

2. INTRODUCTION

This section is a brief summary of the Fischer-Tropsch (F-T) Process. It was written as a forward to the work done under this contract and was not meant to be a complete summary of all the work done in this area. Since Fischer and Tropsch discovered this process approximately sixty years ago hundreds of papers and patents have been written; a comprehensive summary of this area would be beyond the scope of this report. This section is biased in favor of the iron F-T catalyst since this contract is for iron catalyst development. Cobalt is the other common F-T catalyst. It is reviewed in the introduction section of the final report of DOE Contract No. DE-AC22-89PC89869; a contract to UOP for the development of cobalt F-T catalysts.

2.1 FISCHER-TROPSCH BACKGROUND

F-T is one of several processes which use synthesis gas ($H_2 + CO$) as feed. The current sources of synthesis gas are methane and coal. Synthesis gas is an expensive feed even when cheap methane or coal is available such as essentially valueless remote-site methane. This is due to the high capital cost of a synthesis gas plant. Fifty to seventy percent of the total cost of an F-T complex is due to the synthesis gas plant. Additionally, since F-T catalysts demand very pure feed, feed pretreatment can be very expensive as well. To stand these expenses F-T could only compete with high priced petroleum. In today's prices petroleum might have to reach thirty-five dollars a barrel or higher before F-T would be competitive even with a cheap feed for the synthesis gas plant.

F-T is a very non-selective process. A wide carbon number distribution of hydrocarbons and some

oxygenates are formed. Secondary processing is required to convert this multiplicity of products into fuels and chemicals. However, there are advantages to the F-T product. For instance, since the F-T hydrocarbons are essentially linear, a good quality diesel fuel product can be produced with a minimum of secondary processing.

F-T processing has enjoyed several brief periods of popularity. It was used in Germany during World War II to convert coal-derived synthesis gas into transportation fuels when the Allies cut off the Axis power's supply of petroleum. For a while after the war F-T development continued in Germany, mainly in Koebel's laboratory, and in the U.S. by the Bureau of Mines. Thereafter F-T work was scaled back everywhere but in South Africa which faced the continual threat of a petroleum embargo, but had a coal resource and historically cheap labor to mine it. As a result several generations of F-T reactors have been built in South Africa to process coal-derived synthesis gas. Although much of this work has not been published, some South Africans such as Dry have been active in the literature.

F-T enjoyed a second period of popularity in the mid-1970's after the Arab oil embargo. Research projects were then started as part of the worldwide syn-fuels effort at many academic, industrial and government laboratories; there are several reviews which cover this recent work.^{1, 2, 3, 4, 5} Although much of this effort was scaled back by the late 1980's some interest remains, particularly in the area of conversion of synthesis gas from remote-site methane. One large-scale F-T plant has been built to convert synthesis gas from such methane, namely Shell's Indonesian plant which uses tube reactors of narrow dimension to aid heat removal from the very exothermic F-T reactions. Over seventy thousand tubes divided between three reactor assemblies are used!

The Shell plant is an example of F-T by fixed bed processing which is also the type of processing used in the initial German plant in 1935. Fluidized catalyst beds (liquid and gas phase) have also been used. In liquid phase slurry processing part of the heavy products produced during F-T processing (wax) is retained in the reactor as a liquid to fluidize the catalyst under the influence of the reactant gas bubbles and to provide a heat transfer agent for the exothermic F-T reactions. This type of processing is called liquid phase Fischer-Tropsch (LPFT) processing.

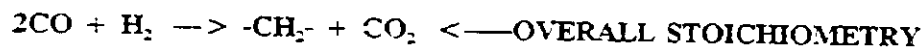
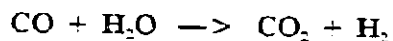
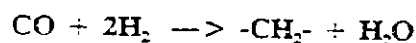
In this contract the means to prepare commercial quantities of an iron-based LPFT catalyst were to be developed. Additionally, the catalyst was to meet certain performance targets, specifically it was to exhibit ≤ 5 mole % methane + ethane selectivity at 88% carbon monoxide + hydrogen conversion 2.4 NL/hr-g iron feed rate. Carbon number distribution among the F-T products is according to the Schulz-Flory distribution which means the amount of product at any carbon number, N , is related by a probability or chain growth number, α , to the amount at carbon number $N-1$. Because of the Schulz-Flory relation this contract's performance target is tantamount to development of a high wax-producing catalyst (low light product selectivity implies more product at high carbon numbers). The reason for a low methane + ethane target is that both of these products are of low economic value; they would probably have to be recycled to the gasifier. In many of the catalyst screening runs only conversions and light product selectivities were determined. Only occasionally were full carbon number range product analyses performed.

During this work feed was used which contained argon internal standard to aid calculations of conversions and selectivities according to Appendix 1. Analyses were performed by two on line gas chromatographs, data from one was used to calculate conversions and C_1 - C_4 hydrocarbon selectivities and that from the other to calculate C_2 - C_4 alcohol selectivities. Contact time plots were

sometimes made; in these cases contact times were calculated according to a method which is also outlined in Appendix 1.

2.2 THE SHIFT REACTION

Iron oxide-derived materials also catalyze the reaction of water with carbon monoxide to form hydrogen and carbon dioxide, the so-called shift reaction. This reaction proceeds at a comparable rate to carbon chain growth,⁶ in some cases considerably faster.² Since water is a product of the F-T reactions shift chemistry is observed during F-T processing. The resulting hydrogen is available to react with CO via F-T chemistry:



The practical significance of the overall stoichiometry above is that low hydrogen synthesis gas such as that from coal can be used without addition of extra hydrogen. Coal-derived synthesis gas has a hydrogen : carbon monoxide molar ratio of about 0.7 which is sufficient for the above stoichiometry ($\text{H}_2 : \text{CO} = 0.5$) with some hydrogen left over to form methane and alkanes which are not taken into account above. Methane-derived synthesis gas, on the other hand, exhibits a hydrogen : carbon monoxide molar ratio of two; cobalt-based catalysts which do not catalyze the shift reaction are most often used for such a feed.

2.3 REACTION MECHANISM

The currently favored F-T mechanism is, in fact, the original mechanism proposed by Fischer and Tropsch.⁷ It involves cleavage of carbon monoxide as the initiation step. This cleavage occurs at surface iron sites and results in the formation of iron carbides and iron oxides. The iron carbide then may build up to the main products of the F-T process which are paraffins and olefins by the steps of hydrogenation and insertion. Iron-bound methyl and methylene radicals thus may be formed from iron-carbide by hydrogenation. Chains may be formed by insertion of methylene radicals into the methyl-iron and alkyl-iron bonds.

Other mechanisms based on intact carbon monoxide have been proposed,^{8,9} but are now out of favor. Although these mechanisms are out of favor, it is true that carbon monoxide can adsorb on metals intact or dissociated. Metals to the left of iron and cobalt in the periodic table adsorb carbon monoxide dissociatively whereas those to their right adsorb it intact.^{4,10} Much of this knowledge is due to work with clean metal surfaces and the addition of carbon monoxide in quantities roughly needed to form a monolayer. However, a working catalyst might not be even closely approximated by such a surface. For instance, metals to the left of iron in the periodic chart do not catalyze the F-T reaction even though they can cleave carbon monoxide. Their lack of F-T activity seems to result because a surface coating of metal oxide is formed which is thermodynamically stable under F-T conditions and inactive for the cleavage of additional carbon monoxide. Metals to the right or below iron, cobalt and nickel, particularly palladium, can be active as methanol synthesis catalysts. This, of course, implies that carbon monoxide reacts with hydrogen as an intact molecule—yielding methanol via hydrogenation.

The non-dissociative F-T mechanism became firmly entrenched in the late 1940's, in large part due to Emmett and co-workers. They provided what at first appeared to be a formidable thermodynamic argument refuting the dissociative mechanism. It was based on data for the formation of hydrocarbons from hydrogenation of bulk phase metal carbides including those of iron and nickel.^{11, 12, 13} Emmett et. al. calculated equilibrium constants for this type of transformation from known free energies including those of bulk phase metal carbides. At normal F-T pressures and temperatures these constants predicted only minimal conversion to hydrocarbons.

The non-dissociative mechanism was in vogue until the late 1970's when fresh theories and evidence supporting the dissociative mechanism were advanced by Rabo and co-workers,^{14, 15} and later by many others as well. Araki and Ponc¹⁶ and Wentreck and co-workers¹⁷ supported a dissociative mechanism for methane formation over nickel surfaces at about the same time. The thinking by these workers was that bulk phase metal carbides should not be invoked to explain transformations occurring on a surface.

Somewhat later rapid dissociation of carbon monoxide on the catalyst surface in the presence of hydrogen became a key aspect of the theory proposed by Biloen, Helle and Sachtler to explain how hydrocarbons are formed by F-T catalysts.¹⁸ Their acceptance of this theory was based on work they did with metals containing surface coverages of ¹³C formed by disproportionation of ¹³CO to ¹³C and ¹³CO₂ at 523°C and 0.5 bar. (This is the "Boudouard" reaction which is also known to occur during activation and use of Fischer-Tropsch catalysts. Although normally not a problem, care must be taken, particularly during catalyst activation with carbon monoxide, that this reaction does not produce excess carbon with a resultant loss in catalyst activity.)

With a measured amount of ^{13}C Biloen, et. al. prepared carbidic materials that were active when reacted with successive batches of $^{12}\text{CO}/\text{H}_2$ each sufficient to consume 20% of the ^{13}C . They found hydrocarbon products which contained ^{13}C under conditions where the carbidic carbon had been demonstrated not to equilibrate back to carbon monoxide. Thus it appears that the surface ^{13}C reacted with hydrogen, putatively forming $^{13}\text{CH}_2$ and $^{13}\text{CH}_3$, the latter of which can form $^{13}\text{CH}_4$ via reaction with hydrogen and higher ^{13}C hydrocarbons via insertion of $^{13}\text{CH}_2$. Rabo and others invoked the dissociative mechanism at about the same time as Biloen, et. al.^{14, 19, 20, 21} The small amounts of oxygenates found in F-T products could arise according to this mechanism by insertion of carbon monoxide into a growing chain, presumably this would be a chain termination step.⁵

Petit and Brady and later Bock have explored the dissociative mechanism by generating carbenes on the surface of F-T metals.^{22, 23, 24} Petit and Brady showed that decomposition of diazomethane in the absence of hydrogen on F-T metals or in the presence of hydrogen on metals that cannot adsorb it dissociatively results in ethylene as the only product. However, decomposition of diazomethane on F-T metals in the presence of hydrogen leads to a normal F-T product slate.

The dissociative mechanism has been criticized recently by Henrici-Olive and Olive, particularly with regard to the relevance of the Petit experiment.^{25, 26} However, Smutek has defended it while emphasizing this experiment.²⁷

Hoffmann and co-workers have reviewed the mechanistic work done up to the mid-1980's and provided an extended Huckel model for F-T catalysis based on the dissociative mechanism.²⁸

Hoffmann treats all of the steps in this mechanism not just the initial carbon monoxide cleavage. He discussed, for instance, the mobility of carbon intermediates on the surface and how that can

relate to the F-T products. Surface mobility is related to d-band filling. The chain propagation step can be visualized as migration of an alkyl group and/or methylene into close proximity allowing facile coupling (chain growth). Hoffmann has made strides toward understanding the theoretical underpinning of F-T catalysis. His theory is predictive, for instance, the differences in product distribution between Co (shorter chains) and Fe (longer chains) is due to different carbon fragment mobility as predicted by the different d-band filling in these two metals.

Biloen²⁹ and others have continued to elucidate the F-T mechanism through use of ^{13}CO . This recent work employs alternate pulses of $^{12}\text{CO}/\text{H}_2$ (D_2) and $^{13}\text{CO}/\text{H}_2$ (D_2) with the same CO : H_2 ratio, the so-called transient response isotopic tracer experiment.^{30, 31} Information regarding the rates of the various reactions in the F-T mechanism can be obtained. For instance, the change in rate constants for propagation and chain termination going from $\text{C}_1 \rightarrow \text{C}_3$ have been estimated for a cobalt catalyst.²⁹ These workers found the rate constant for propagation decreased from 0.045–0.025 s^{-1} and that for termination increased from 0.02–> 0.04 s^{-1} . Mims, et. al. have also employed this method to obtain values for rate constants for both iron and cobalt catalysts.^{32, 33} Krishna and Bell have reviewed this work and presented recent results allowing estimations of activation energies for chain propagation and termination using a ruthenium on titania catalyst.³⁴ They find chain propagation and termination to have activation energies of, respectively, 8 and 20 kcal/mole. Qualitatively, this is not a surprising result because it is known that lower molecular weight products are favored at higher temperatures.

Attempts have been made to apply transient state kinetics to determine F-T rate constants.^{35, 36, 37} This work has been done to try to understand why the turnover numbers for F-T are as much as two orders of magnitude lower than other metal-catalyzed reactions such as hydrogenation.⁸

Dautzenberg³⁴ pulsed synthesis gas followed by hydrogen over a ruthenium catalyst. He adjusted the pulse times and was able to estimate rate constants for the propagation and termination steps. The data in Figure 147 are from this work. Besides the kinetic information, this experiment illustrates the potential of using pulse feeding to change the product distribution obtained from a given catalyst. Clearly, it is possible to obtain products which are on average lower in molecular weight from short pulses. From the kinetic analysis Dautzenberg concludes that the low turnover numbers result from low kinetic rates per site rather than the alternative which is only a fraction of the exposed metal atoms being active (low Taylor number). However, Biloen and Sachtler³⁵ raise questions about underlying assumptions made by Dautzenberg which should be cleared up in future studies.

In summary, the dissociative mechanism now seems to be the accepted one for F-T processing. In addition, Hoffmann's theory is now available which attempts to understand the factors controlling all of the mechanistic steps including the polymerization steps. This is, so far, a theory based on simple assumptions. For instance, the theory uses a metal slab model which assumes a flat surface with atom spacing characteristic of a crystal face. The slab is free of surface bonds other than the surface carbon ones required to build up F-T products. The actual iron F-T catalyst is known to contain metal-oxygen and metal-carbon bonds on the surface. Furthermore, an actual F-T catalyst, iron or cobalt, almost certainly has an irregular surface with "steps" and "kinks" which will probably strongly affect the catalyst performance. However, Hoffmann's theory is comprehensive in that it attempts to cover all steps of the F-T process not just the "dissociative" step. Additionally, it does so in an understandable fashion while using the strong and well-developed logic of molecular orbital theory. It should be expanded not discarded.

The work done to understand the mechanism of the F-T process has produced further insights into how metal crystallites actually function as catalysts and how electronic changes across a row of the periodic chart can pronouncedly affect product selectivity. This can allow powerful insights into the nature of catalysis when coupled with an understanding of what the actual surface layer is on such crystallites. For instance, as Rabo has pointed out,^{14, 25} metals to the left of iron in the periodic table form a stable surface oxide. Once the oxides are formed in the initial stages of processing under F-T conditions the surface can no longer accept oxygen, even under reducing conditions. The surface thus becomes ineffective for cleaving the carbon-oxygen bond. Metals below and to the right of iron, cobalt and nickel (e.g. palladium) are reduced but lack the ability to cleave carbon monoxide. Methanol can result from them under F-T conditions. Iron exists under F-T conditions with both iron-carbon and iron-oxygen bonds on the surface. It is an F-T catalyst as well as a shift catalyst. Cobalt is one element to the right of iron in the periodic chart. Under F-T conditions its surface contains no detectable cobalt-oxygen bonds. Cobalt is an F-T catalyst but not a shift catalyst perhaps because it is not partially oxidized to cobalt oxide. It apparently is in the metallic state during F-T catalysis, probably with a surface covering of carbon. Furthermore, it is intrinsically more selective to methane and other light hydrocarbons than iron. Nickel is one element to the right of cobalt; it also is in the metallic state under F-T conditions. Under F-T conditions its surface also probably contains carbon. Nickel can catalyze the formation of hydrocarbons, but only forms ones heavier than methane with difficulty. It is also not a shift catalyst. One strength of Hoffmann's theory is that it provides an explanation for the difference in carbon number selectivities resulting from catalysts across the row: iron \rightarrow cobalt \rightarrow nickel. Presumably this theory can also be extended to explain why stable surface carbon-oxygen bonds are favored going from right to left across this row.

2.4 CARBON NUMBER SELECTIVITY IN LIQUID-PHASE FISCHER-TROPSCH PROCESSING

The wide range of carbon number products in F-T processing can be understood in terms of the mathematics first used by Schulz³⁸ and Flory³⁹ for condensation polymerization. Thus if a complete product work-up is performed during F-T processing and if a plot is made of log selectivity to each carbon number vs. carbon number, a straight line (single alpha case) or a hyperbolic curve appearing to result from two straight lines (so-called double alpha case) results. Plots of the above type are customarily called Schulz-Flory or Anderson-Schulz-Flory plots. Alpha (α) is the slope of the straight line(s); in Schulz-Flory kinetics it is the probability of a carbon chain of n atoms growing to one of $n + 1$ carbon atoms. Until recently most F-T data was presented as being of the single α type, however, it now appears that most, if not all, F-T catalysts produce the double α type of product distribution, certainly, in LPFT double α appears to be the norm. It is possible that early workers sometimes, at least, reported single α behavior because the breakpoint was at a high carbon number, requiring a complete product analysis to "see" the breakpoint. Such product analysis are facilitated by modern analytical techniques that were not available when the early F-T work was done. Catalysts which are very selective to methane and other light products can produce a product distribution which at least gives the appearance of being single α in nature since undetectable amounts of heavy materials may be formed.

The recent Ph.D. thesis of Yates⁴⁰, who was a student of Satterfield's at the Massachusetts Institute of Technology, contains a review of the experimental evidence for double α behavior. For instance, the first note of it appears to have been at a German pilot plant in 1943 during the "Schwarzheide tests". However, this data was not widely circulated and explanations for the double alpha product

distribution first started to appear years later. For instance, in 1983 Koenig and Gaube⁴¹ theorized it to be due to two different catalyst sites, one promoted by potassium and one not. Later, however, Dictor and Bell⁴² and Satterfield⁴³ observed the double alpha phenomenon with potassium-free catalysts.

Novak and co-workers^{44, 45} have also presented a two active site mechanism, one a condensation site and the other a cracking site. However, Yates points out that Schulz⁴⁶ and Pichler and Schulz⁴⁷ had earlier determined that cracking does not occur significantly on iron or cobalt F-T catalysts.

There is an alternate explanation for the double α effect. Satterfield's group⁴⁰ and Iglesia, et. al. at Exxon⁴⁸ propose that this effect is due to two chain growth processes. One of them is the historic one which involves carbon atom insertions into a growing chain. The other is growth by readsorption of product alkenes followed by their incorporation into chains. Although alkenes are primarily hydrogenated upon readsorption there was ample evidence prior to the mechanistic ideas of Satterfield's and Iglesia's groups that alkenes, particularly ethylene and to a lesser extent propylene and 1-butene can initiate and terminate chain growth.^{46, 49-51} There was also some evidence⁴⁶ that ethylene but not propylene can propagate growing chains as well. The basic concept addressed by Satterfield's and Iglesia's groups is the same, but Iglesia theorizes that alkene participation is related to fugacity implying more participation by higher molecular weight alkenes than Satterfield's and the historic experiments above might imply. It is known that most of the heavy F-T products are alkanes not alkenes, implying that the heavy products are the most strongly readsorbed and are reactive in, at least, the hydrogenation reaction.

Satterfield and his students have developed a mathematical model for the double α case.^{40, 52} It is

not dependent on a given double α mechanism. Included is a nonlinear regression method to assign values called α_1 and α_2 to the hyperbolic curve. These two constants roughly correspond to the values α_1 and α_2 that result from simple linear regression analysis of the apparently straight-line parts of the hyperbola. Yates reports, however, that the linear regression α 's are in error by 5-10% compared to the nonlinear α 's even if the only data used is from several carbon numbers away from the breakpoint. Satterfield, et. al's. method also reports a value X_i which can be likened to a breakpoint, but it can be a fractional number such as 9.4. During this contract a modified form of Satterfield's nonlinear regression analysis was used to calculate values for α_1 , α_2 and X_i (Appendix 2).

No catalyst or set of operational conditions have been discovered that allow good control of carbon number selectivity during F-T processing with iron or cobalt catalysts. Except for methane, it is not possible to make a single carbon number product such as only C_4 's or even a fairly narrow carbon range product such as only $C_4 \rightarrow C_6$. To date changing carbon number selectivity during F-T processing only means changing the magnitude of α , for instance, a change in catalyst composition can shift the product distribution from one that is biased toward low molecular weight products to one that is biased toward higher molecular weight ones or vice versa. However, regardless of the catalyst both high and low molecular weight products will be formed.

Conversion of synthesis gas to C_1 products with other metal catalysts is also possible. For instance, very high methane selectivities can be obtained using a nickel catalyst and very high methanol selectivities can be obtained, for instance, with a palladium catalyst.¹⁴

During this contract Schulz-Flory plots were made when full carbon number range analyses were

performed. However, this is a very time-consuming process and was not done in a routine fashion. Schulz-Flory plots are important because there have been reports that C_1 and C_2 can fall above or below the Schulz-Flory line with some catalysts. This implies that these products can be "uncoupled" from the mathematical formalism of condensation polymerization. Lower levels of methane and/or ethane than predicted by Schulz-Flory would be an extremely important observation considering the objectives of this contract.

2.5 OTHER FISCHER-TROPSCH SELECTIVITIES

F-T processing is highly selective in one respect: the carbon chains are primarily unbranched. This is consistent with chain growth via sequential carbon atom insertions into an iron-carbon bond, with only a small number of insertions by $> C_1$ species. Only low levels of cyclic and aromatic products are formed.

Most of the heavier F-T products are saturated molecules; alkenes can be prominent among the low molecular ones. Of the two most studied F-T catalysts (Fe and Co), iron is more prone to form alkenes than Co. With some iron catalysts, at least, the extent of reduction of iron appears to alter the ethylene/ethane ratio, but not the carbon number selectivity at low conversion. Specifically, more ethylene results from the more highly reduced catalyst (3 vs. 63% iron reduction).⁵³ Incorporation of manganese sometimes improves the selectivity to alkenes in the low molecular weight products and sometimes doesn't.⁵⁴⁻⁶⁶ Operation of an iron/manganese catalyst at low pressure (atmospheric), 420° C and a feed rate of 120 cc/cc catalyst/hour has resulted in 38.3% carbon monoxide conversion and a high aromatics yield of 18%.⁴⁵ Zinc is also purported to favor alkenes in the low carbon number products.⁶⁷⁻⁶⁹

2.6 DESCRIPTION OF THE IRON FISCHER-TROPSCH CATALYST

In its usual manifestation the iron catalyst is unsupported. It is usually furnished as iron oxide, apparently even the slag from iron ore processing may be used as catalyst. The iron oxide catalyst precursor can be reduced (activated) in several ways including pretreatment with the synthesis gas feed itself. Other reductants such as carbon monoxide may also be used. Activation temperature and pressure may be the same as the operating temperature or different. Precursor activation can affect the catalyst activity and α .

Historically, the most important metal adducts for iron F-T catalysts are copper, potassium and silicon. Copper aids the reduction of iron oxide and potassium affects both catalyst activity and selectivity. When copper is used care is taken to get a good distribution of it throughout the bulk iron oxide, for instance, by co-precipitating it with iron. Potassium, on the other hand, is usually added to an iron-copper material in a separate step, for instance, by surface impregnation.

The affect of alkali, particularly potassium, was discovered very early by Fischer and Tropsch.⁷⁰ In their work powdered iron-copper compositions were used which resulted from decomposition and ignition of metal nitrates. Potassium was added separately as potassium carbonate. Catalyst activity increased with increasing potassium level, but so did the catalyst deactivation rate. Later, Pichler studied catalysts resulting from potassium carbonate addition to iron-copper oxides.^{71, 72} Tests were two months long at 235° C and 15 atm. No activity change was noted in going from 0 to 0.25% potassium. Greater than 1% potassium resulted in less active catalysts. As the potassium level was increased the selectivity to wax and oxygenates increased. More recently, Anderson has reviewed the affect of alkali promotion.⁷³ In this later work the activity increase and higher wax

selectivity due to potassium were confirmed.

Although the material furnished to an F-T reactor is best described as unsupported iron oxide with minor metal adducts, it is sometimes called a supported catalyst. This is because silica can be added to give the catalyst structural integrity. The Ruhr catalyst (4.8 wt% silicon) is an example of such a material; it was evaluated as a reference during the current work. Such catalysts are not supported in the usual sense because silicon is usually added during precipitation of the iron oxide, in other words the catalyst does not result from surface impregnation onto silica. Furthermore, regardless of the method of preparation, the level of silica is lower than it would be from impregnation onto silica. In the current work a few catalysts were prepared by coprecipitating low levels of silicon with iron and copper.

Although the iron F-T catalyst is reduced during activation it is not easily described. For instance, there is good evidence that some iron oxide remains in the working catalyst, although the carbon chain growth (F-T) sites appear to involve carbidic iron. There are many iron carbides known and more than one of them have been observed in functioning F-T catalysts, for instance, by Moessbauer spectroscopy. Many workers believe the iron F-T catalyst has more than one catalytic site. These sites could all be carbidic iron sites, each in a different steric and/or electronic environment, or they could be more complex. For instance, more than one iron could be required per site, perhaps with a mixture of iron-carbon and iron-oxygen bonds.

Some theorize that the shift reaction sites, on the other hand, are at places where there is oxidic iron because such sites might aid transfer of oxygen to carbon monoxide. In support of this, the cobalt F-T catalyst is fully reduced during use with no evidence of a cobalt oxide phase, this catalyst does

not catalyze the shift reaction. The possibility exists, therefore, that the F-T and shift sites are different, with one being essentially oxidic and the other carbidic. However, since the reduction and oxidation of carbon monoxide both involve transfer of oxygen atoms it is also likely that in both cases at least transitory iron oxygen bonds are present.

Attempts have been made to learn more about the mechanism of the F-T reactions through studies of the interaction of carbon monoxide and/or hydrogen with clean metal surfaces. Although such surfaces are not the same as an actual functioning F-T (iron oxide/carbide) catalyst useful knowledge may be obtained. For instance, hydrogen adsorption on Fe(100) is affected by potassium: although with and without potassium there are two desorption states (β_1 and β_2) and the total hydrogen coverage does not change, potassium does cause desorption temperatures to increase by about 30° K.⁷⁴ A similar finding of a 30-40° K increase was made for the Fe(111) surface. Separate work confirmed that the sticking probability and binding energy for hydrogen increases linearly as a function of potassium coverage.⁷⁵ Potassium was also found to strengthen the carbon monoxide surface bond (opposite to the affect of carbon, oxygen and sulfur) and to increase the amount of dissociated carbon monoxide. There is also some evidence that potassium can create new carbon monoxide adsorption sites.⁷⁶

It is also clear from the surface studies that the more open crystal faces of a given metal tend to be more active for carbon monoxide dissociation. Work with tungsten, for instance, illustrates carbon monoxide dissociation at 300°K on the tightly packed W(110) surface, but below 200°K on the more open W(100) surface.^{77, 78}

Work function changes have also been measured for promoters such as potassium. Low ionization

potential materials, e. g. alkali metals, donate electron density to a transition metal causing a decrease in the transition metal work function (increased electron density). This effect continues to increase with increasing coverage approaching the work function of the covering material. Specific examples for iron⁷⁹ and nickel⁸⁰ are available. The amount of change in work function follows the ionization potential of the covering material, lower ionization potential (better electron donating) materials are more effective at lowering the work function. The ionization potentials of the alkali metals generally decrease with increasing atomic number.

Metal work function increases are noted upon adsorption of hydrogen or carbon monoxide, indicating loss of electron density from the metal with a resultant addition of electron density to the adsorbed gas. Blyholder's model of CO adsorption is usually used to rationalize how the metal influences carbon monoxide upon adsorption.⁸¹ According to Blyholder electrons from the surface are donated into an antibonding carbon-oxygen bond thus causing this bond to be weakened. At the same time the metal-carbon bond is strengthened resulting in facile carbon-oxygen bond cleavage.

Care must be taken in using the results of experiments with clean metal surface planes to interpret what happens on the surface of a functioning catalyst. However, this is a rapidly growing field of interest with ever-increasing sophistication. For instance, one historic criticism has been that clean metal surface planes do not approximate an actual metal crystallite which can exhibit an irregular surface of "steps" and "kinks". However, Somorjai and others have been actively investigating clean but irregular surfaces.

It is also known that all F-T catalysts result from paramagnetic or ferromagnetic materials,

however, there are many such materials which do not produce active F-T catalysts (Figure 2). The electronic properties associated with the metal d orbitals are important in determining the metal's magnetic properties and probably are also important for F-T catalysis.²⁸ Magnetic measurements of actual iron-based catalysts have been performed during this contract, but more experimental and theoretical work is required.

2.7 CLUSTERS AS CATALYST ANALOGIES

Muetterties believed comparisons could be drawn between known metal clusters and intermediates formed catalysis.⁸² Clusters have played a role in understanding homogeneously-catalyzed hydroformylation. However, they have so far only contributed to an understanding of the first step F-T mechanism.

Metal clusters are multimetallic, ligand-stabilized complexes which exhibit metal-metal bonding. Just after the work of Biloen and the others Muetterties reviewed mechanistic aspects of carbon monoxide hydrogenation, specifically with regard to possible analogies between metal clusters containing carbon monoxide and potential reduction intermediates such as iron carbides.⁸³ He cited known metal carbonyl clusters, particularly those of iron and cobalt which might be used as models for intermediates in reactions such as those occurring during Fischer-Tropsch synthesis. For instance, $[\text{Fe}_4(\text{CO})_{13}\text{H}]$ contains one carbonyl simultaneously bonded to two iron atoms, similar perhaps to a surface carbon monoxide species prior to carbon-oxygen bond cleavage. Another cluster, $[\text{CFe}_5(\text{CO})_{15}]$, contains a carbidic carbon which exists below a basal plane defined by four of the five iron atoms in the cluster. Such clusters might be relatable to the carbide species of Biloen. Complexes containing other ligands, notably cyclopentadienyl, in addition to carbon

monoxide and which might be analogies for F-T intermediates include the bridged complex of manganese: $\text{Cp}(\text{CO})_2\text{Mn}\{\text{CH}_2\}\text{Mn}(\text{CO})_2\text{Cp}$. The methylene bridges a manganese-manganese bond. Such complexes and their possible relation to carbon monoxide hydrogenation including F-T have been reviewed.^{84, 85} However, at the time of the Muetterties review there were no examples of cluster complexes which could be converted from one hydrogenation intermediate analog into another.

The field of cluster analogies has been reviewed again recently by Gates.⁸⁶ He cites work of Chisholm, et. al.⁸⁷ who have discovered a dissociative reaction of carbon monoxide with a tungsten alkoxide complex. The new complex contains both oxidic and carbidic tungsten atoms. Although this is similar to what probably results on a surface when carbon monoxide dissociates, it is not yet an example of a cluster-containing carbon monoxide which can be converted into one with dissociated carbon monoxide. With this cluster initial carbon monoxide bonding must be slow compared to bond cleavage, isolation of the initial complex has not yet been described.

Gates compares Chisholm's work to that of Yates, et. al. who examined the reaction of carbon monoxide on a molybdenum surface.⁸⁸ Yates was able to show that carbon monoxide adsorbs intact at a low temperature but converts to molybdenum oxide/carbide at higher temperatures.

Gates points out that the initial interaction of a reactant with a cluster can be slow compared to reaction with a clean metal surface because the former requires a coordinatively unsaturated cluster. This, in turn, usually means removal of a ligand from a coordinatively saturated precursor which can be slow. Gates says that in a working catalyst reactants and products themselves can fill the role of the departing ligand in a cluster, perhaps making the cluster analogy closer to a real catalyst

than the clean metal analogy.

The cluster analogy for F-T chemistry has been very slow to develop. Clusters are not yet known that can demonstrate even one step in a carbon dioxide reduction process, although carbon monoxide complexation--> cleavage undoubtedly does occur in Chisholm's example. Furthermore, the cluster work to date has been concentrated on finding clusters which model only the initial steps of the carbon monoxide reduction processes. To be helpful in understanding F-T catalysis this work must eventually shed light on the important later steps which determine carbon number selectivity. The goal should be clusters which demonstrate how to obtain a very narrow carbon number distribution such as C₅ to C₁₀.

However, if Hoffmann is correct in thinking about F-T catalysis in terms of extended molecular orbital theory of a several atom thick metal slab there is an even more serious problem with the cluster analogy. Namely, how can the d electrons in a few metal atoms in a cluster ever mimic the behavior of the d electrons in an extended group of metal atoms? According to Hoffmann changes in the d-band electronic state influence the degree of polymerization during F-T synthesis. As stated above, understanding how to control the degree of polymerization should probably be the key objective of future F-T research.

2.8 FISCHER-TROPSCH REACTORS

Commercial F-T plants have traditionally used packed or fluidized bed reactors. In both cases the product liquids and gases are removed from the reactor as fast as they are formed. Provisions such as narrow tube reactor geometry must be provided to remove heat from the very exothermic F-T

reactions. Slurry liquid phase processing is a newer concept although Koebel did seminal work on it in the 1940's and early 1950's at the Rheinprussen Corporation plant at Hamburg Niederrhein, Germany. The driving force behind its development is the ability of the liquid phase to act as a heat transfer agent to remove heat from the reactor. F-T processing is very exothermic.

The first F-T plant was built in Germany in the 1930's. It had a fixed-bed reactor full of catalyst pellets and was operated between 200 and 270° C.⁸⁹ Due to the high exothermicity of the F-T reactions, precise catalyst temperature control was impossible. This resulted in shortened catalyst life. The product liquids were approximately a 50 : 50 mix of naphtha and higher boiling fractions. The most recent fixed-bed plants are in South Africa; they employ Arge reactors which use high catalyst loadings and high space velocities. The product liquids are about 40% naphtha with the balance heavier.

The M.W. Kellogg Co. has developed a type of fluidized-bed reactor called an entrained-bed reactor. It is used in the South African Synthol process. In it the catalyst and syn gas contact at the bottom of the reactor and proceed up together at 300-335° C. Cyclones separate products and catalyst; boilers are used to remove heat. The South Africans have developed two generations of Synthol reactors, Synthol I and II. Synthol II resulted from a cooperative effort with Badger Engineers Inc. to rectify problems associated with Synthol I.⁹⁰ The Synthol reactors are operated to produce a light product which is about 78% naphtha, 7% heavier and the balance gases and oxygenates. The high gasoline yield from this processing implies a high methane yield as well. This is apparently not a problem in South Africa which is short of natural gas. However, in most other places this would be a problem since natural gas is currently in over supply.

South Africa operates its F-T plants to make fuel, but also sells specialty chemicals after separating them from the diverse F-T product. For instance, they sell wax and purified oxygenates. Total product sales coupled with very low priced coal and essentially paid off plants allow them to break even against petroleum at a fairly low price. However, even they admit that they do not break even when petroleum is below about twenty dollars a barrel. Furthermore, some of the markets they sell F-T products into are nearly saturated even with the relatively small amount of product produced in South Africa.

Koebel's LPFT work continued for a while after the Second World War.⁹¹ The plant he and co-workers used contained a 1.55 meter diameter by 8.6 meters tall bubble reactor with internal cooling coils. The slurry of wax and catalyst moved upflow with co-current synthesis gas which contained hydrogen and carbon monoxide in the molar ratio of 0.7. The gas bubbles cause ebullition of the catalyst particles resulting in a well-mixed slurry. There was a recycle loop which allowed removal of wax product and spent catalyst. Fresh catalyst was also added on this loop to maintain catalyst loading at 10-20 wt% of the slurry. At a feed gas linear velocity of 9.5 cm/sec and operating conditions of 268° C and 12 atm. Koebel reported a temperature gradient of only 1° C and a catalyst concentration gradient of 0.2 to 0.6 wt% at 10 wt% average catalyst loading. Carbon monoxide conversion was 91% with 34.5 wt% of the hydrocarbon product in the range C₁—>C₄.

Koebel reported conditions for operating the slurry bubble reactor which produced extraordinary hydrocarbon distributions. For instance, with 50-500 g of catalyst per liter of suspension, catalyst particle size of 0.002—>1 μm, gas flow rate 10-30 times the percent weight of catalyst base metal in the suspension (gas flow expressed as NL/hr/liter of catalyst suspension) and plant operating pressures of 3-150 atmospheres, he reported no methane in the product!⁹² However, in the review

of LPFT which he wrote with Ralek⁹¹ he says about 4% of the total product from the 1952-1953 demonstration plant campaign was methane + ethane. Even this is quite low, particularly in light of the fact that the plant was being operated under conditions favoring production of gasoline not diesel fuel, and the carbon monoxide conversion was 90%. High conversions favor high methane + ethane selectivity.

LPFT research was continued in the U.S. after the Second World War by the U. S. Bureau of Mines.⁷³ After the Bureau of Mines work until the early 1980's additional liquid phase processing research was continued at various laboratories; a review was published in 1983.⁷⁴ Liquid phase processing was aggressively pursued in the 1980's, for instance, Mobil finished an LPFT contract in 1985.⁷⁵ Performance results from this and Koebel's earlier work are compared in Figure 3.

Currently research and development on liquid phase reactors and F-T catalysts to use in them is being done in many laboratories. The hydrodynamics of such reactors as well as kinetic rates of the various processes which have been performed in them have been studied and summarized by Deckwer⁸⁶ and Fan.⁹⁷⁻¹⁰⁰ Catalyst development is currently being sponsored by the DOE at the University of Kentucky and Texas A & M University.

The DOE is also sponsoring an international consortium of private companies for operation of a 0.572 m diameter slurry bubble reactor at LaPorte, Texas. One of the consortium members, Air Products and Chemicals, Inc. (APCI) provides site support. An LPFT reactor of this type is purported to be operational in South Africa, possibly about 1 meter in diameter. In addition, Exxon, Statoil and RENTECH have respectable internal projects for LPFT development. RENTECH have constructed a plant near Denver, Colorado to convert synthesis gas from biogenetic

methane formed at a waste disposal site. Finally, APCI have made a major effort to commercialize the slurry bubble concept for alcohol synthesis before their involvement in the DOE LaPorte consortium.

A slurry autoclave reactor (stirred tank) is usually used to screen LPFT catalysts; it was the only reactor used during this contract. In one case a catalyst was evaluated which later was used in a run at the LaPorte facility. Although this catalyst was not prepared as part of this contract its slurry autoclave pilot plant performance results are included to allow comparison to the performance in the LaPorte test. APCI is separately reporting the LaPorte test which took place in 1992. Some additional catalyst evaluation work was done at UOP in support of the LaPorte testing; these tests are included in Attachment 1. The catalyst performance targets of this contract are for use in a LaPorte type reactor. To estimate such performance from slurry autoclave pilot plant results additional crossover experiments are needed. From such experiments a mathematical model can eventually be derived, possibly based on several slurry autoclave reactors operating in series.

One problem contemplated with LPFT processing is separation of the catalyst from the liquid phase. This is necessitated because the F-T product can contain non-distillable (wax) reaction products. Probably the easiest way to minimize this problem would be to use a catalyst with an α which favors high light ends selectivities (low wax). However, this is a limited solution since a low wax catalyst invariably is excessively selective to methane and ethane. Furthermore, LPFT kinetics favor double α behavior which insures some wax product even from high light end's selective catalysts. In turn, this means catalyst/wax separation will always be necessary. The Mobil work of the mid-1980's showed that a relatively iron-free wax could be produced by known solid-liquid separation

technology. However, the wax still contained several hundred parts per million of iron and even this is sufficient to require a separate iron removal step to protect, for instance, the hydrocracking catalyst used to crack the wax to diesel boiling range material.

Catalyst particle integrity in the F-T reactor is important for LPFT. Particle attrition will magnify the separation problem. However, determining catalyst particle stability is a difficult experimental problem. Determining particle/particle attrition alone might not be enough. Particles could also attrit due to build up of stress from pressure within catalyst pores resulting from formation of long carbon chains. This would be similar to the spalling that the chromium on silica polyethylene catalyst is known to undergo. Direct measure of the rate of attrition of the catalyst particles in the stirred autoclave might also prove erroneous since the particle/particle attrition might be far different than in the slurry bubble reactor. Therefore, catalyst particle integrity data from a slurry bubble reactor will eventually be needed. Only a limited amount of work was done during this contract as a start toward understanding particle integrity.