Low temperature steam reforming of methane over Pd-M alloy catalysts in an electric field

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Abstract: Steam reforming of methane (SR) using Pd supported catalysts proceeds at low temperature by applying an electric field. To elucidate the effect of a supported metal on catalytic activity and selectivity for steam reforming of methane in an electric field, various Pd-M alloy catalysts using $Ce_{0.5}Zr_{0.5}O_2$ support were applied to the reaction. Results revealed that activity and selectivity of Pd-M catalysts varied by the second metal M.

Keywords: Steam reforming of methane, Alloy catalyst, Electric field.

1. Introduction

Natural gas is more clean resource and have less region laterality than oil or coal. Stem reforming of methane (SR) is one of the approaches to utilize methane, a main component of natural gas. SR is the most widely used process for hydrogen production, however, it requires high temperature due to the strong C-H bond of methane. Such a high temperature condition is harsh for catalysts and reforming reactor. Large-scale process of SR has a long history and its technology has been almost established, however onsite hydrogen production in small to medium scale plants has not yet established1). Therefore, it is desired to lower the reaction temperature to solve these problems.

Our previous studies revealed that SR using Pd supported catalysts proceeds at a low temperature of 423 K by applying an electric field (*Electreforming*: ER)2). In the electric field, proton conducts via adsorbed water on the catalyst surface, which is so called the *Grotthuss* mechanism. Then the collision between proton and methane, which was physically adsorbed on Pd, promotes methane dissociative adsorption2). However, detailed effects of supported metal on ER activity have not investigated yet. Therefore, to elucidate the effects of electronic states and structures of supported metal on ER activity, we prepared Pd-M alloy catalysts using $Ce_{0.5}Zr_{0.5}O_2$ (CZO) as a support, and conducted activity tests.

2. Experimental

As a catalyst support, $Ce_{0.5}Zr_{0.5}O_2$ (CZO) was prepared with a complex polymerized method. Precursor of each element was $Ce(NO_3)_3 \cdot 6H_2O$ and $ZrO(NO_3)_2 \cdot H_2O$. Pd and the second metal were supported by a co-impregnation or successive impregnation. Prepared catalysts were characterized by XRD measurements and the Pd-M alloy states were confirmed. Table 1 shows preparation methods and the alloy state. Pd loading amount of the prepared catalysts was 5wt% and the Pd/M molar ratio is shown in Table 1.

For activity tests, a fixed-bed flow-type reactor was used. Before the activity tests, catalysts were reduced under H_2 (20 SCCM) and Ar (80 SCCM) flow at 673 K for 30 min. SR tests were performed using 100 mg of catalyst under CH_4 (10 SCCM), H_2O (20 SCCM) and Ar (70 SCCM) flow at various preset temperatures (473-873 K). For ER, two stainless steel rods were inserted into the reactor as electrodes and the response voltage was observed with an oscilloscope. ER tests were conducted using 100 mg of catalyst under CH_4 (10 SCCM), H_2O (20 SCCM) and Ar (70 SCCM) flow at 423 K with imposing 1-11 mA currents. Product gases were analyzed by a GC-FID and a GC-TCD after removing water by a cold trap. The prepared Pd-M catalysts were characterized by IR, XAFS and XPS.

Table 1 Pd-M alloy catalysts

Pd–M	Pd/M	Method	Reduction temp. / K	phase	crystallite size / nm
Pd		Impregnation	773	Pd	11
Pd-Fe	1	Co-impregnation	1073	$Pd_{0.6}Fe_{0.4}$	10
Pd-Co	1	Successive impregnation	973	$Pd_{0.75}Co_{0.25}$	6
Pd-Ni	1	Successive impregnation	873	$Pd_{0.9}Ni_{0.1}$	11
Pd-Cu	1	Co-impregnation	873	$Pd_{0.9}Cu_{0.1}$	13
Pd-Zn	1	Successive impregnation	873	PdZn	16
Pd-Ga	2	Successive impregnation	1073	Pd_2Ga	9

3. Results and discussion

Figure 1 shows the relationship between temperature and CH_4 conversion for SR and ER. Applying the electric field increased the activity even at low temperature, at which SR hardly proceeded. CH_4 conversion exceeded the equilibrium in the electric field. This was because, in the electric field, the reaction proceeds via an irreversible process including $[H_3C\text{-}H\text{-}H]^+$ intermediates formed by a collision between adsorbed CH_4 on Pd and H^+ conducting on the catalyst surface.

H_2 selectivity for ER varied by the second metal M. In particular, H_2 selectivity for ER increased by the addition of Ni while it decreased by the addition of Co compared to Pd metal without the second metal under the same temperature and CH_4 conversion. Furthermore Pd-Zn/CZO showed catalytic activity only in the electric field. These results indicated that Pd-M alloy catalysts exhibited different behaviors in the electric field.

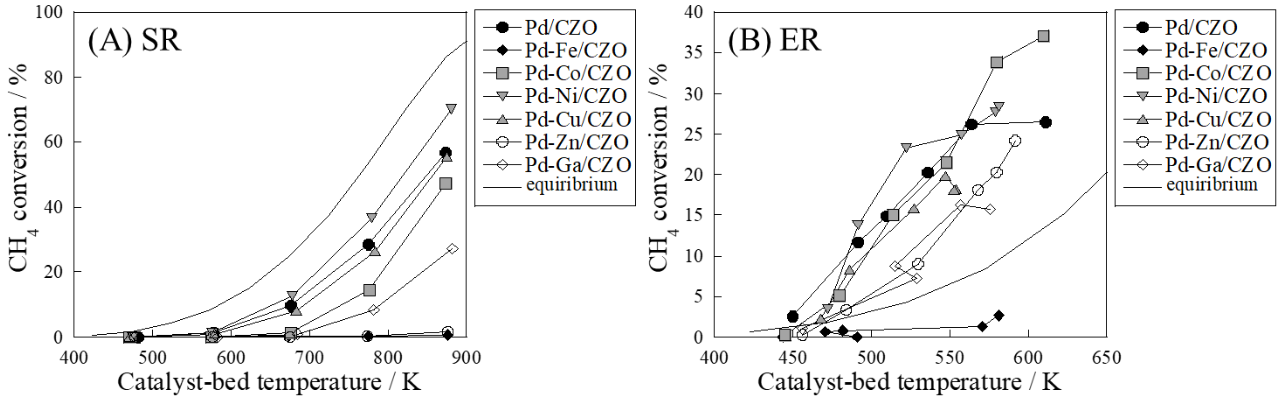

Figure 1. Relationship between catalyst-bed temperature and CH_4 conversion. (A) SR (B) ER.

4. Conclusions

Steam reforming of methane over various Pd-M alloy catalysts with/without an electric field were performed. Application of the electric field increased the activity drastically even at low temperature. The activity and selectivity for SR and ER varied with the second metal M. H_2 selectivity for ER increased by an addition of Ni, and decreased by addition of Co compared with Pd/CZO under the same temperature and CH_4 conversion. Addition of second metal M to Pd/CZO enables to control the activity and H_2 selectivity for ER.

References

1. NEDO, “Hydrogen Energy White Paper”, http://www.nedo.go.jp/library/suiso_ne_hakusyo.html. (Japanese)
2. R. Manabe *et al.*, *Scientific Reports*, 6 (2016) 38007.