Nickel phosphide catalyst for direct dehydrogenative conversion of methane to higher hydrocarbons

<u>Arnoldus Dipu</u>,[a] **Shunya Obuchi,**[a] **Yuta Nishikawa,**[a] **Hitoshi Ogihara,**[b] **Ichiro Yamanaka**[a]*
[a]*Department of Chemical Science and Engineering,Tokyo Institute of Technology, Tokyo , 152-8552, Japan*
[b]*Department of Applied Chemistry, Saitama University, Saitama, 338-8570, Japan*
**Corresponding author: (+81)3-5734-2144, yamanaka.i.aa@m.titech.ac.jp*

Abstract: Various silica supported Ni-Metal catalysts were tested for direct dehydrogenative conversion of methane to higher hydrocarbons (DCM reaction). Products were ethane, ethylene, acetylene, propylene, benzene, toluene and naphthalene. Compared to other Ni-Metal/SiO_2 catalysts, Ni-P/SiO_2 showed higher yields and selectivity to hydrocarbons. Apparent activation energy for CH_4 conversion of 132 kJ/mol on Ni-P/SiO_2 was lower than that of 322 kJ/mol on SiO_2. The Ni-P/SiO_2 catalyst effectively activated a C-H bond of CH_4 and converted to products.

Keywords: Methane, Hydrocarbons, Nickel phosphide.

1. Introduction

Discovery of large natural gas reserve recently has drawn attention for its utilization. Methane which is the main component of natural gas has drawbacks of storage and transportation. Therefore majority of methane is used for power generation and industrial heat source. There have been attempts to convert methane to liquid fuels through multistep processes. However, the process suffers from high energy cost. It is therefore important to develop innovative catalyst for direct conversion of methane to liquid fuels or useful chemicals[1,2]. In this work, we reveal the catalytic activity of silica supported nickel phosphide catalyst for direct dehydrogenative conversion of methane to higher hydrocarbons (DCM reaction).

2. Experimental

Ni-Metal/SiO_2 materials were prepared by a conventional impregnation method. Ni salt and various metal (M) salts of Re, Pd, Fe, Mn, Co, B, Rh, Cs, Pt, Zn, Sb, Cu, Sn, Ag, Ga, Bi, P were dissolved in solvents. The solution was then impregnated on silica. The final mole ratio of Ni/M was 1:1 mol/mol. DCM reaction was performed in a fixed-bed-gas flow system. Pure methane (1.0 atm, 10 mL min^{-1}) was flowed at 1123 K. Products were analyzed using gas chromatographs equipped with thermal conductivity detector and flame ionization detector.

3. Results and discussion

Catalytic activity of various Ni-M/SiO_2 compounds was screened using a fixed-bed-gas flow system. Yields and total selectivity to hydrocarbons are shown in Figure 1a and 1b.

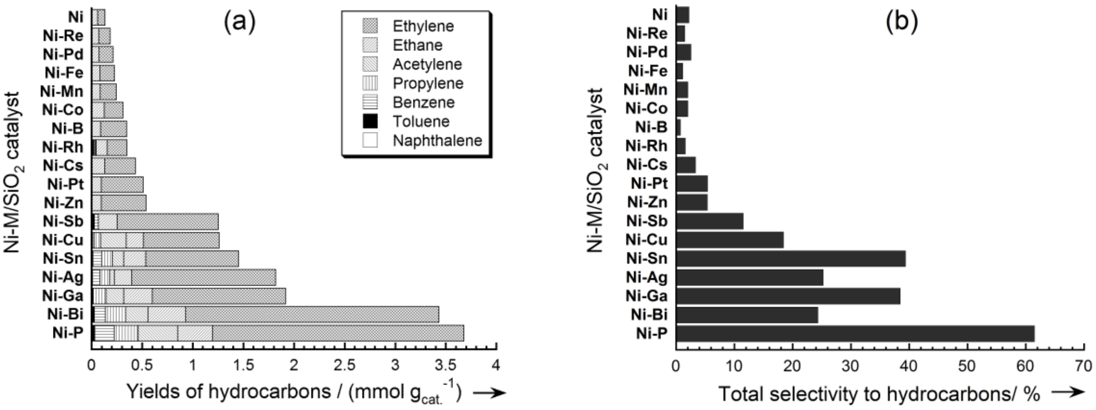

Figure 1. (a) Yields of hydrocarbons and (b) total selectivity to hydrocarbons over Ni-M/SiO_2 for 1.5 h.

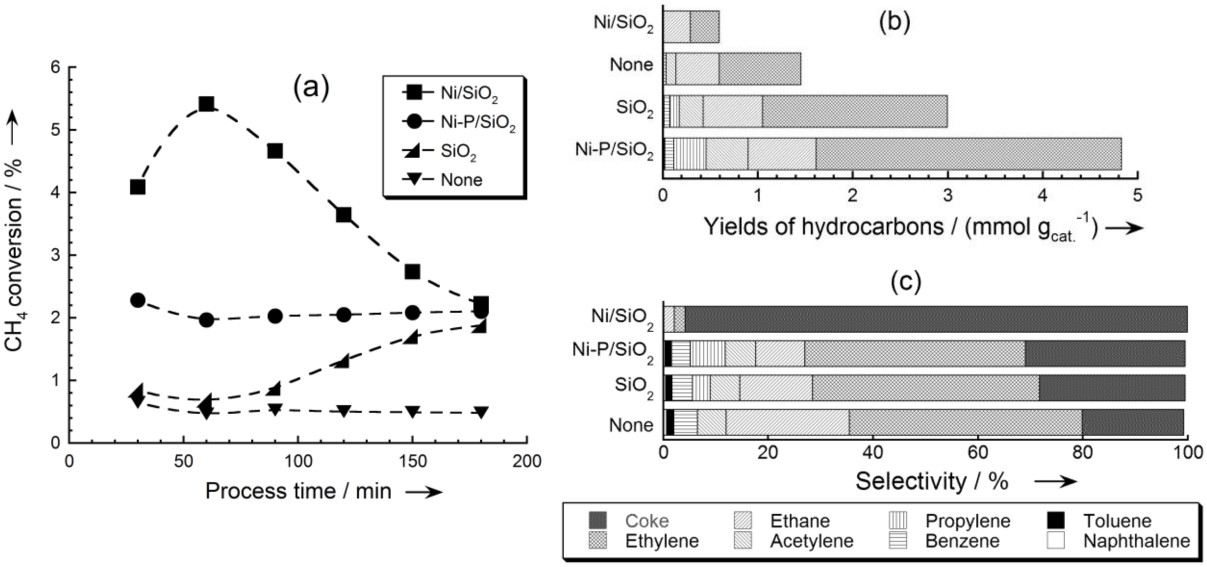

Figure 2. Time course of (a) methane conversion, (b) yields of hydrocarbons and (c) selectivity to hydrocarbons for DCM reaction over SiO$_2$, Ni/SiO$_2$, Ni-P/SiO$_2$.

Ni-P/SiO$_2$ catalyst showed high yields of hydrocarbons of 3.7 mmol g$_{cat}^{-1}$ (Figure 1a) and a highest selectivity to hydrocarbons of 61 % (Figure 1b) among catalysts tested in this work. Ni-Bi/SiO$_2$ catalyst showed a good performance, a higher yield of hydrocarbons, though a lower selectivity. Based on the results, we then focused our study on catalysis of Ni-P/SiO$_2$.

Figure 2 shows (a) time course of methane conversion, (b) yield to hydrocarbon and (c) selectivity to hydrocarbons for DCM reaction over SiO$_2$, Ni/SiO$_2$, Ni-P/SiO$_2$ and without catalyst (none). Methane conversions over Ni-P/SiO$_2$ were stable for 3 h at around 2.0 % as shown in Figure 2a. In Ni/SiO$_2$ catalyst, the highest conversion of 5.4% at 1 h was obtained and the conversion drastically decreased. A large amount of carbon deposition was observed on the Ni/SiO$_2$ catalyst in Figure 2b and c. The serious carbon deposition deactivated the Ni/SiO$_2$ catalyst. In SiO$_2$ catalyst, the conversion gradually increased after 1 h. This increase may be caused by deposited carbon on the surface of SiO$_2$. Previously several researchers had reported the catalysis of activated carbon surface for the DCM reaction[3,4]. A good yield and selectivity to hydrocarbons were observed by using SiO$_2$ in Figure 2b and c.

From Figure 2b and c, Ni-P/SiO$_2$ had the highest yield of hydrocarbons even its selectivity was slightly lower compared to that of SiO$_2$. Effects of reaction temperatures from 1073 K to 1142 K on the DCM reaction by Ni-P/SiO$_2$ and SiO$_2$ were studied. Apparent activation energy for the conversion rate of methane was 123 kJ mol^{-1} on Ni-P/SiO$_2$ and 322 kJ mol^{-1} on SiO$_2$. A C-H bond energy of CH$_4$ is 440 kJ/mol. These facts clearly indicated that the Ni-P/SiO$_2$ catalyst effectively activated a C-H bond of CH$_4$ and promoted the formation of hydrocarbons. We will discuss catalysis of Ni-P/SiO$_2$ and reaction mechanism of the DCM reaction in detail.

4. Conclusions

Ni-P/SiO$_2$ showed higher yields and selectivity to hydrocarbons compared to other Ni-M/SiO$_2$ catalysts. Ni/SiO$_2$ catalyst decomposed methane to carbon and hydrogen. Catalysis of Ni for the conversion of methane drastically changed by the addition of P.

References

1. 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.
2. Y. Nishikawa, H. Ogihara, I. Yamanaka, ChemistrySelect 2(16) (2017) 4572.
3. I. Mochida, Y. Aoyagi, H. Fujitsu, Chem. Lett. (1990) 1525.
4. H. Yagita, A. Ogata, A. Ohbuchi, K. Mizuno, T. Maeda, K. Fujimoto, Catal. Today 29 (1996) 433.