

# Dehydrogenative Conversion of Methane to Higher Hydrocarbons by the Liquid-Metal Indium Catalyst

Yuta Nishikawa<sup>1</sup>, Hitoshi Ogihara<sup>1</sup>, Ichiro Yamanaka<sup>1</sup>

<sup>1</sup> Department of Chemical Science and Engineering, School of Materials and Chemical Technology, Tokyo Institute of Technology, Tokyo, Japan.

\*E-mail: yamanaka.i.aa@m.titech.ac.jp

CH<sub>4</sub> is an abundant energy source in the earth. Most of CH<sub>4</sub> is currently used for combustion to generate electric power and heat because we do not have a chemical utilization technology of CH<sub>4</sub> except for the steam reforming to syngas. This industrial process needs large amount of energy and costs due to a multi-step process. Therefore, the direct conversion of CH<sub>4</sub> to chemicals and a liquid fuel is a promising route for effective utilization of natural gas. However, it is a challenging reaction because of the low reactivity of CH<sub>4</sub>. In dehydrogenative aromatization of CH<sub>4</sub>, Mo/zeolite catalysts have been studied since Wang et al. reported<sup>[1]</sup>, but the deactivation of the catalyst by coke deposition is the key issue to improve the catalytic activity. Recently, Guo et al. reported that single Fe sites in a silica matrix catalyzed conversion of CH<sub>4</sub> to ethylene, benzene and naphthalene without coke deposition at high temperature (> 1223 K)<sup>[2]</sup>. We also reported that the In/SiO<sub>2</sub> catalyst could convert CH<sub>4</sub> into ethylene, propylene and benzene<sup>[3, 4]</sup>. In this study, we will report that the catalyst reactivity and reaction mechanism of dehydrogenative conversion of CH<sub>4</sub> (DCM reaction) by the In/SiO<sub>2</sub> catalyst.

10 wt% SiO<sub>2</sub>-supported metal catalysts (10 wt% M/SiO<sub>2</sub>) were prepared by an impregnation method. The precursors were dried at 393 K and calcined at 773 K in air. Subsequently, the catalyst precursors were reduced with H<sub>2</sub> at 873 K. M/SiO<sub>2</sub> (100 mg) was set in a fixed-bed quartz reactor (I.D. 12 mm) and CH<sub>4</sub> (1 atm, 10 mL min<sup>-1</sup>) was introduced into the reactor at 1173 K. Hydrocarbons and H<sub>2</sub> were analyzed by gas chromatograph.

Fig. 1 shows (a) yields of hydrocarbons and (b) CH<sub>4</sub> conversion in the DCM reaction using 10 wt% M/SiO<sub>2</sub> catalysts at 1173 K. Ga, In and Bi showed good catalytic activity for the DCM reaction. In particular, the In/SiO<sub>2</sub> catalyst was the highest activity among the M/SiO<sub>2</sub> catalysts. In/SiO<sub>2</sub> showed that CH<sub>4</sub> conversion was almost 5 % and a sum of selectivity to hydrocarbons was approximately 75 %. The main products were ethane, ethylene, propylene, benzene, toluene and naphthalene. Selectivity to coke deposition was 25 %. Transition metals such as Ni showed high CH<sub>4</sub> conversion, but the major product was carbon. The melting and boiling points of metallic indium are 430 K and 2345 K. Thus, liquid indium catalyzed the DCM reaction. We will describe kinetic studies for the DCM reaction and the unique catalysis of indium in the presentation.

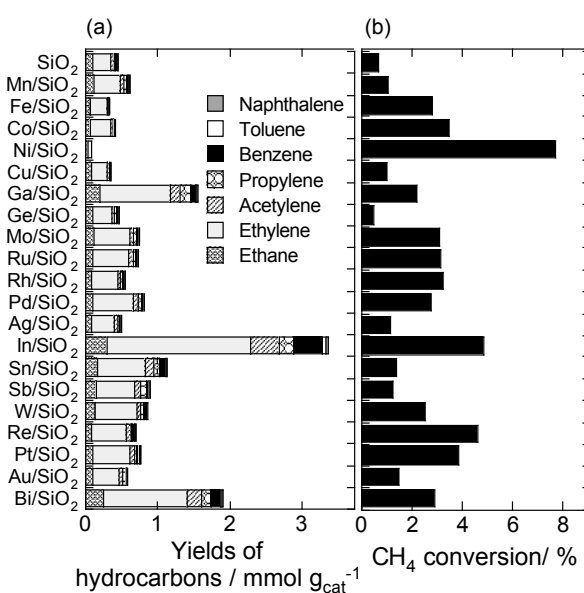


Fig.1 (a) Yields of hydrocarbons and (b) CH<sub>4</sub> conversion in the DCM reaction for 1 h over 10 wt% M/SiO<sub>2</sub> at 1173 K.

## REFERENCES

- [1] L. Wang, L. Tao, M. Xie, G. Xu, J. Huang, Y. Xu, *Catal. Lett.*, 21 (1993) 35.
- [2] X. Guo, G. Fang, G. Li, H. Ma, H. Fan, L. Yu, C. Ma, X. Wu, D. Deng, M. Wei, D. Tan, R. Si, S. Zhang, J. Li, L. Sun, Z. Tang, X. Pan, X. Bao, *Science*, 344 (2014) 616.
- [3] Y. Nishikawa, H. Ogihara, I. Yamanaka, The 116<sup>th</sup> Catal. Symp., Mie, 16-18 Sept. 2015, 1E13.
- [4] Y. Nishikawa, H. Ogihara, I. Yamanaka, The 16<sup>th</sup> ICC, Beijing, 3-8 Jul. 2016, PC074.