Figure 3.3.2.4. X-Ray Powder Diffraction Pattern of the CuO/ZrO_2 = 10/90 mol% Catalyst After Calcination at 350°C in Air

The peak at ≈44° is attributable to the sample holder.

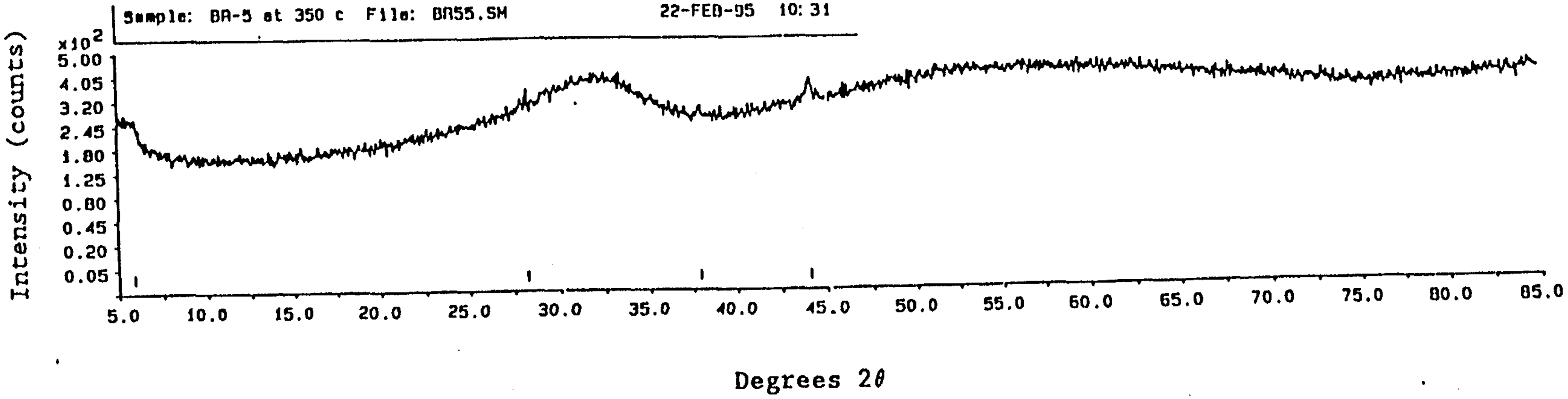
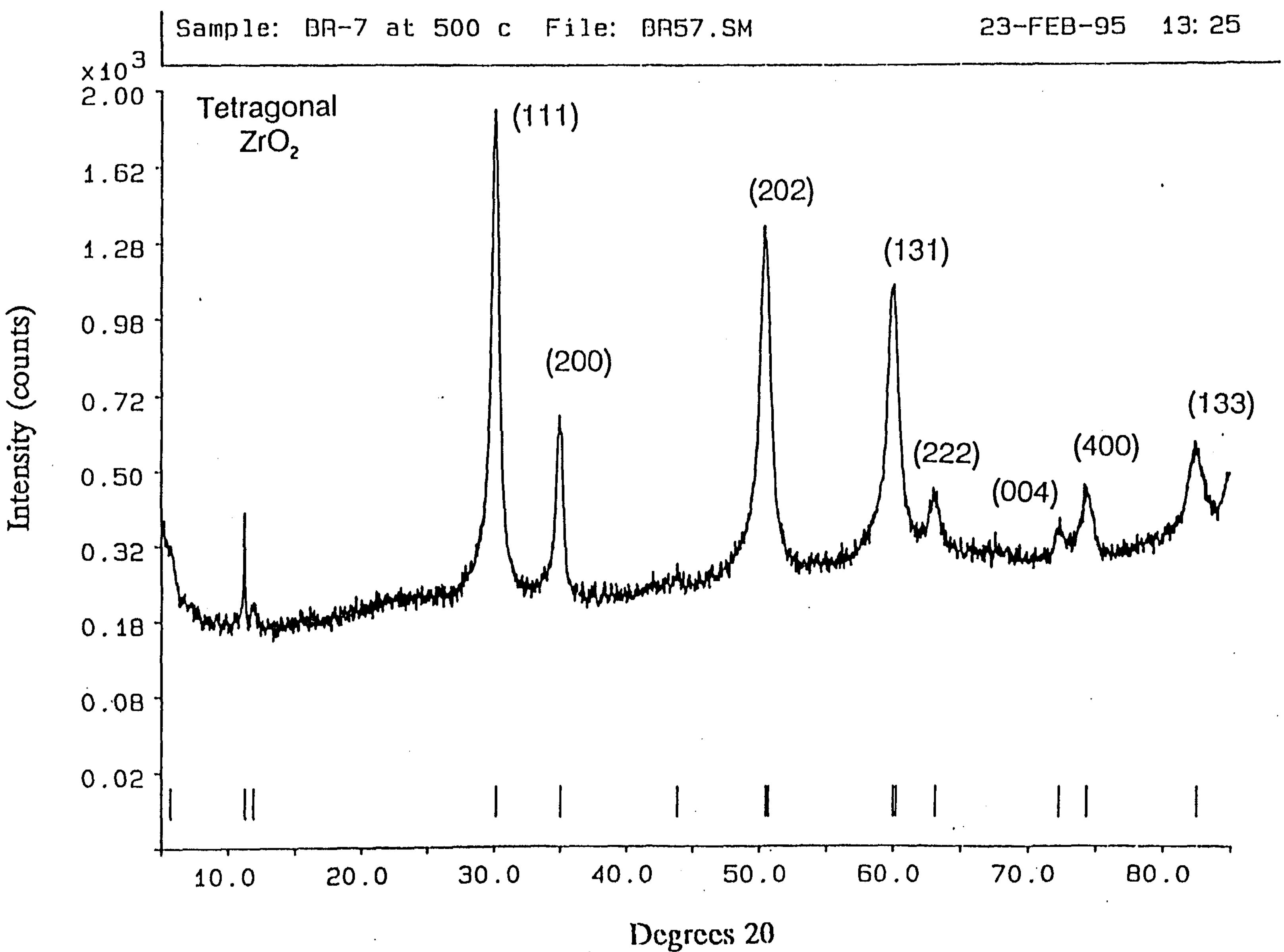


Figure 3.3.2.5. **X-Ray Powder Diffraction Pattern of the CuO/ZrO$_2$ = 10/90 mol% Catalyst After Calcination at 500°C in Air**
The peak at ≈44° is attributable to the sample holder.



catalysts. This strongly suggests that the catalyst performance is enhanced by a tuning of the surface sites in a manner that is not diagnosable in the bulk.

Experimental

The comparison of nitrogen calcination and air calcination of the catalysts was performed on catalysts with compositions corresponding to F6K and F7K (Table 3.3.3.1), which were calcined in flowing air. The corresponding catalysts, calcined under flowing nitrogen, are coded as F6NK and F7NK. The catalysts were prepared by dropping the required amounts of metal nitrate solution into K_2CO_3 (0.2M) basic solution until neutral pH was reached (at precipitation temperature 60°C). The precipitates were washed with deionized water, dried at 130°C (overnight), calcined at 400°C under air or nitrogen flow (3h), pelletized, and sieved. The calcined catalysts were then doped with 4 wt % of K_2CO_3 followed by drying overnight at 130°C. The KOH-precipitated, nitrogen-calcined catalyst reported here is coded as F6KOHN, and it has the same composition as F6K. It was prepared by dropping 2M KOH solution into nitrate solution at 60°C to a final pH of 12. The same process was used for nitrogen calcination as described above.

The reaction testing of the catalysts was carried out at T = 350, 400, 425°C, P = 1000 psi, $CO/H_2 = 1$, GHSV = 2900/h after 24h reduction of the catalyst with 5% H_2/N_2 at 260°C. The reaction was run for over 20 hours at each temperature. X-ray diffraction patterns of the samples before and after reaction were collected on an XRG-3000 diffractometer with CuKα radiation (45 kV and 40 mA) in the range of $2\Theta = 10\text{-}90°$.

Table 3.3.3.1 Catalyst Compositions and Preparation Methods

Catalysts	Compositions	Preparations
F6K	Mn/Cu = 0.5, Zn/Cu = 0.5, Zr/Cu = 2, CoO = 0.2 wt%, 4 wt% K_2CO_3 doping	Coprecipitation by dropping nitrate solution to K_2CO_3 solution. Final pH = 7, washed, air-calcined
F6NK	Same as above	Same as above except nitrogen calcination
F6KOHN	Same as above except no K_2CO_3 doping	Coprecipitation by dropping KOH solution to nitrate solution. Final pH = 12, nitrogen-calcined
F6KOHNK	Same as above except 4 wt% K_2CO_3 doped	Same as above, K_2CO_3 doped after calcination
F6KOHNLi	Same as F6KOHN but with 4 wt% $LiNO_3$ doping	Same as F6KOHN but with $LiNO_3$ doping
F6KOHNCs	Same as F6KOHN but with 4 wt% $CsNO_3$ doping	Same as F6KOHN but with $CsNO_3$ doping

Results and Discussion

1. Nitrogen Calcination vs. Air Calcination

In order to evaluate the effects of nitrogen and air calcination on the catalytic performance of the previously developed catalysts, we prepared the nitrogen-calcined catalyst, F6NK, for comparison with the air-calcined F6K. The experimental results are listed in Table 3.3.3.2

Table 3.3.3.2 Liquid Product Distributions on the Differently Calcined Catalysts

(@ 425°C, 1000 psi, CO/H_2 = 1, GHSV = 2900/h)

Cat	MeOH	EtOH	iPrOH	nPrOH	2BuOH	iBuOH	nBuOH	Other	Yield
					wt%				g/g/h
F6K	10.6	2.9	6.0	15.4	4.6	18.7	1.5	40.2	9.40E-02
F6NK	7.2	5.2	6.0	23.9	6.2	25.2	2.3	24.0	1.10E-01

The nitrogen-calcined catalyst, F6NK, exhibited improved selectivity toward isobutanol. A significant enhancement of the total higher alcohol selectivity also was observed. Accompanying this effect was the enhancement of n-propanol selectivity. These results indicate that the calcination atmosphere in the catalyst preparation plays a critical role in the performance of catalysts for higher alcohol synthesis. In the strictest sense, calcination is heat treatment of an inorganic solid under flowing air. Our findings indicate that the heat treatment is better done under flowing nitrogen.

The activity, hydrocarbon and carbon dioxide selectivity, and stability of F6K and F6NK are shown by the time on-stream plots in Figures 3.3.3.1 and 3.3.3.2. Both catalysts had relatively stable performance during more than 60 hours of reaction. The nitrogen-calcined catalyst showed better low temperature activity than the air-calcined catalyst (350-400°C). The air-calcined catalyst, on the hand, was slightly more active than the nitrogen-calcined catalyst at 425°C.

The XRD patterns of the catalysts calcined under nitrogen are identical to those for the corresponding catalysts calcined under air (see Figures 3.3.3.3 and 3.3.3.4). Therefore, the improved performance of the catalysts by nitrogen calcination does not arise from detectable changes in the bulk crystal structures of these materials, suggesting that a more subtle surface modification is responsible. The XRD pattern in Figure 3.3.3.4 also shows that metallic copper is the major copper phase while all the other components show up as oxide phases. The level of copper agglomeration is not surprising, but must be limited to enhance activity.

2. KOH Precipitation vs. K_2CO_3 Precipitation

Our investigation of the more subtle effects of preparation variables on catalyst performance reveals that the precipitant has a strong effect. To examine KOH as a basic precipitant, the composition of the catalyst was selected to be that of catalyst F6, which was the best composition for isobutanol production in the previously reported factorially designed sample matrix. In these experiments KOH instead of K_2CO_3 for precipitation, and nitrogen instead of air for calcination were employed.

Nitrogen calcination significantly enhanced isobutanol selectivity and total alcohol productivity, as discussed in the last section. However, n-propanol selectivity was still fairly high for the nitrogen-calcined catalysts (see F6NK in Table 3.3.3.3). With KOH as the basic precipitant, not only was the ease of washing and filtering of the precipitated mixture enhanced, but it also produced catalysts that show significant suppression of n-propanol production while maintaining isobutanol selectivity. Another feature that the KOH precipitated catalysts showed is enhanced

Figure 3.3.3.1. Reaction Performance of F6K (300-425°C, 1000 psi, CO/H_2 = 1)

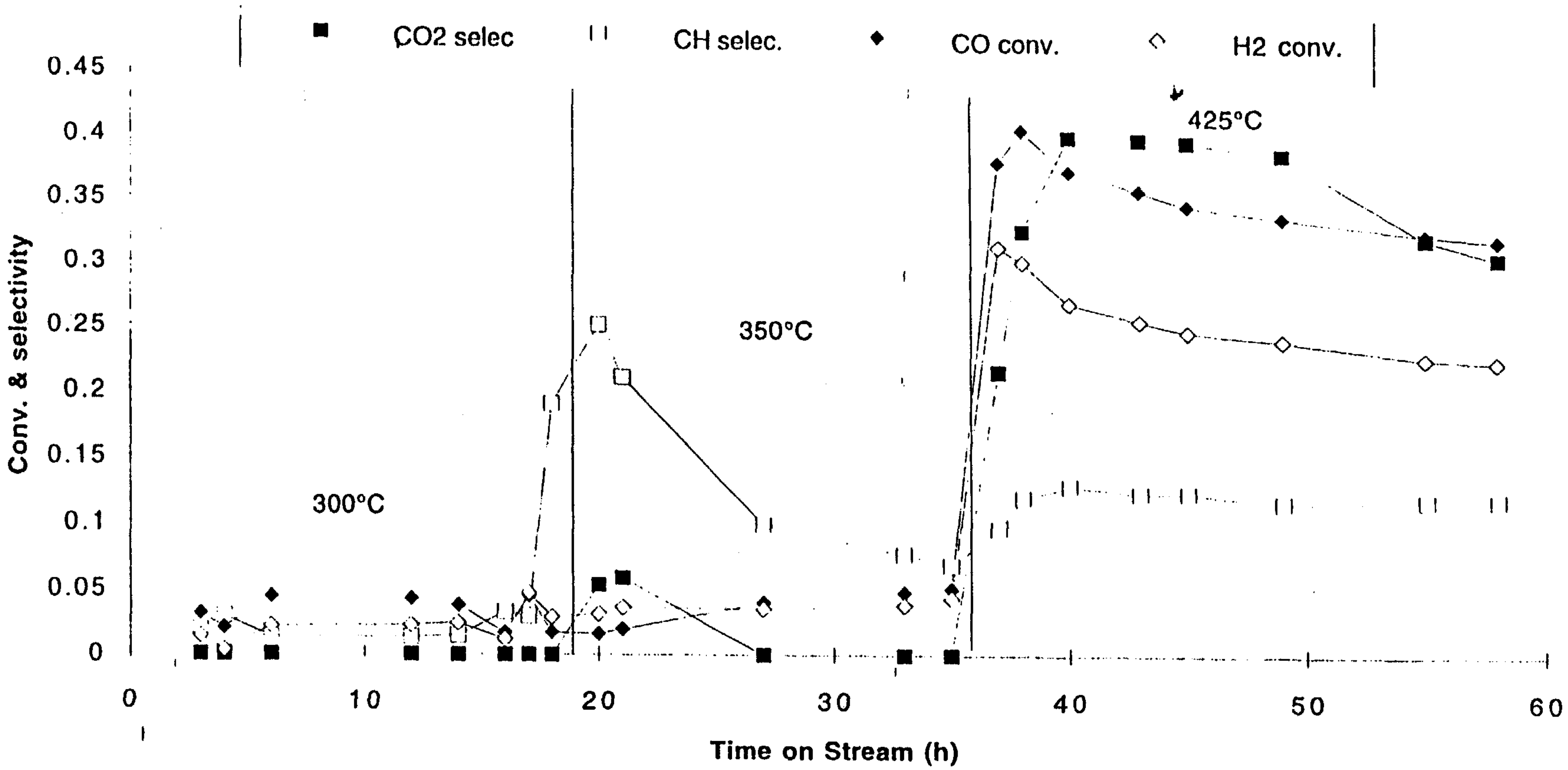


Figure 3.3.3.2. Reaction Performance of F6NK (400-425°C, 1000 psi, CO/H_2 = 1)

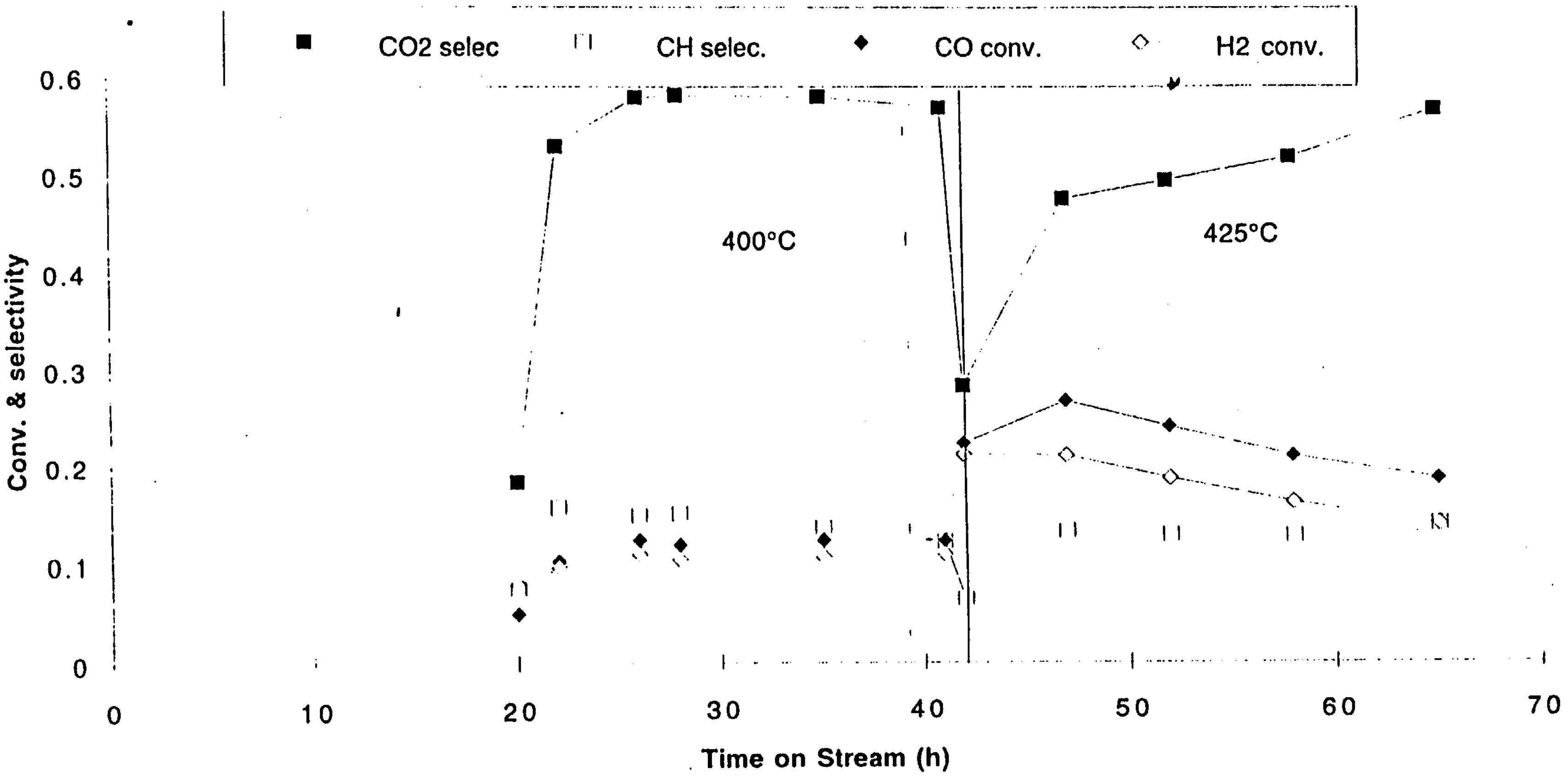


Figure 3.3.3.3. XRD for F6K and F6NK

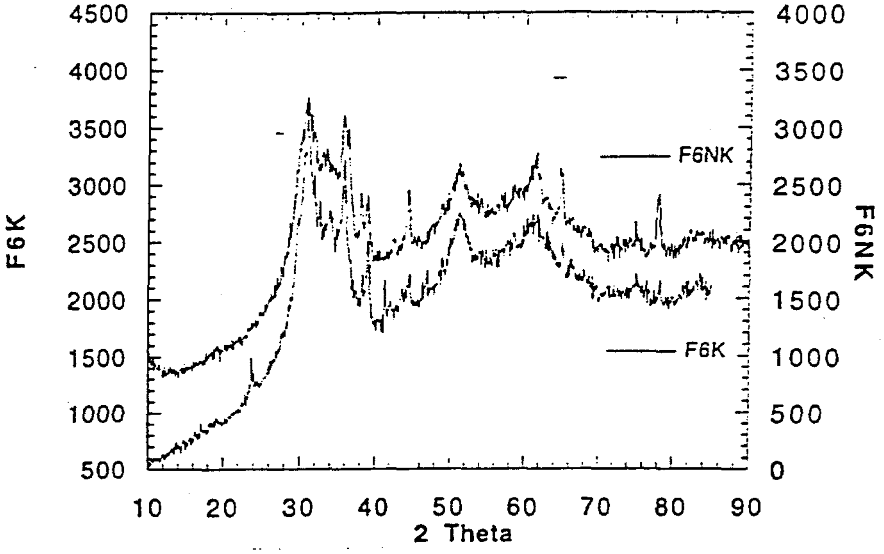
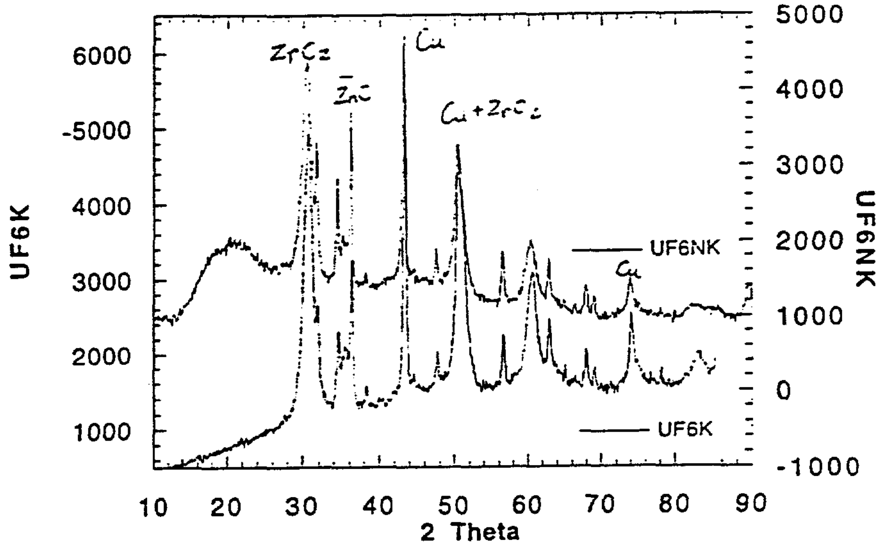


Figure 3.3.3.4. XRD for Used F6K and Used F6NK



low temperature isobutanol selectivity. For K_2CO_3 precipitated catalysts, for example, F6K and F6NK, the highest isobutanol selectivity is observed at 425°C, the upper temperature limit we applied. But KOH precipitated F6KOHN series of catalysts showed the highest isobutanol selectivity at significantly lower temperature, 400°C. The decreased reaction temperature for reaching the highest isobutanol selectivity is obviously beneficial for suppressing n-propanol selectivity and other by-products. This coupled with other results make it clear that it is possible to optimize isobutanol production through a combination of reaction temperature, catalyst composition, catalyst preparation procedure, and other reaction conditions.

Higher final pH (= 12) in the preparation of F6KOHN in contrast with pH = 7 in the F6NK preparation is another factor that should be taken into account when comparing the performance of F6NK and F6KOHN, because the surface acidity (or basicity), which may depend on the precipitation pH, plays an important role in mixed oxide catalysts. However, this cannot be discussed without a more comprehensive experimental result. This should be one of the subjects to be further studied.

The XRD patterns of the catalyst prepared by KOH precipitation are identical with those for the corresponding catalysts prepared by K_2CO_3 precipitation. The XRD patterns in Figure 3.3.3.5 indicate that bulk structures of the precipitated catalysts after calcination are highly amorphous. As observed for K_2CO_3-precipitated catalysts, the bulk structure of the KOH-precipitated catalyst was transformed into highly crystalline metallic copper and the oxide phases of the other components after reduction and with long time on-stream (see Figure 3.3.3.6). The XRD data do not provide a clue to the reason for the enhanced performance of the KOH-precipitated catalysts, indicating that a more subtle surface-modification of the catalyst is responsible for the selectivity rise.

3. *Effects of Alkali Doping for KOH Precipitated Catalysts*

When we made the comparison between the K_2CO_3-precipitated catalyst and the KOH-precipitated catalysts, we were comparing F6NK with the whole series of alkali-doped catalysts (F6KOHNK, F6KOHNLi, F6KOHNCs). In fact, the reaction results on F6KOHNK are an exception in the series since the reaction on it was run at low GHSV (half of the standard run due to leaking at reactor inlet). We expect that the liquid product distribution on F6KOHNK would be similar to that for the Li and Cs doped catalysts if it had been run under normal conditions. We did not repeat the reaction on F6KOHNK because a more consistent conclusion was obtained from comparison of undoped catalyst F6KOHN and the alkali doped catalysts.

F6KOHN, a catalyst left undoped with no alkali metal component, has shown excellent isobutanol selectivity and suppressed n-propanol selectivity (see Table 3.3.3.3). These results suggest that the excess alkali doping does not play a role in improving the isobutanol selectivity and higher alcohol productivity of the previously discussed catalysts. This result is surprising since it is not in agreement with expectation based on the commonly accepted idea that alkali promotion enhances higher alcohol synthesis. A possible reason for the observed result might be that potassium residue from the original KOH-precipitation process provides adequate promotion. This issue will be examined by submitting the catalysts to elemental analysis and other tests for the preserved effect of potassium. With regard to liquid productivity, the undoped

Figure 3.3.3.5. XRD for F6NK and F6KOHN

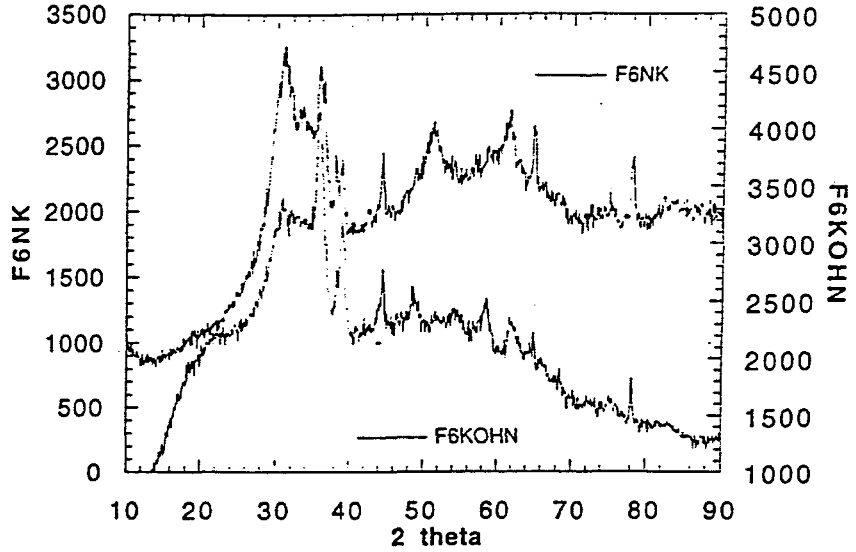
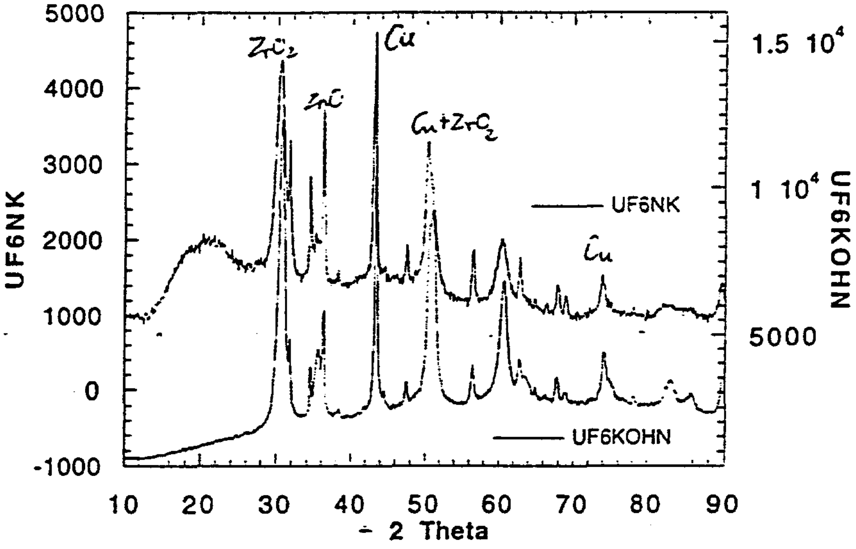


Figure 3.3.3.6. XRD for Used F6NK and Used F6KOHN



catalyst, F6KOHN, has shown the same or even higher (at 400°C or lower temperature) liquid yield compared with Li-, Cs-, or K-doped catalysts. The lower activity might be expected for excess alkali-doped catalysts, if the alkali components cover or block some of the active sites on the catalyst's surface. This too will be investigated.

Time on-stream performance of the F6KOHN series of catalysts is shown in Figures 3.3.3.7 through 3.3.3.10. Generally, this group of catalysts shows relatively stable activity during 60 hours of reaction at 350 to 425°C. Relatively low hydrocarbon selectivity and high carbon dioxide selectivity were observed on all of these catalysts.

The reaction test of F6KOHNLi at 400°C after 20 hours on-stream at 425°C showed that not only was the catalyst significantly deactivated, but the original selectivity pattern observed at 400°C could not be recovered completely (see Table 3.3.3.3 and Figure 3.3.3.8). This indicates that the active sites for isobutanol production may not be stable at higher temperatures, whereas those leading to n-propanol may be increasing. This result, along with the effect of nitrogen calcination and KOH precipitation, further substantiates the role that subtle surface modifications may play in these catalysts.

Table 3.3.3.3 - Liquid Product Distribution on Different Catalysts (wt%)
(@ 1000 psi, $CO/H_2 = 1$, GHSV = 2900/h)

Cat/Temp.	MeOH	EtOH	iPrOH	nPrOH	2BuOH	iBuOH	Other	Yield (g/g/h)
F6NK								
350	65.2	11.3	2.3	17.2	0.5	5.5	1.9	0.003
400	21.7	12.2	5.2	28.9	3.3	17.5	11.3	0.070
425	7.2	5.2	6.0	23.9	6.2	25.2	26.3	0.110
F6KOHNK								
350	45.5	3.8	0.0	5.9	0.0	15.1	29.1	0.028
400	17.4	6.2	0.0	12.5	0.0	13.8	50.1	0.083
425	10.4	3.8	1.0	13.3	0.9	10.1	60.5	0.098
F6KOHNCs								
350	57.4	1.8	0.0	2.8	0.0	15.2	22.9	0.047
400	23.4	3.8	0.0	6.2	0.0	23.6	43.0	0.074
425	12..8	6.6	0.0	14.5	0.0	13.1	51.3	0.105
F6KOHNLi								
350	61.4	1.8	0.0	2.4	0.0	17.7	16.7	0.050
400	25.3	4.5	0.0	5.9	0.0	22.9	41.4	0.078
425	13.6	5.5	0.0	14.3	0.0	13.0	53.6	0.105
400 after 425	26.3	5.7	0.0	16.2	0.0	12.9	38.9	0.050
F6KOHN								
350	69.2	0.0	0.0	1.1	0.0	14.8	14.3	0.060
400	27.3	0.0	0.0	2.0	0.0	24.0	46.7	0.083
425	13.3	2.9	1.4	5.6	0.0	19.3	57.4	0.086

Figure 3.3.3.7. Reaction Performance of F6KOHN (350-425°C, 1000 psi, $CO/H_2 = 1$)

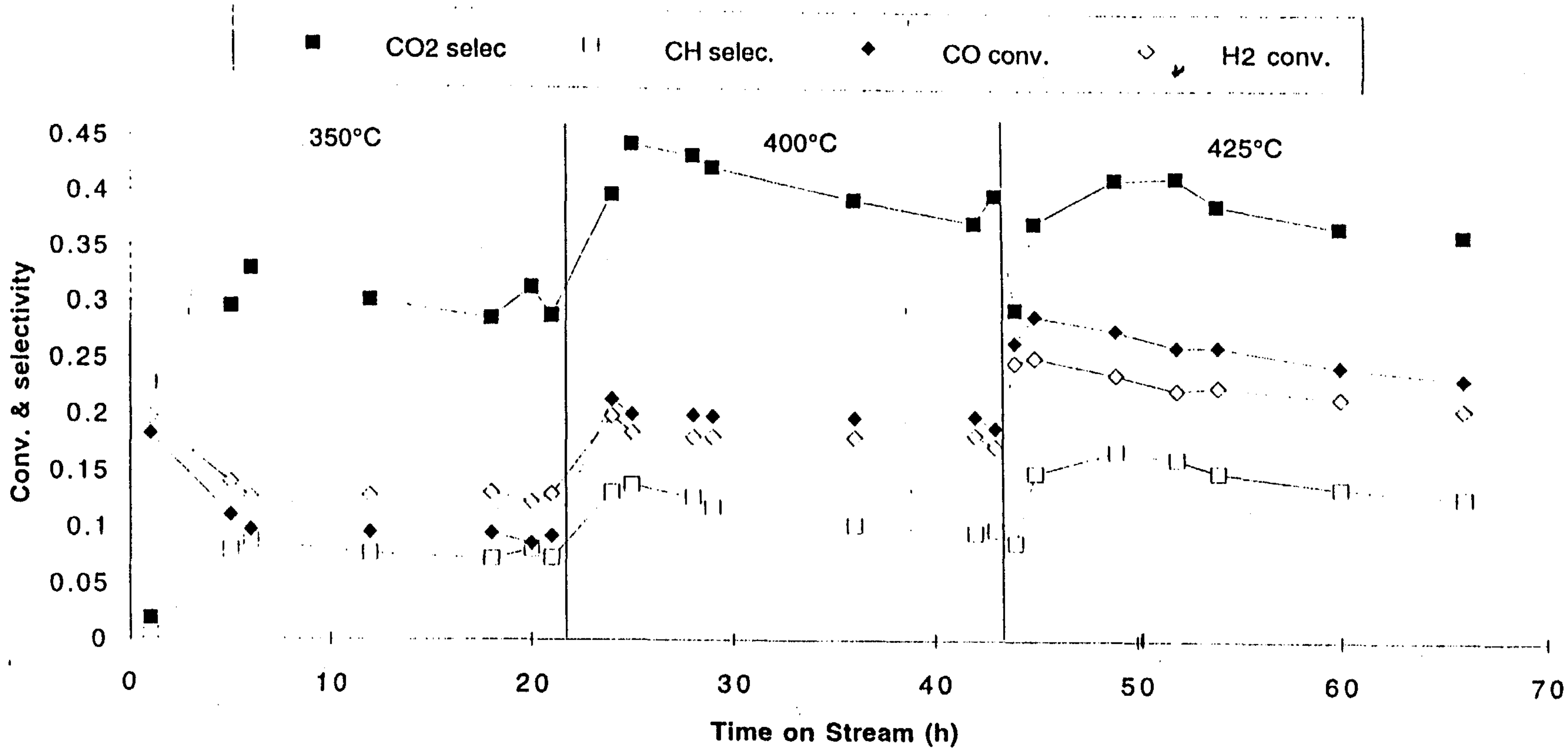


Figure 3.3.3.8. Reaction Performance of F6KOHNLi (350-425°C, 1000 psi, CO/H_2 = 1)

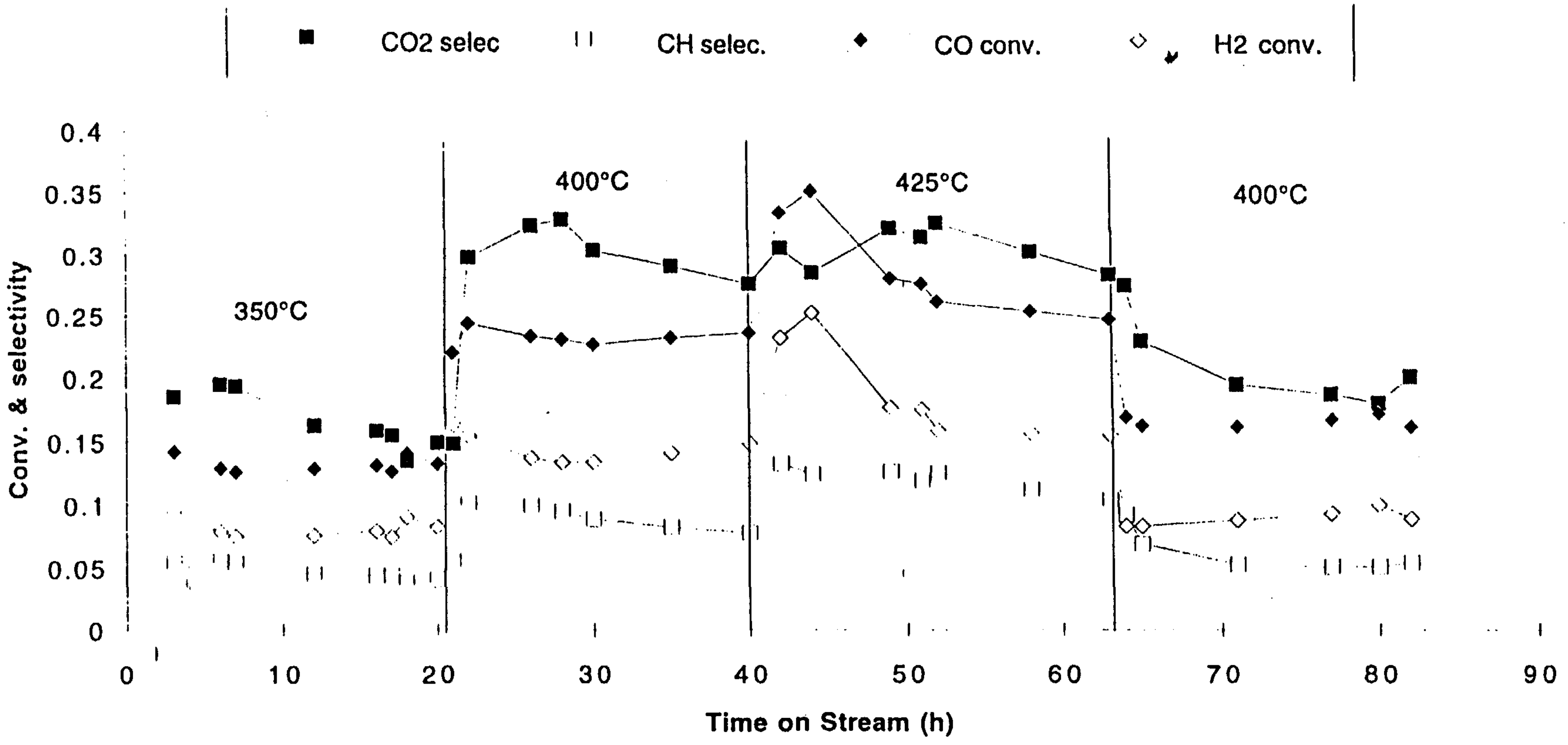


Figure 3.3.3.9. Reaction Performance of F6KOHNK (350-425°C, 1000 psi, $CO/H_2 = 1$)

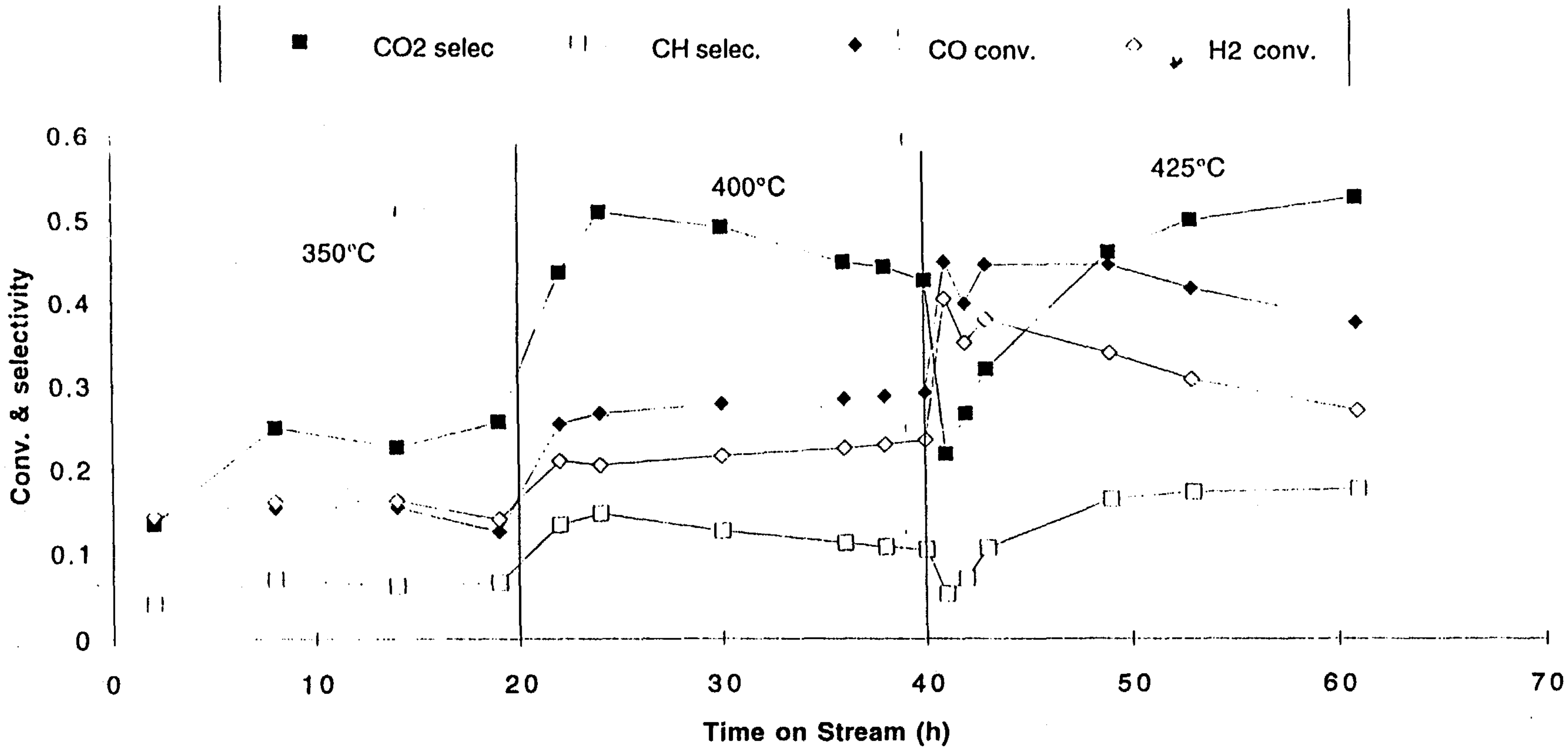
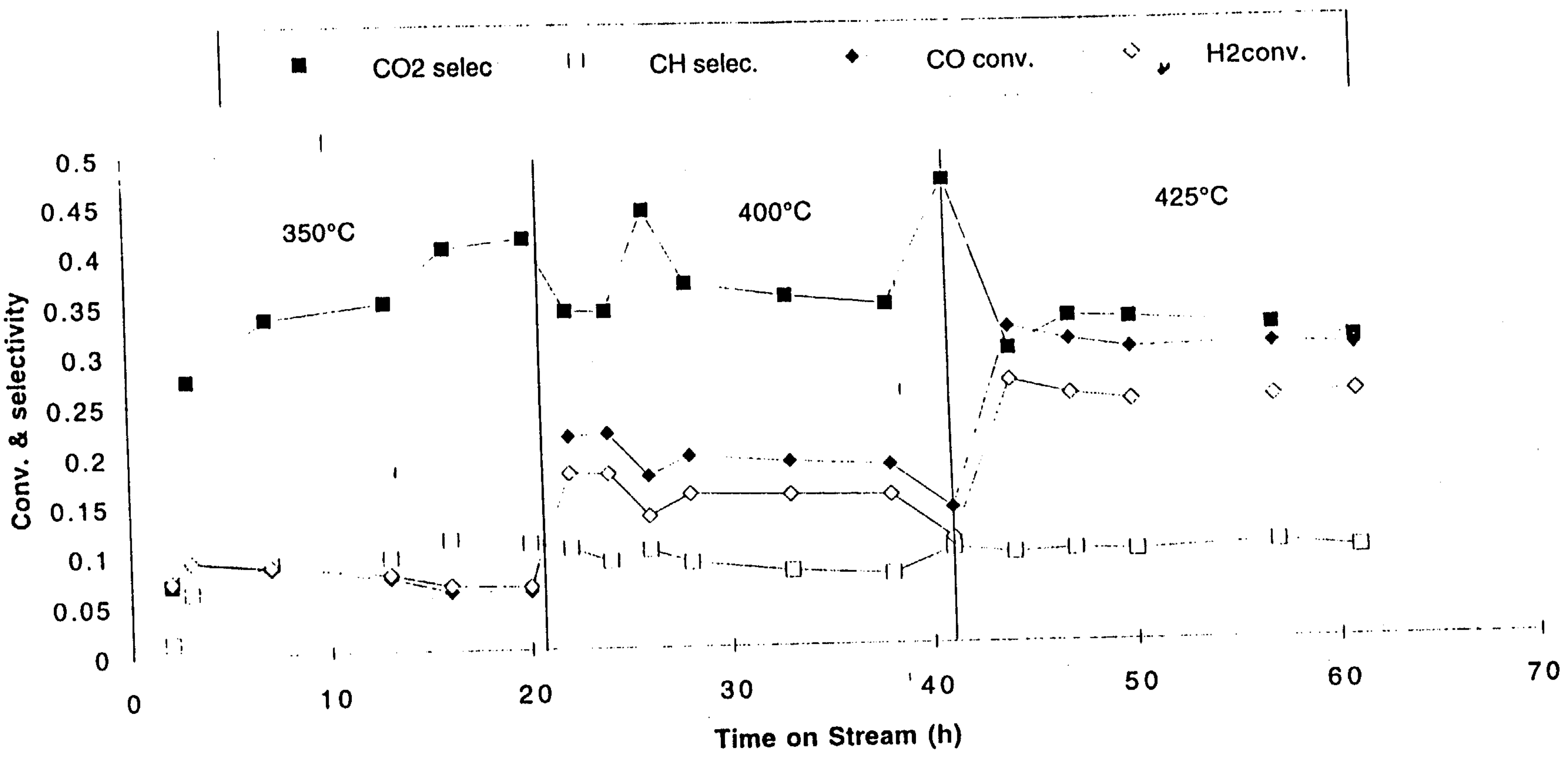


Figure 3.3.3.10. Reaction Performance of F6KOHNCs (350-425°C, 1000 psi, $CO/H_2 = 1$)



Conclusions

Our findings indicate that calcination is better done under nitrogen, which leads to higher isobutanol selectivity and total alcohol productivity. KOH-precipitated catalysts exhibited enhanced low-temperature performance, high isobutanol selectivity and suppressed n-propanol selectivity at lower temperature. Nitrogen calcination and KOH precipitation do not affect the bulk structure of the catalyst, suggesting that a subtle tuning of the surface sites of the catalysts by these variables may be responsible for the enhanced selectivity. Excess alkali metal doping has been proven to show no beneficial promotional effect on our catalysts.

Future Work

In the next quarterly report, we will present further experimental results on the KOH-precipitated F6KOHN catalyst, examining the effects of reaction pressure, space time velocity, and various transition metal dopings on performance.

TASK 4: PROGRAM SUPPORT

The subcontract with Bechtel to carry out process and economic evaluations in support of the Alternative Fuels and Chemicals program was put in place at the end of March. As noted in the previous quarterly, Bechtel's assignments have expanded beyond the area of syngas generation and cleanup. 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 Bechtel's 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 91990-94) 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

B. L. Bhatt participated in a peer review of proposals to DOE's Advanced Coal Research Program for U. S. Colleges and Universities. A review meeting was held in Pittsburgh on January 30.

Detailed data analysis was performed on the results of the Fischer-Tropsch II run recently completed. A report has been written and is being reviewed internally.

An abstract for a paper entitled "Productivity Improvements for Fischer-Tropsch Synthesis" has been accepted for an oral presentation at the 14th North American Catalysis Society Meeting. The paper, which is co-authored by APCI, DOE and Shell personnel, will be presented by B. L. Bhatt at the Hydrocarbons session on June 15.

5.2 Management Activities

The subcontract with Bechtel was in place by the end of the quarter. Their first priority will be to set performance targets for isobutanol synthesis to meet expected future MTBE values.

We continue to strive towards a subcontract with Eastman Chemical. This will be in place, hopefully, within the next quarter.