Low temperature hydrogen production by water splitting using redox reaction in electric field

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Abstract: We have investigated highly active redox material for hydrogen production by water splitting through the redox reaction of metal oxide at 623 K in an electric field (EF). $Ce_{0.67}Cr_{0.33}O_2$ showed high activity for oxygen release to produce lattice oxygen defects in the EF, but did not show the activity for hydrogen production by the reaction between water and lattice oxygen defects. On the other hand, the addition of Pd in $Ce_{0.67}Cr_{0.33}O_2$ structure improved the hydrogen formation rate with maintaining oxygen release activity. As a result of optimization of Pd amount, 5 mol% Pd doped material ($Ce_{0.62}Cr_{0.33}Pd_{0.05}O_2$) showed the highest oxygen release rate and hydrogen formation rate. Doped Pd induced the lattice strain and thereby increasing the reaction rates.

Keywords: H_2 formation, water splitting, electric field

1. Introduction

Hydrogen is used for various purpose such as oil refining, ammonia synthesis, fuel cell and so on. The demand is expected to increase further in the future. Hydrogen is mainly produced by steam reforming (SR), however this method has disadvantages, such as consumption of limited fossil fuels and CO_2 production as a by-product. Therefore, a sustainable process for hydrogen production from abundant feedstocks is required. In this work, we focused on direct hydrogen production by water splitting including the redox reaction of metal oxide (eqs. 1 and 2). To proceed the redox reaction at low temperature, we investigated redox reaction in an electric field (EF).[1)]

$$MO_x \rightarrow MO_{x-1} + 1/2O_2 \qquad \text{[Oxygen release]} \qquad (1)$$

$$MO_{x-1} + H_2O \rightarrow MO_x + H_2 \qquad \text{[Hydrogen production]} \qquad (2)$$

In our previous work, we found that $Ce_{0.67}Cr_{0.33}O_2$ showed high activity for oxygen release to produce lattice oxygen defects in the EF at 623 K,[2)] but did not show the activity for hydrogen production by the reaction between water and lattice oxygen defects. In the present work, to improve the activity for hydrogen production, we prepared various Ce-Cr-M-O systems and evaluated the activity for water splitting. The prepared oxides were characterized by XRD, Raman, XPS and XAFS measurements.

2. Experimental

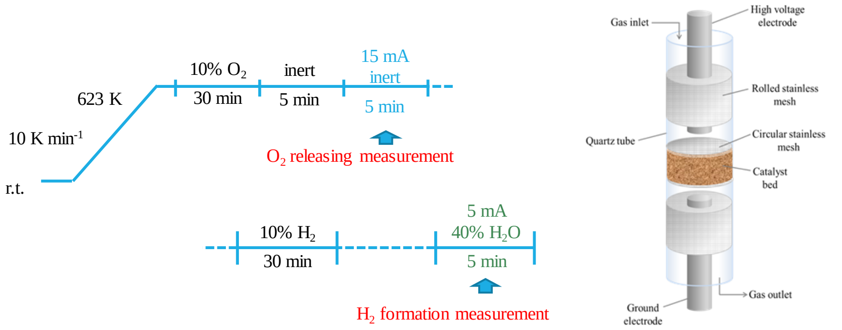
Ce-Cr-M-O system oxides were prepared by a polymerized complex method. The prepared oxides were calcined at 773 K for 5 h. For the activity tests, a fixed-bed flow-type reactor with two stainless steel electrodes was used (Figure 1). Oxide (1.0 g) was sieved to 355-500 μm and was charged into the packed bed. Detailed procedure of activity test is shown in Figure 1. Product gases were analyzed using Q-mass.

3. Results and discussion

To improve the activity for water splitting, effects of addition of noble metal to $Ce_{0.67}Cr_{0.33}O_2$ were investigated. Figure 2 shows results for activity tests using $Ce_{0.66}Cr_{0.33}M_{0.01}O_2$ (M = Ag, Au, Pt, Rh and Pd). Although the addition of noble metal improved the hydrogen formation rate, the oxygen release rate decreased for various oxides. Among them, only the Pd doped material ($Ce_{0.66}Cr_{0.33}Pd_{0.01}O_2$) showed high activities for hydrogen formation and oxygen releasing. From these results, Pd was selected as a suitable additive.

Then, the optimization of doping amount of Pd to $Ce_{0.67}Cr_{0.33}O_2$ was conducted. Figure 3 shows results for activity tests using $Ce_{0.67-n}Cr_{0.33}Pd_nO_2$ (n = 0.01, 0.03 and 0.05) in the EF at 623 K. Both hydrogen formation rate and oxygen formation rate increased with increasing the doped Pd amount. $Ce_{0.62}Cr_{0.33}Pd_{0.05}O_2$ was considered to be a suitable oxide for water splitting, because the oxide structure decomposed and the activity decreased by further addition of Pd.

Raman measurements and Rietveld analyses of the prepared oxides were conducted to evaluate the lattice strain. Results indicated that lattice strain of $Ce_{0.67}Cr_{0.33}O_2$ structure was induced by the Pd doping. The lattice strain might contribute to promote the redox reaction of the $Ce_{0.67}Cr_{0.33}O_2$. Therefore, lattice strain induced by the Pd doping contributes to its high activity for hydrogen production and oxygen release.



Catalyst weight : 1.0g
Temperature : 623K

Applied current
5mA(H_2 formation)
15mA(O_2 release)

Total flow rate : 200 SCCM
Internal standard : Ar(10 SCCM)
Balance : He

Figure 1. Experimental procedure of activity tests and schematic diagram of reactor.

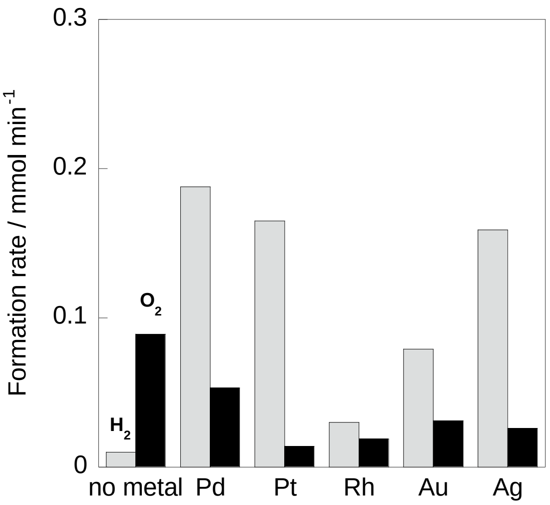


Figure 2. Results of activity tests over $Ce_{0.66}Cr_{0.33}M_{0.01}O_2$ (M = Pd, Pt, Rh, Au, Ag) oxides.

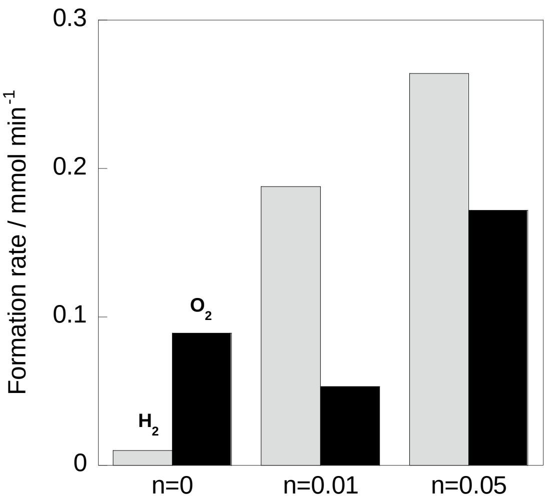


Figure 3. Results of activity tests over $Ce_{0.67-n}Cr_{0.33}Pd_nO_2$ (n = 0, 0.01, 0.03, 0.05) oxides.

4. Conclusions

Addition of Pd to $Ce_{0.67}Cr_{0.33}O_2$ oxide improved the activity for hydrogen production by water splitting at 623 K in the electric field. The activities increased with increasing the Pd doping amount, and 5 mol% Pd doped oxide ($Ce_{0.62}Cr_{0.33}Pd_{0.05}O_2$) showed the highest oxygen releasing rate and hydrogen formation rate. The Pd doping might induce the lattice strain and thereby increasing the reaction rates.

References

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2. K. Ogino *et al.*, *EUROPACAT 2017*, P3.72, (2017).