

DE83015145



STUDY OF FISCHER-TROPSCH SYNTHESIS OVER A SILICA SUPPORTED IRON CATALYST THROUGH THE USE OF REACTIVE SCAVENGERS

TEXAS UNIV. AT AUSTIN

AUG 1983



U.S. Department of Commerce National Technical Information Service

DOE/ER/10720--11 DE83 015145

STUDY OF FISCHER-TROPSCH SYNTHESIS OVER A SILICA-

OF REACTIVE SCAVENGERS

APPROVED BY SUPERVISORY COMMITTEE:

resiloch

NOTICE PORTIONS OF THIS REPORT ARE ILLEGIBLE. It has been reproduced from the best

available copy to permit the broadest possible availability.

REPRODUCED BY: U.S. Department of Commerce National Technical Information Service Springfield, Virginia 22161



Copyright

by

Chia-zuan Jeff Wang

1983

The Government reserves for itself and others acting on its behalf a royalty free, nonexclusive, irrevocable, world-wide license for governmental purposes to publish, distribute, translate, duplicate, exhibit, and perform any such data copyrighted by the contractor.

To my parents

:: ;

.

e

STUDY OF FISCHER-TROPSCH SYNTHESIS OVER A SILICA SUPPORTED IRON CATALYST THROUGH THE USE OF REACTIVE SCAVENGERS

bу

CHIA-ZUAN JEFF WANG, B.S., M.S.

•.

DISSERTATION

Presented to the Faculty of the Graduate School of

The University of Texas at Austin

in Partial Fulfillment

of the Requirements

for the Degree of

DOCTOR OF PHILOSOPHY

THE UNIVERSITY OF TEXAS AT AUSTIN

August 1983

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or passes disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect thuse of the United States Government or any agency thereof.

DISCLAIMER

ACKNOWLEDGEMENTS

I owe more than I can express to Dr. Ekerdi who opened the narrow gate for me in pursuing my advanced education at U.T., Austin. I discovered, on the pathway to the end of this project, that he is a gracious man, accessible and helpful. I am still marveling at his intelligence in guiding my experiments and patience in revising my writing throughout this work. In addition, I experienced the efficiency of "plan your day at dawn" from him, which greatly increased my productivity.

Encouragement from my colleagues in EPS 311 was essential for me during this work. Their efforts transformed EPS 311 from an empty room to "the best little lab in Texas", providing me an enjoyable atmosphere in which to perform my research.

My gratitude goes to the U. S. Department of Energy for finantial support. The kindness of Professors Campion, Rase, Steinfink and Vasilakos to serve on my dissertation committee is highly appreciated.

I am deeply indebted to my parents for their support of my study in the U.S. Special thanks are due my wife for her patience when bad things happened to the experiments and her comfort when bad things happened to me during the past years.

Chia-zuan Jeff Wang

June 1983

STUDY OF FISCHER-TROPSCH SYNTHESIS OVER A SILICA SUPPORTED IRON CATALYST THROUGH THE USE OF REACTIVE SCAVENGERS

Publication No._____

Chia-zuan Jeff Wang, Ph. D. The University of Texas at Austin, 1983

Supervising Professor: John G. Ekerdt

The synthesis of hydrocarbons from H_2 and CO was studied on a silica-supported Fe catalyst. The synthesis was carried out at 1.54 atm and 200 to 255°C in a differential reactor. Conversion of CO never exceeded 2%. The working catalyst was achieved by transforming Fe₂D₃ into a mixture of Fe₃O₄, bulk carbides, and iron under synthesis conditions. Synthesis product distributions and the rate of methane formation are reported. Trends in CO₂ formation and the presence of cyclic hydrocarbons, saturated and unsaturated, suggest the presence of some Fe₃O₄ at the catalyst surface. Cyclohexene addition to the feed generated low concentrations of alkyl-substituted cyclohexene and cyclohexanes consistent with reported scavenging studies over Ru. Pyridine addition to the feed generated alkyl-substituted pyridines. Additional experiments confirmed that scavenged products were not formed

from the interactions between the scavenger and synthesis products on support. The results confirm that the scavengers react with species involved in chain propagation.

Pyridine was used to scavenge $C_1 - C_3$ alkyl species from the catalyst surface. The α -alkylpyridine distributions were dependent upon synthesis variables and demonstrated a dependence which was proportional to the dependence of $C_1^{-C}_3$ Fischer-Tropsch products. These results confirmed that alkyl species are the immediate precursors to synthesis products. Two most probable Fischer-Tropsch mechanisms were used to describe the catalytic behavior and scavenged product distributions. The alkyl fragment dependences were predicted using Langmuir-Hinshelwood expressions for these two mechanisms and were compared against the measured scavenged dependence. Lack of information concerning CO synthesis conditions prevented adsorption characteristics at discrimination between the possible mechanisms.

TABLE OF CONTENTS

•

I.Introduction and Literature Review	1 1 2 3
2.Rate studies	5 8 13
II. Experimental Methods A. Experimental Apparatus 1. Gas handling section 2. Reactor 3. Product collection and analysis B. Experimental Procedures C. Catalyst Preparation and Characterization D. Materials	17 17 19 21 26 27 29
III.Catalyst Characterization and Development of the Scavenging Technique A.Results 1.Catalyst induction 2.Rate measurement and product distributions 3.Scavenging experiments B.Dicussion 1.Catalytic behavior 2.Scavenging technique	30 30 39 42 54 59
IV.Propagation of Fischer-Tropsch Synthesis	63 63 83
V.Conclusion	95 99
Vita	104

•

LIST OF FIGURES

.

.

.

۰

Figu	ire	1.	Possible Fischer-Tropsch reaction mechanism.	11
Figu	Ire	۷.	System Schematic.	18
Figu	ire	3.	Microreactor	20
Figu	ire	4.	Flow diagram of GC operation	22
Figu	ire	5.	Rate of methane formation as a function of time on	
-			stream	32
Fio	Jre	6.	FT synthesis selectivity to low weight hydrocarbon as a	
			function of time on stream	23
Eio.		7	Definite of press all all and colorities as a	55
riyu	ne	1.	frinkly office of the or the selectivity as a	24
F 2		•	Numeral Stream	34
Figu	Jre	ð.	X-ray diffraction patterns	31
Figu	Jre	9.,	Product distribution of the low weight synthesis	
			products at WHSV of 22,274	41
Figu	ire	10.	Typical chromatogram of C _c to C ₁₁ synthesis products	43
<i></i>				
Figi	ure	11.	Chromatogram in the presence and absence of added	
			cycohexene	45
Figu	ure	12.	Chromatogram in the presence of added pyridine	47
Figi	ure	13.	Primary olefin to normal alkane selectivity in the	
•			presence and absence of scavenger	50
Fio	ure	14.	$Log(N_{-}/N_{-})$ versus (n-7) in the presence and absence of	
			cycloborono, scavender	52
Ei.e.		10	$\frac{1}{2} = \frac{1}{2} = \frac{1}$	22
rigi	ure	15.	$\log(M_{C_{-}}/M_{C_{-}})$ versus (n-7) in the presence and absence of	
			n 7	
~			pyridine scavenger.	53
rig	ure	16.	Transformations of iron phase during FT synthesis	55
Fig	ure	17.	C ₁ -pyridine/pyridine and the rate of methane formation	
				rr
			dependence on the partial pressure of $H_2 \cdots$	00
T to a		10	C manualdian (numidian and the mate of methane formation	
· rigu	ire	10.	1 - pyridine/pyridine and the rate of methane formation	
			dependence on the partial pressure of H · · · ·	67
Fiqu	ire	19.	Cpyridine/pyridine and the rate of methane formation	
-				
		• •	dependence on the partial pressure of CO	68
Figu	ire	20.	C ₁ -pyridine/pyridine and the rate of methane formation	
•			dependence of the mentiol processes of CO	c n
- 2			dependence on the partial pressure of LU	09
Figr	ле	Z 1.	Selectivity to higher hydrocarbons during continuous	1 10 - 11
			pyridine injection	71
Figu	ire	22.	Olefin to alkane dependence on the P ₁₁ in the absence of	
			''2	
			pyridine and during continuous pyridine injection.	72

•

,

Figure 23	3.	Olefin to alkane dependence on the P_{CO} in the absence of	
		pyridine and during continuous pyridine injection.	/3
Figure 24	4.	C_2 -pyridine/pyridine and the total rate of C_2	
		hydrocarbon dependence on the partial pressure of H ₂	75
Figure 2	5.	C ₃ -pyridine/pyridine and the total rate of C ₃	
		hydrocarbon dependence on the partial pressure of H ₂	76
Figure 26	6.	C_2 -pyridine/pyridine and the total rate of C_2	
•		hydrocarbon formation dependence on the partial pressure	
F ² 0 ²	-	of CO	77
Figure Z	/.	L_3 -pyridine/pyridine and the total rate of L_3	
		hydrocarbon formation dependence on the partial pressure	70
Figure 28	8.	Distribution dependence of C, and C, scavenged and FT	10
•		products on the partial pressure of Ha.	79
Figure 2	PQ	Distribution dependence of C and C. scavenged and FT	
riguie Li		products on the nextical processor of 1	00
		products on the partial pressure of H2	80
Figure 3	10.	Distribution dependence of C_2 and C_1 scavenged and FT	
F	•	products on the partial pressure of CO.	81
Figure 3	51.	Distribution dependence of L ₃ and L ₂ scavenged and Fi	
		products on the partial pressure of CO	82
•			

. .

. .

. . .

•

.

.

.

.

LIST OF TABLES

ţ

:

Table 1.	Selected Results for Detecting Reaction
	Intermediates15
Table 2.	GC Operation Conditions23
Table 3.	Metal Composition of the Catalyst and Silica -28
Table 4.	X-ray Diffraction Data for CuKa38
Table 5.	Partial Pressure Dependences for
	Alkylpyridine Ratios89
Table 6.	Partial Pressure Dependences for the Chain
	Growth Parameter90
Table 7.	Predicted Partial Pressure Dependences for
	α at the Extremes94

:

.

.

,

I.INTRODUCTION AND LITERATURE REVIEW

A.GENERAL

Coal has been considered a competive carbon source for fuel and chemical feedstocks. Research in the general area covers the spectrum from coal gasification to direct liquefaction. Studies of selective hydrogenation of carbon monoxide, known as Fischer-Tropsch (FT) synthesis, have been directed toward the production of chemical feedstocks and motor fuels. Many research groups have attempted to understand the effects of catalyst composition and synthesis conditions on product distribution and selectivity as well as to establish the reaction mechanisms.

Research in the area of synthesis gas conversion began in the 1920's in Germany. The extensive work of Fischer and Tropsch led to the development of the Fischer-Tropsch synthesis process as it is commonly referred to today. The majority of this effort was directed toward iron and cobalt. The early investigations have been discussed in several reviews (1-3).

Research continues at the present time. With the advent of the modern surface physics techniques, studies of the surface structure of the catalyst and of the adsorbed species on the catalyst have helped to

understand the catalytic chemistry of FT synthesis. Recent studies emphasizing the mechanism have been reviewed by Vannice (4), Ponec (5), Biloen and Sachtler (6), Bell (7), and Rofer-DePoorter (8).

In general, FT synthesis produces predominately linear alkanes and alkenes. The activity, selectivity and mechanism of the synthesis change with the synthesis conditions, temperature and reactant partial pressure, and catalyst composition. These differences are caused by the different chemisorption behavior of CO and H_2 on the various catalysts. For example, strong adsorption of H_2 on Ni leads to Ni as the catalyst for methanation, while weak adsorption of H_p on Ru leads to Ru as the catalyst for high molecular weight hydrocarbons. Studies of CO chemisorption on group VIII, IB, VIB, and VIIB metals have found that dissociative CO chemisorption plays an important role in FT synthesis (9,10). It is well established that the tendency for CO dissociation increases from right to left across a row and bottom to top along a column in the Periodic Table. Variables that increase the metal-CO bonding will increase the tendency of CO dissociation. Therefore the high selectivity to alcohols over Pd, Pt, and Ir (11) is interpretated as due to their low tendency for CO dissociation.

B.FISCHER-TROPSCH SYNTHESIS OVER IRON-BASED CATALYSTS

Iron has long been recognized as an important catalyst for FT

synthesis. It was used for the Schwarzheide test 40 years ago (2) and is still the only commercial catalyst for FT synthesis by SASOL in South Africa. The major products from the SASOL plant are gasoline, diesel, waxes and highly olefinic lighter hydrocarbons. Recent research with iron catalysts has concentrated on the carburization of iron (12-19), promotor effects (20-25), chemisorptive characteristics (20-33) and kinetic behavior (26-34). A detailed discussion of these investigations will be given below.

1. INTERACTION BETWEEN CO/H, AND THE CATALYST

Surface physics analytic techniques have been applied to study the structure and chemistry of the adsorbed reactant gases on iron surfaces (9,10,20-23,35-39), as well as the surface and bulk state of iron during the FT synthesis (25-33). Studies of the chemisorption of H_2 on iron surfaces (22,23,36,37,39) have shown that H_2 is dissociatively adsorbed and that the strength of the adsorption is much weaker than that of CO chemisorption. This leads to the displacement of the hydrogen from the surface by CO (39). Carbon monoxide was found adsorbed molecularly at 27° C and slowly dissociates with increasing temperature, whereas only dissociative adsorption was observed at 112° C (22,35).

Investigations using ultraviolet photoemission spectroscopy (UPS) and infrared spectroscopy (IR) techniques have indicated that CO is adsorbed perpendicularly to the transition metals, in a carbonyl-like

mode with the donation of CO 5 σ electrons to the metal and the backbonding of the metal d electrons to the CO 2 π orbital (9,40,41). The increase of the energy difference between the 1 π and 4 σ orbitals in the molecularly adsorbed CO on iron observed by UPS (20) and the decreased vibrational frequency of C-O bond as observed by IR (40,41) relative to gas phase CO demonstrate that metal-CO bonding leads to weakening of C-O bonding and increases the tendency of CO to dissociate.

Investigations of CO chemisorption on potassium promoted iron catalysts have shown that potassium enchances the bonding energy of molecularly adsorbed CO and increases the amount of CO dissociation (20,22,23). Similar result have been obtained on a potassium promoted FeO surface (32). Dry et al. (23) suggested that the enchancement of metal-CO bonding by potassium was due to the donation of K(4s) electrons to the metal. Benziger and Madix (22) found that this enchancement on Fe(100) by potassium was due to the interaction between the K(4s) orbital and CO(2π) orbital. They also found that the reduction of metal-CO bonding by sulfur, oxygen and carbon adlayers was due to the adspeices' bonding with Fe(3d) orbitals. The Fe(3d) orbitals are involved in backbonding of CO bond which is thought to enchance CO dissociation.

Recent experimental efforts of combining a catalytic reactor with a surface spectroscopy facility (XPS, UPS, AES) on foils and single crystals (26-31) and Mössbauer spectroscopy on dispersed iron catalysts (12-19) have shown that the chemical composition of the iron phase

generally changes during the FT synthesis. Iron was seen to form a mixture of bulk carbides and an inactive carbon overlayer depending on the temperature, H_2/CO ratio, the extent of CO conversion and the duration of the reaction. Characterization of bulk carbides by Mössbauer and XRD have shown that many carbide phases result and the stability of various phases depend on the catalyst particle size, the type of the support, the presence of promotors and the reaction temperature (12,18,19). Inactive carbon overlayer is believed to cause the deactivation of the catalyst (26-31). This inactive overlayer can only be completely removed at temperatures in excess of $420^{\circ}C$ (26,31). The various forms of the iron state are the result of the complex oxidation-reduction reactions among iron oxide, iron and iron carbides. Consequently different catalytic behavior was observed on reduced and unreduced iron oxide (30,31). It has also been suggested that the surface composition changes with synthesis conditions (18,31,46) and that the surface and bulk may exist as different iron phases.

2.RATE STUDIES

Rate measurements of FT synthesis activity have been performed over commercial singlely or multiply promoted catalysts (34,42-46), experimentally prepared supported or unsupported catalysts (14,17,25,30-33,47) and well defined pure iron surfaces (27,28). These catalysts included single crystal, polycrystalline, reduced or

unreduced iron oxides supported on silica or alumina, and fused iron containing Cu, K_2O_3 , K_2O_3 , AI_2O_3 and CaO as promotors.

Dry (43) assuming a near saturation of CO adsorption and a rate determining step of hydrogenation of adsorbed CO on iron, developed a kinetic model for the rate of FT synthesis. At high CO conversion the kinetic expression for the CO conversion is

$$r = k \exp(-E/RT) - \frac{P_{CO} P_{H_2}}{P_{CO} + aP_{H_2O}}$$
(1)

where $a = k_{H_20} / k_{CO}$. In a differential reactor (34) where the production of H_2O can be neglected the rate equation simplifies to

$$r = K P_{H_2}$$
(2)

Vannice (47) observed that the initial rate of methane formation was linearly proportional to the P_{H_2} but was weakly inhibited by P_{CO} and P_{H_2O} . The activation energy for methane formation was determined to range from 20 to 23 Kcal/mole in good agreement with other investigations (43,44,45,47). The apparent activation energy for high molecular weight hydrocarbon formation was found to be smaller than that of methane, therefore selectivity for high molecular weight hydrocarbon decreases with increasing temperature (45).

Product distribution has been found to be independent of CO conversion and H_2/CO ratio for a Cu and K promoted commercial catalyst in an integral reactor (42,44-46). However on a polycrystalline iron surface, the product distribution shifted toward higher molecular weight hydrocarbon as the H_2/CO ratio decreased (28). Satterfield and Huff (42) suggested that the product distribution is a function of iron composition. Conversion dependence and selectivity the water-gas shift (WGS) reaction over several silica-supported iron bimetallic and potassium-promoted iron catalysts was studied by Amelse et al. (17). They found that, depending on the catalyst composition, the methanation activity and WGS rate change with CO conversion and influence each other.

Carbon dioxide formation has been observed to increase with decreasing space velocity, and increasing reactor length (45). These observations support the proposal that CO_2 is a secondary product formed via the WGS reaction. Madon and Taylor (46) proposed that the WGS reaction occurs on the active Fe_3O_4 surface and plays an important role in affecting the catalyst state at high CO conversion. The high production rate of H_2O and CO_2 at high conversion is expected to affect the complex oxidation-reduction reactions that iron undergoes.

The effects of potassium promotion on the kinetic behavior of iron catalysts have been studied (20,25). The results showed that potassium caused a decrease in methanation activity, an increase in the

average molecular weight and olefin to paraffin ratio of the products, and an increase in the WGS activity.

The studies of methanation on iron foils (27,28) have shown that the activity rises rapidly to a maximum, then declines at a smaller steady rate due to the formation of inactive carbon. The comparison of this phenomena between reduced and unreduced iron oxide catalysts have been investigated by Krebs et al. (30) on Fe₃O₄ and by Reymond et al. (31) on Fe₂O₃. In both cases the unreduced oxide catalysts showed a much slower initial rate increase and a much longer and higher steady state activity after a maximum in methanation. Krebs et al. (30) suggested that the competive effects of the hydrogen reduction at 497°C (increasing specific surface area) and the sintering of the catalyst cause the different behavior. Reymond et al. (31) maintained that the faster formation of iron carbide on a reduced catalyst and the complex reduction-oxidation reaction on unreduced iron oxide cause the difference.

3. FISCHER-TROPSCH REACTION MECHANISMS

Early studies of FT synthesis over iron catalysts (2) have shown that the synthesis products satisfy the distribution commonly referred to as a Schulz-Flory distribution. Recent rate studies by Krebs et al. (28), Madon and Taylor (46), and Satterfield and Huff (42) contain similar plots. Satterfield and Huff (42) obtained a linear relation

between the log of the mole fraction of the product C_n and the carbon number, n, extending between 1 and 20 by including oxygenated products. Schulz-Flory plots are an indication that the synthesis proceeds by a stepwise polymerization. Madon and Taylor (46) and Anderson (2) observed a bend in the distribution plots at carbon numbers of 22 and 9-12, respectively. Madon and Taylor proposed that the bend is due to chain growth taking place on different types of sites, each with different chain growth probability. In a recent study, Novak et al. (48) reported that with the readsorption of olefin the overall product distribution is still quite close to a Schulz-Flory distribution.

As the mechanism for FT synthesis was investigated intensively, the discussions have concentrated on two questions, whether CO dissociates before hydrogenation and whether methylene or CD is involved in the chain growth. The earliest mechanism, the so-called "carbide" mechanism was proposed by Fischer and Tropsch and expanded by Craxford and Rideal (1). This mechanism involves the hydrogenation of bulk or surface carbides to form methylene and subsequent polymerization of methylene to form the synthesis product. The ¹⁴CO tracer experiments of Emmett (49-51) discredited the "carbide" mechanism. Synthesis reaction on the ¹⁴CO precarbided catalyst showed only a minor fraction of the synthesis product could be accounted for by bulk or surface carbides. However, because of the difficulty in precisely determining the carbide phase at that time, investigators still consider that chemisorbed carbon is a possible intermediate. Enol (RHCOH) and acyl (RHCO) have also been proposed as the reaction intermediate. Storch et al. (1) postulated that condensation of two enol intermediates, which are formed by the direct hydrogenation of the molecularly adsorbed CO, and the subsequent hydrogenation to form higher molecular weight enol intermediates are propagation steps. Pichler (52) proposed yet another mechanism for propagation. It involves CO insertion into the metal-alkyl bond to form acyl intermediates which are hydrogenated to form the new alkyl intermediates.

As previously discussed, CO dissociates readily when adsorbed on group VIII metals at FT synthesis temperature. Two main mechanisms, presented in Figure 1, have been proposed to account for this finding. Biloen et al. (6,54,55) and Bell and coworkers (7,56-60) proposed that methylene intermediates from hydrogenation of the dissociated CO insert into the metal-alkyl species to produce synthesis products. Ponec (53) and Henrici-Olive and Olive (61,62) suggested that CO insert into the metal-alkyl species to form acyl intermediates. The acyl intermediates are hydrogenated by hydrogen to form higher molecular weight alkyl intermediates. Both mechnisms involve the same initiation step to form methyl groups and methane as well as the same termination steps to form higher synthesis products. Recent studies centered on these two mechnisms over iron catalyst are presented below.

Experimental evidence to support the postulate that the hydrogenation of surface carbon produces methane and \bar{C}_{2+} hydrocarbons

Methylene Insertion $C0_{(g)} - C_{(s)} + C0_{(s)}$ $C0_{(g)} - C_{(s)} + CH_{2(s)} + CH_{3(s)} + CH_{4(g)}$ $C_{(s)} + H_{(s)} - CH_{5(s)} + CH_{2(s)} + CH_{4(g)}$ $CH_{2(s)} + C_{2}H_{5(s)} - C_{n}H_{2n+1(s)} + CH_{2(s)} + CH_{2(s)} + H_{1(s)} + H_{1(s)} + H_{1(s)} + C_{n}H_{2n+1(s)} + CH_{2(s)} + C_{n}H_{2n+1(s)} + C_{n}H_{2n+1(s$

Figure 1. Possible Fischer-Tropsch reaction mechanism.

. Cn H 2n + 2(g)

found from studies over Ni, Co and Ru (53,54). For iron catalysts, 15 Bennett and co-workers (63,64) have found that surface carbon can serve both as a precursor to the formation of Fe₂C as well as methane. Studies over an Fe(110) surface during the synthesis reaction by AES and XPS (29) have identified a CH, phase which was interpretated as the intermediates from the hydrogenation of surface carbidic carbon. Further evidence supporting the methylene insertion mechanism came from the recent work of Brady and Pettit (65,66). They found that ethylene is the only product from the diazomethane reaction over supported Ni, Fe, Co and Ru catalysts. When hydrogen and diazomethane were passed through these catalysts a spectrum of hydrocarbons, similar to the FT synthesis products, were produced. They suggested that diazomethane is decomposed to methylene groups and these methylene groups dimerize to form ethylene in the absence of hydrogen. In the presence of hydrogen, methylene groups are hydrogenated to form methyl groups and methane as well as insert into the metal-alkyl species to produce FT synthesis products.

Support for CG insertion derives from the IR experiments (67) that OH bands have been observed over an Fe/SiO₂ catalyst. The finding of the OH band was postulated as the evidence of the M=C(OH)R intermediates. King (68) questioned this postulate and suggested that the OH band was the result of the accumulation of H_2O on the silica support.

4. DETECTION OF THE REACTION INTERMEDIATES

Chemical scavenging has been considered as an experimental technique to detect the reaction intermediates, because kinetic and surface spectroscopy techniques do not give conclusive evidence for the presence or type reactive intermediates. Essentially, one titrates the reaction intermediates from the surface with a probe (scavenger) molecule. An early example of this was reported by Eidus et al. (69). Benzene was injected into the synthesis gas and produced toluene over Co-Ni and Fe-Cu catalysts. Toluene was not detected in the synthesis products without the injection of benzene, therefore it was postulated as the product from the interaction between the benzene and surface methylene or methyl intermediates.

The interaction between the hydrocarbon fragments and the olefins as the scavengers are supported by the recent advances in organometallic chemistry. A number of reactions between the alkylidene or alkyl ligands on the metal complex and various olefins have been reported (70-73). Ekerdt and Bell (57) used this technique to remove hydrocarbon fragments of varing length from a Ru surface. Compared to the scavenger concentration used by Eidus (10-50%), Ekerdt and Bell used a much smaller concentration ($\leq 2\%$) in order to minimize the possibility of the perturbation of the kinetics and the mechanism of the synthesis reaction. In addition to the detection of alkyl fragments, the injection of the cyclohexene was found to suppress the extent of the hydrocarbon

chain length. The authors suggested that the decreasing chain length was due to the removal of methylene intermediates, which are involved in the chain growth step, by cyclohexene. Baker and Bell (60) continued this technique and included cyclohexene, benzene, cyclopentene, as the sacvengers. Selected results of these experiments to detect the reaction intermediates during FT synthesis are shown in Table 1. These results provide very strong evidence for the presence of methylene and methyl fragments on the catalyst surfaces. The concentration of the scavenged products was reported to depend on the synthesis conditions. Therefore, the scavenged products were interpretated as the products from the interaction between the intermediates and the scavengers.

Pyridine can be selected as a candidate scavenger because it contains a heteroatom, nitrogen, and low concentrations should be easy to discriminate from the multitude of synthesis products. The pyridine ring is difficult to hydrocrack between 200 and 250 °C (74), which will eliminate scavenger decomposition to alkyl fragments. Furthermore, pyridine has been proposed to bond to nickel through the unpaired electrons of the nitrogen and subsequently react with methyl groups to form 2-methylpyridine (75,76). These methyl groups were formed by interaction of H₂/CO or alcohols on the nickel surface.

Studies of the adsorbed states of pyridine on iron films have demostrated that pyridine bonds to a preoxided iron surface through the nitrogen lone pair electrons and to a clean iron surface through π

Catalyst	Scavenger S	Scaveged product	Postulated Re intermediates	ference
Co-Ni Fe-Cu	Benzene	toluene	methyl, methylene	e (69)
Co-ThO ₂ - Kieselgnhr	Benzene cy	ycloheptatriene	methylene	(69)
Ru/SiO ₂	Cyclohexene	norcarane	methylene	(60)
Ru/SiO ₂	cis-2-Butene	l,2-dimethyl cyclopropane	methylene	(60)
Ru/SiO2	1-butene	ethylcyclopropan	e methylene	(60)

Table 1 Selected Results for Detecting Reaction Intermediates

•

.

,

electrons (77). With the strong adsorption it may be expected that pyridine will be a more effective scavenger than cyclohexene because a higher surface concentration of pyridine may be realized. However, pyridine on the iron surface is expected to affect the adsorption of hydrogen and possibly change the catalytic behavior.

The experimental effort of this work consists of two stages. The first stage develops an understanding of the catalytic behavior of FT synthesis and develops the technique of reactive scavenging over the iron catalyst. This is discussed in Chapter III. The second stage used the scavenging technique to gain the better understanding of the elementary processes involved in the FT synthesis over the same catalyst. This will be discussed in Chapter IV.

II.EXPERIMENTAL METHODS

A.EXPERIMENTAL APPARATUS

The apparatus, shown schematically in Figure 2, consisted of three sections: a gas handling section, a reactor, and a product collection and analysis section. Detailed descriptions for each section are presented below.

1.GAS HANDLING SECTION

The reactant gases were metered and blended to the desired composition using manual metering values. The flow rates were determined with Hastings mass flowmeters. Figure 2 depicts an earlier version of the apparatus in which flow rates were determined by monitoring the pressure drop through capillary tubing. Metering values M_5 and M_6 were used to regulate the reactor pressure. Aside from the copper tubing and brass fittings used to connect and regulate carbon monoxide, all tubing, fittings and values were stainless steel. The tubing, values and fittings between the reactor, the trap and the gas chromatograph (GC) were maintained at 90°C to 100°C.





Figure 2. System schematic.

A stream of helium was bubbled through the scavenging reagent in a flask sparger, fitted with a frit. For pulse injection, a glass sparger and a six-port sample injection valve fitted with an 80 μ t loop were used to inject 5 μ moles of gas. For continuous injection, an auxilary feed line was used to combine the helium stream to the feed gases. The sparger was fabricated from copper because saturation was conducted at 1.68 atm. The concentration of the scavenger in the stream was controlled by the sparger temperature and helium flow rate. The helium flow and sparger temperature were maintained at 2 sccm and 0°C, respectively, for all experiments.

2.REACTOR

The reactor, illustrated in Figure 3, was a two-inch section of 0.25 inch OD stainless steel tubing with 0.25 to 0.125 inch Swagelock unions on both ends. Catalyst was contained in the reactor tube by positioning quartz cloth in the union shoulders. The reactor and an 18 inch section of inlet line were immersed in a heated fluidized sand bath. The inlet line served as the reactant gas preheat zone. The catalyst temperature was measured by attaching a thermocouple probe to the exterior of the reactor.

The fluidized sand bath was heated in two ways. Fluidizing air was preheated; the temperature was set 50°C below the desired reactor temperature. Two flexible heating tapes were wrapped around the outside



Figure 3. Microreactor

of the bath and were used to supply different amounts of heat to the bath depending on the location relative to the bottom of the bath. Temperatures were controlled with Omega model 49 controllers. The sand bath temperature at the reactor position was maintained within $\pm 1.0^{\circ}$ C of the desired temperature.

3. PRODUCT COLLECTION AND ANALYSIS

2

Most of the analysis was conducted using a Varian 3760 GC fitted with two packed columns and one capillary column. The flow diagram for the operation of the Varian GC is illustrated in Figure 4. The Chromosorb 106 column, when connected to the thermal conductivity detector (TCD), was used to separate reactants, H_2 and CO, from light products, CO_2 , CH_4 , C_2H_4 , C_2H_6 , C_3H_6 , and C_3H_8 . When connected to the flame ionization detector (FID), this column was used to separate light products when the FT synthesis activity was low. The packed DV-101 column was used to separate C_4 to C_6 hydrocarbons. The OV-101 capillary column was used to analyze C_7 and above hydrocarbons.

A Hewlett Packard 5880A GC equipped with a nitrogen-phosphorus detector (NPD) was used to detect nitrogen containing products. An amine deactivated fused silica glass capillary column loaded with Carbowax (CAM) was used to separate pyridine and alkylpyridines. The operation conditions used in the Hewlett Packard and Varian GC's are given in Table



Figure 4. Flow diagram of GC operation

column .	carrier gas flow rate	detector	temperature program
Chromosorb 106 60/80 mesh 1/8 in x 12 ft	He: 22 cc/min reference column Chromosorb 106	TCD	40°C for 5 min 7°C/min to 200°C 1
Chromosorb 106 60/80 mesh 1/8 in x 12 ft	He:22 cc/min	 FID 	110°C for 6 min 5°C/min to 215°C
20% OV-101 on Chromosorb P-AW 60/80 mesh 1/8 in x 20 ft	He:30 cc/min	 FID 	36°C for 8 min 3°C/min to 130°C
Fused silica glass coated with OV-101 0.235 mm OD x 50 m	 He:0.5 cc/min 	 FID	36°C for 14 min 2°C/min to 170°C
Amine deactivated fused silica glass loaded with Carbowax 0.25 mm ID x 30 m	 H ₂ : 1.1 cc/min 	I I NPD	 40°C for 1 min 30°C/min to 90°C 2°C/min to 114°C

•

Table 2. GC Operation Conditions

.

One cubic centimeter of gas sample was injected into the packed columns through the heated (80-100 $^{\circ}$ C) six-port sample valve. The packed columns were calibrated each day using two certified standard gas mixtures containing CO, CO₂, CH₄, C₂ to C₅ n-alkanes and primary n-olefins, and hexane at different concentrations. Product gas concentrations were determined by comparing the product's peak height to the peak heights for the standards.

A 50 ml pear shaped boiling flask was used to collect products which were trapped at liquid nitrogen temperature. The collected samples were stored in the flask at -10° C for analysis at a later time. Samples were never stored more than 48 hours. These trapped products were analyzed using the capillary columns in the two GC's or in a Finnegan 4023 GC-MS. The products were washed from the sides of the flask and extracted from any water with 0.05 ml of diethylether. A splitless Grob-type injector was used on all instruments and 1.0 to 4.0 µℓ was injected. Three samples were injected for each experiment when using the NPD. The results reported were average values. Amounts of a given nitrogen containing compound were related directly to the NPD signal area.

Elution charateristics for the capillary columns were established using the GC-MS. Component assignment was performed by a computer libray search of the five major fracturing peaks remaining after standard enhacement. The computer is forced to make an assignment
and provides three quantities which represent the confidence of the assignment, fit, refit, and purity. Fit values greater than 900, boiling points expected for the unknown component's retention time, examination of the mass fracturing pattern, and when possible injection of pure components were used to assign the identity to an eluted component.

The capillary columns were operated under identical temperature cycles on the GC's to maintain the same component elution order. Standard mixtures were injected to fix the position of known compounds on a chromatogram. Identification of peaks eluting from the GC were made by comparing the chromatograms for the two instruments. The elution charateristics for the OV-101 capillary column with the GC-MS were well establised. However, the elution characteristics of the CAM column could not be well estalished using the GC-MS. Helium had to be used as the carrier gas on the GC-MS. Carrier flow rate and column temperature could not be optimized to produce the same peak resolution realized with hydrogen as carrier gas on the Varian GC. The GC-MS analysis established that alkylpyridines were eluting and the relative elution order of the alkylpyridines and hydrocarbons.

The NPD only detects nitrogen containing compounds from the trapped products. This greatly simplified component identification and overcame the difficulties encountered using a FID which also detected FT synthesis products. The elution characteristics for pyridine and alkylpyridines were established using pure components.

B.EXPERIMENTAL PROCEDURES

The catalyst powder was pressed into wafers approximately 0.003 inches thick and crumbled before placing in the reactor. Less than 0.5 grams of catalyst were charged to the reactor. Carbon monoxide conversion never exceeded 2% at this catalyst loading.

Iron oxide on silica, Fe_2O_3/SiO_2 , was conditioned for six days by passing a 4/1 H₂/CO mixture over the catalyst at 230°C. This was found sufficient to convert the Fe_2O_3 into a mixture of Fe_3O_4 , carbides and possibly, α -Fe which displayed a stable steady state activity. A conditioned catalyst was always exposed to hydrogen and carbon monoxide between 200 and 250°C to maintain the active form. The catalyst was allowed to adjust to new synthesis conditions for at least 6 hours before data were collected.

Two separate scavenging protocols were employed, pulse and continuous injection. Pulse injection was used mostly in the early experiments which attempted to detect the scavenged products. For these experiments, the H_2/CO ratio was varied between 1 and 9 and total volumetric flow rate varied between 100-200 sccm in order to find an optimal condition to scavenge detectable levels of products. Eighty pulses were added at 30 second intervals into the reactant feed gas. The reactor effluent was trapped at liquid nitrogen temperature for 20 seconds following each injection. The continuous injection was used to

26

study the effects of the synthesis conditions on the alkylpyridine distributions. The total volumetric flow rate was regulated at 100 sccm and the H_2/CO ratio was varied between 0.2 and 5.0. The reactor effluent was trapped continuously for 25 min. For both scavenging protocols, the helium flow rate through the sparger was 2 sccm and an ice bath was used to keep the sparger temperature at $0^{\circ}C$.

C.CATALYST PREPARATION AND CHARACTERIZATION

The supported iron catalyst was prepared by the incipient wettness technique using 2.0 ml of the iron salt solution, per gram of silica, Cab-O-Sil HS-5 (surface area: $325 \text{ m}^2/\text{gm}$). The impregnated support was frozen by pouring liquid nitrogen on it. The frozen mixture was vacuum dried in a rotary evaporator at 60° C for 42 hours and calcined with zero air (79% N₂ and 21% O₂) at 300° C for one hour, followed by 20 hours at 400° C. The catalyst was cooled in the zero air and sieved to sub-325 mesh, then stored in a dessicator.

The iron salt solution was made from 30 ml of distilled water and 27.13 gram of $Fe(NO_3)_3 \cdot 9H_2O$. Metal content was determined by Inductively Coupled Atomic Emission Spectroscopy (analyzed by Mineral Studies Laboratory, Balcones Research Center, University of Texas at Austin). Table 3 presents the results. The catalyst contained 20.44 wt% Fe_2O_3 .

	the second s	
	Silica HS-5	Fe Oxided
		on Silica
(wt %)		
A1203	0.02	0.02
CaO	0.005	0.006
Na ₂ 0	0.11	0.05
к ₂ 0	0.04	0.02
MnO	0.001	0.001
MgO	0.01	0.01
Fe203	0.01	20.44
SiO ₂	99.9	76.5
(µg/g)		
Fe	87	143000
Mn	5	7.6
Ti	25	21
Cu	10	31
Cr	29	29
Ni	25	67
Zn	10	45

Table 3. Metal Composition of the Catalyst and Silica

28

:

Iron, iron oxides and iron carbides were determined using a General Electric model XRD-6 X-ray diffractometer. CuK α radiation diffracting from a graphite monochrometer was used. Particle size of the fresh Fe₂D₃ catalyst, estimated by the line broading technique, was about 240 Å.

D.MATERIALS

Hydrogen (UHP, 99.999%) was passed through a Matheson deoxo cylinder to remove any oxygen. Carbon monoxide (Matheson UHP, 99.8%) was heated to 95°C over molecular sieves to decompose metal carbonyls. Cyclohexene (Aldrich 99%) was purified by distillation over sodium. Pyridine (MCB spectral grade) was used without further purification.

III.CATALYST CHARACTERIZATION AND DEVELOPMENT OF THE SCAVENGING TECHNIQUE

Investigation of the catalytic behavior of iron and the phase transformations of Fe_2O_3/SiO_2 under synthesis conditions are reported and discussed in this chapter. Iron activity and selectivity toward low weight and high weight Fisher-Tropsch (FT) products are presented. Selectivity and phase transformation are used to postulate the surface composition of the working catalyst.

The scavenging technique is also developed in this chapter. Cyclohexene and pyridine are used as scavengers. Scavenging results are combined with appropriate blank tests to demonstrate that FT reaction intermediates are being chemically removed from the surface of the metal phase.

A.RESULTS

1.CATALYST INDUCTION

It is well established that Fe or Fe_3O_4 will convert into one or more carbide phase under synthesis conditions (2,12-19,25,26,30,31). The rates at which the carbide phases convert and the changes in synthesis activity and synthesis selectivity are also reported. Uncertainty in iron phase composition can complicate analysis of data. In an attempt to minimize the uncertainty, the catalyst used in this study, 20.44 wt% Fe_2O_3 /SiO₂ was conditioned under 4/1 H₂/CO (P_{CO}=0.22 atm) at 230 °C for six days prior to use for reactive scavenging experiments and was rarely exposed to temperatures in excess of 250°C.

Time dependent methanation activity and low weight product selectivity are presented in Figures 5 to 7. These figures display FT synthesis data over a 40 day period at a common temperature of 230° C and a weight hour space velocity (WHSV, cm³/hr.g-cat.) of 15,840. The H₂/CO ratio and partial presure of CO varied between 3.8 to 4.3 and 0.20 to 0.23 atmospheres, respectively. Some of the scatter of the data may be due to the slight random variation in reactant partial pressures. After the sixth day this catalyst was also exposed to other pressures and temperatures.

Figure 5 demonstrates the effect the induction period had on methanation activity. After approximately 150 hours the activity reached a steady value. Activity decreased slightly after 400 to 500 hours.

Figure 6 shows that the distribution to total C_2 to C_5 hydrocarbons (branched and normal alkanes and olefins) did not change appreciably during the induction period. Only the C_2 's increased relative to methane during the first 150 hours. These results indicate













that the selectivity to low weight hydrocarbons was relatively independent of total activity. The C₁ to C₅ hydrocarbons increased in activity at approximately the same rate. Carbon dioxide selectivity increased over the first 150 hours and was essentially constant for the remaining 850 hours. The time dependent distribution of C₆+ hydrocarbons was not monitored. High weight products were synthesized during the early stages of induction. A liquid sample collected four hours after exposing Fe_2O_3 to H₂ and CO was found to contain hydrocarbons up to C₁₂, the upper limit investigated.

Figure 7 presents the α -olefin to n-alkane ratio for small hydrocarbons. The ratios pass through a minimum, returning to their initial value after approximately 120 to 140 hours on stream, and continue to increase over the course of the time period studied.

Recent studies on silica supported Fe_2O_3 catalysts (78) have shown that after 20 hours of reaction unreduced catalyst converts to Fe_3O_4 and hydrogen reduced catalyst converts to iron carbides. The conversion of unsupported Fe_2O_3 (31) into Fe_3O_4 and x-carbide was reported at 250°C. Amelse et al. (12) converted 90% reduced Fe_2O_3 into carbides. Unmuth et al. (79) reported that α -Fe $_2O_3/SiO_2$ reduced to Fe_3O_4 prior to reducing to Fe under H_2 at 425°C. In a separate study, Unmuth et al. (15) demonstrated that Fe/SiO₂ was converted to a mixture of carbides at 3/1 H_2/CO and 250°C.

X-ray diffraction (XRD) was used to characterize the state of the catalyst used in this study. The results are presented in Figure &. Composition assignments are based upon published diffraction patterns (80). Table 4 lists the location of the primary peak for the various phases reported by other researchers.

Polyethylene was used to cover the fresh catalyst and the catalyst which had been exposed to hydrogen and carbon monoxide between 200 and 255°C for 56 days. The catalyst was transferred to a glass slide and covered with the 25.4 micron thick polyethylene film in an inert environment to minimize oxidation. Amelse et al. (12) have shown that air oxidation was not rapid, therefore, all other XRD patterns were recorded in the absence of polyethylene.

The fresh catalyst diffraction pattern, pattern a, was identified as α -Fe₂O₃ with an average particle size of 240 Å. The single phase patterns for Fe₃O₄, pattern c, and α -Fe, pattern d, were determined using two separate weight loadings. The Fe₃O₄ pattern was observed after reducing 10 wt% Fe₂O₃/siO₂ at 400°C for six hours under H₂. Continued reduction of the Fe₃O₄ to α -Fe was realized by heating under H₂ for an additional 14 hours at 400°C and one hour at 430°C. The α -Fe pattern presented in Figure 8 was obtained with 20.44 wt% Fe₂O₃/SiO₂ which was subjected to H₂ at 460°C for 24 hours to ensure complete reduction.





:

X-ray diffraction patterns: (a) 20 wt% Fe_2O_3/SiO_2 (covered with polyethylene film), (b) 25.4-um-thick polyethylene film, (c) partially reduced 10 wt% Fe_2O_3/SiO_2 , (d) fully reduced 20 wt% Fe_2C_3/SiO_2 , (e) catalyst after 162 hr of reaction at 4/1 H₂/CO and 230°C, and (f) catalyst after 56 days of use (covered with polyethylene film).

	Phase	28 ^a	T
			([▶] K)
		33.1	
	Fe ₃ 0 ₄	35.4	÷=
	α-Fe	44.5	
	ε'-Fe _{2.2} C	43.4	720
	ε-Fe ₂ C	42.39	650
	x-Fe ₅ C ₂	43.9	525
	θ-Fe ₃ C	41.98	480
a	Diffraction angle for	the primary p	eak (80)

Table 4. X-ray Diffraction Data for $CuK\alpha$

^b Curie temperature

Catalyst was analyzed after exposing 20.44 wt% Fe_2O_3 /SiO₂ for 160 hours to 4/1 H₂/CO, 0.22 atmospheres of CO at 230°C. The peak centered at 20 equal to 35.4° on pattern e indicates the presence of Fe_3O_4 . A weak signal is also seen at 20 equal to 43.4° suggesting the presence of the ε '-carbide phase, $Fe_{2,2}C$.

Pattern f was recorded for a sample which had been exposed to hydrogen and carbon monoxide for 56 days. Catalyst temperature was generally held between 200 and 240°C. The catalyst was exposed to 255°C for approximately 50 hours out of a total of 1340 hours of use. The broad peak centered at 20 equal to 43.5° suggests the presence of several carbide phases. The peak is poory resolved and particle size can not be determined. Niemantsverdriet et al. (18) discussed the carbide phases generated under synthesis conditions. These can included ε' -, ε -, χ - and θ -carbide. The broad shape displayed by the used catalyst on Figure 8 brackets the primary peaks for the first three. The used catalyst pattern has a shoulder at the location for α -Fe suggesting that α -Fe may also be present.

2. RATE MEASUREMENT AND PRODUCT DISTRIBUTIONS

The surface area of the working catalyst was not determined in

this study. Methanation rates are reported per gram of catalyst charged to the reactor. The rate was seen to increase with an increase in temperature and in the H_p/CO ratio.

Changes in the C_2 to C_6 product distribution as a function of synthesis variables are presented in Figure 9 at a common WHSV of 22,274. Only normal alkanes and primary n-olefins are represented because they constituted the major species detected. Branched alkanes and internal olefins were detected at lower concentrations than the normal and primary compounds for C_4 and above.

The selectivity to higher hydrocarbons was seen to decrease with increasing temperature. An increase in the H_2/CO ratio at a constant temperature led to a slight decrease in the selectivity to higher molecular weights. Both observations are consistent with the work of Madon and Taylor (46) at ten atmospheres.

The rate of CO_2 formation increased with increasing temperature and increasing H₂/CO ratio. A similar effect was seen for the rate of methane formation. However, the concentration of CO_2 decreased with increasing temperature and H₂/CO ratio. At all conditions investigated, the amount of CO_2 was less than the amount of CO converted into C_1 to C_6 normal products.



Figure 9. Product distribution of the low weight synthesis products at WHSV of 22,274: only n-alkanes and primary n-olefins are represented.

A GC-MS chromatogram for the C_6 to C_{11} synthesis products is presented in Figure 10. Straight chain α -oleifns are the primary products. The branched alkanes elute first, followed by the α -olefin, normal alkane and a mixture of branched internal olefins.

The chromatogram shows a large peak centered at scan 2420 which was identified as toluene. The toluene was not an impurity introduced during sample collection, handling or injection. The concentration of toluene relative to 1-heptene was observed to vary with synthesis conditions.

Other cyclic and aromatic products were observed. These include: cyclohexene, methylcyclohexene, benzene, styrene, xylenes, methylethylbenzenes, and diethylbenzenes. Additional cyclic products may have formed but were not observed in the region of C_7 through C_{10} . Cyclic C_5 and C_6 alkanes and olefins as well as branched alkanes, olefins and aromatics have been reported over unsupported iron based catalysts (2). The effect of WHSV and synthesis conditions upon the distribution of cyclic hydrocarbons was not studied. Their presence was noted at different conditions; however, their concentration was not accurately determined.

3.SCAVENGING EXPERIMENTS

The present studies have shown that the synthesis products over

÷



Figure 10. Typical chromatogram of C_6 to C_{11} synthesis products: 250°C, 5.5/1 H₂/CO, 0.24 atm P_{co}, 15,600 WHSV.

iron are a complex mixture containing cyclohexene and methylcyclohexene. The feasibility of scavenging was tested by introducing a greater amount of cyclohexene into the reactant feed gas than was observed in the synthesis product stream. Cyclohexene was used because it has been proven to be an effective scavenger over Ru (57).

Figure 11 shows a region of the GC chromatogram for the synthesis product and the cyclohexene scavenged product at $9.7 \text{ H}_2/\text{CO}$ and 220°C . The CO conversion was approximately 0.8% at these conditions and a WHSV of 14,590. The location of methylcyclohexene is indicated on the Figure. The assignment was made by comparison with GC-MS chromatograms, injection of pure compounds and experience with the column elution characteristics. A slight increase in the methylcyclohexene signal was seen upon injecting cyclohexene 120 times. Methylcyclohexene/n-heptane was 0.012 and 0.083 for synthesis and scavenging, respectively.

Small amounts of methylcyclohexene, methylcyclohexane, ethylcyclohexene and ethylcyclohexane were formed upon addition of cyclohexene at H_2/CO ratios between 1.9 and 2.1 and temperatures between 220 and 255°C. The number of pulses and synthesis conditions were varied in an attempt to generate higher concentrations of alkyl-substituted cyclic compounds. In all cases the methyl-substituted compounds were present at a higher concentration than the ethyl-substituted compounds. These attempts were largely unsuccessful.



Figure 11. Chromatogram in the presence and absence of added cycohexene: curve A - scavenged product, curve B - synthesis product, 219°C, 9.7/1 H₂/CO, 0.14 atm CO, 14,590 WHSV.

Pyridine was selected as a candidate scavenger because it contains a heteroatom, nitrogen, and low concentrations would be easy to discriminate from the multitude of synthesis products. Figure 12 presents a GC-MS chromatogram of the trapped products collected during the injection of 60 pulses of pyridine. The synthesis conditions were $1.65 \text{ H}_2/\text{CO}$ at 250° C. The CO conversion was approximately 0.1% at these conditions and a WHSV of 22,275. Peaks for 2-methylpyridine and 2-ethylpyridine are indicated on the Figure. Appropriate blank experiments were performed which established that the alkylpyridines were not impurities.

Additional experiments were performed at different synthesis conditions to confirm the generation of methyl- and ethylpyridines. Injections were reduced from 60 to between 3 and 10 in an attempt to minimize overloading the column with highly polar compounds. Tailing of pyridines was not eliminated, however, these studies indicated that 3 injections were sufficient to produce methyl- and ethylpyridine. The net effect of fewer injections was to increase the hydrocarbon signals on the chromatogram.

Only qualitative observations concerning the relative amount of C_1 and C_2 pyridines and changes in composition with synthesis conditions can be made using the OV-101 capillary column. Elution charateristics of polar compounds from a column designed for nonpolar compounds are such that peak areas could not be accurately assigned to the pyridines. The



Figure 12. Chromatogram in the presence of added pyridine: 255° C, 1.65/1 H₂/CO, 0.58 atm CD, 22,274 WHSV

results showed that the methylpyridine concentration was greater than the ethylpyridine concentration. One expects a higher concentration of methyl fragments on the surface during FT synthesis.

A series of experiments were performed to establish whether the scavengers were reacting with hydrocarbon fragments on the metal phase or with reaction products which may have adsorbed on the silica support. A gas mixture consisting of 7.2% CO, 4944 ppm CH₄ and 500 ppm (nominal) each of CO₂, C₂H₄, C₂H₆, C₃H₆, C₃H₈, C₄H₈, C₅H₁₀, C₅H₁₂, and C₆H₁₄ was directed through the reactor. The reactor contained SiO₂ at 230°C and was operated at a WHSV of 16,000. Pulses of cyclohexene or pyridine were injected into the gas mixture and the effluent was tested for alkyl-substituted scavengers. 2-Methylpyridine was observed at a ratio of 8.9×10^{-4} 2-methylpyridine/pyridine when pyridine were detected.

Additional experiments were performed to determine if the scavengers were decomposing over the iron catalyst and if so whether the decomposition products were alkylating the scavengers. At 230° C and 16,000 WHSV of hydrogen pulses of pyridine were not found to decompose into C₁ to C₅ hydrocarbons. A trace amount of 2-methylpyridine was observed when pulses of pyridine were injected into hydrogen. No other compounds, aside from pyridine, were detected.

Pulses of cyclohexene were also injected into 16,000 WHSV of hydrogen. The catalyst was maintained at 230° C under hydrogen for 24 hours prior to performong these experiments. Hydrogen alone led to methane. The methane signal increased by about 2 ppm and trace amounts, less than 1 ppm, of ethane and propane were observed when pulses of cyclohexene were added to the hydrogen. A very week signal was observed for methylcyclohexene. Methylcyclohexene and C₁ to C₅ hydrocarbons were not observed when cyclohexene was added continuously to helium at a WHSV of 44 at 230° C.

Cyclohexene did interact over the catalyst. In the presence of helium or hydrogen, pulses of cyclohexene converted into a mixture of cyclohexene, cyclohexane and benzene at 230° C. Since the C₁ to C₅ acyclic products were insignificant they can be eliminated as possible additional products. This assumption enables conversion of cyclohexene to be estimated. In the presence of helium, 0.22% of the cyclohexene reacted to cyclohexane, 0.48% reacted to benzene and the balance remained unreacted. Hydrogen had a different effect. Twenty-nine percent of the cyclohexene reacted to cyclohexane and 15% reacted to benzene. The difference between hydrogen and helium was not studied. Both cyclohexene are thermodynamically favored at 230°C, K_{eo}=48,000 and 300, respectively.

Pyridine and cyclohexene had different effects upon the C_2 to C_5 olefin to alkane ratio. Figure 13 presents the α -olefin to n-alkane ratio



Figure 13. Primary olefin to normal alkane selectivity in the presence and absence of scavenger: 230°C, 4/1 H₂/CD, 0.22 atm CO.

during FT synthesis and in the presence of a scavenger. The conversion of CO to C_1 to C_5 hydrocarbon are not reported because of the difficulty in actuating the GC's sample valve as the peak concentration of scavenged product passed through the sample loop. For this reason the ratios presented in Figure 13 during scavenging should be taken as representative of the low weight products during scavenging and not taken as absolute. In general, the total conversion of CO was less in the presence of the sacvenger.

The effect of pyridine and cyclohexene on the high weight products is shown in Figures 14 and 15. Plots of C_n/C_7 versus (n-7) are presented for the FT products in the presence and absence of the scavenger. The concentrations were determined using the four major components for a given carbon number, the normal alkane, the α -olefin and two internal olefins. A basis of C_7 was chosen because this was the first carbon group which was well resolved on the OV-101 capillary column.

Straight lines are not observed for any condition reported in Figures 14 and 15, and the FT lines are not identical for Figures 14 and 15. The difference between FT curves and the nonlinear nature of the plots may be due to incomplete collection of the products in the liquid nitrogen trap and to the fact that only four compounds for any given carbon number were used to determine the concentration, C_n . No attempt was made to interpret this nonlinear performance because of the uncertainty in the magnitude of C_n .



Figure 14. $Log(N_{C_n}/N_{C_7})$ versus (n-7) in the presence and absence of cyclohexene sacvenger: $230^{\circ}C$, $5/1 H_2/CO$, 0.22 atm CO, 16,250 WHSV.



Figure 15. $Log(N_{C_n}/N_{C_7})$ versus (n-7) in the presence and absence of pyridine scavenger.: 230°C, 5/1 H₂/CO, 0.22 atm, 16,250 WHSV.

Figure 15 shows the average molecular weight of C_7 to C_{16} hydrocarbon fraction decreased in the presence of cyclohexene. Figure 16 shows that the average molecular weights of these hydrocarbons increased in the presence of pyridine.

B.DICUSSION

1.CATALYTIC BEHAVIOR

The catalytic behavior of FT synthesis over Fe_2O_3/SiO_2 presented here can be interpretated in terms of the mechanistic pathways shown in Figure 16. Detailed discussions on the reduction of Fe_2O_3/SiO_2 in H₂ flow (82), carburization of Fe/SiO_2 in CO or H_2/CO (12-19) and hydrocarbon formation from H_2/CO over Fe/SiO_2 (14,17,18,25,78) have been given in the literature. It is proposed that active carbon formed from CO dissociation diffuses into bulk iron to form iron carbides and reacts with adsorbed hydrogen to produce hydrocarbons. Mössbauer spectroscopy studies showed that Fe_2O_3 was reduced to α -Fe by H_2 via the Fe_3O_4 phase (18,31,78,82,83). Figure 16 represents a complex mechanism for reduction-oxidation reactions between the iron phases, CO dissociation, carburization and hydrocarbon synthesis. The actual composition of the iron phase is dependent on the temperature, CO conversion and duration of the reaction.





The activity and product distribution trends shown in Figures 5 to 7 suggest that Fe_2O_3/SiO_2 underwent a rapid tranformation into a different active phase during the induction period. Pattern e in Figure 8 obtained from the induced catalyst shows that Fe_2O_3 has reduced to Fe_3O_4 and iron carbides. Furthermore evidence from increasing CO_2 formation during the induction period (see Figure 7) suggests the reduction of Fe_2O_3 to Fe_3O_4 . Carbon dioxide is proposed to form in a secondary process via the water-gas shift reaction. Shift reactivity has been reasoned to indicate the presence of the Fe_3O_4 (46).

The slightly decreasing activity and increasing olefinic nature after the maximal activity in Figures 5 to 7 suggest \therefore slow transformation of the iron phase over the pseudo-steady state period. This slow process involves the transformation of Fe₃O₄ to iron carbides and possibly some α -Fe as well as, as suggested by surface spectroscopic studies (27-31), the transformation of active carbidic carbon to inactive graphitic carbon.

The relative reduction rates between different iron phases shown in Figure 16 can explain why Fe_3n_4 and iron carbide are two major components observed by XRD during the synthesis reaction. Madon and Taylor (46) have suggested that the active surface may be different than the bulk phase. This is suppo ted by the observation of Niemansverdriet et al. (18) who reported detection of oxides at the surface of an iron carbide. The techniques employed in this study indicated a mixture of

bulk phases were present, the surface composition was undetermined as was the particle size of the working catalyst. However, it is believed that the surface carbon will be a major component after induction period (33).

Dissociation of CO can occurr not only on an α -Fe surface but also on iron oxide (32). At the earlier stage of the synthesis reaction, where synthesis activity was low, most of the reactants, CO and H₂ are thought to be consumed in the reduction of Fe₂O₃ and carburization of Fe. As the bulk of catalyst became more and more carbided the catalyst activity increased until reaching the maximum where the inactive carbon began to deactivate the catalyst.

Reymond et al. (31) reported a time dependent increase followed by a decrease in methanation activity for unsupported Fe_2O_3 . Their study at 250°C and 9/1 H₂/CO showed a maximum at 55 hours and no leveling off of the activity over a 20 hours period. The extended activity observed in this study can be explained by the following two explanations. First, the catalyst used in Figures 5 to 7 never exceeded 250°C and that most experiments were performed at temperatures less than 240°C. Low temperature prevents the catalyst from sintering. Secondly, the effect of the silica support slows down the transformations of the iron phase changes and the formation of inactive carbon. This is supported by the work of Blanchard et al. (78) who observed an extended pseudo-steady state activity on silica supported Fe_2O_3 . Increasing formation of C_2 's during the induction period may imply that the probability of ethylene incorporation decreased with the increasing availability of the surface carbon for hydrocarbon production. Ott et al. (26) reported a similar trend for $C_2^{-/}C_2$ and $C_3^{-/}C_3$ ratios (see Figure 6) over unsupported fully reduced iron at 300°C but within a period of 400 to 500 minutes. The change was related to the carburization of the iron and CO conversion.

The trend in rate and concentration for CO_2 are consistent with the postulate that CO_2 is a secondary product (45,46) formed via the water-gas shift reaction

$$H_{2}0 + C0 \rightleftharpoons CO_{2} + H_{2} \tag{3}$$

As the total synthesis rate increases the rate for water, the primary product, increases. If the water-gas shift reaction is at equilibrium $(K_{eq} = 130 \text{ at } 500^{\circ}\text{K})$, then an increase in water will lead to an increase in CO₂. An increase in temperature for the exothermic reaction shifts the equilibrium to the left. Increasing the H₂/CO ratio decreases the equilibrium concentration of CO₂. Shift activity has been reasoned to indicate the presence of the Fe₃O₄ (46).

The presence of cyclic and aromatic compounds demonstrated that complex reactions are occurring during the hydrogenation of CO over Fe-based systems. Dwyer and Somorjai (81) reported that olefins, the

primary products, can readsorb and undergo incorporation into the regular FT products, acyclic hydrocarbons. They referred to this as secondary reaction. The means by which cyclic hydrocarbons and aromatics were formed were not revealed by this study. It seems reasonable to speculate that the primary and secondary products may readsorb and undergo surface rearrangements without incorporating into the growing chains.

2.SCAVENGING TECHNIQUE

The mechanism by which pyridine is alkylated over the iron/silica catalyst is not known but can possibly be inferred from studies over nickel. Formation of 2-methylpyridine from H_2/CO (75) or alcohols (76) over nickel was postulated to proceed via methyl addition to the α -carbon of pyridine, with pyridine bonded to the nickel surface through the nitrogen. Methyl groups were argued to form by interaction of H_2 and CO on the nickel surface. The source of CO was either direct addition with the reactant gas or indirect formation via alcohol decarbonylation. Methyl and higher alkyl fragments, which are expected over iron during FT synthesis, may interact with pyridine in a similar fashion to produce α -alkylpyridines.

In the experiments to investigate the possibility of interaction between the scavenger and the adsorbed hydrocarbon fragments on the silica support, concentrations of C_1 to C_2 compounds in the feed gas

mixture were a factor of five to fifty times greater than the FT products at 230° C. The ratio of methylpyridine/pyridine was a factor of 500 less than the ratio observed during scavenging studies under FT synthesis conditions. These observations suggest that the scavenger was removing hydrocarbon fragments from the metal phase, not products from the support phase, during scavenging under FT conditions.

Hydrogen was found to react with carbon present in or on the iron phase after the cessation of FT synthesis in a manner similar to that reported by Reymond et al. (31). Methane was observed as much as 24 hours after stopping the flow of CO. This observation can explain the formation of 2-methylpyridine and methylcyclohexene during the injection of each scavenger into the H_2 stream. They were probably formed via the reaction between the scavenger and hydrogenated carbon residues.

Kellner and Bell (58) observed linear plots of C_n/C_1 versus (n-1) for FT synthesis over ruthenium. They incorporated this into a machanistic and kinetic description of the synthesis reaction. The linear plot supported the methylene insertion mechanism in which alkyl fragments propagate to the next higher alkyl fragment by inserting CH₂ or terminate by hydrogenation to the alkane or by hydride elimination to the olefin. The slope of the line equals the log of the chain growth probability, α .
A plot of log C_n/C_7 versus (n-7) has the same interpretation as log C_n/C_1 versus (n-1) as long as the propagation and termination rate are independent of carbon number. The steeper the curve the lower the chain growth probability and the lower the average molecular weight of the product.

Three explanations can be given for the decrease of the chain length shown in Figure 14. Cyclohexene dehydrogenation to benzene is suggested by Figure 13. This will act to increase the surface concentration of hydrogen and subsequently the rate of alkyl termination to alkanes. Cyclohexene may react with alkyl fragments to produce the alkylcyclohexenes observed upon injection cyclohexene into the reaction mixture. This introduces a third alkyl fragment termination process. Both of these possibilities will act to increase the net rate of alkyl termination relative to propagation and thereby decrease the magnitude of α and the average molecular weight. The third possible explanation is removal of CH₂ groups in a manner similar to that reported over Ru (57). This will reduce the concentration of CH₂ groups on the surface and simultaneously reduce the rate of propagation. A decrease in the rate of propagation will lead to a lower average molecular weight.

The results shown in Figure 13 suggest that pyridine displaced hydrogen from the surface. This may act to decrease the rate of termination of fragments to alkanes. Additional studies, which will be discussed in the Chapter IV, have shown that the distribution of

alkylpyridines correlate with the FT product distribution, suggesting that pyridine was removing alkyl fragments from the catalyst surface. This may not be enough to compensate for the lower rate of termination by hydrogenation. The net effect of pyridine may be to reduce the total rate of alkyl termination and thereby increase the average molecular weight.

IV. PROPAGATION OF FISCHER-TROPSCH SYNTHESIS

The effect of the synthesis conditions on the distributions of FT products and alkyl fragments using pyridine as the scavenger is presented in this chapter. Two Langmuir-Hinselwood expressions for the two most likely mechanisms for FT propagation are also developed to describe these two sets of distributions. The feasibility of using the measured effects to discriminate between two mechanisms is discussed.

A.RESULTS

All of the product analysis involving the pyridine and alkylpyridines in this chapter were conducted using the Hewlett Packard GC fitted with an NPD and a CAM capillary column. The major components detected in the scavenged samples were pyridine, 2-methylpyridine (2-picoline), 2,6-dimethylpyridine, 2-ethylpyridine, and 2-propylpyridine. The 2,6-dimethylpyridine signal was less than 2.5% of the 2-methylpyridine signal. 2-Butylpyridine was detected occasionally, however, the signal to noise ratio for this peak was insufficient for quantitative purposes. In addition, a trace amount of 4-ethylpyridine and what is thought to be a methylethylpyridine were observed. The last two component signals were too weak to quantify.

As discussed previously, conditioned catalysts were analyzed by XRD and found to consist of bulk iron carbides and possibly Fe_3O_4 . The surface was not analyzed; the presence of Fe_3O_4 at the surface was postulated on the basis of water-gas shift (WGS) activity. The means by which pyridine adsorbed on the surface may be inferred from the fact that almost all products were substituted at the 2 position. This suggests that pyridine adsorbed through nitrogen on the iron oxide surface.

The details and efficiency of the reaction between adsorbed pyridine and alkyl are unknown. The reaction to $2-C_n$ -pyridine is thought to occur between an n-alkyl fragment containing n carbon atoms and pyridine. The scavenged distributions C_n -pyridine/ C_{n+1} -pyridine decreased rapidly with increasing n and butylpyridine was difficult to detect. This decrease may be caused by the actual distribution of alkyl fragments and/or by steric limitations between a larger alkyl fragment and pyridine. Steric limitations are suspected; however, because known alkyl distributions could not be generated the steric effects could not be quantified. Scavenging experiments were performed at one temperature to avoid assigning alkyl distribution changes with temperature to possible changes in the relative rates of the scavenging reactions.

The absolute amount of pyridine injected was held constant. The amount collected and ultimately injected into the capillary column varied because these operations required several manual manipulations. A suitable internal standard could not be identified, therefore, for

consistency all alkylpyridine signals were normalized with the signal of pyridine. These normalized signals were used to examine the effects of the synthesis variables on the alkyl fragments. The trends reflected changes in surface alkyl concentrations; the absolute magnitude of a scavenged distribution at one set of conditions did not reflect the absolute magnitude of the surface alkyl distribution.

The effects of reactant partial pressure on the sum of 2-picoline and two times 2,6-dimethylpyridine to pyridine (C1-pyridine/pyridine) and methanation activity for continuous and pulse injection are shown in Figures 17-20. The partial pressures were selected to produce H_2/CO ratios of roughly 5/1 to 1/1 for P_{co} equal to 0.257 atm or P_{H_2} equal to 0.77 atm and roughly 1/1 to 0.2/1 for P_{CO} equal to 1.027 atm or \bar{P}_{H_2} equal to 0.308 atm. The methanation rate was slightly suppressed in the presence of pyridine; the partial pressure dependences appeared the same in the presence or absence of pyridine. The rate suppression was expected since pyridine was titrating methyl fragments from the surface. The similar partial pressure dependencies demostrates that FT synthesis continued in the presence of pyridine and suggests that the surface concentration of pyridine was not too large. FT activity was always recovered in the absence of pyridine.

Figure 17 and 18 demonstrate that the rate of methane formation had a greater H_2 partial dependence than did C_1 -pyridine. Differences between the slopes of the C_1 -pyridine lines on Figure 17 and 18 were



Figure 17. C_1 -pyridine/pyridine and the rate of methane formation dependence on the partial pressure of H_2 : (---) represents the methane formed in the absence of pyridine and (...) represents methane formed during pulse injection of pyridine.



Figure 18. C_1 -pyridine/pyridine and the rate of methane formation dependence on the partial pressure of H_2 : (---) represents the methane formed in the absence of pyridine and (...) represents methane formed during continuous pyridine injection.



figure 19. C₁-pyridine/pyridine and the rate of methane formation dependence on the partial pressure of CO : (---) represents the methane formed in the absence of pyridine and (...) represents methane formed during pulse injection of pyridine.



Figure 20. C_3 -pyridine/pyridine and the rate of methane formation dependence on the partial pressure of CO : (---) represents the methane formed in the absence of pyridine and (...) represents methane formed during continuous pyridine injection.

1~

69

. .

probably caused by the different injection techniques. Pulse injection reflects the removal of methyl fragments under nonconstant gas and surface pyridine surface concentration. Both techniques are presented here to demonstrate that the scavenged distributions are affected by the manner in which the scavenger is added to the feed. Continuous injection is prefered because the surface scavenger concentration is constant and scavenged distributions are expected to be better characterized with this technique. The continuous injection technique is used throughout the remainder of this chapter.

Figures 19 and 20 demonstrate a negative CO partial pressure dependence on both the methanation rate and on the C_1 -pyridine/pyridine ratio. The dependence was nearly the same at a constant partial pressure of H₂. Causes for the different methanation dependence at the two H₂ partial pressures could be caused by slight changes in the iron surface composition. These differences were not investigated.

The effect of continuous pyridine injection on the hydrocarbon chain length and the olefin/alkane selectivity are presented in Figures 21-23. There was no noticeable change for low weight products whereas there tended to be more propagation of alkyl fragments for the high weight products during scavenging. These trends were observed earlier where the change at high weights was assigned to suppressed alkyl termination to alkanes. The suppressed termination was caused by the postulated displacement of hydrogen from the surface by pyridine.







Figure 22. Olefin to alkane dependence on the P_H in the absence of H₂ pyridine and during continuous pyridine injection.



Figure 23. Olefin to alkane dependence on the P_{CO} in the absence of pyridine and during continuous pyridine injection.

The olefin/alkane ratio increased with increasing partial pressure of CO and decreasing partial pressure of H₂. In all cases the low weight FT products were more olefinic during continuous pyridine exposure. The partial pressure dependences were nearly the same in the presence and absence of pyridine. The changes with CO and pyridine may both be due to a displacement of surface hydrogen by either species. Wedler et al. (39) found that CO displaced preadsorbed H₂ from polycrystalline iron films. Such a displacement would increase the olefin to alkane ratio.

The effects of reactant partial pressure on C_2 and C_3 FT products and 2-ethylpyridine (C_2 -pyridine) and 2-propylpyridine (C_3 -pyridine) are presented in Figures 24-27. The FT rates were less and the partial pressure dependences appeared unchanged in the presence of pyridine. The partial pressure dependence on H₂ was less for the C_n -pyridine than for the corresponding rate of total C_n production. The C_n -pyridine and C_n hydrocarbons displayed a negative dependence on the partial pressure of CO; the C_n -pyridine dependence was more negative.

Figures 28-31 present the distribution dependences of the alkylpyridines and the FT products on reactant partial pressure. Except for the data collected at P_{co} of 0.257 atm and H_2/CO ranging from 1.5 to 5 on Figure 29 the distribution of scavenged products and the ratios of the hydrocarbon rates displayed nearly the same pressure dependences. The similarity suggested that the pyridine reacted with a product



Figure 24. C_2 -pyridine/pyridine and the total rate of C_2 hydrocarbon dependence on the partial pressure of H_2 : (---) represents C_2 formed in the absence of pyridine and (...) represents C_2 formed during continuous pyridine injection.



Figure 25. C_3 -pyridine/pyridine and the total rate of C_3 hydrocarbon dependence on the--partial--pressure of H_2 : (---) represents C_3 formed in the absence of pyridine and (...) represents C_3 formed during continuous pyridine injection. (...) represents C_3 formed during continuous pyridine injection.



Figure 26. C_2 -pyridine/pyridine and the total rate of C_2 hydrocarbon formation dependence on the partial pressure of CO: (---) represents C_3 formed in the absence of pyridine and (...) represents C_3 formed during continuous pyridine injection.



Figure 27. C_3 -pyridine/pyridine and the total rate of C_3 hydrocarbon formation dependence on the partial pressure of CO: (---) represents C_3 formed in the absence of pyridine and (...) represents C_3 formed during continuous pyridine injection.

. .



Figure 28. Distribution dependence of C_2 and C_1 scavenged and FT products on the partial pressure of H_2 .



Figure 29. Distribution dependence of C_3 and C_2 scavenged and FT products on the partial pressure of H_2 .



Figure 30. Distribution dependence of C_2 and C_1 scavenged and FT products on the partial pressure of CO.



Figure 31. Distribution dependence of C_3 and C_2 scavenged and FT products on the partial pressure of CO.

precursor. Previous work in Chapter III established that pyridine was not reacting with FT products rather reaction intermediates.

B.DISCUSSION

The mechanisms outlined in Figure 1 contain alkyl intermediates; therefore, the fact that alkyl fragments were scavenged does not disprove either mechanism. The removal of alkyl fragments and the similar pressure dependences for alkylpyridines and FT products establish that alkyl species are the immediate precursors to products. The central question is whether the partial pressure dependences of the alkylpyridines enable one to establish the mechanism. This requires that Langmuir-Hinshelwood type rate expressions be constructed for both mechanisms. These expressions are used to determine the concentration of alkyl fragments which will be compared against the experimental alkylpyridine distributions.

Hydrogenation of the dissociated surface carbon is expected to form methane and C_{2+} hydrocarbons. The discussion in Chapter III suggeted that the coverage of surface carbon was very large and essentially constant. This is supported by the observation of the large carbon reservoir over iron (33). The methyl and methane forming steps according to this mechanism can be expressed as:

> (1) $CD_{(g)} + S \iff CO$ (2) $CO + S \iff C + O$

(3) $H_{2(g)} + 2S \rightleftharpoons 2H$ (4) $C + H \rightleftharpoons CH + S$ (5) $CH + H \rightleftharpoons CH_2 + S$ (6) $CH_2 + H \rightleftharpoons H_3 + S$ (7) $CH_3 + H + CH_{4(g)} + 2S$

where S denotes a vacant surface site, (g) denotes a gas phase species and all other species are adsorbed.

Assuming constant carbon coverage, θ_{c} , eliminates the need to perform an oxygen balance. The site balance is assumed to be approximately by the following equation

$$1 = \theta_{\rm C} + \theta_{\rm H} + \theta_{\rm CO} + \theta_{\rm V} \tag{4}$$

where θ_V represents the fraction of vacant sites. Only reactants, carbon and vacant sites are considered for simplicity and because intermediates have not been detected by spectroscopic means. Carbon monoxide is considered because negative CO partial pressure dependences were found for FT synthesis rates. Uncertainty concerning hydrogen coverage suggests it be considered. If the coverage of hydrogen and CO are represented by Langmuir isotherms

$$\theta_{\rm H} = (K_{\rm 3}P_{\rm H_2})^{0.5} \theta_{\rm V};$$
 (5)

 $\theta_{\rm CO} = \kappa_1 \rho_{\rm CO} \theta_{\rm V}; \tag{6}$

$$\theta_{V} = \frac{1 - \theta_{C}}{1 + (K_{3}P_{H_{2}})^{0.5} + K_{1}P_{CO}};$$
(7)

where K is an equilibrium constant.

The methylene insertion mechanism is based on one developed by Kellner and Bell (59) and is written as

(8)
$$CH_3 + CH_2 \longrightarrow C_2H_5 + S$$

(9) $C_n + CH_2 \xrightarrow{k_{p_n}} C_{n+1} + S$
(10) $C_n + S \xrightarrow{k_{o_n}} C_nH_{2n}(g) + H + S$
(11) $C_n + H \xrightarrow{k_{A_n}} C_nH_{2n+2}(g) + 2S$

where C_n refers to an alkyl species containing n carbon atoms and k_{p_n} , k_{O_n} , and k_A refer to propagation, olefin termination and alkane termination, respectively. The above reactions are considered to be irreversible under FT conditions.

Several assumptions are required to solve for θ_{C_n} . Reactions 4 and 6 are assumed to be in equilibrium. Letting reaction 5 in addition to 4 and 6, or only reaction 4 be at equilibrium produces a methanation hydrogen dependence of 2.0. The experimental value was 1.4. The steady-state approximation is applied to CH₂ and C₂ and higher alkyl species. Finally, the propagation and termination rate constants are independent of chain length, a common assumption for FT synthesis. The resulting expressions for methylene insertion are

$$\boldsymbol{\theta}_{CH} = \kappa_4 \boldsymbol{\theta}_C (\kappa_3 \boldsymbol{P}_{H_2})^{0.5}; \qquad (8)$$

$$\theta_{CH_2} = \frac{k_5 \theta_{CH} \theta_{H}}{k_{-5} \theta_{V} + k_p K_6 (\theta_{H} / \theta_{V}) \theta_{CH_2} \sum_{n=0}^{\Sigma \alpha^n} t_{n=0}};$$

 $\theta_{CH_3} = \theta_1 = K_6 (K_3 P_{H_2})^{0.5} \theta_{CH_2};$ (10)

 $\theta_{n} = \alpha^{n-1} \theta_{1}; \qquad (11)$

⁰n+1 ----- = a ;

θ_n

(12)

(9)

$$a = \frac{k_p \theta_{CH_2}}{k_p \theta_{CH_2} + k_0 \theta_V + k_A \theta_H}, \qquad (13)$$

where a is the chain growth parameter.

The CO insertion mechanism is based on a mechanism developed by Olive and Olive (61,62). Reactions 1 to 7 are used as are 10 and 11. The details of the propagation reaction are unknown. The steps shown below assume that CO insertion is slow and all subsequent hydrogenation/dehydration steps are rapid. There is no precedence for this other than acyl fragments have never been detected during FT synthesis.

(12)
$$CH_3 + CO \rightarrow COCH_3 \rightarrow C_2H_5 + H_2O$$

.

(13)
$$C_n + CO + CDC_n + C_{n+1} + H_2O$$

The rate at which C_2H_5 forms by reaction 12 is given by

$$\frac{d\theta_2}{dt} = k_{12}\theta_{CH_3}\theta_{CD}$$
(14)

The same assumptions are made for the CO insertion mechanism: reactions 4 and 6 are at equilibrium, a steady -state approximation holds

for C_2 and higher alkyl fragments, and rate constants are independent of chain length. The resulting expressions for CD insertion are

$$\theta_{CH} = \kappa_4 \theta_C (\kappa_3 P_{H_2})^{0.5}; \qquad (B)$$

$${}^{\theta}CH_2 = {}^{K}_4 {}^{K}_5 {}^{\theta}_c {}^{K}_3 {}^{P}_{H_2};$$
(15)

$$\theta_{CH_3} = \kappa_6 \kappa_5 \kappa_4 \theta_C (\kappa_3 P_{H_2})^{1.5};$$
 (16)

$$\alpha = \frac{k_{I}^{\theta}CO}{k_{I}^{\theta}CO + k_{O}^{\theta}V + k_{A}^{\theta}H}$$
(17)

Equations 11 and 12 also result.

The ratios of θ_{n+1}/θ_n are given by α . The ratios C_2 -pyridine/ C_1 -pyridine and C_3 -pyridine/ C_2 -pyridine are expected to be proportional to the concentrations of θ_1 to θ_3 . Therefore, the ratio of alkylpyridine signals should have the same dependence on the synthesis variables as does α . The results of Figures 27-30 are summarized in Table 5, where a negative hydrogen and positive carbon monoxide dependence are observed.

The predicted partial pressure dependences for the α 's derived for methylene and CO insertion, equation 13 and 17, respectively, are

Table 5. Partial Pressure Dependences for Alkylpyridine Ratios.

.

Ratio C _{n+1} -pyr C _n -pyr	P _{co} (atm)	^P H2 (atm)	Nominal	_x (a)	y(a)						
			H ₂ /CO range								
						2/1	1.027		0.2-0.5		-0.19
						2/1	0.257		0.7-5		-0.20
2/1		0.770	1-5	0.17							
2/1		0.308	0.2-1	0.22							
3/2	1.027		0.2-0.5		-0.03						
3/2	0.257		0.7-0.5		-0.27						
3/2		0.770	1-5	0.07							
3/2		0.308	0.2-1	0.17							

.

(a) x and y are defined as $C_{n+1}^{-pyr/C} P_{n}^{-pyr=gP} C_{0}^{x} P_{H_{2}}^{y}$

.

.

Table 6. Partial Pressure Dependence for the

Chain Growth Parameter



.

given in Table 6. These were arrived at by considering the individual dependences for θ_{H} , θ_{CO} , θ_{V} and $\theta_{CH_{2}}$. A brief discussion of this follows.

The partial pressure dependence for θ_{CO} , θ_{H} , and θ_{V} depend upon the significance of the terms in the denominator of equation 7. Arakawa and Bell (25) were unable to detect adsorbed CO over iron with infrared spectroscopy. They offered two interpretations: 1) molecular CO adsorbed parallel to the surface in a manner which would not produce an infrared absorption band, and 2) molecular CO coverage was very low. The inhibitory effect of increasing CO pressure on FT activity and olefin/alkane selectivity suggests that CO does adsorb on the surface. The limit of CO saturation invoked over Ru (56) can not be justified; therefore, the magnitude of K_1P_{CO} is assumed to be of order unity or less. At 0°C adsorbed hydrogen is displaced from polycrystalline iron film by gas phase CO (39). This observation suggests that K_1P_{CO} is greater than $(K_3P_{H_p})^{D.5}$.

The vacant site term, θ_V , is assumed to have a negative P_{CO} dependence, denoted as β in Table 6, and a weaker negative dependence on P_{H_2} , which is neglected. The dependence for θ_H and θ_{CO} are found by combining those indicated in equations 5 and 6, respectively, with the assumed dependences for θ_V . A positive 0.5 P_{H_2} dependence and negative P_{CO} dependence, β , are assumed for θ_H . A negligible P_{H_2} dependence for θ_C and θ_C are found by θ_C .

The pressure dependence for θ_{CH_2} can in principle be determined using equation 9. This equation includes α which has a partial pressure

dependence. Alternately, the dependence for θ_{CH_2} can be estimated from the predicted value for θ_{H} , equation 10, and experimental methane data presented in Figures 18 and 20. The rate of methane formation can be represented by the following expression

The experimental data predict



Equations 18 and 19 are combined to give



The results of Table 6 can be used to estimate the partial pressure dependence in the limits that α is approximately zero and unity. When α equals unity propagation is much faster than termination such that only the first term need be considered in the denominator. When α equals

(19)

zero, the termination rates exceed the propagation rate. This is anticipated at high H_2/CD ratios where alkane formation dominates. Therefore, at α equal zero only the last term in each denominator was considered. Table 7 lists the anticipated dependences.

Satterfield and Huff (42) reported values for α over an iron catalyst. The values were obtained from Schulz-Flory plots of experimental data. They observed that α was constant with CO conversion and H₂/CO ratio and appeared to be a function of iron composition. The latter observation is supported by Krebs et al. (30). The growth parameter, α , was not measured over the catalyst used in these studies; however, it is reasonable to assume that it had a value between 0.4 and 0.7. This implies that the actual partial pressure dependence will be intermediate between the values shown in Table 7.

The results in Table 5 demonstrate that the hydrogen dependence was negative and of order 0.2. Both mechanisms predict a negative P_{H_2} dependence reasonably close to this value. The experimental partial pressure ratio for P_{CO} was of positive order 0.2. Both mechanisms predict a value which is positive. The unknown P_{CO} dependence of θ_V , β , is bounded by one and zero. For values of β greater than 0.25 the methylene insertion mechanism predicts smaller values for the P_{CO} dependence than does the CO insertion mechanism.

Table 7.	Predicted Partial Pressure	Dependences
	for α at the Extremes.	

	Mechanism	Pco	PH2	
limα→1	Methylene Insertion	0	0	
lim α → 1	CO Insertion	0	0	
lim α → O	Methylene Insertion	28-0.5	-0.1	
lim ∝ → O	CO Insertion	1	-0.5	

More information is required about CO adsorption and coverage at reaction conditions over iron catalysts before a value of β can be determined. Without this value it is not possible to discriminate between the mechanisms by measuring the partial pressure dependence of the reaction intermediates. This probably results from the fact that both mechanisms share common intermediates and common termination steps.

The details of the mechanisms and the assumptions used to derive θ_{i} expressions seem reasonable. Not all possible combinations of equilibrium and steady-state assumptions for various reactions or intermediate species were tried. Other combinations of elementary reaction equilibria and reversible versus irreversible reaction mechanisms were investigated. The combination presented above produced the experimentally determined negative P_{H_2} and positive P_{CO} dependence of α , whereas others did not. While this does not substantiate the proposed mechanisms the hydrogen partial pressure correspondence adds credence to the mechanisms.

V.CONCLUSION

The studies over 20 wt% Fe_2O_3/SiO_2 have shown that the iron phase converts into the same type of iron phases seen by other groups starting with Fe, Fe_2O_3 , and Fe_3O_4 . Activation of the supported Fe_2O_3 in H_2/CO at temperatures less than 250°C resulted in a catalyst which displayed steady activity for at least 700 hours. The bulk phase was identified as a mixture of Fe_3O_4 , carbides and possibly some α -Fe. The surface composition was not measured using surface sensitive spectroscopies. However, the conversion characteristics of CO_2 and the presence of aromatics suggest that some Fe_3O_4 was present at the surface of the carbides.

Synthesis products were analyzed through C_{16} . The primary products were the straight chain α -olefins. As the carbon number increased the complexity of the acyclic products increased to the level that branched alkanes constituted a larger fraction of synthesis products. Cyclohexene, methylcyclohexene, benzene, and alkyl-substituted benzenes were also observed as FT synthesis products. This suggests that even at low CO conversion in a differential reactor a complex set of reactions is present over iron.
Cyclohexene and pyridine were added to the reactant feed gas to scavenge alkyl fragments from the surface. Both scavengers were alkylated, methyl substitution was greater than ethyl substitution. Pridine was much more efficiently alkylated, 3 injections producing a measurable signal versus the 120 injections of cyclohexene required to see a minor increase in methylcyclohexene. Control experiments established that the alkyl-substituted scavengers result from the interaction of the scavenger with alkyl fragments on the iron phase.

Pyridine was used to study the effects of the synthesis conditions on the distributions of the alkyl fragments adsorbed on the catalyst surface. Pyridine did not significantly affect FT activity therefore the scavenged alkyl species were representative of the species present during synthesis in the absence of pyridine. The scavenged product distributions were thus used to determine the dependence of the reactant partial pressure on the alkyl species. This research has demonstrated that the postulated alkyl species are indeed reaction intermediates for the FT synthesis reaction and are the immediate precursors to alkanes and olefins.

Reaction mechanisms were postulated to develop Langmuir-Hinshelwood kinetic expressions for alkyl fragment concentrations. The experimental and predicted distributions were used to examine postulated mechanisms. Both mechanisms displayed the same qualitative dependences on the reactant partial pressures. Quantitative

97

dependences could not be used to discriminate between the two mechanisms because the P_{CO} dependence was unknown and could not be measured independently. The research does support a mechanism in which alkyl fragments are involved in the propagation step.

REFERENCE

1.	Storch, H. H	I., Golumbia	:, H.,	and Ander	-son, R. B	., " he	
	Fischer	-Tropsch and	nd Rela	ited Synth	nesis", Wi	ley, New	York,
	(1951).						

- Anderson, R. B., in "Catalysis" (P. H. Emmett, Ed.), Vol. 4, Reinhold, New York, (1956).
- 3. Pichler, H., and Hector, A., "Kirk-Othmer Encyclopedia Chem. Tech. IV", <u>446</u> (1964)
- 4. Vannice, M. A., Catal. Rev. Sci. and Eng. 14, 153 (1976).

5. Ponec, V., Catal. Rev. Sci. and Eng. 18, 151 (1978).

- 6. Biloen, P., and Sachtler, W. M. H., Adv. in Catal. 30, 163 (1981)
- 7. Bell, A. T., Catal. Rev. Sci. and Eng. 23, 203 (1981).
- 8. Rofer-DePoorter, C. K., Chem. Rev. 81, 447 (1981).
- Broden, G., Rhodin, T. N., Brucker, C., Benbow, R., and Hurych, Z., Surf. Sci. <u>59</u>, 593 (1976).
- Ponec, V., and van Barneveld, W. A., Ind. Eng. Chem. Prod. Res. Dev. <u>18</u>, 268 (1979).
- Poutsma, M. L., Elek, L. F., Ibarbia, P. A., Risch, A. P., and Rabo, J. A., J. Catal. <u>52</u>, 157 (1978).
- 12. Amelse, J. A., Butt, J. B., and Schwartz, L. H., J. Phys. Chem. 82, 558 (1978).
- 13. Raupp, G. B., and Delgass, W. N., J. Catal. <u>58</u>, 348 (1979).
- 14. Raupp, G. B., and Delgass, W. N., J. Catal. 58, 361 (1979).
- 15. Unmuth, E. G., Schwartz, L. H., and Butt, J. B., J. Catal. <u>63</u>, 404 (1980).
- 16. Stanfield, R. M., and Delgass, W. N., J. Catal. <u>72</u>, 37 (1981).
- 17. Amelse, J. A., Schwartz, L. H., and Butt, J. B., J. Catal. <u>72</u>, 95 (1981).
- 1B. Niemantsverdriet, J. W., van der Kraan, A. M., van Dijk, W. L., and van der Baan, H. S., J. Phys. Chem. <u>84</u>, 3363 (1980).

19.	Le Caer, G., Dubois, J. M., Pijolat, M., Perrichon, V., and Busslere, P., J. Phys. Chem., <u>86</u> 4799 (1982).
20.	Broden, G., Gafner, G., and Bonzel, H. P., Surf. Sci. <u>84</u> , 295 (1979)
21.	Bonzel, H. P., and Krebs, H. J., Surf. Sci. <u>109</u> , L527 (1981).
22.	Benziger, J., and Madix, R. J., Surf. Sci., <u>94</u> , 119 (1980).
23.	Dry, M. E., Shingles, T., Boshoff, L. J., and Oosthuizen, G. J., J. Catal. <u>15</u> , 190 (1969).
24.	Dry, M. E., Shingles, T., and Botna, C. S. van H., J. Catal. <u>17</u> , 341 (1970).
25.	Arakawa, H., and Bell, A. T., Ind. Eng. Chem. Process Des. Dev. <u>22</u> , 97 (1983).
26.	Ott, G. L., Fleisch, T., and Delgass, W. N., J. Catal. <u>65</u> , 253 (1980).
27.	Dwyer, D. J., and Somorjai, G. A., J. Catal. <u>52</u> , 291 (1978).
28.	Krebs, H. J., and Bonzel, H. P., Surf. Sci. <u>88</u> , 269 (1979).
29.	Bonzel, H. P., and Krebs, H. J., Surf. Sci. <u>91</u> , 499 (1980).
30.	Krebs, H. J., Bonzel, H. P., Schwarting, W., and Gafner, G., J. Catal. <u>72</u> , 199 (1981).
31.	Reymond, J. P., Meriaudeau, P., and Teichner, S. J., J. Catal. <u>75</u> , 39 (1982).
32.	Kelemen, S. R., Kaldor, A., and Dwyer, D. J., Surf. Sci. <u>121</u> , 45 (1982).
33.	van Dijk, W. L., and van der Baan, H. S., J. Catal. <u>78</u> , 24 (1982)
34.	Dry, M. E., Shingles, T., and Boshoff, L. J., J. Catal. <u>25</u> , 99 (1972)
35.	Broden, G., Gafner, G., and Bonzel, H. P., Appl. Phys. <u>13</u> , 333 (1977).
36.	Wedler, G., Geuss, K. P., Colb, K. G., and McElhiney, G., Appl. Surface Sci. <u>1</u> , 471 (1978).
37.	Chornet, E., and Coughlin, R. W., J. Catal. <u>27</u> , 246 (1972).

- 38. Wedler, G., Colb, K. G., McElhiney, G., and Heinrich, W., Appl. Surface Sci. 2, 30 (1978).
- 39. Wedler, G., Colb, K. G., Heinrich, W., and McElhiney, G., Appl. Surface Sci. <u>2</u>, 85 (1978).
- 40. Bradshaw, A. M., Surf. Sci. <u>80</u>, 215 (1979).
- 41. Blyholder, G., J. Phys. Chem. 79, 756 (1975).
- 42. Satterfield, C. N., and Huff, G. A., Jr., J. Catal. <u>73</u>, 187 (1982).
- 43. Dry, M. E., Ind. Eng. Chem. Prod. Res. Dev. 15, 282 (1976).
- 44. Atwood, H. E., and Bennett, C. O., Ind. Eng. Chem. Process Des. Dev. <u>18</u>, 163 (1979).
- 45. Feimer, J. L., Silveston, P. L., and Hudgins, R. R., Ind. Eng. Chem. Prod. Res. Dev. <u>20</u>, 609 (1981).
- 46. Madon, R. J., and Taylor, W. F., J. Catal. <u>69</u>, 32 (1981).
- 47. Vannice, M. A., J. Catal. <u>37</u>, 462(1975).
- 48. Novak, S., Madon, R. J., and Suhl, H., J. Catal. <u>77</u>, 141 (1982).
- 49. Kummer, J. T., DeWitt, T. W., and Emmett, P.H., J. Am. Chem. Soc. 70, 2632 (1948).
- 50. Kummer, J. T., Browning, L.C., and Emmett, P.H., J. Chem. Phys. <u>16</u>, 739 (1948).
- 51. Browning, L.C., DeWitt, T. W., and Emmett, P.H., J. Am. Chem. Soc. <u>72</u>, 4211 (1950).
- 52. Pichler, H., Adv. Catal. 4, 271 (1952).
- 53. Ponec, V., Catal. Rev. Sci. Eng. <u>18</u>, 151 (1978).
- 54. Biloen, P., Helle, T. N., and Sachtler, W. M. H., J. Catal. <u>58</u>, 95 (1979).
- 55. Biloen, P., J. Roy. Neth. Chem. Soc., 99, 33 (1980).
- 56. Ekerdt, J. G., and Bell, A. T., J. Catal. <u>58</u>, 170 (1979).
- 57. Ekerdt, J. G., and Bell, A. T., J. Catal. <u>62</u>, 19 (1980).
- 58. Kellner, C. S., and Bell, A. T., J. Catal. <u>67</u>, 175 (1981).

- 59. Kellner, C. S., and Bell, A. T., J. Catal. <u>70</u>, 418 (1981).
- 60. Baker, J. A., and Bell, A. T., J. Catal. 78, 165 (1982).
- 61. Henrici-Olive, G., and Olive, S., Angew. Chem. Int. Ed. Engl. 15, 136 (1976).
- 62. Henrici-Olive, G., and Olive, S., J. Mol. Catal. <u>16</u>, 111 (1982).
- 63. Reymond, J. P., Merideau, P., Pommler, B., and Bennett, C. O., J. Catal. <u>64</u>, 163 (1980).
- 64. Matsumoto, H., and Bennett, C. O., J. Catal., <u>53</u>, 331 (1978).
- 65. Brady, R. C., and Pettit, R. J., Am. Chem. Soc. <u>102</u>, 6181 (1980).
- 66. Brady, R. C., and Pettit, R., J. Am. Chem. Soc. <u>103</u>, 1287 (1981).
- 67. Blyholder, G., and Neff, L. D., J. Phys. Chem. <u>66</u>, 1664 (1962).
- 68. King, D. L., J. Catal. <u>61</u>, 77 (1980).
- 69. Eidus, Ya. T., Russ. Chem. Rev. 36, 338 (1967).
- 70. Evitt, E. R., and Bergman, R. G., J. Am. Chem. Soc. <u>101</u>, 3973 (1979).
- 71. Fellman, J. D., Rupprecht, G. A., Wood, C. D., and Schrock, R. R., J. Am. Chem. Soc. <u>100</u>, 5962 (1978).
- 72. Stevens, A. E., and Beauchamp, J. L., J. Am. Chem. Soc. <u>100</u>, 2584 (1978).
- 73. Grubbs, R. H., and Miyashita, A., J. Am. Chem. Soc. <u>100</u>, 7428 (1978).
- 74. Satterfield, C. N., and Cocchetto, J. F., AIChE J. 21, 1107 (1975).
- 75. Myerly, R. C., and Weinberg, K. G., J. Organ. Chem. <u>31</u>,2008 (1966).
- 76. Reinecke, M. G., and Kray, L. R., J. Am. Chem. Soc. <u>86</u>, 5355 (1964).
- 77. Kishi, K., Chinomi, K., Inoue, Y., and Ikeda, S., J. Catal. <u>60</u>, 228 (1979).
- 78. Blanchard, F., Reymond, J. P., Pommier, B., and Teichner, S. J., J. Mol. Catal. <u>17</u>, 171 (1982).

79. Unmuth, E. E., Schwartz, L. H., and Butt, J. B., J. Catal. <u>61</u>, 242 (1980).

•

- 80. Berry, L. G., Ed., "Powder Diffraction File, Inorganic Material." International Centre for Diffraction Data, Swarthmore, Pa., 1979.
- 81. Dwyer, D. J., and Somorjai, G. A., J. Catal. <u>56</u>, 249 (1979).
- 82. Raupp, G. B., and Delgass, W. N., J. Catal. 58, 337 (1979).
- B3. Niemantsverdriet, J. W., and van der Kraan, A. M., J. Catal. <u>72</u>, 385 (1981).

-

VITA

Chia-zuan Jeff Wang was born in Pingtung, Taiwan, on October 31, 1951, the son of Mr. Kang-ang Wang and Mrs. Su Liau Wang. In September, 1971, he entered National Cheng Kung University in Taiwan. After obtaining the degree of Bachelor of Science in Chemical Engineering in June 1975, he was commisioned as a secondary lieutenant through the R.O.T.C. for two years. On October 30, 1977, he was married to Joyce Yi-Yun Lee in Taiwan. In January 1978, they both entered the Graduate School of The University of Missouri-Columbia. They obtained degrees of Master of Science in Chemical Engineering and of Master of Education in Curriculum and Instruction, respectively. In January 1980, he entered The Graduate School of the University of Texas at Austin.

This dissertation was typed by the author.