



## Development of membrane reactor for Fischer-Tropsch synthesis using Fe-based catalyst and ZSM-5 membrane

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### Introduction

To achieve carbon neutrality by 2050, it is essential to develop technologies to produce useful chemicals and fuels directly from CO<sub>2</sub>. One method to produce liquid fuels directly from CO<sub>2</sub> is the Fischer-Tropsch (FT) synthesis. This reaction is catalyzed to produce hydrocarbons from H<sub>2</sub> and CO, with Fe and Co as the main catalyst components. Here, since Fe is also active in the reverse water gas shift reaction, it is possible to produce hydrocarbons directly from CO<sub>2</sub> by FT synthesis. However, it is known that in the FT synthesis, a large amount of water produced simultaneously with hydrocarbons reduces the partial pressure of the feedstock and the reaction rate[1]. Since the FT synthesis is a high-temperature, high-pressure reaction, the separation membranes used must be highly durable and hydrophilic. ZSM-5, a type of zeolite, was selected as a membrane material. The objective of this study was to demonstrate the effectiveness of the membrane reactor using Fe-based catalyst and ZSM-5 membrane by introducing the membrane reactor into FT synthesis and comparing it with a conventional reactor.

### Experimental

Two kinds of feedstocks, H<sub>2</sub>/CO and H<sub>2</sub>/CO<sub>2</sub> gas mixtures, were employed for the FT synthesis. The catalysts used were Fe/γ-Al<sub>2</sub>O<sub>3</sub> for H<sub>2</sub>/CO and K-Fe/γ-Al<sub>2</sub>O<sub>3</sub> for H<sub>2</sub>/CO<sub>2</sub>. These catalysts were prepared by precipitation and impregnation methods based on the method of Wan *et al.*[2] Na-ZSM-5 membranes were synthesized on α-Al<sub>2</sub>O<sub>3</sub> tubular support by hydrothermal synthesis. To evaluate the water permselectivity through Na-ZSM-5 membrane under FT synthesis reaction conditions, permeation separation tests were conducted by feeding FT synthesis products to the Na-ZSM-5 membrane under reaction conditions. The fixed-bed reactor in the first stage was filled with 0.2 g of Fe/γ-Al<sub>2</sub>O<sub>3</sub> and Na-ZSM-5 membrane (membrane area 6.28 × 10<sup>-4</sup> m<sup>2</sup>) was introduced into the membrane module in the second stage. A H<sub>2</sub>/CO = 2/1 gas mixture was fed at 20 mL min<sup>-1</sup> at 533 K and 0.9 MPa. Ar was also introduced as sweep gas inside the tubular support at 20 mL min<sup>-1</sup>. The reaction temperature was set at 533 K for H<sub>2</sub>/CO, and at 573 K for the H<sub>2</sub>/CO<sub>2</sub>. Hydrogen reduction of catalyst was performed at 673 K for 10 h before the reaction.

### Results and discussion

To demonstrate the efficacy of membrane reactor, membrane reactor and reference tests were then performed using H<sub>2</sub>/CO at 533 K and 0.9 MPa. The catalyst amount was 0.4 g in the first stage and 0.2 g in the second stage, and the feed flow rate was 20 mL min<sup>-1</sup>. Fig. 1 compares the CO conversion. In the reference test using stainless steel tubes, the average CO conversion was 47.7 % (including 34.0 % conversion to hydrocarbons and 13.7 % to CO<sub>2</sub>). In contrast, in the test using Na-ZSM-5 membranes, the average CO conversion was 59.2 % (including 42.4 % conversion to hydrocarbons and 16.8 % conversion to CO<sub>2</sub>). A remarkable increase of more than 10 % in CO conversion was observed compared to the conventional reactor. Thus, the reaction enhancement effect of the membrane reactor was successfully demonstrated experimentally.

For H<sub>2</sub>/CO<sub>2</sub> feed, a membrane reactor was also tested for FT synthesis. K-Fe/γ-Al<sub>2</sub>O<sub>3</sub> catalyst of 0.6 g was used for both front and back stages, and the feed flow rate was 20 mL min<sup>-1</sup>. Fig. 2 compares the CO<sub>2</sub> conversion for each test. In the reference test, the CO<sub>2</sub> average conversion was 35.8%. In the reference test (including 32.1% conversion to hydrocarbons and 3.7% conversion to CO). In contrast, in the membrane reactor

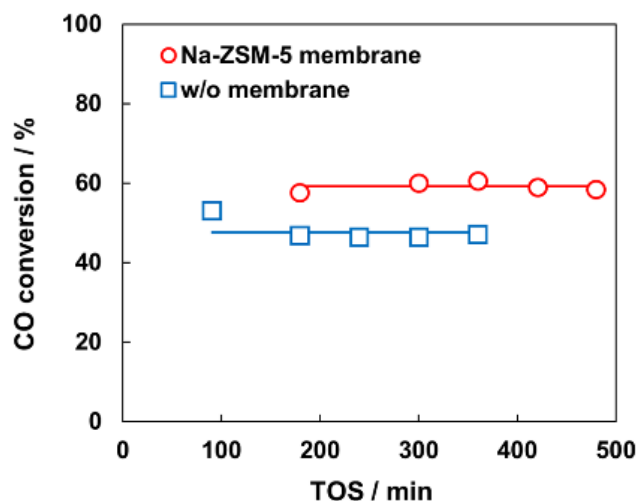


Fig. 1 Comparison of CO conversion with and without Na-ZSM-5 membrane.



test, the CO<sub>2</sub> average conversion was 61.3 % (including 57.9 % conversion to hydrocarbons and 3.4 % conversion to CO), which is an increase of more than 25 % in the CO<sub>2</sub> conversion compared to the conventional reactor. Clearly, the membrane reactor can significantly accelerate the reaction of H<sub>2</sub>/CO<sub>2</sub>.

In order to show the kinetic reaction enhancement effect of the membrane reactor, the activity tests were conducted using only the front-end fixed-bed reactor at 573 K and 0.9 MPa for the H<sub>2</sub>/CO<sub>2</sub> feed with Ar and H<sub>2</sub>O. The Ar fraction in the feed was varied from 0 to 50 % and the H<sub>2</sub>O fraction from 0 to 15 %. Fig. 3(a) shows the CO<sub>2</sub> conversion in the H<sub>2</sub>/CO<sub>2</sub>/Ar feed and Fig. 4(b) shows the CO<sub>2</sub> conversion in the H<sub>2</sub>/CO<sub>2</sub>/H<sub>2</sub>O feed. For the case of using Ar, the CO<sub>2</sub> conversion decreased from 23.6 to 18.2% with increasing Ar fraction. On the other hand, in the case of using H<sub>2</sub>O, the CO<sub>2</sub> conversion decreased significantly from 24.5 to 1.30 % with increasing H<sub>2</sub>O fraction. Comparing the CO<sub>2</sub> conversion for these feed at the same fraction of 10 %, the CO conversion was 22.4 % for the H<sub>2</sub>/CO<sub>2</sub>/Ar feed and 9.46 % for the H<sub>2</sub>/CO<sub>2</sub>/H<sub>2</sub>O feed, suggesting that H<sub>2</sub>O had a greater effect on the reaction rate than the feedstock partial pressure. Without the addition of H<sub>2</sub>O, the conversion recovered to 18.3 % after H<sub>2</sub> reduction of catalyst. It was considered that H<sub>2</sub>O causes a decrease in the reaction rate from both in situ inhibition effect due to competitive adsorption with CO<sub>2</sub> and oxidation of catalyst.

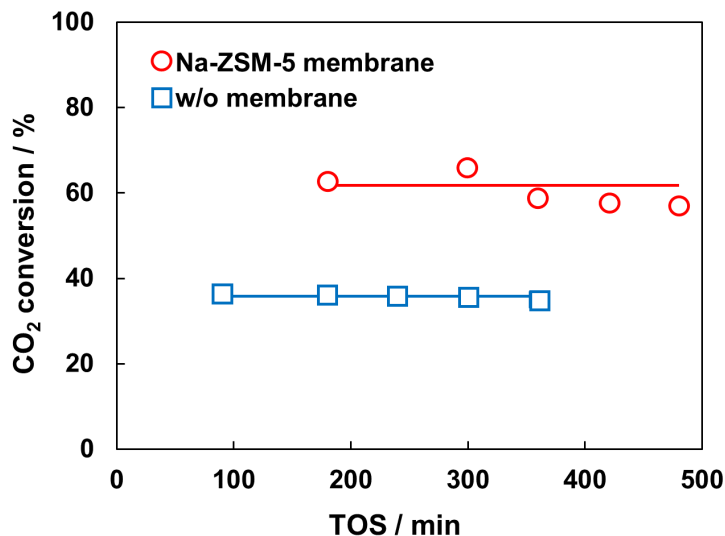


Fig. 2 Comparison of CO<sub>2</sub> conversion with and without Na-ZSM-5 membrane.

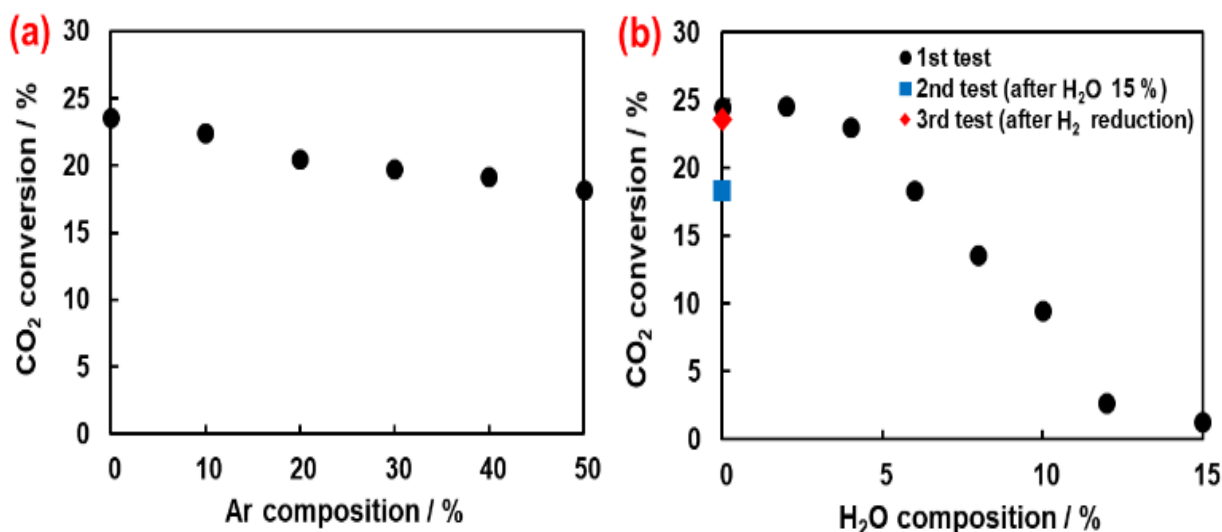


Fig. 3 CO<sub>2</sub> conversion with (a)H<sub>2</sub>/CO<sub>2</sub>/Ar and (b)H<sub>2</sub>/CO<sub>2</sub>/H<sub>2</sub>O.

## References

- [1] M.P. Rohde et al., "Fisher-Tropsch synthesis with in situ H<sub>2</sub>O removal - Directions of membrane development," *Microporous Mesoporous Mater.*, 115 123-136 (2008).
- [2] H. Wan et al, "Promotional effects of Cu and K on precipitated iron-based catalysts for Fischer-Tropsch synthesis. *Mol. Catal. A: Chem.*, 283, 33-42 (2008).