

## Conversion of CH<sub>4</sub> Into H<sub>2</sub> At 300°C Using Pd/MnO<sub>2</sub> Catalyst Made With An Effect of Water Oxidation

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### Introduction

Hydrogen (H<sub>2</sub>) is a representative clean energy, and inexpensive methods for producing it will increasingly be required in the market. Currently, a major H<sub>2</sub> is obtained by using a method in which a methane gas (CH<sub>4</sub>) as a main ingredient of a natural gas is brought into contact with a steam at 700 to 800°C whereby allowing it to be reformed into H<sub>2</sub>. Nevertheless, this steam reforming method allows about 10 to 20% of the CH<sub>4</sub> to remain unreformed, although it allows for CH<sub>4</sub> to H<sub>2</sub> reforming rate as high as 80% or more. Accordingly, various attempts have been made in studies to convert the remaining CH<sub>4</sub> to H<sub>2</sub> by utilizing the residual heat of the steam reforming method. For example, Lodeng et. al. studied a catalytic method <sup>[1]</sup> in which alumina with metal microparticles, such as cobalt, nickel and iron, were used for a catalytic performance for reforming CH<sub>4</sub>. However, cobalt poses a problem of water solubility and the nickel and the iron suffer from a reduced catalytic performance due to a promoted oxidation of the surface. Therefore, when considering an actual natural gas as a resource for the H<sub>2</sub> production, it is a practical and critical problem how noble metal catalysts such as platinum (Pt) and palladium (Pd) can be used at a low cost while maintaining CH<sub>4</sub> reforming performance. Using an alumina as a carrier, the stability is ensured chemically and crystallographically even at a temperature as high as 700°C, but unfortunately a toxic carbon monoxide (CO) is produced as a by-product when reforming CH<sub>4</sub> to H<sub>2</sub>. Also when using as a carrier a carbon material such as an activated carbon, the carbon itself undergoes calcination with no resistance against a temperature of several hundred degrees Celsius if oxygen is mixed in the CH<sub>4</sub>. In view of the described above, a technology enabling H<sub>2</sub> production by a catalyst of nano-particles Pd is highly demanded. Pd is least expensive among the noble metals employed effectively in obtaining H<sub>2</sub> by reforming CH<sub>4</sub>. We show here a novel catalyst (Pd/MnO<sub>2</sub>) that is Pd chemically deposited onto the surface of a manganese dioxide having a ramsdellite-type crystal structure (RMO) and used as a reformed catalyst <sup>[2]</sup>.

### Experimental

First, an aqueous solution of Pd(OH)<sub>2</sub> with the Pd concentration of 1000mg/L was provided. Then, the RMO is added and suspended to this aqueous solution. Upon this, an alkali reagent such as an aqueous solution of NaOH is added dropwise while stirring the aqueous solution of Pd(OH)<sub>2</sub> to ensure that the pH4.8 or higher was maintained for about 24 hours. As a result, the palladium was deposited chemically as metallic nano-particles onto the surface of RMO to give Pd/MnO<sub>2</sub>. Fig. 1 shows the TEM image of a Pd/MnO<sub>2</sub> particle. The metallic state of deposited Pd was confirmed by X-ray photoelectron spectroscopy and inelastic neutron

scattering. The experimental setup for reforming CH<sub>4</sub> is shown in Fig. 2. The powder of 0.2g Pd/MnO<sub>2</sub> was packed into a Pyrex glass tube of 6 mm inner diameter. The Pd/MnO<sub>2</sub> in this glass tube was heated to 300°C. This temperature was kept while the gas mixture of CH<sub>4</sub> (10% concentration) and an argon (90% concentration) humidified by the passage through a bubbler filled with 30mL of a distilled water was introduced continuously at a flow rate of 20mL/min, thereby heating for 4 hours. Also, a gas chromatograph was connected to the glass tube for quantifying the concentration of the gas produced.

### Results and discussion

In Fig. 1, nanometer size Pd particles deposited in a high density onto the surface of RMO are observed. The reaction yielding the Pd deposition can be described by the following reactions that based on an oxidation of hydroxide ion in water.

1st anodic reaction:  $\text{OH}^- + \text{MnO}_2 \rightarrow \text{MnOOH} + 1/2\text{O}_2 + \text{e}^-$

2nd anodic reaction:  $\text{MnOOH} \rightarrow \text{MnO}_2 + \text{H}^+ + \text{e}^-$

Cathode reaction:  $\text{Pd}^{2+} + 2 \text{e}^- \rightarrow \text{Pd}$

Overall reaction:  $\text{Pd}^{2+} + \text{OH}^- \rightarrow \text{Pd} + 1/2\text{O}_2 + \text{H}^+$

The H<sub>2</sub> concentration of 3.6% was detected constantly in the gas after the passage of CH<sub>4</sub>/Ar through and the contact with the catalyst in the glass tube. The concentration of CO was lower than the detection limit, and the concentration of O<sub>2</sub> was under 20μL/L in the production gas. During the experiment, the crystal structure and the composition of the RMO as a carrier for the Pd catalyst were changed to a manganese oxide Mn<sub>3</sub>O<sub>4</sub>. However, the conversion efficiency from CH<sub>4</sub> to H<sub>2</sub> was maintained constantly at 200mL H<sub>2</sub> /hr g under similar conditions in the both cases of Pd/MnO<sub>2</sub> and Pd/Mn<sub>3</sub>O<sub>4</sub>. In addition, using these manganese oxides as the carrier for the Pd catalyst was effective in inhibiting production of the by-product CO.

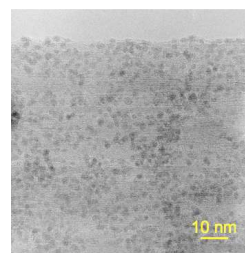


Fig. 1 TEM photograph of the Pd/MnO<sub>2</sub> particle prepared with an effect of water oxidation. Dark: single nano-particles of metallic Pd. Bright: a micro-particle of the MnO<sub>2</sub> (RMO).

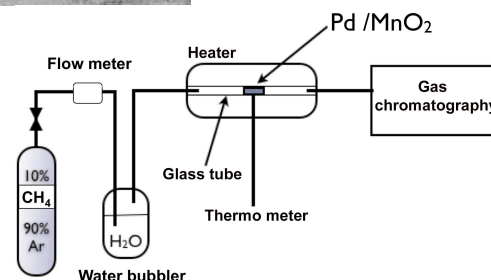


Fig. 2 Schematic illustration of experimental setup. 0.2 g of catalysts (i.e. Pd/MnO<sub>2</sub>, Pd/Mn<sub>3</sub>O<sub>4</sub>) were tested at 300°C. Flow of CH<sub>4</sub> gas balanced with Ar was supplied and maintained at 20mL/min.

### References

- [1] R. Loden, et. al., Catalytic partial oxidation of CH<sub>4</sub> to H<sub>2</sub> over cobalt catalysts at moderate temperatures, *Applied Catalysis A: General*, **333**, 11-23, (2007).
- [2] H. Koyanaka, et. al., PCT/JP2011/064573, Catalysts reforming methane gases into hydrogen and methods for synthesizing the same, and methods for reforming methane gases using said catalysts, Kyoto University 2010/6/28, 2011/6/24.