

FISCHER-TROPSCH SYNTHESIS IN SUPERCRITICAL PROPANE

D. B. Bukur^{1*} and X. Lang²

¹*Texas A&M University at Qatar
Chemical Engineering Program
P.O. Box 23874
Doha, Qatar*

²*Department of Chemical Engineering
Texas A&M University
College Station, TX 77843-3122
U.S.A.*

dragomir.bukur@qatar.tamu.edu Fax: (974) 423-0011

The objective of this study is to determine effects of co-feeding a 1-olefin on activity and selectivity of an iron Fischer-Tropsch catalyst (Ruhchemie LP 33/81 with nominal composition 100 Fe/5 Cu/4.2 K/25 SiO₂ in parts by weight) during both conventional Fischer-Tropsch synthesis (FTS) and FTS under supercritical conditions. We used propane as the supercritical fluid and 1-dodecene (1-C₁₂H₂₄) in this test. Motivation for this study was the work of Fujimoto and co-workers¹ who reported that suppression of methane and enhancement of high molecular weight hydrocarbons selectivities occurs with co-feeding of 1-olefins (1-heptene, 1-tetradecene, or 1-hexadecene) during supercritical FTS (SFTS), but not during the conventional FTS (silica supported Co in supercritical n-pentane).

Table 1 summarizes process conditions for run FA-1075. In period 1, the reaction was conducted at the baseline conditions (conventional FTS). In period 2, 1-dodecene was introduced at a feed rate of 1.67 cm³/h, which corresponds to 4 mol% of CO feed rate, while maintaining the synthesis gas flow rate, reaction temperature and pressure at baseline values (conventional FTS with co-feeding of 1-dodecene). In period 3, the feed rates of synthesis gas and 1-dodecene were maintained at the same values as in period 2, while propane was introduced at total system pressure of 5.5 MPa (SFTS with co-feeding of 1-dodecene). In period 4, the flow of 1-dodecene was terminated, while other conditions were the same as in period 3 (SFTS in propane at 5.5 MPa). In period 5, FTS was carried out at the baseline conditions to check for changes in activity and selectivity relative to the initial period 1.

Table 1. Experimental Conditions for Run FA-1075^a.

Period	Time on Stream (h)	Total Pressure (MPa)	Type of Operation
1	22 to 70	1.48	Conventional FTS
2	71 to 127	1.48	Conventional FTS co-feeding of 1-dodecene
3	128 to 218	5.5	SFTS with propane co-feeding of 1-dodecene
4	219 to 296	5.5	SFTS with propane
5	297 to 331	1.48	Conventional FTS

^aReaction temperature, synthesis gas partial pressure, gas space velocity and H₂ to CO feed ratio were maintained at 250°C, 1.48 MPa, 2 NI/g-cat· h, and 0.67, respectively. Flow rates (at STP): syngas - 117 cm³/min; propane - 350 cm³/min; 1-dodecene - 1.7 cm³/h.

Results

Selected results are shown in Table 2. During conventional FTS at baseline conditions the (H₂+CO) conversion was about 59%. Upon introduction of 1-dodecene (period 2) the (H₂+CO) conversion decreased to 52%. Decrease in activity may be attributed to reduction of partial pressure of syngas and partial coverage of active sites by 1-dodecene. During supercritical FTS (SFTS) with propane and 1-dodecene at 5.5 MPa and 250°C (period 3), the (H₂+CO) conversion was 54%. When the 1-dodecene feed was discontinued (period 4) the (H₂+CO) conversion increased to 57%. In period 5 (297 to 331 h on stream), corresponding to conventional FTS at the baseline conditions, the (H₂+CO) conversion was 46%, indicating catalyst deactivation during 300 h of testing.

Selectivities of CH₄, C₂-C₄ and C₅⁺ hydrocarbons (as %C-atom selectivity to hydrocarbons) are also shown in Table 2. Hydrocarbon selectivities (based on gas phase analysis) did not vary significantly from period 1 to period 4 (i.e. they were independent of the mode of operation). In period 5, selectivities of CH₄ and C₂-C₄ were slightly higher than those in period 1, due to deactivation of the catalyst.

Table 2. Summary of Results for Run FA-1075

TOS, h	60	110	200	270	325
Total pressure, MPa	1.48	1.48	5.5	5.5	1.48
Type of operation	Period 1	Period 2	Period 3	Period 4	Period 5
H ₂ conv, %	57.8	54.0	54.7	55.7	49.8
CO conv, %	59.4	51.3	53.1	58.1	44.2
(H ₂ +CO) conv, %	58.8	52.4	53.7	57.2	46.4
H ₂ /CO usage ratio	0.65	0.70	0.69	0.65	0.75
Mol % ^a CH ₄	5.8	5.7	6.0	5.7	6.6
Mol % ^a C ₂ -C ₄	19.1	20.0	17.2	18.9	24.7
Mol % ^a C ₅ ⁺	75.1	74.3	76.8	75.4	68.7

^a from gas phase composition

Total olefin and 2-olefin contents during different periods of run FA-1075 have exhibited the following trends. At a given carbon number, the total olefin content decreased in the following order: SFTS > SFTS with co-feeding of 1-dodecene > conventional FTS with co-feeding of 1-

dodecene > conventional FTS, whereas 2-olefin content decreased in the following order: conventional FTS > conventional FTS with co-feeding of 1-dodecene > SFTS with co-feeding of 1-dodecene > SFTS with propane.

Selectivity of the primary FTS reaction products (1-olefins) was greater during SFTS, which is in agreement with results obtained in previous studies at Texas A&M University²⁻⁴. Presence of 1-dodecene during conventional FTS (Period 2) also enhanced selectivity of 1-olefins, but the effect was not as profound as that during operation with supercritical propane. This effect may be attributed to lower surface concentrations of high molecular weight olefins in the presence of a large amount of 1-dodecene which adsorbs on the surface (competitive chemisorption on FTS sites).

In contrast to Fujimoto et al.¹ we did not observe suppression of methane selectivity and enhancement of selectivity of high weight molecular hydrocarbons, during SFTS with co-feeding of 1-dodecene. It seems that 1-olefin readsorption is much smaller on iron based catalyst used in the present study than on cobalt FTS catalyst used by Fujimoto and co-workers.

[1] K. Fujimoto, L. Fan, K. Yoshii, *Topics in Catal.* **1995**, 2, 259-266

[2] X. Lang, A. Akgerman, D. B. Bukur, *Ind. Eng. Chem. Res.* **1995**, 34, 2707-2712

[3] D. B. Bukur, X. Lang, A. Akgerman, Z. Feng, *Ind. Eng. Chem. Res.* **1997**, 36, 2580-2587

[4] D. B. Bukur, X. Lang, L. Nowicki, *Ind. Eng. Chem. Res.* **2005**, 44, 6038-6044.