Noble metal catalysts highly-dispersed on Sm-doped ceria for the application to internal reforming solid oxide fuel cells operated at medium temperature

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Steam reforming of CH_4 on microcrystalline metal catalysts dispersed on Sm-doped ceria (SDC) was investigated with the intention of the application to an anode for internal reforming-type solid oxide fuel cells to be operated at medium temperature. Ru- or Ir-dispersed SDC exhibited high catalytic activities and low activation energies; these are potential candidates for that application. The high dispersion of microcrystalline noble metal catalysts results in such a high catalytic activity even with a significantly small amount of noble metal.

Keywords: microcrystalline catalyst; steam reforming; methane; internal reforming; solid oxide fuel cell

1. Introduction

Solid oxide fuel cells (SOFC) are promising electrochemical devices for efficient and clean generation of electric power. A schematic illustration of the SOFC is shown in fig. 1. Oxygen gas is ionized to oxide ions at the cathode of the SOFC, and the oxide ions discharge at the anode by the reaction with reactive hydrogen or carbon monoxide which may be reformed from source fuels such as natural gas or coal. The reactive fuel gases are usually formed before the introduction to the anode, as shown in fig. 1b. Owing to the high temperature operation, however, the cells have a potential of a direct reforming of source fuels into reactive gases at the anode, as illustrated in fig. 1a. For example, methane can be steam-reformed endothermically into hydrogen and carbon monoxide. The exhaust heat, produced in the cell due to an irreversibility in the process of electric power generation, can be utilized efficiently in the reforming reaction at the anode.

At present, the operating temperature of conventional SOFC is restricted to

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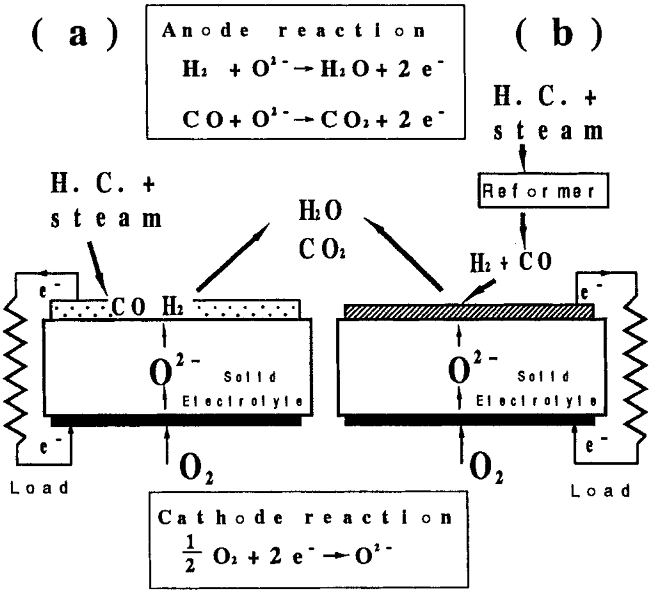

Fig. 1. Schematic illustration of SOFC utilizing hydrocarbons (H.C.) as the fuel: (a) internal reforming SOFC and (b) SOFC with an external fuel reformer.

very high temperature of about 1000°C because of the low ionic conductivity of yttria-stabilized zirconia (YSZ) used as the solid electrolytes [1]. Since the high temperature operation causes many serious problems, such as physical and chemical degradations of the constructing materials resulting in a limitation of choice of them, it is desirable to operate SOFC at a medium temperature around 800°C.

As well known, however, the lower operating temperature causes an increase both in the ohmic loss at the solid electrolytes and the polarization loss at the anode and cathode. Also, it should be noted that the Ni-YSZ cermet anode, which has been widely employed in SOFC, exhibited low catalytic activity [2] or a rapid degradation of the activity [3] even at 1000°C when the internal reforming reaction of methane-containing fuel gases was performed. It is probably due to the low specific surface area of the Ni catalyst. Therefore, the development of some active catalysts for the steam-reforming reaction is essential for the internal reforming SOFCs. Although high catalytic activities of noble metals supported on insulating oxide such as SiO_2, TiO_2 or Al_2O_3 for the steam reforming of CH_4 have been reported [4], they cannot work as the anode in SOFC because of their character of electric and/or electronic insulators. Therefore, it is important to develop an anode which satisfies the requirement both of a small electrochemical polarization and a high reforming activity to fuel gases such as CH_4.

We have proposed a new concept which realizes high performance anode and cathode for SOFC operating at medium temperature around 800°C [5]. Mixed conducting oxide particles, samaria-doped ceria (SDC) were employed as the anode material on which only a small amount of noble metal catalysts were highly dispersed. As the cathode material, Sr-doped $LaMnO_3$ (LSM) particles catalyzed with microcrystalline Pt were employed. It was found that both the catalyzed anode and cathode exhibited reduced polarization losses in the electrochemical reaction of pure H_2 and O_2, respectively.

In this paper, we will report the catalytic activities of the catalyzed-SDC for the steam reforming reaction of methane with the intention of the application as the anode in the internal reforming-type SOFC, shown in fig. 1a, operated at medium temperature.

2. Experimental

The catalyst support used was a powder of samaria doped ceria $(CeO_2)_{0.8}(SmO_{1.5})_{0.2}$ (SDC). The SDC was prepared from cerium and samarium nitrates (99.9% purity) by the following manner [6]. Mixed cerium and samarium hydroxides were obtained by the addition of ammonia solution to the mixed solution of the metal nitrates at 80°C, followed by filtering and then drying the resulting precipitates. The SDC was obtained by heating the precipitates at 400°C for 2 h and finally calcining at 1300°C for 10 h. In order to avoid that the reforming of CH_4 is controlled by the diffusion processes of CH_4 or products in catalyzed particles, the SDC powder with a small particle diameter of 105–180 μm was prepared by classifying with sieves after grinding the sinters.

Metal salt solutions containing a constant wt% of each metal ion were prepared by dissolving H_2PtCl_6, $RuCl_3$, $Rh(NO_3)_3$, $NiCl_2{\cdot}6H_2O$ or $H_2IrCl_3{\cdot}6H_2O$ into 2-propanol–H_2O (3 : 1 by volume). Microcrystalline noble metals (Pt, Ru, Rh, Ni, Ir) were dispersed on the SDC particles mentioned above by impregnating one of the above metal salt solutions so as to give 2 wt% metal loading, followed by thermal treatments at 600–1200°C for 2 h in a flow of hydrogen gas. The particle size of the microcrystalline catalyst was evaluated by Scherrer's equation from the full width at height medium (FWHM) of the X-ray diffraction.

In order to get the conversion of methane sufficiently small compared with the equilibrium one, the catalyzed SDC powder was diluted with non-catalyzed SDC powder of similar diameter, and the mixture was packed in a quartz tube (inner diameter: 4 mm) with a constant volume (0.05 cm^3), resulting in the amount of the supported catalysts ranging from 50 μg (Ru) to 1.5 mg (Ni). A reduction treatment of the catalysts was performed in advance at 1000°C for 1–2 h in a hydrogen stream. An appropriate ratio of steam to CH_4 (S/C ratio) is necessary to avoid the deposition of carbon during the steam reforming reaction. Preliminary experiments of the reforming by changing the S/C ratio showed that no carbon deposited at S/C ratio higher than 1.5 for the catalysts examined in this work. Hereinafter, the S/C ratio was kept at 2.0 for all the experiments.

The steam reforming was carried out, at first, with use of 20 vol% of hydrogen in the inlet gas at 1000°C. Contents of H_2, CO, CO_2 and unreacted CH_4 in the exhaust gas were determined by gas chromatography. The introduction of hydrogen was stopped after the catalytic activity became constant, and the steady state activity was evaluated at 600–1000°C under a series of reactant gas flow rates. The catalytic stability of each catalyst without adding hydrogen in the inlet gas was also monitored over 20 h.

As a reference to the present catalysts, we also examined the catalytic activity of the conventional Ni-YSZ cermet (particle diameter = 105–180 μm, Ni content = 20 wt%), which was prepared from 8 mol% YSZ (Tosoh) and NiO (2 μm) by calcination at 1400°C for 5 h in air, followed by the reduction of NiO in hydrogen atmosphere at 1000°C.

3. Results and discussion

X-ray diffraction analyses of the catalyzed SDC showed that the particle sizes of supported catalysts ranged from 14 to 28 nm as summarized in table 1.

The steam reforming of methane over various conventional catalysts has been reviewed [7]. At least two reactions are needed to represent the system,

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \tag{1}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{2}$$

and combining eqs. (1) and (2) yields

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2 . \tag{3}$$

The reaction kinetics for the steam reforming reaction of CH_4 over Ni-Al_2O_3 catalysts has been proposed [8],

$$-\mathrm{d}[CH_4]/\mathrm{d}t = k[CH_4](1 - K'/K) , \tag{4}$$

where k, K and K' are the rate constant, the conventional equilibrium constant and the corresponding molar ratio for the reactants and products present under the

Table 1
Average diameter, specific surface area, and catalytic properties of noble metal microcrystals dispersed on SDC for steam reforming of methane

Metal	Diameter [a] (nm)	Specific surface area, A [b] (m^2/g)	k/A at 800°C [c] (ml/m^2 min)	Activation energy [d] ($kJ\ mol^{-1}$)
Ir	15.4	17.3	4.53×10^4	104
Ru	19.1	26.0	3.48×10^4	145
Rh	22.7	21.2	1.39×10^4	124
Pt	28.1	10.0	2.25×10^3	174
Ni	14.8	45.8	1.35×10^3	135

[a] Determined from FWHM of X-ray diffraction.

[b] Calculated by assuming that metal particles were of spherical shape with the average diameter given in this table and the specific density.

[c] Rate constant at 800°C per unit surface area of metal given in this table.

[d] Calculated from Arrhenius plots of k shown in fig. 3.

actual operating conditions, respectively. The term $(1 - K'/K)$ takes into account the reverse reaction, which becomes important when the operation is close to the equilibrium. The observed K'/K depended on the contact time of CH_4, the reforming temperature and the activity of supported catalysts, but it was ranging from about 10^{-6} at 600°C to 1×10^{-3} for the longest contact time at 1000°C in all the present experimental conditions; K'/K was small enough to be ignored. Considering the material balance in the reaction (3) and the S/C ratio $= 2$, the molar concentration of CH_4, $[CH_4]$, is represented as a function of the initial concentration, C_0, and the conversion, x,

$$[CH_4] = 3C_0(1 - x)/(3 + 2x) . \tag{5}$$

By integration of eq. (4) with an appropriate assumption of $(1 - K'/K)$ being constant due to the negligibly small ratio of K'/K for the experimental condition, we obtain the following relationship:

$$-[5 \ln(1 - x) + 2x]/(1 - K'/K) = 3k\rho V/F , \tag{6}$$

where x, ρ, V and F stand for the conversion of methane, loading density of catalyst, apparent volume of the catalytic bed and volumetric gas supply rate, respectively, and V/F represents the contact time. The reaction kinetics of the present catalysts is well represented by eq. (4), as is indicated by the linear shape of the plots of the value of the left-hand side of eq. (6) as a function of V/F for all of the catalyzed SDC, as is shown, for example, in the case of Ir-SDC in fig. 2. The experimental data were not expressed by any other rate equations cited in ref. [9], taking into account the diffusion processes of reactants or products and the inhibition by strongly adsorbed reaction products. From the slope of the line, the rate con-

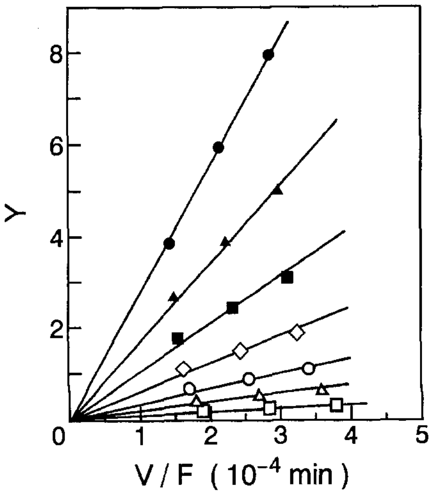

Fig. 2. Plots of the value of the left-hand side of eq. (6), $Y = -[5 \ln(1 - x) + 2x]/(1 - K'/K)$, versus V/F in the steam reforming of CH_4 on the Ir-SDC catalyst. Steam/CH_4 ratio = 2.0, amount of Ir = 200 μg, (●) 950°C, (▲) 900°C, (■) 850°C, (◇) 800°C, (○) 750°C, (△) 700°C, (□) 650°C.

stants *k* were determined for each supported catalyst as the function of reaction temperatures.

Fig. 3 shows Arrhenius plots of the rate constant per unit weight of loaded catalyst in the steam reforming reaction of CH_4 for various noble metal catalysts loaded on SDC. At 1000°C, Ru-SDC showed the highest rate constant and the rate constants for various catalysts decreased in the order of Ru>Ir>Rh>Ni>Pt. At 800°C, the rate constant for Ir-SDC becomes comparable to that for Ru-SDC due to the small activation energy of the former. The rate constant per unit metal surface area of each catalyst (k/A) at 800°C is shown in table 1 in order to compensate for the difference in the metal particle sizes among the supported catalysts, and the activation energies calculated from fig. 3 are also shown in the same table. The activation energy of 135 kJ mol^{-1} on Ni-SDC coincides well with that of 130 kJ mol^{-1} in the absence of diffusion effects reported for Ni-Al_2O_3 [10]. The apparent activation energies listed in table 1 are independent of the operating temperature and range from 104 to 174 kJ mol^{-1}, which are reasonably large compared with a small activation energy for the diffusion process. Hence, it is indicated that the reaction rate was not controlled by the diffusion processes of reactants or products in the catalyzed particles but by the kinetic process on the metal catalyst. The activities of Ru- and Ir-SDC are more than one order of magnitude higher than that of Pt-SDC at 800°C. The low activation energy obtained for Ru or Ir is favorable as compared with Pt for the medium temperature operation of the internal reforming type SOFC.

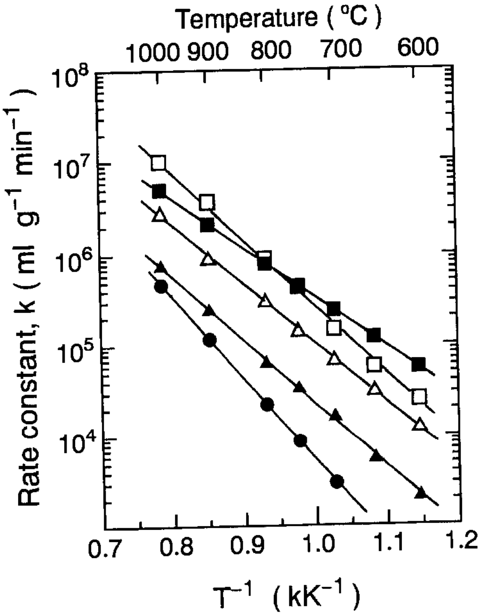

Fig. 3. Arrhenius plots of rate constants (k) based on the unit weight of each metal supported on SDC. Steam/CH_4 ratio =2.0, (□) Ir, (△) Rh, (▲) Ni, (●) Pt.

Fig. 4 shows typical changes of CH_4 conversion with time in the case of Ni-SDC, Ir-SDC and Ni-YSZ catalysts. Although the Ni-YSZ cermet exhibited a high conversion of CH_4, about 90% at 1000°C, under the external supply of 20 vol% hydrogen, the activity was reduced with time and finally to zero without external addition of hydrogen. Recently, Koide et al. [3] have reported that a degradation of the catalytic activity of the Ni-YSZ cermet commences to occur rapidly even at the open circuit condition of the CH_4-internal-reforming SOFC, and also that the discharge of the cell, which increases the oxygen partial pressure at the anode by the formation of water as the reaction product, accelerates the deterioration. These facts suggest that an oxidation of Ni in the cermet is one of the predominant reasons for the degradation. On the other hand, such a degradation of the catalytic activity was not observed, not only on the noble metal catalyzed SDC but also on the Ni-SDC, and their activities were very stable with time (fig. 4). The specific surface area of the dispersed Ni, which is several-hundreds times higher than that of Ni in the cermet, or the substrate of SDC may protect the dispersed Ni from the successive oxidation by steam along the gas stream. We concluded that Ni-YSZ cermet itself does not work as an internal reforming catalyst unless a proper amount of hydrogen is contained in the inlet reacting gas stream, and highly dispersed Ni on SDC works well in the internal reforming of CH_4 without any addition of hydrogen in the fuel stream in advance.

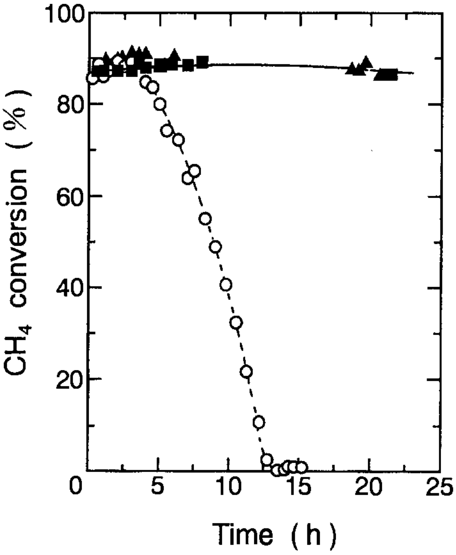

Fig. 4. Typical changes of the conversion ratios of CH_4 with time at 1000°C on Ni-YSZ cermet and catalyzed SDC with Ni or Ir. Steam/CH_4 ratio =2.0, $F = 84.9$ ml/min, (○) Ni-YSZ cermet, amount of Ni = 15.94 mg, (▲) Ni-SDC, amount of Ni = 1.5 mg, (■) Ir-SDC, amount of Ir = 0.2 mg. Mixing of hydrogen (20%) was stopped at 2 h for Ni-SDC and at 4 h for Ni-YSZ cermet and Ir-SDC.

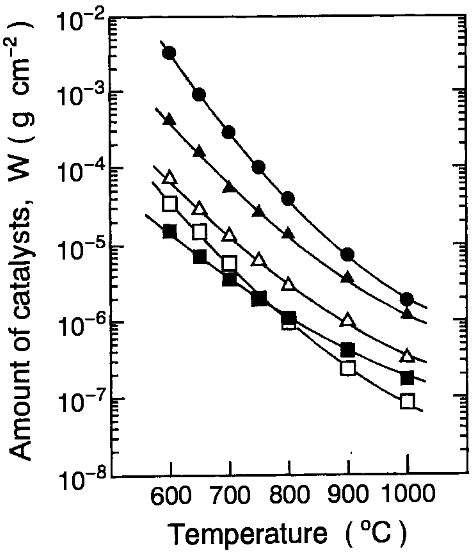

Fig. 5. Calculated amount of catalysts (W) required for SOFC operation at 0.3 A cm^{-2} with 80% CH_4 utilization. Microcrystalline metal catalysts were highly dispersed on SDC powder supports. Steam/CH_4 ratio =2.0, (□) Ru, (■) Ir, (△) Rh, (▲) Ni, (●) Pt.

In the internal reforming SOFC, the amount of the catalyst on the anode can be minimized by achieving a sufficient contact between fuel gases and the catalysts with well-designed anode structure. Based on the rate constants k obtained above, the minimum amount of noble metal catalysts required for the CH_4-internal reforming in SOFC can be calculated in the following manner. We assume that only hydrogen gas produced by the reactions (1) and (2) is consumed by the anode reaction ($H_2 + O^{2-} \rightarrow H_2O + 2e^-$), and that 3 mol of H_2 are produced with consumption of 1 mol of CH_4 although the amount of hydrogen produced should be anything in between three and four times the amount of CH_4 consumed. The anode reaction consumes hydrogen at a rate of 2.09 ml(at STP)/cm^2 min in the fuel cell operated at the current density of 0.3 A/cm^2. When the utilization of CH_4 = 80% at the current density, the amount of each catalyst required to convert CH_4 with a rate of 2.09/(3 × 0.8), i.e. 0.87 ml(at STP)/cm^2 min, was calculated, and the results are shown in fig. 5. It increases exponentially with decreasing temperature. However, Ru- or Ir-dispersed SDC required only about 1 μg/cm^2 of these precious metals to produce hydrogen equivalent to 0.3 A/cm^2 at 800°C in this estimation, which is about 1/100–1/1000 of that used for the conventional phosphoric acid fuel cells. Since these catalyzed SDC exhibited excellent anodic polarization properties for pure hydrogen in an SOFC [5], they must show high activities in both the catalytic and the electrocatalytic reactions under the internal reforming condition when the anode structure can be well designed. The studies of the anode layer catalyzed with the above catalysts are in progress using methane as the fuel.

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