Methanol synthesis by zeolite membrane assisted reactive separation technology

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Abstract: Reactive separation combined with a zeolite membrane was conducted for methanol synthesis using a conventional catalyst. It was confirmed that the reaction thermodynamic equilibrium limitations were broken, resulting in a higher methanol yield in our small-scale pilot plant. The maximum CO conversion to methanol reached over 80% at 503 K and 3 MPaG, which is higher than the equilibrium conversion at the same temperature and 10 MPaG. The membrane performance for the reactive separation of methanol synthesis was stable under practical severe reaction conditions for several hundred hours.

Keywords: methanol synthesis, reactive separation, zeolite membrane

1. Introduction

Methanol synthesis has recently attracted much attention in the following aspects: 1) applicability of various raw materials, 2) fixation of carbon dioxide as chemicals[1].

In the conventional process, methanol synthesis reaction is carried out under high pressure conditions because per pass methanol yield is limited by thermodynamic equilibrium. Hence, the problems such as insufficient conversion rate, large amount of recycled gas, and high construction cost due to the high pressure[2] in the process are inevitable as the result of thermodynamic equilibrium.

To improve the per pass conversion and to lower the reaction pressures, one of the effective solutions is to remove methanol from the equilibrium reaction mixture using a separation membrane[3, 4]. In order to apply a separation membrane to methanol synthesis, it is necessary to develop a pin-hole-free membrane that is durable in the presence of water and methanol vapor at high temperatures and pressures. Durable sealing technology for ceramic membranes is also necessary[5]. Furthermore, designs of membrane reactor and reactive separation system are also important.

We have successfully developed a sealing technology being durable under methanol synthesis conditions, which we will report and discuss elsewhere. In this presentation, we report the durability of our zeolite membrane and the conversion-enhancing effect by reactive separation for methanol synthesis.

2. Experimental

Reactive separation study was carried out with our originally designed membrane reactor, in which a separation membrane was installed. Figure 1-(a) shows a schematic diagram of the membrane reactor, Figure 1-(b) shows the zeolite membrane set on the reactor flange, and Figure 1-(c) shows the appearance of our small-scale pilot plant.

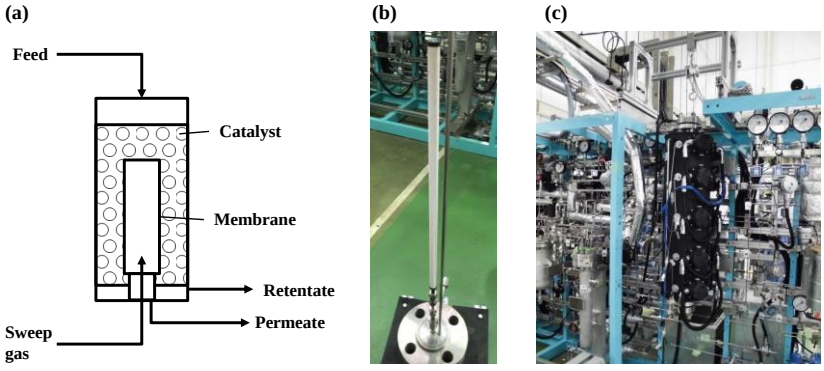

Figure 1. (a) Schematic diagram of the membrane reactor. (b) Zeolite membrane set on the flange. (c) Small-scale pilot plant.

Reactive separation tests were typically conducted at 503 K and 3 MPaG. The internal pressure of the membrane was 0.1 MPaG. The mixture of H_2/CO was supplied with a typical composition of 2/1 (molar ratio). The feed gas containing CO_2 was also tested. The performance of the reactive separation was calculated based on the analysis of both permeate and retentate gases.

3. Results and discussions

Demonstration of the reactive separation was successful by using our originally designed membrane reactor with the zeolite membrane installed. The conversion of CO reached over 80% at 503 K and 3 MPaG, whereas the thermodynamic equilibrium conversion is 54%. To obtain the conversion over 80% under an equilibrium condition, 10 MPaG is necessary at 503 K. We also confirmed that the reactive separation can be applied to the methanol synthesis from H_2/CO_2 and that the conversion of CO_2 was significantly improved beyond the equilibrium conversion, although a certain amount of water was formed as a by-product. From these results, it was confirmed that the membrane reactor and the reactive separation system worked as we designed.

Figure 2 shows the result of the life test. During the life test for 500 h, the conversion stably exceeded the equilibrium conversion rate. It means that the performance of the zeolite membrane was stable in the presence of water and methanol vapor at a high temperature and pressure for 500 h.

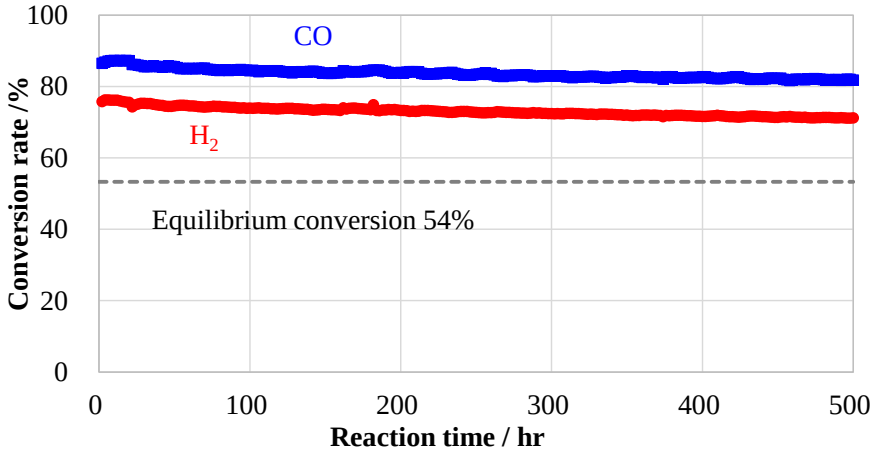

Figure 2. H_2 and CO conversion in the small scale pilot reactive separation process for methanol synthesis. Conditions: Temperature, 503 K; Pressure, 3 MPaG (outside the membrane) and 0.1 MPaG (inside the membrane); Feed gas, H_2/CO = 2/1; catalyst, Cu-ZnO-Al_2O_3; W/F, 597 kg h/kmol; A/V, 18 m^{-1}.

4. Conclusions

Reactive separation tests were conducted for methanol synthesis using a zeolite membrane. It was confirmed that the conversion of CO was improved over the thermodynamic equilibrium. The zeolite membrane showed almost stable performance for 500 h. In addition, it was also confirmed that the reactive separation system could be applied to CO_2 hydrogenation for methanol synthesis, although there formed a certain amount of water vapor as a by-product.

Acknowledgements

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