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# CO + $H_2$ REACTION OVER NITROGEN-MODIFIED IRON CATALYSTS

Quarterly Technical Progress Report for the Period
January 1—March 31, 1984

By
W. Nicholas Delgass

Work Performed Under Contract No. FG22-82PC50804

Purdue University
West Lafayette, Indiana

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PREPARED FOR THE

U. S. DEPARTMENT OF ENERGY

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# ABSTRACT

We have found that the nitride catalysts lose substantial amounts of nitrogen during the initial minutes of Fischer-Tropsch synthesis. In order to further study the stability of these catalysts, we have concentrated on the decomposition of the nitride in hydrogen. In addition, we have prepared a range of $\epsilon$-$Fe_xN$ $(2 < x < 3)$ phases. The Mössbauer parameters from these phases will aid in the identification and fitting of the transient $\epsilon$ phases formed during the carburization of $\zeta$-$Fe_2N$.

Extremely rapid nitrogen loss has been observed from $\zeta$-$Fe_2N$ in $H_2$ at 523 K both in constant velocity Mössbauer and in transient mass spectrometer experiments. In order to study the phase change from $\zeta$-$Fe_2N$ to $\alpha$-Fe in more detail, the hydrogenation temperature was decreased to 473 K and intermediate samples were quenched in liquid nitrogen to lock in the phase distribution for subsequent Mössbauer study. The spectra show complete conversion to $\alpha$-Fe at or before 21 minutes at 473 K. The intermediate samples show evidence of an extremely sharp gradient; only a very small amount of $\gamma'$ or $\epsilon$ phase is observed. Thus, a moving front model of the phase transformation appears to be appropriate.

Mass spectroscopy of the hydrogenation of $\zeta$-$Fe_2N$ at 523 K showed similar behavior to that of both the $\gamma'$ and $\epsilon$ phases, in which an active surface species and a slowly activating one were observed. The $H_2$ was replaced by $D_2$ in this experiment in order

to observe partially hydrogenated surface species in the initial spike of ammonia. All $NH_xD_y$ (x + y = 3) species were observed in this spike, indicating extremely rapid surface H/D exchange with gaseous ammonia. The fragmentation pattern of $NH_3$ in the mass spectrometer was also determined and will be used to calculate initial $NH_x$ surface contributions.

# 1. OBJECTIVES AND SCOPE

## 1.1 BACKGROUND

The feasibility of utilizing synthesis gas ($CO + H_2$) 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 fused promoted iron and precipitated iron catalyst is said to shift the product distribution to one exhibiting lower molecular weight fractions and enhanced alcohol yields (1,2). Iron nitrides with high initial activity and significant stability over weeks of experimentation are also reported (1,2). On the other hand, simultaneous introduction of ammonia ($NH_3$) with synthesis gas produces nitrogeneous 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 (3,4). 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, are aiding in the identification of the various iron nitride phases and allow examination of their stability during reaction. The Mössbauer results are forming a 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. XRD studies will supplement the Mössbauer effect in identifying the bulk iron nitride phases.

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 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 are being used to determine nitride phase stability and to correlate these phases to reaction selectivity.

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 analysis 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 invoked by the presence of $NH_3$.

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

## 2. TECHNICAL PROGRESS

### 2.1 MÖSSBAUER PARAMETER REVIEW

Several investigators have used the Mössbauer effect to help characterize the iron nitride phases. Other spectroscopic methods include x-ray diffraction and magnetization studies. An appreciation of the reported Mossbauer spectra of iron nitrides aids us in interpreting our Mössbauer results [5]. We consider here an update of our previous spectral parameter review, but limit the reported spectra to $\gamma'$- and $\epsilon$-iron nitrides. The third major phase, $\zeta$-$Fe_2N$, is well established to be a paramegnetic doublet at 300 K. The characterization of the remaining two phases is not, however, so facile and is a contentious subject in the literature to date.

So, although the eight line spectrum of $\gamma'$-$Fe_4N$ is well established, the actual assignment of electronically different iron sites in this nitride is still under debate. Shirane <u>et al</u>. [6], Gielen and Kaplow [7], and Maksimov <u>et al</u>. [8] consider two superimposed six line patterns in the analysis of the γ′-nitride. Other researchers, however, support a third site in the analysis. Nozik et al. [9], Lo and coworkers [10], Foct et al. [11], and Clauser [12] are among such investigators. The exact assignment of this third site is, however, unresolved within this group of researchers. Two explanations exist, either the IIA and IIB sits are electronically different, or the inequality arises from a ninety degree difference in the EFG-magnetization vector angle between atoms on adjacent sides of the cubic unit cell. Maksimov and coworkers [8], in fact, only report two indentifiable iron sites in the $Fe_4N$ lattice but remark that the difference between the IIA and IIB sites may be masked by the estimated error in their reported parameters. Table I highlights the Mössbauer parameters reported for γ′-$Fe_4N$ by the aforementioned researchers.

The wider range of nitrogen composition for the ϵ-iron nitrides further complicates this characterization by the Mossbauer effect. These hexagonal close packed nitrides exhibit an average bulk nitrogen concentration ranging from approximately 26 at % to 33.3 at %. Special quenching or preparation techniques can produce hexagonal unit cells with nominal compositions below the room temperature 26 at % limit [13]. Overall inhomogeneity of ϵ-nitrides, where the nitrogen is distributed through the iron lattice only statistically, creates a wider variation of magnetic fields at the iron nucleus than is encountered in either γ′-$Fe_4N$ or α-Fe. Recent work [14-15] reports increasing peak widths with distance from the center of the isomer shift. Thus, constraining of peak dips to 3:2:1 (with equal width) is no longer valid for randomly orientated Fe powders under such conditions. Other interpretations of ϵ-iron nitride spectra are given by DeCristofaro and Kaplow [16], Eichel and Pitsch [17] and Foct *et al*. [11]. The reported bulk compositions and Mössbauer parameters are summarized in Table II.

As evidenced by Tables I and II, the characterization of even the more defined $\gamma'$-$Fe_4N$ stoichiometry is not trivial. Particle size distributions, sample inhomgeneity and synthesis conditions play a role in altering the Mössbauer parameters. A given nitride may then be characterized differently despite an equivalent nominal stoichiometry or identical x-ray diffraction pattern. Care must be exercised in interpreting such parameters, and the sample condition and pretreatments should be clearly cited.

## Table 1

## MÖSSBAUER PARAMETERS FOR $\gamma'$-Fe$_4$N

| Iron Identity | Temp. (K) | Isomer Shift (mm/s) | Quadrupole Splitting (mm/s) | Hyperfine Field (kOe) | Reference |
|---|---|---|---|---|---|
| Fe-I | 300 | +0.24 | 0.0 | 340.6 | 9 |
| Fe-II-A | 300 | +0.52 | −0.22 | 215.5 | 9 |
| Fe-II-B | 300 | −0.15 | +0.43 | 219.2 | 9 |
| Fe-I | 300 | | | 340±5 | 8 |
| Fe-II | 300 | | | 216±5 | 8 |
| Fe-I | 300 | +0.30±.08 | | 345±10 | 6 |
| Fe-II | 300 | +0.45±.06 | | 215±10 | 6 |
| Fe-I | 300 | +0.24 | 0.0 | 340 | 12 |
| Fe-IIA | 300 | +0.30 | −0.22 | | 12 |
| Fe-IIB | 300 | +0.30 | +0.43 | | 12 |
| Fe-I | 300 | +0.01±0.05 | 0.0 | 339±4 | 7 |
| Fe-II | 300 | +0.11±0.1 | +0.2±0.4 | 202±7 | 7 |
| Fe-I | 300 | +0.25±.01 | 0.0 | 339±1 | 10 |
| Fe-IIA | 300 | +0.30±.01 | −0.12±.02 | 217±1 | 10 |
| Fe-IIB | 300 | +0.30±.01 | +0.12±.02 | 217±1 | 10 |
| Superpara. | 300 | +0.29±.01 | 0.0 | 0 | 10 |
| Fe-I | 77 | +0.36±.02 | 0.02±.02 | 370±2 | 11 |
| Fe-II | 77 | +0.40±.02 | −0.25±.02 | 234±2 | 11 |
| Fe-II | 77 | +0.41±.02 | 0.12±.02 | 235±2 | 11 |

Table 2

MÖSSBAUER PARAMETERS FOR $\epsilon\text{-Fe}_x\text{N}$

| Nitride | Iron Identity | Temp. (K) | IS (mm/s) | QS (mm/s) | HFS (kOe) | Reference |
|---|---|---|---|---|---|---|
| $\epsilon\text{-Fe}_x\text{N}$ | 1nn | well | ... | ... | 298 | 16 |
| | 2nn | below | ... | ... | 238 | 16 |
| | 3nn | $T_c$ | ... | ... | 130 | 16 |
| $\epsilon\text{-Fe}_{2.67}\text{N}$ | Fe-I | 300 | +0.26 | ... | 273 | 14 |
| | Fe-II | 300 | +0.34 | ... | 205 | 14 |
| | Fe-III | 300 | +0.40 | ... | 99.5 | 14 |
| | Fe-I | 4.2 | +0.40 | ... | 330 | 14 |
| | Fe-II | 4.2 | +0.48 | ... | 258 | 14 |
| | Fe-IIIA | 4.2 | +0.54 | ... | 140 | 14 |
| | Fe-IIIB | 4.2 | +0.52 | ... | 64 | 14 |
| $\epsilon\text{-Fe}_{2.47}\text{N}$ | Fe-II | 300 | +0.35 | ... | 186 | 14 |
| | Fe-III | 300 | +0.41 | ... | 84 | 14 |
| | Fe-II | 4.2 | +0.47 | ... | 259 | 14 |
| | Fe-IIIA | 4.2 | +0.57 | ... | 142 | 14 |
| | Fe-IIIB | 4.2 | +0.60 | ... | 66 | 14 |
| $\epsilon\text{-Fe}_{3.2}\text{N}$ | Fe-II | 295 | +0.24 | ... | 298 | 17 |
| | Fe-II | 295 | +0.33 | ... | 238 | 17 |
| $\epsilon\text{-Fe}_{4.4}\text{N}$ | Fe-I | 77 | +0.29±.03 | 0.0±.03 | 298±2 | 11 |
| | Fe-III | 77 | +0.34±.01 | 0.02±.01 | 222±1 | 11 |
| $\epsilon\text{-Fe}_{2.5}\text{N}$ | Fe-II | 77 | +0.45±.05 | -0.03±.05 | 243±3 | 11 |
| | Fe-III | 77 | +0.45±.06 | 0.00 | 85±5 | 11 |
| $\epsilon\text{-Fe}_{2.66}\text{N}$ | Fe-II | 300 | +0.34 | 0.0 | 220 | 15 |
| | Fe-III | 300 | +0.41 | 0.0 | 112 | 15 |
| | Fe-Q | 300 | +0.40 | ... | 0 | 15 |

## 2.2 SUMMARY OF RESULTS

### 2.2.1. $\epsilon$-$Fe_xN$ Catalysts

The wide distribution of nitrogen stoichiometries in the $\epsilon$-iron nitride was discussed in the previous section. Different iron sites may be predicted, depending upon the statistical distribution of nitrogen within the bulk lattice. The hyperfine splitting for each site will vary with localized nitrogen content. An appreciation of the variation of spectral parameters of the Fe-N system, notably in the $\epsilon$-$Fe_xN$ region, may be necessary in order to clearly understand the spectral variations occurring with incorporation of carbon into the catalyst lattice. We have observed that during Fischer-Tropsch synthesis (at 523 K in $3H_2/CO$ synthesis gas) the initial transient period (15 minutes) is characterized by a major nitrogen content depletion, rather than by carbon incorporation. The rapid loss of bulk nitrogen from a nitrogen rich $\zeta$-$Fe_2N$ to an $\epsilon$-$Fe_xN$, under synthesis condition is documented [14,18]. The ability to distinguish the $\epsilon$-iron nitride over which the reaction then proceeds thus becomes important.

In an attempt to produce an informative sequence of $\epsilon$-iron nitrides, we performed the experiment illustrated by Figure 1. Here one sees the sequential leaching of nitrogen from the zeta nitride. The starting phase was produced by nitriding a freshly reduced $\alpha$-Fe wafer with pure ammonia (100 ml/min) at 673 K. The gas phase ammonia concentration was then diluted to 91% by adding

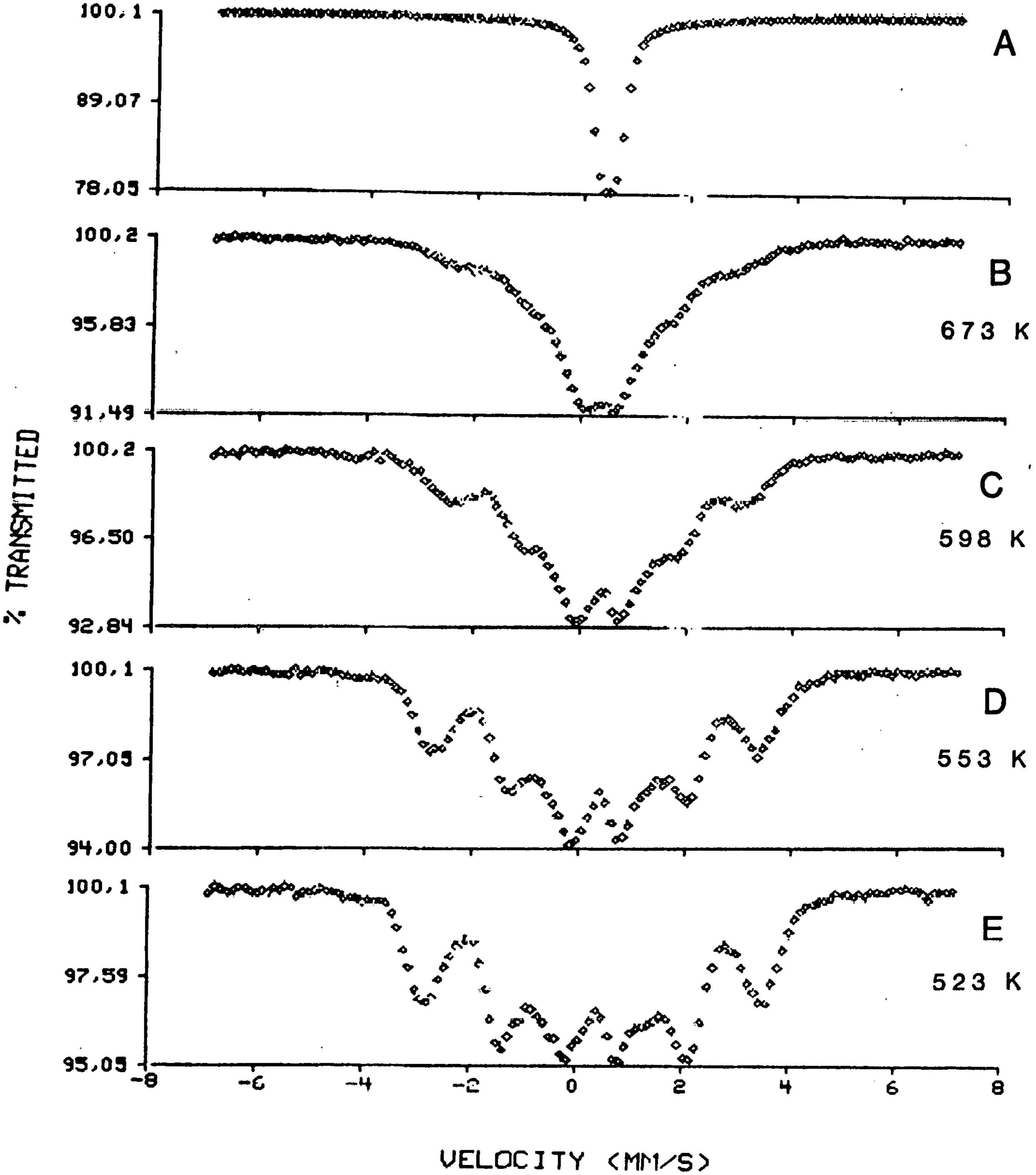

Figure 1: Mössbauer spectra (298 K) of ε-iron nitrides
A) Starting ε/ζ-$Fe_2N$ then consecutively annealed in
91% $NH_3$ for 6 hours at respective temperatures (B-E)

hydrogen and make up ammonia to a 150 ml/min total flow rate. The sample was then annealed at 673 K in 91% $NH_3$ for approximately 6 hours. The Mössbauer spectrum of this new ε phase is shown in Figure 1B. An additional six hour annealing cycle did not produce a noticeable change in this spectrum. The sample was then sequentially annealed in 91% $NH_3$ for 6 hours, but at progressively lower temperatures. Figure 1C, D and E show the spectra from 598K, 553 K, and 523K annealing treatments respectively. This sequence further demonstrates that the synthesis of a higher nitrogen containing nitride may be accomplished by an increase in the synthesis temperature. Additionally, a similar effect is seen for an increase in ammonia concentration when the temperature is kept constant. In the temperature range 450-725K, the lines of equal nitriding potential are therefore represented by a decreasing ammonia mole fraction with increasing temperature. This trend follows the nitriding envelopes presented by Eisenhutt and Kaupp [19] in their early study of iron nitrides.

The spectra shown in Figure 1 span a nitrogen concentration ranging from 33.3 at % N to an estimated 29 at % N. Although final least squares fit spectral parameters are not yet available for these spectra, certain trends are worth mentioning. The magnetic splittings of the two major 6 line patterns expected in the Figure 1 spectra, $H_{Fe-II}$ and $H_{Fe-III}$, increase from 0 to approximately 190 and 100 kOe in Figure 1E. The exact increase in the peak intensities of the Fe-II and Fe-III sites with decreasing N content is difficult to determine exactly without the completion of computer fittings. The prominence of the inner two peaks is probably complicated by a paramagnetic doublet, whose quadropole splitting also appears to increase with decreased nitrogen content. These and others more exact trends should be confirmed after fitting and will then form the basics for the analyses of samples carburized previously.

### 2.2.2 Intermediate Phases in Denitriding

The transient nature of iron nitride denitriding is fast in hydrogen rich atmospheres at the present synthesis temperatures (523 K) and greater. The mechanism of phase change and nitrogen migration from the bulk to the surface is thus difficult to follow under such conditions through Mössbauer effect measurements. In an attempt to slow the rate of nitrogen removal kinetics, the gas phase was kept as pure hydrogen while the denitriding temperature was reduced from 523 K. The experiment was partly successful and serves as an upper bound estimate as to the behavior of the bulk nitride exposed to hydrogen rich atmospheres.

Figure 2 shows the room temperature Mossbauer spectra of a $\zeta$-$Fe_2N$ sample denitrided in hydrogen at 473 K for 2.5, 5.0, 10.0 and 21.0 minutes. After the specified exposure to $H_2$, each sample was liquid nitrogen quenched to prevent further loss of nitrogen. Hydrogen was flowed during the quench. After the room temperature spectrum had been acquired, the sample was then nitrided for approximately 6 hours in flowing $NH_3$ at 673 K to

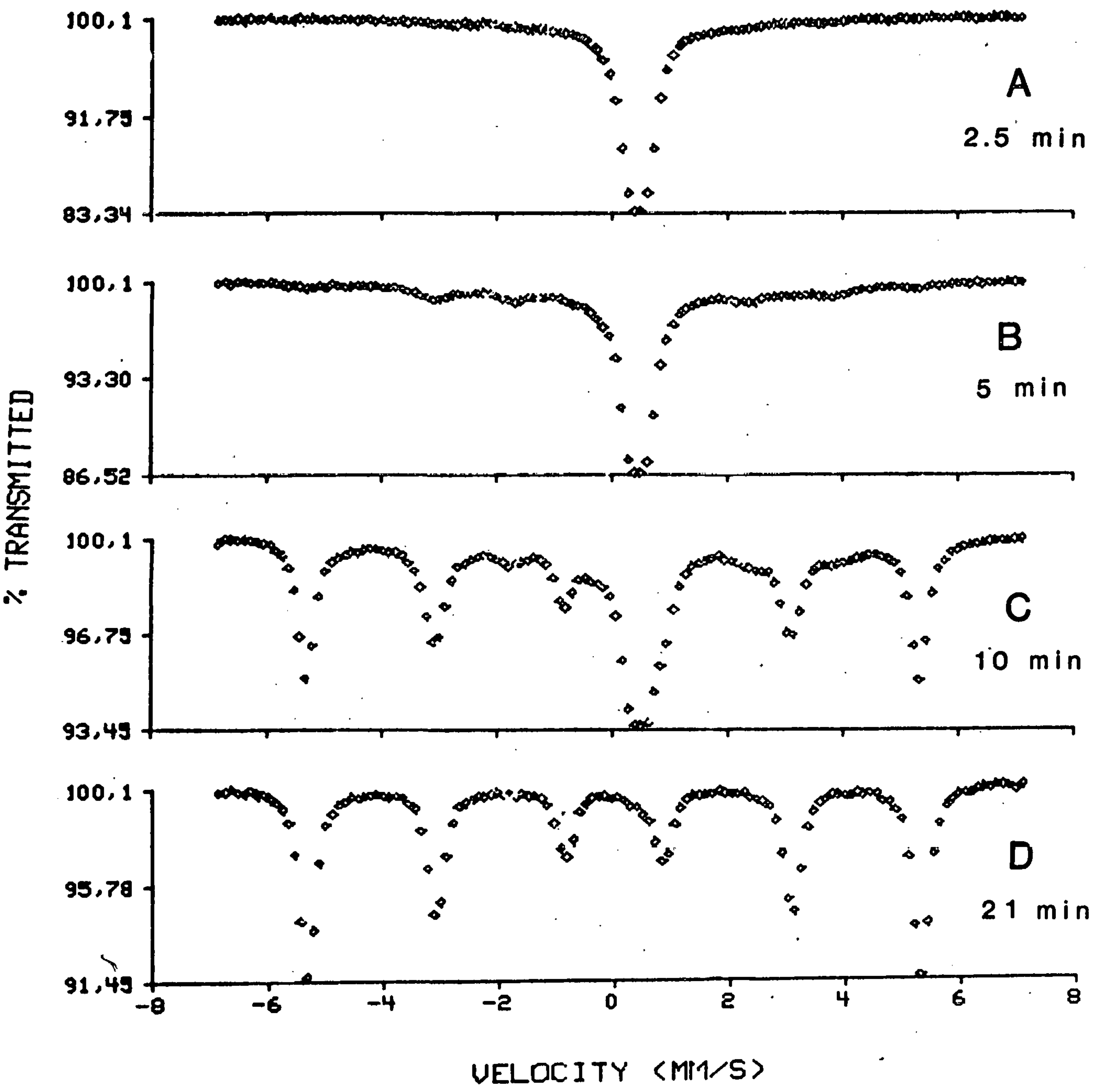

Figure 2: Mössbauer spectra (298 K) of ζ-$Fe_2N$ denitriding in $H_2$ at 473 K for progressively longer time periods.

reestablish the homogeneous $\zeta$-$Fe_2N$. The sample was then cooled in flowing ammonia to 473 K before switching to hydrogen. Total denitriding to $\alpha$-Fe is seen to occur in 21 minutes or less and corresponds well to constant velocity measurements of $\zeta$-$Fe_2N$ loss in $H_2$ at 473 K.

The two intermediate spectra, 2B and C, accentuate the denitriding phenomenon. The former shows a slight change of the initial $\zeta$-$Fe_2N$ phase to an intermediate nitride with very broad peaks. An additional five minutes of hydrogen then produces substantial amounts of $\alpha$-Fe. The broad center peak (doublet) shows that the nitrogen rich $\epsilon/\zeta$-$Fe_2N$ phase is presumably covered by a $Fe^o$ domain. Quantities of an intermediate nitride are clearly visible in 2C. The small amount of this intermediate ($\gamma'/\epsilon$) phase further shows the rapid nature of this transition from $\zeta$-$Fe_2N$ to $\alpha$-Fe, and also serves as an indication of the steep N concentration gradient between the two major phases.

The inhibition of this rapid denitriding must be accomplished if the catalyst is to retain its nitride structure and associated kinetics. Conditions and treatments for stabilizing the nitrides will be considered and emphasized in future work.

### 2.2.3 Transient Kinetics by Mass Spectrometry

Transient denitriding behavior of $\zeta$-$Fe_2N$ in $H_2$ has been further investigated by mass spectrometry. Results of the denitriding behavior of $\gamma'$-$Fe_4N$ and $\epsilon$-$Fe_{2.7}N$ have been reported in previous progress reports (20,21). In addition, extremely rapid decomposition of $\zeta$-$Fe_2N$ has been observed in our previous Mössbauer studies.

From the hydrogenation (decomposition) of $\gamma'$-$Fe_4N$, $\epsilon$-$Fe_xN$ (21) and in the present case $\zeta$-$Fe_2N$, it is apparent that there are two distinct nitrogen species associated with the virgin nitride. An active and presumably partially hydrogenated surface species reacts to form a first small spike of $NH_3$, and then a second slow activating species builds to maximum $NH_3$ production. The active, partially hydrogenated $NH_x$ species could appear due to a rate limiting step during the nitriding process; obviously, ammonia must adsorb and decompose through this species to become the nitride. Drechsler and coworkers (22) and Grunze <u>et al</u>. (23) have in fact found evidence for an NH species in the decomposition of $NH_3$ on iron single crystal surfaces.

If this active species is indeed partially hydrogenated, decomposition of the $\zeta$-$Fe_2N$ nitride in $D_2$ should yield $NH_xD_y$ ($x+y = 3$) ammonia in the short spike. Figure 3 shows the result of switching to a pulse of $D_2$ from the argon, followed by a step to $H_2$. As can be seen in the $D_2$ pulse, partially hydrogenated $NH_xD_y$ species are observed indicating the presence of $NH_x$ ($x \neq 0$) species on the surface prior to the step to $D_2$. Also, from the variety of $NH_xD_y$ ($x + y = 3$) species ranging from $NH_3$ to $ND_3$, it is evident that H/D exchange was occurring in the ammonia as it traveled across the catalyst bed.

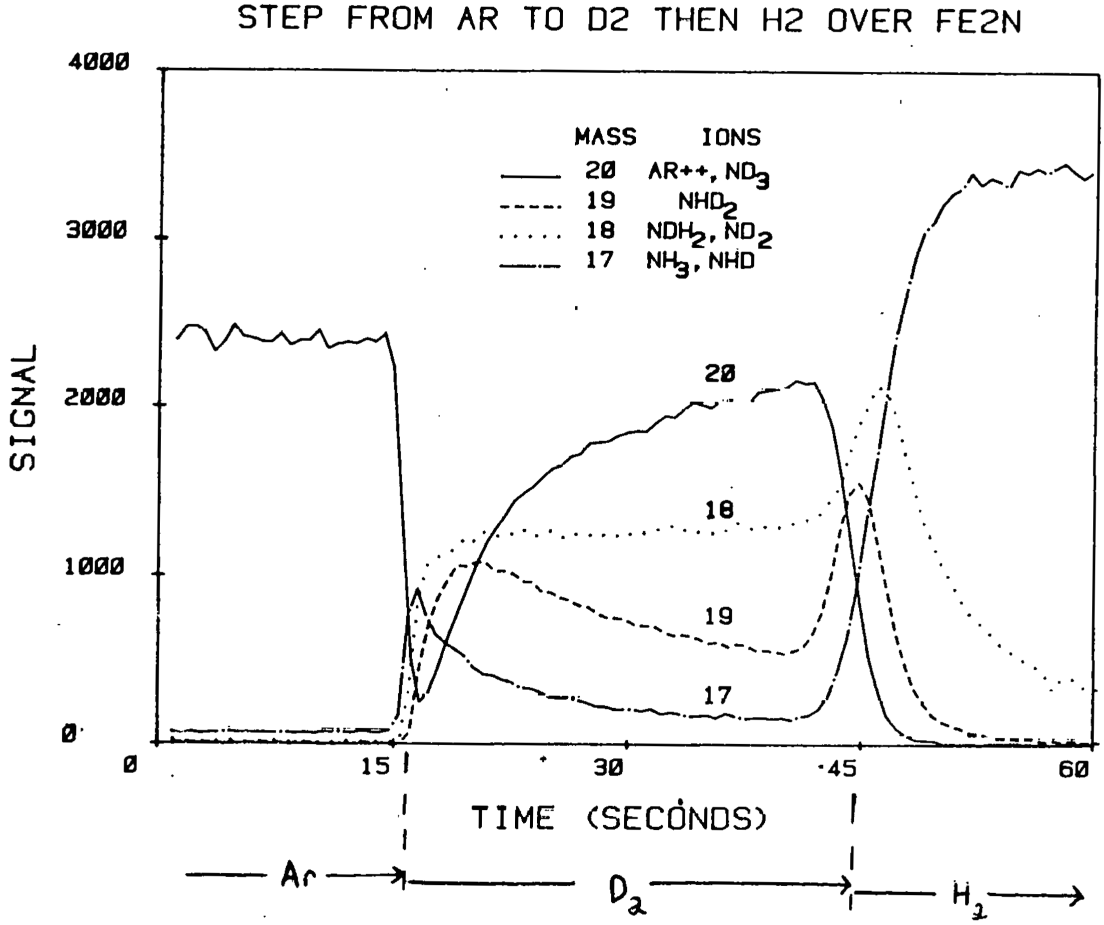

Figure 3: Denitriding of $\zeta$-$Fe_2N$ in a pulse of $D_2$ followed by $H_2$ at 523K. The masses shown are the deuterated isotopes of ammonia with contributions due to the fragment ions shown in the legend.

The different masses shown in Figure 3 have contributions due both to the parent molecule and to fragments formed in the mass spectrometer. In order to subtract out the fragment contributions, a fragmentation table (Table III) was developed from calibration $NH_3$ data. The calibration was made immediately after the $D_2$ experiment. Computer programs designed to deconvolute the data of figure 3 from the fragmentations of Table III are currently being debugged. The final result will be data in which the total amount of N and H can be estimated in the short spike in order to determine the degree of hydrogenation (the value of x) in the $NH_x$ species.

## Table 3.

Fractions of Parent Molecule Contributions to Masses Due to Fragmentations.

| Mass | $H_2$ | HD | $D_2$ | $NH_3$ | $NDH_2$ | $ND_2H$ | $ND_3$ | Ar |
|---|---|---|---|---|---|---|---|---|
| 2 | 1.00 | | | | | | | |
| 3 | | 1.00 | | | | | | |
| 4 | | | 1.00 | | | | | |
| 15 | | | | 0.014 | 0.009 | 0.005 | | |
| 16 | | | | 0.346 | 0.120 | 0.009 | 0.014 | |
| 17 | | | | 0.64 | 0.231 | 0.231 | | |
| 18 | | | | | | 0.64 | 0.346 | |
| 19 | | | | | 0.64 | | | |
| 20 | | | | | | | 0.64 | 0.133 |
| 40 | | | | | | | | 0.867 |

## 3. FUTURE RESEARCH

Research during the forthcoming three month period will be twofold; a continuation of search for stable reaction conditions, and a continuation, if not completion, of computer fittings of the Mössbauer parameters. This latter direction will be directly aided by the analysis of recent ε-nitride phase spectra. The former direction, conditions for increased nitride stability, will continue to develop the study of lower hydrogen ratio synthesis conditions. In addition, we will consider the inclusion of gas phase ammonia during the synthesis reaction. This potential stabilizing treatment, however, may require significant $NH_3$ concentrations and could alter the distribution of hydrocarbon products.

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# 5. APPENDICES

## 5.1 Distribution List

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