containing 1 liter of water. This procedure is done under vigorous stirring, at a temperature of 353 K and a constant pH (resp. 9, 10 or 1 liter). After the addition, which normally takes 90 min, the suspension is stirred for 12-14 h, filtered, suspended again in 1 liter of deionized water and stirred for 1 h. After this washing procedure the solid is filtered again and pelletized in teflon matrices (3 x 3 mm). Subsequently the pellets are dried at 400 K for 12 h. The pellets were calcined in a quartz tube using flowing air (heating rate 5°/min; 3 h constant at 600 K).

Impregnation with 0.25 wt% Pd(acac)2 is performed in acetonitrile solution (30 ml) without stirring. After disappearance of the yellow color, the solution is decanted. After drying under flowing air at ambient temperature the pellets are calcined as described above.

This set of twelve catalysts includes Falter's best catalysts compared to other less active and less selective ones described in his thesis. Their behavior will enable us to compare the present isobutanol unit with the former one.

Analysis of these samples, using AAS, BET and XRD is in progress and will be presented when all data are available. As mentioned before, a laboratory spray dryer has been installed, and, in addition to pelletizing, some of the above described catalysts were spray dried for later use under slurry conditions.

2. Semibatch (Discontinuous) Slurry Reactions

In order to gain information about the catalysts in a shorter time, semibatch reactions are carried out. For this purpose more laboratory autoclaves are needed. Within the next week the institute workshop will finish new autoclaves that can withstand a pressure of 300 bars and temperatures up to 700 K. With this setup, catalysts can be screened for their selectivity towards oxygenated products, especially isobutanol and methanol.

3. Objectives of Catalyst Design

To optimize the catalysts it is important to obtain information regarding composition, surface, porous structure and crystalline or amorphous phases.

The good properties of the alkaline-promoted Zr/Zn/Mn-system have been shown. Falter found that the pH of the precipitation has a major impact on catalyst behavior. However, it was not clear in what way pH change influenced the catalyst. For that reason current research aims at investigating one specific variable, keeping the others constant.

The final alkaline content in the Falter catalyst after precipitation is determined by the washing procedure. The influence of this factor has been investigated by preparing a set of catalysts at constant pH, only varying the amount of washing water. Another approach to introduce an exact amount of alkaline metal would be the impregnation of an alkaline free catalyst. To meet with this objective we plan to synthesize alkaline-free Zr/Zn/Mn catalysts.

Precipitations are performed using complexing agents, e.g., mono- and bidentate ligands, containing oxygen or nitrogen. In fact, ammonia and hydroxyl can be regarded as the smallest ligand representatives. Therefore precipitations with aqueous ammonia solutions were investigated. Finding a pH-value at which Mn^{+2} is nearly fully precipitated as the hydroxide,

without dissolving $Zn(OH)_2$ as an ammonia-complex, has not yet been accomplished. Further reactions with other amine bases, for example, tetramethylammoniumhydroxide (TMAH), are planned.

As bidentate complexing agents, ammonium oxalate, aminoacids or hydroxyacids are well suited. With ammonium oxalate an almost quantitative precipitation was observed.

The generation of porosity by thermal decomposition reveals an additional effect of these complexing agents which can be controlled by steric modifications.

4. Inert Liquids

In the continuing research for a suitable inert liquid for slurry operations,synthesizing a decalin analogue with a higher boiling point was attempted in order to improve the separation characteristics in the continuous three phase system. Starting from 2-methylnaphthaline, the fully saturated product, 2-methyldecalin could be obtained quantitatively by hydrogenation reaction with $Pd/Al_2O_3(5\%)$ at 560 K and 200 bars. The product was characterized by MS. In stability tests with syngas at 620 K and 200 bars, this compound showed the same behavior as decalin.

TASK 4: PROGRAM SUPPORT

Much of the planned work in this task will be carried out Bechtel. A subcontract with Bechtel is currently being arranged and is expected to be in place by the end of the next quarter. Although Bechtel's principal responsibilities will lie in the area of syngas generation and cleanup, Air Products iis currently negotiating to add a further, high priority item to its slate. A combination of reduced manpower at Air Products coupled with Bechtel's abilities in the area of process innovation and techno-economic evaluation is leading to their assuming prime responsibility for the work under Task 4.1, Research Support Studies. A FY95 deliverable in this section is the preparation of isobutanol synthesis catalyst performance requirements for coal-based, resid-based and natural gas-based coproduction routes to MBTE. The target in the Alternative Fuels I contract (1990-94) was 50 gms/hr of isobutanol per kg catalyst, this in turn leading ultimately to a MTBE price of $1.20/gal. With a revised target of MTBE @ $.70/gal for 1995-2000, the new performance requirements need calculating as guidance for the university programs at Aachen, Delaware, and Lehigh.

TASK 5: PROGRAM MANAGEMENT

5.1 Reports and Presentations

A draft topical report entitled "Catalytic Dehydration of Isobutanol in a Slurry-Phase Reactor" was sent to DOE for review. This report described the LaPorte 8/93 results of dehydrating a feed of mixed alcohols, predominately isobutanol, to isobutylene, the necessary precursor to MTBE.

Monthly technical progress reports for October, November, and December were prepared and submitted to DOE.

The results of the second Fischer-Tropsch campaign at LaPorte were summarized and submitted in abstract form for presentation at the 14th North American Meeting of the Catalysis Society. The paper, entitled "Productivity Improvements for Fischer-Tropsch Synthesis," will be co-authored by DOE, Shell and Air Products personnel.

5.2 Management Activities

- Preaward work started in October at Air Products on the new cooperative program with DOE entitled "Alternative Fuels and Chemicals from Synthesis Gas." The Cooperative Agreement is not expected to be in place until December, however, DOE has formally notified us of their willingness to allow cost reimbursement back to October 3. The universities of Lehigh, Aachen, and Delaware will roll their work over from the Alternative Fuels I contract although their official subcontracts will not be in place until early spring. Eastman and Bechtel's subcontracts will also probably not start until then.

  At the end of December, DOE approved the Cooperative Agreement. The program will be funded in full for FY95, $8.8 million in total.

- A confidentiality agreement was signed between Air Products and Syncrude Technology (STI). Technical discussions were held through December between Air Products, STI, and DOE-PETC personnel for a proposed F-T run at LaPorte. The objective of the run would be to evaluate performance of catalyst-reactor system to confirm the design basis. A preliminary process flow diagram has been developed based on STI's desired operational envelope. Four line specifications were generated for new equipment required at LaPorte. Equipment and materials cost for the modifications was estimated at $425,000. The total cost of the run is expected to be $2,028,000.

- Bogdan Slomka from Iowa State University visited LaPorte in early November. He has been working on sonic-assisted cross-flow filtration. For removal of solids from coal liquefaction products, they have demonstrated a 2.7 fold increase in filtrate flux with sonic treatment. They plan to evaluate the F-T spent slurry from LaPorte (F-T I) next.

- A visit to Institut Francais du Petrole (IFP) revealed that they have stopped work on their (linear) higher alcohols process because of the unfavorable economics relative to MTBE production. They have switched their syngas work over to Fischer-Tropsch chemistry.

- An abstract was submitted for a presentation of the F-T II results at the 14th North American Meeting of the Catalysis Society. The paper entitled "Productivity Improvements for Fischer-Tropsch Synthesis" will be co-authored by Shell and DOE personnel.

Quarterly Progress Report III: Preparation, Examination and Characterization of the Factorially Designed Catalyst Matrix

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University of Delaware

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April 12, 1995

For the Period October–December 1994

Summary: Factorially designed catalysts are prepared for the evaluation of the effects of variation in the primary oxide components on the activity and selectivity of higher alcohol synthesis catalysts. Namely, a two level , three factor full factorial design was performed on the ratios of MnO/CuO, ZrO_2/CuO, and ZnO/CuO, which resulted in an eight sample catalyst matrix. All these catalysts were examined between 300-425°C and at 1000 psi of total reaction pressure. The XRD patterns of the catalysts before and after use were collected to characterize their solid state structures. Gas components and liquid products were analyzed by on- and off-line GCs to derive conversion and selectivity data. Experimental results showed that each of the factors indeed had significant influence on the higher alcohol synthesis performance of the catalysts, which in turn provided important information for optimizing the catalyst composition toward better isobutanol productivity. Basically, chemometric treatment of the reaction data indicated that increasing the ZrO_2/CuO ratio and decreasing the MnO/CuO ratio significantly enhanced the isobutanol selectivity and suppressed the n-propanol production. The XRD patterns of the used catalysts show the presence of crystalline metallic copper, ZrO_2, ZnO, and MnO with different relative intensities depending on their contents. In contrast the fresh samples before reduction and reaction display low crystallinity and more amorphous-like diffraction patterns.

Introduction

In this quarter, our reaction testing and characterization mainly focused on the factorially designed catalysts for evaluation of the individual components of the previously examined catalysts. The basic idea is to systematically change the metal oxide compositions to explore the effects of them on the higher alcohol synthesis selectivity and activity with specific interest on isobutanol production from CO hydrogenation. With the help of the chemometric evaluation of the reaction data, we were able to determine the major effects of the oxide components on higher alcohol synthesis. X-ray diffraction was carried out to characterize the bulk structural changes of the catalysts. The performance of the catalysts in a stainless-steel reactor and copper-lined reactor also were compared.

Experimental

The catalyst design and preparation are as follow: according to the literature and our previous results, CuO, MnO, ZnO and ZrO_2 are most essential components of the higher alcohol synthesis catalysts, especially for isobutanol synthesis, therefore, we chose the MnO/CuO, ZnO/CuO, and ZrO_2/CuO ratios as our main factors and we changed their ratios from high to low levels. This results in a three factor, two level full factorial sample matrix. The catalyst preparation procedure was reverse precipitation, i.e., the catalysts were prepared by dropping corresponding amounts of metal nitrate solution into the K_2CO_3 basic solution until a neutral pH was reached. The precipitates were then washed with deionized water, dried at 130°C (overnight), calcined at 400°C (2h in air), pelletized and sieved. Each sample also included a fixed amount of CoO. The calcined catalysts were doped with 4wt% of K_2CO_3. The coding and basic compositions of the catalysts are listed in the Tables 1 and 2.

After finishing the catalyst preparations of the factorially designed sample matrix, we carried out the reaction testing of the catalysts at T=300-425°C, P=1000psig, CO/H_2=1, and at a GHSV=2800/h.

Results and Discussions

Chemometric Evaluation of the Catalysts

Generally, this set of catalysts shows significantly different performance than the last set of six catalysts reported in the previous two quarterly reports. This difference arises from the significant changes that we have made in component levels.

Examination of the reaction data collected from the factorially designed sample matrix has been carried out by the chemometric regressional method. The compositions and alcohol productivities of the factorially designed catalysts are listed in the Tables 2 and 3. Clearly, n-propanol is the major higher alcohol product on the most of the catalysts, which is also shown in the detailed selectivity data listed in the Table 4. However, by changing the oxide compositions, n-propanol was successfully suppressed and the isobutanol selectivity was significantly enhanced on F5K and F6K, where we employed a high ZrO_2/CuO ratio and a low MnO/CuO ratio. The effects of the MO_X to CuO ratios on the alcohol productivities become even evident when we applied the multiple linear regressional analysis to the experimental data to evaluate the effect of each factor on the isobutanol productivity quantitatively:

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_1x_2 + b_5x_1x_3 + b_6x_2x_3 + b_7x_1x_2x_3$$

Here y is the isobutanol productivity; x_1, x_2, x_3 are the MnO/CuO, ZrO_2/CuO, and ZnO/CuO factors and the b's are regressional coefficients. The coefficients obtained from regression analysis are listed in the Table 5.

Clearly, the first order terms represent the main contributions to isobutanol productivity. Not surprisingly, the MnO/CuO and ZrO_2/CuO ratios turn out to be the most significant. Their signs indicate that a decrease in the MnO/CuO and an increase in the ZrO_2/CuO ratios would improve the productivity of isobutanol. The second order terms reflect the interactions between the factors. Therefore, decreasing the interaction between MnO and ZrO_2 by decreasing the MnO/CuO ratio also would be helpful for isobutanol production. Similarly, we performed the regressional analysis

on the isobutanol selectivity and n-propanol selectivity. The results of the evaluation are listed in the last two rows of the Table 5.

Therefore, an increase in the ZrO_2/CuO ratio, and a decrease in the MnO/CuO ratio. both first order terms, would be beneficial for enhancing isobutanol selectivity and suppressing n-propanol selectivity. This is crucial since as we have pointed out in our previous reports, these catalysts as originally composed did produce high levels of n-propanol indicating that the slow step between C_1 and C_2 alcohols was effectively catalyzed. Hence, it seemed logical to explore a means to shifting the selectivity more favorably towards isobutanol. These results constitute the first indications of how this may be achieved. The second order terms are showing similar effects on the isobutanol selectivity as discussed above. However, second order interactions are relatively more complex, especially for n-propanol selectivity. They may have a major effect on the product selectivity in the limiting cases of the first order terms. Therefore, we can optimize the product selectivity by adjusting the component ratios as defined by the factorial design, which helps us to minimize the catalyst screening process and to get to a more fundamental evaluation of the catalysts. But this small factorial design is by no means complete. For a complete evaluation of the catalysts, we would need to examine more factors on such a systematic basis.

Performances of the Catalysts

The performances of the catalysts discussed in this report are summarized in the Table 6. Generally, CO and H_2 conversions are low (less than 10%) when temperature is lower than 350°C, but the conversions are drastically increased at 425°C. At a temperature higher than 350°C, the CO_2 selectivity could be as high as 50%, which is a apparently due to fast water gas reaction at high temperature. The CO_2 formation could be beneficial in that the reaction would remove the water produced by the FT reaction and higher alcohol synthesis reaction. However, the contribution from FT reaction to the production of water and hydrocarbon is not very significant, which can be inferred from the hydrocarbon selectivity data listed in the Table 6. The hydrocarbon selectivity is generally less than 15% even at temperatures as high as 425°C.

Most of the catalysts discussed here are tested at three different temperature levels and over a period of 20 hours at each temperature, therefore, total reaction time on stream for the catalysts is over 60 hours. During this period, the catalysts showed fairly stable CO and H_2 conversions. CO_2 and hydrocarbon selectivities (see the plots of catalytic performance versus reaction-time-on-stream in Figures 1 to 9.)

Stainless Steel Reactor versus Copper Lined Reactor

In order to examine the possible influence of stainless steel reactor materials on the hydrocarbon productivity during the synthesis reaction, we have tested a copper-lined reactor. The experimental results do not show any significant difference between the two types of reactors with regard to total CO conversion, oxygenate selectivity, or hydrocarbon selectivity (see F6K and F6K/Cu in Tables 4 and 6, and Figures 6 and 7.) This result is reassuring since our previously reported data were taken in an unlined stainless steel reactor tube, and the similar performance of the two types of reactor now rules out the possible catalytic contribution of the reactor materials. Nonetheless, we will use the copper lined-reactor to run all reactions from this point forward to avoid the possible background reactions from the stainless steel reactor.

X-ray Powder Diffraction Characterization of the Catalysts

All of the catalysts, 8 fresh samples prior to the reduction and reaction, and the 8 corresponding samples after reduction and use in the actual catalytic reaction, have been subject to XRD measurement in the range of 2 Theta from 10 to 90 degree at 30mA and 40KV. The approximate compositions of the samples are listed in the Table 2. All of the fresh catalyst samples show low crystallinity and more amorphous-like XRD features. But after reduction and use in the higher alcohol synthesis reaction, the samples show sharp XRD lines. This provides an indication of the phase transformations that occur during reduction and the course of reaction.

Not copper oxide but metallic copper is observed on the XRD patterns of the used catalysts. The relative intensities of the XRD lines correspond well to the original content of the materials.

No other metal phase is detected by XRD on the used samples. The metal oxide phases that can be seen on the used catalysts include MnO, ZrO_2 and ZnO. Among these, MnO's XRD lines are always relatively weak even at loadings of 43 wt%. ZnO's XRD lines are relatively strong and sharp; ZrO_2 shows strong XRD lines at high loading but they are always somewhat broadened. The XRD patterns of the catalysts before and after reactions are shown in the Figures 10 to 17.

For the catalysts with high ZrO_2/CuO and low MnO/CuO ratios, F5K and F6K, which have shown enhanced isobutanol selectivity, the XRD patterns show very weak to unobservable MnO lines but relatively strong ZrO_2 diffraction lines (see Figures 14 and 15.) There are other minor XRD lines in the XRD patterns of the used catalysts that have not been identified, but which might be due to spinel formation during the catalytic reaction.

Future work

From these experimental results using the chemometric design we have gotten important information with regard to the critical compositional factors that can lead to optimizing these catalysts for isobutanol production. Exploring the effects of the other components and factors of the catalysts and reactions, specifically, the alkali metal oxides (such as Li, K, Cs), the minor transition metal components (such as Co, Rh, Ir, Pd), different preparative procedures (such as precipitation pH, temperatures), and calcination conditions (such as air versus N_2 calcination) will be important aspects of the future work of this project.

Table 1. Sample matrix

MO_n/CuO ratio	F1K	F2K	F3K	F4K	F5K	F6K	F7K	F8K
MnO/CuO	+1	+1	+1	+1	-1	-1	-1	-1
ZrO_2/CuO	+1	+1	-1	-1	+1	+1	-1	-1
ZnO/CuO	+1	-1	-1	+1	+1	-1	+1	-1

Note: All the catalysts are composed of MnO, ZrO_2, ZnO, CuO in addition to the constant amounts of Co and K_2CO_3, "+1" and "-1" represent the MO_n/CuO ratio of 2 and 0.5, respectively.

Table 2. Approximate compositions (wt%) of the factorially designed catalysts(calculation)

	F1K	F2K	F3K	F4K	F5K	F6K	F7K	F8K
MnO	22.5	27.9	43.8	31.8	6.8	8.8	10.4	16.3
ZrO_2	39.1	48.4	19.0	13.8	47.0	61.3	18.1	28.3
ZnO	25.8	8.0	12.6	36.5	31.1	10.1	48.0	18.7
CuO	12.6	15.7	24.6	17.9	15.2	19.8	23.4	36.6

Table 3. Alcohol productivity of the catalysts (425°C, 1000psi, CO/H_2=1) (mg/g/h)

Catalysts	MeOH	EtOH	iPrOH	nPrOH	2BuOH	iBuOH	nBuOH
F1K	9.96	4.55	9.23	32.0	5.04	8.49	2.71
F2K	9.14	6.20	6.41	19.0	3.47	6.09	1.68
F3K	4.34	7.68	6.77	20.8	3.64	4.75	3.23
F4K	10.7	8.49	9.54	20.0	6.56	4.92	1.49
F5K	15.7	3.87	5.42	13.8	5.81	13.7	2.32
F6K	9.68	2.44	5.17	13.2	3.85	16.2	1.32
F7K	1.38	2.94	8.83	11.6	11.0	6.44	2.76
F8K	2.55	1.85	10.8	16.4	15.1	7.13	3.96

Table 4. Analysis of Liquid Products

Cat	*MeOH*	*EtOH*	*iPrOH*	*nPrOH*	*2BuOH*	*iBuOH*	*nBuOH*	*Other*	*yield (g/g/h)*
F1K	8.3%	4.1%	8.3%	28.7%	4.6%	7.5%	2.4%	36.1%	1.23E-01
F2K	9.0%	6.5%	6.8%	20.0%	3.7%	6.3%	1.7%	46.0%	1.05E-01
F3K	4.5%	8.3%	7.4%	22.7%	4.0%	5.1%	3.4%	44.5%	1.01E-01
F4K	7.5%	6.3%	7.0%	14.8%	5.0%	3.6%	1.1%	54.8%	1.49E-01
F5K	12.5%	3.3%	4.7%	11.8%	5.1%	11.5%	1.9%	49.2%	1.29E-01
F6K	10.6%	2.9%	6.0%	15.4%	4.6%	18.7%	1.5%	40.2%	9.40E-02
F6K/cu	11.5%	4.1%	4.4%	16.0%	3.4%	15.1%	1.5%	44.0%	8.80E-02
F7K/cu	7.5%	8.3%	9.5%	30.6%	4.4%	8.8%	3.0%	28.0%	1.02E-01
F8K/cu	10.0%	8.5%	7.5%	28.9%	5.4%	12.2%	6.3%	21.2%	8.00E-02

Note: Reaction conditions: 425°C, 1000psi, CO/H_2=1.
F6K/cu indicates F6K in copper lined reactor.

Table 5. Coefficients obtained from the multiple linear regressional analysis

	b_0	b_1	b_2	b_3	b_4	b_5	b_6	b_7
i-BuOH product.	8.48	-2.42	2.67	-0.07	-1.44	0.71	0.06	0.49
iBuOH selec.	7.8	-2.8	2.2	-1.0	-1.0	0.93	-0.38	1.0
nPrOH selec.	16.8	2.8	0.45	-1.1	2.1	1.3	2.2	1.6

Table 6. Performance of the Factorially Designed Catalysts

Catalysts	*T ℃*	*CO Conv.*	*H_2-Conv.*	*Yield (g/g.h)*	*Selectivity*		*C_2OH+ in liquid*
					CO_2	*HC*	
F1K	300	3.1%	2.9%	0.004	5.7%	0.7%	2.1%
	350	4.7%	4.3%	0.030	35.0%	6.4%	12.9%
	425	32.8%	23.7%	0.120	40.2%	10.7%	55.6%
F2K	300	1.7%	1.1%	/	11.6%	1.7%	
	350	5.4%	3.2%	0.012	29.7%	7.5%	20.7%
	425	31.5%	22.4%	0.110	31.2%	10.0%	45.0%
F3K	300	2.5%	0.3%	/	9.0%	1.7%	
	350	7.2%	3.7%	0.008	20.2%	5.8%	22.3%
	425	39.7%	29.0%	0.096	38.4%	17.1%	51.1%
F4K	300	3.6%	3.7%	0.012	6.1%	1.0%	4.0%
	350	6.4%	6.0%	0.025	30.1%	7.7%	14.3%
	425	42.9%	32.1%	0.160	42.1%	16.5%	37.8%
F5K	300	3.8%	3.3%	0.002	6.2%	0.8%	
	350	5.9%	4.8%	0.022	27.3%	5.5%	
	425	37.9%	25.8%	0.129	39.1%	9.9%	38.2%
F6K	300	3.8%	2.4%	/	0.0%	1.5%	
	350	4.8%	3.8%	0.015	0.0%	7.7%	
	425	32.4%	22.8%	0.094	32.1%	11.9%	49.2%
F6K/cu	350	4.0%	3.6%		0.0%	8.0%	
	425	28.0%	17.0%	0.088	33.4%	12.3%	44.6%
F7K/cu	350	7.0%	2.4%	0.017	0.0%	6.9%	-
	425	25.5%	16.7%	0.102	23.1%	14.8%	64.5%

Figure 1. Reaction on F1K (425°C, 1000psi, CO/H2=1)

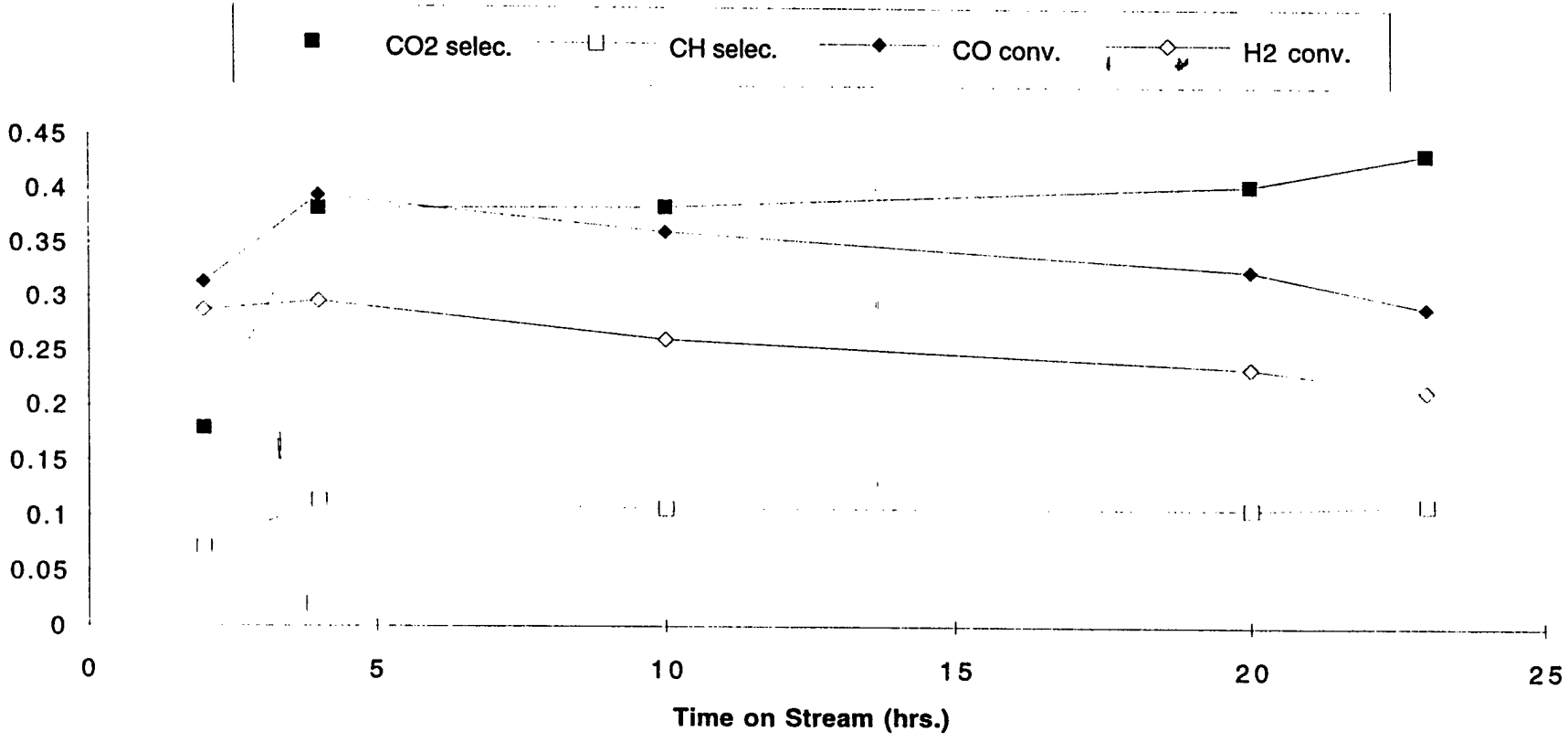

Figure 2. Reaction on F2K (425°C, 1000psi, CO/H2=1)

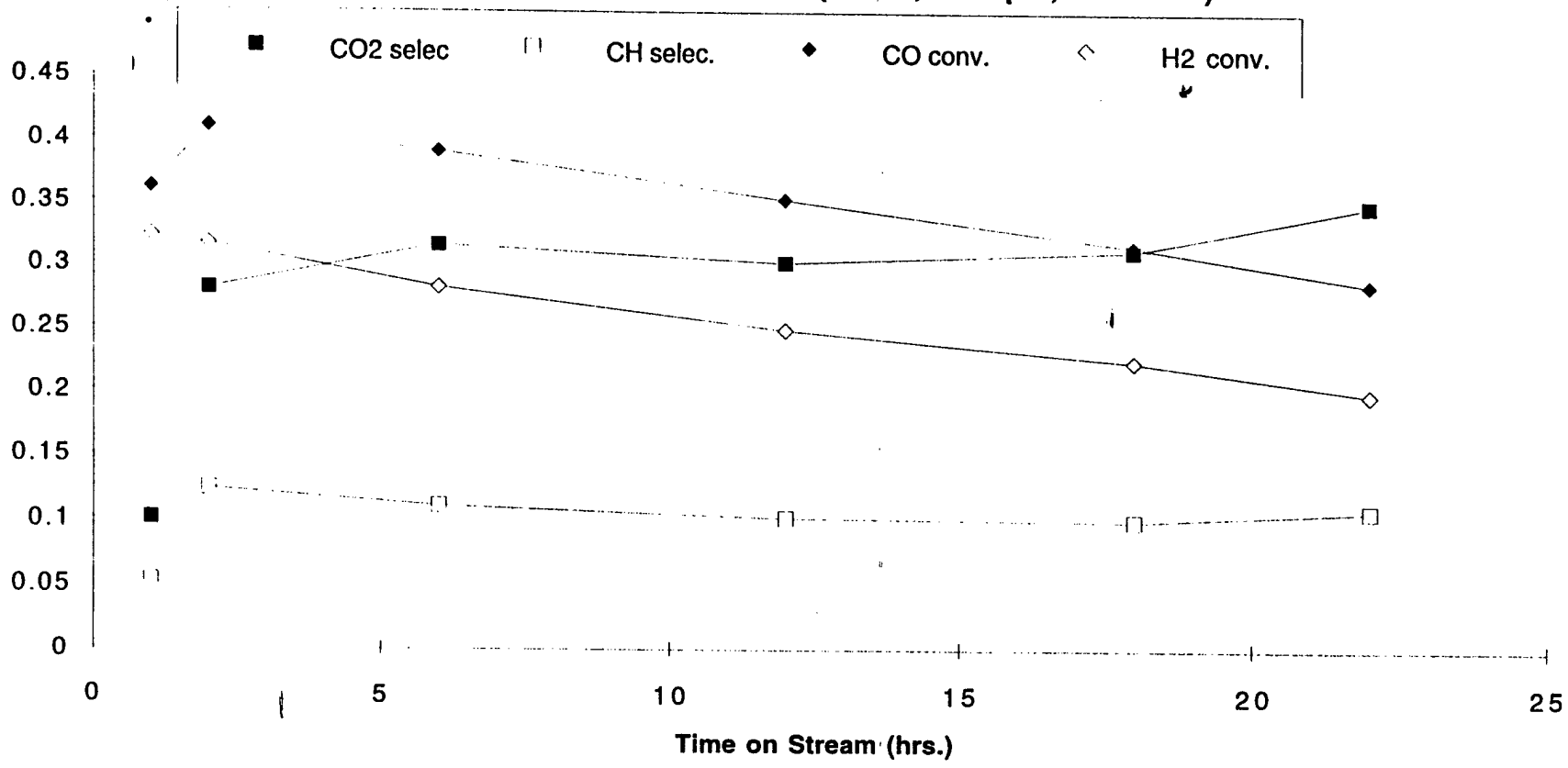

Figure 3. Reaction on F3K (425°C, 1000psi, CO/H2=1)

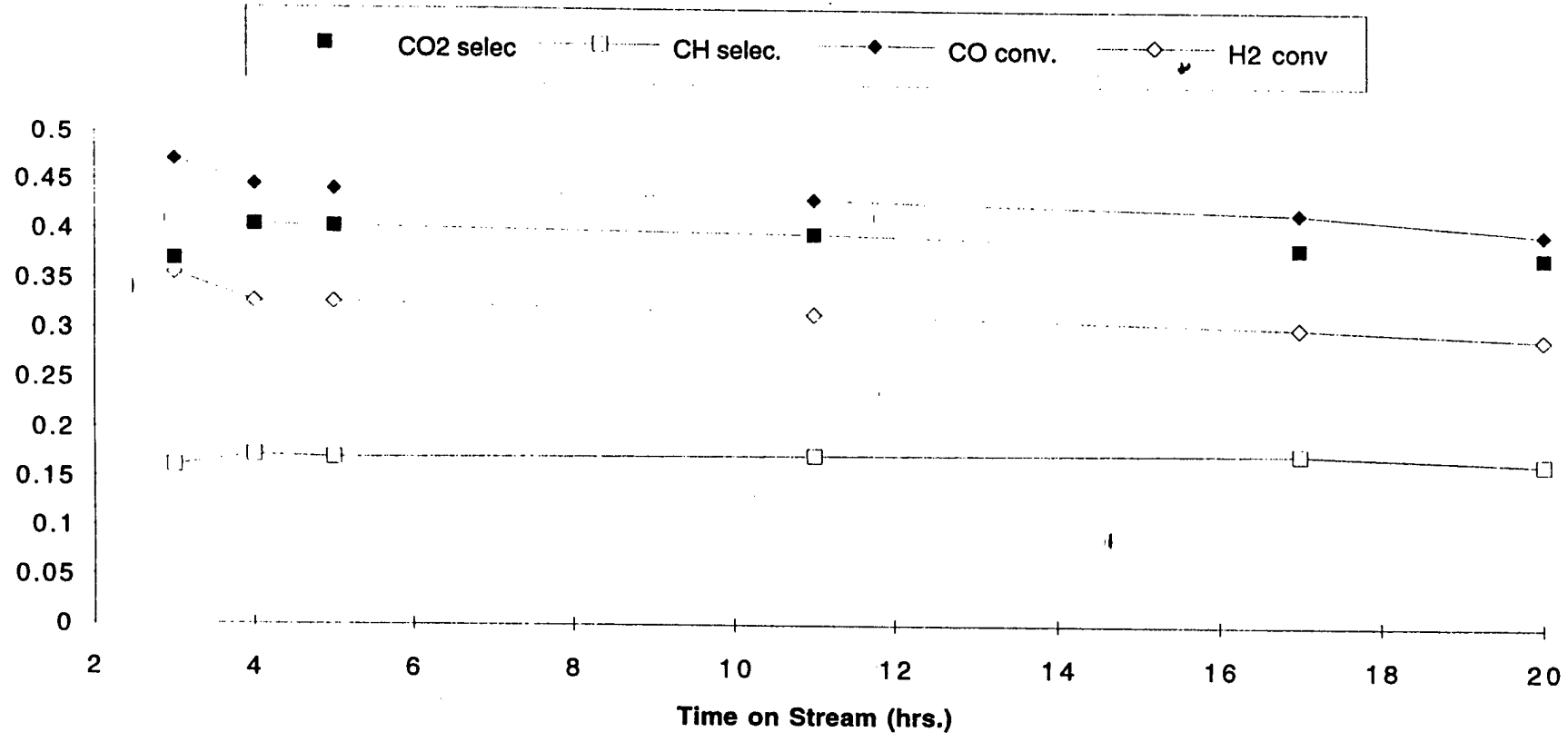

Figure 4. Reaction on F4K (425°C, 1000psi, CO/H2=1)

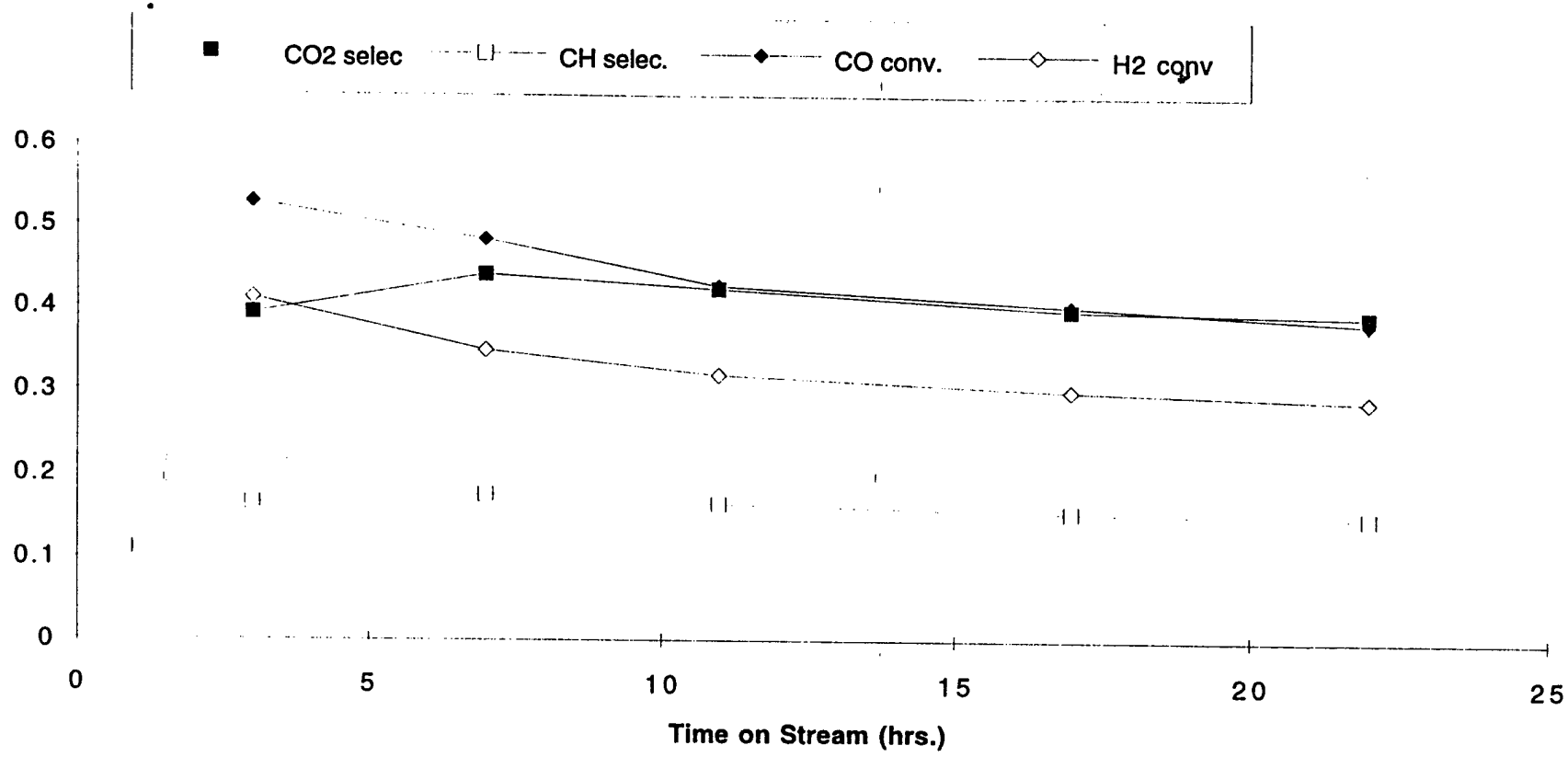

Figure 5. Reaction on F5K (425°C, 1000psi, CO/H2=1)

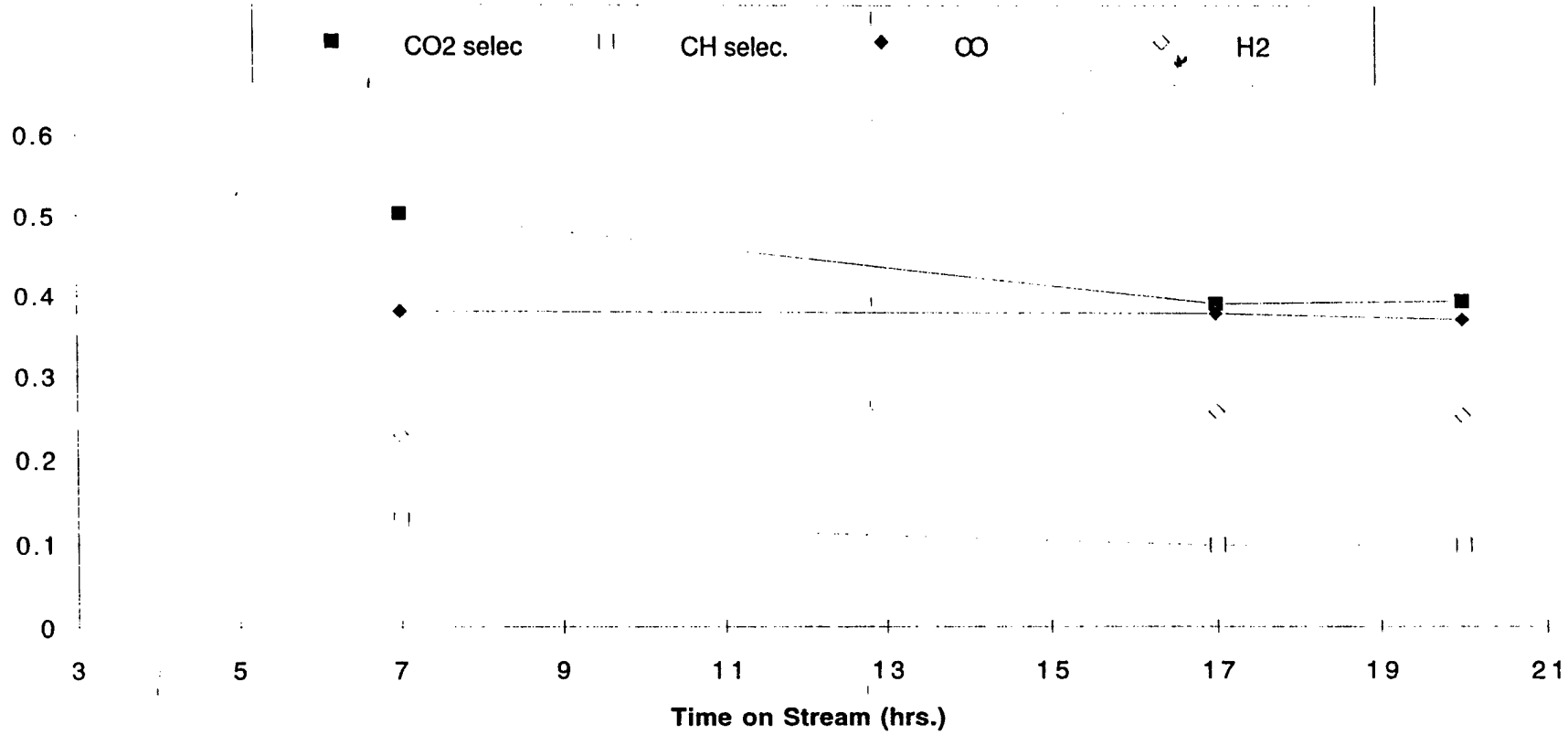

Figure 6. Reaction on F6K (425°C, 1000psi, CO/H2=1)

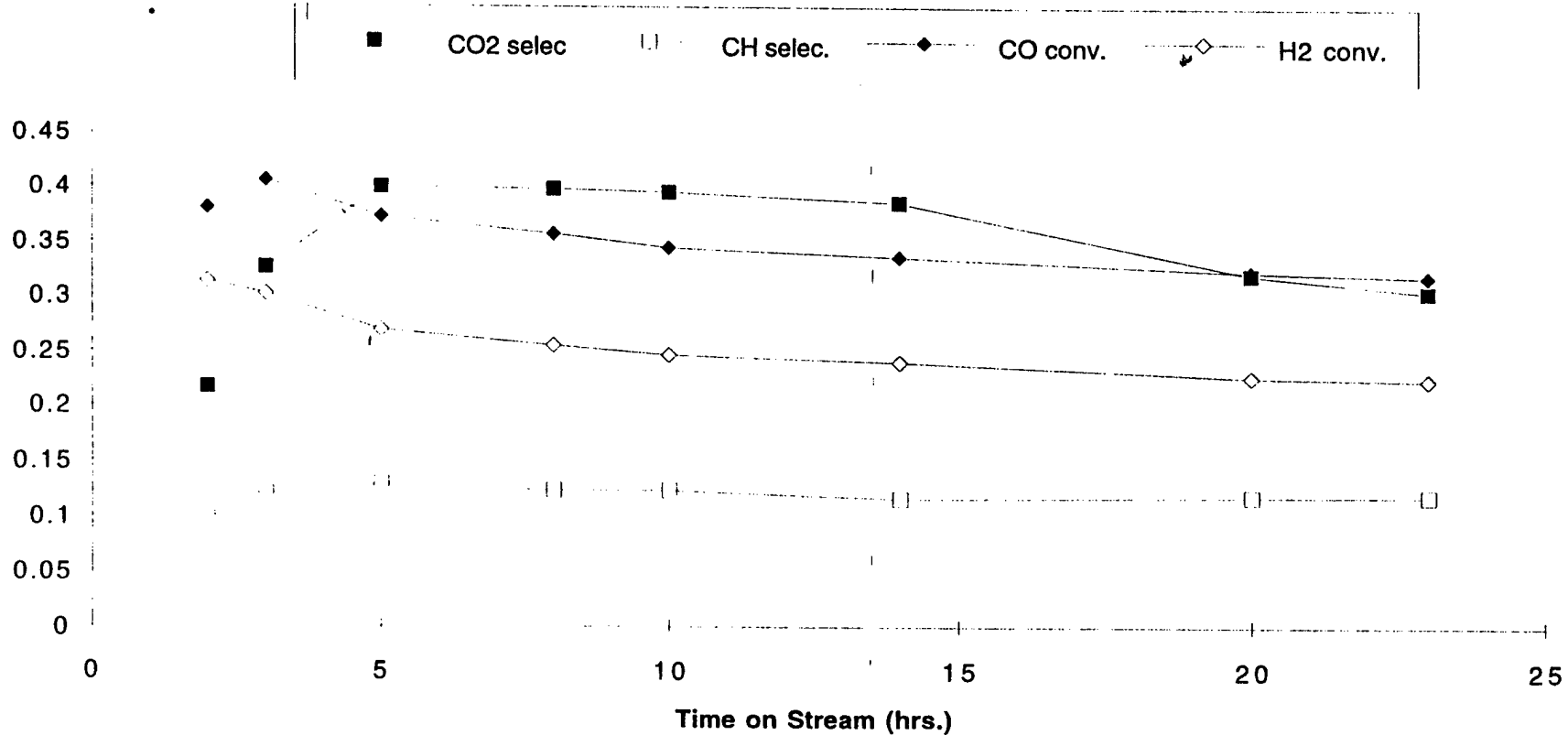

Figure 7. Reaction on F6K (cu)(425°C, 1000psi, CO/H2=1)

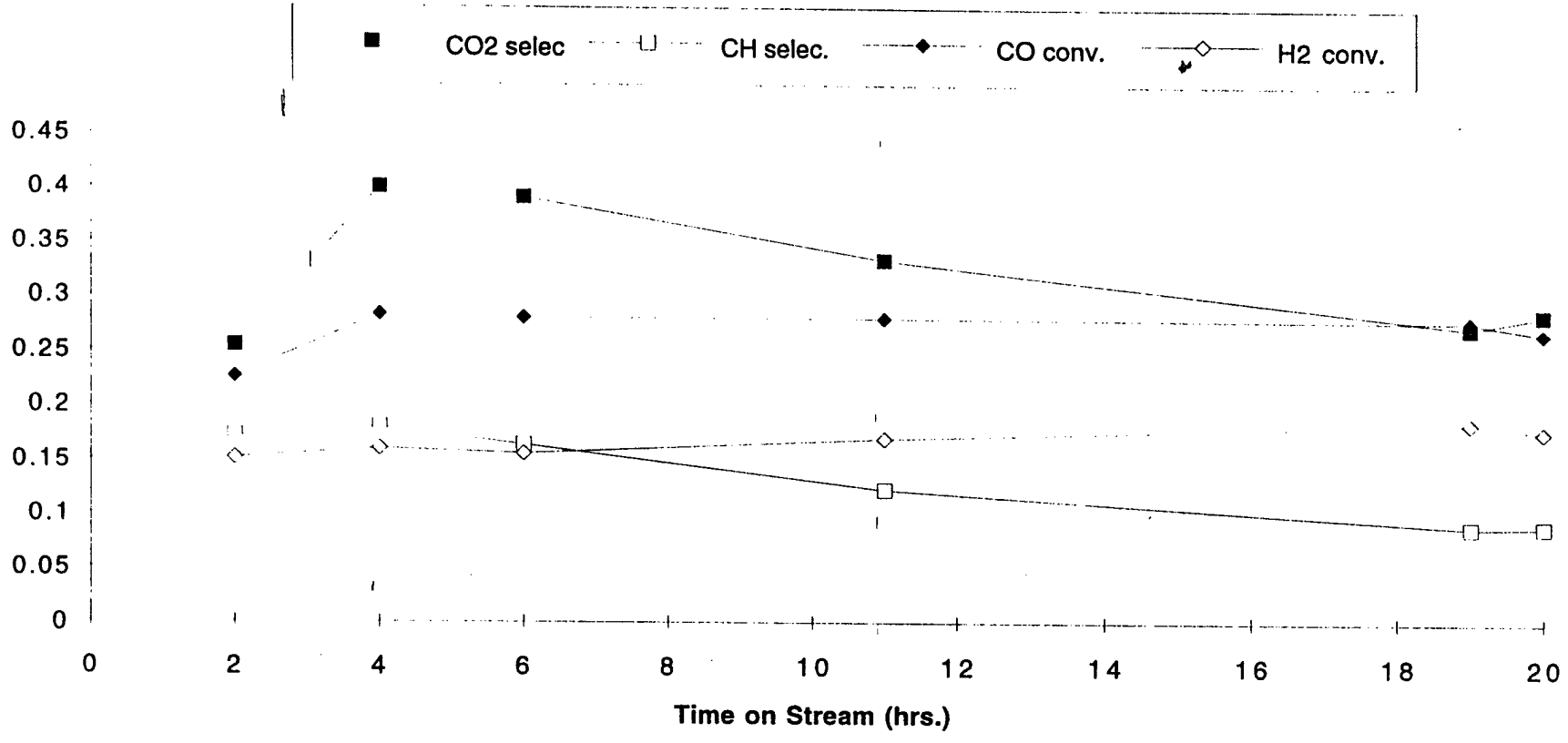

Figure 8. Reaction on F7K (425°C, 1000psi, CO/H2=1)