Table 3.3.7 Product Distribution Observed over the 3 mol% Cs/Cu/ZnO/Cr$_2$O$_3$ Catalyst with H$_2$/CO = 0.45 Synthesis Gas at 310°C, 7.6 MPa, and with GHSV = 5,450 l(STP)/kg cat/hr. MeOH = methanol, EtOH = ethanol, PrOH = 1-propanol, BuOH = 1-butanol, PentOH = 1-pentanol, HexOH = 1-hexanol, 2m-PrOH = 2-methyl-1-propanol, 2m-BuOH = 2-methyl-1-butanol, 2m-PentOH = 2-methyl-1-pentanol, 2m-HexOH = 2-methyl-1-hexanol, 2-PrOH = 2-propanol, 2-BuOH = 2-butanol, 3m-2-BuOH = 3-methyl-2-butanol, 3-PentOH = 3-pentanol, 2m-3-PentOH = 2-methyl-3-pentanol, MF = methyl formate, MAC = methyl acetate, MPR = methyl propionate, MiBu = methyl isobutyrate, and MBU = methyl butyrate.

Species	Productivity (g/kg cat/h)	Species	Productivity (g/kg cat/h)
Primary Alcohols:		Methyl Esters:	
MeOH	231.0	MF	8.3
EtOH	22.3	MAC	7.4
PrOH	28.6	MBR	5.6
BuOH	6.1	MiBU	6.7
PentOH	1.3	MBU	2.8
HexOH	1.0		
2m-PrOH	28.0	Hydrocarbons:	
2m-BuOH	5.0	Methane	5.1
2m-PentOH	1.5	Ethene	0.02
2m-HexOH	1.5	Ethane	5.9
		Propene	0.1
Secondary Alcohols:		Propane	1.8
		Buta(e)nes	1.7
2-PrOH	0.1	Penta(e)nes	0.6
2-BuOH	1.5	Hexa(e)nes	0.6
3m-2-BuOH	2.9		
3-PentOH	2.1		
2m-3-PentOH	1.8	Others:	
		DME	1.8
Aldehydes:		C$_{7+}$ oxygenates	22.5
Acethaldehyde	0.7		
Propanaldehyde	1.1		
Isobutanaldehyde	0.9	CO$_2$	638.2
Ketones:			
Acetone	0.2	H$_2$O	3.4
2-Butanone	1.5		
3m-2-Butanone	1.7		
3-Pentanone	1.9	% CO conversion	20.2%
2m-3-Pentanone	3.0		

The 4 mol% $Cs/ZnO/Cr_2O_3$ catalyst was tested with GHSV = 12,000 l/kg cat/hr while all other reaction conditions were maintained constant for this high temperature catalyst (see Tables 3.3.4 and 3.3.5). The observed product space time yields are given in Table 3.3.8, in which the total CO conversion corresponds to 7.0%. Again, it is notable that the productivity of the linear C_2-C_6 alcohols was much lower over the high temperature Cu-free catalyst than over the Cu-based catalysts (see Tables 3.3.4, 3.3.5, and 3.3.7). As expected, the space time yields of methanol and isobutanol are between those at higher and lower GSVS, which are given in Tables 3.3.4 and 3.3.5.

Table 3.3.8 Space Time Yields (g/kg catal/hr) of Higher Alcohols and Other Products over the 4 mol% $Cs/ZnO/Cr_2O_3$ Catalyst at 405°C and 7.6 MPa from $H_2/CO = 0.75$ Synthesis Gas with GHSV = 12,000 l/kg catal/hr. The small quantities of aldehydes and ketones formed over this catalyst have been added to the productivities reported for the parent alcohols.

Product*	12,000 l/kg catal/hr
MeOH	132.8
EtOH	2.1
PrOH	8.7
BuOH	0.8
PentOH	0.5
HexOH	0.2
2m-PrOH	69.1
2m-BuOH	7.9
2m-PentOH	7.0
2m-HexOH	0.7
2-BuOH	1.2
3m-2-BuOH	0.9
3-PentOH	0.7
2m-3-PentOH	5.4
Methylformate	1.2
Methylacetate	0.8
DME	4.5
C_{7+} Oxygenates	79.1
CH_4	3.9
C_2-C_4 HC	15.0
%CO Conv.$_{(CO2-free)}$	4.9

*m = methyl. CO_2 and H_2O are also formed but are not listed.

Cu/ZrO₂ Catalysts

Zirconia-based catalysts are being investigated for their potential as alcohol synthesis catalysts. A series of CuO/ZrO_2 catalysts having different Cu/Zr molar ratios were prepared by aqueous coprecipitation at constant pH and temperature, as described in the previous quarterly progress report.

Initial testing of zirconia-supported copper catalysts for alcohol synthesis from H_2/CO synthesis gas employed a $CuO/ZrO_2 = 10/90$ mol% catalyst. The catalyst was calcined at 350°C for 3 hr, was X-ray amorphous, and had an initial surface area of 149 m²/g. After the catalyst (2 g mixed with Pyrex beads for dilution) was loaded into the reactor, it was reduced in flowing 2 vol% H_2/N_2 at 330°C for 4 hr at ambient pressure.

This unpromoted Cu/ZrO_2 catalyst was tested under both methanol synthesis conditions for comparison with the Cu/ZnO catalyst ($H_2/CO = 2.33$) and higher alcohol synthesis conditions ($H_2/CO = 0.45$). The levels of CO conversion were rather low, and the space time yields of the products observed are given in Table 3.3.9. It is clear that methanol and dimethylether were the dominant products formed over this catalyst under the reaction conditions employed. At the higher temperatures, small quantities of higher alcohols were also formed. Comparison of the first and last tests that utilized the same reaction conditions indicated that the catalyst had become more active and more selective toward alcohols during the testing program.

A second catalytic test utilizing a fresh portion of the $CuO/ZrO_2 = 10/90$ mol% catalyst (2.0 g) calcined at 350°C was initiated to determine the reproducibility of the activity and selectivity observed in the first test with this catalyst. The influence of carbon dioxide and of steam in the reactant mixture on the catalytic activity of the Cu/ZrO_2 catalyst will be determined during the next quarter of research and will be reported in the next quarterly progress report.

Overall 4QFY95 Objectives

Future plans for Task 3 will focus on the following areas:

(i)   Continue studies of increasing the conversion of H_2/CO to higher alcohols by promotion of the $C_1 \rightarrow C_2$ carbon chain growth step over Cs-promoted $Cu/ZnO/Cr_2O_3$ and MoS_2 catalysts,

(ii)   Enhance the $C_2 \rightarrow C_3 \rightarrow C_4$ carbon chain growth steps over $Cs/Cu/ZnO/Cr_2O_3$ catalysts, and

(iii)   Prepare and test high surface area Cu/ZrO_2 catalysts, both Cs-doped and undoped, that are candidates for the synthesis of C_1-C_5 alcohols, in particular branched products such as isobutanol.

Table 3.3.9 The Space Time Yields (g/kg catal/hr) of the Products Formed over the 10 mol% Cu/ZrO_2 Catalyst. Testing was carried out at 7.6 MPa with H_2/CO = 0.45 and 2.33 and with GHSV = 5500 and 6120 l/kg catal/hr. The %CO converted to products is also given for each test.

GHSV H_2/CO °C Product	6120 2.33 250	6120 2.33 310	5500 0.45 310	5500 0.45 330	5500 0.45 350	6120 2.33 250
MeOH	24.1	50.3	150.0	117.5	82.5	40.4
DME	5.3	70.0	18.0	32.2	43.4	0.4
H_2O		7.6	1.5	2.6	4.2	0.7
MF		0.9			0.8	
EtOH			0.8	0.6	1.0	
PrOH		0.4		3.7	3.3	2.5
i-BuOH				1.7	1.5	
%CO Conv.	1.4	4.8	3.4	3.0	2.7	1.9

3.3.3 Study of Reaction Conditions and Promotion of Group VIII Metals for Isobutanol Synthesis (University of Delaware)

Introduction

The basicity of a dopant compound is thought to be an important variable that can be utilized to beneficially tune the surface properties of promoted catalysts for higher alcohol synthesis. With this in mind, we compared LiOH as a dopant with our previous results on a $LiNO_3$-doped catalyst. The results demonstrated were again that excess alkali-doping did not lead to an enhancement in higher alcohol productivity. In contrast, those results on the effect of pressure and GHSV on higher alcohol synthesis are quite consistent with the literature. Increasing GHSV leads to enhancement of methanol production and suppression of higher alcohol formation. Higher GHSV, that is, lower residence time, decreases the time required for the slow chain propagation step on the surface, thus leading to less higher alcohols. Reaction pressure has similar effects on catalytic performance. Higher pressure shifts the equilibrium toward methanol production. Interesting results were observed in the study of the Group VIII metal promoted catalysts: while most of the metals show little effect on catalytic activity and selectivity, cobalt exhibits significant promotion on activity and stability of the catalysts, which reveals the unique and important role of the minimal amount of cobalt in our catalysts.

Experimental

The LiOH-promoted catalyst was prepared by incipient-wetness impregnation of F6KOHN with a LiOH solution. As reported before, F6KOHN was prepared by KOH precipitation of the mixed-nitrate solution at 60°C (composition: Zr/Cu = 2, Mn/Cu = 0.5, Zn/Cu = 0.5, CoO = 0.2 wt%), calcined at 400°C under nitrogen. The catalyst used in the experiments varying GHSV

and pressure was F6KOHNLi, which was prepared as above except that it was doped with LiNO₃. The catalyst precursor for studying Group VIII metal promotion was AF6KOHN, prepared as F6KOHN except that no cobalt was included. The Group VIII metal-promoted catalyst were denoted as MAF6KOHN, where M = Co, Rh, Ir, Fe, Ni, or Pd. The Group VIII metals were impregnated on the catalyst precursor by incipient-wetness method, at a 0.2/wt % level. The solutions used for the impregnations were: an aqueous nitrate solution of cobalt, nickel, or iron; an aqueous ammonium solution of $PdCl_2$; and a CH_2Cl_2 solution of $Rh(CO)_2$ acac (acetylacetonate) or $Ir(CO)_2$acac, respectively. The alkali-doped or metal-promoted catalysts were dried at 100-130°C overnight (no further calcination) before they were loaded into the reactor.

The standard reaction test procedure used in this study was: catalyst reduction at 260°C with $5\%H_2/N_2$ for 24 hours; reaction conditions of 950-1000 psi, $CO/H_2 = 1$, T = 350, 400, 425°C (~ 20 hr at each temperature), and GHSV = 2900/hr. For GHSV and pressure effects tests, the catalyst was run at 350°C, GHSV = 6700/h, and P = 1000 psi for 20 hours first, then at 400°C, GHSV = 6700/hr, and P = 1000 psi for 20 hours. The pressure was then increased to 1400 psi and the catalyst was run for about 20 hours while temperature and GHSV were maintained; finally, the temperature was raised to 425°C and the reaction was carried out for another 20 hours while P = 1400 psi and GHSV = 6700/hr. The reaction data for 600 psi were collected from another set of experiments with fresh catalyst. For all reaction tests, liquid product was released and collected from a condenser (-10°C) after each reaction period, and then it was analyzed by GC.

The compositions and preparation methods of the catalysts reported here are summarized in Table 3.3.10.

Table 3.3.10 Compositions and Preparation Methods of the Catalysts

Catalysts	Compositions	Preparations
F6KOHNLi	Mn/Cu = 0.5, Zn/Cu = 0.5, Zr/Cu = 2, CoO = 0.2 wt%, 4 wt% LiNO₃ doping	Coprecipitation by dropping KOH solution to nitrate solution. Final pH = 12, nitrogen-calcined and LiNO₃ doped.
F6KOHNLiOH	Same as above except LiNO₃ replaced by 4 wt% LiOH doping	Same as above except LiOH doping
F6KOHN	Same as F6KOHNLi except no doping	Same as F6KOHNLi except no doping
AF6KO0HN	Same as above but no cobalt was included	Same as above except no cobalt was included
RhAF6KOHN	Same as above but doped with 0.2 wt% Rh	AF6KOHN doped with Rh
IrAF6KOHN	Same as AF6KOHN but doped with 0.2 wt% Ir	AF6KOHN doped with Ir
FeAF6KOHN	Same as AF6KOHN but doped with 0.2 wt% Fe	AF6KOHN doped with Fe
CoAF6KOHN	Same as AF6KOHN but doped with 0.2 wt% Co	AF6KOHN doped with Co
NiAF6KOHN	Same as AF6KOHN but doped with 0.2 wt% Ni	AF6KOHN doped with Ni
PdAF6KOHN	Same as AF6KOHN but doped with 0.2 wt% Pd	AF6KOHN doped with Pd

Results and Discussion

LiOH Doping vs. LiNO₃ Doping

Since the alkali doping affects the acidity (basicity) of the catalyst surface, we expect that the composition of the alkali metal precursor could have some effect on performance of the catalysts. For this reason we tested a catalyst doped with LiOH solution, instead of $LiNO_3$ solution, as was used in the other Li-doped catalysts. The comparison of LiOH- and $LiNO_3$-doped catalysts is given in Table 3.3.11.

The time-on-stream plot in Figure 3.3.3 shows that the LiOH-doped catalyst behaves like the other doped or undoped F6KOHN catalysts, that is, relatively stable activity and selectivity, high CO_2 selectivity, and relatively low hydrocarbon selectivity.

Table 3.3.11 Liquid Product Selectivity (wt%) on LiNO₃- and LiOH-Doped Catalysts (@1000 psi, CO/H₂ = 1, GHSV = 2900/h)

Catalyst	T°C	MeOH	EtOH	nPrOH	iBuOH	Other	yield (g/g/h)
LiNO₃-doped	350	61.4	1.8	2.4	17.7	16.7	0.050
F6KOHN	400	25.3	4.5	5.9	22.9	41.4	0.078
	425	13.6	5.5	14.3	13.0	53.6	0.105
LiOH-doped	350	68.6	1.6	2.4	13.6	13.8	0.048
F6KOHN	400	24.3	5.5	8.0	19.0	43.2	0.082
	425	13.2	5.6	13.2	11.2	56.8	0.109

As with previous experiments, we found that doping with excess alkali produces little or no beneficial effect on our catalyst and may even be detrimental to higher alcohol synthesis, independent of the alkali precursor's composition.

Effects of GHSV and Reaction Pressure

Gas hourly space velocity (GHSV) and reaction pressure are two important variables for higher alcohol synthesis reaction. They could affect pathways of surface reactions and the thermodynamic equilibrium of the system, and have therefore been examined extensively in the higher alcohol synthesis literature. It was reported that relatively low GHSV is helpful for higher alcohol production since the relatively long residence time would allow more surface species to undergo chain growth to higher alcohols. The chain propagation step is always needed for any proposed mechanism for higher alcohol synthesis from CO hydrogenation. The effect of pressure is mostly addressed through thermodynamic equilibrium calculations. Higher pressure is more favorable for methanol formation than for the formation of higher alcohols. Hence, high pressure increases total alcohol productivity and probably higher alcohol productivity in terms of space time yield, but it does not enhance alcohol selectivity. In order to evaluate the effects of these factors on our catalysts, we tested them on catalyst F6KOHNLi. The experimental results are summarized in Table 3.3.12.

Table 3.3.12 Effects of Pressure and GHSV on the Alcohol Selectivity (wt%) and Yield of F6KOHNLi (@CO/H$_2$ = 1)

P (psi)	GHSV (l/h)	T°C	MeOH	EtOH	nPrOH	iBuOH	Other	Yield (g/g/h)
1000	2900	350	61.4	1.8	2.4	17.7	16.7	0.050
1000	2900	400	25.3	4.5	5.9	22.9	41.4	0.078
1000	2900	425	13.6	5.5	14.3	13.0	53.6	0.105
1000	6700	350	79.8	0.0	2.1	9.2	8.9	0.067
1000	6700	400	37.2	2.5	4.3	17.5	38.5	0.105
1400	6700	400	38.4	6.0	12.7	11.5	31.4	0.177
1400	6700	425	22.5	8.0	19.0	8.3	42.2	0.183
600	6700	350	70.4	0.0	1.7	12.9	15.0	0.025
600	6700	400	33.4	2.5	4.0	20.2	40.0	0.050
600	6700	425	20.6	4.3	8.4	15.2	51.4	0.050

When GHSV increases from 2900/hr to 6700/hr, methanol selectivity increases from 61.4 to 79.8% at 350°C and from 25.3 to 37.2% at 400°C; isobutanol selectivity decreases at the same time. These shifts in selectivity are not favorable for higher alcohol synthesis. However, a major advantage seen here is that the liquid yield is enhanced significantly with the increased GHSV. While isobutanol selectivity is not reduced excessively by more than doubling the GHSV, isobutanol yield is slightly enhanced, for example, from 17.9 to 18.3 mg/g/hr at 400°C. Therefore, some benefits in yield may accrue if we properly manage the GHSV in a certain range.

Another factor that is closely related to GHSV is the reaction pressure, which can alter the performance of the catalysts by changing the residence time of reactants on the surface. Table 3.3.11 provides the experimental results of the pressure effects on our catalysts.

With increasing reaction pressure from 1000 psi to 1400 psi, the higher alcohol selectivity patterns on the catalyst change significantly. Isobutanol selectivity is reduced, for example, at 400°C, from 17.5 to 11.5 wt%, while n-propanol selectivity is increased from 4.3 to 12.7%. Therefore, increased pressure favors n-propanol formation, but suppresses isobutanol selectivity. The clear advantage of applying higher pressure to the reaction is the great enhancement in total liquid productivity; for example, the productivity of the catalyst is almost doubled when pressure is raised from 1000 to 1400 psi at 400°C. When we consider the effect of pressure on the basis of isobutanol productivity (space time yield) instead of selectivity, we see the advantage of higher pressure. For example, increasing the pressure from 1000 to 1400 psi leads to enhancement of isobutanol yield from 18.4 to 20.4 mg/g/hr at 400°C, while isobutanol selectivity decreases significantly.

When the same catalyst was tested under a lower pressure of 600 psi, not only was a dramatically decreased liquid yield observed, but also little enhancement of isobutanol selectivity was realized. It seems that relatively high pressure is an essential requirement for efficient isobutanol production.

From these experimental results, it is reasonable to expect that a proper combination of high pressure and high GHSV could lead to high isobutanol yield, although low GHSV and moderate pressure are favored for higher isobutanol selectivity.

Time-on-stream plots in Figures 3.3.4 and 3.3.5 show stable performance of the catalyst, F6KOHNLi, under various GHSVs and pressures. From Figure 3.3.4 we can see another important advantage of applying higher pressure to the reaction. When the pressure was increased from 1000 to 1400 psi, not only were the CO/H_2 conversions increased, but also CO_2 and hydrocarbon selectivities were suppressed. This also points to the advantage of applying higher pressure, since we are seeking as low a hydrocarbon selectivity as possible.

Unfortunately, since we could not achieve pressures higher than 1500 psi (limited by CO gas tank pressure), it is impossible to take full advantage of these pressures/GHSV variables to optimize the performance of our catalysts for the best isobutanol yield.

Importance of Cobalt in Catalysts

A minor amount of cobalt in higher alcohol synthesis catalysts is considered a critical compositional factor. Cobalt's effect is discussed mechanistically as a chain growth promoter in the literature and in our previous work. However, questions such as the way global performance of a catalyst changes if other similar transition metals are used to replace the cobalt have not been carefully examined. The balance of this report will address this question using our most recent experimental results.

A series of catalysts was designed, prepared and examined to evaluate the effect of cobalt and other Group VIII transition metal promoters on the performance of these catalysts. The catalyst precursor, denoted as AF6KOHN, was made with exactly the same composition and preparation procedure as F6KOHN, except that cobalt was not included. With this as a starting material, various transition metals were impregnated onto the precursor using the incipient wetness method. The derived catalysts are coded as MAF6KOHN, where M = Co, Rh, Ir, Fe, Ni, or Pd, respectively. General performance of these catalysts is summarized in Table 3.3.13, and the time on-stream plots of them are provided in Figures 3.3.7-3.3.13.

Excluding the cobalt component from the catalyst increases the activity of the catalyst at low temperature (350°C), but higher temperature performance of the catalyst is also suppressed significantly. See CO conversion and liquid yield of the catalysts F6KOHN and AF6KOHN in Table 3.3.13. The poor high-temperature performance of the "no cobalt" catalyst is seen even more clearly when the time-on-stream plots of F6KOHN (cobalt coprecipitated) and AF6KOHN (no cobalt) are compared in Figures 3.3.6 and 3.3.7. Although the higher alcohol selectivity did not severely decline by excluding cobalt from the catalyst, the decreased total liquid yield, isobutanol selectivity, CO and H_2 conversions, and increase in hydrocarbon selectivity with increasing reaction temperature clearly show the important role played by cobalt at higher reaction temperature. Since higher alcohols were best produced at relatively high temperature, these results indicate that the minor amount of cobalt component in the catalyst is critical to maintaining high isobutanol yields.

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The behavior of the cobalt-doped catalyst, CoAFKOHN, confirmed the role played by cobalt in the catalyst, since it exhibited an activity pattern similar to that of the cobalt coprecipitated catalyst, F6KOHN (see Figures 3.3.6 and 3.3.8). Both catalysts, F6KOHN and CoAF6KOHN, exhibited increased CO conversion and liquid yield with increasing reaction temperature. However, the isobutanol selectivity on CoAF6KOHN was not as high as on F6KOHN (Table 3.3.13), which could be due to poorer cobalt dispersion on the doped catalyst.

Attempts to modify the performance of catalyst AF6KOHN by doping it with Rh or Ir proved ineffective. The Rh- or Ir-doped catalysts were slightly less active and less selective compared with the unpromoted catalyst, AF6KOHN, and their general performance was very similar to the unpromoted catalyst, AF6KOHN, (see Table 3.3.13 and Figures 3.3.9 and 3.3.10). However, the transition metal precursors used and the treatment of the catalysts after doping of the precursor could be responsible for the ineffective promotion of the catalysts by Rh and Ir. The catalysts were prepared by incipient wetness impregnation of AF6KOHN with $Rh(CO)_2acac/CH_2Cl_2$ or $Ir(CO)_2acac/CH_2Cl_2$. No further pretreatment was carried out except to dry the materials at 100°C before reduction and reaction. This treatment might not be vigorous enough to produce sufficient interaction of the promoter with oxide surface. Therefore, further experiments are needed to examine the effect of calcination on the doped catalysts.

Ni or Pd promotion of the catalysts also did not improve the alcohol selectivity and productivity. Like the Rh- or Ir-promoted catalysts, Ni- or Pd-promoted catalysts have shown performance similar to the unpromoted catalyst AF6KOHN, that is, low isobutanol selectivity and decreased activity with increasing temperatures (see Table 3.3.12 and Figures 3.3.11 and 3.3.12). An exceptional result is observed with the Fe-promoted catalyst, FeAF6KOHN. The minor amount of Fe doping results in high CO conversion and high liquid yield, even at low temperature (350°C); see Table 3.3.12 and Figure 3.3.13. Unfortunately, few alcohols are produced in the reaction. The liquid, which appears as two phases, contains water and other hydrocarbon components. Hence, Fe promotion does not seem worth further exploration.

The ineffective promotion by most of the Group VIII transition metals studied to date undoubtedly arises from a combination of factors such as the precursors of the promoters and thermotreatment after doping. A more thorough examination of these approaches will be studied and reported in the future. However, the effective promotion of the catalysts by cobalt is a conclusive result largely independent of these secondary factors.

Conclusions

Basic alkali dopant LiOH, like the other alkali dopants studied before, shows no promotion for higher alcohol synthesis. Pressure and GHSV can significantly affect catalyst activity and selectivity. While low GHSV and moderate pressure favor improved isobutanol selectivity, properly selected high GHSV and high pressure can have the advantage of increasing isobutanol yield. Cobalt is an important promoter for maintaining high activity and selectivity for higher alcohol synthesis. In contrast with cobalt, most of the other Group VIII transition metals are ineffective promoters of our catalysts by the methods of doping and calcination used to date.

Future Work

Future work will focus on further examinations of precipitation methods, post treatment of the catalyst precursor, and reduction of the copper level in the catalyst to avoid agglomeration and to improve space time yield.

Table 3.3.13 Comparison of Performance of Group VIII Metal Doped-Catalysts

Catalysts	T°C	CO Conv. %	Yield g/g/h	MeOH wt%	nPrOH wt%	iBuOH wt%	Other wt%
F6KOHN	350	9.30	0.060	69.2	1.1	14.8	14.3
	400	18.9	0.083	27.3	2.0	24.0	43.6
	425	23.4	0.086	13.3	5.6	19.3	54.4
AF6KOHN	350	15.7	0.121	60.6	0.0	15.0	24.4
	400	11.4	0.075	30.4	2.3	20.8	46.5
	425	10.0	0.043	18.1	5.1	17.9	58.9
RhAF6KOHN	350	10.4	0.118	69.5	0.0	10.5	20.0
	400	8.10	0.080	38.1	2.0	20.4	39.6
	425	5.50	0.048	26.3	4.3	19.0	50.4
IrAF6KOHN	350	12.3	0.110	65.4	1.0	10.9	22.7
	400	11.7	0.068	33.3	1.8	18.7	46.2
	425	8.70	0.050	21.0	3.9	16.8	58.3
FeAF6KOHN	350	39.6	0.118				
	400	45.1	0.148				
	425	35.0	0.100				
CoAF6KOHN	350	8.2	0.050	65.7	2.0	8.3	23.9
	400	12.4	0.081	21.0	9.9	14.2	55.0
	425	22.4	0.106	12.7	15.7	8.1	63.5
NiAF6KOHN	350	10.7	0.095	59.0	2.2	11.6	27.2
	400	12.7	0.071	28.0	4.9	17.8	49.3
	425	10.3	0.054	19.9	5.6	17.1	57.3
PdAF6KOHN	350	17.2	0.142	53.8	1.7	14.5	30.0
	400	13.0	0.103	25.7	4.1	17.4	52.7
	425	10.7	0.058	19.7	6.0	17.5	56.8

Figure 3.3.3 Reaction Performance of F6KOHNLiOH (350-425°C, 1000 psi, CO/H2 = 1)
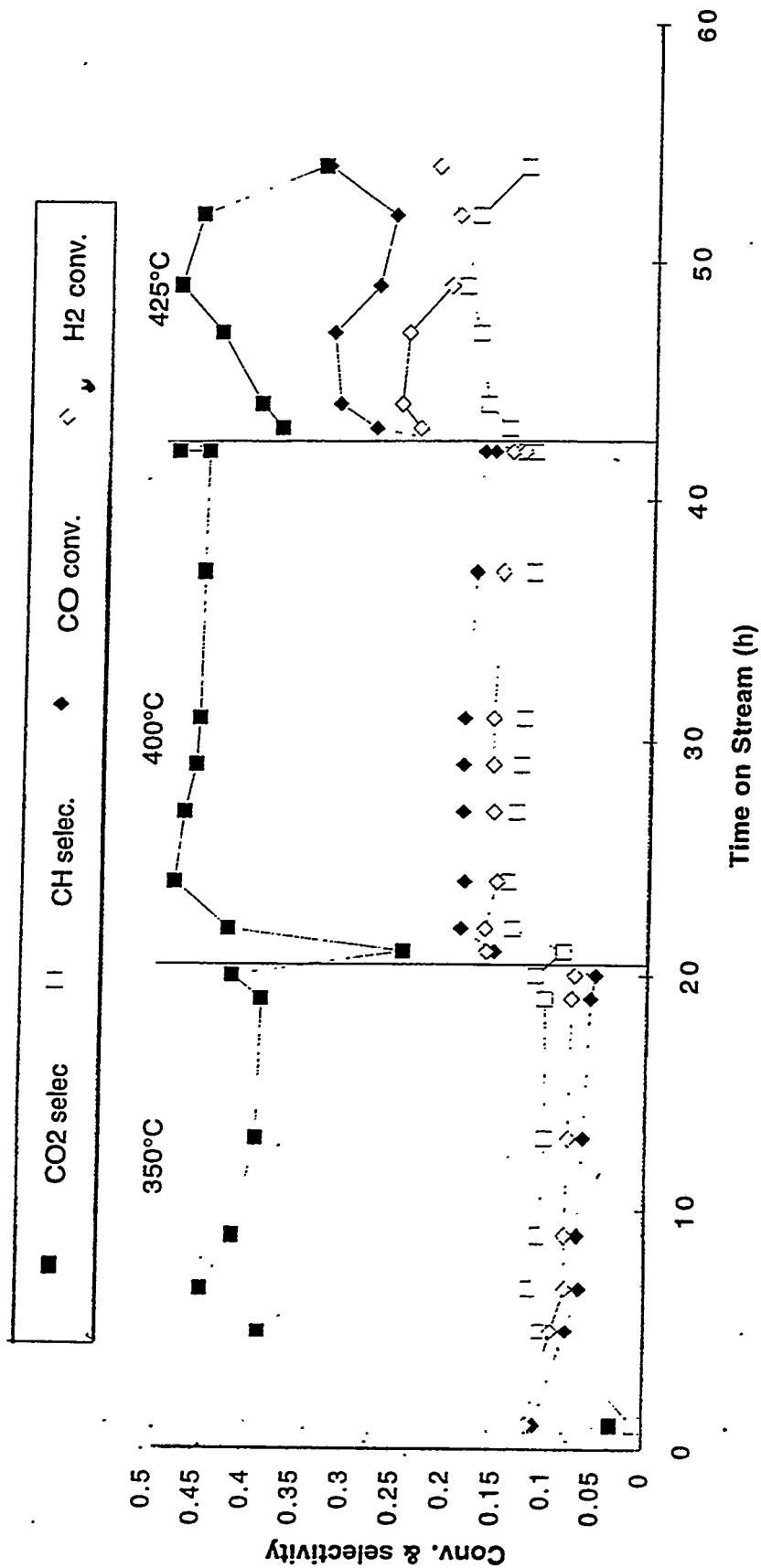
Figure 3.3.4 Effect of Pressure on the Performance of F6KOHNLi (GHSV = 6700/h, CO/H2 = 1)
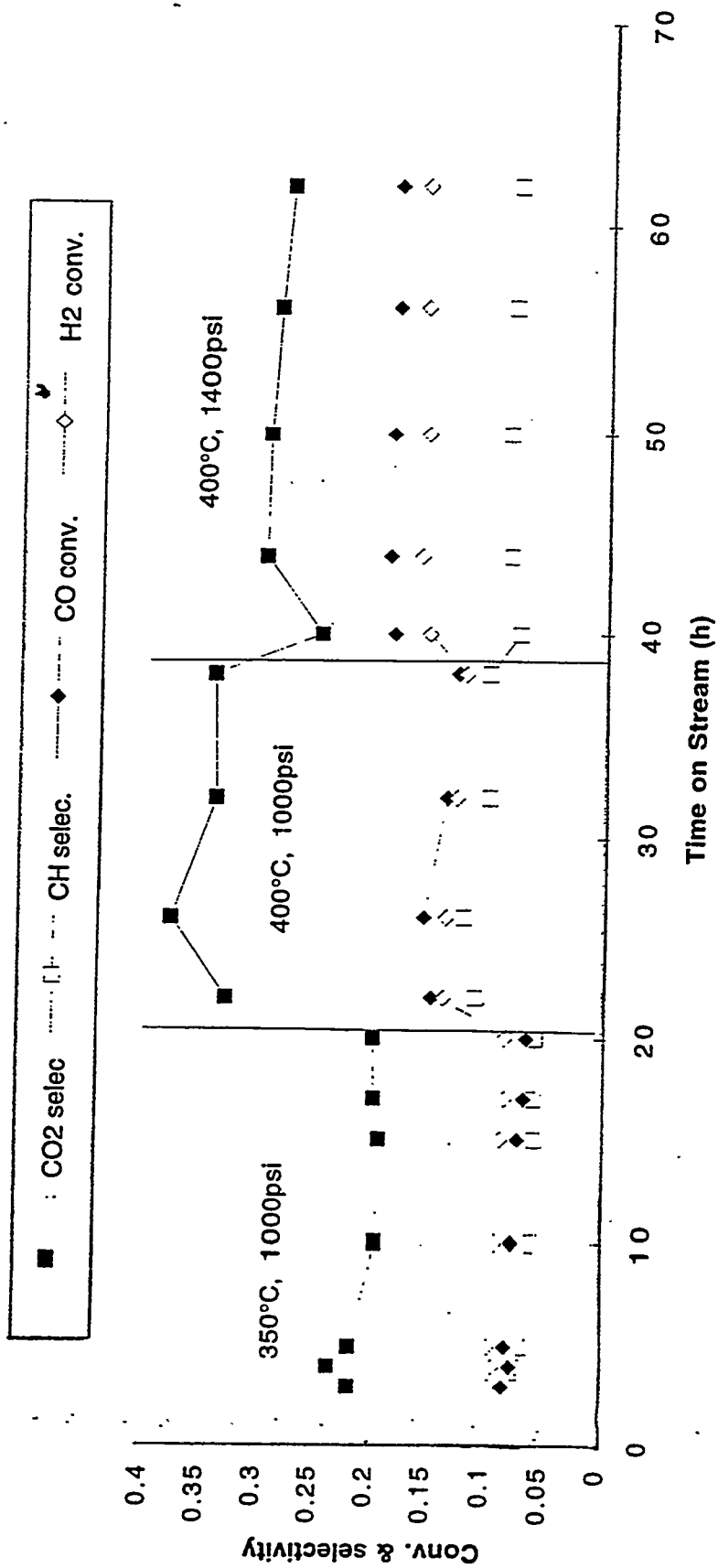

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Figure 3.3.5 Reaction Performance of F6KOHNLi at Low Pressure (350-425°C, 600 psi, CO/H2 = 1)
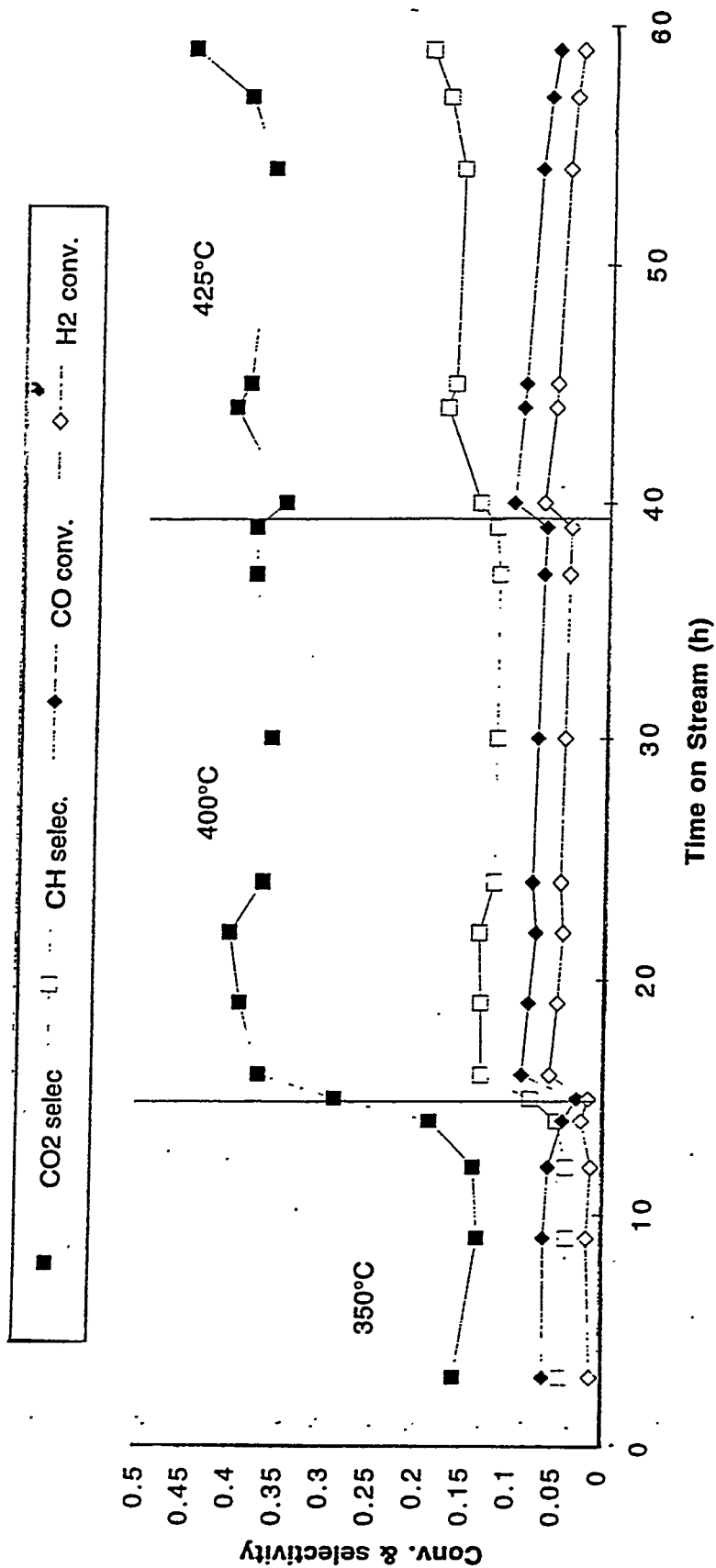
Figure 3.3.6 Reaction Performance of F6KOHN (350-425°C, 1000 psi, CO/H2 = 1)
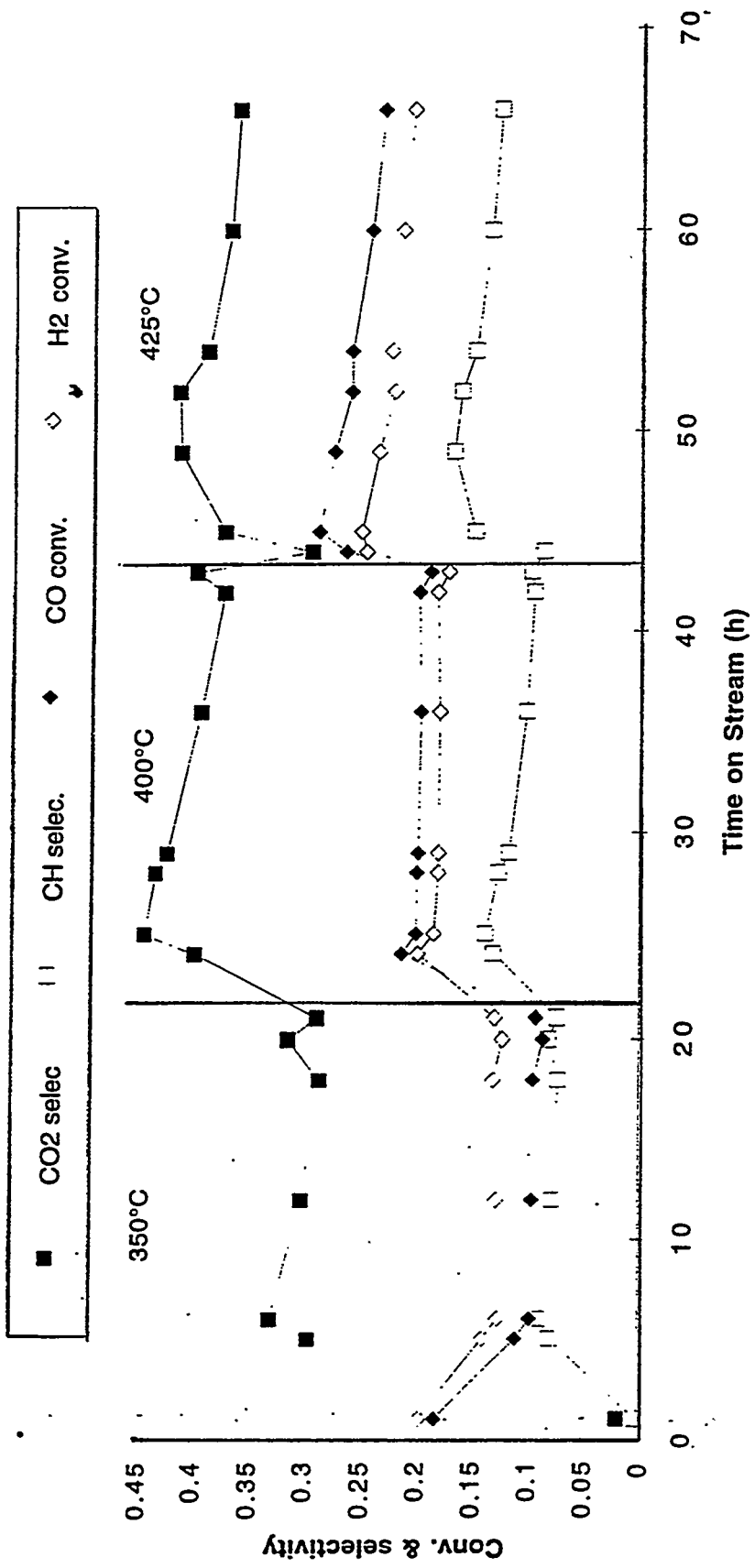
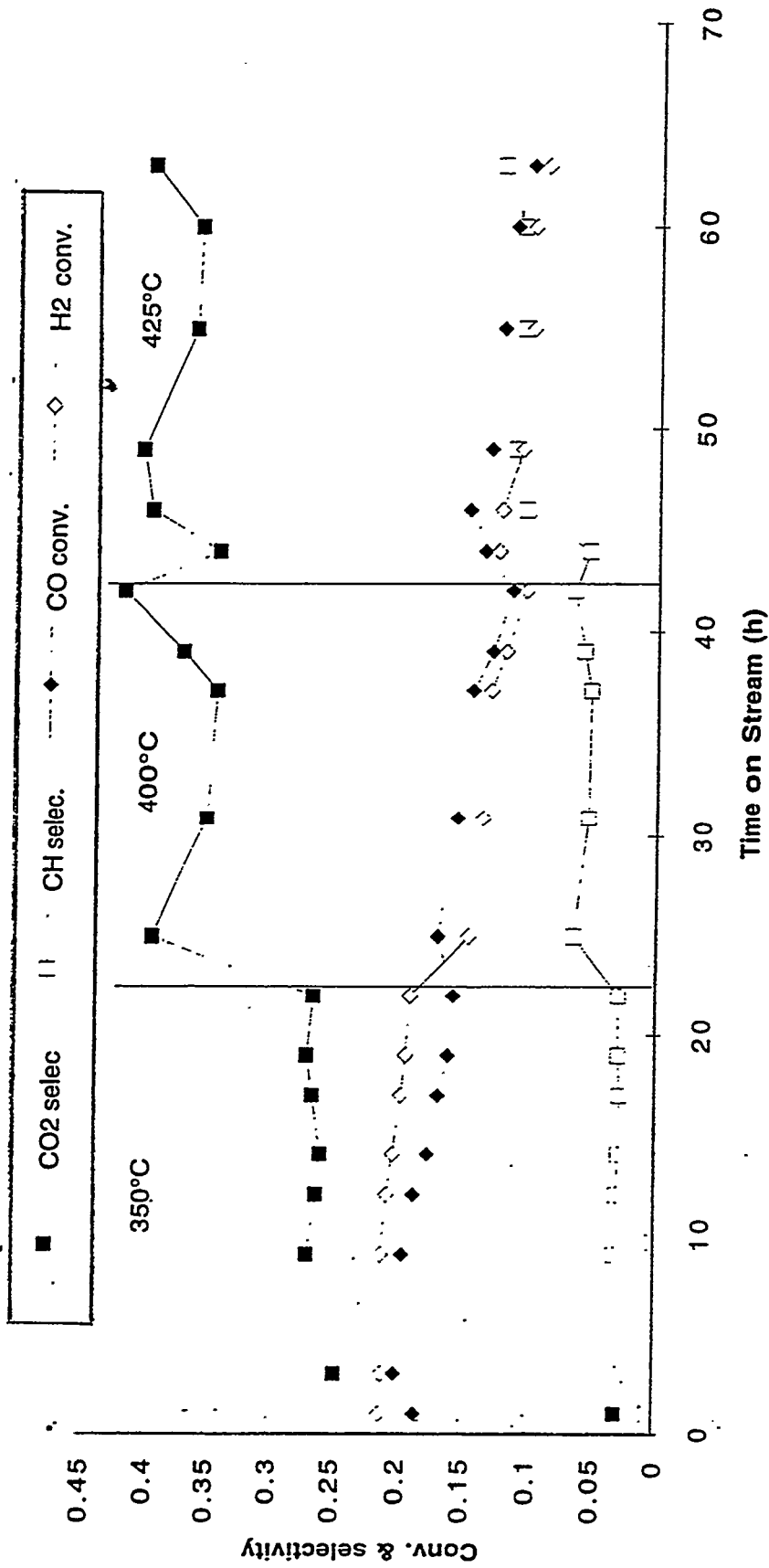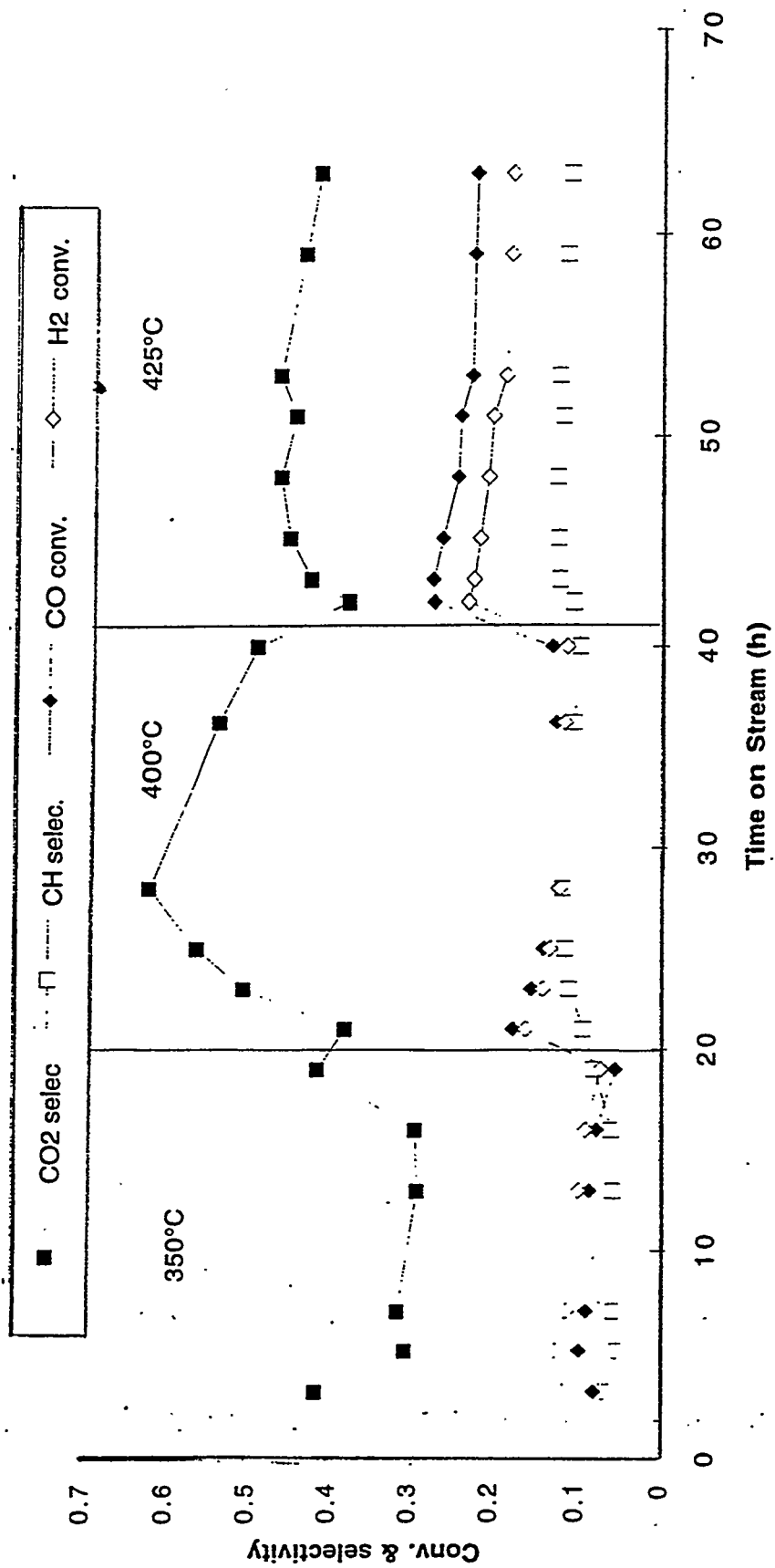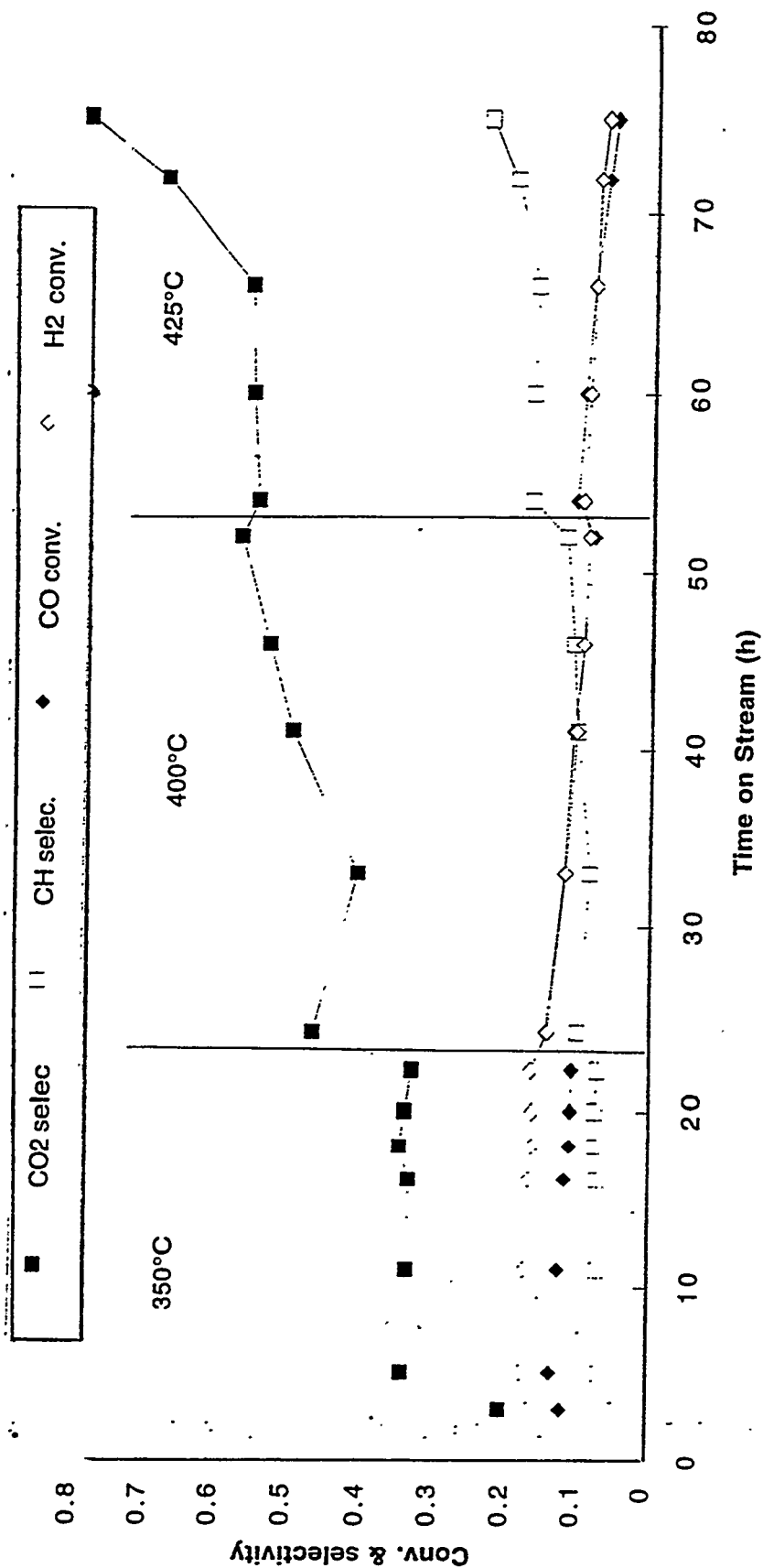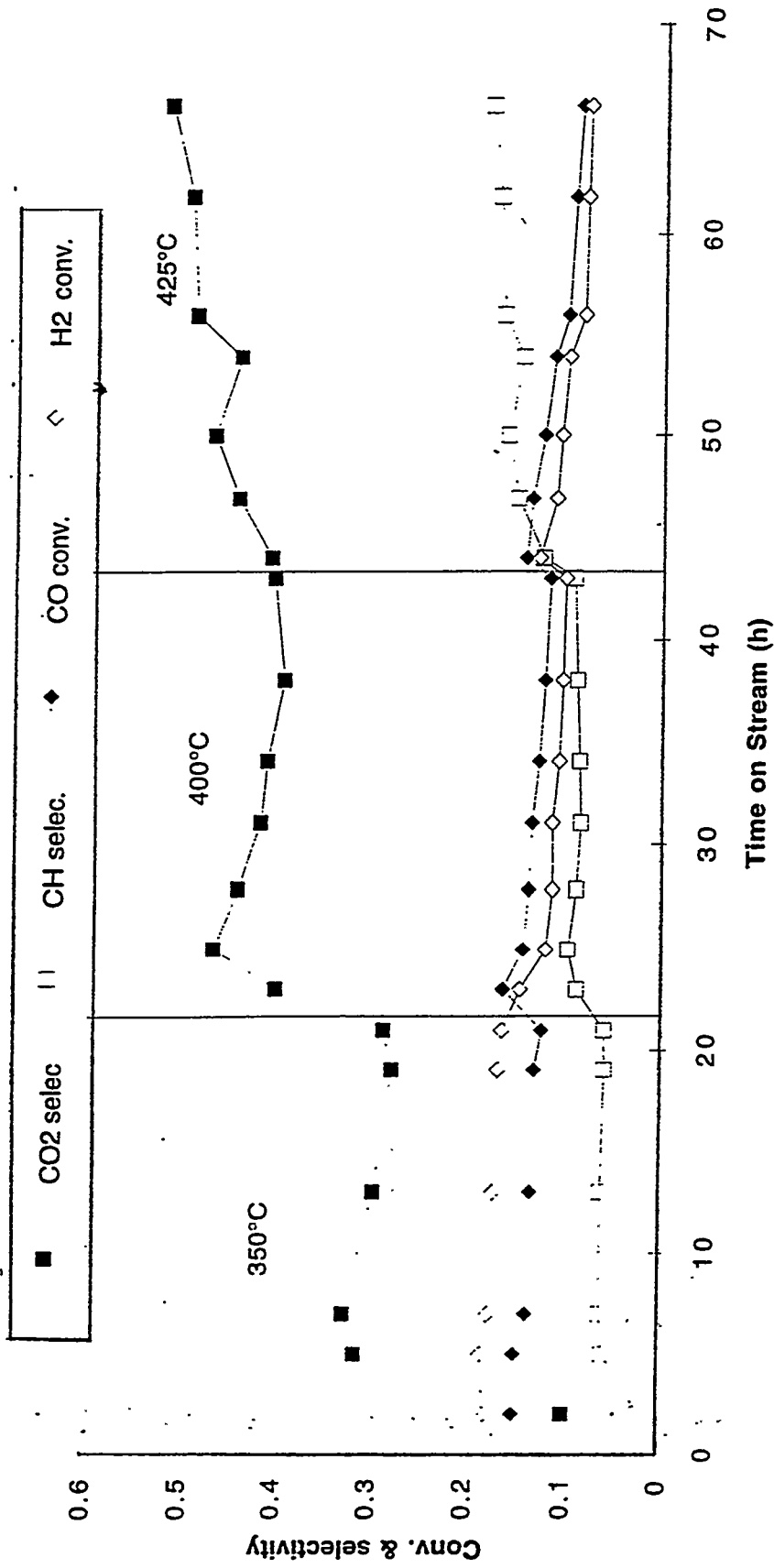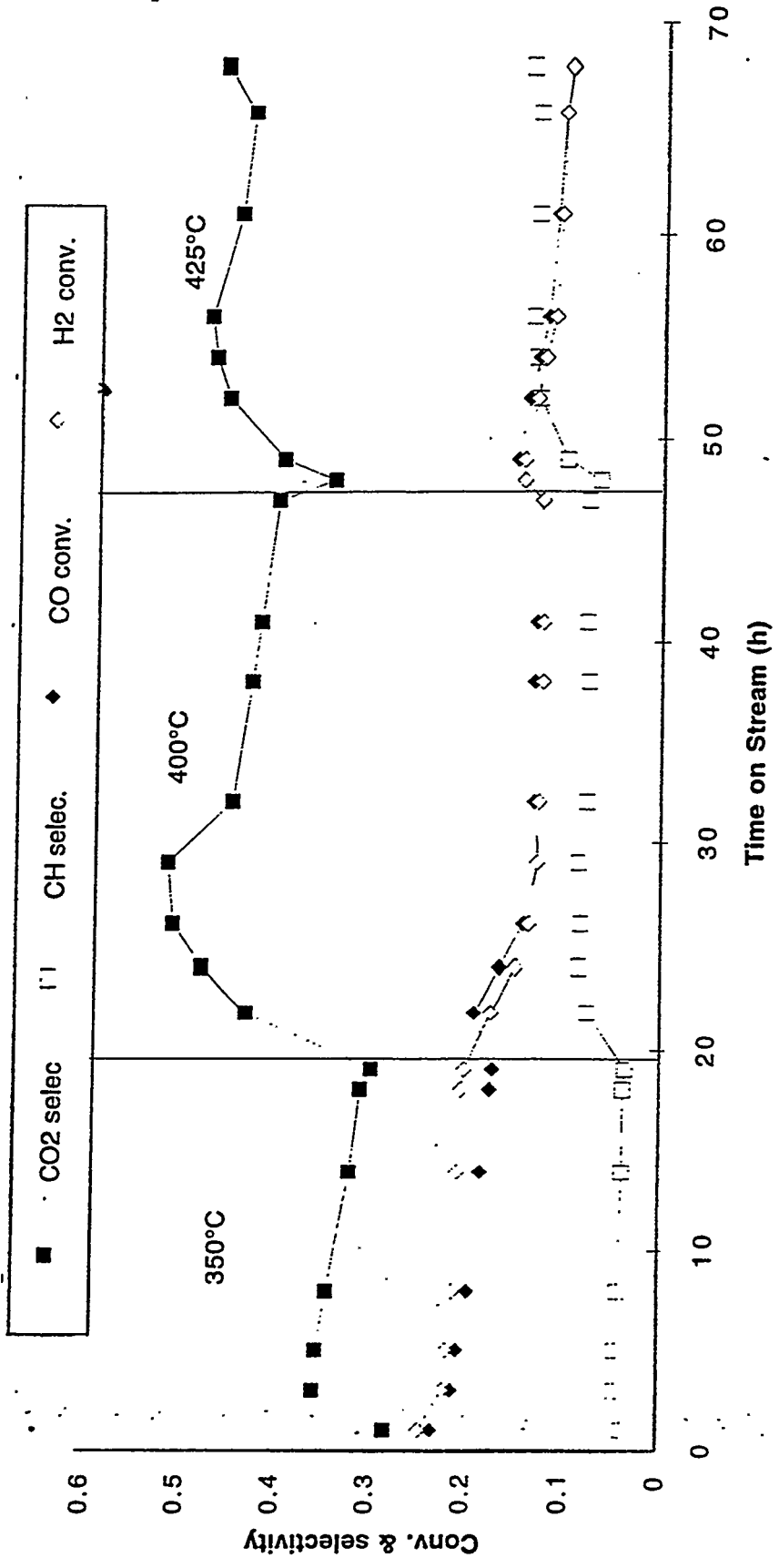Figure 3.3.7 Reaction Performance of AF6KOHN (350-425°C, 1000 psi, CO/H2 = 1)

Figure 3.3.8 Reaction Performance of CoAF6KOHN (350-425°C, 1000 psi, CO/H2 = 1)

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Figure 3.3.9 Reaction of Performance of RhAF6KOHN (350-425°C, 1000 psi, CO/H2 = 1)

Figure 3.3.10 Reaction Performance of IrAF6KOHN (350-425°C, 1000 psi, CO/H2 = 1)

Figure 3.3.11 Reaction Performance of PdAF6KOHN (350-425°C, 1000 psi, CO/H2 = 1)

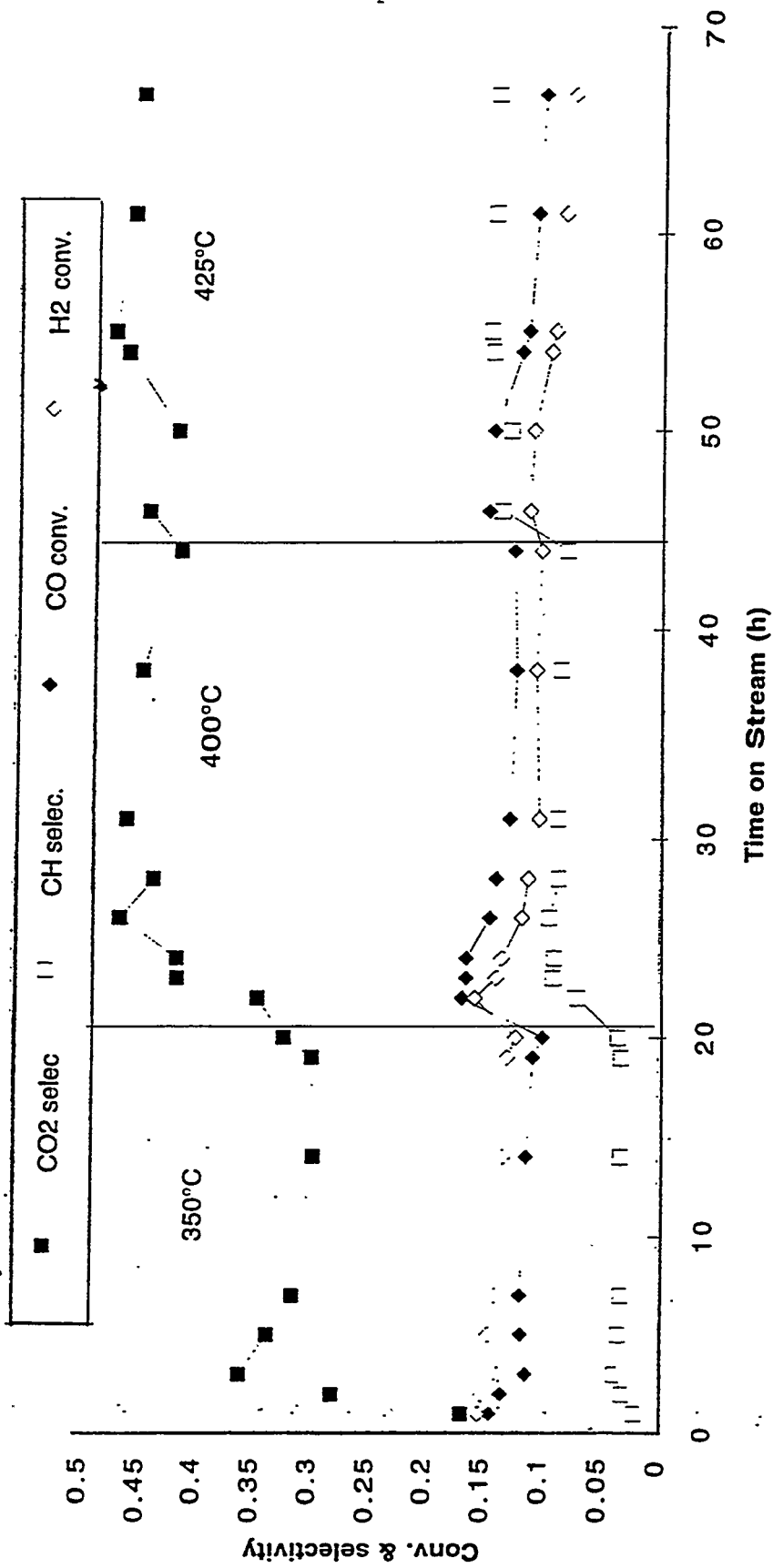**Figure 3.3.12 Reaction Performance of NiAF6KOHN (350-425°C, 1000 psi, CO/H2 = 1)**
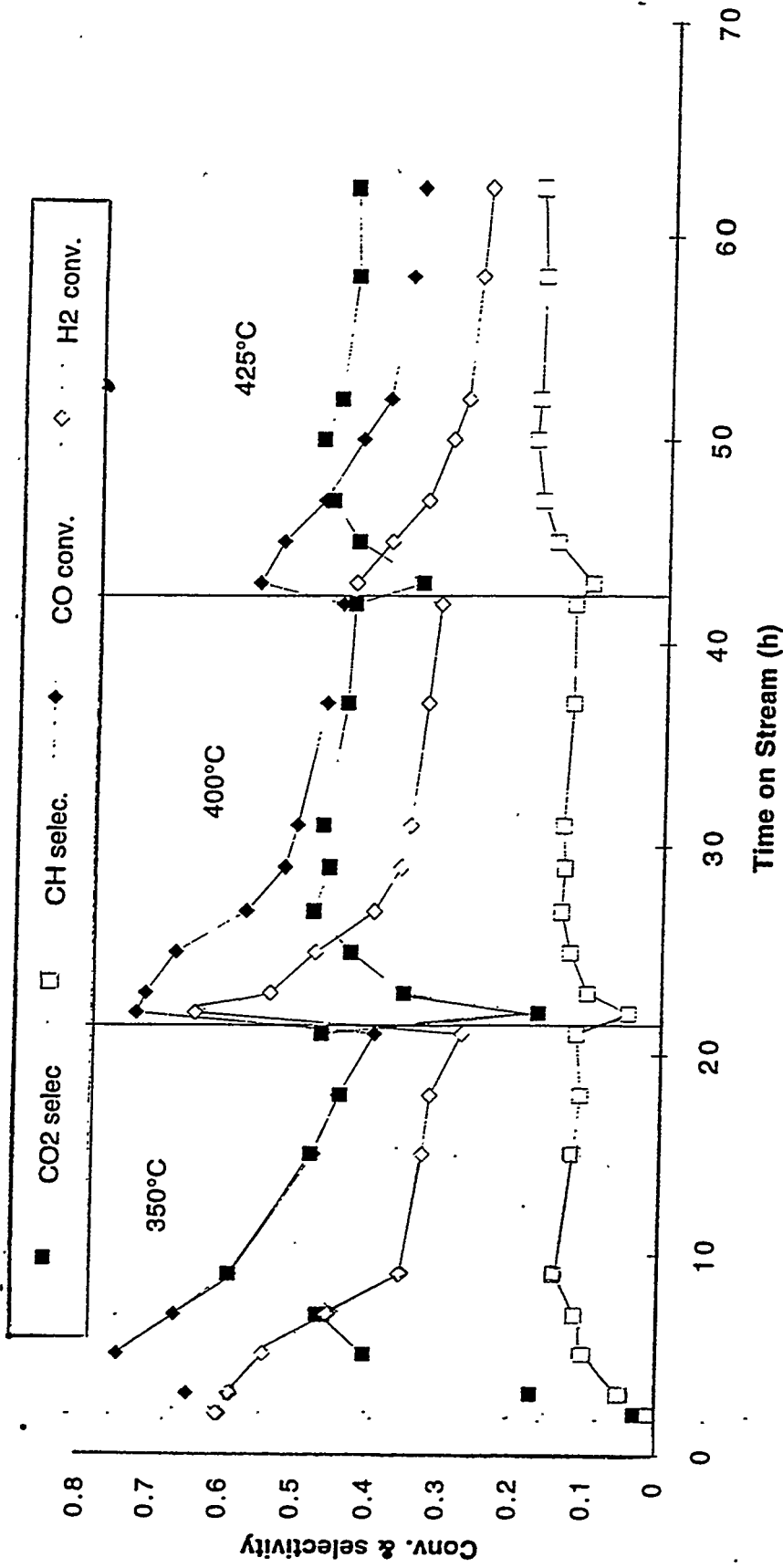
Figure 3.3.13 Reaction Performance of FeAF6KOHN (350-425°C, 1000 psi, CO/H2 = 1)

TASK 4: PROGRAM SUPPORT

Bechtel began work late in the quarter on the program support items specified in the last quarterly report. Some of their preliminary results are covered in the June monthly report. The work will be written up in more comprehensive fashion in the next quarterly report.

TASK 5: PROJECT MANAGEMENT

Reports and Presentations
A draft topical report was issued on the results of the Fischer-Tropsch II demonstration run recently completed. Comments have been received from DOE personnel on the report. The suggestions will be incorporated in the final report.

B. L. Bhatt presented a paper entitled "Productivity Improvements for Fischer-Tropsch Synthesis" at the 14th North American Meeting of the Catalysis Society. The paper, which was co-authored by Shell and DOE personnel, was well received.

Monthly reports for April, May, and June were prepared and submitted to DOE as scheduled. A draft Quarterly Report (No. 2) for the period January 1995 through March 1995 has been prepared.

Management Activities
The R&D subcontract with Eastman Chemical was finally organized and ratified by all parties. Congratulations to all for a Trojan effort!