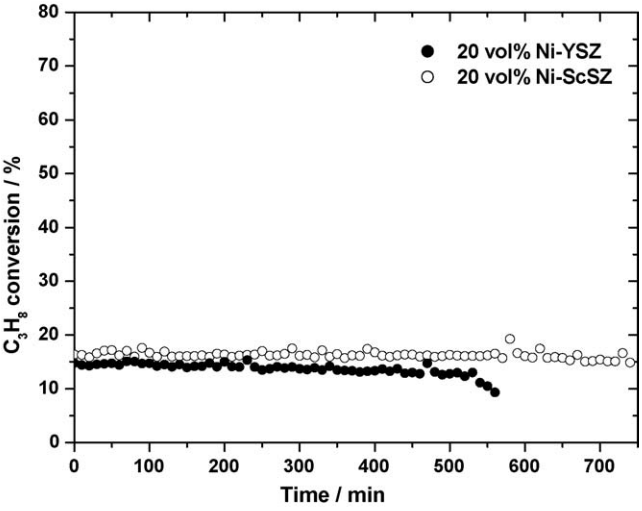

Fig. 8. C_3H_8 conversion as a function of time on stream for steam reforming of C_3H_8 at 600 °C over Ni–YSZ and Ni–ScSZ. Reaction conditions: C_3H_8 30%, H_2O 10%, N_2 60%; S.V. = 20,000 l kg^{-1} h^{-1}.

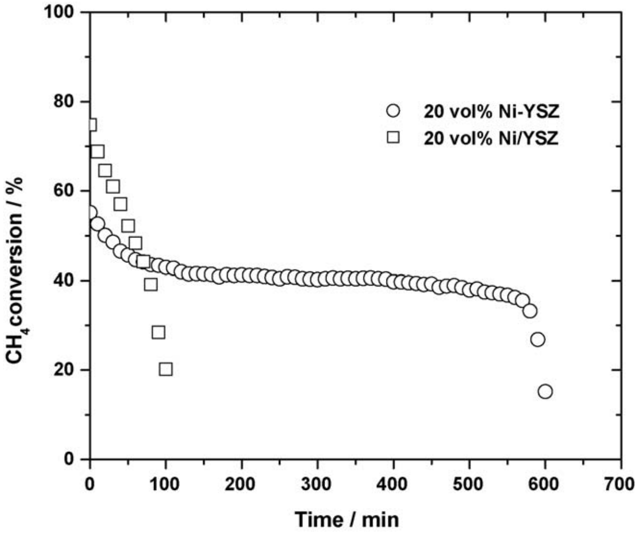

Fig. 10. CH_4 conversion as a function of time on stream for steam reforming of CH_4 at 700 °C over Ni–YSZ and Ni/YSZ. Reaction conditions: CH_4 10%, H_2O 6%, N_2 84%; S.V. = 20,000 l kg^{-1} h^{-1}.

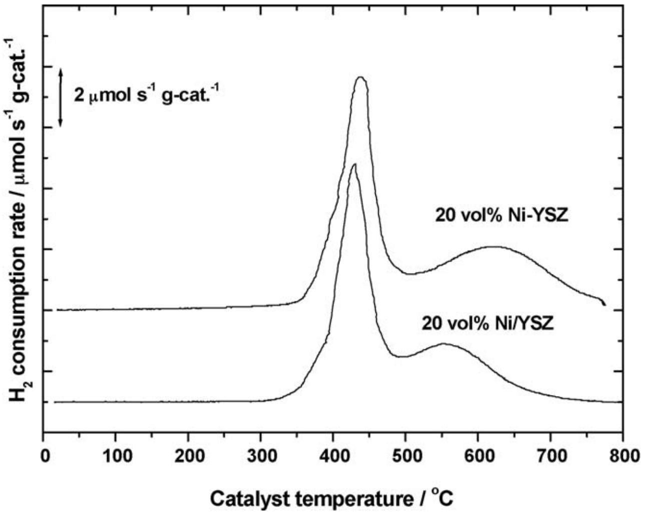

Fig. 11. TPR profiles of Ni–YSZ and Ni/YSZ. Measurements were conducted at a heating rate of 10 °C min^{-1} in 5% H_2/Ar.

compared at the high space velocity condition. The degradation with carbon deposition was tested for Ni–YSZ and Ni/YSZ catalysts in the long-term operation. The degradation more rapidly proceeded for the case of Ni/YSZ than Ni–YSZ. Since the surface of Ni was more effectively exposed to the fuel in the case of impregnated catalyst, the higher activity was achieved during methane steam reforming reaction. However, the impregnated Ni/YSZ catalyst was apt to be suffered from the carbon deposition. This result will be also explained by the difference in the interaction between Ni and oxide as is observed in TPR profiles (Fig. 11).

4. Conclusions

The catalytic activity of the cermet catalysts was investigated in the present study for the application to the internal reforming operation of solid oxide fuel cells. The activity and carbon deposition behavior were compared for Ni–YSZ and Ni–ScSZ catalysts. It was noted that the oxide materials mixed with Ni significantly affected carbon deposition rate and amount. The amount of deposited carbon was smaller for the case of the Ni–ScSZ catalyst; thus the stable long-term operation and smaller amount of deposited carbon were confirmed. The amount of Ni and preparation procedure also affected the carbon deposition behavior. Especially, the high content of Ni in the cermet significantly facilitated the deposition of carbon on the surface. This behavior should be important for the cermet catalysts for the application as the anode to the stable internal operation of SOFCs.

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