1. Ethanol Production

Ethanol, which is receiving much attention as an alternative fuel\(^1\),\(^2\), is produced mainly by fermentation of biomass carbohydrates such as sugarcane and corn\(^2\)\(^4\). Ethanol is anticipated for use as a clean and renewable energy resource. To avoid competition with food production, ethanol production processes from non-food biomass, such as cellulose and bagasse have also been developed. Alternatively, ethanol is producible from syngas (CO\(_\text{g}\) + H\(_2\text{g}\))\(^5\). Because syngas is obtainable through biomass gasification\(^6\),\(^7\), syngas-derived ethanol is also regarded as a renewable source. Direct electrochemical conversion of CO\(_2\) to ethanol using a Cu/carbon electrocatalyst has also been reported\(^8\)\(^9\). By this electrochemical reaction, surplus electricity in power generation by renewable energy can be stored as ethanol. Consequently, large amounts of ethanol are expected to be obtained from renewable feedstocks at low cost. Furthermore, because ethanol is stable and liquid at ambient temperatures, it is a promising candidate for use as an energy carrier.

2. Bioethanol Utilization as Energy

Ethanol is proposed for use as an automobile fuel by mixing with gasoline\(^10\). For utilization in automobiles, ethanol must be dehydrated and purified by azeotropic distillation with large energy loss to obtain \( \geq 99.5 \text{ wt\%} \) ethanol. Reportedly, this distillation process consumes about 700 kJ mol\(^{-1}\)\(^{10,11}\), which corresponds to ca. 50 % of combustion enthalpy of ethanol (\( \Delta H_c = 1278 \text{ kJ mol}^{-1} \)). Consequently, considering the distillation process, the energy efficiency is not so high (Fig. 1(left)).

Direct hydrogen production from low-concentration ethanol aqueous solution (20-50 wt%) by ethanol steam reforming (Eq. (1)) after simple distillation has been proposed to avoid such large energy loss\(^12\)-\(^16\). In addition, hydrogen is regarded as a candidate for next-generation secondary energy use with fuel, fuel cells, and fuel cell vehicles\(^17\),\(^18\). Therefore, development of efficient hydrogen production processes from biomass-derived ethanol can contribute directly to expand the enhanced utilization of renewable energy.

\[
\text{C}_2\text{H}_5\text{OH}(g) + 3\text{H}_2\text{O}(g) \rightarrow 2\text{CO}_2(g) + 6\text{H}_2(g) \\
\Delta H^\circ_{f,298} = 173.0 \text{ kJ mol}^{-1} \tag{1}
\]

Moreover, because ethanol steam reforming is an endothermic reaction, the combustion enthalpy of reformate after the reforming increases by 173.0 kJ mol\(^{-1}\) (\( \Delta H_c = 1451 \text{ kJ mol}^{-1} \)), compared with that before the
reforming (Fig. 1(right)). Figure 2 shows an exergy diagram of ethanol steam reforming. The exergy rate is defined as the ratio of Gibbs free energy (potential useful work) over the combustion enthalpy. For exergy calculation, the environment temperature is defined as 298 K and reference compounds are H2O(l) and CO2(g). Therefore, in Fig. 2, combustion enthalpy and exergy of C2H5OH(1) and 6H2(g) were calculated based on HHV (higher heating value). Because latent heat of vaporization of ethanol solution (S/C = 1.5: C2H5OH(1) + 3H2O(1)) is 175 kJ mol-ethanol–1, enthalpy gain from C2H5OH(1) is 348 kJ mol–1. From Figs. 1 and 2(a), if ethanol steam reforming can proceed using low grade waste heat, then the enthalpy and exergy of the waste heat are recoverable for storage as hydrogen energy(19). Consequently, low-temperature ethanol steam reforming can be a clean and efficient process for hydrogen production from renewable resources using waste heat generated in automobiles and industries.

To date, various transition metal supported catalysts such as Rh, Pt, Pd, Ni, and Co have been investigated for ethanol steam reforming(13–15). Because noble metal catalysts are expensive, Ni and Co catalysts are attracting much attention(20–22). Earlier research has found that Co-based catalysts show high activity and stability at 823 K(23–26), as summarized in Fig. 3. Consequently, ethanol steam reforming is anticipated as a highly efficient energy production process.

However, the waste heat consists mostly of heat in the low-temperature region of 373–473 K, with total heat value of about 0.7 EJ, which accounts for approximately 3.5% of the primary energy supply in Japan(27). From the viewpoint of recovery of the unused waste heat energy, the reaction should proceed in a low-temperature region, such as 373–473 K. However, catalysts showing both high activity and low carbon deposition have not been reported for such low temperatures. Therefore, novel low-temperature reaction processes for effective ethanol steam reforming are strongly required.
3. Low-temperature Ethanol Steam Reforming in an Electric Field

For ethanol steam reforming to proceed below 473 K, external energy input is required. As presented in Fig. 2(b), input of a small amount of electrical power would enable the reaction to proceed at 423 K with recovery of enthalpy and exergy of the low-grade waste heat. According to the G-T diagram (Fig. 4), it is necessary to input energy into the system to lower the reaction temperature below 473 K ($\Delta G > 0$). To overcome that issue, we have proposed “electrocatalytic reaction in a direct current (DC) electric field” as a novel low-temperature catalytic reaction system. We have succeeded in facilitating various endothermic catalytic reactions such as steam reforming, dry reforming, and dehydrogenation, even at low temperatures below 473 K by applying an electric field to the catalyst bed. Therefore, we investigated the ethanol steam reforming in the electric field.

In this study, the supported Pt catalysts were used because it showed high activity for ethanol steam reforming in the electric field. Effects of the Pt loading amount, support, reaction temperature and imposed current on the activity and selectivity were examined. The reaction mechanism and the related energy efficiency were also investigated.

3.1. Effects of the Pt Loading Amount and Support

Ethanol steam reforming in the electric field was conducted using a fixed bed continuous flow quartz tube reactor (6 mm i.d.) equipped with two stainless steel rod electrodes (SUS 304, 2 mm o.d.). Figure 5 portrays a schematic diagram of the reactor. As reactant, 20 wt% ethanol aqueous solution (S/C: steam/carbon ratio = 5) was fed to the reactor using a syringe pump.

Figure 6 shows the ethanol conversion and H$_2$ yield at various catalyst-bed temperatures in ethanol steam reforming over 1 wt% Pt/Ce$_{1-x}$Zr$_x$O$_2$ ($x$ = 0, 0.25, 0.5, 0.75) catalysts with the electric field. In the electric field, the tested Pt/Ce$_{1-x}$Zr$_x$O$_2$ catalysts showed almost equal temperature dependence of conversion and H$_2$ yield. In addition, a stable electric field is applicable to Pt/CeO$_2$ compared to Pt/Ce$_{1-x}$Zr$_x$O$_2$. It is noteworthy that Pt/CeO$_2$ catalyst with the electric field showed stable activity at least 2 h with low carbon deposition (7.5 mg g$_{cat}$ h$^{-1}$). Therefore, Pt/CeO$_2$ catalyst was used for various analyses.

Then, to clarify the role of the supported Pt, activity tests were conducted in the electric field using Pt/CeO$_2$ catalysts with various Pt loading amounts. As shown in Table 1, bare CeO$_2$ support showed very low activity. Conversion and H$_2$ yield increased concomitantly with
increasing Pt loading amounts. These results indicated that the supported Pt is an active site for ethanol steam reforming in the electric field\(^{34}\).

### 3.2. Electric Field Effects on Activity and Selectivity

As shown in **Fig. 6**, on the Pt/CeO\(_2\) catalyst, conversion and H\(_2\) yield increased remarkably by imposing an electric field in the low-temperature region below 573 K\(^{34,35}\). It is noteworthy that application of the electric field enabled the reaction to proceed even at a temperature lower than 473 K, although conventional catalytic reactions proceed only slightly at such low temperatures because of thermodynamic limitations (\(\Delta G > 0\)).

**Figure 7** presents changes in the product selectivity against the catalyst-bed temperature with or without the electric field. As portrayed in **Fig. 7(a)**, acetaldehyde selectivity was high in the low temperature range without the electric field. However, as portrayed in **Fig. 7(b)**, in the electric field, CO\(_2\) selectivity was high, even at a low temperature. Moreover, the ratio of (CO + CO\(_2\))/CH\(_4\) in the electric field was higher than that in the conventional catalytic reaction. These results indicate that imposition of the electric field resulted not only in promotion of acetaldehyde steam reforming (CO + CO\(_2\) formation) but also in suppression of acetaldehyde decomposition (CH\(_4\) formation)\(^{34}\). Based on the results described above and on results described in the literature\(^{25}\), a possible reaction scheme can be proposed as presented in **Fig. 8**\(^{35}\).

### 3.3. Effects of Imposed Current

Effects of imposed current on activity and selectivity were investigated. **Table 2** presents results of activity tests over Pt/CeO\(_2\) catalyst at 423 K under various imposed currents (0-9 mA). The conversion and H\(_2\) yield increased with higher imposed current\(^{34}\). Although the catalyst-bed temperature increased with higher imposed current because of the Joule heat, the higher imposed current caused higher conversion and H\(_2\) yield at

![Fig. 7](image)

**Fig. 7** Conversion and Product Selectivity in the Ethanol Steam Reforming over Pt/CeO\(_2\) Catalyst: (a) without the electric field, (b) with the electric field\(^{34,35}\)

![Fig. 8](image)

**Fig. 8** Possible Reaction Scheme for Ethanol Steam Reforming in an Electric Field\(^{35}\)

### Table 1: Ethanol Steam Reforming in an Electric Field over Pt/CeO\(_2\) Catalysts with Various Pt Loading Amounts\(^{34,35}\)

| Pt loading amount [wt\%] | Conversion [%] | H\(_2\) yield [%] |
|--------------------------|----------------|------------------|
| 0                        | 1.4            | 0.5              |
| 0.5                      | 22.1           | 17.1             |
| 1.0                      | 27.4           | 27.3             |
| 3.0                      | 35.9           | 35.4             |

Catalyst weight, 200 mg; furnace temperature, 423 K; imposed current, 3 mA; S/C, 5; time on stream, 10 min.

### Table 2: Effect of the Imposed Current over Pt/CeO\(_2\) in the Electric Field\(^{34}\)

| Imposed current [mA] | Voltage [kV] | Power [W] | Catalyst-bed temp. [K] | Conv. [%] | H\(_2\) yield\(^{a}\) [%] | \(\Delta H_r^{b}\) [J s\(^{-1}\)] | Energy efficiency\(^{c}\) [%] | Faradaic number\(^{d}\) [-] | Energy demand\(^{e}\) [MJ kg-H\(_2\) \(^{-1}\)] |
|----------------------|--------------|-----------|------------------------|----------|--------------------------|-----------------|-----------------|----------------|-----------------|
| 0                    | -            | -         | 423                    | <0.1     | <0.1                     | 0.00            | -               | -              | -               |
| 2                    | 0.45         | 0.9       | 500                    | 19.4     | 16.6                     | 0.08            | 9.2             | 171            | 127             |
| 3                    | 0.37         | 1.1       | 505                    | 27.4     | 27.3                     | 0.14            | 12.6            | 187            | 95              |
| 5                    | 0.34         | 1.7       | 547                    | 38.0     | 46.1                     | 0.21            | 12.2            | 190            | 86              |
| 7                    | 0.27         | 1.9       | 565                    | 44.7     | 52.2                     | 0.25            | 13.3            | 154            | 85              |
| 9                    | 0.23         | 2.1       | 573                    | 46.4     | 61.0                     | 0.28            | 13.4            | 140            | 79              |

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

a) H\(_2\) yield [%] = (mol of produced H\(_2\))/((mol of input ethanol) x 3).

b) \(\Delta H_r\) [J s\(^{-1}\)]: endothermic enthalpy of reaction.

c) Energy efficiency [%] = \(\Delta H_r\)/(input power) \times 100.

d) Faradaic number = (mol of formed H\(_2\))/((mol of input electron) x 2).

e) Energy demand [MJ kg-H\(_2\) \(^{-1}\)] = (input power)/(formation rate of H\(_2\)).
almost equal catalyst-bed temperatures (Fig. 9)\(^{34)}\).

The apparent activation energy of elementary reactions was calculated from the Arrhenius plot. Figure 10 presents Arrhenius plots for (a) ethanol dehydrogenation \((\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} + \text{H}_2)\), (b) acetaldehyde decomposition \((\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO})\), and (c) acetaldehyde steam reforming \((\text{CH}_3\text{CHO} + \text{H}_2\text{O} \rightarrow 2\text{CO} + 3\text{H}_2)\). Table 3 shows the calculated apparent activation energy. Imposing the electric field lowered the apparent activation energy of three reactions, which indicates that the electric field promoted these reactions. Especially, the apparent activation energy of acetaldehyde steam reforming greatly decreased concomitantly with increase of the imposed current. The electric field preferentially promoted acetaldehyde steam reforming. Thereby, the Pt/CeO\(_2\) catalyst with higher imposed current showed a higher H\(_2\) yield\(^{34)}\).

### 3.4. Reaction Mechanism

#### 3.4.1. Isotope Effect

To evaluate the electric field effects on activation of adsorbed water or OH\(_x\) species, activity tests using D\(_2\)O were conducted with or without the electric field. As presented in Fig. 11(a), the reaction rate of ethanol dehydrogenation using D\(_2\)O was almost equal to that obtained using H\(_2\)O, even when the electric field was applied. By contrast, as presented in Fig. 11(b), the reaction rate of acetaldehyde steam reforming obtained using D\(_2\)O was lower than that using H\(_2\)O only when the electric field was applied. Consequently, in the electric field, an isotope effect for acetaldehyde steam reforming was observed. From these results, one can infer that the electric field contributed to the activation of adsorbed water and/or OH\(_x\) species\(^{35)}\).

#### 3.4.2. In-situ DRIFTS Measurements

To investigate the behavior of adsorbed species on the catalyst surface in an electric field, in-situ diffuse reflectance infrared Fourier transformed spectroscopy (DRIFTS) measurements were conducted using the Pt/CeO\(_2\) catalyst. The apparatus for the in-situ DRIFTS measurements was described in earlier reports\(^{29),34)}\).

| Imposed current [mA] | (a) Dehydrogenation | (b) Decomposition | (c) Steam reforming |
|----------------------|---------------------|-------------------|---------------------|
| 0 (w/o EF)           | 50.4                | 62.5              | 59.8                |
| 2                    | 38.4                | 45.4              | 39.4                |
| 3                    | 30.7                | 34.8              | 32.2                |
| 5                    | 27.4                | 36.6              | 21.6                |
| 7                    | 22.7                | 36.4              | 20.3                |
| 9                    | 23.3                | 29.4              | 18.7                |

Catalyst weight, 200 mg; furnace temperature, 423 K; S/C, 5; time on stream, 10 min.

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**Fig. 9** Changes in (a) Conversions and (b) H\(_2\) Yields against Catalyst-bed Temperature in the Ethanol Steam Reforming over Pt/CeO\(_2\) without or with the Electric Field (0-9 mA)\(^{34),35)}\)

**Fig. 10** Arrhenius Plots for (a) Ethanol Dehydrogenation, (b) Acetaldehyde Decomposition and (c) Acetaldehyde Steam Reforming in the Ethanol Steam Reforming over Pt/CeO\(_2\) with or without the Electric Field with Various Imposed Currents (2-9 mA)\(^{34),35)}\)
As presented in Fig. 12 (a), at 423 K without the electric field, ethanol was adsorbed as ethoxide species. Then, applying the electric field caused decreased peak intensity of ethoxide species and increased that of acetate, CO(ad.), and CO₂ (Fig. 12 (b)). Results demonstrate that the electric field promoted conversion of ethoxide to acetate. Reportedly, the acetate species is an intermediate of ethanol steam reforming; it is reactive in the presence of H₂O²⁵). Therefore, surface reaction between the adsorbed species and steam in the electric field was investigated. As presented in Fig. 12 (c), introducing steam under the electric field decreased the peak intensity of the acetate species. Results indicated that surface reaction between the adsorbed acetate species and H₂O or OH₃ species (by steam reforming) was promoted in the electric field. Consequently, in-situ DRIFTS measurements indicate clearly that the electric field promoted not only the formation of acetate species from ethoxide but also steam reforming of the formed acetate species³⁴),³⁵). Results show that ethanol steam reforming proceeds in the electric field, even at low temperatures.

Figure 13 shows a proposed reaction mechanism based on results of activity tests using D₂O and in-situ DRIFTS measurements. Because acetate species were formed even in the absence of steam, the lattice oxygen (O₃) of CeO₂ support might contribute to oxidation of ethoxide to acetate. We reported earlier that lattice oxygen participates in the oxidation of hydrocarbons, even at low temperatures, when the electric field was applied²²). Therefore, promotion of the redox reaction by the electric field using the lattice oxygen is expected to contribute to oxidation of ethoxide to acetate species. Thereby, steam reforming was promoted at low temperatures.

3.5. Energy Efficiency of Ethanol Steam Reforming in an Electric Field

Finally, we calculated the energy efficiency of the ethanol steam reforming in the electric field. Table 2 presents results obtained from activity tests conducted at 423 K with various imposed currents. Imposing a higher current caused higher enthalpy gain (ΔHᵣ). Energy efficiency ( = ΔHᵣ/(input power)) was also increased concomitantly with increasing applied current because the reaction was promoted not only electro-chemically but also catalytically in this reaction system²⁸). Energy efficiency of the reaction using 9 mA current reached 13.4 %, although further improvement is necessary to recover the energy of low-grade waste heat. Moreover, energy demand for hydrogen production was 79 MJ kg⁻¹H₂ (423 K, 9 mA), which was sufficiently lower than the combustion enthalpy of hydrogen (143 MJ kg⁻¹H₂). Results show that hydrogen was produced efficiently in this novel electrocatalytic process by ethanol steam reforming using less energy at a low temperature such as 423 K.

4. Conclusion

Hydrogen production from renewable resources is
important for next-generation energy resources. Here we report catalytic properties, reaction mechanisms, and energy efficiencies of low-temperature hydrogen production by catalytic ethanol steam reforming in an electric field. By application of an electric field to Pt/CeO$_2$ catalyst, ethanol steam reforming proceeds even at low temperatures such as 423 K. In this catalytic system, the supported Pt was an active site. In the electric field, even at low temperatures, conversion, H$_2$ yield, and CO + CO$_2$ selectivity were high. Applying the electric field lowered the apparent activation energy of three elementary reactions: ethanol dehydrogenation, acetaldehyde decomposition, and acetaldehyde steam reforming. In particular, the electric field preferentially promoted acetaldehyde steam reforming. Mechanistic study clarified that the electric field assisted the formation of adsorbed acetate species and activation of the adsorbed OH species, and thereby promoted steam reforming of the formed acetate species. Energy demand for hydrogen production in this electrocatalytic process was sufficiently low, at 79 MJ kg$^{-1}$H$_2$, which was about half of the combustion enthalpy of hydrogen.

Consequently, combination of catalyst with the electric field is an effective approach for lowering the reaction temperature of endothermic reaction. It is expected to realize efficient direct hydrogen production from ethanol at low temperatures. Although the energy efficiency remains low at present, further advances in scientific understanding and improvement of energy efficiency are expected to open the door to highly efficient hydrogen production from renewable resources using low grade waste heat with recovery of exergy.

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