Development of Advanced Methane-Utilization Technology with Microwave Heating

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Abstract: There are a lot of methane hydrate in the sea near Japan. As a way of the utilization of methane, there has a lot of processes that converting methane into hydrogen. We study the new process "Direct conversion of methane". This process can be obtained the high purity hydrogen and functional carbon. In this study, we evaluated the activity for the other metal species as methane decomposition catalyst, and assessed the electrochemical properties of its carbon.

Keywords: Microwave Heating, Hydrogen, Functional Carbon

1. Introduction

Some researchers found that there are a lot of methane hydrate in the sea near Japan. As a way of the utilization of methane, there has many processes that converting methane into hydrogen. For example, steam reforming of methane is a major process all over the world. This reaction of this process is as follows:

$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H^0 = +206$ [kJ/mol] $\qquad CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H^0 = -41$ [kJ/mol]

The strong point is that the process can produce the large amount of hydrogen per unit time. On the other hands, the weak point is that the process discharges carbon dioxide. Since the gas is disliked because of greenhouse gases, we developed a new process (direct conversion of methane) [1,2]. This reaction of this process is as follows:

$CH_4 \rightarrow C + 2H_2 \qquad \Delta H^0 = +76$ [kJ/mol]

A new process is used microwave and the catalyst (Nickel – Molybdenum Carbide – HZSM-5 as the methane decomposition components and Silicon Carbide as the microwave absorber). The strong point is that the process cannot discharge the carbon dioxide in principle.

The objective of this research is to evaluate the activity for other metal species as methane decomposition catalyst and to assessed the electrochemical properties of its carbon.

2. Experimental

Firstly, we made catalyst and stacked it into the reaction tube (**Figure. 1**). The catalyst preparation was carried out the simple way with physical mixed commercial reagent powder. Nickel (30 wt%), HZSM-5 (38 wt%) and Molybdenum Carbide (2 wt%) have poor absorption for microwave, whereas Silicon Carbide (30 wt%) is an excellent microwave absorber. Secondly, we introduced methane into a reaction tube (methane flow rate = 50 mL・min.$^{-1}$, S.V. = 110.7 hr^{-1}) and examined catalytic activity using by Gas Chromatograph (GC). The reactor is multi-mode type microwave (μReactor Ex, Magnetron) made by Shikoku Instrumentation Co., Ltd. Finally, we analyzed used catalyst by Gas Chromatograph – Mass Spectrometer (GC-MS), X-Ray Diffraction (XRD), Linear Sweep Voltammogram (LSV), Transmission Electron Microscope (TEM) and Raman spectrometer (Raman).

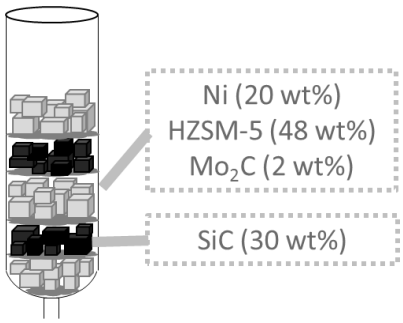

Figure 1. Catalytic packed bed.

3. Results and discussion

3-1. The catalytic Activity for other metal species.

Figure 2 shows nickel was the most excellent catalyst of five metal species. Moreover, copper and niobium hardly converted methane to hydrogen. We found the energy for forming a solid solution of carbonaceous [3] varies in inverse proportion to the hydrogen yield (R^2 = 0.971). Consequently, the generated CH_x originated from CH_4 was taking into metal species, therefore, carbon solid solution nickel was made during the reaction.

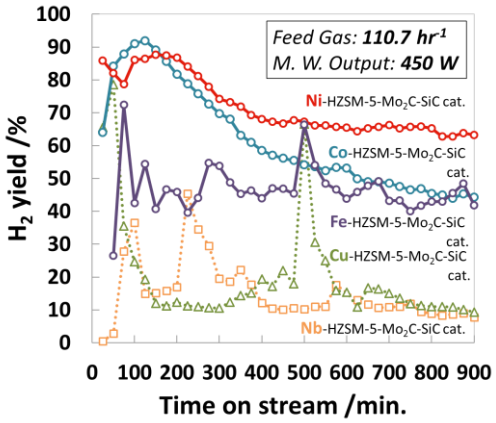

Figure 2. The comparison of metal component for HZSM-5-Mo_2C-SiC catalysts on hydrogen yield plotted against time-on-stream on 450 W (M.W. output), S.V.=110.7 hr^{-1}

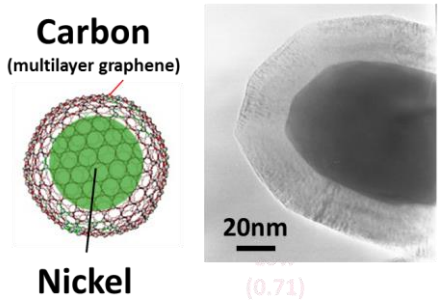

Figure 3. The image measured by TEM of the generated carbon.

Figure. 3 shows the carbon was laminated around the Ni particle. We name this species the "*Metal – Carbon Nano Onion* (*Metal - CNO*)". For that reason, coke deposition hardly occurred over HZSM-5.

3-2. The catalytic activity for Oxygen Reduction Reaction in Porous Microelectrode

We investigated the carbon in non-aqueous solvent, and an Oxygen Reduction Reaction (ORR) at the prepared carbon-based particles treated with acidic solution was evaluated by using a porous microelectrode (PME) based on electrochemical methods [4]. The objective of this section is to evaluate electrochemical characteristic for the "*Metal - CNO*" outside Nickel by Linear Sweep Voltammograms.

As a result, we obtained the linear sweep voltammograms of "*Metal – CNO*" in ORR. According to **Figure 4**, it has the same capabilities at Pt/C electrode. Therefore, we are considering new fuel cell of the application of its electrode.

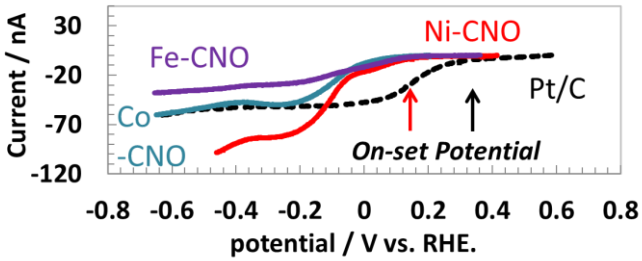

Figure 4. Linear sweep voltammograms of ORR in 0.1 M-Na_2SO_4 saturated with O_2 (Scan rate = 10 mV/sec).

4. Conclusions

Nickel is the most excellent catalyst of five metal species (Ni, Co, Fe, Cu, Nb). Moreover, the energy for forming a solution of carbonaceous varies in inverse proportion to the activity for methane decomposition. In addition, we found that the carbon originated from methane has the activity for ORR.

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