FISCHER TROPSCH SYNTHESIS IN SUPERCRITICAL FLUIDS

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QUARTERLY TECHNICAL PROGRESS REPORT

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I. Objectives for the Fourth Quarter, Year 3:

A. Fischer Tropsch Reaction Related Studies

Our objective for this quarter was to compare performance of the Ruhrchemie catalyst in different modes of operation: fixed bed reactor (conventional and supercritical mode of operation), and stirred tank slurry reactor.

B. Diffusion Coefficients of F-T Products in Supercritical Fluids

Our objectives for this quarter were to measure the molecular diffusion coefficients and effective diffusivities with different solvent-solute pairs to get a better understanding of the interaction of Fischer-Tropsch synthesis products and help to quantify the reaction kinetics. We then will attempt to find a model to predict the molecular diffusion coefficients to a high degree of accuracy so we may be able to predict both the molecular diffusion coefficient and thus the effective diffusivity a priori.

II. Accomplishments and Problems, Fourty Quarter, Year 3:

A. Fischer Tropsch Reaction Related Studies

During the course of this project the Ruhrchemie LP 33/81 catalyst (100 Fe/5 Cu/4.2 K/25 SiO_2 on mass basis) was tested in a fixed bed reactor in both conventional and supercritical modes of operation. Also, this catalyst was tested previously in our laboratory in fixed bed and stirred tank slurry reactors (conventional mode of operation) during the work on DOE Contract No. DE-AC22-89PC89868. In all tests the catalyst was reduced in situ with H_2 at 220°C, 7500 cc/min for 1 h, and ambient pressure (fixed bed reactor test) or 0.8 MPa (slurry reactor test). Results from these tests at baseline set of process conditions: 250°C, 2 Nl/g-cat/h, syngas partial pressure of 1.48 MPa, and synthesis feed gas with H_2/CO molar ratio of about 0.67, are summarized below.

Fischer-Tropsch Synthesis in Fixed Bed Reactors - Conventional Mode of Operation

Seven tests were conducted in fixed bed reactors, and selected results are given in Table 1. Results from individual tests are given together with mean values and standard deviations for each of measured quantities (CO and syngas conversions, usage ratio (UR), apparent reaction rate constant (k), and lumped hydrocarbon selectivities: CH_4, C_2-C_4, C_5-C_{11} and C_{12}+). Although there are some variations between individual tests, the data are well represented by

mean values from all seven tests. Standard deviations as a percentage of the mean value range from 5.4 % (usage ratio) to 15.7 % (methane selectivity). Thus, the mean values from all tests can be used for comparison of results obtained in other modes of operation.

Olefin selectivities (total olefin content and 2-olefin selectivity) as a function of carbon number for individual tests are shown in Figures 1 and 2. Mean values from six different sets are also shown in these two figures. As can be seen the differences in olefin selectivities between different tests are rather small, and the mean values can be used as an illustration of catalyst performance in fixed bed reactors at baseline conditions.

Fischer-Tropsch Synthesis in Fixed Bed Reactors - Supercritical Mode of Operation

Four tests (three with supercritical propane and one with supercritical n-hexane) were conducted in this mode of operation. Partial pressure of syngas was constant in all four tests (1.48 MPa), whereas total pressure varied between 4.1 MPa (run FA-2984) and 7 MPa (run FA-0844) as shown in Table 2. Results from individual tests illustrating catalyst activity and selectivity are summarized in Table 2. Mean values and standard deviations are also provided to illustrate variability of results. Values of the apparent reaction rate constant had the highest variability (standard deviation was about 20.6 % of the mean value), followed by methane selectivity (14.6 % variation from the mean). Gaseous hydrocarbon selectivity (C_2-C_4 hydrocarbons) in run FA-2984, with supercritical n-hexane, was much lower (10.2 %) than that obtained in the three tests with supercritical propane (15-17.2 %). This is attributed to high solubility of C_2-C_4 hydrocarbons in supercritical n-hexane, and is not the result of intrinsic catalyst selectivity.

Olefin selectivities (total olefin content and 2-olefin selectivity) as a function of carbon number for individual tests are shown in Figures 3 and 4. Mean values from four sets of data are also shown in these figures. As can be seen the differences in olefin selectivities between different tests are small (except for high ethylene selectivity in run FA-1075), and the corresponding mean values are representative of catalyst performance in fixed bed reactors under supercritical conditions.

Fischer-Tropsch Synthesis in a Stirred Tank Slurry Reactor

Only one test was conducted in the stirred tank slurry reactor (run SB-1370) following reduction with hydrogen. Baseline conditions (250°C, 2 Nl/g-cat/h, 1.48 MPa, $H_2/CO = 0.67$) were maintained during the first 350 h on stream, and results from five mass balances illustrating variations of catalyst activity and selectivity with time-on-stream (TOS) are shown in Table 3 and Figures 5 and 6.

Catalyst activity (Table 3, conversions and k values) and 2-olefin selectivity (Figure 6) increased slightly with time whereas hydrocarbon selectivity shifted towards lower molecular weight products, however, the magnitude of these changes was rather small and mean values will be used for comparison with results obtained in fixed bed reactors.

Comparison of Catalyst Performance in Different Modes of Operation

Comparison of activities and hydrocarbon selectivities (lumped hydrocarbon distribution) is given in Table 4, whereas comparison of olefin selectivities (total olefin content and 2-olefin selectivity) is given in Figures 7 and 8.

Average values of CO and syngas conversions from seven fixed bed reactor tests in conventional mode of operation were about 10 % greater than the corresponding average values obtained from four tests in supercritical mode of operation. However, the average value of the apparent reaction rate constant in the supercritical mode of operation was slightly higher (about 5 %) than the corresponding average for conventional mode of operation. For a given test in both conventional and supercritical modes of operation, it was found that the apparent rate constant is either the same or slightly higher in the supercritical mode of operation. Usage ratios, which represent a measure of water-gas-shift activity, are the same in both modes of operation. The general conclusion from these results is that the catalyst activity is slightly higher in the supercritical mode of operation, due to higher diffusivities of reactants in supercritical fluids relative to conventional mode of operation (pores filled with liquid hydrocarbon wax). Syngas and CO conversions were significantly lower in a stirred tank slurry reactor (STSR), due to the fact that the catalyst activity was lower (143 mmol/g-Fe/h/MPa vs. 209 - 220 mmol/g-Fe/h/MPa in fixed bed reactors) and due to differences in flow patterns (perfect mixing vs. plug flow behavior). It is believed that low catalyst activity in run SB-1370 is due to lower degree of iron reduction in the STSR. Catalyst activity

in run SB-1370 continued to increase with time-on-stream (Table 3) due to creation of active sites during FTS. Also, the CO pretreated Ruhrchemie catalyst (run SA-0888) had the apparent rate constant of 193 mmol/g-Fe/h/MPa (Bukur et al., 1990), which is only about 10 % less than that obtained in fixed bed reactors (H_2 reductions). These observations support the hypothesis that low activity in run SB-1370, is due to incomplete reduction of the catalyst.

Hydrocarbon selectivities in the fixed bed reactor were similar in both modes of operation. Methane selectivity in the STSR was lower than in the fixed bed reactor, due to better temperature control in the former. Also, the gasoline (C_5 - C_{11} hydrocarbons) yield is higher in the STSR.

The consensus from many studies with iron catalysts is that 1-alkenes and, to a smaller extent, n-alkanes are the primary products of FTS (Dry, 1981; Dictor and Bell, 1986; Donnelly and Satterfield, 1989; Schulz and Gokcebay, 1984). The 1-alkene may subsequently be hydrogenated to an n-alkane, isomerized to the 2-alkene or readsorbed to initiate further chain growth.

As can be seen in Figures 1, 3, 5 and 7, the total olefin content dependence on carbon number of hydrocarbon products passes through a broad maximum (C_3 - C_5 range). This shape is believed to be due to either secondary hydrogenation of 1-alkenes (Schulz and Gokcebay, 1984; Dictor and Bell, 1986) or 1-olefin readsorption and subsequent chain termination to paraffins (Zimmerman et al., 1992; Madon and Iglesia, 1993). Ethylene is more reactive than other low molecular weight olefins, whereas the decrease in olefin content with increase in molecular weight has been attributed to their greater adsorptivity (Anderson, 1956; Dictor and Bell, 1986), higher solubility resulting in longer residence time in a slurry reactor (Donnelly and Satterfield, 1989; Schulz and Gokcebay, 1984), lower diffusivities (Yokota and Fujimoto, 1991; Lang et al., 1995) and/or 1-olefin readsorption (Zimmerman et al., 1992; Madon and Iglesia, 1993). The increase in olefin isomerization activity with increase in carbon number (Figures 2, 4, 6 and 8) is due to the same factors which affect the 1-olefin hydrogenation and/or readsorption activity. The longer residence time of high molecular weight 1-alkenes either in the catalyst pores or in the reactor itself increases probability for secondary reactions (hydrogenation, isomerization and 1-olefin readsorption).

The total olefin content was the highest (Figure 7) and the 2-olefin selectivity was the lowest (Figure 8) in the supercritical mode of operation. This is attributed to higher diffusivities of high molecular weight 1-olefins in supercritical fluids than in the liquid filled pores during the conventional FTS in either the fixed bed or the stirred tank slurry reactor. The olefin content was lower and the olefin isomerization activity was higher in the fixed bed reactor than in the slurry reactor (SB-1370). These differences in olefin selectivities are partly caused by differences in conversion levels, since higher conversions favor secondary reactions.

Effect of Process Conditions on Olefin Selectivity

During the reporting period we have written a paper (submitted to Chemical Engineering Science) on the effect of process conditions (gas space velocity, reaction temperature, and syngas feed composition) on olefin selectivity during FTS in supercritical propane. This is based on results obtained in run FA-1724 with the Ruhrchemie LP 33/81 catalyst (Quarterly Technical Progress Report July - September, 1994). A copy of the paper . is attached.

B. Diffusion Coefficients of F-T Products in Supercritical Fluids

We previously had reported on the methodology to extract molecular diffusion coefficients from experimental data in Taylor dispersion at high temperatures. We also previously reported on the method for determining the effective diffusivity at high temperatures. These methodologies have been verified to be accurate by repetition of experimentation. Due to equipment failure this quarter, not many new experiments were completed. However runs were still completed with varying solvents at 523-543 K and 900-1500 psi . These results are given in Table 5.

We also began the predictive methodology for molecular diffusion coefficients in supercritical fluids. The diffusion coefficient can be correlated to the rough hards spheres diffusion, $D_{12,RHS}$, which is governed by the equation:

$$D_{12} \approx D_{12, RHS} = A_{12}D_{12, SHS} \qquad (0 < A_{12} \leq 1)$$

where $D_{12,SHS}$ is the smooth hard spheres diffusivity and A_{12} is the translational rotational

coupling parameter. Further this equation can be written as:

$$D_{12, RHS} = A_{12} \left(\frac{D_{12, SHS}}{D_{12, E}} \right) D_{12, E} \qquad (0 < A_{12} \leq 1)$$

where $D_{12,E}$ is the Enskog diffusivity for dense gases. The ratio of smooth hard sphere to enskog diffusivity, a correction factor for correlated velocities and cage effects, is determined either by molecular dynamics simulations or by semie-mpirical correlations. The Enskog diffusivity is given by the equation:

$$D_{12, E} = \frac{D_{12, HSG}}{g(\sigma_{12})}$$

where the radial distribution factor is portrayed by:

$$g(\sigma_{12}) = \frac{1}{1-\xi} + \frac{3\xi\sigma_1}{(1-\xi)^2(\sigma_1+\sigma_2)} + \frac{\xi^2\sigma_1}{2(1-\xi)^3\sigma_2}$$

This is a very accurate way of determining the Enskog diffusivity for dense gases. However, a better correlation is needed for calculating the smooth hard sphere to Enskog ratio (the correction factor) and the translational rotational coupling parameter.

The first area was to work on correlating the smooth hard sphere to enskog ratio emloying the molecular dynamics and exprimental diffusion data available in the literature. All available supercritical fluid diffusion coefficient measurements were formed into a database and correlated to their given molecular weight, molecular radii, and density ratio's. Unfortunately, most supercritical systems are not covered in the molecular ratio spectrum of the literature data on molecular dynamics. Thus we first attempted to use a correlation by Sung and Stell (1984) to predict the molecular dynamics results. This led to possible problems, since the correlation

was developed for self diffusion and does not seem to extrapolate well to uncorrelated species. It was thus determined that molecular dynamics simulations were needed to be completed in the correct range in order to develop a predictive equation.

We also submitted a manuscript based om our studies to the Journal of Chemical Engineering and Data, which is accepted for publication and is in press. A copy of the manuscript is included in the appendix.

III. Plans for the First Quarter, Year 4 (No Cost Extension Period).

A. Fischer Tropsch Reactor Assembly

We have completed all planned activities related to reaction studies for this project, and no further activities are planned.

B. Diffusion Coefficients of F-T Products in Supercritical Fluids

We will attempt to find a model to predict the molecular diffusion coefficients to a high degree of accuracy so we may be able to predict both the molecular diffusion coefficient and thus the effective diffusivity a priori. To accomplish this a set of molecular dynamics simulations will be carried out in the range of the literature data. This will allow us to develop an emperical formula to correlate the molecular diffusion coefficent to ratios of mass, size, and density. More runs with propane and hexane are also scheduled for the upcoming period to give a broader base of Fisher Tropsch systhesis molecular diffusion data.

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Yokota, K. and Fujimoto, K., "Supercritical Phase Fischer-Tropsch Synthesis Reaction. 2. The Effective Diffusion of Reactant and Products in the Supercritical-Phase Reaction", Ind. Eng. Chem. Res., **30**, 95-100 (1991).

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Table 1: Ruhrchemie Catalyst Activity and Selectivity during Conventional FT Synthesis in Fixed Bed Reactors

Test ID	FA-3509	FA-0113	FA-3143	FA-0844	FB-1644	FA-2984	FA-1075	MEAN	Std. Dev.
TOS (h)	150-350	40-70	40-70	240-260	40-70	40-70	40-70		
CO conversion (%)	68.1	73.8	58.8	50.5	61.9	57.9	59.8	61.5	7.5
(H_2+CO) conversion (%)	64.5	71.9	59.5	51.1	61.6	59.9	58.8	61.0	6.3
(H_2/CO) usage ratio	0.62	0.60	0.68	0.68	0.66	0.70	0.65	0.66	0.04
k (mmol/g-Fe/h/MPa) [a]	216	241	206	170	220	207	202	209	21.6
Hydrocarbon Selectivity (wt%)									
CH_4	6.2	6.1	7.0	5.5	7.6	6.8	4.8	6.3	1.0
C_2-C_4	19.8	16.8	17.7	15.9	18.5	19.4	16.6	17.8	1.5
C_5-C_{11}	30.3	19.8	25.0	23.9	24.5	27.4	20.2	24.4	3.7
$C_{12}+$	43.7	53.3	50.2	54.7	49.4	46.4	58.4	51.5	5.6

Note: Process conditions: 250°C, 1.48 MPa, 2.0 Nl/g-cat/h, $H_2/CO = 0.67$.

[a]: Apparent reaction rate constant for a first-order reaction in hydrogen, based on measured usage ratio.

Table 2: Ruhrchemie Catalyst Activity and Selectivity during Supercritical FT Synthesis in Fixed Bed Reactors

Test ID	FA-0844	FA-1724	FA-2984	FA-1705	MEAN	Std. Dev.
TOS (h)	92-215	70-140	69-192	220-296		
Total Pressure (MPa)	7.0	5.5	4.1	5.5		
Supercritical medium	propane	propane	hexane	propane		
CO conversion (%)	55.1	48.5	66.0	58.1	56.9	7.3
(H_2+CO) conversion (%)	53.6	50.2	65.6	57.2	56.6	6.6
(H_2/CO) usage ratio	0.62	0.73	0.64	0.65	0.66	0.05
k (mmol/g-Fe/h/MPa)[a]	174	198	279	231	221	45.5
Hydrocarbon Selectivity (wt%)						
CH_4	5.3	5.7	6.9	7.2	6.2	0.9
C_2-C_4	15.4	17.2	10.2b	15.0	15.8	1.3
C_5-C_{11}	20.3	23.7	36.9b	25.1	23.0	2.5
C_{12}+	59.0	53.4	46.0b	52.7	55.0	3.5

Note: Process conditions: 250°C, 1.48 MPa (syngas), 2.0 Nl (syngas)/g-cat/h, H_2/CO = 0.67.

a: Apparent reaction rate constant for a first-order reaction in hydrogen, based on measured usage ratio.

b: excluded from the calculation of the mean.

Table 3: Ruhrchemie Catalyst Activity and Selectivity during Conventional FT Synthesis in a Stirred Tank Slurry Reactor Test SB-1370

TOS (h)	65	134	181	253	350	MEAN	Std. Dev.
CO conversion (%)	35.3	36.3	39.5	39.8	38.5	37.9	2.0
(H_2+CO) conversion (%)	36.6	37.6	40.0	40.2	39.9	38.9	1.6
(H_2/CO) usage ratio	0.72	0.72	0.68	0.68	0.72	0.70	0.02
k (mmol/g-Fe/h/MPa)[a]	133	139	147	148	150	143	7.2
Hydrocarbon Selectivity (wt%)							
CH_4	4.0	5.2	4.7	5.2	4.8	4.8	0.5
C_2-C_4	15.3	16.0	16.7	15.9	18.2	16.4	1.1
C_5-C_{11}	25.5	27.1	33.1	28.7	31.2	29.1	3.1
$C_{12}+$	55.2	51.7	45.5	50.2	45.8	49.7	4.1

Note: Process conditions: 250°C, 1.48 MPa, 2.0 Nl/g-cat/h, H_2/CO = 0.61 - 0.70.

a: Apparent reaction rate constant for a first-order reaction in hydrogen, based on measured usage ratio.

Table 4: Comparison of Ruhrchemie Catalyst Performance in Different Modes of Operation

	Conventional FTS		Supercritical FTS
	Fixed Bed Reactor	Slurry Reactor	Fixed Bed Reactor
CO conversion (%)	61.5 ± 7.5[b]	37.9 ± 2.0	56.9 ± 7.3
(H_2+CO) conversion (%)	61.0 ± 6.3	38.9 ± 1.6	56.6 ± 6.6
(H_2/CO) usage ratio	0.66 ± 0.04	0.70 ± 0.02	0.66 ± 0.05
k (mmol/g-Fe/h/MPa)[a]	209 ± 21.6	143 ± 7.2	221 ± 45.5
Hydrocarbon Selectivity (wt%)			
CH_4	6.3 ± 1.0	4.8 ± 0.5	6.2 ± 0.9
C_2-C_4	17.8 ± 1.5	16.4 ± 1.1	15.8 ± 1.3
C_5-C_{11}	24.4 ± 3.7	29.1 ± 3.1	23.0 ± 2.5
$C_{12}+$	51.5 ± 5.6	49.7 ± 4.1	55.0 ± 3.5

Note: Process conditions: 250°C, 1.48 MPa (syngas), 2.0 Nl (syngas)/g-cat/h, $H_2/CO = 0.67$.

a: Apparent reaction rate constant for a first-order reaction in hydrogen, based on measured usage ratio.

b: mean ± std. dev.
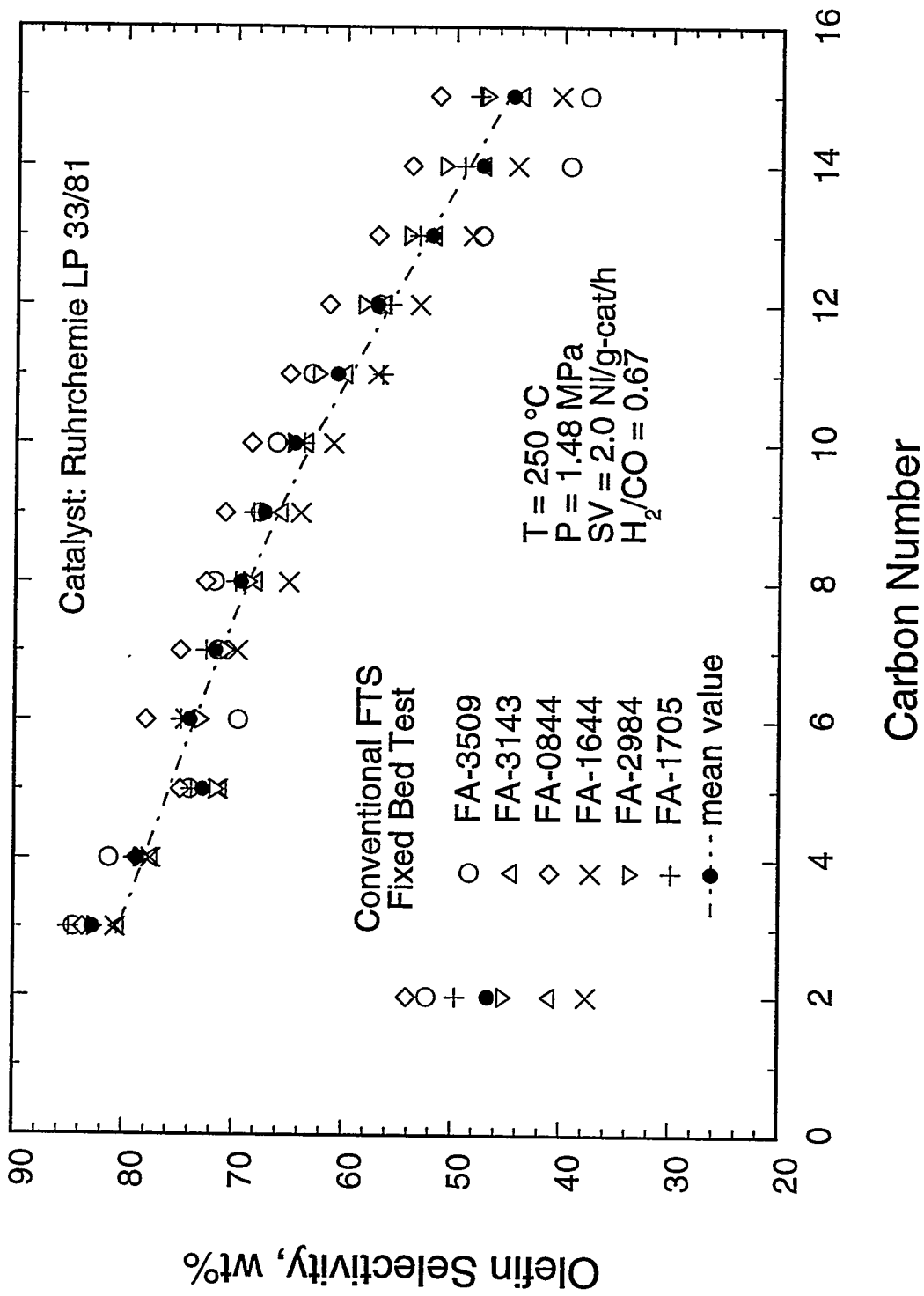
Figure 1. Comparison of olefin selectivities from different tests - Conventional FTS in fixed bed reactors.
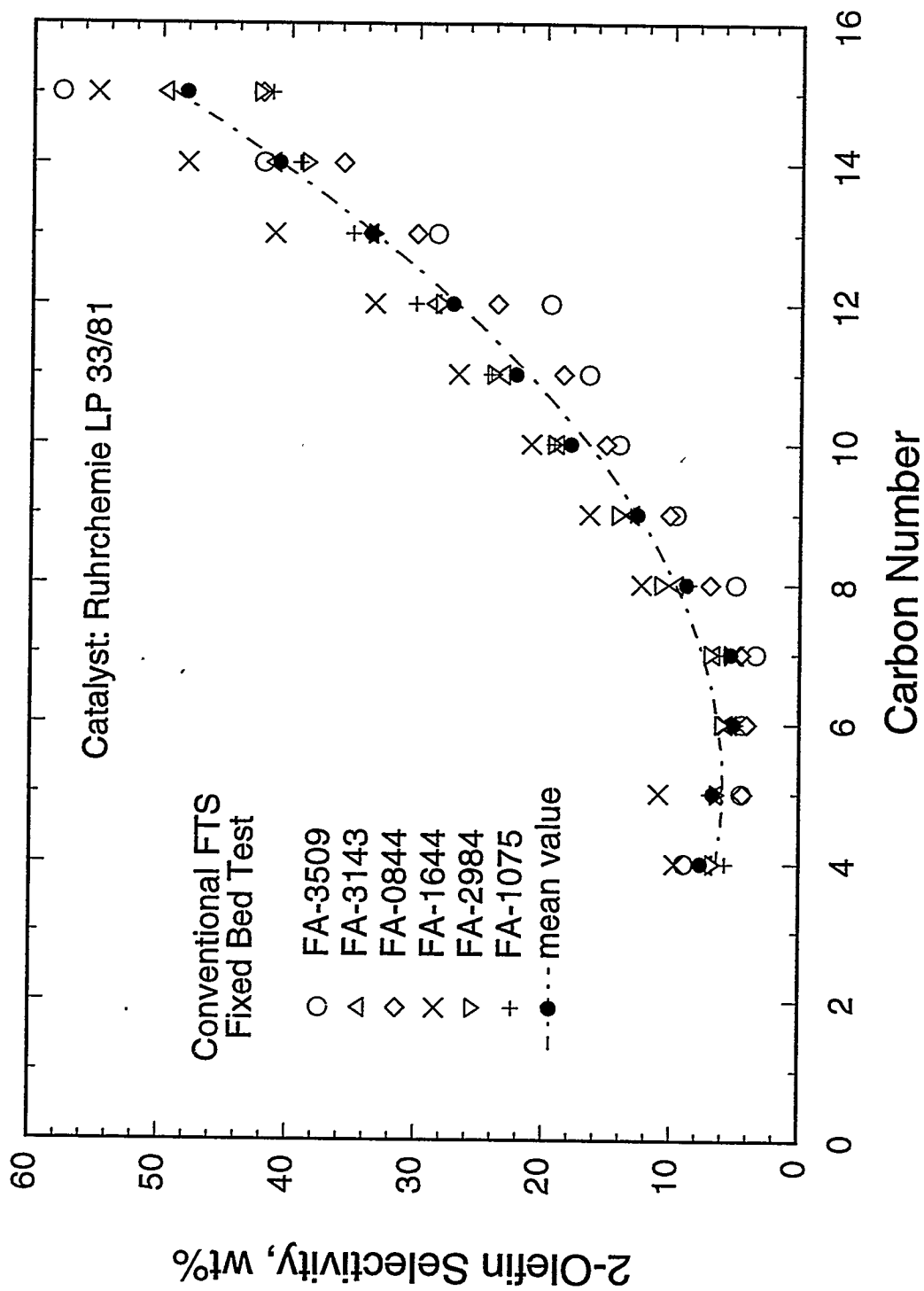
Figure 2. Comparison of 2-olefin selectivities from different tests - Conventional FTS in fixed bed reactors.
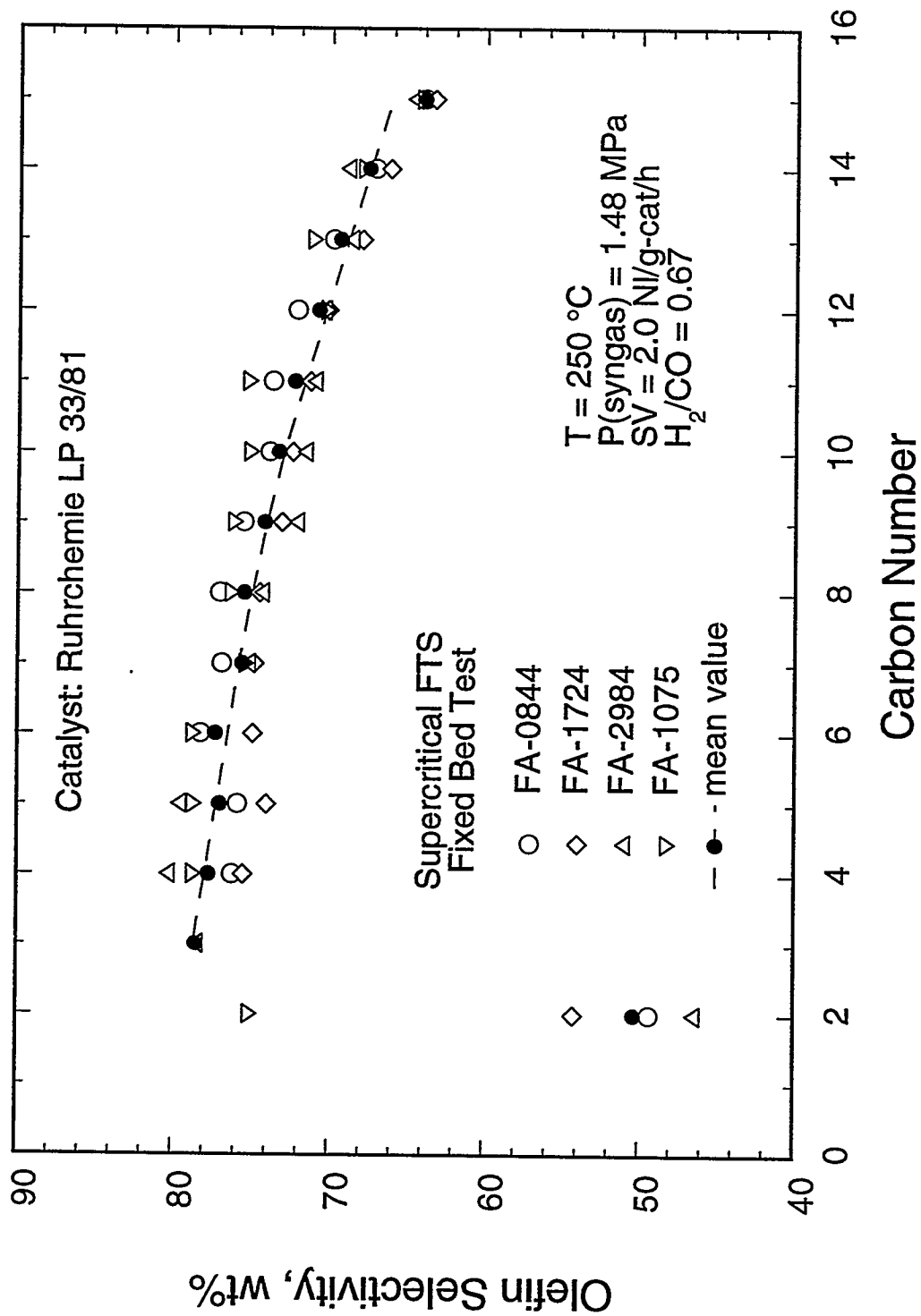
Figure 3. Comparison of olefin selectivities from different tests - Supercritical FTS in fixed bed reactors.
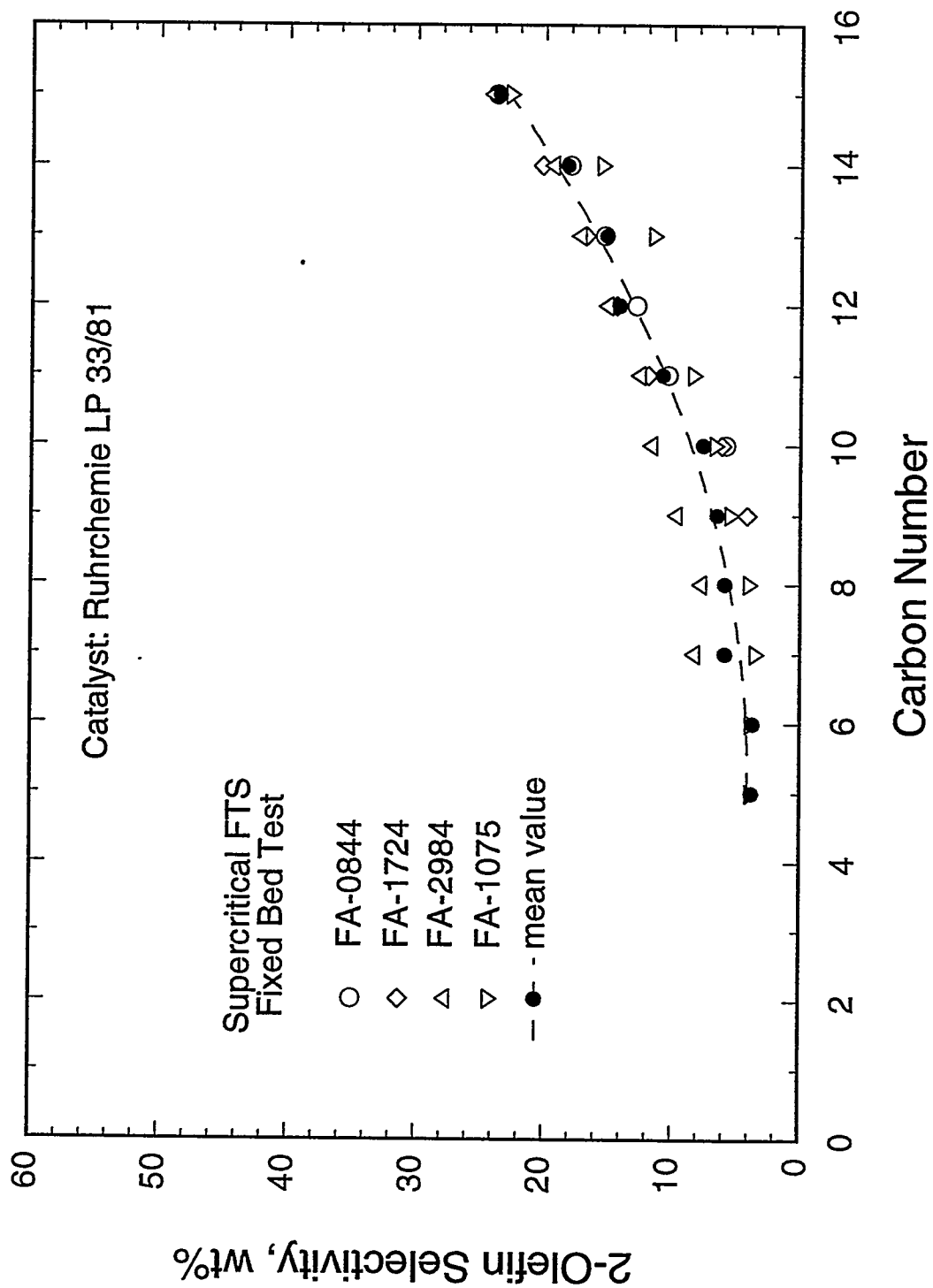
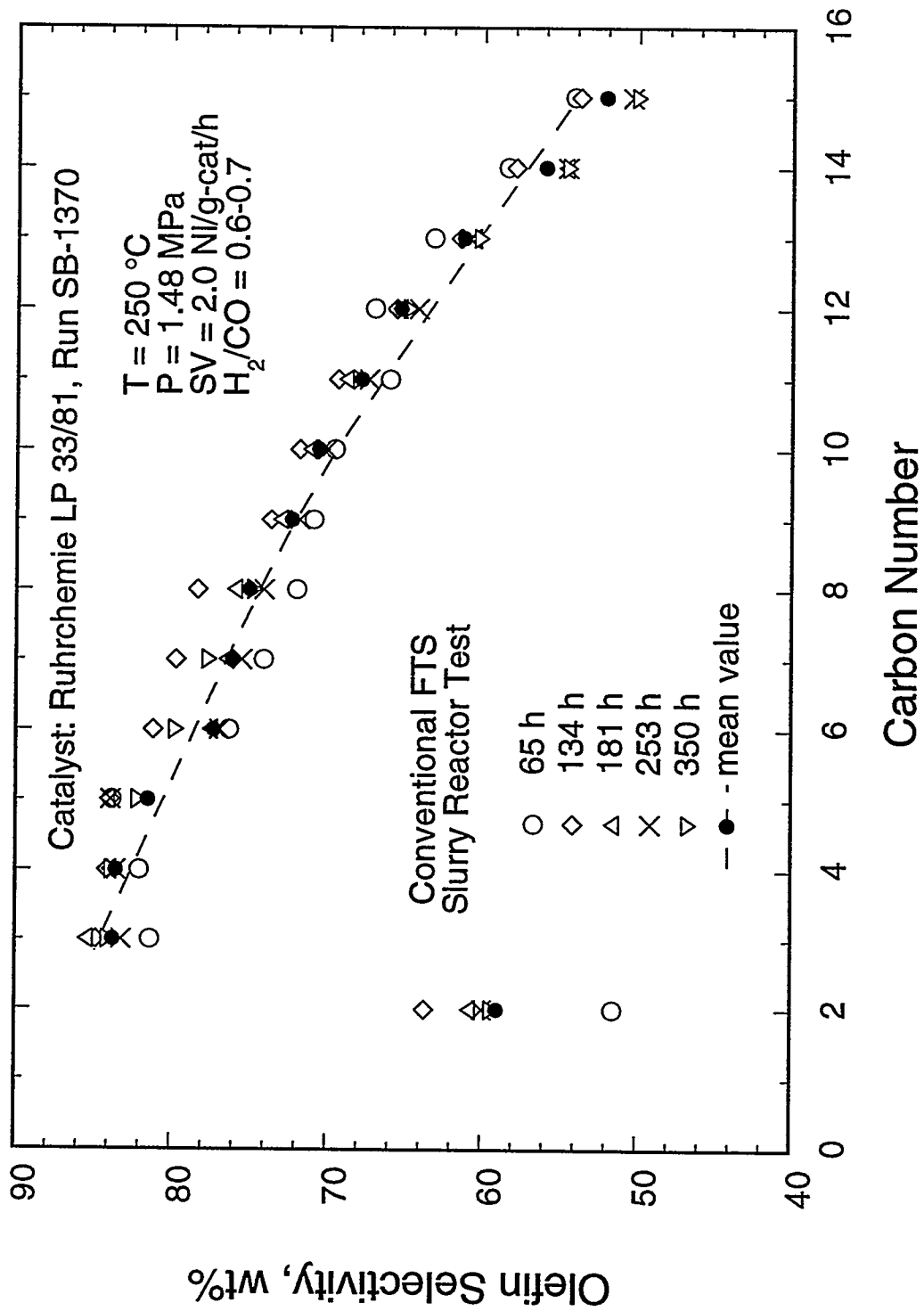Figure 4. Comparison of 2-olefin selectivities from different tests - Supercritical FTS in fixed bed reactors.

Figure 5. Olefin selectivities during conventional FTS in a stirred tank slurry reactor.
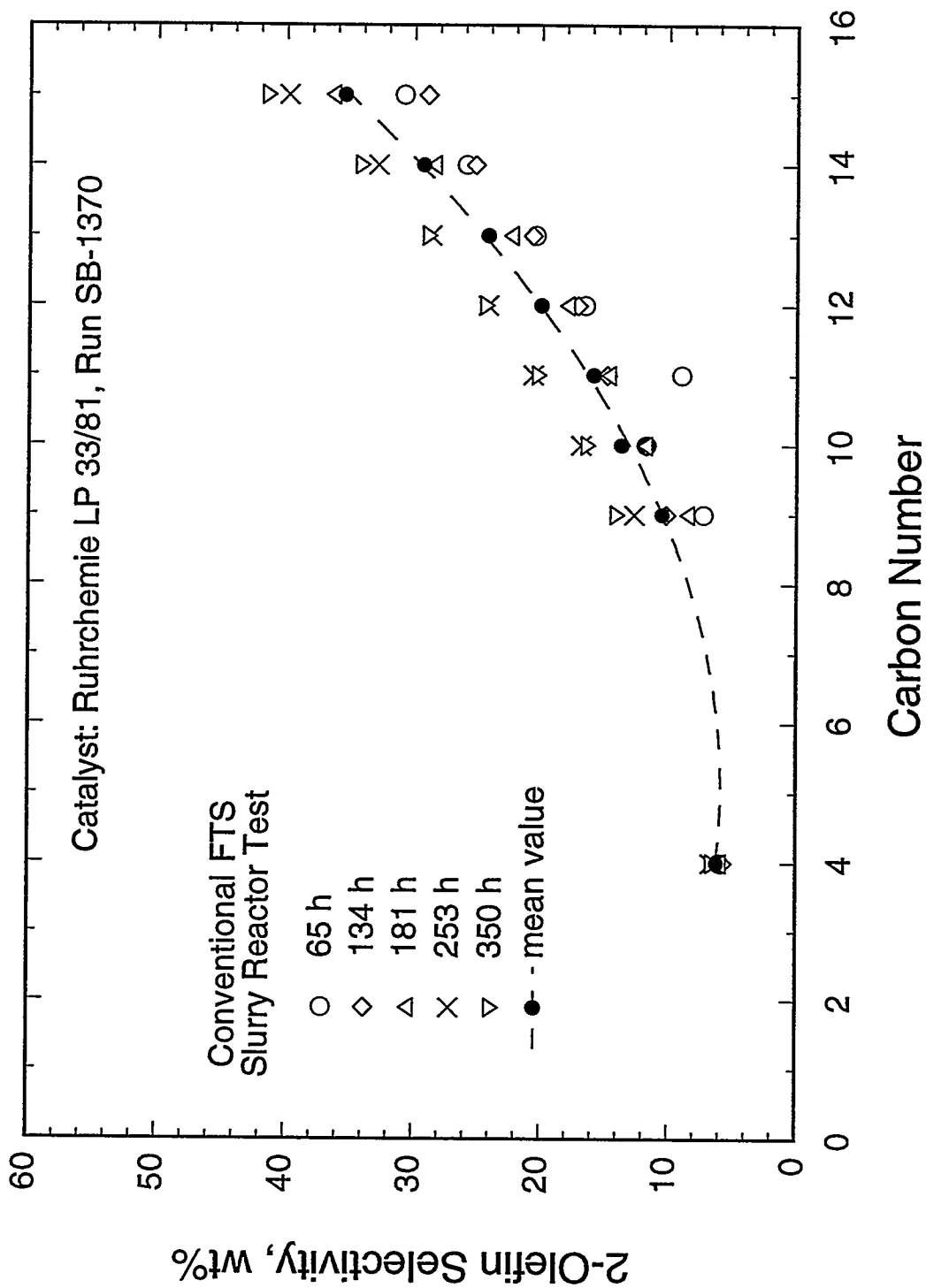
Figure 6. 2-Olefin selectivities during conventional FTS in a stirred tank slurry reactors.
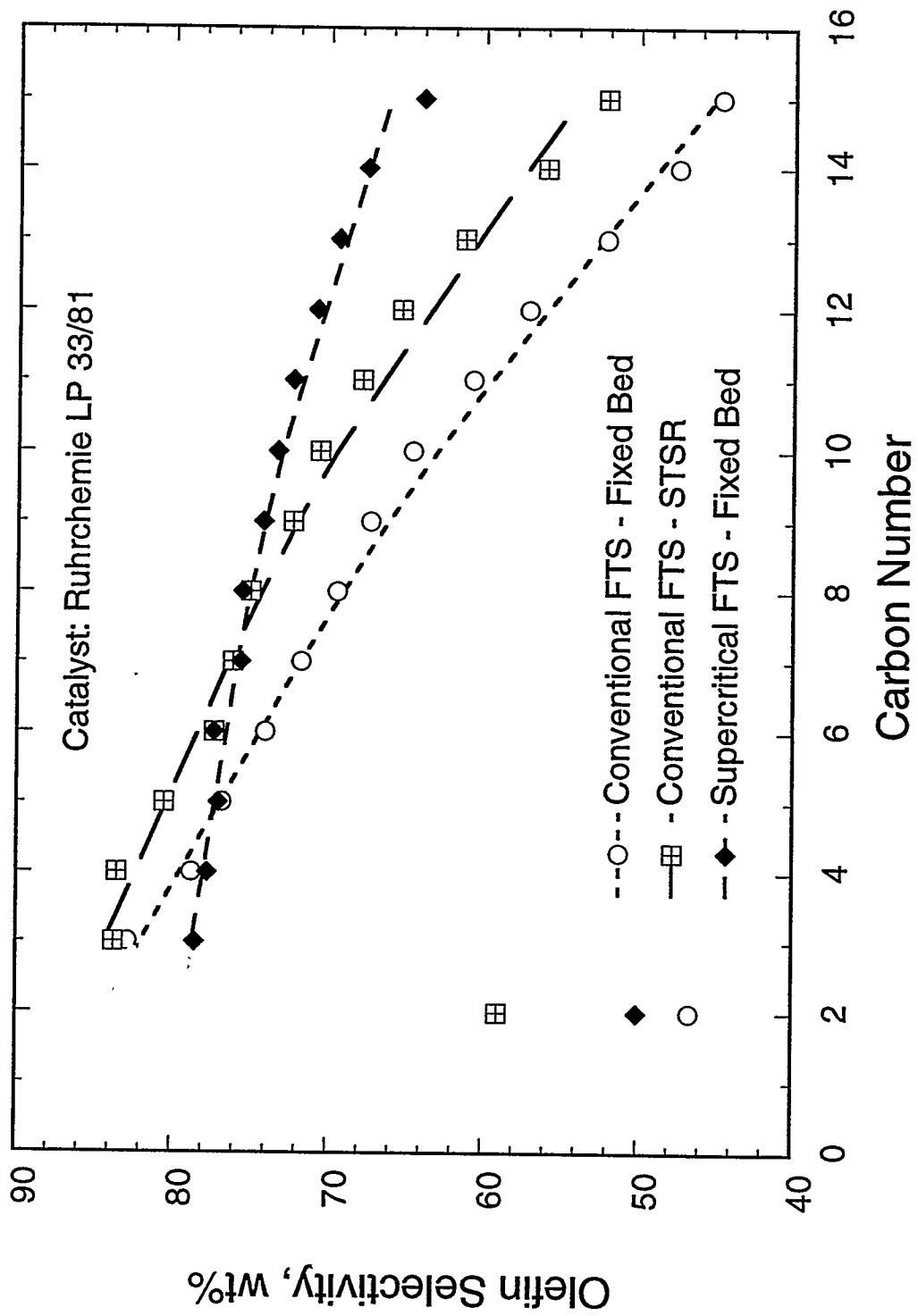
Figure 7. Comparison of olefin selectivities from three different modes of FTS operation
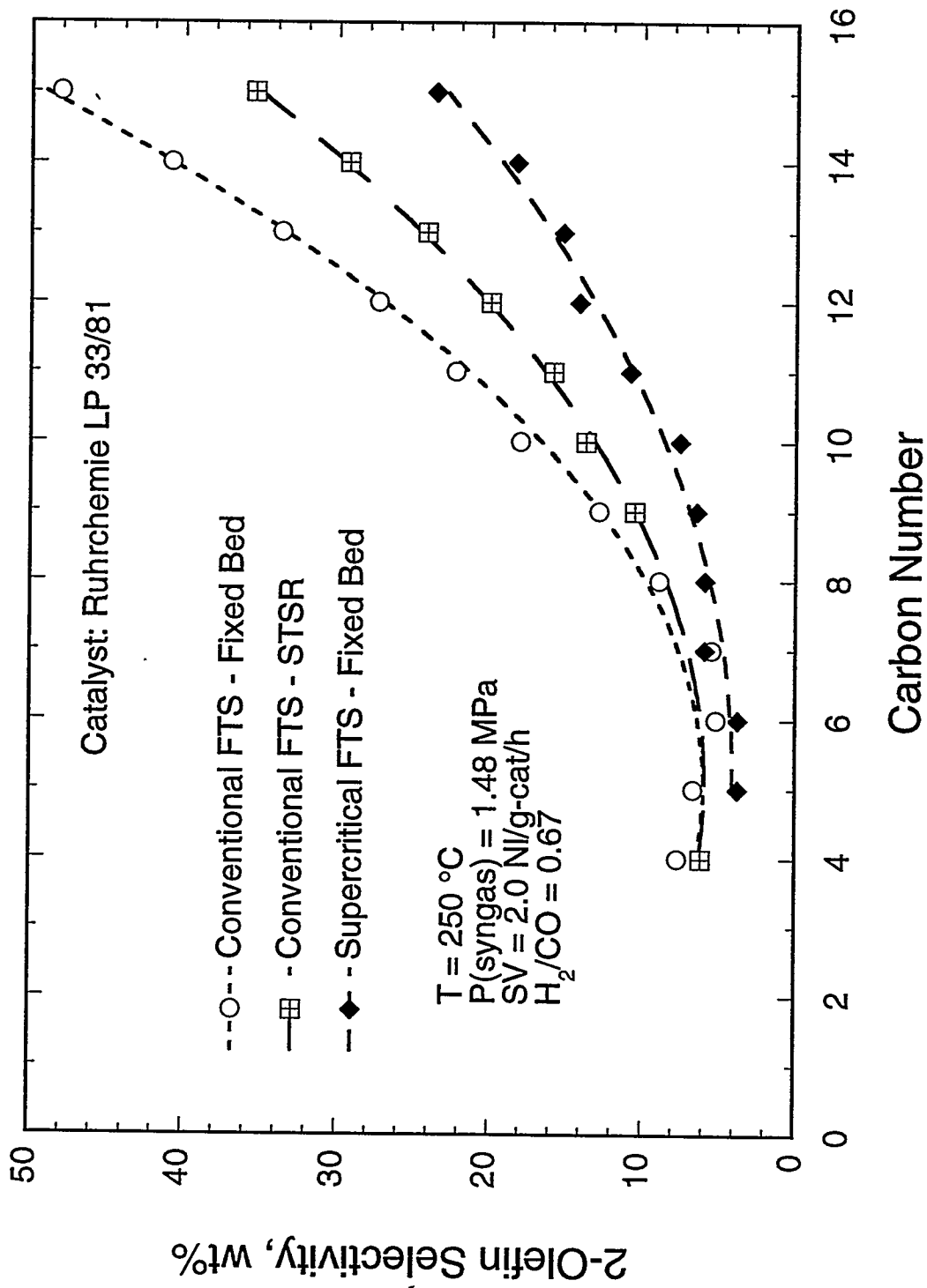
Figure 8. Comparison of 2-olefin selectivities from three different modes of FTS operation

Table 5. Molecular Diffusion Coefficients and Effective Diffusivities for 1-Octene/Hexane and 1-Octene/Propane

Temperature (K)	Pressure (bar)	Solvent	D12 *108 (m2/s)	Deff 108 (m2/s)
523	103.4212	Hexane	2.75 ± 0.011	0.289 ± 0.027
523	62.4659	Propane	31.0 ± 1.69	2.872 ± 0.234
533	62.4659	Propane	37.0 ± 5.85	4.394 ± 0.499
543	62.4659	Propane	31.5 ± 1.15	3.499 ± 0.254

Molecular Diffusion Coefficients and Effective Diffusivities of Octene in Supercritical Ethane in Relation to Fischer-Tropsch Synthesis

submitted to

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Appendix A

FISCHER-TROPSCH SYNYHESIS IN SUPERCRITICAL PROPANE -

Effect of Process Conditions on Olefin Selectivity

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