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CO + H SUB 2 REACTION OVER NITROGEN-MODIFIED IRON CATALYSTS. QUARTERLY TECHNICAL PROGRESS REPORT, OCTOBER 1, 1984-DECEMBER 31, 1984

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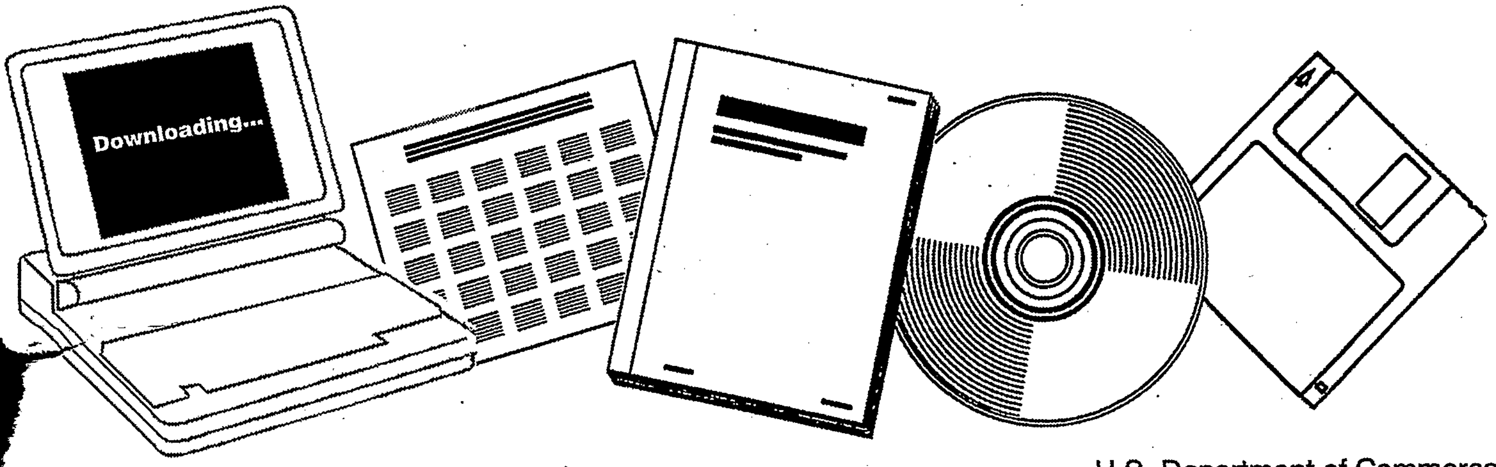

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$CO+H_2$ Reaction Over Nitrogen-Modified Iron Catalysts

Quarterly Technical Progress Report
for the Period Oct. 1, 1984 - Dec. 31, 1984

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PREPARED FOR THE

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ABSTRACT

Preoxidizing a freshly prepared ς–Fe_2N catalyst resulted in unique Fischer-Tropsch behavior. Characterization of this catalyst by Mösbauer spectroscopy indicated contributions from both ς–Fe_2N and Fe_3O_4. The kinetic behavior of this preoxidized catalyst revealed a remarkable enhancement in the C_4 and C_5 hydrocarbons as compared to the kinetics over the ς nitride. Transient kinetic studies by mass spectrometry determined the bulk stoichiometry of a prenitrided catalyst after 12 hours of reaction in 3/1 H_2/CO at 523 K by monitoring the H_2O, NH_3 and CH_4 produced during temperature programmed reduction in H_2. The ϵ–$Fe_{2.7}N$ catalyst lost 24% of its nitrogen. The ς–Fe_2N catalyst lost 15% of its nitrogen.

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 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 nitrogeneous compounds (2). Furthermore, and probably of greater importance, this addition of ammonia effects a reduction in the overall chain length of compounds in the product spectrum. 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 identify the various iron nitride phases and allow for examination of their stability during reaction. The Mössbauer 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 Mössbauer 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 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 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 *Summary of Results*

In this report, we investigate a preoxidized ς-Fe_2N catalyst and the resulting Fischer-Tropsch behavior. This catalyst was prepared by oxidizing a fully nitrided ς-Fe_2N in 1 % O_2/He at 473 K for 6 minutes. Mössbauer spectroscopic analysis of this catalyst revealed both a prominent center peak characteristic of ς-Fe_2N, and the nine line spectrum characteristic of Fe_3O_4. This magnetically split material accounted for 30% of the spectral area.

The kinetic behavior of this preoxidized catalyst revealed a remarkable enhancement in the C_4 and C_5 hydrocarbons during the first hour of synthesis as compared to the kinetics over the ς nitride at the same conditions, 3/1 H_2/CO at 523 K and atmospheric pressure. Activity was enhanced for the preoxidized catalyst vs. the ς nitride catalyst initially, and the activities were comparable after 45 minutes. The oxide phase was stable over the first hour of synthesis.

In separate experiments we have determined the bulk stoichiometry of prenitrided catalysts after 12 hours of reaction in $3H_2/CO$ at 523 K. Using mass spectrometry, the reaction products of water, ammonia or methane were monitored while exposing a used and passivated catalyst to hydrogen in a temperature ramp from 473 - 673 K. These products were produced selectively in the order of H_2O, NH_3 and CH_4 during the hydrogenation reaction. The ϵ catalyst lost 24% of the original nitrogen contained in an ϵ-$Fe_{2.7}N$ catalyst, whereas a ς-Fe_2N catalyst lost only 15% of its original nitrogen after 12 hours of reaction. Since nitrogen in the bulk is totally lost in as little as 5 minutes in pure hydrogen, the stability of bulk nitrogen in H_2/CO mixtures is readily apparent.

2.2 *Kinetic Behavior of Preoxidized* ς-Fe_2N

Preoxidation of iron catalysts has been reported to markedly improve activity as compared to conventional iron catalysts (3). The Fe_2O_3 phase, however, is inactive until reduced to lower oxidation states in synthesis gas (4), suggesting that it is the partially oxidized surface phases that are of catalytic interest. Preoxidation of an original ζ-Fe_2N catalyst offers a new route to the preparation of a partially oxidized surface.

The preoxidized nitride catalyst was prepared by oxidizing a fully nitrided ζ-Fe_2N in 1% O_2/He at 473 K for 6 minutes. The CO hydrogenation kinetics over this catalyst and over a zeta-nitride were monitored during the first hour of reaction. The synthesis conditions were atmospheric pressure, $3H_2/CO$, 523 K, and 66 ml/min total gas flow rate at ambient conditions. Discussion of the behavior of the nitride bulk, monitored by Mössbauer spectroscopy, follows these kinetic discussions.

When compared to kinetics over zeta nitride at the same conditions, the preoxidized nitride catalyst is seen to produce significantly more C_4 and C_5 hydrocarbons during the first hour (see Table 1). The first GC analysis at .17 hr shows the zeta forming no hydrocarbons above prolyene and being 90% selective towards CO_2 production. The CO conversion over the preoxidized catalyst is twice as great as that over the zeta nitride during this first analysis, and is even greater on a CO_2 free CO conversion basis.

By 0.75 hour, overall CO conversions are nearly equal. The olefin to paraffin ratios of each catalyst are essentially the same for C_2 and C_3 selectivity, but 30% larger for C_4 selectivity over the preoxidized catalyst. The preoxidized nitride is more than twice as selective towards total C_4 and C_5 hydrocarbon make, but is approximately 20% less selective towards $C_1 - C_3$ production. Indeed, the nitride produces some 12% C_4 hydrocarbons, yet only 8% C_3 product. Should the active surface indeed by an iron nitride, this trend for higher molecular weight products is contrary to that seen by Anderson (1), but similar to the trend observed by Yeh *et al.* (6).

TABLE 1

Iron and Pre-oxidized ζ-iron Nitride Kinetics at 523 K

Initial Phase	Time (hr	CO Conversion (%)	Molar Selectivity (%)										Olefin/Paraffin Ratio		
			C_1	CO_2	$C_2^=$	C_2	$C_3^=$	C_3	$1C_4^=$	nC_4	$2C_4^=$	C_5	$C_2^=/C_2$	$C_3^=/C_3$	$C_4^=/C_4$
a	.17	0.37	6.1	89.8	1.3	0.4	2.4	---	---	---	---	---	3.5	---	---
b	.17	0.85	19.9	54.9	3.1	1.7	3.9	0.4	6.5	3.8	3.6	2.2	1.8	9.1	2.7
a	.81	1.16	46.1	24.7	5.7	4.9	8.3	1.6	1.9	1.8	0.9	0.2	1.2	5.1	1.6
b	.73	1.20	39.6	28.6	4.7	4.2	6.7	1.3	5.2	4.0	3.1	2.6	1.1	5.0	2.1

a ≡ α - Fe, b ≡ preoxidized ζ-Fe_2N

2.3 *Phase Behavior of Preoxidized* ζ-Fe_2N

The six minute treatment in 1% O_2 at 473 K has a marked effect on the nitride bulk, as seen by Figure 1a. While the prominent center peak is the contribution from the remaining Fe_2N, two large hyperfine fields are clearly visible. These two offset fields have isomer shifts of .29 and .65 mm/s, hyperfine splittings of 486.4 and 457.3 kOe, and no quadrupole interaction. These parameters are consistent with magnetic Fe_3O_4. According to Greenwood and Gibb (7), Fe^{3+} in tetrahedral sites (A sites) and Fe^{+3} plus Fe^{+2} in octahedral sites (B sites) exhibit fields of 491 and 453 kOe respectively. The residual background to Figure 1a is computer fit with equal statistics to two different environments. Both procedures predict a 216 kOe field with isomer shift between 0.33 and 0.35 mm/s. Due to the broadness of the peaks for this site, with half widths of 0.8 mm/s and greater, the existence of a quadrupole interaction could not be ascertained. This fit gives a 17% area contribution from this site. A lower area is predicted by a second fit because it uses an extremely broad ($\Gamma/2 > 9$ mm/s) superparamagnetic species accounting for almost 25% of the spectral area. Both fits require a central (IS = .34 - .43), broad ($\Gamma/2 = 1.1 - 1.6$ mm/s) doublet. This is too broad to be attributed solely to the nonmagnetic Fe-Q species. Including a forth magnetic site of approximate 70 kOe field (ϵ-III) in either fit gives nonphysical peak positions. The broadness of the doublet could arise from a superposition of the Fe-Q species and a magnetically unresolved ϵ-III site, although an oxynitride species can not be ruled out. Some relaxation effects are probably being seen and the ill-defined nature of these sites arises from attempting to fit them to full Lorentzian line shapes.

The spectrum of the catalyst after 50 minutes of synthesis (Figure 1b) shows that

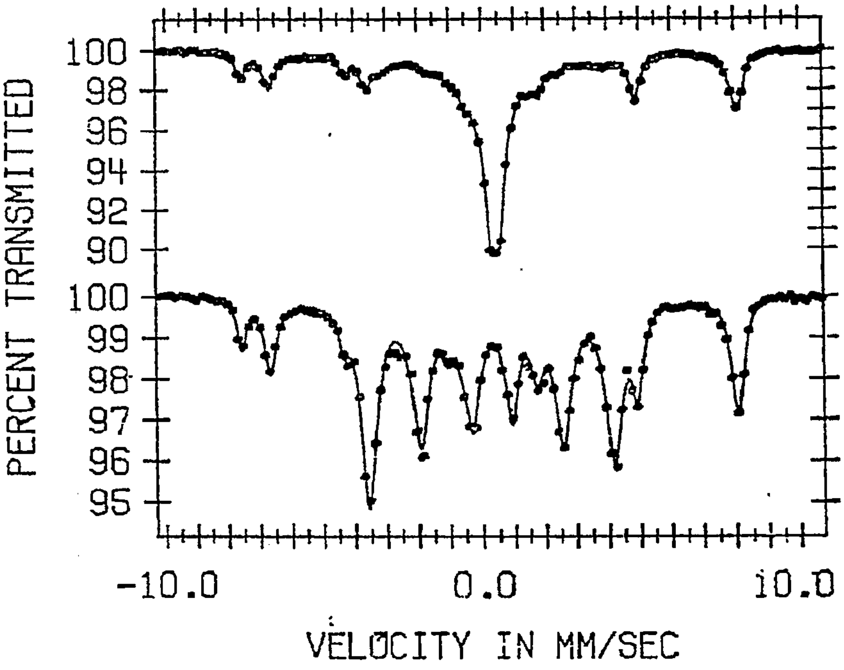

Figure 1. Mössbauer Spectra of Pre-oxidized ζ-Fe_2N Reacted at 523 K.

a) ζ-Fe_2N treated in 1% O_2/He at 473 K for 6 minutes

b) Pre-oxidized ζ-Fe_2N treated in $3H_2/CO$ for 50 minutes

TABLE 2

Mössbauer Parameters for Pre-oxidized ζ-Fe_2N

Figure	Iron Identity	IS (mm/s)	QS (mm/s)	HFS (kOe)	LW (mm/s)	RA (%)	Total Area
1a	Fe_3O_4 A	0.29	0.00	486.4	0.30	10.2	.2702
	B	0.65	0.00	457.3	0.52	22.9	
	ε-II	0.35	0.00	217.3	1.19	16.6	
	ζ-III	0.43	0.27	---	0.39	24.7	
	Fe-Q+	0.43	0.34	---	1.68	25.6	
		unresolved				3.6	
1b	Fe_3O_4 A	0.28	0.00	485.2	0.33	9.1	.2700
	B	0.66	0.00	454.9	0.47	19.8	
	ε-II	0.31	0.00	238.8	0.62	55.3	
	ε-III+	0.37	0.00	172.3	0.59	11.2	
	Fe-Q	0.31	1.19	---	0.33	4.6	

the two Fe_3O_4 sites remain, but the orthorhombic Fe_2N phase has been depleted. The total spectral area of site A and site B oxide is 15% less in the spent catalyst. In addition, two magnetic fields (239 and 172 kOe) and a 4-5% Fe-Q contribution are found. The two magnetically ordered sites could be fitted without quadrupole interactions. On a basis of their isomer shifts alone, a 2 and 3 nn ϵ-nitride assignment is likely. The magnitude of the 172 kOe HFS, however, makes an homogeneous ϵ-II and ϵ-III assignment difficult. A one nitrogen nearest neighbor ϵ-I site, although reported by Chen *et al.* (7) and DeCristofaro and Kaplow (8), has not been seen before in this nitride system. Furthermore, the well developed 239 kOe peaks (Figure 1b) favor an absence of domain inhomogeneity. A plausible assignment for this more intense field is low nitrogen containing ϵ-nitride ($\sim Fe_{2.75}N$), and although an ϵ-III site must be associated with this stoichiometry, its lower intensity and smaller field could be masked by higher field components. The 172 kOe contribution has isomer shift too large for ϵ'-carbide, and carbide formation is not expected in high nitrogen containing nitrides. The presence of an oxynitride cannot be discounted. Without low temperature spectra, and associated Debye temperatures, further phase identification is too speculative.

The different behavior of the nitride bulk in this pre-oxidized sample compared to the behavior of non-oxidized ϵ-nitrides clearly indicates a stabilizing effect of the oxygen upon the nitride bulk during reaction. Although the surface phase cannot be authoritatively assigned to a uniform Fe_3O_4 covering, a comparison of kinetic trends over oxidized iron surfaces is helpful. Teichner *et al.* (3,9) have reported preoxidized iron catalysts to be more active toward hydrocarbon synthesis than reduced iron. Krebs and coworkers (10) studied magnetite during CO hydrogenation but did not characterize the catalyst during reaction. Indeed, the kinetics over the pre-oxidized ζ–Fe_2N are similar to kinetic results over an Fe_3O_4 surface reported by Knoechel (11). The preoxidized nitride was operated at a higher CO conversion than the Fe_3O_4 surface, but still produced higher olefin to paraffin ratios. Additional characterization of the pre-oxidized nitrides during reaction will be necessary, and, based upon the unusual product distribution, worthwhile.

2.4 *Hydrogenation of Catalysts After Reaction*

How different are iron nitride catalysts after 12 hours of reaction in H_2/CO at 523 K? If the bulk nitride were completely gone by this point, the catalysts might be expected to have the same behavior after they equilibrate from the loss of nitrogen. Figure 2 shows that this is not the case, however, since ammonia can still be produced from the used ϵ–$Fe_{2.7}N$ catalyst.

In this experiment the reactant is hydrogen, and the initial temperature is low (473 K). The catalyst has previously been used for 12 hours of reaction in 3/1 H_2/CO at 523 K, and then passivated in helium and finally exposed to air. Part of the catalyst was oxidized, and therefore produces water during the decomposition in hydrogen. The decomposition also produces methane from carbide that formed during synthesis, but the rate of production was extremely small during the entire course of the experiment, and is not shown in Figure 2. At the end of the experiment (15 minutes), methane was beginning to rise, indicating that the carbide was finally available for hydrogenation. It is not clear why carbide hydrogenation took so long to commence, but the significant background level of water might be a cause of the inhibition. Unreactive surface graphite could also block methanation sites. Our other transient studies suggest that NH_3

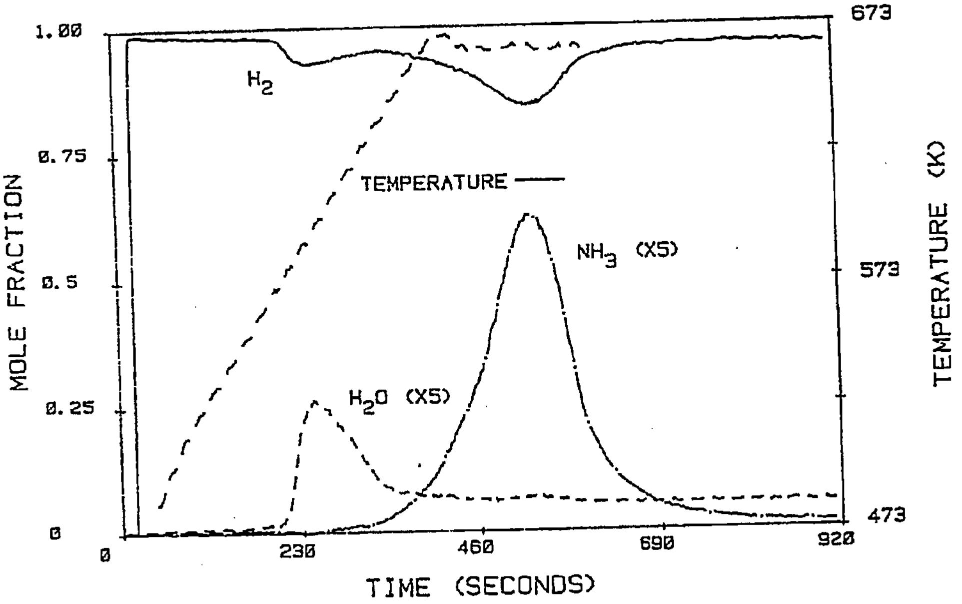

Figure 2. Hydrogenation of ε-$Fe_{2.7}N$ Catalyst After 12 Hours of Synthesis.

is produced exclusively when both N and C are available to react with hydrogen at the surface. This selectivity could also play a role in the present experiments.

Figure 3 displays the analogous experiment over used ς-Fe_2N. Here, the amount of water is much less (note the scale difference between H_2O in Figures 2 and 3), indicating that the passivation procedure for this catalyst was more effective at preserving the bulk. Also, methane appears in Figure 3, after both ammonia and water have virtually disappeared. Much more ammonia was produced over the carburized ς catalyst as well. As will be shown subsequently, a greater percentage of nitrogen from the ς-nitride survived during 12 hours of Fischer-Tropsch synthesis.

Interestingly, the product formed during the temperature ramp is quite selective to hydrogen at different periods of the decomposition. In both Figure 2 and 3 water is the first product, appearing at approximately 573 K and at a maximum production rate at 600 K. Ammonia, meanwhile, begins to appear when water starts to decline. Methane waits until both these products have disappeared. The order of the products could be the result of a number of processes. Since the catalyst was passivated, oxygen is at the surface, and is available to hydrogen first. From the kinetic experiments of the initial minute of synthesis at 523 K over the ϵ nitride, we know that water is not produced in significant quantities until the rate of ammonia production declines. This would suggest that the rate of ammonia production is higher than water production with all reactants available on the surface. In Figure 2 and 3 however, nitrogen is apparently not available at the surface of the passivated catalyst, since the reaction favors water initially. As soon as enough of the surface is open to the nitride (or carbonitride) core, ammonia comes barreling out, leaving carbon behind. Carbon, slower to react, must

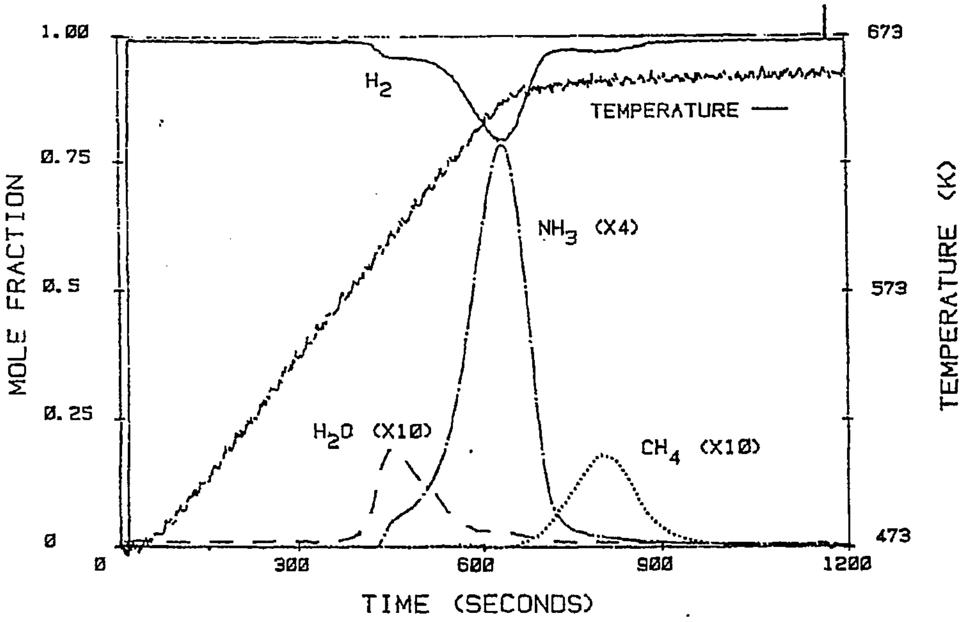

Figure 3. Hydrogenation of ε-$Fe_{2.7}N$ Catalyst After 12 Hours of Synthesis.

wait for available surface hydrogen. Diffusion could be a factor, since carbon is slower to diffuse than nitrogen (12,13), but at these high temperatures the diffusion rates are too rapid (10^{-10} cmsp2/sec in α-Fe for nitrogen) to account for the delay.

The integrated amounts of the products give a rough estimate of the stoichiometry of the catalyst after 12 hours of synthesis. For the original ϵ–$Fe_{2.7}N$ catalyst, the amount of nitrogen left after 12 hours of synthesis corresponds to a Fe/N ratio of 5.0, indicating that 24% of the original nitride has been lost. Oxygen accounts for Fe/O ratio of 10, which is substantial enough to place considerable uncertainty in the assessment of stoichiometry. During the passivation process, both nitrogen and carbon could have been lost. For ς–Fe_2N, the Fe/N ratio of 2.4 after reaction, indicates that only 15% of the original nitride has been lost. The Fe/O ratio is 25, which is not very significant. The Fe/C ratio is also 25, indicating that very little of the nitride has actually been carburized. The stoichiometry for the ς sample is thus $Fe\ N_{0.42}C_{0.04}O_{0.04}$, and adds to a net interstitial stoichiometry of Fe_2X, in fair agreement with carbide stoichiometries by Anderson and researchers at Northwestern (6). In order to estimate the carbon in the ϵ sample, we assume a Fe_2X stoichiometry, and thus the stoichiometry becomes $Fe\ N_{0.2}C_{0.2}O_{0.1}$. It is not known how oxygen replaces the other species, or if it simply adds as an oxide overlayer. These stoichiometries are somewhat nitrogen rich in comparison with those estimated by Wilson (14) using Mössbauer spectroscopy. After 12 hours of reaction, the catalysts had apparently reached a kinetic steady state with regard to the Fischer-Tropsch reaction. We see from these experiments, however, that a great deal of nitrogen still remains in the bulk, as predicted by the early experiments of Anderson (1). By exposing these used catalysts to hydrogen at higher (> 600 K) temperatures, nitrogen immediately vacates the bulk. Apparently the bulk nitrogen lies poised to react during the Fischer-Tropsch reaction, but carbon monoxide in the gas phase and the resulting carbon overlayer prevents decomposition.

3. FUTURE RESEARCH

We are continuing efforts in the area of computer fitting of complicated carbonitride peaks in Mössbauer spectra. Computer modeling of the denitriding process is also underway. We also will study the effects of ammonia as a reactant in $NH_3/CO/H_2$ mixtures on the production of hydrocarbons and nitrogen containing organics.

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5. APPENDICES

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