Temperature effect on the selectivity for C3 and C4 Olefins in Fischer-Tropsch synthesis with a Ru catalyst

Takashiro Muroi[a*], Hiromasa Fujii[a], Atsushi Watanabe[a], Chuichi Watanabe[a]

[a] Frontier Laboratories; Koriyama, Fukushima, 963-8014, Japan

[*] 024-935-5100, muroi@frontier-lab.com

Abstract: Effect of the reaction temperature on Fischer-Tropsch synthesis (FTS) using Ru/Al_2O_3 catalyst was examined to obtain selectivity for C3 and C4 olefins which are valuable compounds as petrochemical feedstocks. FTS was carried out by using a micro-reactor coupled with GC/MS by varying the temperature from 180 ºC to 320 ºC . Maximum C3' and C4' yields show 240 ºC and 250 ºC respectively. The low hydrogen mole ratio gives high olefin selectivity.

Keywords: Fischer-Tropsch synthesis, propylene, butane, Ru catalyst, micro reactor, Reaction temperature

1. Introduction

FTS was developed in 1920s to produce transportation fuel using coal gas. Since natural gas reserves are higher than oil reserves and lower price than oil, the large plants have been constructed in natural gas countries. Other hand light olefins such as propylene and butene are desired as raw material in chemical industry. We have studied to get higher C3 and C4 olefins yield at different reaction temperature and hydrogen mole ratio on FTS using Ru/Al_2O_3 catalyst by using a micro-reactor coupled with GC/MS. to obtain selectivity for C3 and C4 olefins.

2. Experimental

A micro-reactor (Single µ-Reactor; Rx-3050SR, Frontier Laboratories Ltd., Japan) was coupled with GC/MS as shown in Figure 1. A mixed gas of hydrogen with carbon-monoxide (H_2/CO) was fed into the micro-reactor (flow rate = 9 mL/min) containing a catalyst bed (3 mm i.d. × 15 mm length) where Ru catalyst (5%Ru/Al_2O_3, 90 mg, 50 µm in size, N. E. Chemcat corp.) was loaded. Catalytically converted gases flowed from the reactor to a GC inlet and diluted by a He flow (51 mL/min). The split ratio was (59/1) and a fraction (1 mL/min) was introduced into either a deactivated evolved gas analysis (EGA) tube, (0.15 mm i.d., 2.5m) tube for real-time monitoring or a GC column for separation analysis.

In real-time monitoring, reaction temperature was increased from 100ºC to 400ºC at a rate of 10 ºC/min, and reaction products were detected continuously by MS via EGA tube which was kept at 300ºC to prevent condensation of products with a high boiling point.

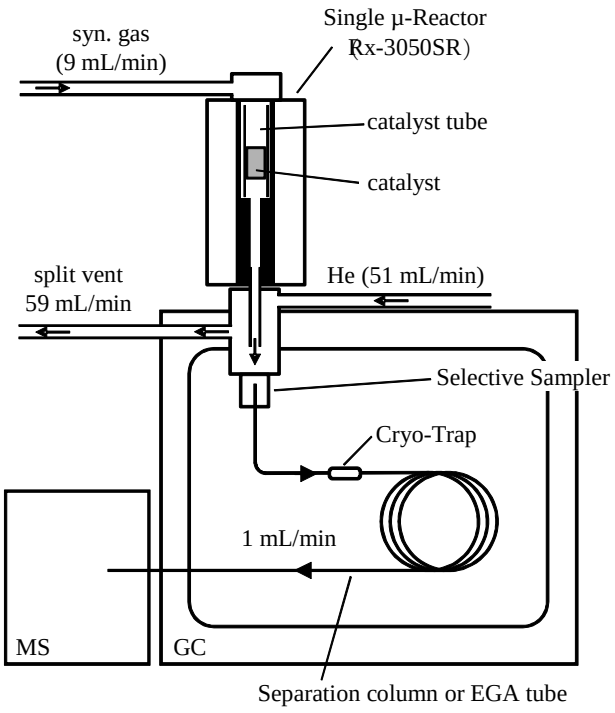

Figure 1. Schematic illustration of instrument used in this study consisted of micro reactor and GC/MS.

Separation analysis was done to examine the distribution of hydrocarbons obtained by varying the reaction temperature from 180ºC to 320ºC by a 10ºC step. Reaction products at each temperature were collected for 1 min by using a flow switching device (Selective Sampler, SS-1010E, Frontier Laboratories

Ltd.) and the collected products were once trapped by putting a former part of a column into a liquid nitrogen at -196ºC before separation analysis, then swept into the GC separation column, followed by GC/MS analysis.

3. Results and discussion

The results obtained by real-time monitoring, it is clear that C3 and C4 are produced in the temperature range from 180ºC to 320ºC. Since the obtained data was peak area of MS, propylene (*m/z*=42), propane (*m/z*=44), butene (*m/z*=43), butane (*m/z*=41), to determine the yield is calculated with propylene standard gas and mass fragment ratio information of NIST library. The data shows C3, C4 yield wt% to the feeds at $H_2/CO=2$. (Fig.2)

The highest peak area of propylene shows at 240 ºC, y ield is 5.5%. The highest peak area of butene (1-butene, trans-2-butene, cis-2 butene) shows 8.5% yield at 250 ºC. The highest yield of propane is 8.8% at 270 ºC. The highest yield of butane shows 5.4% at 260 ºC. We have got 5% of C3' and 7.5% of C3, 8.5% of C4' and 5% 0f C4 , total C3+C4 is 26% at 250 ºC. Ru catalyst gives higher C3-C4 at 240-260 ºC. For the reference, the Fe catalyst needs 330-350 ºC to get C2-C4 [1], C3' and C4' olefins can be produced lower than 250 ºC. The phenomenon proofs FT synthesis is proceeded chain reaction of carbene ligand and hydrogenation.

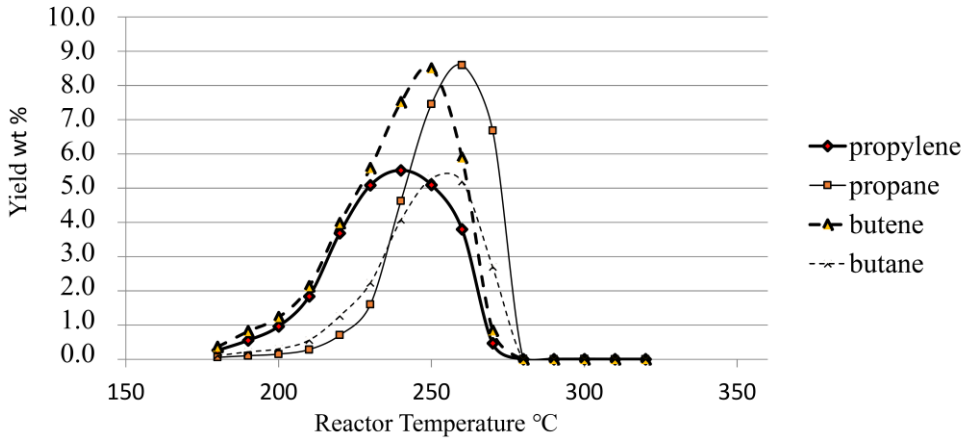

Figure 2 C3, C4 Yield at Reactor Temperature

Next, we examined the selectivity of C3' and C4' using different H_2/CO mole ratio at the same reaction condition. As shown in Table-1, C3', C4' could not find at 3.5 of H_2/CO, all of them were hydrogenated. At 1.25 of H_2/CO gives C3'/C3 is 3.6 and C4'/C4 is 2.3. In case of 0.8 of H_2/CO gives almost olefins, however we find the catalyst activity is declined at short time because of carbon deposition.

These data suggest that the control of temperature and hydrogen mole ratio, and the control of hydrogenation activity of catalyst gives more olefins yield.

Table-1 Olefins yield at different Hydrogen mol ratio

H_2/CO mol ratio	C3'/C3	C4'/C4
3.5	0.0	0.0
2.0	2.6	1.8
1.25	3.6	2.3
0.8	13.8	6.2

References

1) Jager, B., AlChE Meeting, New Orleans March 31 to April 4, 2003