



CO+H SUB 2 REACTION OVER NITROGEN-MODIFIED IRON CATALYSTS. QUARTERLY TECHNICAL PROGRESS REPORT, APRIL 1, 1984-JUNE 30, 1984

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CO+H₂ Reaction Over

Nitrogen-Modified Iron Catalysts

Quarterly Technical Progress Report for the Period Apr. 1, 1984 - Jun. 31, 1984

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PREPARED FOR THE

U.S. DEPARTMENT OF ENERGY

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ABSTRACT

The steady state Fischer-Tropsch behavior over the iron nitrides at 523 and 450 K was compared to the kinetics over iron at similar conditions. At 523 K, 3/1 H₂/CO at atmospheric pressure, the e and ζ nitrides give higher olefin to paraffin ratios and CO₂ activities than iron and the V ' nitride. At 458 K the high olefin to paraffin yield of the higher nitrides is preserved after an induction period. Detailed Mossbauer analysis of the catalysts used at 458 K showed < 20% incorporation of carbon and allow structural interpretation of carbon movement into, and nitrogen removal from, the nitride lattice. Quantitative analysis of the NH_xD_{3-x} species leaving a fresh nitride surface after a surtch to D₂ yields NH as the average composition of the surface nitrogen-containing species.

1. DBJECTIVES 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 catalystscatalysts 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 (1,2). On the other hand, simultaneous introduction of ammonia (NH₃) 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). 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. <u>In-situ</u> Nossbauer studies identify the various iron nitride phases and allow for examination of their stability during reaction. The Mossbauer results 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 NH₃ pulses. Along with ultrahigh vacuum studies, the transient kinetics of NH₃ 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. Mossbauer and simultaneous kinetics of prenitrided iron catalysts will be used to determine nitride phase stahility 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 NH₃ 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_o will be investigated.
 - v. The effects of NH₃ 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_2 .

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

2. TECHNICAL PROGRESS

2.1 Summary of Results

Research during this period of study has concentrated on steady state kinetics over the nitrides at 523 and 458 K and the phase changes at 458 K as monitored by Mossbauer Spectroscopy. In addition, the decomposition of a ζ -Fe₂N nitride in D₂ was analyzed in an effort to identify a partially hydrogenated surface species that might exist during nitriding in NH₂.

The <-fe_N decomposition in deuterium experiment indeed revealed the existence of partially hydrogenated surface N species. Integration of the partially hydrogenated NH_xD_{3-x} molecules accounted for one monolayer's worth of hydrogen suggesting NH as the average composition of the surface species. Additionally, it was demonstrated in this experiment that contributions of fragmentations to the mass abundance data can be subtracted out with computational methods and fragmentation tables.

Steady state kinetic behavior over the separate mitrides at 523 K in 3/1 H_2 /CO at atmospheric pressure did not reveal startling differences between the mitrides and iron. In the case of \tilde{v} -Fe₄N, activity and selectivity was not measurably different than that over iron after eight hours of synthesis. The e-Fe_x and ξ -Fe₂N catalysts, however, produced more olefins, methane and CO₂ at a measurably higher activity than α -Fe. The data from the first few hours of synthesis showed significant differences between all catalysts.

The FT kinetic behavior for the nitrides at 458 K also showed higher olefin to paraffin ratios for the nitrides versus iron after an initial induction period. This induction period over the nitrides was characterized by extremely low activity (CO₂ is the only significant product) and the production of a nitrogen-containing organic species not yet identified.

The fitted Mossbauer spectra at this temperature reflect substantially less nitrogen loss than in previous experiments at higher temperature. Carbon in neighbors to iron contribute less than 20% of the spectral area after an hour of synthesis, and progressively less carbon is incorporated into the higher N containing nitrides. The identification of e-II and e-III carbonitride sites was part of the development of this analysis.

2.2 \leq -Fe₂N Decomposition

In our last report (4), we presented the results of a transient experiment on ξ -Fe₂N denitriding in deuterium at 250° C. The resulting transient production of partially deuterated ammonia species during the D₂ pulse gave indication of a surface NH_x species that formed from the decomposition of ammonia during nitriding. Further analysis of this experiment is depicted in figure 1, in which the signal/mass overlap of different species

has been subtracted out to yield the true species shown. Examinetion of this figure indeed discloses the existence of partially deuterated ammonia species in the D_p pulse.

In order to arrive at the results in figure 1, fragmentation table was developed from NH₃ calibration data. The calibration was made immediately after the D₂ experiment. For m masses and n species, the experimental data (DATA, Masses vs. time) and the fragmentation data (FRAG, Mass vs. species) can be combined to yield the deconvoluted species results (DECONV, species vs mass). In matrix algebra terms,

FRAG DECONV = DATA

man nat mat

0T

BECONV - (FRAG^TFRAG)⁻¹FRAG^TDATA

nxt nxm mxn nxm mxt where the superscript "T" refers to transpose, and the superscript "-1" refers to the inverse. The extensive matrix algebra was readily done by computer.

Interestingly, the first production of emmonia is in the form of NH_3 , which is surprising considering that no gas phase hydrogen is present. This phenomenon is undoubtedly due to extremely rapid H/D exchange in the ammonia molecule as it progresses down the catalyst bed. Specifically, the D₂ wavefront arrives at the front of the bed, and a deuterated ammonia molecule is produced by reaction at the catalyst surface. At the wavefront, the gas phase D₂ concentration is low and is therefore



Figure 1 Denitriding of a ζ -Fe_N catalyst in D at 523 K. The catalyst was prepared² in pure NH₃ at ²623 K, followed by the argon purge at 523 K.

completely consumed by reaction An ammonia molecule, therefore, travels in a pure argon gas phase with many opportunities to return to the catalyst surface and H/D exchange with NH_U species, thus producing NH $_{
m S}$ at the effluent of the reactor. As time moves on, the D_n front moves down the bed and correspondingly a progressively higher D/H ratio exists at the surface, thus producing some NH_o D molecules that can survive to the end of the bed. This series of increasingly deuterated stoichiometries is seen in figure 1, where the NH, spike is followed by a NH₃D spike, then $\mathrm{NHD}_{2},$ and finally $\mathrm{ND}_{2},$ corresponding to the changing D/H ratio along the catalyst bed. Another example of this "plug flow reactor" phenomenon, where the length of the bed plays a role in the kinetics and effluent composition, is the transient step change of a CO/H₂ mixture into pure H₂ over a reduced iron catalyst (5). CD is adsorbed along the wavefront and the leading edge is rich in H_2 , thus producing a spike of CH_4 seen in the effluent. The same experiment performed over an iron nitride (5), however, produces no spike of CH_a undoubtedly due to blockage of surface sites by the same NH, species seen in the ${
m D}_2$ pulse experiment.

Integration of the partially deuterated species up to the switch to H_2 in figure 1 will yield the stoichometry (value of x) in NH_x . In this calculation NHD_2 was extrapolated beyond the step to H_2 and corrections were made for the HD impurity in the D_2 (0.7%) and also the NH_3 background in the mass spectrometer. A value of 1±0.5 monolayers worth of hydrogen was evolved in the form of the ammonia species during the D_2 pulse, thus tentatively

designating the surface species as NH.

There is considerable uncertainty in the integration, however, and the surface need not contain a single species but could have more than one with an average concentration of NH. This result agrees well with detection of NH species in ammonia decomposition by Drechsler (6) and Grunze (7), and kinetic isotope measurements by Dzaki (8).

2.1.2 Steady State Fischer-Tropsch Reaction over the Iron Nitrides

It is clear that the available data on the kinetics of the Fischer- Tropsch reaction over the iron nitrides is scant (1,9). In addition the available data is not consistent. Anderson reports a shift to lower molecular weight products and higher activity over promoted e-Fe_xN nitride at 7.8 atm in synthesis gas, whereas recent studies at Northwestern (9) show a shift to higher molecular weight products and comparable activity at 7.8 atm and lower activity at 1 atm over an e-Fe₂N catalyst. In an effort to clarify some of these issues, steady state data was taken for 12 hrs over each of the nitride phases separately. The conditions were held at 1 atm pressure, $3/1 H_2/CO$ at $250^{\circ}C$ with a flow rate of 50 ml/min over approximately 200 mg of catalyst precursor, thus yielding a CO conversion of 1 - 10% to products.

Figure 2 displays the activity results referenced to the surface area of reduced Fe $(4.3m^2/g)$ as found by BET. Interestingly, the initial activity is high for all three nitrides,



Figure 2

Fischer-Tropsch activity to $C_1 - C_5$ hydrocarbons over iron and the nitrides. Reaction was at atmospheric pressure in 3/1 H₂/CO at 523 K.

indicating that the initial state of the nitride is more active than Fe metal. In kinetic data listed in a previous report (10), the first point was low, in contrast to the results here. This seemingly contradictory result can be clarified by examining mass spectrometric data for the first few minutes of synthesis. These results show that the hydrocarbon production builds to a maximum only after the removal of surface nitrogen species. If the first sample was taken during this short period of nitrogen removal, the resulting FT activity would indeed be low. The length of this period is probably affected by conversion level and reactor design (CSTR or PFR), but in any case many changes occur during the first minutes of synthesis.

In addition, hydrocarbon selectivity over the nitrides indicates that the surface is somewhat hydrogen deficient during the first minutes of synthesis. The olefin/paraffin ratio at 4 minutes is higher than at 40 minutes, in spite of the fact that the conversion has decreased. The products are substantially methane poor, especially for %'-Fe₄N. This behavior is perhaps indicative of a competition between carbon and nitrogen hydrogenation. It must be noted, however, that the activity for these nitrides is high, even though the data indicate that surface hydrogen concentration is low.

As Figure 2 shows, after eight hours of synthesis at these conditions, activity for all the catalysts reaches an essentially steady state. The position of a secondary maximum in activity increases in time for Fe, %'-Fe_dN, and e-Fe_{p p}N respectively, corresponding to an increase in nitrogen content. A maximum for ζ -Fe₂N may exist, but data in the 360-540 minute range is not yet available for this catalyst.

Table 1 lists the activity and selectivity results for all catalysts after approximately 12 hours. The TON (CO₂ free) values reflect the activity results at the 12 hr point in figure 2. Diefin/paraffin comparisons must be tempered by the total conversion level; high conversion lowers the olefin/paraffin ratio. Also, the selectivity results reflect total CO conversion with CO₂ included, therefore the relative selectivity between hydrocarbons will seemingly be less pronounced for high CO₂ conversion (note the e-Fe_{2 2}N results).

The major overall conclusion from Table 1 is that the behavior of the steady state catalysts are largely the same. The activity of the ϵ -Fe_{2.7}N and ξ -Fe₂N catalysts are respectively 2 and 1.6 times as much as that of Fe and V'-Fe₄N, which suggests a significant advantage for the high nitrogen-containing catalysts.

Other observations that can be made from Table 1: (1) Fe and V'-Fe₄N do not have significant differences in activity or selectivity after twelve hours of synthesis.

(2) The e-Fe_{2.7}N and ξ -Fe₂N catalysts produce more methane and correspondingly less C₂ hydrocarbons than Fe or V'-Fe₄N; relative selectivity to the C₃ and higher hydrocarbons does not appear to be significantly

****	Fe	γ´-Fe ₄ N	ε-Fe _{2.7} N	ς-Fe ₂ N
Total Conversion %	1.2	1.2	3.2	2.0
TON*	10.2	9.6	22.6	16.4
TON (CO ₂ free)	8.4	7.7	16.6	14.0
% CO Conversion to pr	oducts			
co ₂	17.6	20.0	26.7	14.8
CH ₄	33.2	32.3	35.1	39.1
C ₂	22.0	20.1	15.3	18.0
C ₃	17.7	14.6	14.1	16.5
C ₄	8.8	7.4	6.4	8.8
<u>Oelfin/paraffin ratio</u>				
C ₂	1.03	1.01	0.49	0.99
C ₃	5.19	4.92	3.66	7.21
C ₄	3.22	2.22	1.75	2.93

TABLE 1Activity and selectivity results after 12 hours of synthesis at 523 K

* TON = turnover number = CO molecules converted/site sec includes all hydrocarbons to C₅

affected.

(3) The turn over number to CO_2 is increased over the e and ξ catalysts compared to Fe and ξ' .

(4) The olefin/paraffin ratio is enhanced for ζ -Fe₂N for all carbon chain lengths, as compared to Fe and \forall' -Fe₄N, even considering the high conversion level in the ζ -mitride. The ratio for e-Fe_{2.7}N is too strongly affected by the high conversion level over this catalyst to be comparable.

These conclusions are in agreement with some of those listed by the Northwestern group (9), namely higher olefin/paraffin ratio and higher CO_2 production over an ϵ , ξ -Fe₂N catalyst. We have found, however, that the activity is somewhat higher for the high-nitrogen containing catalysts, although the difference is not substantial.

2.4 <u>Kinetic Behavior at 458 K</u>

Kinetics representative of the single phase nitrides are obtained by following CO hydrogenation in $3H_2/CO$, 458 K, and a total gas flow rate of 50 ml/min, measured at ambient conditions. The chromatographic analysis compares catalyst performance on the basis of CO conversion to CO_2 and C_1 through C_5 hydrocarbons. Molar selectivities are normalized to the total molar production. Due to small concentrations of C_4 hydrocarbons, the C_4 olefin to paraffin ratio is not included. No alcohol production was



detected and the lower methanol concentration limit in $3H_2/CO$ is 2×10^{-6} %. Table 2 gives the kinetic results for the Fischer-Tropsch reaction over iron and over V'-, e-, and **3-iron nitrides**.

The first QC sample at 10 minutes (.17 hr) after the switch to synthesis gas indicates a difference in kinetic behavior between the nitrides and iron. Over the iron catalyst, more than 23% of the products are hydrocarbons. No hydrocarbon production is detected over any of the nitrided catalysts, and the carbon monoxide conversion, ×_{CO}, is derived from the Boudouard and water gas shift reactions. A significant, unidentified broad peak with an approximate retention time of 11.5 minutes is, however, present in the nitride chromatograms. This peak is absent from analyses after the 0.17 hr injection. It is unlikely that ammonia, which has a 10 minute retention time in the series Porapak Q and Porapak R column, is solely responsible for this peak. The presence of other nitrogen containing gasses is suspected.

The percentage CO conversion exhibits a trend; lower conversions occur with increasing nitrogen content, from 0.110% over iron to 0.066% over ξ -Fe₂N. Two explanations could account for this. The dissociation of carbon monoxide could evoke a dual reaction: (1) carbon incorporation into the bulk and (2) surface carbon deposition. An hydrogenation pathway is minimal at 100% CO₂ selectivity. As carbon diffusion is slower in denser nitride phases, a decrease in the first reaction could lower the overall rate of CD dissociation. However, if the formation of

Iron and Iron Nitride Kinetics at 458 K

TABLE 2

01efin/Paraffin Ratio C₂=/C₂ C₃=/C₃ 5.2 4.8 5.1 7.9 8.6 5.3 111 1 2.8 2.9 9.1 10.6 8.5 4.4 5.7 1 1 0.2 2.0 1 1 0.1 111 ł 111 0.1 ပို့ 2CA 1 0.1 111 E]] 1 1 nC, 0.2 0.100.2 111 111 111 0.1 6 5 Molar Selectivity (x) $c_2 = c_2 = c_3 = c_3 = 1c_4$ 4.0 1.2 1+1 9.0 æ. 111 111 -0.6 0.9.0 0.4 0.6 1 222 2.0.4 2.0.4 3.1 111 111 111 0000 0000 0.5 0.5 1.1 0.9 76.7 1.9 0.7 114 0.00 0.0 0.0 0 8.4 0 4 0 4 0 --- 100.0 ------- 100.0 ---| | | 80.6 84.4 85.2 85.7 10.6 80.4 3 11.5 81.7 3 12.9 75.8 4 --- 100.0 602 2 11.7 8.4 9.1 7.6 చ్ CO Conversion (%) .155 .137 .147 137 11080 Time (hr) 00.1 11 1.33 Initial Phase í۵. 23

 $\alpha \equiv \alpha - Fe$, $\gamma^{t} \equiv \gamma - Fe_{q}N$, $\varepsilon \equiv \varepsilon - Fe_{\chi}N$, $\zeta \equiv \zeta - Fe_{2}N$

. 17 exists between the two pathways, this explanation is inadequate. The CD would dissociate at the same rate, and more surface carbon would accumulate. A surface nitrogen competition effect is more likely to occur if nitrogen and carbon dissociation (recombination) sites are equivalent. As higher bulk nitrogen compositions should correspond to larger surface N concentrations under equilibrium conditions, the catalytic sites on ξ -Fe₂N should experience a greater proximity of N than would those of χ' -Fe₄N. In a competition between CD dissociation and N removal, an increased nitrogen content should retard the reaction of CO and reduce the H availability. At sufficiently low nitrogen removal rates, N diffusion from the bulk to the surface would be sufficiently rapid to prevent immediate depletion of surface N.

The second and third reaction measurement points, are characterized by increasing hydrocarbon production over the nitrides. The lack of an unidentified nitrogen compound peak implies that CD hydrogenation has slowed the N removal rate. Although reaction over the e-nitride was temporarily interrupted by a stability problem with the GC, and the break in reaction continuity probably affected the catalyst, the level of CO conversion is comparable between all four phases at the second injection and between the nitrides at the third. The selectivities of the nitrides, barring ethylene and propylene, after 1.3 hours are quite similar to the iron selectivity after 0.75 hours. An induction period over the nitrides may exist; one in which hydrocarbon production starts after a decrease in the rate of N

removal.

The remaining difference between the iron and nitrides is in the olefin to paraffin ratios. The mean $C_2 = C_2$ and $C_3 = C_3$ ratios over iron are 2.8 and 5.0, respectively. Table 2 shows C_2 and C_3 selectivities to olefins are higher for the nitrides, especially V'- and ξ - nitride. The increase is not as significant over the s-nitride and may be due to the interruption in kinetic analysis. The ethylene to ethane ratio, particularly, is at least twice as high over the nitrides when compared to the iron. If olefin selectivity is indicative of large surface carbon pools, or a low hydrogen to carbon ratio on the surface, this trend is explained as the effect of initial competition between surface N-H and C-H reactions on the subsequent surface C/H ratio. Lower hydrogen availability would increase hydrocarbon unsaturation.

Barring the initial behavior when the nitride catalysts are first exposed to synthesis gas, and the higher $C_2 = C_2$ ratio, the nitride surfaces behave similarly to the iron surface. Although it is incorrect to extrapolate kinetic selectivities to higher temperatures, it is nonetheless interesting to note that Anderson and coworkers reported enhanced clefin production by promoted, fused iron nitrides (2).

2.5 Phase Behavior at 458 K

The bulk catalyst phases are characterized by Mossbauer spectroscopy both before and after synthesis reaction. The room temperature spectra indicate the stability of the catalyst. This

analysis tests the claim that the preceding kinetic results are indicative of the individual starting bulk phases.

2.5.1 α-Fe

The room temperature Mossbauer spectra of the fresh and spent iron catalyst are presented in Figure 3. The Mossbauer parameters of the computer fits are given in Table 3. The starting catalyst is essentially reduced α -Fe whose six peaks can be fitted to 3:2:1.1:2:3 intensity and equal width constraints.

Unconstrained fitting, however, shows greater than expected spectral area in the two innermost peaks. This asymmetry is attributed to an oxide - one which persists after four hours of reduction at 573 K. This is more likely to be an unreduced species, rather than a reoxidized surface species because Mossbauer spectra of all reduced wafers were taken in positive pressures of $H_{\rm p}$.

The spectra of this iron catalyst, after forty-five minutes of synthesis (Figure 3b), can be fitted with two different structural approaches. Both methods predict an 80% spectral area for α -Fe with the reduced 20% distributed as carbide phases. This residual is analyzed as either a combination of e'- and x (I, II, and III) carbides or as a combination of e'- and Fe_xC carbides. Niementsverdriet <u>et al.</u> (11) favor analysis with the amorphous Fe_xC carbide. They note that this transition carbide is characterized by a hyperfine field below ~275 kDe and that it transforms to other carbides scon after the disappearance of the





Mössbauer Spectra of c-Fe Reacted at 458 K. 3

- α -Fe treated in 3H₂/CO for 45 minutes a) b)

Mössbauer Parameters (298 K) for Catalysts Reacted at 458 K

TABLE 3

2975 .3567 .3162 3664 2151 Total 27.3 34.3 (1.7) 26.5 10.1 20.7 50.5 25.2 3.6 20.7 44.5 22.3 12.5 100.0 80.2 ₹£ 0.59 0.77 0.53 0.53 0.42 LN (m/s) 0.30 0.45 0.45 0,43 0,43 0,89 0.33 0.32 193.2 102.2 (335.9) 214.2 338.7 217.6 214.4 339.0 217.3 215.2 329.4 329.4 HFS (k0e) 0.00 0.00 -0.07 1.06 (s/mm) 0 0.00 unresolved -0.14 -0.14 1.11 0.00 -0.14 +0.36 1.41 0.00 IS (mm/s) 0.32 0.40 0.35 0.33 0.0 0.24 0.31 0.29 0.37 $\begin{array}{c} 0.23 \\ 0.30 \\ 0.35 \\ 0.35 \end{array}$ 0.00 Iron Identity crFe carbide 7'-1 7'-11A 7'-11B Fe-Q γ.-Ι Υ'-ΙΙΑ Υ'-ΙΙΒ Fe-Q Ţ E-11 E-111 e-0 g-Fe 1-~ ~ Figure 5a 4b 4a 3a 3b

TABLE 3 (Continued)

.3700 .4544 Total Area 48.2 20.3 (1.6) 9.6 12.4 (1.2) 17.4 22.9 53.4 6.3 88 (%) 0.78 0.53 0.53 0.53 0.44 0.44 (0.16) LM (mm/s) 0.86 1.36 0.34 0.63 207.5 115.1 (341.3) ---243.4 91.6 (155.4) 209.9 HFS (k0e) as for Figure 4.1d (s/ww) Sp 0.00 0.00 1.11 -0.05 (-1.36) -0.31 -0.31 0.28 0.89 IS (mm/s) 0.32 0.41 0.35 0.35 0.35 0.45 (0.40) 0.35 0.45 0.45 0.28 e-II e-III γ'-I Fe-Q e-III(CB) e-III(CB) unknown Iron Identity 6-0 Fe-Q 111-2 Figure 5b6a 6b

 α -Fe. The Fe_x U in Figure 5.2b would have a magnetic splitting of approximately 234 kOe. The x-Fe₅C₀ carbide analysis approach will suffice as well, but the small contribution from each site, approximately 5% relative area, does not permit an authoritative assignment of the cartide. On the assumption that the iron and carbide have equal recoil-free fractions, one concludes, however, that the α -Fe is roughly 20% carbided after 45 minutes of reaction.

2.5.2 V-Fe_

The $^{**}\text{-}\mathsf{Fe}_4^{}\mathsf{N}$ catalyst was prepared by mitriding a reduced wafer in 80% NH $_{
m S}$ at 598 K for 6.5 hours. The room temperature spectrum of this catalyst is presented in Figure 4a and the Mossbauer parameters are given in Table 3. Two superimposed six line patterns, a zero nearest neighbor (340 kDe) and a two nearest neighbor (215 kOe), fit the spectrum adequately, but the fit is improved by considering two 2nn sites (IIA and IIB). IB line with the theoretical analysis by Clauser (12), the two inequivalent 2nn magnetic sites are constrained to have relative intensities in the ratio 2:1. In addition, initial peak position assignments are made so as to bias the fitting to yield fields with opposite sign quadrupole interactions. The spectral area ratio in Figure 4a is 0.93:1.00:2.00 (I:IIB:IIA), as compared to the ideal 1.1:2 ratio for stoichiometric &'-Fe₄N. In fitting this %'-nitride spectrum, it is necessary to include a central doublet with an isomer shift of 0.37 mm/s and quadrupole splitting of 1.11 mm/s. The doublet, designated Fe-Q, accounts for



Figure 4

4 Mössbauer Spectra of γ '-Fe_dN Reacted at 458 K.

a) γ' -Fe₄N

b) treated in $3H_2/CO$ for 85 minutes

12.5% of the spectral area. Low temperature analysis should discorr between this contribution arising from a small particle nitride or a non magnetic s-nitride. The reducing atmosphere of the NH_3/H_2 nitriding mixture precludes such a large amount of iron oxide phase.

The Mossbauer characterization of the V'-Fe₄N catalyst after 80 minutes reaction at 458 K is shown in Figure 4b and spectral parameters are given in Table 3. Only the eighteen peaks from the V'-nitrdie, and the Fe-Q doublet, could be determined from the computer fit. The IS, WS, and HFS values for these three sites are in accordance with the starting catalyst. The 2nn sites, although still constrained to a 2:1 relative area ratio, are 10-15% greater in area than those in the fresh V'-Fe_AN. The area of the V^{*} Onn site is unchanged. An additional carbonitride or carbide contribution, unresolved at the present spectrum resolution, would account for this increased area fraction. A better statistical fit is given if one reverses the -1:2 QS symmetry expected in pure %'-mitride. A similar fitting to the virgin $%'-Fe_{a}N$ spectrum would not converge. Even during synthesis reactions at 523 K over the V'-nitride, no differentiation between the XII carbide site (~218 kOe) and the ¥'-II sites could be made. So, although some V'-carbonitride and carbide formation is expected, the probable inhomogeneity of the phase prevents its identification in the spectrum fit. Furthermore, a decrease in the non-magnetic contribution is seen between Figure 4a and 4b. The increase in the quadrupole splitting from 1.1 to 1.4 mm/s,

signifies greater charge asymmetry at this Fe site. One can speculate that addition of carbon in the vicinity of this site can reorder a portion of the domain as magnetic and further polarize the electronic state of the paramagnetic domain. The degree of carbon incorporation would account for less than 10% of the spectral area. As such, the kinetics are representative of a bulk %'-Fe₄N.

2.5.3 e-Fe_N

The e-nitride catalyst was synthesized by nitriding a reduced wafer in 91% NH, at 653 K for 6 hours. The Mossbauer parameters for the computer fit to the room temperature spectrum (Figure 5a) are given in Table 3. In addition to the e-II and e-III fields, a small %' Onn contribution is evident. The small spectral area of this site (1.7%) is responsible for the deviation from the expected HFS value (~340 kBe). The associated 2nn site, identified as Y'/epsilon-II in Table 5.2, although characterized by a typical %' magnetic splitting of 214.2 kOe, is not solely a V'-II site. The 1.7% area contribution from V'-I limits the total Fe₄N area to below 8%. Constraining the area of this six line pattern to three times that of the higher δ' field, rather than reducing the %' 2nn area, increases the Onn area unreasonably. Therefore, we attribute this two nearest neighbor contribution to an inhomogeneous mixture of V' precipitates in hop e-Fe_.N. The e-nitride inhomogeneity can be visualized by considering a distribution of hyperfine fields. The variation in statistical placement of nitrogen neighbors in the first





Mössbauer Spectra of ϵ -Fe_XN Reacted at 458 K.

- a)
- ^{e-Fe}2.49^N treated in 3H₂/CO for 85 minutes b)

(nearest) higher coordination shells of each iron atom will generate nonuniform fields at their nuclei. Chen <u>et al</u>. (13) and DeCristofaro and Keplow (14) favor this distribution of magnetic fields approach. The nonmagnetic Fe-Q site should thus correspond to underestimated innermost peak intensities encountered when fitting field broadened spectra with 3:2:1 area constraints. Yeh <u>et al</u> (15), in addition to fitting with an HFS distribution, also require a nonmagnetic doublet in their room temperature Mossbauer spectra.

The e-mitride catalyzed CO hydrogenation for approximately 1.5 hours. The room temperature spectrum of the spent catalyst (Figure 5b) still exhibits a small $\forall - \text{Fe}_4 \text{N}$ contribution. A majority of the starting mitride, e-II, e-III, and Fe-Q, is also retained. The hyperfine fields of e-II and e-III are higher than those in the starting mitride, indicative of N loss. Furthermore, the spectral area of the e-III site has decreased from 34 to 20%.

The computer fitting also identified three new magnetic species in the carburized sample. A low spectral area and overlapping peak positions of the third site, however, does not warrant its discussion. The remaining two species, ϵ -II and ϵ -III, are attributed to ϵ -carbonitride sites having two and three interstices occupied. Foct <u>et al</u>. (16) identified a (CNV) carbonitride with a isomer shift of 0.30 mm/s and a magnetic field of 243 kOe. The ϵ -II site has similar parameters. The actual identification of these transition carbonitrides requires a

greater reaction length so that greater definition is given each proposed site. One may say though, that Fe sites with carbon neighbors account for roughly 20% of the spectral area.

2.5.4. - FegN

A ξ -nitride catalyst was synthesized by flowing pure NH $_3$ at 673 K for 8 hours over a reduced iron powder. The computer fitted room temperature Mossbauer spectrum is given in Figure 6a. The Mossbauer parameters (lable 3) for this fit indicate a single phase paramagnetic <-Fe_pN. The spectrum of the catalyst after 80 minutes of reaction (Figure 6b) exhibits magnetic ordering in addition to pure 2-nitride. By subtracting the 2-Fe_pN contribution and expanding the spectrum scale, the background becomes substantially more clear (Figure &c). Two magnetic fields and a single doublet are predicted in fitting this 'residual'. The two magnetic sites have hyperfine splittings characteristic of iron with 2 and 3 nearest nitrogen neighbors. The lower field site has a quadrupole splitting of -0.30 mm/s, and could not be fit with a physically meaningful zero quadrupole split six line pattern. Nor could a separate magnetically ordered site be introduced into the fit. This 108.1 kDe field is attributed to overlap between an e-III site and a less intense e-carbonitride site, probably of NNC structure. As a spectral area of ten percent of more is normally detectable, the carbonitride contribution to spectral area of the reacted \diamondsuit -Fe₂N may be estimated as less than This would be less than the spectral areas of carbon phases 10%. in iron, W-nitride, and e-nitride.



Figure 6

- Mössbauer Spectra of ζ-Fe₂N Reacted at 458 K.
- a) z-Fe₂N
- b) treated in 3H₂/CO for 85 minutes
- c) as above less non-magnetic components

3. Future Research

Research in the next 3 month period will emphasize the computer fitting of complicated carbonitride peaks in Mossbauer spectra. Transient mass spectral analysis of the decomposition in hydrogen of pre-nitrided catalysts after Fischer-Tropsch synthesis will give additional information on the stoichiometry of the bulk phase during reaction. The effect of pre-carbiding a nitride on the subsequent synthesis reaction will also be investigated.

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