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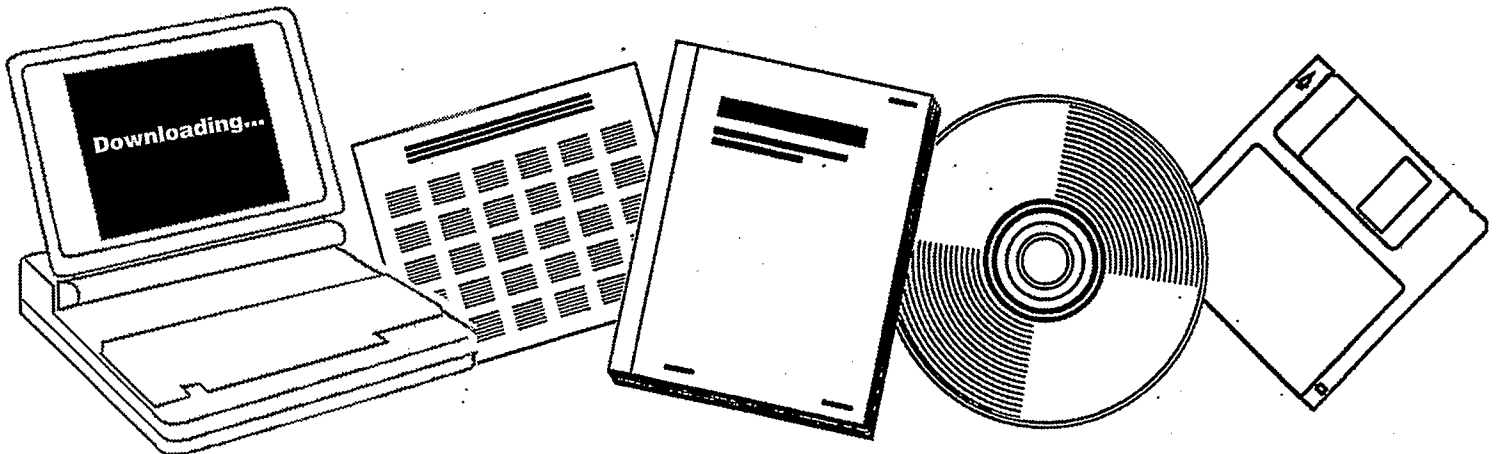
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**CO + H SUB 2 REACTIONS OVER
NITROGEN-MODIFIED IRON CATALYSTS.
QUARTERLY TECHNICAL PROGRESS REPORT,
AUGUST 1, 1982-DECEMBER 31, 1982**

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

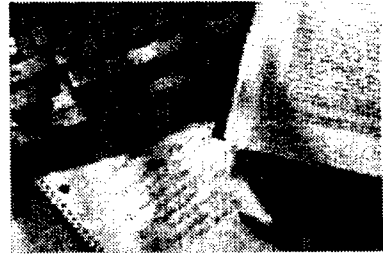
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CO + H₂ Reactions Over

Nitrogen-Modified iron Catalysts

Quarterly Technical Progress Report
for the Period Aug 1, 1982 - Dec 31, 1982

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PREPARED FOR THE
U.S. DEPARTMENT OF ENERGY

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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. In this first quarterly period of a three year program, two students have been assigned to the project and have begun assimilation of the literature and upgrading of equipment. Initial Mossbauer spectroscopic and kinetic experiments on bulk iron nitrides show our ability to prepare and identify the γ' -Fe₄N phase and follow its stability during Fischer-Tropsch synthesis. Kinetic and characterization experiments will be the major emphasis of this first phase of the work.

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. Pre-nitriding 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 (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 Mossbauer studies, already in progress, will identify the various iron nitride phases and allow for examination of their stability during reaction. The Mossbauer 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 NH_3 pulses. Along with ultrahigh vacuum studies, the transient kinetics of 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 affecting 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) Mossbauer 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 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 analyses will examine surface stoichiometry and reaction intermediates. Interaction between the nitrided phases and adsorption bond strengths of CO and H_2 will be investigated.
- v) The effects of NH_3 addition to the reactant stream will be similarly followed by UHV and transient tracer studies to determine possible alterations in reaction pathways evoked by the presence of NH_3 .

Computer modeling may be undertaken at several stages, particularly to simulate the effect of NH_3 interaction as discussed above.

2. TECHNICAL PROGRESS

2.1. LITERATURE REVIEW

2.1.1. General Properties of Nitrides

The transition metal carbides and nitrides can possess certain catalytic advantages relative to their parent transition metals. Recent literature shows that these carbides and nitrides sometimes have higher levels of activity, better activity maintenance and overall selectivity to lower molecular weights, and a greater resistance to poisoning in Fischer-Tropsch synthesis (4). Anderson (1), for example, cites examples of greater activities and altered selectivities of iron nitrides. This result is presented in greater detail below.

Both nitrides and carbides exhibit high melting points (5) and are extremely brittle and hard. When subjected to mechanical attrition, therefore, these materials exhibit low weight losses. In addition, the nitrides show the tendency to conduct electrons and react to magnetic fields in a manner similar to transition metals.

The actual mode of bonding, subject of many bond theory calculations (6,7), is still not adequately described. Sophisticated

theories will be required to explain this complex subject. The following section discusses the structural aspects of the iron-nitrogen system.

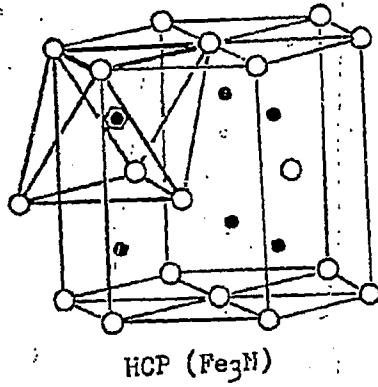
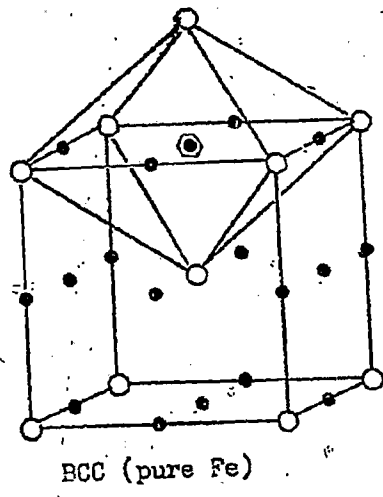
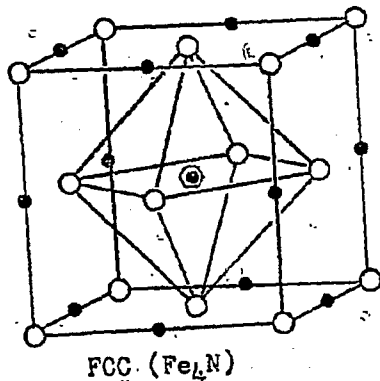
2.1.2. Iron-Nitrogen Phases

Studies of the iron-nitrogen phases by Jack (8) and Anderson (9) have yielded well documented characteristics of the system. Investigations of the iron-carbonitrides have not been so successful. Table One outlines the four major iron nitride phases present at low temperatures (below 490°C). The table, as presented by Anderson (9), provides for each primary phase the associated nitrogen weight %, atomic ratio \bar{N} (ratio N atoms to Fe atoms) and the expected unit cell arrangement. A representation of the unit cells is provided in Figure One, showing body-centered-cubic (bcc), face-centered-cubic (fcc), and hexagonal-close-packed (hcp) arrangements.

TABLE ONE: LOW TEMPERATURE PHASES OF IRON NITRIDE

Phase	Approximate Stoichiometry	N wt %	\bar{N} , atom ratio*	Unit cell
α	Fe	< 0.2	< 0.008	bcc
γ'	Fe ₄ N	5.7-6.1	.241-.259	fcc
ϵ	Fe ₃ N	7.3-11.1	.314-.498	hcp
ϵ'	Fe ₂ N	11.1-11.3	.498-.508	orthorhombic

* \bar{N} is defined as the ratio of nitrogen atoms to iron atoms.



- Fe position
- Possible N position
- ⊙ N position (octahedral interstice)

FIGURE ONE: Unit Cells of Iron Nitrides

The actual locations of the nitrogen atoms are the interstices between the iron positions. Exact stoichiometries are not defined, although the three phases γ' , ϵ and ζ respectively correspond to approximately Fe_4N , Fe_3N and Fe_2N . The compositional dependence of the iron-nitrogen system is presented in Figure Two. This phase diagram covers compositions up to 12 wt % N (ζ -nitride) and temperatures from 300°C through 700°C . Some analogies may be drawn from the iron-carbon system, particularly for low concentrations of the non-metal.

The nitrogen, as shown by Figure Two, exhibits low solubility in the cubic body-centered α -iron, reaching a maximum of 0.4 atom % N at 590°C . The solubility increases markedly in γ -iron (fcc) at temperatures above 900°C . With less than one nitrogen atom per ten iron atoms, a 50% portion of octahedral holes in the fcc iron lattice remains available for interstitial occupation by the nitrogen.

Continual increasing of the nitrogen content at these elevated temperatures (above 700°C) will yield ϵ -phase iron nitride, having a hexagonal-close-packed arrangement. The nitrogen is distributed among the octahedral holes once again. Slow equilibrium cooling at approximately 20 atomic % nitrogen will yield γ' -iron nitride at temperatures below 680°C . This is the Fe_4N phase, and exhibits a cubic (fcc) arrangement. At lower nitrogen contents, below 20% yet above 590°C , an equilibrium between γ and γ' phases will exist.

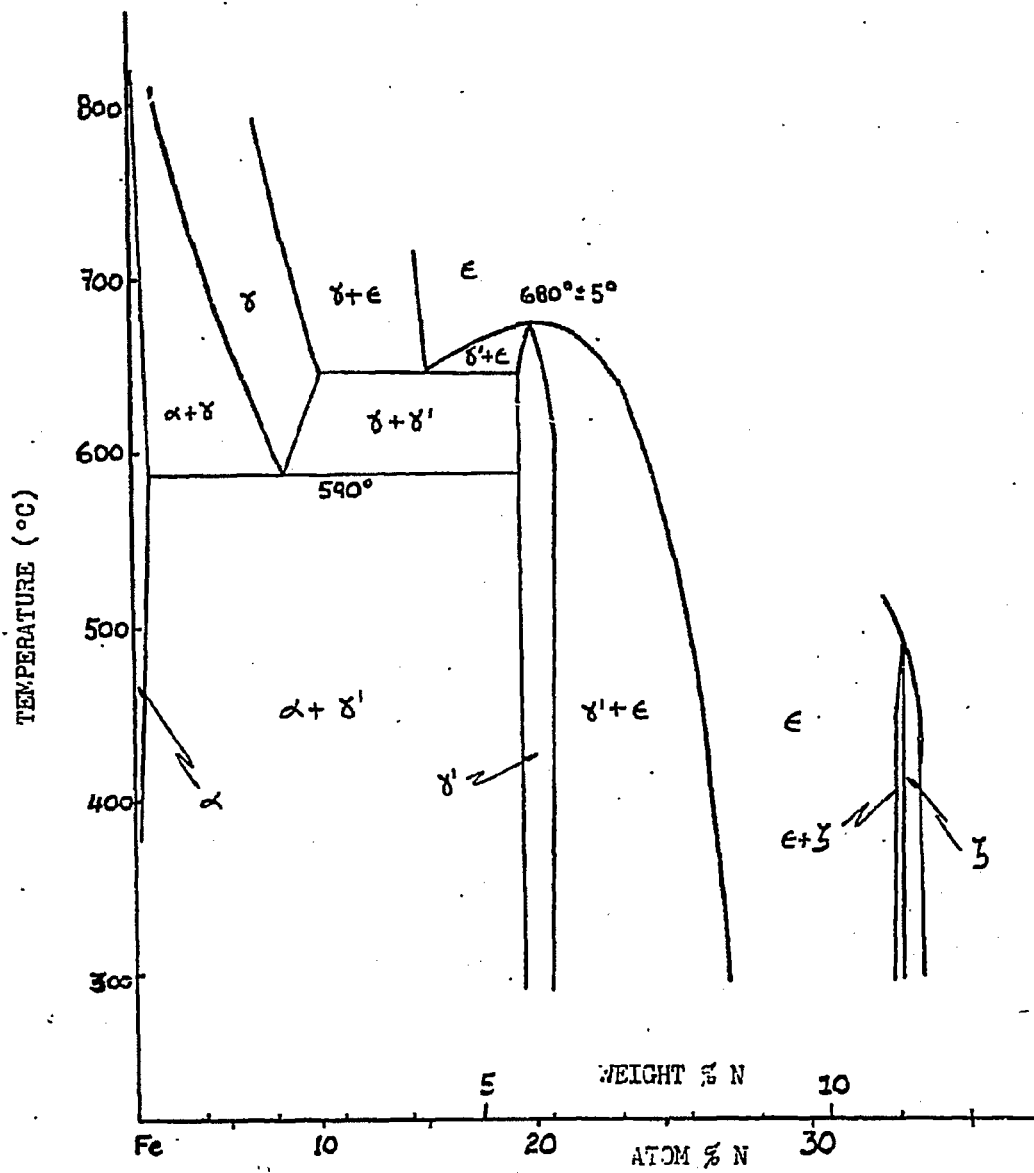


FIGURE TWO: The Iron-Nitrogen Phase Diagram

The nitrogen martensite (α' phase) will be formed by rapidly cooling the γ -phase (which is termed nitrogen austenite in analogy to the Fe-C compound). This N martensite will form a two phase solution with α -iron. The martensite has iron atoms arranged tetrahedrally and is reported to contain up to a maximum 9.4 N per 100 Fe atoms (7).

Occurring at approximately 33 atomic % nitrogen is the orthorhombic ζ -phase. This is stable at temperatures below 500°C and represents the nitride phase with the greatest nitrogen content, corresponding to the formula Fe_2N . The narrow two phase (ζ and ϵ) region separates this orthorhombic phase from the hcp ϵ -phase. The unit cells will be similar in form except the ζ phase exhibits an elongated axis in the c direction transforming the orthohexagonal cell to orthorhombic.

Nitriding of α -iron, at say 450°C, would exhibit these four distinguishable nitride phases. The α -nitride phase would occur immediately upon N addition, but would yield to a mixture of α and γ' after approximately 0.05 atom % nitrogen had been added. The pure γ' -nitrogen would only then be encountered at 20 atom % as mentioned previously. Further nitriding would form the ϵ and ζ phases plus their respective two phase regions. Thus, nitriding at 400-450°C would enable the four major phases to be accessible. The nitriding procedures used in this work will be at these and lower temperatures, and will be discussed below.

2.1.3. Preparation of Iron Nitrides

The preparation of iron nitrides has been considered by Bouchard et al. (13), Juza (12), Jack (8), and by Anderson (9). The iron must first be reduced before significant nitriding can proceed. Thus, the nitrides are prepared by passing ammonia over reduced iron. Juza showed that an unreduced sample is only slowly reduced by the passage of ammonia, with little or no take-up of nitrogen. Anderson reported that the orthorhombic ζ phase (Fe_2N) can be achieved at temperatures less than 350°C , at a space velocity of 750 volumes of ammonia (STP) per volume catalyst per hour. Anderson reported the fastest rate of nitriding at 350°C , achieving the limit of the ζ phase in 10 hours. At higher temperatures of nitriding, only the ϵ phase (Fe_xN , $2 < x \leq 3$) can be obtained. A higher limit of N:Fe ratio can be obtained at higher space velocities. An alternative method of nitriding is to pass ammonia and hydrogen over the reduced catalyst. The presence of hydrogen lowers the effective partial pressure of nitrogen, thus producing a lower N/Fe ratio nitride. In this manner, γ' - Fe_4N can be produced by passing a 7:1 mixture of NH_3 and H_2 over reduced iron at 350°C . Table Two summarizes preparation methods.

TABLE TWO: PREPARATION OF IRON NITRIDES

Phase	Reactants	Temp. °C	Time Hr.	Ref.
ζ - Fe ₂ N	Fe/NH ₃	350	10	(9)
ϵ - Fe _x N	Fe/NH ₃ /H ₂	350	<10	(13)
ϵ - Fe _x N	Fe/NH ₃	>350	>10	(9)
γ' - Fe ₄ N	Fe/NH ₃ /H ₂	350	3	(13)

2.1.4. Catalytic Properties of Iron Nitrides

Studies of the Fischer-Tropsch synthesis over iron nitrides are rare. Anderson, during the 1950's (9) and in review in 1980 (1), concluded that iron nitrides are more active than conventional iron catalysts. In addition, he found greater selectivity toward shorter chain hydrocarbons, and an increase in the yield of alcohols. Bennett et al. (11) recently investigated synthesis over many catalysts, including iron nitrides, and reached similar conclusions.

Anderson conducted experiments at a pressure of 7.8 atmospheres over a fused iron catalyst at 240°C, with a 1:1 H₂/CO feed. His results show almost no production of high molecular weight hydrocarbons (> 464°C b.p.) over the nitrided ϵ -Fe_xN catalyst, while 10-20% of the hydrocarbons are high molecular weight in the experiment over reduced iron (1). The activity for the nitride was twice that of the reduced catalyst, and the nitride catalyst did not lose activity significantly over 10

weeks of testing. In contrast, the reduced iron catalyst steadily decreased in activity over the same period. The nitrides also remained remarkably stable over weeks of testing in synthesis gas, in which nitrogen was slowly replaced by carbon during the synthesis, forming iron carbonitrides.

Synthesis over the nitrided catalyst yielded significant amounts of alcohols, up to 30% of the condensed phases, or 20% of the total product exclusive of water and carbon dioxide. The alcohols were largely primary and straight chain, with ethanol the most abundant (40%) of the total.

From thermodynamics, the low molecular weight alcohols are less favored than the longer chain products. Methanol synthesis from CO and H₂ has a positive change of standard free energy at 230°C ($\Delta G^\circ = + 5.1$ kcal/mol) and is therefore not favored as a product. Ethanol, however, is favored, $\Delta G^\circ = - 6.8$ kcal/mol. Anderson's experiments at 240°C indeed reflect a preference for the longer chain alcohols, since methanol was a minor product. In addition, the standard free energy change increases with temperature, causing production to become less favorable at higher temperatures.

Bennett investigated many catalysts for Fischer-Tropsch synthesis, including fused iron, iron nitrides, cobalt, iron/copper alloy and lathe turnings (11). He concluded that "nitrided fused iron catalysts look most promising". The nitrided catalysts produced significant quantities of alcohols, the C₂ and C₃ alcohols

notably most abundant, as expected from the thermodynamics.

Nitrided iron has been largely ignored as a Fischer-Tropsch catalyst, although it was proven to be worthy of interest. The behavior of the iron nitrides in Fischer-Tropsch synthesis, namely the reasons behind the selectivity, the increased activity and the unusual stability, is not at present given in the literature. Keys to predicting this behavior are in the determinations of the catalytically important nitride phases and examination of their chemical and surface properties.

2.2 SUMMARY OF RESULTS

The main effort in this first quarter of the grant period has been assignment and orientation of personnel, initiation of equipment upgrades and preliminary Mossbauer studies of the bulk nitrides. Two excellent first year students, Albert Hummel and Alan Wilson, joined the project last fall. Both are completing the core course sequence this spring and have begun research. Albert Hummel will emphasize kinetic studies of the iron nitrides. Alan Wilson's work will center on Mossbauer studies of the catalysts.

Several modifications and upgrades of equipment are described in the original proposal. The power supply for the axial electron gun for Auger spectroscopy has been ordered and delivered. Because of rapid changes in the computer market we have reevaluated our proposed computer upgrade. The general approach and specific main hardware items proposed still seem

optimum and the orders will be written shortly. Funds from another grant have permitted us to replace the old multichannel analyzer with a new and more sophisticated data analysis system for the Mossbauer spectrometer. The system is being checked out now and will improve the reliability of the Mossbauer experiments undertaken in this work.

We have initiated experiments on iron nitrides with a series of Mossbauer and kinetic runs on prenitrided iron powder. The catalysts were prepared by mixing 30 mg of α -Fe₂O₃ with 270 mg of SiO₂ and pressing the mixed powders into a self supporting wafer. The wafer was reduced in the Mossbauer cell in H₂ at 120°C for one half hour and at 400°C for 4 hours. The silica acted as a diluent for the reduced iron powder. The catalysts were then exposed to H₂/NH₃ mixtures to produce the desired nitrides. After the Mossbauer spectrum of the nitride was recorded at room temperature, a Fischer-Tropsch synthesis experiment was started. The catalyst was first heated to 250°C in the NH₃ and H₂ mixture. A switch of the flowing gas to a H₂/CO/He mixture started the synthesis run. After six hours of reaction, the catalyst was cooled in reaction gas and then another Mossbauer spectrum was taken.

Attempts to make the ϵ nitride gave unexpected results. The Mossbauer spectrum the the nitrided catalyst has a strong singlet, suggestive of the ζ rather than the ϵ nitride. These experiments need further evaluation.

Three hour treatment of the reduced catalyst in 4/1 NH_3/H_2 at 350°C was expected to produce the γ' - Fe_4N phase (13). The Mossbauer spectrum showed that 2/3 of the iron was still in the metallic state after this treatment. Further nitriding at 400°C for 2.5 hours gave spectrum A in Figure Three. The splitting of the outermost lines in this spectrum identifies the major phase as γ' , but the relative intensities of the inner lines suggest that other nitride phases are present as well. Spectrum B, taken after the Fischer-Tropsch reaction, shows loss of some of the γ' phase (decrease in the intensity of the outer peaks) and the growth of a new phase which is probably a carbonitride. Complete analysis of these spectra will require further experiments. Comparison of these results to those for the other nitrides prepared in this group suggest that the γ' nitride is the most stable at the reaction conditions used.

3. Future Research

Experiments have begun as planned in the original proposal. In this first phase of the work, the nitride stabilities and the kinetics will be the prime areas of study. The stability studies will rely heavily on the Mossbauer effect as a method of phase identification. As appropriate, x ray diffraction will also be used. We will continue with the bulk nitrides, but expect also to evaluate nitriding effects in supported iron systems. The kinetic studies will begin with steady state experiments to evaluate selectivity changes associated with nitride formation. We are eager to begin transient kinetic analysis also, however,

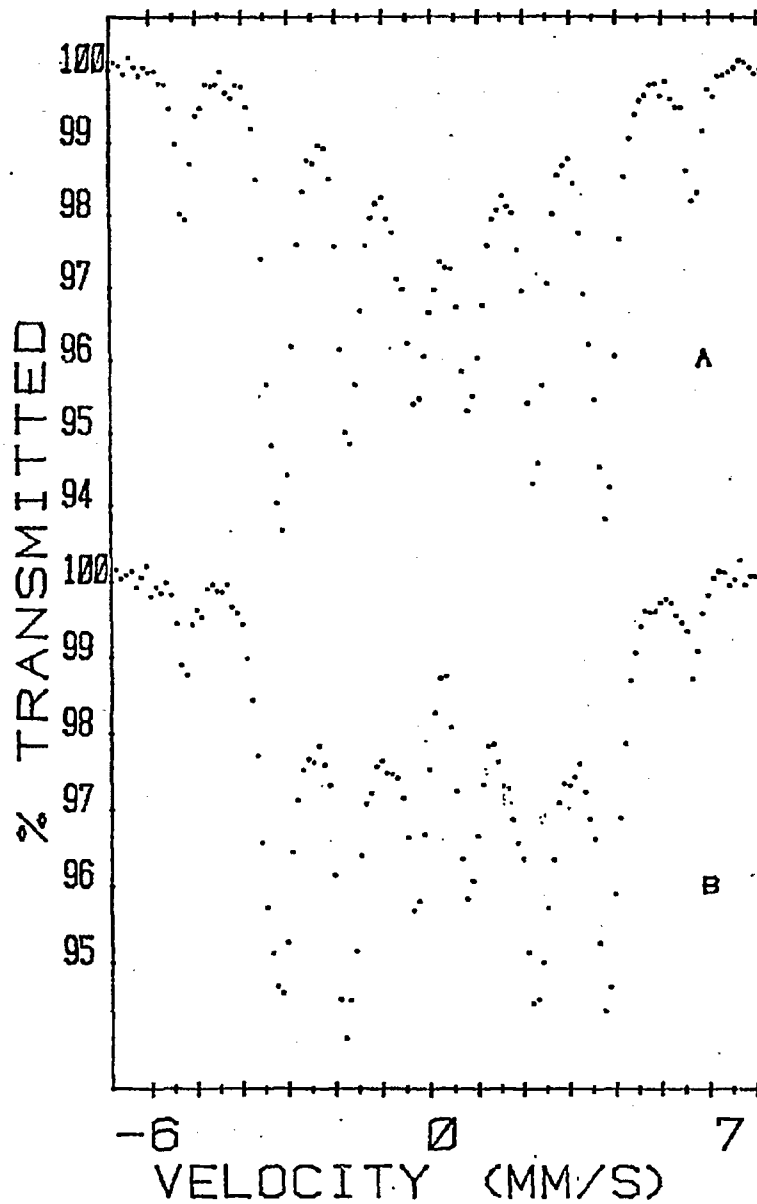


Figure Three: Room temperature Mössbauer spectra. A) After nitriding. B) After Fischer-Tropsch synthesis.

and intend to start with studies of the surface nitride stoichiometry. (In preparation for those and other transient experiments, we are beginning attempts to model the transient behavior of the system on the computer. We expect that the computer "experiments" will allow us to test various approaches to studying the system and permit a more streamlined program of actual experiments. This capability should be especially valuable in mechanistic studies where the responses of trial sequences of elementary steps can be tested to show the most sensitive experiments.

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5. APPENDICES

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