

Reforming of Aqueous Methanol using Double Cylinder Type Reactor

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1. Introduction

Hydrogen is produced by water electrolysis using renewable energy, and is regarded as an ideal energy carrier. Organic hydride is adequate for hydrogen to store, transport and utilize because of its advantages on safety and easiness-to-treat as well as of its effectiveness on energy and cost. Recently, methanol is also considered as a storable and transportable hydrogen carrier by reforming reaction of methanol aqueous solution. Moreover, it is reported that methanol is produced using carbon dioxide. Therefore, hydrogen energy utilization system using reforming reaction of methanol aqueous solution is efficient system from the view point of carbon capture and utilization. In our previous study, nanosized metal particles supported on carbon, immersed with liquid substrate, were heated externally under boiling conditions. Superheated liquid could contact with the catalyst active sites immediately after the evolution of bubbles, into which the reaction products had been enforced to desorb under boiling conditions with sharp temperature gradient. Gaseous hydrogen was disturbed by liquid film to meet the catalyst again. In this study, catalytic reforming reaction of methanol aqueous solution was investigated using Pt/ACC (Activated Carbon Cross) catalyst.

2. Methods

The Pt/ACC (5wt%-Pt) catalyst was prepared by a conventional impregnation method. The BET specific surface area, pore volume, and average pore size of activated carbon cross (ACC) using this study were 2403 m² g⁻¹, 1.027 cm³ g⁻¹, and 1.710 nm, respectively. Potassium tetrachloroplatinate (II) (K₂PtCl₄) was used as precursor, and sodium borohydride was used as reducing agent. The catalytic reforming of methanol aqueous was carried out using double cylinder flow-type reactor. Figure 1 shows the design of double cylinder type reactor. The methanol aqueous solution was supplied to the reactor at room temperature. The substrate has the mole ratio of methanol / water of 1.0. The catalyst and substrate were heated cartridge heater inside the double cylinder reactor. Also, the outside of the reactor was heated using ribbon heater. The flow rate of substrate was operated between 0.2 – 2.0 mL min⁻¹, temperature of reactor was operated 250 , 280 and 350 °C.

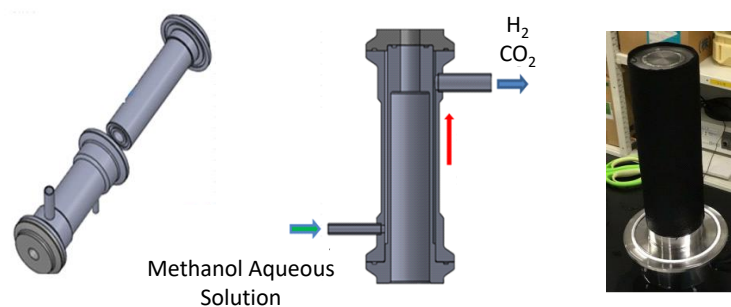


Figure 1. Design of double cylinder type reactor.

3. Results and discussion

Figure 2 shows the effect of flow rate of substrate on generation rate of gas for various temperatures. The rate of generation gas was increased with increasing reaction temperature, and reforming reaction of aqueous methanol was enhanced with increasing temperature.

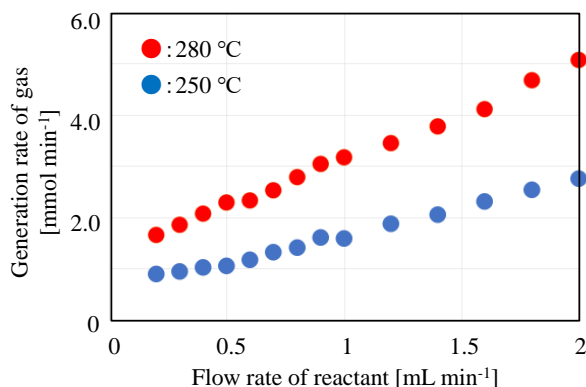


Figure 2. Effect of flow rate of substrate on generation rate of gas.

Figure 3 shows the effect of flow rate of substrate on generation rate of gas at 350 °C. At first, the rate of generation gas was increased with increasing flow rate of substrate. However, it is found that optimal value of flow rate for reforming reaction of aqueous methanol using this reactor exists. Saito *et al.* have proposed superheated liquid-film concept for efficient hydrogen generation process from organic chemical hydrides using batch-wise catalytic reactor^[1]. The reaction rate of hydrogenation was higher in the superheated liquid-film state in comparison to either suspended or sand-bath state. It is considered that the relationships between flow rate of substrate and volume of Pt/ACC catalyst influence the activities of reforming reaction of aqueous methanol in flow-type reactor.

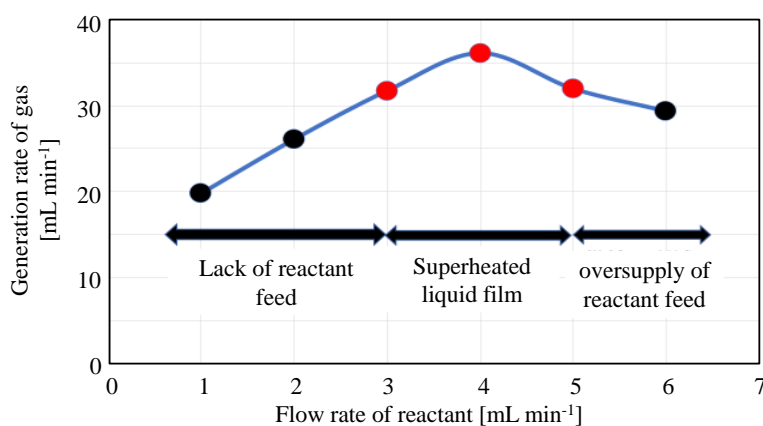


Figure 3. Effect of flow rate of substrate on generation rate of gas at 350 °C.

4. Conclusions

Aqueous solutions of methanol were reformed with carbon-supported metal catalysts rapidly under superheated liquid-film conditions. The role of catalysts, properly-wetted with aqueous methanol, or of heating conditions of nucleate boiling was satisfactorily testified in a specially-designed double-tube flow reactor, equipped with platinum on carbon-cloth support.

References

- [1] Y. Saito, K. Aramaki, S. Hodoshima, M. Saito, A. Shono, J. Kuwano, K. Otake, Chem. Eng. Sci. 63 (2008) 4935-4941