4. RESULTS AND DISCUSSION

One objective of this contract was development of the means to prepare an iron-based LPFT catalyst at the rate of 100 lbs/day. This production rate has been met with a pilot plant which produces metal oxides via precipitation. For the catalyst preparation procedure developed, a high rate of filtration is essential. There is room for improvement in the current method through reducing the amount of water injected in the reactor and/or addition of higher capacity filters.

Catalyst evaluations were performed in a slurry autoclave pilot plant; good progress has been made toward achieving the catalyst performance targets. Means are not yet available to accurately predict how the performance in a slurry autoclave correlates with that in a slurry bubble reactor, however, in one case fresh samples of the same catalyst were evaluated in both the slurry autoclave reactor and the large slurry bubble reactor at LaPorte, Texas. There was pretty good correlation between the one stage of slurry processing and the bubble reactor from the standpoints of conversion and selectivity at the same temperature and feed rate. However, this must be confirmed by additional crossover experiments.

Slurry autoclave conversions with the best catalysts of this contract at target processing conditions were below the slurry bubble conversion target. However, the methane + ethane selectivities were well within the target limitations; this can probably be taken advantage of by processing at slightly higher than target temperatures and/or pressures to achieve higher conversions while still maintaining target methane + ethane selectivity.

Potassium is a key component of the iron F-T catalyst; it influences both activity and selectivity. The way potassium works has been studied by many workers. In some work potassium has been added as potassium metal, particularly for work done on clean iron surfaces with potassium metal coverages up to about one monolayer. In other cases, such as actual F-T catalysts ionic potassium has been added. It should not be a surprise if these different types of potassium produce different results. During this contract means were developed to simplify addition of potassium ion. In so doing ways of achieving better selectivity control were also discovered.

There is considerable evidence from surface studies that carbon monoxide is adsorbed both intact and dissociatively by iron even at temperatures below those used for F-T processing. Private discussions with J. Rabo have expanded upon his findings during work leading to the two earlier-cited papers.[14, 15] In this work he found that under F-T conditions iron and cobalt catalysts cause dissociation of about 80% of the carbon monoxide, whereas with palladium only 0.1% is dissociated.

One mechanism which has been given for dissociation involves back bonding of electrons from the metal d-band into an antibonding orbital of carbon monoxide, thus weakening the carbon-oxygen bond. Anything which enhances the d-band electron density, such as metallic potassium, will facilitate this backbonding. In addition, donation of electrons to the d-band will enhance the bonding of carbon and oxygen to the surface, also contributing to cleavage of the carbon-oxygen bond.

Many experiments have been done to elucidate the mechanism of the F-T reaction. Within the last decade most workers seem to have concluded that the body of experimental evidence favors the dissociative mechanism of Rabo whereby the initial step is cleavage of carbon monoxide into iron carbide and iron oxide as above. Quite a bit is known about the subsequent steps, for instance, measurements have been made of initiation and propagation rates and very good product analyses have been done. However, the nature of these steps is not as clearly known as that of the initial step. An understanding of the factors which control the propagation step is particularly required to prepare more selective catalysts.

Hoffmann has attempted to close the dissociative mechanism with a series of steps resulting from careful development of a model based on extended molecular orbital theory. He involves the d-band electrons of the metal surface. Hoffmann does not discuss the role of potassium, however, an attempt will be made herein to understand how potassium affects the catalyst in terms of Hoffmann's picture.

According to Hoffmann, the critical propagation step is dependent upon the migration abilities of adsorbed alkyl and carbenoid species which result from hydrogenation of the metal carbide formed during the dissociation step. The migratory aptitudes are affected by the extent of filling of the metal d-band; Hoffmann's calculations indicate mobility is lower for higher d-band filling. Since longer carbon chains are expected from higher mobilities, and since in going from left to right across the transition metal series (Fe—>Co—>Ni) the d-band is being filled, one expects to see progressively shorter chains across this series. This is observed; nickel, in fact, is usually considered a methanation rather than an F-T catalyst.

One would like to understand the effect of potassium on the iron F-T catalyst in terms of the

Hoffmann model. It is known that potassium salts cause longer chains to form on iron. If only d-orbital filling needs to be invoked to explain this, then the effect caused by ionic potassium is to remove electrons from the d-band. Work cited above with potassium metal indicated that carbon-oxygen bond cleavage in carbon monoxide is facilitated by electron donation from potassium metal. If potassium salts do, on the other hand, subtract electron density from the metal d-band they cannot facilitate carbon-oxygen bond cleavage by the above mechanism. One must, therefore, derive an alternate explanation for the shift and F-T reaction rate enhancements observed in most cases from low to medium levels of potassium salts.

Contemporary thinking is that physisorption of carbon monoxide onto the working catalyst is slow compared to carbon-oxygen bond cleavage. In this context an increase in the overall rate would result from an increase in the rate of physisorption of carbon monoxide which, in turn, will depend upon the rate at which it can displace the species which cover the surface and which are expected to be mainly reaction products such as olefins. Carbon monoxide is more polar than those products which it has to replace. The flow of electrons from the iron d-band to potassium cation might make the surface less nucleophilic (basic) and reduce the ability of the surface to hold the relatively non-polar reaction products. This mechanism would have to be further modified to explain why high levels of potassium ion begin to cause loss in catalyst activity.

In the work with potassium laurate it was shown that low levels of potassium effectively catalyze the shift reaction but not the F-T reactions. This likely indicates a less complex active site for shift catalysis, for instance, one including just one potassium ion. Thus every potassium added initially can produce another active shift catalysis site. On the other hand, two or more potassiums in near proximity might be required for a F-T active site. Such sites would only begin to form in quantity at relatively high levels of potassium.

The loss in activity with high levels of potassium carbonate-derived potassium might be due to loss of catalyst active sites by making them too concentrated in potassium, e. g., maybe two or three proximal potassium ions are good but four or more are bad. The key finding with potassium laurate was that even at high potassium levels activity was maintained. This indicates that the laurate anion, when it is present instead of the oxide anion, causes a change in catalyst properties, perhaps by sterically separating proximal potassiums. This certainly is not the only possible explanation. For instance, if cationic potassium effects activity and selectivity by an electron effect such as above, it stands to reason that different anions would have the ability to modify this electronic interaction.

Performance results during this contract are summarized in a set of conversion/selectivity plots attached as Figures 153 to 159. Such plots allow different catalysts to be compared in such a way that changes in selectivities with conversion are taken into account. It is known that at high conversion selectivities to light products increase. The hydrogen/carbon monoxide usage ratio is less than the feed hydrogen to carbon monoxide ratio, resulting in a hydrogen rich environment at high conversions. It is reasonable that this might favor formation of higher hydrogen content products such as low molecular weight hydrocarbons.

The key catalyst performance target of this contract is low methane + ethane selectivity (≤ 5 mole %) at high conversion (88% CO + H_2). The most important of the attached plots are, therefore, those which compare methane and ethane selectivities. For instance, Figure 153 contains data pertaining to methane selectivities for a series of catalysts resulting from use of either potassium carbonate or laurate. High potassium levels result in the lowest methane selectivities. Unfortunately, high potassium also usually means lower activity necessitating heroic means such as above target temperatures or below target feed rates to achieve high conversion. However, one high potassium catalyst maintained high activity while still exhibiting low methane selectivity. It resulted from impregnation/calcination of a small amount of potassium (1 g : 100 g iron) followed by periodic additions of a solution of potassium laurate in isopropanol/heptane. This catalyst evinced a low ethane selectivity (Figure 154). It was superior to high potassium catalysts resulting only from impregnation/calcination of potassium carbonate or addition of potassium laurate, although in the latter case the superiority was only in conversion activity. The catalyst resulting from addition of a solution of potassium laurate to a potassium-free catalyst exhibited low methane selectivity at high potassium level and high conversion when the high conversion was obtained by increasing the temperature. This was surprising because temperature increases usually cause big increases in a catalyst's intrinsic methane selectivity, temperature increases, therefore, are usually avoided as a way to increase conversion.

Other selectivities are summarized in Figures 155 to 160. These show that the conclusions formed above with methane are similar to those with other paraffins up to butane. Alkene selectivities, on the other hand, do not seem to be affected much by the different methods of potassium addition.

A key finding of this phase of the work was that a combination of potassium carbonate impregnation/calcination followed by addition of a solution of potassium laurate resulted in low methane and ethane selectivities and also high activity even at high potassium levels. A second finding was that addition of all the potassium as a potassium laurate solution during a run produced a lower selectivity catalyst at a given conversion and potassium level than addition of all the potassium as potassium carbonate. Unfortunately in this case the activity was low even at a high potassium level.

The use of other organo-potassium salts produced less striking results. Use of a solution of potassium nonylphenolate during a run with a catalyst initially containing 1.0 g potassium/100 g iron from potassium carbonate impregnation resulted in changes in conversions and selectivities that somewhat mirrored the changes due to addition of a solution of potassium laurate to a similar catalyst, however, the magnitudes of these changes were much smaller with potassium nonylphenolate. A potassium benzoate solution was also used in one run. In this case there was no change in the conversion or hydrocarbon products, but there was an increase in the selectivity to carbon monoxide.

Pretreatment with carbon monoxide resulted in more active catalysts than ones activated with synthesis gas. The reason for this is not clear although it is known from work using clean metal surfaces that different crystal planes have different abilities to catalyze bond cleavage, for instance, carbon-oxygen bond cleavage. It is possible that the iron carbide phase(s) present after carbon monoxide activation are different from the phase(s) present after synthesis gas activation. Presumably the University of Kentucky studies being done under their DOE contract will provide comparisons of the products from various types of iron oxide reductions via Moessbauer and other techniques.

The first of the two carbon monoxide activations was performed with potassium, as potassium laurate, present at the start. The second such activation had no potassium present at the start and, as expected, the catalyst was only slightly more selective for light end products. The activity with and without potassium, however, was not greatly different. The potassium laurate solution was added intermittently during the run with the initially potassium-free catalyst. These additions initially resulted in slightly increased catalyst activities, but eventually appeared to cause activity loss. The maximum carbon monoxide conversion during the potassium additions was 93% which was the highest achieved during this work. During the potassium additions, as the conversion increased, a small decrease in the methane selectivity was noted, but there was virtually no change in the other light end product selectivities. Overall, potassium seems to have less affect on a carbon monoxide activated catalyst.

Conversion/selectivity plots comparing results from the earlier synthesis gas activation to the first of the carbon monoxide activations (C_1, C_2, and C_3 hydrocarbons) are in Figures 160 to 164. When plotted on this basis both the ethane and propane selectivities seem higher than would be expected from continuing the curve resulting from the earlier work when potassium laurate was added at the start with a synthesis gas activated catalyst. The methane selectivity, although high, appears to fall on the continuation of this earlier line. It would appear that carbon monoxide activation produces a fundamentally different material than synthesis gas activation.