1. Introduction

The improvement of thermal efficiency in vehicles is necessary to solve worldwide issues such as global warming and increasing consumption of fossil fuels. Most of the total energy consumption in automobiles is reduced by exhaust gas loss, cooling loss, and friction loss. The actual energy efficiency has not exceeded 30%. Especially, the exhaust gas loss is approximately 30% of the total fuel energy. Exhaust gas in a lean-burn condition contains steam, CO₂ and O₂; the temperature is not so high (473-673 K). Such low-temperature gas, which has a low exergy rate, has not been used as a heat source. Therefore, we aim to use an exhaust gas recirculation (EGR), and propose a catalytic syngas production system from exhaust gas because the catalytic syngas production such as steam reforming and dry reforming of methane, which are endothermic reactions, can gain enthalpy, as described by the following equations:\(^1\)

\[
\text{SR: } \text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO} \\
\Delta H^{0}_{298} = 205.9 \text{ kJ mol}^{-1} \tag{1}
\]

\[
\text{DR: } \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{H}_2 + 2\text{CO} \\
\Delta H^{0}_{298} = 247.2 \text{ kJ mol}^{-1} \tag{2}
\]

Recently, lean-burn combustion, by which oxygen concentration at the exhaust outlet exceeds 5% in the condition of \(\lambda = 1.3\), in gasoline combustion engines, has received attention from automobile manufacturers because of its low exhaust gas temperature and high fuel efficiency. Considering the utilization of exhaust gases and low temperature heat, tri-reforming (TR)\(^2\): a mixed reaction with steam reforming (SR)\(^4\) and dry reforming (DR)\(^3\) and partial oxidation (POx) is an option for the purpose. Although SR and DR are endothermic reactions and can gain enthalpy, the partial oxidation and complete combustion of methane are large exothermic reactions and loses enthalpy, as presented in the following equation.

\[
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \\
\Delta H^{0}_{298} = -890.4 \text{ kJ mol}^{-1} \tag{3}
\]

Therefore, a selective reforming reaction with suppressed methane combustion is necessary to gain enthalpy using the lean-burn exhaust gas. Produced syngas by TR can be re-injected into the engine, where it can improve combustion efficiency in automobile engines. Walker\(^5\) reported that TRM (TR of methane) cannot proceed under 1023 K. In these situations, novel processes such as catalytic reactions using plasma, photocatalysis, and electrocatalysis should be developed to recover exergy from low-temperature heat emissions.
Recently, our group found low-temperature catalytic reactions proceeding in an electric field, even in a low temperature range (room temperature to 473 K)\(^{26-35}\).

For this study, we selected methane as a model fuel considering aspects of the low cost by virtue of the rapid development of shale gas resources, and the wide utilization of natural gas such as natural gas vehicles (NGVs) in the Middle East, the US, and other countries. Methane has the most stable tetrahedral structure among hydrocarbons. Therefore, catalysts showing high TRM activity at low temperatures might be applied to other hydrocarbons contained in gasoline and diesel fuel. This study investigated the TRM reaction in the electric field over various Ni-supported catalysts. And we succeeded in promoting SR and DR with suppressing methane combustion even at 473 K in an electric field. So we conducted characterizations using X-ray diffraction (XRD), field emission-transmission electron microscope (FE-TEM), scanning transmission electron microscope-energy dispersive X-ray fluorescence spectrometer (STEM-EDX), and \(H_2\)-temperature-programmed reduction (\(H_2\)-TPR) to clarify the causes of suppressed combustion ability on these catalysts.

2. Experimental

2.1. Catalyst Preparation

Ce\(_{x}\)Zr\(_{1-x}\)O\(_2\) (\(x = 0.25, 0.50\) and 0.75), La\(_y\)Zr\(_{1-y}\)O\(_2\) (\(y = 0.1\) and 0.25), Y\(_{0.1}\)Zr\(_{0.9}\)O\(_2\), and Mg\(_{0.5}\)Ti\(_{0.5}\)O\(_2\) were prepared using a polymerized complex method using citric acid and ethylene glycol\(^{27,29,32}\). The citric acid and ethylene glycol (Kanto Chemical Co., Inc.) were dissolved in water. Then metal nitrate precursors (Kanto Chemical Co., Inc.) were added to the solution. The molar ratios of metal, citric acid, and ethylene glycol were 1 : 3 : 3. The water volume was 250 mL. The prepared solution was evaporated in a water bath at 353 K overnight. Then the solution was dried on a hot plate with stirring. The resultant powder, which was calcined at 673 K for 2 h with a ramping rate of 5 K \(\text{min}^{-1}\), was finallycalcined at 1123 K (10 K \(\text{min}^{-1}\)) for 10 h. MgO (JRC-MGO-4) and ZrO\(_2\) (JRC-ZRO-3) were provided by the Catalysis Society of Japan and were used as received.

As an active site, X wt\%Ni (\(X = 0.25-5\)) was loaded on oxide supports using an impregnation method with water as an impregnation solvent. First, water (20 mL) and oxide supports (0.99 g) were added to a 300 mL round-bottom flask and were stirred for 2 h using a rotary evaporator \(\text{in vacuo}\). Subsequently, Ni(NO\(_3\))\(_2\)·6H\(_2\)O (0.253 g) dissolved into water (10 mL) were added to the flask and were stirred again for 2 h. The suspension was then dried. Then the powder was dried overnight at 393 K, and was calcined at 773 K for 2 h with a ramping rate of 5 K \(\text{min}^{-1}\). In addition, the Ni-Mg/La\(_{0.1}\)Zr\(_{0.9}\)O\(_2\) catalysts were prepared using an impregnation method. Mg was supported as a second metal on the Ni/La\(_{0.1}\)Zr\(_{0.9}\)O\(_2\) catalyst. In this work, the effect of the impregnation order of Ni and Mg on the catalytic performance was investigated. Ni/Mg/La\(_{0.1}\)Zr\(_{0.9}\)O\(_2\) (sequential impregnation), Mg/Ni/La\(_{0.1}\)Zr\(_{0.9}\)O\(_2\) (sequential impregnation), and Ni-Mg/La\(_{0.1}\)Zr\(_{0.9}\)O\(_2\) (co-impregnation) were prepared.

The preparation of Ni/Mg/La\(_{0.1}\)Zr\(_{0.9}\)O\(_2\) was conducted as follows: First, water (20 mL) and oxide supports (0.99 g) were added to a 300 mL round-bottom flask and were stirred for 2 h \(\text{in vacuo}\) with a rotary evaporator. Subsequently, Mg(NO\(_3\))\(_2\)·6H\(_2\)O (0.253 g) dissolved in water (10 mL) was added to the flask and was stirred for 2 h again. The suspension was dried. Then the powder was dried overnight at 393 K. Then the powder was calcined at 773 K for 2 h with a ramping rate of 5 K \(\text{min}^{-1}\). For the preparation of Ni/Mg/La\(_{0.1}\)Zr\(_{0.9}\)O\(_2\) catalyst, Mg/La\(_{0.1}\)Zr\(_{0.9}\)O\(_2\) catalyst was impregnated with an aqueous solution of Ni(NO\(_3\))\(_2\)·6H\(_2\)O.

For the preparation of the Mg/Ni/La\(_{0.1}\)Zr\(_{0.9}\)O\(_2\) catalyst, Ni/La\(_{0.1}\)Zr\(_{0.9}\)O\(_2\) catalyst was impregnated with an aqueous solution of Mg(NO\(_3\))\(_2\)·6H\(_2\)O to obtain. Then it was dried and calcined at 773 K for 2 h.

For the preparation of the Ni-Mg/La\(_{0.1}\)Zr\(_{0.9}\)O\(_2\), La\(_{0.1}\)Zr\(_{0.9}\)O\(_2\) was impregnated with a mixed aqueous solution of Ni(NO\(_3\))\(_2\)·6H\(_2\)O and Mg(NO\(_3\))\(_2\)·6H\(_2\)O.

To investigate the effect of solvent on a Ni particle dispersion on the La\(_{0.1}\)Zr\(_{0.9}\)O\(_2\) support, Ni(aq)/Mg/La\(_{0.1}\)Zr\(_{0.9}\)O\(_2\) using an acetone as a solution was also prepared. Mg/La\(_{0.1}\)Zr\(_{0.9}\)O\(_2\) was impregnated with an acetone solution of Ni(NO\(_3\))\(_2\)·6H\(_2\)O.

2.2. Activity Test

Catalytic activity tests with an electric field were conducted with a fixed bed flow-type reactor equipped with a quartz tube (6.0 mm i.d.) as described in an earlier report\(^{32}\). The catalyst was sieved into 355-500 mm and was charged in the reactor (200 mg). The catalyst was used without pre-reduction. The reactant feed gases were methane, oxygen, carbon dioxide, H\(_2\)O, and Ar (CH\(_4\) : O\(_2\) : CO\(_2\) : H\(_2\)O : Ar = 6 : 1 : 2 : 2 : 9, total flow rate: 200 SCCM). For the electric field accompanying the reaction, two stainless steel electrodes (2.0 mm o.d.) were inserted contiguously to the catalyst bed in the quartz tube reactor. A DC power supply was used to impose an electric field to the catalyst bed with 3.0 mA current. The imposed voltage depends on the electric properties of the catalyst. Current and voltage profiles were measured using an oscilloscope (TDS 3052B; Tektronix Inc.). The furnace temperature was 473 K, which was close to the exhaust gas temperature at low load of the automobile. After passing a cold trap, the product gases were analyzed using gas chromatograph with flame ionization detector (GC-FID, GC-14B; Shimadzu Corp.) with a Porapak N packed column after methanation by a Ru/Al\(_2\)O\(_3\) catalyst and gas chromatograph with thermal conductivity detector.
(GC-TCD, GC-2014; Shimadzu Corp.) with a molecular sieve 5A packed column. The calculation formulae for reactant conversion, CH4 conversion for combustion, and CH4 conversion for reforming (SR and DR) are presented below.

Reactant conv. = \frac{F_{\text{Reactant, in}} - F_{\text{Reactant, out}}}{F_{\text{Reactant, in}}} \times 100 \quad (4)

CH4 conv. for combustion = \frac{1}{2} \times \left( F_{\text{CH4, in}} - F_{\text{CH4, out}} \right) \times 100 \quad (5)

CH4 conv. for reforming = \frac{F_{\text{H2, in}} - F_{\text{H2, out}}}{F_{\text{CH4, in}}} \times 100 \quad (6)

CH4 conversion for combustion is calculated on the assumption that oxygen is consumed only by combustion of methane (CH4 + O2 → CO2 + 2H2O). CH4 conversion for reforming is calculated from the total consumption rates of methane and the methane consumption rate for combustion. The difference between total enthalpy of the output and that of input was defined as ΔHr. The only by-product except CO, CO2, H2 and H2O for the TRM reaction in the electric field was deposited carbon. Carbon balances were calculated from the supply rate for CH4 and CO2, and the carbon balances were almost 98–102 %. Hydrogen balances were calculated from the supply rate for CH4 and H2O, and the hydrogen balances were also almost 98–102 %.

### 2.3. Characterization of Catalyst

Crystalline structures of catalysts were characterized using powder XRD (Smart Lab, Rigaku Corp.) operating at 40 kV and 40 mA with Cu Ka radiation. The 2θ angle was scanned at 20° min⁻¹ for the range of 10° < 2θ < 90°. Specific surface areas of catalysts were measured using N2 adsorption and were calculated using BET method (Gemini VII, Micromeritics Instrument Corp.) after pre-treatment at 473 K in N2 atmosphere for 2 h. The catalyst surface was observed using FE-TEM (JEM-2100F; Hitachi Ltd.) operating at 200 kV acceleration voltage and 0.1 nm resolution value. A sample was dropped on a collodion (NP-C15; Okenshoji Co., Ltd.) after ultrasonic dispersion in 99.5 % ethanol (Kanto Chemical Co., Inc.). Furthermore, element mappings of O, Mg, Ni, La, and Zr were observed using STEM-EDX (HF-2200; Hitachi Ltd.). H2-TPR was measured (TGA-50; Shimadzu Corp.) for the reduction behavior of Ni metal after pre-treatment at 773 K (20 K min⁻¹) in Ar for 30 min. H2-TPR was conducted from 323 to 1223 K by the ramping rate of 5 K min⁻¹ in 20 vol%H2/Ar.

### 3. Results and Discussion

#### 3.1. Screening Tests for Tri-reforming of Methane in an Electric Field

First, to discover suitable catalysts for the TRM reaction, 1 wt%Ni catalysts supported on various oxides under a kinetic condition at 473 K in an electric field were investigated to assess their catalytic activities. The gap of voltage was 200 V and the decline of the voltage with time on stream was not observed. Among various basic oxides, we selected MgO, CeO2, ZrO2, Ce0.25Zr0.75O2 (x = 0.25, 0.50 and 0.75; denoted as Ce-ZrO2), La0.1Zr0.9O2 (y = 0.1 and 0.25 denoted as La-ZrO2), or Mg0.5Ti0.5O2 as a catalyst support in this work because Ni supported on these supports showed high catalytic activity for the TRM reaction in the conventional catalytic system (not imposing the electric field). Results are presented in Table 1. Among these catalysts, 1 wt%Ni/MgO showed the highest TRM activity (total CH4 conv. = 32.3 %) and 1 wt%Ni/La0.1Zr0.9O2 (LZO) also showed higher activity. However, over the 1 wt%Ni/MgO catalyst, electric power consumption to impose the electric field was high, and the electric field was not stable because of the high electric resistance of the catalyst.
the TRM reaction with the electric field are not markedly differ-
presents catalytic activities for various amounts of Ni
LZO catalyst showed low TRM activity (total CH4 conv.
we inferred that LZO is a suitable catalyst support for
of methane. For heat recovery (i.e. \( \Delta H_r > 0 \)), it is neces-
suppression combustion without decreasing
MgO. Over the 1 wt%Ni/LZO catalyst, high catalytic ac-
total CH4 conv. = 20.7 %) was achieved with high elec-
the electric efficiency without forming a discharge. The
electric power consumption over Ni/LZO was one-
remained exothermic (\( \Delta H_r = 0.02 \text{ kJ min}^{-1} \)) because

Table 2 Catalytic Activities in an Electric Field over Ni/LZO Catalyst with Various Ni Loadings\(^a\)

| Ni loading amount [wt%] | Power [W] | CH4 conversion [%] | O2 conv. [%] | Reforming selectivity [-] | H2/CO [-] | \( \Delta H_r \) [kJ min\(^{-1}\)] | BET surface area\(^a\) [m\(^2\) g\(^{-1}\)] |
|------------------------|----------|-------------------|--------------|--------------------------|----------|-----------------|-----------------|
| 0                      | 2.7      | 3.7               | 1.9          | 1.8                      | 27.9     | 46.9            | 1.8             | -0.033         | 10.4          |
| 0.25                   | 3.4      | 12.8              | 7.0          | 5.8                      | 91.1     | 44.9            | 1.2             | -0.113         | 11.1          |
| 0.50                   | 4.1      | 18.2              | 7.5          | 10.7                      | 80.4     | 58.2            | 1.6             | -0.079         | 10.8          |
| 1                      | 2.6      | 20.7              | 8.2          | 12.5                      | 100      | 56.3            | 2.7             | -0.091         | 13.8          |
| 5                      | 1.8      | 18.7              | 7.6          | 11.2                      | 100      | 55.8            | 3.6             | -0.098         | 15.4          |

\( \text{a) Feed gas CH}_4 \colon \text{O}_2 \colon \text{CO}_2 \colon \text{H}_2\text{O} \colon \text{Ar} = 6 : 1 : 2 : 2 : 9, \text{total flow rate: 200 SCCM, input current: 3.0 mA, catalyst weight: 200 mg, furnace temperature: 473 K.}\)
b) Determined by N\(_2\) physisorption.

Table 3 Catalytic Activities over 1 wt%Ni-(Mg, Ca, Sr, Ba)/LZO in the Electric Field\(^b\)

| Supported metal | Power [W] | CH4 conversion [%] | O2 conv. [%] | Reforming selectivity [-] | H2/CO [-] | \( \Delta H_r \) [kJ min\(^{-1}\)] |
|----------------|----------|-------------------|--------------|--------------------------|----------|-----------------|
| 1 wt%Ni        | 2.6      | 20.7              | 8.2          | 12.5                      | 100      | 56.3            | 2.7             | -0.091         |
| 1 wt%Mg        | 2.5      | 4.5               | 1.9          | 2.6                      | 27.1     | 56.7            | 1.6             | -0.038         |
| 1 wt%Ni-1 wt%Mg | 2.0     | 15.7              | 3.9          | 11.8                      | 54.6     | 74.6            | 2.2             | -0.020         |
| 1 wt%Ni-1 wt%Ca | 1.8     | 9.6               | 3.8          | 5.8                      | 57.9     | 39.5            | 2.7             | -0.051         |
| 1 wt%Ni-1 wt%Sr | 2.4     | 16.4              | 6.7          | 9.7                      | 92.9     | 50.1            | 3.8             | -0.090         |
| 1 wt%Ni-1 wt%Ba | 1.3     | 15.5              | 7.2          | 8.2                      | 100      | 26.3            | 3.3             | -0.112         |

\( \text{a) Feed gas: CH}_4 \colon \text{O}_2 \colon \text{CO}_2 \colon \text{H}_2\text{O} \colon \text{Ar} = 6 : 1 : 2 : 2 : 9, \text{total flow rate: 200 SCCM, input current: 3.0 mA, catalyst weight: 200 mg, furnace temperature: 473 K.}\)

To suppress the methane combustion, we tried to add various group II elements on the 1 wt%Ni/LZO. Table 3 presents results of activity tests over 1 wt%Ni-M/LZO catalysts (M = Mg, Ca, Sr, Ba; Ni-M/LZO) prepared using co-impregnation method in the electric field at 473 K to confirm the effect of second metal addition on the catalytic activity and suppression of methane combustion. Table 3 shows that, by adding group II elements, O2 conversion decreased (methane combustion was suppressed) in the following order: \( \text{Ni only (100 %)} = \text{Ni} + \text{Ba (100 %)} > \text{Ni} + \text{Sr (92.9 %)} > \text{Ni} + \text{Ca (57.9 %)} > \text{Ni} + \text{Mg (54.6 %)} \). Moreover, the combustion activity (CH\(_4\) conv. for combustion) for Ni-Mg/LZO catalyst (3.9%) declined to less than that for Ni/LZO catalyst (8.2%). However, the reforming activity for Ni-Mg/LZO catalyst (CH\(_2\) conv. for reforming: 11.8%) was almost equal to that for Ni/LZO catalyst (12.5%), although the reforming activity decreased in Ba (8.2%), Sr (9.7%), or Ca (5.8%) added to Ni/LZO. As Table 3 shows, 1 wt%Mg/LZO catalyst showed low TRM activity (total CH\(_4\) conv. = 4.5%), indicating that the co-supported Mg itself had low activity for TRM. Results show that the addition of Mg to Ni/LZO catalyst suppressed methane combustion while maintaining reforming activity, thereby minimizing enthalpy loss by combustion (\( \Delta H_r = -0.02 \text{ kJ min}^{-1} \)).

To investigate carbon deposition over Ni/LZO and Ni-Mg/LZO, temperature programmed oxidation (TPO) measurements were conducted. After 60 min reaction
in the electric field at 473 K, 3.84 mg g-cat⁻¹ over 1 wt%Ni/LZO catalyst was detected. Conversely no carbon was detected on Ni_Mg/LZO. Therefore, the amount of deposited carbon after the TRM reaction in the electric field was small because of its low reaction temperature.

3.2. Optimization of Ni/Mg/LZO Catalysts for Suppressing Methane Combustion

To optimize the loading amounts of Mg for Ni_Mg/LZO catalysts, tri-reforming of methane in the electric field over Ni_Mg/LZO with various Mg loadings were conducted as presented in Table 4(A). Methane combustion activity was stable with increasing Mg loading amount (CH₄ conv. for combustion: 3.9 % → 3.3 %). The reforming activity decreased drastically and concomitantly with increasing Mg loading (CH₄ conv. for reforming: 11.8 % → 6.6 %). Thereby, the value of reforming selectivity decreased concomitantly with increasing Mg loading. As presented in Fig. 1 (XRD pattern), the peak intensities of MgO phase increased concomitantly with increasing Mg loading amounts. Excess amounts of Mg loading might cover the active site of Ni particles, thereby, the reforming activity of Ni particle was suppressed by excess Mg addition. Consequently, the reaction enthalpy decreased by increasing Mg loading. From these results, we inferred 1 wt% as the most appropriate amount for Mg co-supported on Ni/LZO catalyst to increase reforming selectivity.

Next, we elucidated the effects of impregnation sequences of Ni and Mg on catalytic activity. For comparison with Ni-Mg/LZO (co-impregnation), Ni/Mg/LZO (Mg → Ni) and Mg/Ni/LZO (Ni → Mg) were prepared using a sequential impregnation method with water as an impregnation solvent. Table 4(B) presents results for catalytic activity tests over these three catalysts. Methane combustion activities for these three catalysts were almost identical. However, the impregnation sequences affected the methane reforming activity as Ni/Mg/LZO (13.8 %) > Ni-Mg/LZO (11.8 %) > Ni/Mg/LZO (9.4 %). Next, to improve the reforming activity, we investigated the effect of Ni precursor in the Ni/Mg/LZO on the catalytic activity. As shown in Table 4, Ni(ac)/Mg/LZO catalyst, prepared using acetone as an impregnation solvent, showed higher reforming activity than Ni/Mg/LZO catalyst, prepared using aqueous solution of Ni nitrate. In addition, the value of the reforming ratio (CH₄ conv. for reforming/CH₄ conv. for combustion) increased on Ni(ac)/Mg/LZO catalyst (74.6 → 79.8 %). Therefore, Ni(ac)/Mg/LZO catalyst selectively promoted methane reforming.

| Supported metal | Power [W] | CH₄ conversion [%] | O₂ conv. [%] | Reforming selectivity [-] | H₂/CO [-] | ΔHᵣ [kJ min⁻¹] |
|----------------|----------|--------------------|-------------|---------------------------|-----------|---------------|
|                |          | total | for combustion | for reforming |             |              |               |
| 1 wt%Ni_1 wt%Mg | 2.0      | 15.7 | 3.9 | 11.8 | 54.6 | 74.6 | 2.2 | -0.020 |
| 1 wt%Ni_3 wt%Mg | 2.6      | 12.9 | 3.2 | 9.7 | 37.9 | 73.1 | 1.4 | -0.021 |
| 1 wt%Ni_5 wt%Mg | 2.1      | 9.8  | 3.3 | 6.6 | 45.3 | 66.4 | 1.7 | -0.038 |

Table 4 Catalytic Activities for TRM in the Electric Field over (A) Various Loading Amounts of Mg on Ni/LZO and (B) Ni-Mg/LZO in Various Preparation Methods

![XRD Patterns](image)
and suppressed methane combustion, and brought an endothermic result ($\Delta H > 0$; $\Delta H = +0.004$ kJ min$^{-1}$).

To investigate the combustion suppression effect of Ni(ac)/Mg/LZO under higher contact time ($W/F_{CH4}$) conditions, the effect of contact time on TRM activity and $\Delta H$ over Ni(ac)/Mg/LZO catalyst at 473 K in the electric field was investigated in Table 5. As presented in Table 5, methane reforming activity increased continuously, concomitantly with increased contact time, although methane combustion activity increased slightly. As a result, the TRM reaction proceeded over Ni(ac)/Mg/LZO catalyst at a neutral thermic region ($\Delta H = -0.003$ to +0.004 kJ min$^{-1}$) with suppressed excess combustion, even at a higher contact time. These results indicate that the reforming reaction proceeded selectively on the surface of Ni(ac)/Mg/LZO catalyst in the electric field.

### 3.3 Effects of the Electric Field and Temperature on Tri-reforming Activity

To examine the electric field effects on the catalytic activity, we conducted the TRM reaction over the Ni/LZO and Ni(ac)/Mg/LZO catalysts with or without the electric field. Figure 2 presents conversion of methane (for reforming and for combustion) and $\Delta H$ with and without the electric field at various temperatures. In the catalytic reaction without the electric field, the methane conversions were almost zero in the low temperature range ($<673$ K). However, the TRM reaction proceeded even at furnace temperatures as low as 473 K when the electric field was imposed. Consequently, imposing the electric field to the catalyst bed enabled proceeding of the low temperature reaction at the temperatures of the exhaust gas (473-673 K). From the results of operando-diffuse reflection infrared Fourier transform spectroscopy (operando-DRIFTS), proton hopping via adsorbed water on the catalyst surface occurred with the electric field, known as the Grothuss mechanism, and the surface protonics by the application of electric field served an important role in the enhancement of SRM. Referring these results, this mechanism would be applied to TRM because of the existence of H$_2$O as a reactant gas.

Furthermore, to elucidate the effect of temperature in the electric field on the activity for reforming and combustion, we investigated the reaction over Ni(ac)/Mg/LZO in the electric field at 473-773 K. The voltage was declined from 900 to 800 V with increasing reaction temperature from 473 to 573 K. But the voltage was stable at 800 V over 573 K. The voltage increased from 900 to 800 V with increasing reaction temperature from 473 to 573 K. But the voltage was stable at 800 V over 573 K. Consequently, $\Delta H$ decreased by increasing external temperature by the enhancement of combustion. At 473 K, Ni(ac)/Mg/LZO catalyst can suppress combustion by virtue of the low reaction temperature in the electric field.

### 3.4 Characterization for Ni(ac)/Mg/LZO Catalyst

As described above, the Ni(ac)/Mg/LZO catalyst selectively promoted methane reforming with suppression of methane combustion on TRM reaction in the electric field at 473 K. To clarify the reason for the methane combustion suppression, the structure and reducibility for Ni(ac)/Mg/LZO catalyst were evaluated using scanning transmission electron microscope-energy disper-

| W/F$_{CH4}$ [g-cat h mol$^{-1}$] | Power [W] | CH$_4$ conversion [%] | O$_2$ conv. [%] | Reforming selectivity [-] | H$_2$/CO [-] | $\Delta H$ [kJ min$^{-1}$] |
|-------------------------------|-----------|-----------------------|----------------|---------------------------|-------------|------------------|
| total                         |           | for combustion        | for reforming  |                           |             |                  |
| 1.3                           | 2.9       | 19.7                  | 3.9            | 15.8                      | 47.4        | 79.8             | +0.004           |
| 2.7                           | 2.3       | 26.7                  | 5.3            | 21.4                      | 67.2        | 80.1             | -0.003           |
| 4.0                           | 2.3       | 29.6                  | 6.0            | 23.6                      | 79.0        | 79.5             | 1.9              | 0.004           |

Reaction condition: feed gas, CH$_4$: O$_2$: CO$_2$: H$_2$O: Ar = 6: 1: 2: 2: 9, total flow rate: 67-200 SCCM, input current: 3.0 mA, catalyst weight: 200 mg, furnace temperature: 473 K.

Fig. 2 Temperature Dependence of Catalytic Activities over 1 wt%Ni(ac)/1 wt%Mg/LZO Catalyst with or without the Electric Field
sive X-ray spectroscopy (STEM-EDS), HAADF, and H2-TPR measurements.

Figure 3 depicts scanning electron microscope (SEM) and HAADF images and the EDS mappings of Ni and Mg over Ni/LZO and Ni(ac)/Mg/LZO. As depicted in Fig. 3, the average Ni particle size on Ni(ac)/Mg/LZO was 25 nm, which was almost identical to those on Ni/LZO (20 nm) and Ni/Mg/LZO (20 nm). Therefore, the supported Ni particle size had no effect on suppressing the methane combustion. Additionally, the results of the EDS mappings of the Ni(ac)/Mg/LZO catalyst indicated that Mg was highly dispersed. The location of Mg completely overlapped that of Ni. In earlier reports, NiO-MgO solid solution was well known to form highly dispersed Ni metal particles after reduction\(^{36,38}\). These results indicate that the co-supported Mg particle might form an adjacent or solid-solution structure to the Ni particle and that it might also contribute to methane combustion suppression. This structure could not be observed using XRD because of its small particle size. The formation of NiO-MgO solid solution should be investigated in future.

To investigate the effect of the Ni-Mg adjacent structure on the reducibility of Ni, H2-TPR measurement was conducted on LZO support, Ni/LZO, and Ni(ac)/Mg/LZO (portrayed in Fig. 4). As portrayed in Fig. 4 (b), two reduction peaks at 573 K and 973 K were observed on Ni/LZO. A low-temperature peak (573 K) was assigned to weakly interacted Ni oxide with LZO support. A report of the relevant literature described that bare NiO also showed a reduction peak at around 573 K over Ni/ZrO\(_2\)\(^{39}\). A high-temperature peak (973 K) was assigned to the strongly interacted Ni oxide with LZO support. However, on the Ni/Mg/LZO catalyst, as portrayed in Fig. 4 (c), the low-temperature peak disappeared. The amounts of the total weight loss in H2-TPR on each catalyst were the following: LZO, 0.080 wt%; Ni/LZO, 0.405 wt%; and Ni(ac)/Mg/LZO, 0.325 wt%. The theoretical value was calculated as 0.27 wt%, assuming that the supported NiO was fully reduced to Ni metal. The experimental value of weight loss on Ni/LZO and Ni(ac)/Mg/LZO was higher than that of theoretical value. As portrayed in Fig. 4...
(a), weight loss was observed even on the bare LZO support, indicating that the LZO support was also reduced at around 973 K.

The high-temperature reduction peak was mainly attributable to the reducibility of Ni oxide interacted strongly with LZO support. It was considered that Ni oxide was stabilized on Ni(ac)/Mg/LZO, even in the reaction atmosphere, by virtue of the formation of an adjacent structure to a Mg particle with a Ni oxide. It might contribute methane combustion suppression.

4. Conclusion

Tri-reforming of methane (TRM) was conducted in an electric field. Results of screening tests showed that La0.1Zr0.9O2 (Ni/LZO) catalyst was the most appropriate support in the electric field. To increase the ratio of reforming/combustion, the addition of second metal strongly with LZO support, indicating that Ni oxide was stabilized on Ni(ac)/Mg/LZO, even in the reaction atmosphere by virtue of the formation of an adjacent structure to a Mg particle with a Ni oxide. It might contribute methane combustion suppression.

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要  旨

低温電場中での担持 Ni 触媒によるメタントリッパルフォーミングにおける燃焼抑制

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担持ニッケル触媒を用いたメタンのトリリファーミング（水
蒸気改質＋二酸化炭素改質＋部分酸化）について，473 K とい
う低温で電場中にて検討した。自動車の排気ガス循環システム
を用いた車上改質によるエネルギー回収を狙っているため，高
いメタン転化率と燃焼の抑制に優れた触媒が求められる。

Ni(ac)/Mg/La0.1Zr0.9O2 触媒は，473 K においても高いメタン転化
率を示しながらメタン燃焼を抑制した。Ni/La0.1(Zr0.9O2 上のマ
ゲネシウムについて種々のキャラクタリゼーションを行っ
た。マグネシウムの添加は，Ni と Mg の近接構造を形成し
これがメタン燃焼抑制につながっていることが分かった。

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