Hydrogen Production by Steam Reforming of Ethanol over Pt/CeO$_2$ Catalyst in Electric Field at Low Temperature

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Catalytic ethanol steam reforming was investigated over Pt/CeO$_2$ catalyst in an electric field at low temperature, and the effect of the electric field and controlling factors for the activity and selectivity were examined. With the electric field, ethanol steam reforming proceeded at temperatures as low as 423 K, at which the conventional catalytic reaction hardly proceeded. Supported platinum acted as an active site for ethanol steam reforming. Conversion of ethanol and H$_2$ yield drastically increased with the electric field, and apparent activation energies for ethanol dehydrogenation, acetaldehyde decomposition, and acetaldehyde steam reforming were lowered by the electric field. *In-situ* DRIFTS measurements revealed that the adsorbed ethanol formed reactive acetate species with the electric field even at low temperature, which improved hydrogen selectivity. This process can produce hydrogen from bioethanol using less energy at low temperatures, such as 423 K, with high efficiency.

**Keywords**
Hydrogen production, Low temperature system, Electric field, Bioethanol, Steam reforming, Platinum catalyst

1. Introduction

Biomass-derived ethanol (bioethanol) is expected to become an important renewable resource	extsuperscript{1).} Bioethanol is currently produced mainly by fermentation of mono-sugars	extsuperscript{2),} which entails the use of large quantities of water. Bioethanol is commonly mixed with gasoline for utilization in automobiles	extsuperscript{3)}, so the ethanol must first be purified by distillation. Unfortunately azeotropic distillation of bioethanol consumes external heat of about 50-60 % of the combustion enthalpy of ethanol (1277.4 kJ mol	extsuperscript{-1}). To avoid such large energy loss, one-step production of hydrogen by ethanol steam reforming could be developed as a highly efficient energy production process	extsuperscript{4,5).} The hydrogen product represents a secondary energy storage to support the need for sustainable energy sources	extsuperscript{6,7).} Moreover, ethanol steam reforming is an endothermic reaction, as shown in Eq. (1), so the reformate has a higher heating value of about 1450.9 kJ mol	extsuperscript{-1} (1277.4 + 173.5) after ethanol steam reforming.

\[
\text{C}_2\text{H}_5\text{OH}(g) + 3\text{H}_2\text{O}(g) \rightarrow 2\text{CO}_2(g) + 6\text{H}_2(g) \quad \Delta H_{298} = 173.5 \text{ kJ mol}^{-1}
\]  

Ethanol steam reforming could significantly increase the exergy rate for storage as hydrogen	extsuperscript{8).} Exergy rate is defined as the ratio of Gibbs free energy (potential useful work) over the combustion enthalpy (energy supplied). The main reaction pathway of ethanol steam reforming is believed to involve the three reactions shown in Eqs. (2)-(4)	extsuperscript{9~13).}

Dehydrogenation of ethanol

\[
\text{C}_2\text{H}_5\text{OH}(g) \rightarrow \text{CH}_3\text{CHO}(g) + \text{H}_2(g) \quad \Delta H_{298} = 64.3 \text{ kJ mol}^{-1}
\]  

Steam reforming of acetaldehyde

\[
\text{CH}_3\text{CHO}(g) + \text{H}_2\text{O}(g) \rightarrow 2\text{CO}(g) + 3\text{H}_2(g) \quad \Delta H_{298} = 191.5 \text{ kJ mol}^{-1}
\]  

Water gas shift

\[
\text{CO}(g) + \text{H}_2\text{O}(g) \rightarrow \text{CO}_2(g) + \text{H}_2(g) \quad \Delta H_{298} = -41.2 \text{ kJ mol}^{-1}
\]  

However, side reactions such as ethanol dehydration, decomposition of acetaldehyde and acetone formation also proceed (Eqs. (5)-(7))	extsuperscript{41,15}. The formation of by-products and the deactivation of catalytic activity by coke formation pose severe problems.
Ethanol dehydration
\[ \text{C}_2\text{H}_5\text{OH}(g) \rightarrow \text{C}_2\text{H}_4(g) + \text{H}_2\text{O}(g) \]
\[ \Delta H_{298} = 45.5 \text{ kJ mol}^{-1} \] (5)

Decomposition of acetaldehyde
\[ \text{CH}_3\text{CHO}(g) \rightarrow \text{CH}_4(g) + \text{CO}(g) \]
\[ \Delta H_{298} = -14.4 \text{ kJ mol}^{-1} \] (6)

Acetone formation
\[ 2\text{CH}_3\text{CHO}(g) \rightarrow \text{CH}_3\text{COCH}_3(g) + \text{CO}(g) + \text{H}_2(g) \]
\[ \Delta H_{298} = 12.4 \text{ kJ mol}^{-1} \] (7)

Highly active and selective catalysts have been developed for ethanol steam reforming, including supported noble metal (Pt, Pd, Rh) catalysts (Pt, Pd, Rh) catalysts (16)-(19), cobalt catalysts (20)-(22) and nickel catalysts (23)-(25). Two solutions have been proposed to increase catalytic activity, and suppress coke formation and side reactions in ethanol steam reforming: addition of a second element (5), (9), (11), (25), (27); and controlling the properties of the catalyst support (5), (25), (26), (28), (29). However, both high ethanol conversion and low carbon deposition are difficult to achieve at low temperatures (<573 K).

Recovery of waste heat at a low temperature is difficult after heat exchange in high temperature catalytic processes. Such heat loss is one of the reasons for the lower total energy efficiency of chemical processes. Application of high temperatures is a serious problem in small commercial chemical processes without a heat exchanger because of the high heat losses, so a catalytic process that operates at lower temperature without a heat exchanger is desirable for high energy efficiency. If this reaction could proceed at low temperature using waste heat, a novel process for effective hydrogen production could be established.

Previously, we proposed catalytic reactions in an electric field at low temperatures at which conventional catalytic reaction cannot take place (30), (31). The application of an electric field is different from plasma, and provides milder conditions and has properties of lower consumption energy and no emission spectra (32). Recently, we reported that endothermic reactions such as steam reforming of methane, reverse water gas shift and steam reforming of ethanol can proceed even at temperatures as low as 423 K (30)-(34). Moreover, the molar amount of reactants activated from one electron is much greater than in the stoichiometric reaction (i.e. electrolysis and other electrochemical reactions), so this catalytic reaction in the electric field represents a non-Faradaic electro-catalytic reaction.

The present study investigated ethanol steam reforming for hydrogen production in an electric field over Pt supported catalyst at low temperature. The effects of reaction temperature, imposed current and other parameters were examined on the catalytic activity and selectivity. In addition, Pt/CeO\(_2\) catalysts with various Pt loading amounts were compared to investigate the role of the supported Pt. Surface-adsorbed species were investigated using in-situ DRIFTS (diffuse reflectance infrared Fourier transform) study. The energy efficiencies for this reaction system were also investigated.

2. Experimental

2.1. Catalyst Preparation
CeO\(_2\) (JRC-CEO-1; Catalyst Society of Japan) was used as the catalyst support, and platinum as the active metal because of their high catalytic activities in an electric field (31). Pt was loaded on the catalyst support by an impregnation method. The catalyst support was soaked in distilled water for 2 h. Then a solution of Pt(NH\(_3\))\(_4\)(NO\(_3\))\(_2\) was added. After the slurry was stirred at room temperature for 2 h, the water was evaporated with heating and stirring. The obtained powder was dried in an oven at 393 K for 20 h in air and calcined in a muffle furnace at 973 K for 12 h in air.

2.2. Activity Test
Catalytic activity tests were conducted in a fixed bed flow quartz tube reactor (6 mm i.d./8 mm o.d.) under atmospheric pressure. A schematic image of the reaction system is shown in Fig. 1. The catalyst (200 mg) was sieved into 355-500 \(\mu\)m particles and charged into the reactor. To induce the electric field, two stainless steel rods (SUS304; 2 mm o.d.) were inserted from either end of the catalyst bed as electrodes, and a thermocouple was inserted into the catalyst-bed to measure the reaction temperature. Before the activity test, the catalyst was pretreated under an Ar atmosphere at 423 K for 1 h. The electric field was induced using a constant DC current (2-9 mA). The electric field was defined and controlled by the input current, and the voltage depended on the nature of the catalyst (i.e. elec-

![Fig. 1 Schematic of the Reactor](image)
The substrate 9.1 mol% ethanol solution (steam to carbon molar ratio: S/C = 5.0) was supplied (4.7 μmol min⁻¹) using a micro-feeder (JP-V4; Furue science) and evaporated in a pre-heating zone with carrier gas (Ar: 80 SCCM) and internal standard gas (N₂: 20 SCCM). Liquid products (H₂O, CH₃CHO, CH₃COOH, unreacted C₂H₅OH) were trapped in aqueous 2-butanol at 273 K. Product gases after passing the cold trap were analyzed using a GC-TCD (GC-2014; Shimadzu Corp.) with a Porapak QS packed column and a methanizer (Ru/Al₂O₃ catalyst). Liquid products were analyzed using an on-line GC-FID (GC-2014; Shimadzu Corp.) with a Porapak Q packed column before passing the cold trap.

The ethanol conversion and product yields were calculated by the following equations. The maximum H₂ yield was 200 % following Eq. (10).

\[
\text{Ethanol conversion} (%) = \frac{\text{carbon mole of total products}}{\text{carbon mole of input ethanol}} \times 100
\]

\[
\text{Yield of product} (%) = \frac{\text{carbon mole of product}}{\text{carbon mole of input ethanol}} \times 100
\]

\[
\text{H₂ yield} (%) = \frac{\text{mole of produced hydrogen}}{\text{mole of input ethanol}} \times 3 \times 100
\]

The amount of deposited carbon after the activity test was measured by TPO (temperature programmed oxidation). The catalyst after the activity test (15 mg) was sieved into particles of 355-500 μm and placed into a quartz tube. The catalyst was heated to 1173 K at 10 K min⁻¹ under 10% O₂ gas (O₂: 10 SCCM, N₂: 90 SCCM) and analyzed using an infrared gas analyzer (CGT-7000; Shimadzu Corp.) with measurement of CO and CO₂.

### 2.3 Characterization

Crystalline structures of the prepared catalysts were characterized by XRD (X-ray diffraction, Ultima III; Rigaku Corp.) operated at 40 kV and 40 mA with Cu Kα radiation (λ = 1.5406 Å). Specific surface areas of the catalysts were measured by nitrogen adsorption with the BET method (Gemini VII 2390; Micromeritics).

**In-situ DRIFTS** (diffuse reflectance infrared Fourier transform) spectroscopy was performed with a FT-IR spectrometer (FT/IR-6200; Jasco Corp.) with a MCT detector cooled by liquid nitrogen at a resolution of 4 cm⁻¹ and 44 scans per spectrum. The sample was sieved into particles of 355-500 μm and placed into a DRIFTS reactor-cell (DR-600Ci; Jasco Corp.) with a ZnSe window. All obtained spectra were transformed from absorbance to Kubelka-Munk (KM).

For DRIFTS measurements with the electric field, a Teflon IR cell and Pt wire electrodes were used. The IR cell was heated to 423 K in an inert gas flow (Ar: 58 SCCM) and a background spectrum was measured. Then, ethanol or acetaldehyde (2 SCCM) was passed for 30 min at 423 K with a carrier gas (Ar: 58 SCCM). After purging at 423 K for 30 min in Ar flow (58 SCCM) to remove gas phase species, IR measurements were conducted. Thereafter, the electric field (3 mA) was induced through the electrodes for 10 min and IR spectra were measured at 423 K.

For DRIFTS measurements without the electric field during temperature-programmed desorption of ethanol or acetaldehyde, a SUS304 IR cell was used. Background measurements were conducted at 423 K in an inert gas flow (Ar: 58 SCCM). After ethanol or acetaldehyde (2 SCCM) was passed for 30 min at 423 K with a carrier gas (Ar: 58 SCCM) and Ar purging (58 SCCM) for 30 min, the IR spectrum was measured. Then, the sample was heated to a designated temperature of 473-573 K and kept at that temperature for 10 min in Ar flow (58 SCCM). After cooling to 423 K in Ar flow, the IR spectrum was recorded.

Surface reactions between adsorbed ethanol and water in the electric field were also investigated using DRIFTS. H₂O (8 SCCM) was introduced for 30 min with a carrier gas (Ar: 52 SCCM) at 423 K without the electric field after adsorption of ethanol. Thereafter, the electric field was induced (3 mA) at 423 K in H₂O/Ar flow and IR spectrum was measured.

For comparison, the surface reaction between adsorbed ethanol and water without the electric field was also investigated. The IR cell was heated to 548 K in Ar flow, and the background spectrum was measured. After adsorption of ethanol and Ar purging at 548 K, the IR spectrum was measured. Thereafter, H₂O (8 SCCM) was introduced with a carrier gas (Ar: 52 SCCM) at 548 K and the IR spectrum was measured.

To identify the adsorbed species, D₂ gas (2 SCCM) was introduced at 423 K for 10 min without the electric field after adsorption of ethanol and inducing the electric field (3 mA) at 423 K. After H atoms of adsorbed species were exchanged with D atoms, a peak shift to a lower wavenumber was observed.

### 3. Results and Discussion

#### 3.1 Effects of Electric Field and Reaction Temperature on Catalytic Activity of Ethanol Steam Reforming

In our previous investigations, Pt/CeO₂ had higher catalytic activity for hydrogen production by steam reforming in an electric field at low temperature. To investigate the catalytic activity for ethanol steam reforming, reactions with or without an electric field was conducted over Pt/CeO₂ catalyst at various temperatures. Figure 2 shows the ethanol conversions and H₂ yields at various catalyst-bed temperatures. In these experiments, hydrogen, carbon dioxide, carbon monox-
ide, acetaldehyde, methane, acetone and ethylene were observed, and the carbon balances were almost 100%.

In the catalytic reactions without an electric field, ethanol conversion and H2 yield were almost zero at low temperature range around 423 K. In contrast, the catalytic reactions with an electric field (electreforming) showed high activity (conversion: 27.4%, H2 yield: 27.3%) even at the low furnace temperature of 423 K (catalyst-bed temperature increased to 505 K due to Joule heat produced by the induced electric field). Pt/CeO2 catalyst in the electric field showed higher activity than catalyst without the electric field at the same temperature (\(<573 \text{ K}\)), so the effect of Joule heat by the induced electric field was not important in the system.

Figure 3 shows changes in the conversion and product selectivity with catalyst-bed temperature. In the conventional catalytic reaction without an electric field, CH3CHO selectivity was high (81.0%) at the low catalyst-bed temperature of 473 K (Fig. 3(a)). Conversion, CO + CO2 selectivity and CH4 selectivity increased, and CH3CHO selectivity decreased with higher catalyst-bed temperature. On the other hand, in electreforming, CH3CHO selectivity was low (13.0%) and CO + CO2 selectivity was high (55.1%) even at the low catalyst-bed temperature of 479 K (Fig. 3(b)). Moreover, the ratio of CO + CO2 selectivity to CH4 selectivity in electreforming ((CO + CO2)/CH4 = 1.65; at 479 K) was higher than that in the conventional catalytic reaction ((CO + CO2)/CH4 = 1.06; at 473 K), which indicated that steam reforming of acetaldehyde was promoted, and decomposition of acetaldehyde or methanation was suppressed by applying the electric field at low temperature. These results indicate that applying the electric field resulted in promoting efficient hydrogen production in the low temperature range even at 423 K.

3.2 Effect of Pt Loading Amount

To evaluate the effect of Pt loading, ethanol steam
reforming in an electric field over Pt/CeO2 catalyst with various Pt loadings were conducted as summarized in Table 1. The \( r_{D/r_{0}} \) in Table 1 represents the ratio of the rate of steam reforming of acetaldehyde to the rate of decomposition of acetaldehyde (Eq. (11)). This \( r_{D/r_{0}} \) ratio is an indicator for evaluating the selectivity for the steam reforming of acetaldehyde. Selective steam reforming of intermediate acetaldehyde is crucial in the steam reforming of ethanol as shown above. The WGS ratio in Table 1 represents the extent of the water gas shift reaction (Eq. (12)).

\[
r_{D/r_{0}} \left( \frac{\text{rate}}{\text{rate}_{0}} \right) = \frac{f(\text{CO}) + f(\text{CO}_2) - f(\text{CH}_4)}{f(\text{CH}_4)} \quad (11)
\]

\[
\text{WGS ratio}(\%) = \frac{f(\text{CO}_2)}{f(\text{CO}) + f(\text{CO}_2)} \times 100 \quad (12)
\]

As shown in Table 1, in the case of no Pt loading, ethanol conversion and \( \text{H}_2 \) yield were extremely low and selectivities for ethylene and acetone were relatively high. Higher Pt loading on CeO2 from 0.5 to 3 wt% resulted in increased ethanol conversion and \( \text{H}_2 \) yield and suppressed formation of CH3CHO, CH4 and acetone. This result indicated that the reaction rates of steam reforming of acetaldehyde, acetaldehyde decomposition and water gas shift reaction increased with higher Pt loading resulting in increased \( \text{H}_2 \) yield.

3.3. Effect of the Imposed Current

To evaluate the effect of the imposed current on catalytic activity and selectivity, ethanol steam reforming was conducted over Pt/CeO2 catalyst at 423 K in an electric field with current of 2-9 mA as summarized in Table 2. The ethanol conversion and \( \text{H}_2 \) yield increased with higher current. Increases in the current resulted in slightly decreased voltage, but the input power (current \( \times \) voltage) increased. Therefore, catalyst-bed temperature increased because of Joule heating with the higher input power.

Figure 4 shows the changes in ethanol conversion and \( \text{H}_2 \) yield with catalyst-bed temperature under various imposed currents (2-9 mA) at different furnace temperatures (363-573 K). Higher current resulted in higher conversion and \( \text{H}_2 \) yield at almost the same temperature in the low temperature range (<573 K). Therefore, the imposed current affected not only the activity but also the selectivity.

The apparent activation energy of elementary reactions was calculated from the Arrhenius plot using Pt/CeO2 catalyst with various currents (2-9 mA). Figure 5 shows the Arrhenius plots for ethanol dehydrogenation, acetaldehyde decomposition, and acetaldehyde steam reforming. Apparent activation energy was calculated according to the slope of the Arrhenius plot, as summarized in Table 3. Induced electric field lowered the apparent activation energy for all three reactions, indicating these reactions were promoted by the electric field. In particular, the imposed current had a high impact on the apparent activation energy for steam reforming of acetaldehyde. Higher imposed current reduced the apparent activation energy, so acetaldehyde steam reforming was preferentially promoted by the electric field, and the catalyst showed high \( \text{H}_2 \) yield.

Table 1: Catalytic Activity for Ethanol Steam Reforming in an Electric Field over Pt/CeO2 Catalysts with Various Pt Loadings

<table>
<thead>
<tr>
<th>Pt loading [wt%]</th>
<th>Voltage [kV]</th>
<th>Power [W]</th>
<th>Catalyst-bed temp. [K]</th>
<th>Conv. [%]</th>
<th>( \text{H}_2 ) yield [%]</th>
<th>Selectivity [%]</th>
<th>( r_{D/r_{0}} )</th>
<th>WGS ratio [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.25</td>
<td>0.8</td>
<td>500</td>
<td>1.4</td>
<td>0.5</td>
<td>1.0, 2.6</td>
<td>14.5</td>
<td>4.9</td>
</tr>
<tr>
<td>0.5</td>
<td>0.35</td>
<td>1.1</td>
<td>513</td>
<td>22.1</td>
<td>17.1</td>
<td>11.8, 26.0</td>
<td>40.6</td>
<td>17.2</td>
</tr>
<tr>
<td>1</td>
<td>0.37</td>
<td>1.1</td>
<td>505</td>
<td>27.4</td>
<td>27.3</td>
<td>8.3, 29.3</td>
<td>52.6</td>
<td>9.1</td>
</tr>
<tr>
<td>3</td>
<td>0.40</td>
<td>1.2</td>
<td>518</td>
<td>35.9</td>
<td>35.4</td>
<td>5.7, 33.7</td>
<td>52.6</td>
<td>7.7</td>
</tr>
</tbody>
</table>

Catalyst weight, 200 mg; furnace temperature, 423 K; current, 3 mA; S/C, 5.0; time on stream, 10 min.

Table 2: Effect of the Imposed Current over Pt/CeO2 in an Electric Field

<table>
<thead>
<tr>
<th>Imposed current [mA]</th>
<th>Voltage [kV]</th>
<th>Power [W]</th>
<th>Catalyst-bed temp. [K]</th>
<th>Conv. [%]</th>
<th>( \text{H}_2 ) yield [%]</th>
<th>( \Delta H_r^{\circ} ) [kJ/mol]</th>
<th>Energy efficiency [%]</th>
<th>Faradaic number [-]</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>-</td>
<td>423</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>0.00</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>0.45</td>
<td>0.9</td>
<td>500</td>
<td>19.4</td>
<td>16.6</td>
<td>0.08</td>
<td>9.2</td>
<td>171</td>
</tr>
<tr>
<td>3</td>
<td>0.37</td>
<td>1.1</td>
<td>505</td>
<td>27.4</td>
<td>27.3</td>
<td>0.14</td>
<td>12.6</td>
<td>187</td>
</tr>
<tr>
<td>5</td>
<td>0.34</td>
<td>1.7</td>
<td>547</td>
<td>38.0</td>
<td>46.1</td>
<td>0.21</td>
<td>12.2</td>
<td>190</td>
</tr>
<tr>
<td>7</td>
<td>0.27</td>
<td>2.1</td>
<td>563</td>
<td>44.7</td>
<td>52.2</td>
<td>0.25</td>
<td>13.3</td>
<td>154</td>
</tr>
<tr>
<td>9</td>
<td>0.23</td>
<td>2.1</td>
<td>573</td>
<td>46.4</td>
<td>61.0</td>
<td>0.28</td>
<td>13.4</td>
<td>140</td>
</tr>
</tbody>
</table>

Catalyst weight, 200 mg; furnace temperature, 423 K; S/C, 5.0; time on stream, 10 min.

\( a) \) \( \Delta H_r \): endothermic enthalpy of reaction.

\( b) \) Energy efficiency (\%) = \( \Delta H_r / (\text{input power} \times \text{current}) \times 100. \)

\( c) \) Faradaic number = (mol of formed \( \text{H}_2 \) / (mol of input electron) \times 2).
yield with high current at the same catalyst-bed temperature. The promotion of acetaldehyde steam reforming by the electric field might be caused by the activation of surface adsorbed water and promotion of acetate species formation. On the other hand, dehydrogenation of ethanol and decomposition of acetaldehyde showed less promotion effect by applying the electric field, because activation of surface adsorbed water is not included for these reactions.

3.4. In-situ DRIFTS Study for Adsorbed Species

3.4.1. Effect of Electric Field on Adsorbed Species

To investigate the reaction mechanism for the elec-
Electroforming of ethanol over Pt/CeO₂ catalyst, in-situ DRIFTS measurements were conducted. Figure 6 shows the DRIFTS spectra over Pt/CeO₂ catalyst at 423 K with or without the electric field after adsorption of ethanol and Ar purging (30 min). Assignments of the adsorbed species were based on the literatures and the H-D exchange reaction (see Section 3.4.2). Ethanol adsorbed on the catalyst at 423 K without the electric field resulted in formation of monodentate and bidentate ethoxide species, which were identified by CH stretching of CH₃ and CH₂ (around 2900 cm⁻¹), CH₃ bending (around 1400 cm⁻¹) and CO stretching (1114 cm⁻¹ and 1044 cm⁻¹). The band at around 1240 cm⁻¹ was assigned to δ(OH) of adsorbed molecular ethanol species and/or ν(CO) of adsorbed molecular acetaldehyde species. Small bands corresponding to acetate species (νₐs(OCO) = 1595 cm⁻¹, νₐs(OCO) = around 1400 cm⁻¹) and carbonate species (νₐs(OCO) = 1658 cm⁻¹, νₐs(OCO) = around 1400 cm⁻¹) were also observed.

Induced electric field caused increases in the peak intensities of acetate species and adsorbed molecular species (1595, 1450-1350, 1240 cm⁻¹) and decreases in that of ethoxide species (around 1100 cm⁻¹). Moreover, the peaks of adsorbed CO (around 2000 cm⁻¹) and CO₂ (around 2300 cm⁻¹) were increased significantly. These results suggest that conversion of ethoxide species to acetaldehyde, acetate species, CO and CO₂ was promoted by the electric field.

As described above, electroforming of ethanol proceeds via an acetaldehyde intermediate, which is formed by ethanol dehydrogenation. Therefore, DRIFTS measurements were conducted after adsorption of “acetaldehyde” (not ethanol) and Ar purging (30 min) at 423 K. Figure 7 shows the DRIFTS spectra with or without the electric field. With the electric field after adsorption of acetaldehyde, the peaks of adsorbed acetaldehyde species (1606, around 1400 cm⁻¹), adsorbed molecular acetaldehyde species (1735, around 1200 cm⁻¹), adsorbed CO (around 2000 cm⁻¹) and CO₂ (2360 cm⁻¹) were observed. Although the spectrum closely resembled the spectra shown in Fig. 6, the peaks around 1600 cm⁻¹ (νₐs(OCO) vibration of acetate species) were larger. Therefore, the peaks around 1600 cm⁻¹ are associated with intermediates derived from acetaldehyde. These results suggest that the adsorbed species derived from ethanol were converted promptly to the adsorbed species derived from acetaldehyde with the electric field even at low temperature, such as 423 K. In-situ DRIFTS measurement also indicated that ethanol dehydrogenation was promoted in the electric field.

3.4.2 Identification of Adsorbed Species

In order to identify the adsorbed species at 1300-1700 cm⁻¹, H-D exchange reaction of adsorbed species with D₂ gas was conducted. Figure 8 shows in-situ DRIFTS spectra of adsorbed acetate or carbonate species over Pt/CeO₂ catalyst after adsorption of ethanol and imposing the electric field at 423 K, and then introduced D₂ gas without the electric field. Before introduction of D₂ gas, bands at 1656, 1595, 1440-1410 cm⁻¹ were observed. By introducing D₂ gas, the band at 1595 cm⁻¹ was shifted to lower wavenumber at 1585 cm⁻¹ while peak shifts of the other bands could not be observed. Previously, it was reported that the peaks of acetate species shifted to lower wavenumber about 10 cm⁻¹ by H-D exchange reaction. Therefore, it is confirmed the peak at 1595 cm⁻¹ is attributed to acetate species (νₐs(OCO)) and the peaks at 1656 cm⁻¹ is attributed to carbonate species (νₐs(OCO)). In this study, symmetric OCO stretching vibrations of acetate species and carbonate species, which was observed at around 1400 cm⁻¹, could not be identified because of...
overlapping of these peaks.

In-situ DRIFTS measurements revealed that not only conversion of the adsorbed ethoxide species to the adsorbed acetate species but also the promotion of steam reforming reaction of the adsorbed acetate species significantly (as shown in Fig. 9) in the electric field even at low temperature, such as 423 K. Consequently, ethanol steam reforming proceeded in the electric field at low temperature, such as 423 K.

3.5. Energy Efficiency of Electreforming

To evaluate the efficiency of the electrons supplied by the electric field, the Faradaic number, the number of the \( \text{H}_2 \) molecules formed per electron supplied by the electric field, was calculated. If hydrogen formation was promoted electrochemically, the Faradaic number would be 0.5, because formation of a hydrogen molecule from two protons requires two electrons. However, the Faradaic number was 140-190 in this reaction system as shown in Table 2. Therefore, the reaction was not only promoted electrochemically, but also catalytically activated by the electric field. In addition, electreforming can be conducted at low temperatures, so can use waste heat. Therefore, in the electreforming of ethanol, hydrogen can be produced using less energy at low temperatures such as 423 K with high energy efficiency.

4. Conclusion

Ethanol steam reforming was conducted over Pt/CeO\(_2\) catalyst in an electric field (electreforming) at low temperature. Ethanol steam reforming proceeded at low temperature, such as 423 K, under electreforming, whereas the conventional catalytic reaction without the electric field hardly proceeded. Moreover, CH\(_3\)CHO selectivity was low and CO + CO\(_2\) selectivity and \( r_{\text{H}_2}/r_D \) ratio were higher in electreforming than in the conventional catalytic reaction, which indicated that steam reforming of acetaldehyde was promoted by the electric field. The supported platinum worked as an active site and had a great impact on the activity and selectivity for ethanol steam reforming in the electric field. Electreforming with higher current showed higher conversion and \( \text{H}_2 \) yield than with lower current at almost the same catalyst-bed temperature, because apparent activation energies for ethanol dehydrogenation and acetaldehyde steam reforming were lowered by higher current. In-situ DRIFTS measurements revealed that both conversion of the adsorbed ethoxide species to the adsorbed acetate species and steam reforming reaction of the adsorbed acetate species was promoted significantly in the electric field even at low temperature, which improved hydrogen selectivity. The Faradaic number was 140-190 in this reaction system, which means that the reaction was promoted not only electrochemically, but also catalytically by electrons supplied by the electric field. This electreforming process for bioethanol can produce hydrogen using less energy at low temperature, such as 423 K, with high energy effi-

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**Fig. 8** In-situ DRIFTS Spectra of Adsorbed Acetate Species over Pt/CeO\(_2\) Catalyst after Adsorption of Ethanol at 423 K in the Presence or Absence of D\(_2\)

**Fig. 9** In-situ DRIFTS Spectra over Pt/CeO\(_2\) Catalyst under H\(_2\)O Atmosphere after Adsorption Ethanol (a) without the Electric Field at 548 K and (b) with the Electric Field at 423 K
ciency.

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References
要  旨

セリア担持白金触媒を用いた低温電場中でのエタノール水蒸気改質による水素製造

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セリア担持白金触媒を用いて低温電場中でエタノール水蒸気改質を行い、活性や選択性に及ぼす電場の効果を検討した。従来の触媒反応では反応が進行しない423 Kという低温においても、電場を印加することでエタノール水蒸気改質が進行した。白金はエタノール水蒸気改質の活性点として働くことが示された。電場印加によって三つの素反応（エタノール脱水素、アセトアルデヒド分解、アセトアルデヒド水蒸気改質）の活性化エネルギーは低下し、エタノール転化率や水素収率が増加した。特に、アセトアルデヒド水蒸気改質が印加電流値の増加に伴って423 Kという低温でも選択的に促進された。電場印加によって低温でも反応性の高いアセテート吸着種が形成されることがin-situ DRIFTS測定により示され、これが水素収率の向上に寄与した。本触媒プロセスによってバイオエタノールから水素の低温での製造が可能となる。