1. OBJECTIVE

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Develop a supported cobalt-ruthenium catalyst for Fischer-Tropsch (F-T) processing of synthesis gas.

1.2 OVERVIEW

The eventual goal of this research is a high activity cobalt-based catalyst for use in slurry bubble reactors. A potential catalyst of this type has been developed using a modified Y zeolite and a pore-filling impregnation method. This approach was used when it was found that high activity catalysts could not be prepared by the original, reverse micelle, approach.

The experimental sections of this report describe preparation and evaluation of both the reverse micelle and Y zeolite-supported catalysts. Reverse micelle catalysts were prepared on a number of different supports. The Y zeolite catalysts were prepared on a support resulting from steaming and acid-washing Y zeolite. The resulting material is essentially crystalline with Y zeolite type channels but large (50-100 Å) amorphous "cages". The current high activity catalysts resulted from impregnation of higher levels of cobalt onto the modified Y zeolite than were used in an earlier similar catalyst developed by Union Carbide during previous DOE contracts.

Ruthenium is known to produce a very high activity F-T catalyst alone, however, it is too expensive for such a use. Thus it has been suggested to use it in small amounts in cobalt-based catalysts a an activity promoter. During the reverse micelle work no strong evidence for ruthenium promotion was found; this work indicated that the reverse micelle method results in poor dispersion of ruthenium into cobalt crystallites. Because the Y zeolite approach was only started midway through the contract, time was not available to fully explore the effect of small amounts of ruthenium on catalyst performance.

Most catalysts were only screened in a pilot plant which contained a tube reactor to quickly assess activity and selectivity. However, an evaluation was made of the high activity Y zeolite-type catalyst in a slurry autoclave plant, a type of test that results in a longer run.

2. INTRODUCTION

This section is a brief summary of cobalt-catalyzed Fischer-Tropsch (F-T) processing. 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 require more space than is available in this report.

2.1 FISCHER-TROPSCH BACKGROUND

The Fischer-Tropsch (F-T) process is one of several which use synthesis gas (H_2 + CO) as feed. A complex product is formed. F-T usually employs either an iron or cobalt catalyst although ruthenium and nickel have also been used. In addition, multimetallic catalysts such as cobalt-ruthenium have been described. Currently synthesis gas is available from methane or coal; in either case it is an expensive feed, largely due to the high capital cost of a synthesis gas plant. Fifty to seventy percent of the total cost of a F-T complex will be due to the synthesis gas plant. Since F-T catalysts require very pure feed, feed pretreatment is an additional expense. To stand these expenses F-T can only compete with high, rather than the current low, priced petroleum.

F-T processing was used in Germany during World War II to convert coal-derived synthesis gas into transportation fuels when the Allies cut off their supply of petroleum. Following the war only the South Africans who faced the continual threat of a petroleum embargo continued to develop F-T processing. They pessess a coal resource and historically cheap labor to mine it. As a result, several generations of F-T reactors have been built there to process coal-derived synthesis gas. Although much of this work has not been published, Dry, among others, have been active in the literature.

F-T research gained momentum in the mid-1970's after the Arab oil embargo. Projects were then started at many academic, industrial and government laboratories as part of the worldwide synthetic fuels effort; there are 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 methane-derived synthesis gas conversion, since part of the world's methane resource is in remote areas where there is no market for it. One large-scale F-T plant has been built to convert synthesis gas from such methane into transportation fuel, namely Shell's Indonesian plant. It 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 of 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 feed 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.

2.2 COMPARISON OF IRON AND COBALT FISCHER-TROPSCH CATALYSTS

In this contract novel cobalt-based F-T catalysts were the goal, specifically ones containing cobalt and minor amounts of ruthenium. Cobalt and iron catalysts are different in many respects. The former are usually supported whereas the latter are usually derived from bulk iron oxide. Small amounts of other metals are used in both catalysts but the ones used are not the same for both catalysts. Both catalyst types are reduced prior to use, however, the cobalt catalyst requires higher temperatures (300° C or higher vs. 260-280° C). The working cobalt catalyst is entirely in the zerovalent state, while iron works in at least a partially oxidized state. The cobalt catalyst operates about 200° C compared to about 270° C for the iron catalyst. This is an important difference, it means that the iron catalyst can be reduced in the F-T reactor whereas the cobalt catalyst usually has to be reduced in a separate vessel capable of withstanding the higher reduction temperature.

Iron catalyzes the shift reaction (carbon monoxide with water to produce hydrogen and carbon dioxide); cobalt doesn't. Some workers believe this reaction is catalyzed by iron oxide sites on the iron catalyst.

The equation below illustrates the stoichiometry of the preponderant F-T reactions (alkane formation):

$$CO + 2H_2 \longrightarrow -CH_2- + H_2O$$

According to this stoichiometry a 2 : 1 molar ratio of hydrogen to carbon monoxide is required; this is the ratio resulting from partial oxidation of methane:

$$2CH_4 + O_2 \longrightarrow 2CO + 4H_2$$

Cobalt is the catalyst of choice for such-derived synthesis gas. Iron, however, is used for hydrogen-poor synthesis gas, most especially that from coal (≈ 0.7 molar ratio of hydrogen to carbon monoxide), since the shift reaction has the effect of producing hydrogen from product water. (At the expense of some of the carbon!)

2.3 CALCULATIONS

The conversions and selectivities calculation method used in this work (Appendix 1) requires argon internal standard in the feed. The data required to calculate conversions and $C_1 \rightarrow C_4$ hydrocarbon and carbon dioxide selectivities were obtained throughout the runs with an on line gas chromatograph. A second on line gas chromatograph, which performed a different analysis method, was used to obtain the data needed to calculate $C_2 \rightarrow C_4$ alcohol selectivities.

2.4 REACTION MECHANISM

The F-T products are mostly alkanes, alkenes and oxygenates of wide molecular weight range. The mechanism describing their formation is complicated. Apparently relatively large metal crystallites are needed, small ones can produce high levels of methane. The cobalt catalyst is usually supported and formation of sufficiently large crystallites (50-100 Å) can be a problem. The initial work during this contract was directed toward forming 50-100 Å cobalt aggregates via impregnation of cobalt-containing reverse micelles. Subsequent work was also directed toward forming these sorts of aggregates but by using a support with 50-100 Å pores. The support used was steamed and acidwashed Y-zeolite.

The currently favored F-T mechanism is the original one of Fischer and Tropsch.[6] It involves cleavage of carbon monoxide as the first step. This cleavage occurs at surface cobalt sites and results in surface carbon and oxygen. Most of the oxygen ends up as water although some oxygenate molecules also result. The carbon builds up to the main products of the F-T process which are alkanes and alkenes by the steps of hydrogenation and insertion. Surface-bound methyl and methylene radicals may thus be formed from carbon by hydrogenation. Chains may be formed by insertion of methylene radicals into the surface-bound methyl and alkyl radicals.

A 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,[7, 8] and later by many others as well. Araki and Ponec[9] and Wentrcek and co-workers[10] supported a dissociative mechanism for methane formation over nickel surfaces at about the same time. Rapid dissociation of carbon monoxide on the catalyst surface in the presence of hydrogen is a key aspect of the theory proposed by Biloen, Helle and Sachtler to explain how hydrocarbons are formed by F-T catalysts.[11] Their acceptance of this theory was based on work they did with metals containing surface coverages of ^{13}C formed by disproportionation of ^{13}CO to ^{13}C and $^{13}CO_2$ at 5[illegible]° C and 0.5 bar. They prepared carbidic materials with measured amounts of ^{13}C that were active when reacted with successive pulses of $^{12}CO/H_2$ 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 $^{13}CH_2$ and $^{13}CH_3$, the latter of which can form $^{13}CH_4$ via reaction with hydrogen and higher ^{13}C hydrocarbons via insertion of $^{13}CH_2$. Others invoked the dissociative mechanism at about the same time as Biloen, et. al.[12, 13, 14] 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.[15, 16, 17] 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 by Henrici-Olive and Olive, particularly with regard to the relevance of the Petit experiment.[18, 19] However, Smutek has defended it while emphasizing this experiment.[20]

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.[21] This model covers all of the steps in this mechanism not just the initial carbon monoxide cleavage. They discuss, for instance, the mobility of carbon intermediates on the surface and how that can relate to the F-T products. In their logic 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, et. al. have made strides toward understanding the theoretical underpinning of F-T catalysis with a theory that 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. This theory is also interesting since all F-T catalysts result from paramagnetic or ferromagnetic materials, and metal d-band electrons also determine a material's magnetic properties (Figure 1). Understanding why some materials are magnetic but not F-T catalysts should be a goal of future experiments.

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 T-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 is apparently in the metallic state during F-T catalysis, possibly 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 possibly contains a carbon layer. 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—>cobalt—>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.

In summary, the dissociative mechanism now seems to be the accepted one for F-T processing. In addition, the Hoffmann theory is 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 effect 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 first, "dissociation", step. Furthermore, it provides an explanation for the difference in carbon number selectivities across the row: iron--> cobalt--> nickel.

2.5 CARBON NUMBER SELECTIVITY

The wide range of carbon number products in F-T processing can be understood in terms of the mathematics first used by Schulz[22] and Flory[23] 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 reported single α behavior because the breakpoint was at a high carbon number, requiring a complete product analysis to "see" the breakpoint. Such product analyses 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, such as cobalt catalysts, 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.

Yates[24] presented a review containing a discussion 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. Thus, in 1983 Koenig and Gaube[25] theorized it to be due to two different catalyst sites, one promoted by potassium and one not. Later, however, Dictor and Bell[26] and Satterfield[27] observed the double alpha phenomenon with potassium-free catalysts.

Novak and co-workers[28, 29] have also presented a two active site mechanism, one a condensation site and the other a cracking site. However, Yates points out that Schulz[30] and Pichler and Schulz[31] 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 group[24] and Iglesia, et. al. at Exxon[32] propose that this effect is due to two chain growth processes. One of them is the historic one which involves one carbon atom insertion 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.[24, 33-35] There was also some evidence[30] 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.[34, 24] 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.

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 $C_4 -> C_6$. 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.[7]

2.6 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 a metal-carbon bond, with only a small number of insertions by $>C_1$ species. Only low levels of cyclic and aromatic products are formed, although in special cases aromatics yield can be as high as 18%.[37]

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.

2.7 COBALT CATALYST DESCRIPTION

The cobalt catalyst is usually supported and results from reduction of supported cobalt salt(s). Manganese and zirconium are commonly-used promoter metals for cobalt. Anderson has reviewed the cobalt catalyst up to the early 1980's.[38] He gives the composition of key cobalt catalysts and cites earlier reviews of this type of catalyst. According to Anderson, Fischer's cobalt/thoria/magnesia catalyst is the forerunner of all supported, cobalt-containing F-T catalysts. Much early work was devoted to removing thoria from this composition culminating in catalysts supported on zirconia-magnesia and titania-magnesia. Kieselguhr was also a support component for some of the earliest cobalt catalysts.

By the time of the Anderson review, there were many other cobalt catalysts including ones on supports such as silica and alumina as well as others supported on the historic materials above. There had also been extensive studies of the performance of such catalysts under a multiplicity of conditions.

Much of the recent F-T work has, in fact, been concentrated on cobalt- rather than iron-based catalysts. This is due to the current abundance of cheap methane and the utility of the cobalt catalyst for conversion of methane-derived synthesis gas.

Exxon, for instance, have done extensive research on this type of catalysis since at least the early 1980's. Some of their more recent patents describe cobalt-manganese spinels which can be promoted by copper.[39, 40] Copper apparently promotes conversion, manganese also promotes conversion and also causes a lowering in the selectivity to methane. These catalysts apparently exhibit the low selectivity to carbon dioxide expected from cobalt-based catalysts. However, the carbon dioxide selectivity appears to be somewhat higher than typically obtained with cobalt catalysts. Presumably a spinel (Co_2MnO_4/1% Cu) will allow more cobalt to be loaded into the reactor per unit volume of catalyst than a supported catalyst. Interestingly, copper-promoted iron-manganese spinels have also been patented as low methane and carbon dioxide selective catalysts.[41]

Exxon have also done a considerable amount of work on cobalt and cobalt-ruthenium catalysts supported on titania. Their cobalt-ruthenium work follows earlier work by Kobylinski (Gulf-Chevron) who also investigated cobalt and cobalt-ruthenium catalysts but used other supports.[42-45] This type of catalyst often has other metals such as zirconium present as adducts.[46] Both sets of workers found that a small amount of ruthenium can promote catalyst activity and selectivity to C_5+ products. They believe these effects are due to small amounts of ruthenium lodged in cobalt crystallites. Special efforts were, therefore, made during catalyst preparations to insure that cobalt and ruthenium were in intimate contact. Exxon believes ruthenium has the ability to keep the catalyst surface free of deactivating molecules, perhaps through reaction of them with hydrogen. Exxon have also found that ruthenium-containing catalysts are more easily regenerable; they believe the explanation is the same as above. Exxon have provided a recent review of their work and that of earlier workers.[47]

Many other supports have been used for the cobalt catalyst. For instance, alumina has been used by Exxon as a second stage catalyst in a two stage F-T process.[46] In this scheme the first stage is operated at a lower pressure than the second stage. The use of alumina in this example is based on Exxon's finding that alumina-supported catalysts are more active at relatively low pressures than other supported cobalt catalysts.

Lapidus and co-workers have also recently investigated alumina-supported catalysts[48] and compared them to ones supported on silica. They found that the extent of calcination affected the ultimate selectivity of the catalyst. Extensive calcination decreased the liquid product selectivity of a silica-supported catalyst, whereas it increased that of an alumina-supported one.

Shell have also been active recently in the area of cobalt-catalyzed F-T processing. This has led to the F-T plant in Sintulu, Malaysia which is the only commercial F-T plant outside of South Africa. It processes methane-derived synthesis gas with an unknown catalyst which, however, is likely supported and cobalt-based.

A recent Shell patent describes a catalyst activation procedure.[49] This procedure is for activation of fresh catalysts and reactivation of spent ones as well. It incorporates treatment with hydrogen at pressures in excess of those previously used for such catalyst treatments. It is written to cover simple one stage activations but also the multistage one of Kobylinski, it. al. which is called ROR (reduction/oxidation/reduction).[50]

Additional recent work on silica-supported catalysts is due to Ishihara and co-workers.[51] The particular catalysts studied were ones containing cobalt and nickel, with the extreme examples being either all cobalt or all nickel. Activity was maximal for the 50 : 50 cobalt : nickel catalyst. Surprisingly the methane selectivity was not a linear function of the amount of nickel, rather it was a minimum for the 50 : 50 catalyst. However, even at a minimum it was still a high 30%. The selectivity minimum might, in part at least, be do to the high conversion obtained with the 50 : 50 catalyst, since methane selectivity during cobalt catalysis is known to decrease as conversion increases.

2.8 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, since 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.[52] 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 synthesis 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.[53] The Synthol reactors are operated to produce a light product which is about 78% naphtha, 7% heavies 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 probably 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.[54] 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 $C_1 \longrightarrow > C_4$.

Koebel reported conditions for operating the slurry bubble reactor which produced extraordinary hydrocarbon distributions. For instance, he observed no methane product with 50-500 g of catalyst per liter of suspension, catalyst particle size 0.002—>1 nm, 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.[55] However, in the review of LPFT which he wrote with Ralek[54] it is said that about 4% of the total product from the 1952-1953 campaign with the demonstration plant 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, <u>and</u> the carbon monoxide conversion was 90%. High conversions favor high methane + ethane selectivity.

LPFT processing was continued in the U.S. after the Second World War by the U.S.Bureau of Mines.[56] After the Bureau of Mines work until the mid 1980's additional liquid phase processing research was continued at various laboratories; a review was published in 1983.[36] Liquid phase processing was aggressively pursued in the 1980's, for instance, Mobil finished an LPFT contract in 1985.[57] Performance results from this and Koebel's earlier work are compared in Figure 2.

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 Deckwer[58] and Fan.[59-62] 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 Co., 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 garbage site. Finally, Air Products Co. 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 certify LPFT catalysts, however, this is a time-consuming way to screen new catalysts. Although the eventual goal of the research done under the current contract is a catalyst for LPFT use, the actual state of development of the reverse micelle and zeolite-supported catalysts at the outset was not very far advanced and extensive catalyst screening was anticipated. In fact, most of the catalyst evaluations in this report were screening in nature and were performed by a quick fixed-bed catalyst evaluation procedure. However, a few of the zeolite-supported catalysts were sufficiently developed by the end of this contract to warrant evaluation in the slurry autoclave plant.

One problem contemplated with LPFT processing is separation of the catalyst from the liquid phase. This separation is necessary because the F-T product can contain wax reaction products that cannot be removed from the catalyst by distillation. 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. The Mobil work of the mid-1980's (iron catalyst) 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.

Separation of catalyst from wax will have to be addressed with a supported LPFT catalyst as well as non-supported catalysts such as Mobil's iron catalyst. There might be some advantages due to a supported cobalt catalyst. First of all, cobalt catalysts do not produce as much wax as iron catalysts due to their bias toward low molecular weight products. Secondly, cobalt tends to be more active per atom than iron so less catalyst will have to be loaded to achieve a given conversion target. Lastly, one might be able to choose a support that is more stable to attrition than bulk phase iron catalysts resulting in fewer fines in the wax.

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. During the cobalt catalyst research no work was done on catalyst particle integrity since only a few slurry autoclave runs were performed.