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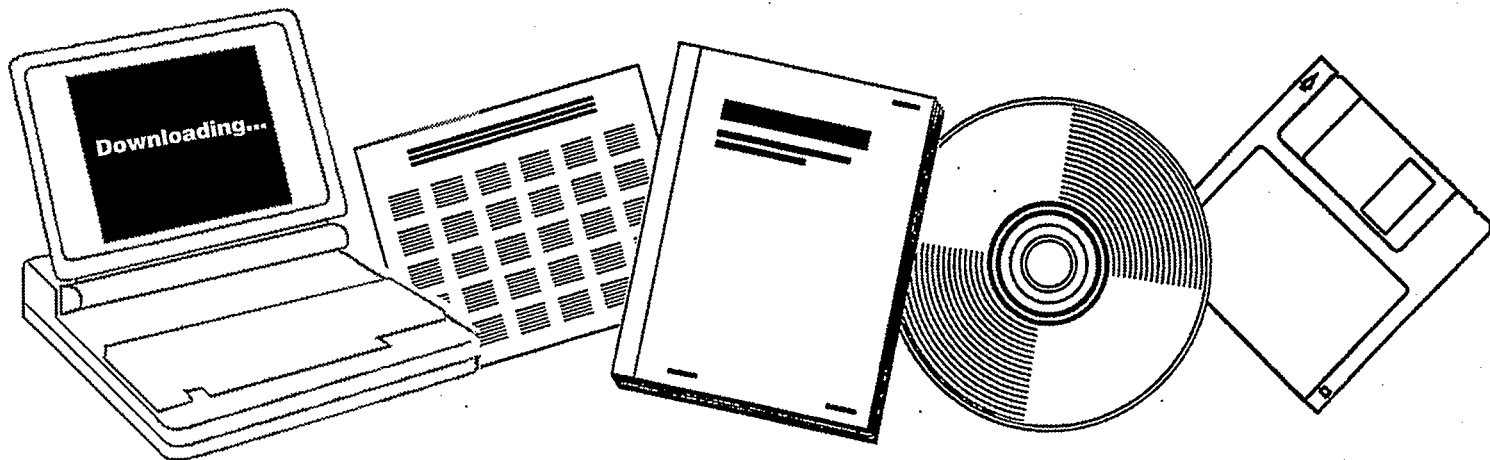
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**CO + H SUB 2 REACTION OVER  
NITROGEN-MODIFIED IRON CATALYSTS.  
QUARTERLY TECHNICAL PROGRESS REPORT, APRIL  
1, 1983-JUNE 30, 1983**

PURDUE UNIV., LAFAYETTE, IN. SCHOOL OF  
CHEMICAL ENGINEERING

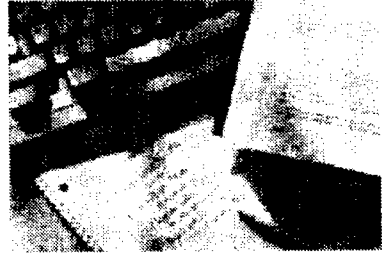
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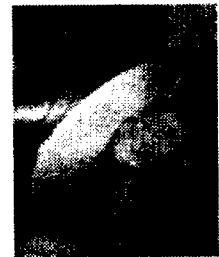
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CO + H<sub>2</sub> Reaction Over

Nitrogen-Modified Iron Catalysts

Quarterly Technical Progress Report  
for the Period April 1, 1983 - June 30, 1983

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Purdue University  
West Lafayette, Indiana 47907

PREPARED FOR THE

U. S. DEPARTMENT OF ENERGY

**MASTER**

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## ABSTRACT

The objective of this work is to examine the effects of nitrogen, as nitride and as a gas-phase reactant, on hydrocarbon synthesis reactions over iron catalysts. This is the third quarterly period of a three-year program. Procedures for preparing the pure  $\gamma'$ -Fe<sub>4</sub>N and  $\zeta$ -Fe<sub>2</sub>N bulk phases have been refined and these phases have been confirmed by Mössbauer spectroscopy. After four hours of Fischer-Tropsch reaction with a 3/1 mixture of H<sub>2</sub>/CO at 523 K both unsupported nitrides form new phases, presumably carbonitrides, retaining little of the original nitride structure. A pure  $\gamma'$ -Fe<sub>4</sub>N was prepared from a highly dispersed iron on carbolac. Mössbauer spectrum of this sample after reaction showed considerable retention of the nitride phase. The stability of this catalyst was further reflected in a steady reactivity and selectivity during synthesis, in contrast to the gradual activity loss over the unsupported catalysts. Kinetic measurements suggest a hydrogen deficient surface during the first minutes of exposure to synthesis gas. These preliminary studies identify the short time behavior of the catalysts as worthy of more thorough study by transient methods.

## 1. OBJECTIVES AND SCOPE

### 1.1 BACKGROUND

The feasibility of utilizing synthesis gas ( $\text{CO} + \text{H}_2$ ) via the Fischer-Tropsch reaction pathway for the production of fuels and chemicals is well established. The SASOL ventures, for example, take advantage of abundant coal resources to produce both desirable synthetic automotive fuels and basic chemical feedstocks. The applicability of these chemical transformations is nonetheless limited. The present procedure requires extensive processing if the production of non-essential byproducts is to be avoided. The discovery and subsequent usage of improved catalysts would therefore be advantageous.

Experimental results published in the current literature show that nitrogen affects the performance of iron catalysts—catalysts which find widespread use in the Fischer-Tropsch synthesis route. Prenitriding of the iron catalyst has been reported to shift the product distribution to one exhibiting lower molecular weight fractions and enhanced alcohol yields (1). On the other hand, simultaneous introduction of ammonia ( $\text{NH}_3$ ) with synthesis gas produces nitrogenous compounds. Furthermore, and probably of greater importance, this addition of ammonia effects a reduction in the overall chain length of compounds in the product spectrum (2,3). It is of considerable interest, therefore, to study these and other characteristics of nitrided iron catalysts in order to gain a basic understanding of their



behavior. Discovery of the new pathways in Fischer-Tropsch synthesis afforded by nitrogen will add to the fundamental knowledge from which future synthesis-catalysts can be derived.

## 1.2 OBJECTIVES

The scope of the program may be broken down into two main areas of concern. Firstly, consideration must be given to the role of the surface nitrogen in

- i. altering the product distribution and
- ii. stabilizing catalyst activity

of the synthesis reactions. In-situ Mössbauer studies, already in progress, will identify the various iron nitride phases and allow for examination of their stability during reaction. The Mössbauer results will form the basis for detailed kinetic tracer experiments involving transient and isotope labeling analyses. Ultrahigh vacuum work using SIMS and AES will supplement the Mossbauer and kinetic characterizations.

The second area of consideration will involve the kinetic and catalytic effects observed during the addition of ammonia to the synthesis gas stream. Transient work will be ideal for observing initial activity changes occurring as a result of  $\text{NH}_3$  pulses. Along with ultrahigh vacuum studies, the transient kinetics of  $\text{NH}_3$  addition will help clarify which steady state experiments would be most productive. The various analytical methods will define interactions between surface and bulk

nitrogen, and their role in effecting new reaction pathways.

The primary experiments which define our route to understanding which parameters influence the selectivity and alter the activity of synthesis reactions may, therefore, be outlined as follows:

- i. Mössbauer and simultaneous kinetics of prenitrided iron catalysts will be used to determine nitride phase stability and to correlate these phases to reaction selectivity. The initial pressure of one atmosphere may later be increased.
- ii. Similar analysis of the effects of addition of  $\text{NH}_3$  to the reactant stream will be performed.
- iii. Transient analysis and isotope tracer studies of synthesis reactions over prenitrided catalysts will determine surface nitride stability. The stoichiometry at the surface and influence of nitriding on CO dissociation will be sought.
- iv. Ultrahigh vacuum analysis will examine surface stoichiometry and reaction intermediates. Interaction between the nitrided phases and adsorption bond strengths of CO and  $\text{H}_2$  will be investigated.
- v. The effects of  $\text{NH}_3$  addition to the reactant stream will be similarly followed by UHV and transient tracer studies to determine possible alterations in reaction

pathways invoked by the presence of  $\text{NH}_3$ .

Computer modeling will be undertaken to aid in quantitative interpretation of transient data.

## 2. TECHNICAL PROGRESS

### 2.1 LITERATURE REVIEW

#### 2.1.1 Carbolac-supported Iron

Vannice and coworkers (4-6) have used carbolac supported iron in their studies of the CO hydrogenation reaction. This carbon black, as patented by Hucke (7), retains many properties associated with activated carbon and glassy carbon supports. The material is characterized by a high surface area ( $\sim 1000\text{m}^2/\text{g}$ ), good electron conduction and a highly controllable porosity (4). The uniform and narrow pore distribution of this carbon black provides considerable advantage over the polymodal pore distributions found in activated carbons. Catalytically active metals may be added during the actual carbolac manufacturing or more commonly via incipient wetness or similar impregnation techniques.

A partial characterization of iron supported upon carbolac by Mössbauer Spectroscopy has already been successfully undertaken by Jung et. al., (6) and by Niemantsverdriet (8). These investigators have shown by CO chemisorption and Mössbauer spectroscopy that 5 wt% iron on carbolac consists of very small iron particles (2.2 nm). Vannice (4) reports that CO hydrogenation

over this catalyst yields a product several fold higher in olefin concentration compared to that from other Fe catalysts. The catalyst also shows a four fold increase in activity per gram of iron over iron supported upon either silica or alumina. We are interested in whether nitriding of such a supported iron catalyst would provide any additional benefits.

### 2.1.2 Carburization During Fischer-Tropsch Synthesis

The Fischer-Tropsch synthesis has been studied extensively over reduced iron, revealing the unique characteristic that its activity is initially low and increases to a maximum (9-12). This behavior is undoubtedly due to the formation of iron carbides during synthesis, a process which is analogous to the formation of iron carbonitrides from initially nitrided iron. Models that explain the activity behavior of iron and the simultaneous formation of the carbide are therefore instructive in the case of iron carbonitride formation.

Three explanations concerning iron during synthesis have been proposed in the literature. In the "carbide" model, iron is not active for F-T synthesis unless it is "activated" by a bulk carbide structure. Raupp and Delgass(2) have shown that the activity of iron can closely match the carburization of the bulk, and therefore suggested that the bulk carbide influences the number of active sites on the surface. This model, however, does not explain why preoxidized iron, which resists carburization, or an FeRu alloy, which does not form a bulk carbide, both show a

high initial activity.

Niemantsverdriet, et. al., (11-12) therefore propose the "competition" model, in which an activated carbon species participates in three reaction pathways; carburization, hydrogenation, and deactivation. Initially the carburization step dominates the overall activity until diffusion of carbon is inhibited by the formation of the bulk carbide. This model assumes the dissociation of CO to be a relatively slow step or that the carbon coverage is self limiting.

The "slow activation" model (11-12) assumes CO dissociation is faster than subsequent reactions, thus providing ample carbon for all reaction pathways. Hydrogenation occurs only through a preferred complex that is formed at a slow rate. This model is not supported by the FeRu and preoxidized iron experiments since there is no reason why these catalysts should preferentially form the required complex (11).

The selectivity of hydrocarbon products over iron is dependent on both conversion and the nature of the catalyst. Published data indicate that as conversion is increased, the olefin to paraffin ratio decreases (10). In addition, the type of support effects both the distribution of products and the time dependent activity although these effects could be due primarily to particle size changes (9-11). The factors that influence activity and carburization of iron will undoubtedly also affect the Fischer-Tropsch synthesis behavior of the iron nitrides. We

have now begun the process of examining these effects.

## 2.2 SUMMARY OF RESULTS

The previous study by Mössbauer spectroscopy of bulk iron nitrides has been expanded to include a carbon black (carbolac) supported iron catalyst. Preparation procedures for two of the three iron nitride phases have been refined to produce nearly pure  $\gamma'$  ( $\text{Fe}_4\text{N}$ ) and  $\delta$  ( $\text{Fe}_2\text{N}$ ) from bulk iron samples. Steady state kinetic analyses of these two phases have been undertaken. A nearly pure  $\gamma'$  iron nitride supported upon carbon has also been produced. Preparation, Mössbauer spectra, and kinetic analyses of these catalysts are discussed below.

### 2.2.1 Catalyst Preparation

The preparation procedure for the bulk iron nitride catalysts has been detailed previously (13). Preparations discussed below involve slight modification of these procedures. To begin with, a new source of iron oxide precursor was prepared because our original supply was depleted. Additional  $\alpha\text{-Fe}_2\text{O}_3$  had been supplied by BASF, but these supplies were determined to be catalytically inactive. Scanning Electron Microscopy EDAX analysis of this material showed substantial sulfur contamination of two separate samples;  $\text{S} = 0.43 \pm .05 \text{ wt\%}$  and  $0.20 \pm .06 \text{ wt\%}$ . These samples showed no increase in catalytic activity after cyclic oxidation and reduction sequences at 723 K in flowing  $\text{O}_2$  and  $\text{H}_2$  respectively. The particles probably sintered during this procedure. The subsequent decrease in surface area combined with

sulfur contamination account for an essentially inactive sample.

Thus, we resorted to preparing an iron oxyhydroxide precursor by precipitation of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  with ammonium hydroxide,  $\text{NH}_4\text{OH}$ . The hydroxide was added dropwise to a .17 M  $\text{Fe}(\text{NO}_3)_3$  solution (pH  $\sim$  3.5). The solution was kept at a temperature of  $348 \pm 2$  K under constant mechanical agitation. The  $\text{NH}_4\text{OH}$  was added continuously, precipitating the dark brown iron compound, until the pH of the solution reached 7.0 (batch 1) or 10.5 (batch 2). Agitation was continued at 348 K to ensure solution uniformity. The suspension was vacuum filtered, washed with distilled water and air dried at ambient conditions for 90+ hours. The resulting brittle black cake was ground with an agate mortar and pestle and calcined for 24 hours in  $\text{O}_2$  at  $388 \pm 5$  K (batch 1) or in air for 4 hrs at 573 K (batch 2). A nitrogen BET at 77 K of the inactivated precursor gave an estimated surface area of  $357 \pm 10$   $\text{m}^2/\text{g}$  for batch 1 and  $123 \pm 10$   $\text{m}^2/\text{g}$  for batch 2.

The iron on carbon support was prepared from a high surface area (950  $\text{m}^2/\text{g}$ ) carbolac carbon black supplied by Cabot Corporation. A 5 wt% iron on carbolac was obtained from M.A. Vannice at Penn State, and we prepared a calculated 8.2 wt% iron on carbolac by using a standard incipient wetness technique (14).

### 2.2.2 Mössbauer Effect Characterization

Nitriding in an ammonia rich (85%  $\text{NH}_3$  in  $\text{H}_2$ ) stream at atmospheric pressure and 673 K for three hours yielded a nearly

pure bulk  $\gamma'$ -Fe<sub>4</sub>N phase. The room temperature Mössbauer spectrum of this phase is shown in figure 1a. This spectrum resembles closely those  $\gamma'$ -Fe<sub>4</sub>N Mössbauer spectra reported by Lo et.al., (15) and by Gielen and Kaplow (16). The two outside peaks at approximate Doppler velocities of -5.2 and 5.8 mm/s are characteristic of the  $\gamma'$  nitride.

The intensity of these outside peaks is significantly greater than that shown in the mixed nitride phase ( $\epsilon$  and  $\gamma'$ ) spectrum reported by us previously (13). This indicates preparation of a more pure  $\gamma'$  nitride phase by the new procedure. The low temperature, 85 K, Mössbauer spectrum of this single phase material is shown in figure 1b. Essentially similar to the room temperature spectrum, this spectrum shows the increase in the recoil free fraction through an increase in the percent absorption of the observable peaks. The temperature dependency of the isomer shift is also apparent from this figure. Upon reaction at 523 K for four hours in a 3H<sub>2</sub>/CO synthesis mixture, the room and low temperature Mössbauer spectra, figures 1c and d respectively, were obtained. The decrease in the quantity of  $\gamma'$ -Fe<sub>4</sub>N after reaction is shown by a substantial decrease in percent absorption of the two characteristic outer peaks in both the room and low temperature spectra. A corresponding emergence of new peaks at around  $\pm 2$  mm/s indicate the formation of a new, non-Fe<sub>4</sub>N structure, probably a carbonitride. Computer fitting of these spectra, which will aid in the elucidation of structures present in this sample, is in progress.



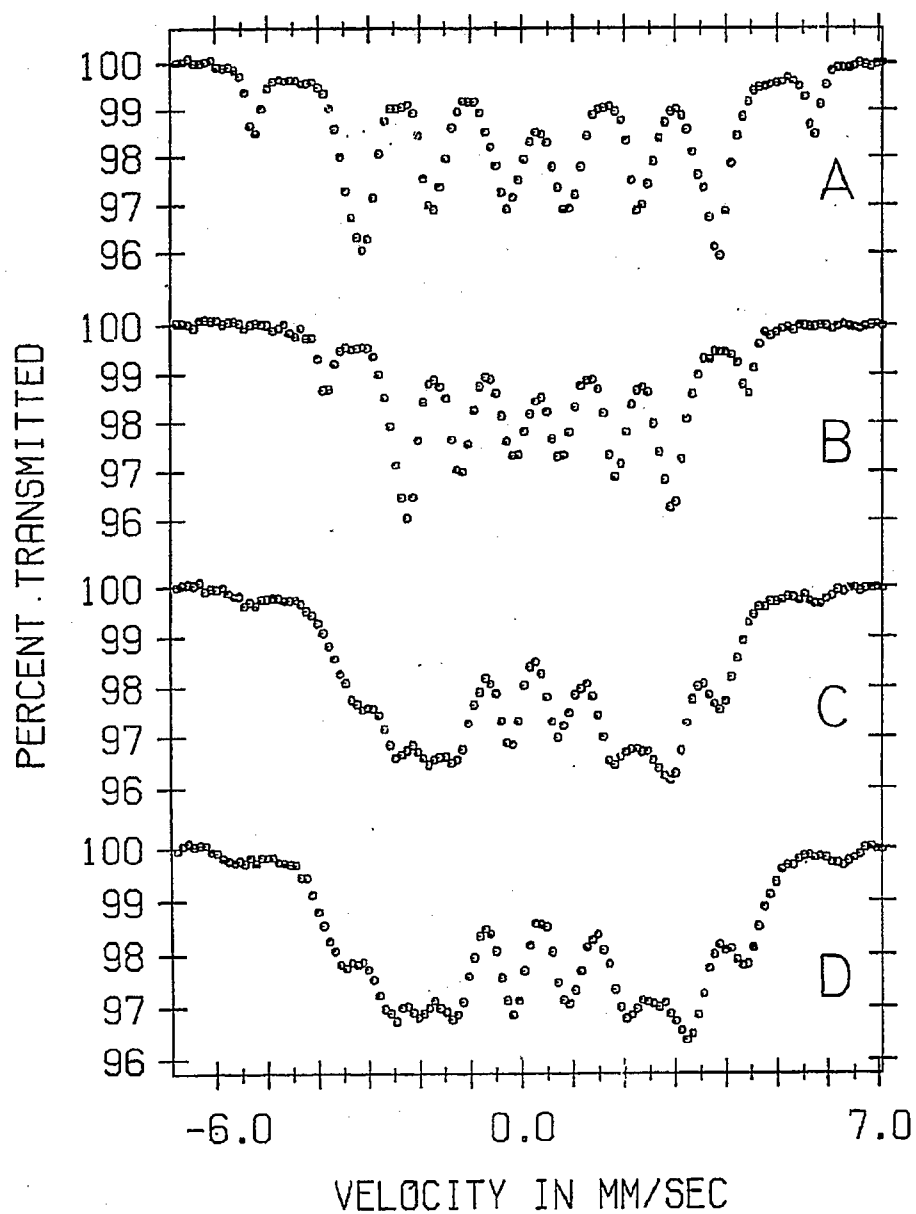


Figure 1: Mössbauer spectra of bulk  $\gamma'$ -Fe<sub>4</sub>N  
a) 298 K spectrum and b) 85 K spectrum  
reacted in 3H<sub>2</sub>/CO at 523 K for 4hr  
c) 298 K spectrum and d) 85 K spectrum.

We also investigated the stability of  $\gamma'$ - $\text{Fe}_4\text{N}$  nitride with respect to oxidation. A 21%  $\text{O}_2$  in He gas mixture was flowed over the bulk iron nitride for 1 1/4 hours at 298 K. The Mössbauer spectra obtained before and after the exposure to  $\text{O}_2$  were identical. Thus, with respect to Mössbauer effect sensitivity, the effects of transportation of the  $\gamma'$  nitride through ambient conditions should be negligible.

For comparison to the above bulk iron nitride, a  $\gamma'$ - $\text{Fe}_4\text{N}$  phase was also produced from the 5 wt% iron on carbolac precursor. Other investigators (4-6, 8) have suggested that severe reduction schedules are needed for complete reduction. Such a procedure can lead to sintering. Figures 2a and b show the effect of an increase of 25°K in reduction temperature. The Mössbauer spectrum of the 16 hour reduction in  $\text{H}_2$  at 723 K (figure 2a) shows only minor existence of the six line pattern which characterizes large particle  $\alpha$ -Fe. Figure 2b portrays the identical catalyst reduced at 748 K and here the existence of both large and small iron particles is clearly visible.

Nitriding of the sample shown in figure 2b for 6 hours in 75%  $\text{NH}_3$  in  $\text{H}_2$  at 633 K yielded a strong  $\gamma'$  nitride component (see figure 2c). The Mössbauer spectrum of this catalyst after reaction in  $3\text{H}_2/\text{CO}$  at 523 K for 4 hours is shown in Figure 2d. This latter spectrum shows remarkable stability of the small particle  $\gamma'$ - $\text{Fe}_4\text{N}$  when it is compared to the  $\gamma'$ - spectrum of bulk iron nitride after reaction. Small peaks appear to occur at approximately -2.5 and + 3.0 mm/s which may be indicative of

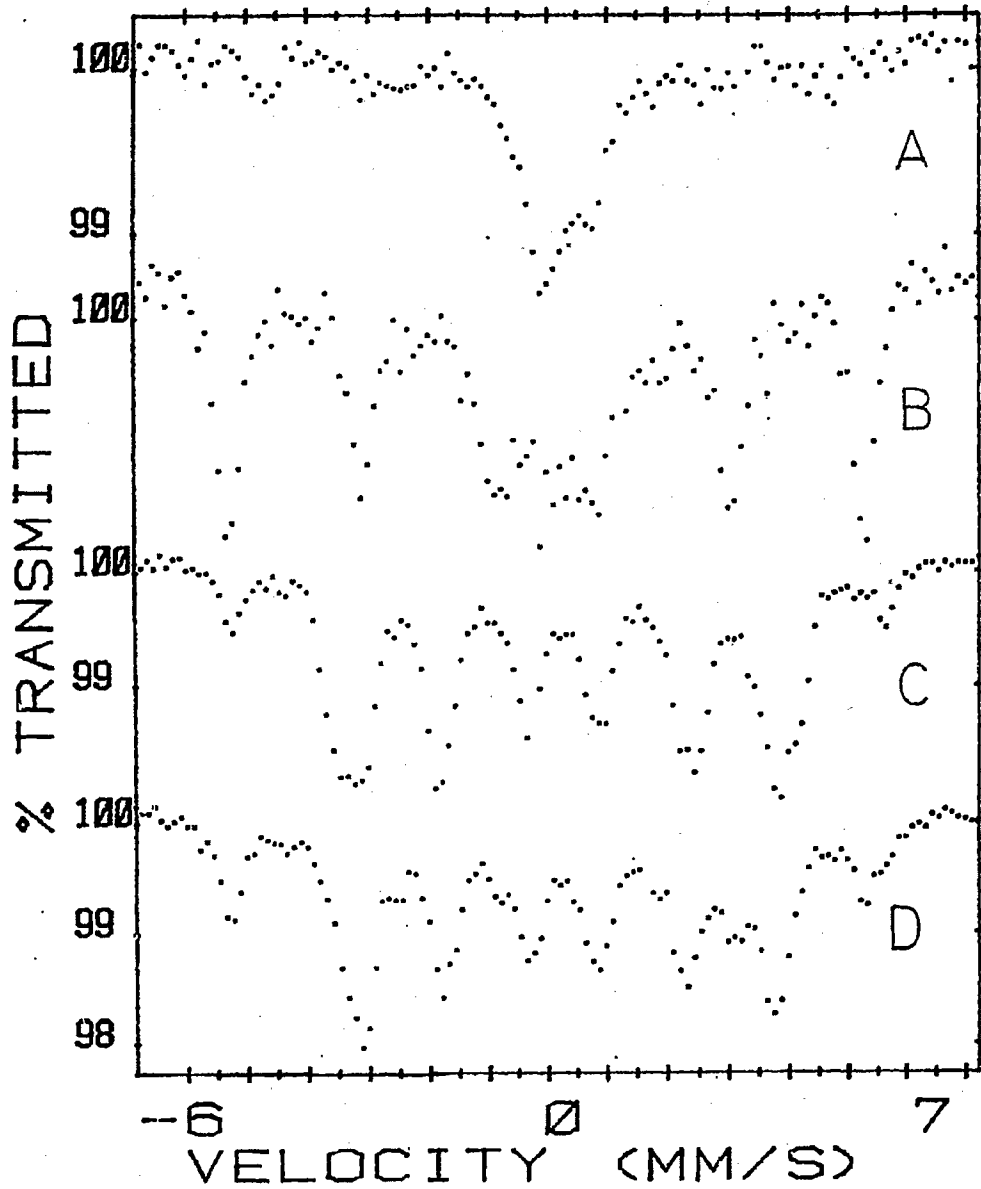


Figure 2: Mössbauer spectra (298 K) of 5 wt% Fe on carbolac after reduction in  $H_2$  for 16hr at a) 723 K and b) 748 K then c) 6hr  $2/75\% NH_3$  at 623 K then d) 4hr reaction in  $3 H_2 / CO_3$  at 523 K.

carbonitride formation. Slight reduction to  $\alpha$ -Fe is probable as can be seen in the  $-5$  mm/sec region, but most of the iron is still  $\gamma'$ -Fe<sub>4</sub>N. This stability during reaction is surprising considering the iron particle size. Smaller iron particles should carburize more rapidly than bulk iron at identical reaction conditions, but they have not.

A high nitrogen containing nitride, an approximation of  $\zeta$ -Fe<sub>2</sub>N, has also been prepared from unsupported iron. Figure 3a shows the Mössbauer spectrum of a reduced  $\alpha$ -Fe wafer nitrided at 673 K in 90% NH<sub>3</sub> in H<sub>2</sub> for 3 hours and then treated an additional 2 hours with pure ammonia at 623 K. A decreased velocity range has been employed to improve resolution and to emphasize the doublet peak. This doublet is characteristic of high nitrogen containing  $\epsilon/\zeta$ -Fe<sub>2</sub>N, but is no longer visible after carburization. Figure 3b shows the Mössbauer spectrum of this essentially pure  $\zeta$ -Fe<sub>2</sub>N after 4 hours of reaction in 3H<sub>2</sub>/CO at 523 K.

A comparison of this spectrum against figure 1c, the spectrum of the bulk  $\gamma'$  nitride after reaction, shows several noticeable differences. The peaks appearing in the latter spectrum at velocities  $-2.5$  and  $3.0$  mm/s are either absent or severely reduced in intensity in the  $\zeta$  nitride spectra. Furthermore, figure 1c shows a spectrum with a spectral area 15-20% greater than that shown in  $\zeta$  nitride spectra (figure 3b). Clearly after a 4 hour reaction period these catalysts still have different chemical structures. Computer fittings of spectra are in progress to help identify the contributing components in these and other

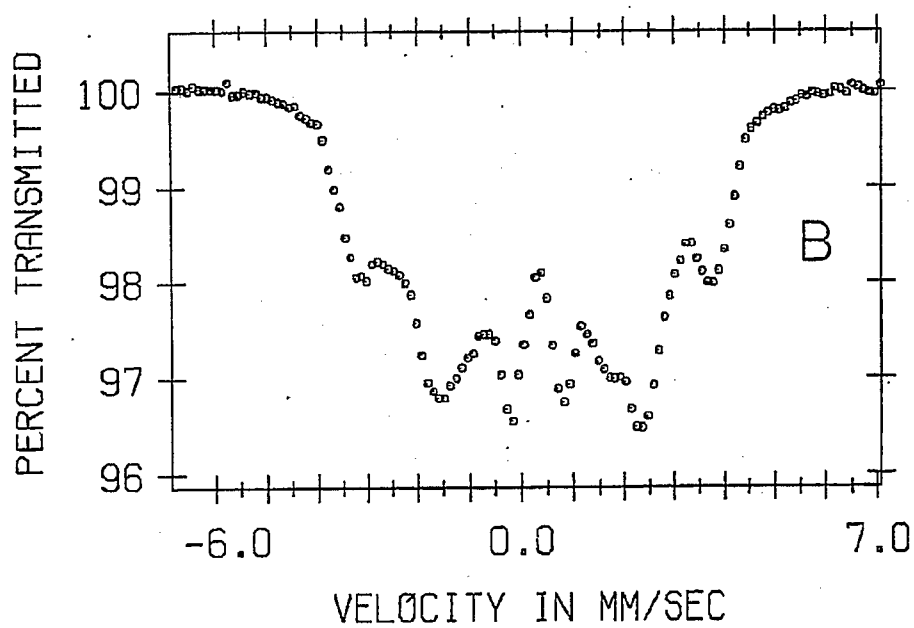
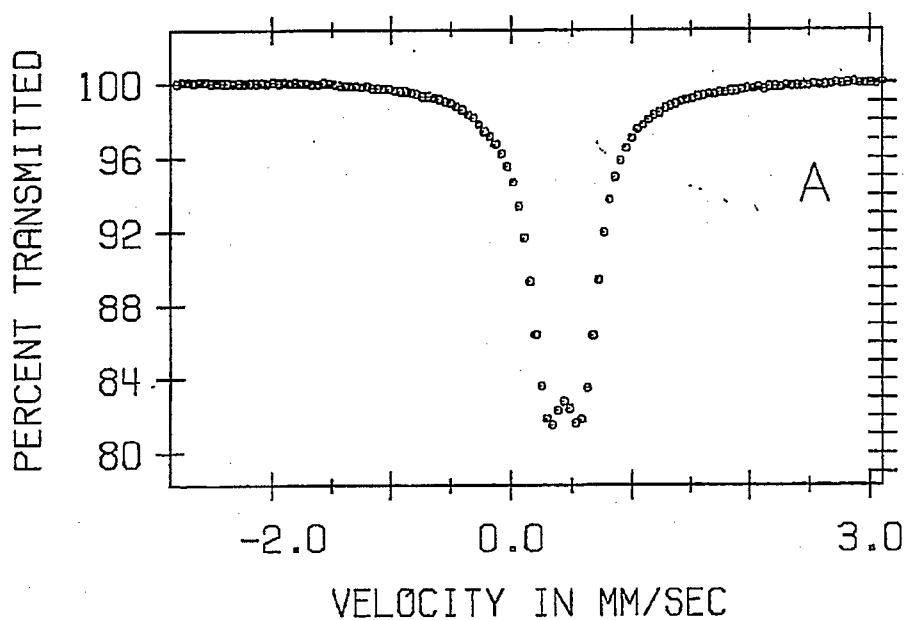


Figure 3: Mössbauer spectra (298 K) of bulk  $\gamma$ - $\text{Fe}_2\text{N}$   
a) 3hr 90%  $\text{NH}_3$  at 673 K then  
2hr 100%  $\text{NH}_3$  at 623 K and then  
b) 4hr reaction in  $3\text{H}_2/\text{CO}$  at 523 K.

nitride samples. The influence of the different nitrides on activity and products on the CO hydrogenation reaction is considered below.

TABLE I  
Initial activity Data for Unsupported Catalysts

|                                       | Fe   | Fe <sub>4</sub> N |
|---------------------------------------|------|-------------------|
| Amt. catalyst precursor               | .1g  | .1g               |
| flow rate H <sub>2</sub> /CO (ml/min) | 60   | 60                |
| min. after initiation of run          | 2.5  | 3.5               |
| CO conversion to CH <sub>4</sub> (%)  | 1.35 | 0.53              |
| C <sub>2</sub> H <sub>6</sub>         | 0.15 | 0.15              |
| C <sub>3</sub> H <sub>8</sub>         | 0.12 | 0.04              |
| C <sub>2</sub> H <sub>4</sub>         | n.d. | 0.09              |
| C <sub>3</sub> H <sub>6</sub>         | n.d. | 0.26              |

n. d. - not detectable

### 2.2.3 Kinetic Results

In this stage of experimental work, the steady state Fischer-Tropsch (FT) synthesis behavior of  $\alpha$ -Fe,  $\gamma'$ -Fe<sub>4</sub>N,  $\zeta$ -Fe<sub>2</sub>N and Fe/Carbolac was studied. The results of this study can be separated into two regions, an initial (<10min) region of FT synthesis and a slow development (~5hrs) region. In all cases the oxidized catalyst precursor was reduced in flowing H<sub>2</sub> at 400°C for at least 4 hrs. Surface area determination of the

reduced catalyst is in progress.

During the initial minutes of FT synthesis over iron and all of the iron nitrides studied, the activity started low and increased, reaching a maximum during the first hour of synthesis. In the case of iron, this behavior could be explained by the "competition" model, where carburization competes with hydrogenation for active adsorbed carbon. The competition model can also account for the nitride behavior, but a more thorough analysis of reaction of surface nitrogen with  $H_2$  must be undertaken before firm conclusions can be reached.

Table 1 lists the CO conversion to various products during the initial region of activity for the unsupported catalysts. As found in published results, unsupported iron produces an abundance of methane in this region. In contrast, the  $\gamma\text{-Fe}_4\text{N}$  produces a wider range of products. It appears that the nitride surface is hydrogen deficient during the initial minutes of synthesis, perhaps due to a competition with hydrogenation of surface nitrogen. Transient experiments will elucidate this possibility.

Figure 4 shows the conversion and olefin/paraffin ratio results for unsupported Fe and  $\gamma\text{-Fe}_4\text{N}$ . Both catalysts were prepared from .1g of the iron oxide precursor, and were subjected to the same reaction conditions. Note that because of the very low conversion and small chromatograph peaks, the first olefin/paraffin data points for iron were not resolvable. It is

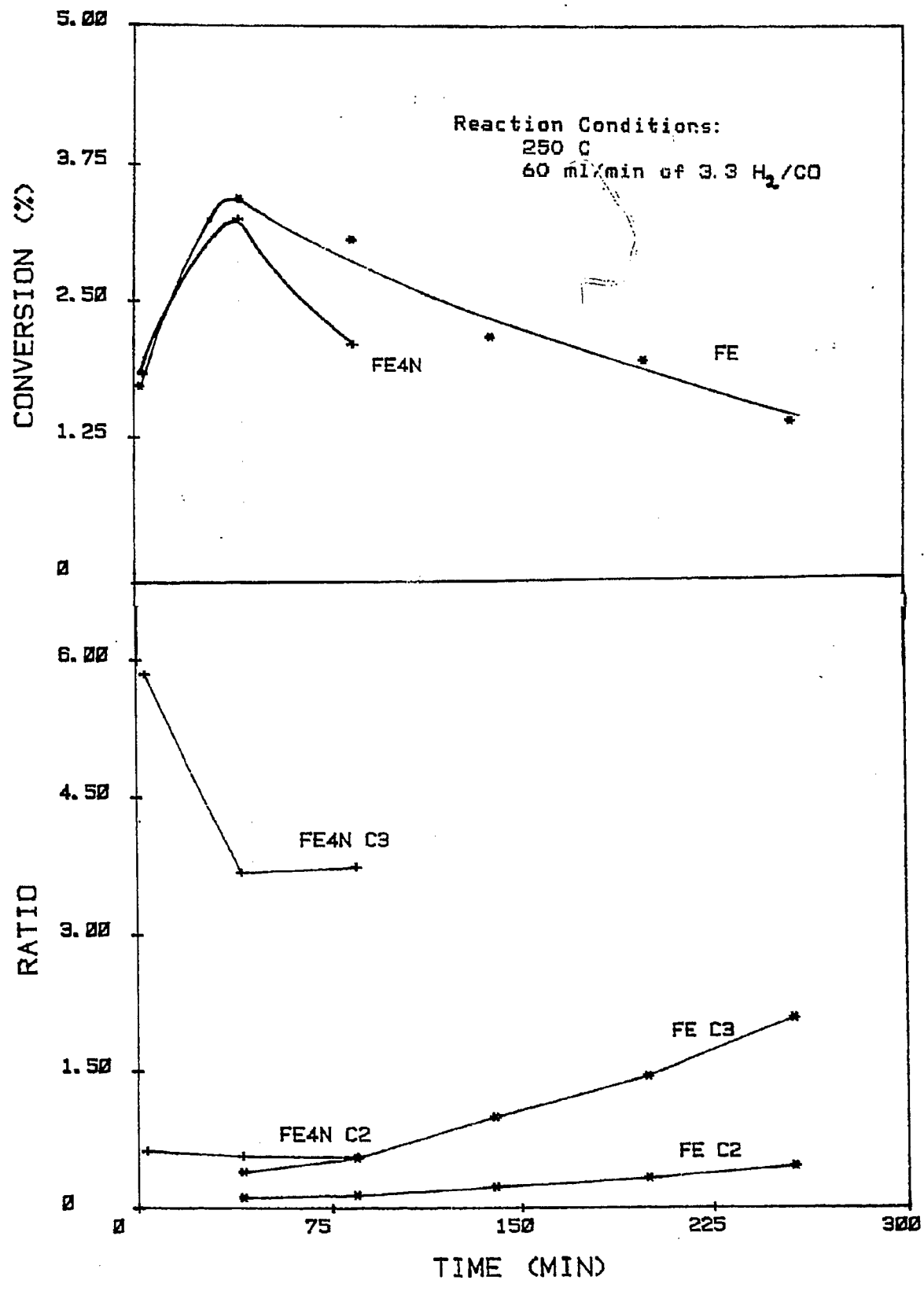


Figure 4: Time dependency of CO conversion and olefin/paraffin ratio of unsupported Fe and bulk Fe<sub>4</sub>N catalysts. Both catalysts prepared from 0.1g iron oxide precursor.



clear, however, that even at longer times the production of propylene is significantly enhanced in the nitride compared to pure iron.

Figure 5 shows the kinetic results of synthesis over  $\gamma'$ -Fe<sub>4</sub>N made from 25 mg of the iron oxide precursor and run in the Mössbauer reactor. The data reflect the same trend as the results for the nitride in figure 4. The overall activity goes through a maximum and slowly drops, and the relative difference between the C<sub>3</sub> and C<sub>2</sub> olefin to paraffin ratio is the same. Since the conversion in this sample is less than for the nitride in figure 4, the olefin/paraffin ratios are accordingly higher. The short time data points for C<sub>3</sub> and C<sub>4</sub> were also unattainable because of the low initial conversion.

The carbolac-supported  $\gamma'$ -Fe<sub>4</sub>N shows both activity and selectivity trends distinctly different from those of the bulk nitrides under similar reaction conditions. In contrast to the  $\zeta$  and  $\gamma'$  bulk phase reactivity, the activity of the carbolac catalyst reaches a steady maximum after the first fifteen minute period. This stability is further reflected in the catalyst's product selectivity. The time dependent C1-C4 product distribution is shown in figure 6. This comparison of selectivities at increasing reaction times clearly shows the stable nature of the catalyst after the initial half hour transient period. We intend to investigate this phenomenon more completely by considering Fe/SiO<sub>2</sub> catalysts in order to differentiate between bulk and supported iron nitride kinetic trends.

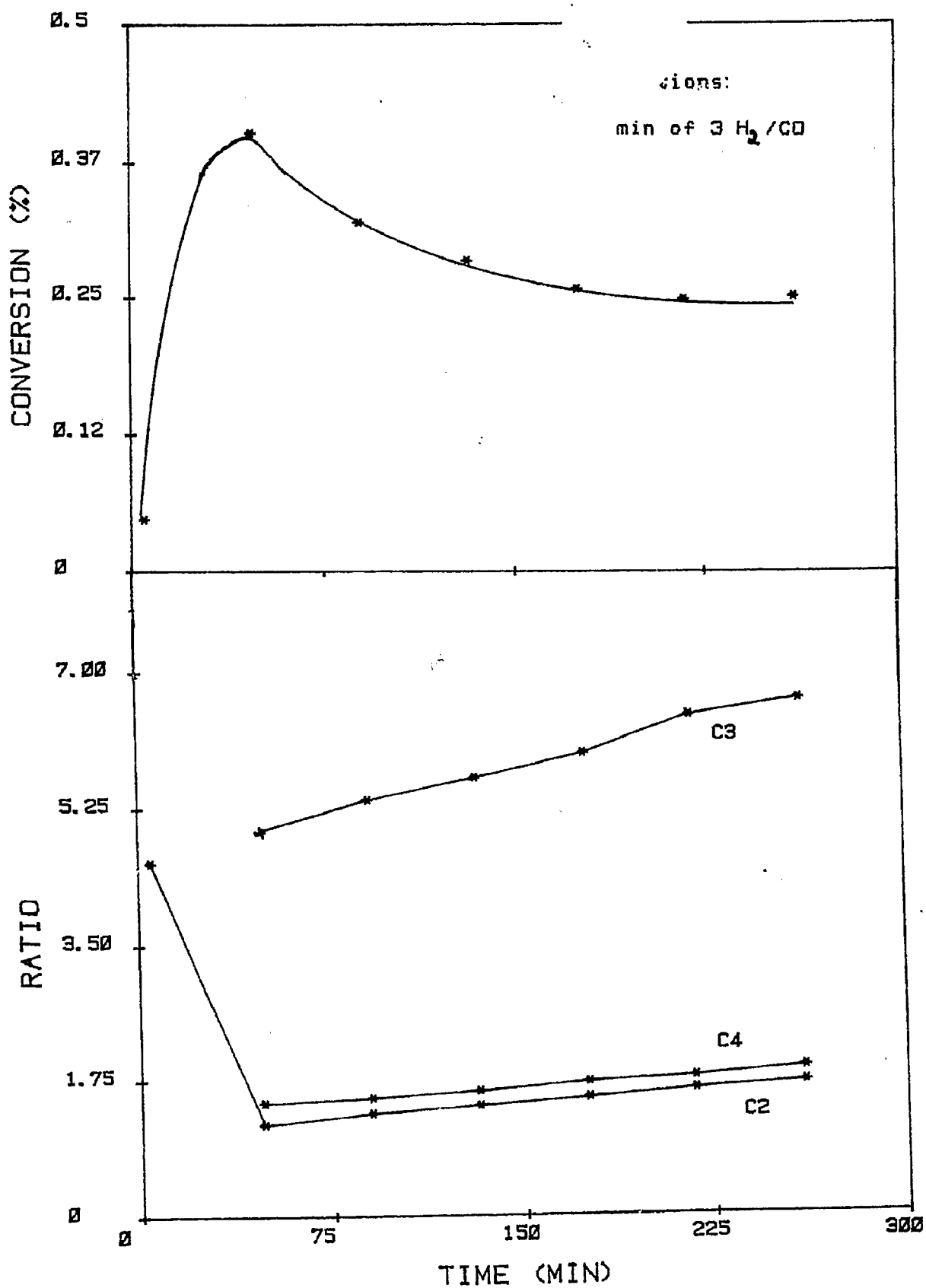


Figure 5: Time dependency of CO conversion and olefin/paraffin ratio of bulk Fe<sub>4</sub>N prepared from 0.025g of iron oxide precursor.

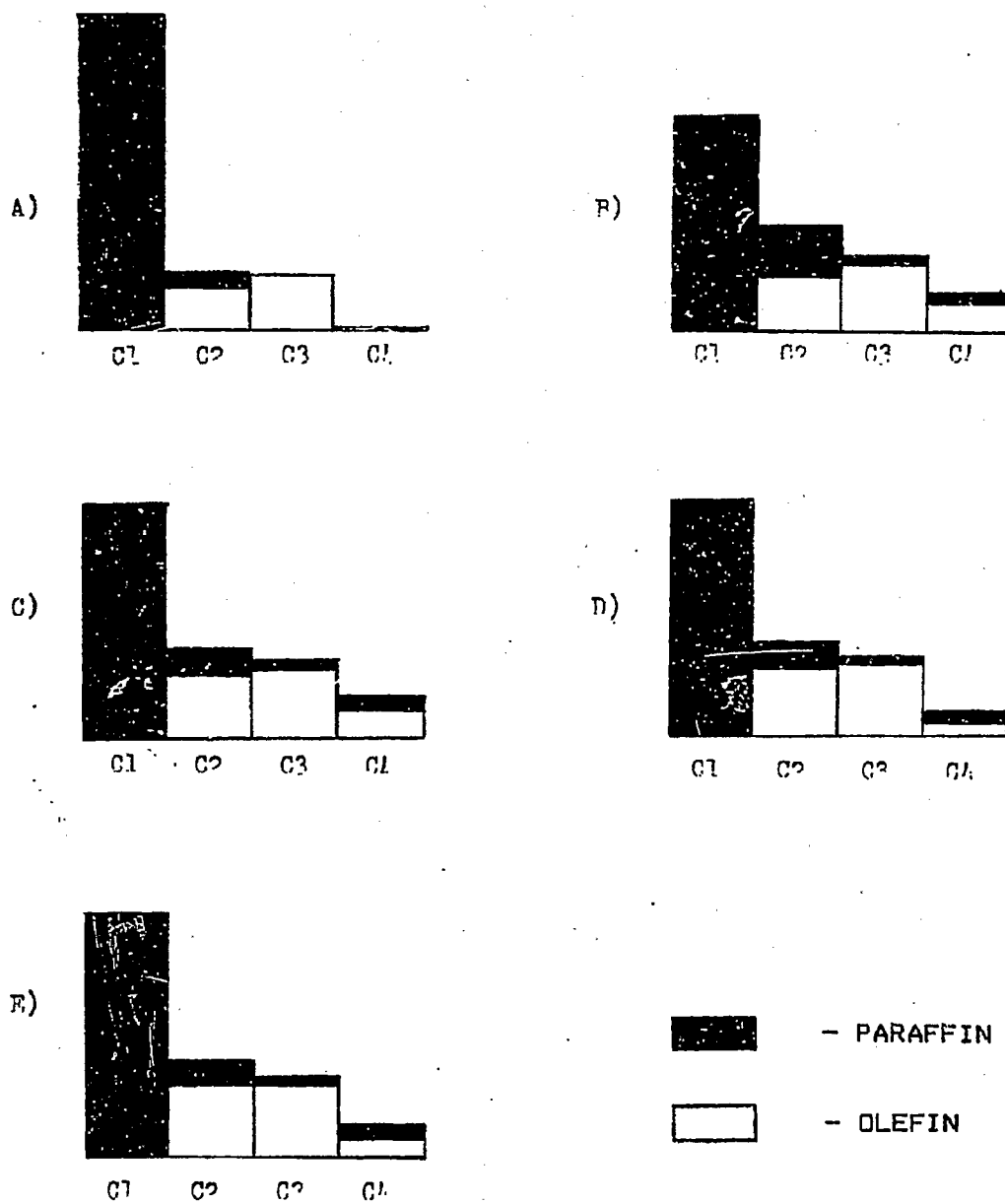


Figure 6: Selectivities of 5 wt% Fe on carbolac. Reduced for 16hr in  $H_2$  at 748 K then 6hr 75%  $NH_3$  at 623 K. Product distribution after a) 0.07 hr, b) 0.61 hr, c) 1.15 hr, d) 1.70 hr and e) 3.88 hr in  $3H_2/CO$  at 523 K.

## FUTURE RESEARCH

Our first task is to complete the studies of the stability and kinetic characteristics of the iron nitride phases. In view of the results obtained for iron on carbon, we will compare the behavior of the unsupported iron nitride phases to that for iron nitrides on silica and carbon. Studies of the short time (minutes) kinetics over these catalysts will utilize the transient kinetic facilities. By using isotopes, material balances and transient responses we expect to elucidate surface nitrogen stability and effects of the presence of nitrogen on the stoichiometry of the adsorbed phase and kinetics of the surface reactions.

Together these studies should provide a thorough evaluation of the capabilities and potential of the iron nitrides for synthesis at 1 atmosphere. With this information secured we will decide whether to pursue higher synthesis gas pressures or continuous addition of  $\text{NH}_3$  to the feed gas during reaction in order to further alter product selectivity.

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## 5. APPENDICES

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