Evaluation of surface protonics on $Ce_{0.25}Zr_{0.75}O_2$ by AC impedance measurement

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Abstract:

To decrease the high reaction temperature of the conventional catalytic reactions, the process with application of the electric field to the catalyst bed has been investigated. When this process was applied to methane steam reforming over 1wt%Pd/CeO_2, the activity increased drastically even at low temperature such as 423 K. Additionally, Zr doped CeO_2 ($Ce_{0.25}Zr_{0.75}O_2$) showed the highest activity for methane steam reforming in the electric field. Furthermore, it was revealed that proton conduction on the catalyst surface: surface protonics promoted the reaction even at low temperatures. Therefore, AC impedance measurements over CeO_2 and $Ce_{0.25}Zr_{0.75}O_2$ were conducted to evaluate the surface protonics.

Keywords: AC impedance measurements, Surface protonics, Methane steam reforming

1. Introduction

Hydrogen has been anticipated as a secondary energy source because it is converted easily into electric power. Catalytic steam reforming is one of the main process to produce hydrogen. The formula of the reaction is presented below when methane is used as a raw material of hydrocarbon.

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \qquad \Delta H^0_{298} = 164.9\ \mathrm{kJ\ mol^{-1}}$$

Since this reaction is conducted at high temperatures due to thermodynamics and kinetics, the process with application of the electric field to catalyst bed has been investigated. This process enables the catalytic reactions to proceed at low temperatures. From the results of imposing the electric field to methane steam reforming over 1wt%Pd/CeO_2, it was revealed that Pd supported catalyst demonstrated high activity even at low temperatures such as 423 K, compared to the thermal catalytic reaction without the electric field.1) In addition, various supports for Zr doped CeO_2 were prepared. As a result, $Ce_{0.25}Zr_{0.75}O_2$ support showed the highest activity for methane steam reforming in an electric field.1) Besides, *in-situ* IR measurements detected the rotation spectrum of adsorbed water, suggesting that proton conduction via adsorbed water on the catalyst surface, so-called surface protonics, occurred by the *Grotthuss* mechanism during the electric field application.2) Based on the above, it was considered there is a close relationship between surface protonics and the mechanism of catalytic reaction in the electric field. Therefore, AC impedance method was applied to the catalyst supports of CeO_2 and $Ce_{0.25}Zr_{0.75}O_2$ to extract and evaluate surface protonics.

2. Experimental

For AC impedance measurements, almost 60% relative density of CeO_2 pellet and $Ce_{0.25}Zr_{0.75}O_2$ pellet were prepared. Pt ink was painted on both sides of these two pellets in order to attach electrodes. Only Ar gas was supplied in a dry condition, and wet Ar gas (P_{H2O} = 0.026 atm) was supplied in a wet condition. Electrochemical impedance spectroscopy (EIS) measurements were conducted between the temperature range of 398–673 K, with the frequency range of 10^{-3}-10^6 and amplitude of 0.1V RMS in a measurement cell (Probostat, NorECs AS, Norway) with a 2-electrode 4-wire set up connected to a Novocontrol alpha-A impedance spectrometer with a ZG4 interface. The impedance data were analyzed using an equivalent circuit fitting software (ZView ver. 3.5a; Scribner Associates Inc.).

3. Results and discussion

To elucidate the temperature dependency on the conductivity of CeO_2 and $Ce_{0.25}Zr_{0.75}O_2$, EIS measurements were conducted at various temperatures in dry and wet conditions. Results are presented in Figures 1 and 2. In a dry condition, both CeO_2 and $Ce_{0.25}Zr_{0.75}O_2$ demonstrated the same tendency. The conductivities of bulk and grain boundary decreased with the decreasing temperature, as presented in Figure 1. Also in a wet condition, the conductivities of surface bulk and surface grain boundary showed the same tendency. As shown in Figure 2, the conductivity decreased along with the decreasing of temperature at the temperature range over 523 K. However, the conductivity increased along with the decreasing of temperature at the temperature range under 523 K. These tendencies can be explained by the effect of surface protonics. In a wet condition, the conductivity increases at low temperatures below 523 K because the amount of adsorbed water on the catalyst surface increases at low temperatures. Therefore, it was considered these tendencies reflected the protonics derived from adsorbed water on the catalyst surface.

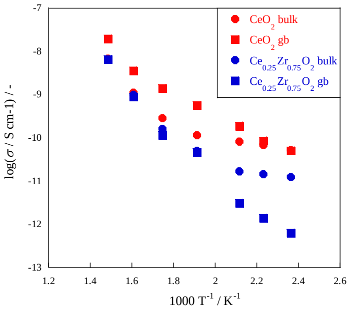

Figure 1. Temperature dependence on conductivity in dry condition.

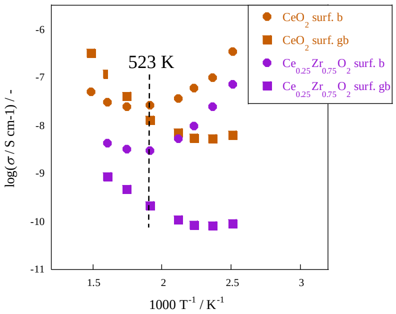

Figure 2. Temperature dependence on conductivity in wet condition.

Next, to compare the proportion of surface protonics component of CeO_2 with that of $Ce_{0.25}Zr_{0.75}O_2$, a parameter η which indicates the ratio of the total surface conductivity to the total bulk internal conductivity was used. The definition of η is presented below.

$$\eta = \frac{\sigma_{surf.\ \mathrm{b}} + \sigma_{surf.\ \mathrm{gb}}}{\sigma_{\mathrm{b}} + \sigma_{\mathrm{gb}}} \quad \text{(b: bulk, gb: grain boundary)}$$

The calculated η at various temperatures are shown in Figure 3. As shown in Figure 3, η for $Ce_{0.25}Zr_{0.75}O_2$ showed higher values than that for CeO_2 at the low temperature range under 523 K. These results indicate that surface protonics on $Ce_{0.25}Zr_{0.75}O_2$ occurred more vigorous than that on CeO_2, resulting in higher activity for methane steam reforming in the electric field.

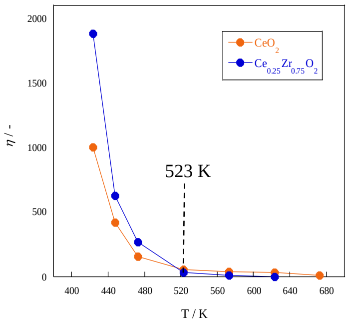

Figure 3. Temperature dependence on η (the proportion of surface protonics)

4. Conclusions

In a dry condition, both CeO_2 and $Ce_{0.25}Zr_{0.75}O_2$ presented the same tendency: the conductivity of bulk and grain boundary decreased along with the decreasing of temperature. Also in a wet condition, both of them demonstrated the same tendency: at the temperature range over 523 K, the conductivity decreased along with the decreasing of temperature. On the other hand, at the temperature range under 523 K in wet conditions, the conductivity increased along with the decreasing of temperature. These tendencies were considered the protonics derived from adsorbed water on the catalyst surface contributed the increase of conductivity in the low temperature range. In addition, through the comparison for the proportion of surface protonics component of CeO_2 and $Ce_{0.25}Zr_{0.75}O_2$, it was revealed that the proportion of $Ce_{0.25}Zr_{0.75}O_2$ exceeded that of CeO_2 at the low temperature range under 523 K. These results provide some evidences that surface protonics plays an important role for promoting methane steam reforming at low temperatures in the electric field, and surface protonics on $Ce_{0.25}Zr_{0.75}O_2$ occurred more vigorous than that on CeO_2.

References

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