Elucidation of the reaction mechanism on dry reforming of methane in an electric field by in situ DRIFTs†

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With increasing expectations for carbon neutrality, dry reforming is anticipated for direct conversion of methane and carbon dioxide: the main components of biogas. We have found that dry reforming of methane in an electric field using a Pt/CeO2 catalyst proceeds with sufficient rapidity even at a low temperature of about 473 K. The effect of the electric field (EF) on dry reforming was investigated using kinetic analysis, in situ DRIFTs, XPS, and DFT calculation. In situ DRIFTs and XPS measurements indicated that the amount of carbonate, which is an adsorbed species of CO2, increased with the application of EF. XPS measurements also confirmed the reduction of CeO2 by the reaction of surface oxygen and CH4. The reaction between CH4 molecules and surface oxygen was promoted at the interface between Pt and CeO2.

1. Introduction

As expectations for the achievement of carbon neutrality continue to rise worldwide, the effective use of biomass resources is attracting attention as one means of achieving that goal. Biogas obtained from anaerobic fermentation is composed mainly of methane and carbon dioxide, both of which are known to be greenhouse gases. A promising technology is one that could directly convert methane and carbon dioxide into high value-added substances such as synthesis gas by dry reforming (DRM: eqn (1)). However, because of thermodynamic and kinetic constraints, the conventional catalytic process for dry reforming requires temperatures higher than 1000 K. Moreover, the reaction is known to be prone to carbon deposition.

DRM: CH4 + CO2 → 2CO + 2H2, ΔHox=298 = 247 kJ mol⁻¹ (1)

The reaction mechanism of CO2 in these reactions has been well-studied through in situ DRIFTs measurements. CO2 dissociates on the active metal via carbonyl species and supports oxides using oxygen vacancies via intermediates such as carbonate and formate. Chen et al. reported that CO was formed via carbonate, which is adsorbed species of CO2 using CeO2 lattice oxygen defects, in DRM using Pt–Ni supported CeO2. Bobadilla et al. revealed that the reaction proceeds via formate species as the key intermediate in RWGS (reverse water gas shift) of Pt-loaded CeO2.

In addition, various unconventional studies have been conducted in recent years to promote the conversion of CO2 by application of external stimuli such as electricity, magnetic fields, and light. Wang et al. reported that Xe lamp irradiation to Cu-loaded CeO2 increases the amount of lattice defects of CeO2 and shows high CO2 reduction performance. Zhu et al. reported that plasma application accelerates the formation and decomposition of the intermediate formate in DRM using Au-loaded CeO2. Consequently, a process that accelerates the reaction by providing an external stimulus is becoming a more attractive CO2 conversion technology.

Under these circumstances, our group has proposed a catalytic reaction in an electric field (EF) in which direct current is applied by inserting electrodes at the top and bottom edges of the catalyst layer to promote the reaction. We earlier reported various effects of enhanced activity and lowered apparent activation energy at low temperatures in DRM, and RWGS, and CO2 methanation. However, details of the reactivity of CO2 and its adsorption ability in the EF have not been clarified. Therefore, in situ DRIFTs measurements were taken for this study to confirm EF effects on the CO2 conversion reaction by examining changes of intermediates when the EF is applied during a DRM reaction.

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2. Experimental

2.1 Catalyst preparation

The catalyst of 1 wt% Pt-supported ceria (1 wt% Pt/CeO₂) was prepared using an impregnation method. We used ceria (CeO₂; JRC-CER-1) supplied by the Catalysis Society of Japan as a support. Pt was loaded on the support using the following procedure. First, Pt(NH₃)₄(NO₃)₂ (Sigma-Aldrich Corp.) was dissolved in distilled water. The powder of CeO₂ support was added to the solution and was stirred for 2 h. Subsequently, the solution was dried at 393 K for 24 h. The obtained powder was calcined at 773 K for 3 h. The obtained sample was pressed and sieved using 355–500 µm mesh. Subsequently, it was reduced with 20% H₂ diluted with Ar at a 100 SCCM flow rate at 723 K for 30 min.

2.2 In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

*In situ* DRIFTs measurements were taken with an FT-IR spectrophotometer (FT/IR-6200; Jasco Corp.) equipped with a ZnSe window and MCT-M detector cooled with liquid nitrogen. Spectra were recorded with 4 cm⁻¹ resolution and 50–200 times scans. The DRIFT cell was made of PTFE, which is an insulator for inserting two electrodes as described in an earlier report. After a pelleted catalyst of 50 mg (without EF) or 110 mg (with EF) was set in the DRIFT cell, the EF was applied with 3 mA of direct current. A schematic image of the DRIFT cell was described in an earlier report. The background spectrum was recorded under Ar flow at 90 SCCM at 473 K without EF. During the experiment, CH₄ and CO₂ were supplied respectively at 10 SCCM. They were diluted with Ar at 90 SCCM at 473 K.

2.3 Activity test

Catalytic activity tests were conducted with a fixed bed flow type reactor as presented in Fig. S1† A 6.0 mm-diameter quartz tube was used, with 300 mg of the catalyst charged in it. A thermocouple was inserted into the catalyst bed at the bottom. The reaction temperature was fixed at 473 K. The temperature was controlled with the thermocouple of the catalyst bed, which includes the Joule heat with EF. For that reason, electrical heating of the catalyst bed is negligible in this case. The feed gas (Ar : CH₄ : CO₂ = 2 : 1 : 1) was supplied with the total flow rate of 80 SCCM. A direct current voltage power supply was used to apply the EF. The current and applied voltage were monitored using a digital phosphor oscilloscope (TDS2100; Tektronics Corp.). After passing a cold trap, the reacted gas was analyzed using GC-FID, TCD (GC-2014; Shimadzu Corp.) with a Porapak Q column and a methanizer. The conversion, yield, and input power were calculated by some equations (see ESI†).

2.4 Characterization

Powder X-ray diffractometry (XRD, RINT-Ultima III; Rigaku Corp.) was used to characterize the crystalline structure of catalysts before and after the activity test. The anode voltage and current were 40 kV, 40 mA, respectively, with Cu-Kα radiation. Fig. S2† shows XRD patterns of catalysts before and after the activity test. The diffraction peaks at 28.6, 33.0, 47.4, 56.4, 69.3, and 76.7° were assigned respectively to the CeO₂ crystal facets of (111), (200), (220), (311), (222), and (400). No significant change in the crystalline structure occurred during the reaction.

The nitrogen physical adsorption desorption isotherm of catalysts was measured using a surface area analyser (Gemini VII; Micromeritics Instrument Corp.) at 77 K. The specific surface area was obtained using the BET method. The specific surface area of the catalyst before the activity test was 158 m² g⁻¹.

The Pt particle size was measured using a field-emission electron microscope (FE-TEM, JEM-2100F; Jasco Corp.) with an accelerating voltage of 200 kV. The particle size was determined using ImageJ software. The average diameter of the Pt particles was 1.5 nm.

XPS measurements were taken (PHI 5000 Versa Probe II; ULVAC-PHI Corp.) with a monochromatic Al-Kα X-ray source. Before the measurement, samples were pretreated with H₂ (H₂ : Ar = 1 : 4; 100 SCCM total flow rate) and O₂ (O₂ : Ar = 1 : 4; 100 SCCM total flow rate) at 693 K for 30 min. Subsequently, they were exposed to CH₄, CO₂, and Ar flow, respectively, for 20 min. In each flow, the EF was applied for 10 min at 3 mA. The samples were transported to the instrument using a transfer vessel while avoiding exposure to air. The obtained binding energies were calibrated using C 1s assigned to C–H or C–C (284.8 eV). The peak fittings were conducted using the Shirley method. The Ce⁴⁺ fraction was calculated using the equation shown in ESI†.

2.5 DFT calculation

All Density Functional Theory (DFT) calculations were performed using the Vienna *Ab initio* Simulation Package (VASP) 5.4.4 with the PAW (Projector Augmented Wave) potentials. The Perdew–Burke–Ernzerhof (PBE) of the generalized gradient approximation (GGA) was used as the functional, and the van der Waals force was corrected by DFT-D3. The plane wave cutoff was set to 400 eV, and the on-site Coulomb interaction of Ce 4f orbitals was taken into account using the DFT+U method with U = 5.0 eV. As reciprocal space sampling, (5 × 5 × 5) and (1 × 1 × 1) k-points were sampled using Gaussian smearing for CeO₂ bulk and slab, respectively, and 0.08 Å⁻¹ k-points were sampled using the first order Methfessel–Paxton method for Pt bulk. All sampling points were decided with Monkhorst–Pack method.

The calculated lattice constant of CeO₂ bulk was 5.437 Å with an error of 0.4% from the experimental value. The CeO₂(111) slab was represented by the three repeated layers of (3 × 6) supercells with 20 Å vacuum layers. The lowest layer was fixed during the structural optimization. The calculated lattice constant of Pt bulk was 3.909 Å with an error of 0.4% from the experimental value. A Pt rod were prepared from the (111) and (100) planes of the Pt bulk as the side and top, respectively, and placed on a CeO₂ slab to express Pt/CeO₂ surface. The O₂...
molecules in the gas phase were placed in a $10 \times 10 \times 10 \text{ Å}$ box and calculated at $T$ point. All calculation models were depicted using VESTA. Here, the oxygen vacancy formation energies were calculated according to the following equation.

$$E_{\text{Vox}} = E(\text{Pt/CeO}_2 \text{ without O}) + \left( \frac{1}{2}E(\text{O}_2) - E(\text{Pt/CeO}_2) \right)$$

(2)

Here, $E_{\text{Vox}}$, $E(\text{O}_2)$, and $E(\text{Pt/CeO}_2)$ are the energy of the formation energy of the oxygen defect, the oxygen molecule, the Pt/CeO$_2$ model, the Pt/CeO$_2$ model after the oxygen defect formation, respectively.

3. Results and discussion

3.1 Catalytic activity

First, activity tests were performed to evaluate the activity with EF at low temperatures. Yabe et al. reported DRM activity with EF: the reaction proceeds at a temperature as low as 473 K for Ni-supported La-doped ZrO$_2$ with EF. As the catalyst, Pt/CeO$_2$ was selected because CeO$_2$ has been studied for other reactions with EF, such as methane steam reforming and dehydrogenation of methylcyclohexane. Then, Pt/CeO$_2$ catalysts with various supported amounts of Pt were investigated (Fig. S4†), and 1wt%Pt/CeO$_2$ showed highest activity and was selected for suitable catalyst. Table 1 presents the catalytic activity of 1wt% Pt/CeO$_2$ at 473 K. The activities at different temperatures are presented in Table S1.† Fig. S5† shows the relation between reaction temperature and conversion in DRM (left), the Arrhenius plot (middle), and H$_2$/CO ratio (right). The conversion of CH$_4$ and CO$_2$ at 473 K was more than 15% (it is conducted in a kinetic region), whereas the reaction did not proceed without EF at this temperature. The cause of catalyst deactivation, the amount of carbon deposition, was negligible because the carbon balance was almost 100%. No carbon formation on the catalyst was apparent after the reaction. The apparent activation energy calculated from the Arrhenius plot (Fig. S5†) without EF was 104 kJ mol$^{-1}$, but it was markedly lower with EF: only 4.82 kJ mol$^{-1}$. As reported from an earlier study, the H$_2$/CO ratio with EF was high in the low-temperature range. In addition, the power efficiency, the value obtained by dividing the gained enthalpy during the reaction by the applied power, was calculated as around 20%. As described above, the 1wt%Pt/CeO$_2$ showed high activity for DRM at 473 K in the electric field. Therefore, we investigated the reaction pathway related to this process using various methods including DRIFTs.

3.2 Effects of EF on CO$_2$ adsorption

To elucidate reasons why DRM proceeds effectively even at such low temperatures, in situ DRIFTs measurements were performed to observe the changes in CO$_2$ adsorption state before and after applying the EF. The adsorption of CO$_2$ on CeO$_2$-based catalysts has been well-studied. Many reports have assigned the peaks of carbonaceous species. The assignment of carbonaceous species used for this study and their values in the literature are shown in ESI.‡‡ We assigned peaks in the range of 1800–2100 cm$^{-1}$ to carbonyl species adsorbed onto Pt, but they are not shown in the table. In this measurement, we applied the EF to the catalyst in the CO$_2$ flow and compared the spectra before and after the application of EF. Fig. 1 shows (a) DRIFT spectra before and after the application of EF and (b) the difference spectrum obtained by subtracting the spectrum without EF from that with EF. As shown in Fig. 1(b), the peak area at around 1160 cm$^{-1}$ was increased by the application of EF. The peaks at 1160, 1131, 1074, and 1031 cm$^{-1}$ are assigned

![Fig. 1](image-url)
respectively as monodentate, bridged, polydentate, and bidentate carbonate peaks (see ESI†). The increase of the peak area at around 1160 cm\(^{-1}\) signifies that the number of carbonate species adsorbed onto CeO\(_2\) increased because of application of the EF.

In general, CO\(_2\) adsors on metal oxides and forms adsorbed species such as carbonate and bicarbonate.\(^{75-77}\) DFT calculations and various experimentally obtained results revealed that lattice oxygen defects enhance the adsorption of gas-phase CO\(_2\).\(^{75-77}\) Lattice oxygen in the catalyst support dissociates CH\(_4\) in the DRM reaction, leading to the formation of oxygen vacancies.\(^{75-78,79}\)

Consequently, the reaction of CH\(_4\) with lattice oxygen is expected to be an important factor supporting oxygen vacancy formation. Therefore, to investigate the effects of CH\(_4\) on the formation of lattice oxygen defects with or without EF, we took XPS measurements and evaluated the reducibility of CeO\(_2\). We then compared the fractions of Ce\(^{3+}\) and Ce\(^{4+}\) of 1wt%Pt/CeO\(_2\) after exposing catalysts to CH\(_4\), CO\(_2\), and Ar flow, respectively with and without EF at 473 K. Table 2 shows the calculated Ce\(^{3+}\) fraction of 1wt%Pt/CeO\(_2\) spent in each condition. Fig. S7† presents the obtained XPS spectra. In the Ce 3d spectrum, three doublet peaks at \((u''': 916.6, v'': 898.2), (u''': 907.5, v'': 888.8),\) and \((u: 900.7, v: 882.3)\) eV are assigned to Ce\(^{4+}\); two doublet peaks at \((u': 903.8, v': 885.2), (u0: 899.3, v0: 880.7)\) eV are assigned to Ce\(^{3+}\).\(^{80}\) Table 2 shows that the fraction of Ce\(^{3+}\), after being kept in the CH\(_4\) flow with EF, was larger than that without EF. The increase in the Ce\(^{3+}\) fraction in the CH\(_4\) flow suggests that the oxygen species were removed easily by reaction with CH\(_4\) in the EF, resulting in the formation of more lattice oxygen defects. Fig. S8† depicts changes in DRIFT spectra before and after application of the EF under the CH\(_4\) flow. Fig. S8† (b) shows that the peak area of carbonate species increased. The increase of the carbonate species signifies that CH\(_4\) consumed lattice oxygen, which is the only oxygen source, resulting in the formation of lattice oxygen defects.

The increase of Ce\(^{3+}\) fraction by application of the EF in Ar flow was 0.5%, which is much less than that in the CH\(_4\) flow. Therefore, the oxygen species are not released simply by application of the EF, but are released by the reaction with CH\(_4\) in the EF. Therefore, the oxygen of CeO\(_2\) is regarded as activated by the EF. Thus the reaction of lattice oxygen with CH\(_4\) is promoted, thereby forming the oxygen defect.

The fraction of Ce\(^{3+}\) increased from 17.5% to 18.3% after applying the EF in the CO\(_2\) flow, indicating an increase of carbonate species by CO\(_2\) adsorption. According to Yi et al.,\(^{81}\) Ce\(^{3+}\) decreases along with the carbonate species formation because the carbonate species are formed by oxidation of the adsorbed CO\(_2\) by the surface oxygen of the CeO\(_2\) support. Therefore, the reduction of Ce in the EF in the CO\(_2\) flow also supports enhancement of the CO\(_2\) adsorption.

The enhanced reactivity of oxygen in the EF was confirmed using oxygen isotope exchange test. Fig. S9† portrays results of the oxygen isotope exchange test. For this measurement, the EF was applied to the catalyst in the CO\(_2\) flow after the surface oxygen species in CZO were filled with \(^{16}\)O. Then a mass spectrometer was used to analyze the produced gas. As shown in Fig. S9† after the application of EF, the amount of \(^{18}\)O\(_2\) decreased immediately. Simultaneously, \(^{16}\)O\(^{18}\)O appeared. However, the appearance of \(^{16}\)O\(_2\) was slight. These results indicate that lattice oxygen is not removed merely by applying EF. Rather, it is removed by reaction with the gas species. This result also supports the increased reactivity of the oxygen in the EF.

### 3.3 Reactivity of carbonate species

Next, an alternating feed test between CO\(_2\) and CH\(_4\) was conducted to elucidate the behaviour of CO\(_2\) and CH\(_4\) in the DRM reaction with and without EF. In the alternating feed test, CO\(_2\) and CH\(_4\) were switched; GC was used to analyze the produced gas. Fig. 2 shows the calculated formation rate of CO after switching the gas with EF. Actually, CO was not observed without EF, although it was formed with EF. The CO formed after either the CO\(_2\) or CH\(_4\) supply. This CO formation signifies that oxidation of CH\(_4\) and reduction of CO\(_2\) occur on Pt/CeO\(_2\) with EF. In both gas feeds, the amount of the produced CO decreased with the time course. The oxidation and reduction performance of the catalyst decreased with time because of the continuous supply or consumption of oxygen. From earlier results and research, we assumed the role of lattice oxygen in this test. In the CH\(_4\) flow, lattice oxygen was removed by CH\(_4\). Then depletion of the activated oxygen caused the decrease of the produced CO amount. However, CO\(_2\) filled the lattice oxygen defect in the CO\(_2\) flow. The amount of produced CO decreased along with the decrease of the lattice oxygen defects.

![Fig. 2](image-url) CO formation rate after switching between CO\(_2\) and CH\(_4\) over 1wt%Pt/CeO\(_2\) catalyst with EF; 80 SCCM total flow rate (CH\(_4\) : Ar = 1 : 3 under CH\(_4\) flow, CO\(_2\) : Ar = 1 : 3 under CO\(_2\) flow) at 473 K.

Table 2  Relative ratio of surface contents of Ce\(^{3+}\)

| Condition          | Surface content of Ce\(^{3+}\)/% |
|--------------------|---------------------------------|
| CH\(_4\) flow without EF | 16.8                           |
| CH\(_4\) flow with EF    | 19.4                           |
| Ar flow without EF      | 16.2                           |
| Ar flow with EF         | 16.7                           |
| CO\(_2\) flow without EF | 17.5                           |
| CO\(_2\) flow with EF    | 18.3                           |
In situ DRIFTs measurements were conducted in the CO₂, CH₄ alternating feed test to observe the reactivity of the carbonate species. Fig. 3 portrays the change in spectra in the test between CH₄ and CO₂ (a) with EF, (b) without EF, and the difference in the spectrum before and after CH₄ supply (c) with EF, (d) without EF. The peaks assigned to carbonate species decreased by stopping the CO₂ supply, irrespective of the presence of EF. A similar decrease in the carbonate peak was observed when the supply gas was switched from CO₂ to Ar without EF (Fig. S10 and S11†). Without EF, CO was not formed when the CO₂ gas feed was switched to CH₄ or Ar flow, suggesting that carbonate species desorbed as CO₂. However, when the EF was applied, CO was formed, suggesting that some of the carbonate species reduced and dissociated as CO.

3.4 Oxygen release ability of CeO₂

DFT calculations were performed to investigate the tendency of oxygen defect formation on Pt-loaded CeO₂. Fig. S15† shows the calculated oxygen defect locations, and Table S3 shows the oxygen defect formation energy at each location. The formation energy of the oxygen defects became higher as the distance from Pt increased. The results show that the oxygen defects are more easily generated at the interface of Pt and CeO₂ than other locations. This result supports the reaction of CO₂ at the interface of Pt and CeO₂ because the oxygen defects are more easily generated near the interface, and the generated oxygen defects facilitate the adsorption of CO₂ near the interface.† Note that the sign of the value does not mean whether it is spontaneous or not, because the energy of half of the oxygen molecule is used as the energy of the oxygen atom and the term of pressure, and the temperature is not taken into account in the calculation of the oxygen defect formation energy.

3.5 Discussion

From these results, we consider the effect of EF on DRM and the reaction mechanism.

3.5.1 Effect of EF. In situ DRIFTs measurements revealed the effect of the EF on CO₂ adsorption. As shown in Fig. 1, the peak area of carbonate species increased by application of the EF, indicating that application of the EF enhanced the CO₂ adsorption. The XPS measurement results also support the enhancement of CO₂ adsorption on CeO₂ (Table 2).

It is reported that the enhancement in CO₂ adsorption is related to the oxygen activity of the oxide support. Chen et al. investigated the adsorption and oxidation, redox behaviour of CO and CO₂ on CeO₂ using DFT calculations. They reported that highly reactive surface oxygen, which Ce weakly bonds, lowers CO₂ adsorption and carbonate species formation barriers. In addition, results of several studies suggest that EF promotes the activation of the oxygen in the oxide support. High catalytic activity due to the activated oxygen on supports by applying EF was reported in the OCM reaction using CeO₂ and in the TWC catalytic reaction of exhaust gases using cerium zirconium oxides (Ce₀.₇Zr₀.₃O₂) as support. Therefore, we considered that lattice oxygen was activated by the EF, and promoted CO₂ adsorption.

The XPS measurements taken for this study revealed that CH₄ molecules react with surface oxygen, consume them, and thereby reduce CeO₂ more with EF than without EF (Table 2). This improved reactivity of CH₄ with surface oxygen might be attributed to the enhanced reactivity of the oxygen by the EF.

Next, the CO₂, CH₄ alternating test shows the CO₂ dissociation ability of CeO₂. When the gas was switched from CO₂ to Ar without EF, the carbonate species desorbed as CO (Fig. S9 and S10†). When the gas was switched to CH₄ without EF, the carbonate species also desorbed as CO₂ and CO did not form. However, CO was formed when the supply gas was switched to CH₄ with EF, indicating that a part of the carbonate species reacted and desorbed as CO (Fig. 2 and 3). These results indicate that the EF promotes dissociation of CO₂ adsorbed on CeO₂.

3.5.2 Active site. DFT calculations showed that oxygen defect is likely to form on CeO₂ at the interface of Pt and CeO₂. Previous research suggest that oxygen defect promotes CO₂ adsorption. Thus, CO₂ adsorption tends to occur on CeO₂ at the interface of Pt and CeO₂.

On the other hand, CH₄ dissociates on Pt at the interface of metal (Pt) and support (CeO₂) with EF and without EF. CH₄ and CO₂ with high reactivity at the interface of Pt and CeO₂ suggests that active site of this reaction is the interface of Pt and CeO₂.

3.5.3 Reaction mechanism. From these results, we considered the possible DRM mechanism.

First, with the EF, the reaction of CO₂ is considered to proceed by the Mars–van Krevelen (MvK) mechanism using the lattice oxygen of the support. Yabe et al. have shown that the dissociation of CO₂ proceeds via the lattice oxygen in the EF by
%18O isotope test. This indicates that the dissociation of CO₂ by
the MvK mechanism proceeds at low temperatures with EF.

Contrarily, CH₄ dissociation proceeds on Pt. Previously,
many reports have suggested the rate determining step (RDS) of
the reaction of CH₄. Otsuka et al.¹⁶ showed that CH₄ dissociation
and recombination proceed much faster than the oxidation
of CH₄ on CeO₂ and Pt/CeO₂ by the CH₄,C₄D₄ exchange test. Wei
and Iglesia¹⁷ also suggested C–H bond activation on Pt is reversible,
using the CH₄, C₄D₄ exchange test in DRM reaction. Thus, the oxidation of H species formed after CH₄ dissociation
is necessary for the reaction to proceed. Das et al.¹⁸ have also
reported that reaction of CH₄ and lattice oxygen is the RDS in
the DRM reaction. Therefore, we considered that the RDS in this
reaction is oxidation of the H species. The EF promotes the reaction to activate lattice oxygen.

From these results, we considered the possible DRM mechanism as follows.

(1) Methane dissociation on Pt⁹⁰

\[
\text{CH}_4(\text{g}) \rightarrow \text{CH}_4(\text{Pt}) \\
\text{CH}_4(\text{Pt}) \rightarrow \text{CH}_4(\text{Pt}) + x\text{H(PT)}
\]

(2) Diffusion of H species⁹⁰,⁹¹

\[
\text{CH}_4(\text{Pt}) + \text{O(lattice)} \rightarrow \text{CH}_3(\text{Pt}) + \text{O(lattice)} – \text{H} \\
\text{CH}_3(\text{Pt}) + \text{O(lattice)} \rightarrow \text{CH}_2(\text{Pt}) + \text{O(lattice)} – \text{H} \\
\text{CH}_2(\text{Pt}) + \text{O(lattice)} \rightarrow \text{CH}(\text{Pt}) + \text{O(lattice)} – \text{H} \\
\text{CH}(\text{Pt}) + \text{O(lattice)} \rightarrow \text{H(PT)} + \text{O(lattice)} – \text{H}
\]

(3) Methane desorption as CO⁹⁶

\[
\text{C(Pt) + O(lattice)} \rightarrow \text{CO} + V_{ox}
\]

(4) CO₂ adsorption

\[
\text{CO}_2(\text{g}) + \text{O(lattice)} + V_{ox} \rightarrow \text{CO}_3(\text{CeO}_2)
\]

(5) Hydrogenation of CO₂ species

\[
\text{CO}_2(\text{CeO}_2) + \text{H(PT, CeO}_2) \rightarrow \text{HCO}_3(\text{CeO}_2)
\]

(6) Desorption of carbonate species

\[
\text{HCO}_3(\text{CeO}_2) \rightarrow \text{CO(CeO}_2) + \text{H}_2\text{O(g) + O(lattice)} + V_{ox}
\]

(7) Refilling of oxygen vacancy

\[
V_{ox} + \text{H}_2\text{O} \rightarrow \text{O(lattice)} + 2\text{H(CEO}_2)
\]

(8) Formation of H₂

\[
2\text{H(CEO}_2) \rightarrow \text{H}_2(\text{g})
\]

Here, V_{ox} and O{lattice} denote oxygen vacancy and lattice oxygen, respectively.

First, the EF effect is to enhance the oxygen activity of oxide support because the adsorption of CO₂ was promoted significantly by EF application (eqn (8)). The activated surface oxygen reacts easily with C and H species dissociated from CH₄ and forms oxygen defects (eqn (5)–(7)).

The activated oxygen and the oxygen defects of oxide support both contribute to enhancement of the CO₂ adsorption. Finally, the adsorbed CO₂ forms carbonate species, reacts, and desorbs as CO. The remaining oxygen species again work as the oxidant of CH₄. Consequently, the DRM reaction in the EF proceeds via a redox cycle of CeO₂ support.

4. Conclusion

The effect of the electric field (EF) on DRM reaction was investigated using 1wt%Pt/CeO₂ by activity tests, in situ DRIFTs, XPS, and DFT calculation. 1wt%Pt/CeO₂ showed high activity for DRM with EF, even at 473 K, at which thermal catalysis proceeds only slightly. In situ DRIFTs measurements in CO₂ flow revealed that the adsorbed species of CO₂ increases when the EF is applied. This increase signifies that the adsorption of CO₂ is promoted by the EF. XPS measurements of the catalysts after the treatment in CO₂ atmosphere with EF suggest the enhancement of CO₂ adsorption on CeO₂. In addition, XPS measurements of catalysts after exposure to CH₄ flow with EF confirmed that the Ce⁴⁺ fraction of CeO₂ increased, indicating that CeO₂ support was reduced after the reaction of surface oxygen and CH₄ molecules in EF, even at 473 K. These results suggest that the oxygen in the oxide support was activated in the EF. Furthermore, the reaction of CH₄ and the surface oxygen was promoted, thereby forming lattice oxygen defects and CO. The activated oxygen in the EF and the resulting lattice oxygen defects by the reaction with CH₄ molecules promote CO₂ adsorption. The reaction is considered to proceed at the interface of Pt and CeO₂. DFT calculations also support the reaction mechanism of DRM at the interface of Pt and CeO₂.

In summary, the reaction mechanism of DRM in the EF was inferred as presented below. The EF can improve the oxygen activity and can therefore promote the reaction of CH₄ molecules and surface oxygen at the Pt–CeO₂ interface, forming the oxygen defects. Both the activated oxygen and the oxygen defects of oxide support enhance the adsorption of CO₂, forming more carbonate species on CeO₂ in the EF. Finally, CO₂ molecules dissociate to form CO via the carbonate species.

Conflicts of interest

There are no conflicts to declare.

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