

# Synthesis of Lower Olefins from Synthesis Gas over Active Carbon-Supported Iron Catalyst

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Lower olefins (C<sub>2</sub>-C<sub>6</sub>) are important basic chemicals as raw materials of plastics and packaging materials, and the demand of these compounds will increase further. To produce them from other resources than petroleum, a number of studies have been made over modified Fischer-Tropsch Synthesis (FTS) catalysts, which are mainly Fe-based ones [1]. The present authors have found that an iron catalyst promoted with a small amount of copper and potassium supported on active carbon (Fe-Cu-K/AC) is active for FT synthesis, and high selectivity of olefins are obtained [2,3]. In the present work, catalyst modification by metal addition was performed and effect of H<sub>2</sub>/CO ratio in the feed gas was examined for the selective synthesis of lower olefins from syngas.

Supported iron catalysts were prepared by co-precipitation with aqueous solutions [1]. Metal additives were introduced by simultaneous co-precipitation. FTS reaction runs were conducted with a flow type fixed bed apparatus under pressure. Catalysts were reduced with syngas (H<sub>2</sub>/CO = 1) at 300°C for 2 h under atmospheric pressure. The standard reaction conditions were temperature, 300°C; pressure, 2.0 MPa-G; W/F, 4.1 g h mol<sup>-1</sup>; H<sub>2</sub>/CO = 1. All the products were analyzed with GC-TCD and GC-FID on line.

Figure 1 shows the hydrocarbon distribution obtained over metal added catalysts. All the metal additives enhanced the lower olefin selectivity, and the most effective one was manganese. The selectivity to the lower olefins increased from 25% without additive to 33% with Mn. Figure 2 shows effect of H<sub>2</sub>/CO ratio in the feed gas on hydrocarbon distribution. When the ratio was increased over unpromoted catalyst, lower

olefin selectivity decreased, and selectivity to paraffins, especially methane, increased largely. In contrast, the lower olefin selectivity increased with increasing the ratio to reach about 40% at H<sub>2</sub>/CO = 4. Also, hydrocarbon yield increased from 55% to 84%, and thus the lower olefin yield reached to 34%. Although selectivity to the lower paraffins was also increased, it was no less than about 20% at the ratio. From XRD, SEM, and EPMA studies, it is suggested that hydrogenation ability to olefins of Fe species in the Mn-promoted catalyst should be reduced, and thus the olefin selectivity was enhanced. It may also be possible that the surface concentration of CO becomes higher by Mn which can adsorb CO, and the hydrogen concentration is reduced.

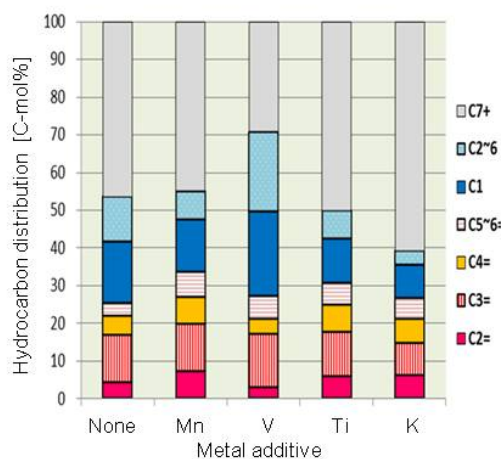


Fig. 1 Effect of Metal Additives.

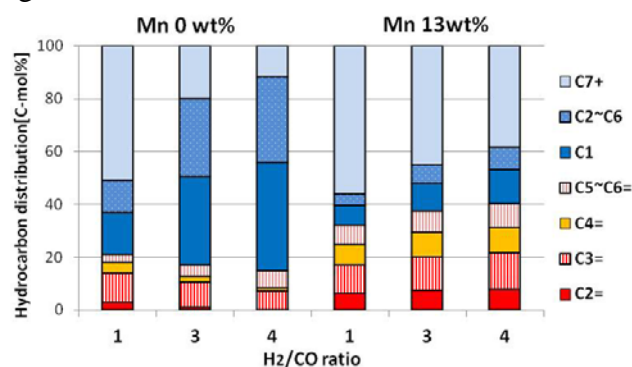


Fig. 2 Effect of H<sub>2</sub>/CO ratio.

## REFERENCES

- [1] H.M.T. Galvis and K.P. de Jong, ACS Catal., 3 (2013) 2130.
- [2] K. Asami, A. Iwasa, N. Igarashi, S. Takemiya, K. Yamamoto, K. Fujimoto, Catal. Today, 215 (2013) 80.
- [3] Y. Kawahara, K. Komiyama, K. Asami, J. Jpn. Petrol. Inst., 60 (2017) 95.