Direct conversion of methane into methanol over Cu-CHA

Sae Ha Lee[a] , Sung June Cho[b], Eun Duck Park[a]*

[a]*Department of Chemical Engineering and Department of Energy Systems Research, Ajou University, Suwon, 16499, Republic of Korea*

[b]*Department of Applied Chemical Engineering and the Research Institute for Catalysis, Chonnam National University Buk-gu, Gwang-ju Korea*

**E-mail: edpark@ajou.ac.kr*

Abstract: The copper ion-exchanged chabazite (CHA) was investigated to convert methane directly into methanol. Compared with the previous works in which a high-temperature treatment step with air or an inert gas is required to produce methanol by using water as an extracting agent and/or oxidant in a cyclic process, we could remove the activation step to remove moisture and further produce methanol continuously from methane and water in the continuous process.

Keywords: Methane, Methanol, Cu-CHA, Continuous process

1. Introduction

Methane is a major component in the natural gas and its valorization as a chemical feedstock has recently attracted much attention because its production rate has increased due to the development of shale gas. Until now, all the commercial chemical transformations of methane are carried out indirectly via synthesis gas, a mixture of CO and H_2, which requires lots of energy. Therefore, the direct conversion of methane has been sought to overcome the disadvantage of the indirect process in different ways [1, 2]. One of the proposed methods is the conversion of methane into methanol using metal-containing zeolites, inspired by the methane monooxygenase system in nature [3, 4]. Theoretically the C-H bond in methane can be activated even at low temperatures, but its dissociation energy is too large to stabilize the reaction intermediates such as methanol and formaldehyde resulting in low their yields. In the previous works, copper ion-exchanged zeolites have been reported to be active for direct conversion of methane into methanol through a number of step processes in which formation of catalytically active species, methoxy species formation, and its extraction with water [5-7]. However, this discontinuous step process is problematic from the practical viewpoint. In this work, we applied the Cu-SSZ-13 catalyst to convert methane into methanol directly and realized the concept on the continuous process to produce methanol from methane and steam.

2. Experimental

0.3 g of Cu-SSZ-13 was charged into the fixed-bed tubular reactor. After oxidation by air at 400 ℃, high-purity methane gas was fed into the reactor for 30 min at a flow rate of 30 mL/min under 1 bar. Methanol was obtained by contacting the catalyst with a mixture gas of 90 mol% steam and 10 mol% helium at a flow rate of 460 mL/min for 2 h. The methanol produced was collected in a condenser at -10 ℃ at the bottom of the reactor. The methanol concentration was determined using gas chromatograph equipped with flame ionization detector. All these cycles were repeated to obtain the steady-state methanol yield.

Separately, a continuous process was realized in which high-purity methane gas containing saturated water vapor at 20 ℃ was fed into the reactor with a flow rate of 30 mL/min. The methanol concentration was determined with mass spectroscopy.

3. Results and discussion

In the cyclic experiments, the effect of reaction temperature with methane on the methanol yield was examined. It is remarkable that the methanol yield is very critically dependent on the reaction temperature. The methanol yield increases with increasing reaction temperature and reached the ceiling value at above

350 ℃ (Fig. 1(A)). On the other hand, there is no noticeable difference in the methanol yield according to the activation gas at 400 ℃. A similar methanol yield was obtained even methane was used as an activation gas instead of air (Fig. 1(B)). This implies that the activation step is not necessary for this cyclic process. Methane and steam can be contacted with the catalyst alternatively to produce methanol. To simplify the process further, a continuous process in which methane and steam are fed into the reactor at the same time to produce methanol was proposed. The effect of the reaction temperature was also examined. As shown in Fig. 1(C), the production rate of methanol is strongly dependent on the reaction temperature. The methanol production rate increases with the reaction temperature, reaches the maximum value at 350 ℃, and then decreases with further increasing the reaction temperature.

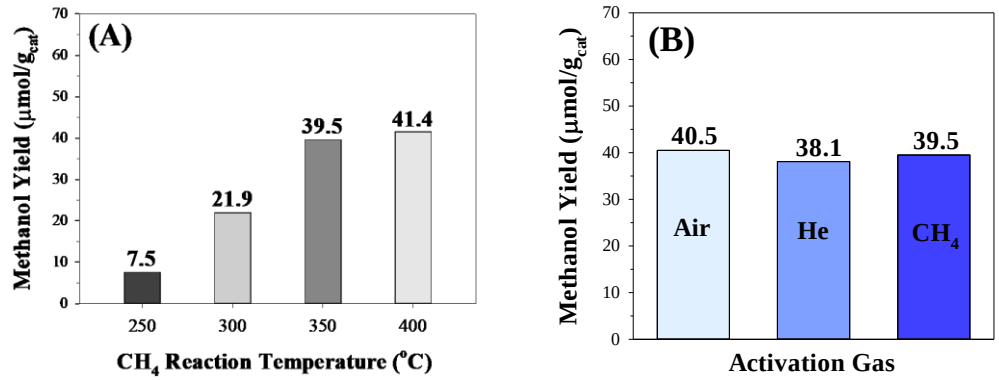

Figure 1. Methanol yields in the cyclic process ((A) and (B)).

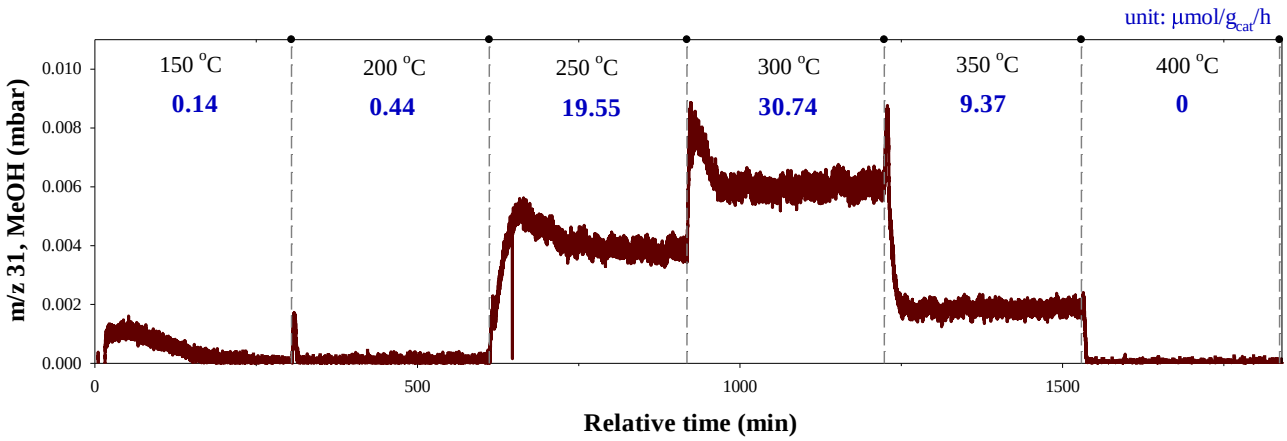

Figure 2. Mass spectra as a function of reaction time during methane conversion in the continuous process.

4. Conclusions

In the cyclic process to produce methanol from methane over Cu-SSZ-13, the methanol yield increases with the reaction temperature with methane and reaches the ceiling value at above 350 ℃. However, oxygen does not appear to be necessary to activate this catalyst. The continuous production of methanol can proceed over this catalyst using methane and steam, which is also strongly affected by the reaction temperature. The maximum methanol production rate was observed at 350 ℃.

References

1. E.G. Nisbet, E.J. Dlugokencky, P. Bousquet, Science 343 (2014) 493.
2. K. Aasberg-Petersen, I. Dybkjær, C.V. Ovesen, N.C. Schjødt, J. Sehested, S.G. Thomsen, J. Nat. Gas Sci. Eng. 3 (2011) 423.
3. L. Que, W.B. Tolman, Nature 455 (2008) 333.
4. R. Balasubramanian, S.M. Smith, S. Rawat, L.A. Yatsunyk, T.L. Stemmler, A.C. Rosenzweig, Nature 465 (2010) 115.
5. B. Ipek, R.F. Lobo, Chem. Commun. 52 (2016) 13401.
6. K. Narsimhan, K. Iyoki, K. Dinh, Y. Román-Leshkov, ACS Cent. Sci. 2 (2016) 424.
7. D.K. Pappas, E. Borfecchia, M. Dyballa, I.A. Pankin, K.A. Lomachenko, A. Martini, M. Signorile, S. Teketel, B. Arstad, G. Berlier, C. Lamberti, S. Bordiga, U. Olsbye, K.P. Lillerud, S. Svelle, P. Beato, J. Am. Chem. Soc. 13 (2017) 14961.