DIVISION 5. Results.

Section A. Preparation and Characterization of Inorganic Oxide Modified-Carbon Molecular Sieves.

In this research program we have sought to prepare novel shape-selective materials comprised of carbon molecular sieves and selected inorganic oxides, which we refer to as Inorganic Oxide-Modified Carbon Molecular Sieves or IOM-CMS materials. Using the IOM-CMS materials and the methods developed to prepare them, we prepared IOM-CMS versions of both supported and unsupported catalysts and began testing these materials in the Fischer-Tropsch reaction for lower levels of wax production. In this section we describe the results of our investigation into the preparation and characterization of the different types of IOM-CMS materials.

An incentive for conducting this investigation was that in the proposed IOM-CMS materials we would be able to combine the best properties of both inorganic oxide support media with the molecular sieving properties of the carbon. The inorganic oxides, such as alumina, silica, silica-alumina, titania, and titania:zirconia have a variety of desirable and flexible properties not available with pure carbon. These variable properties include: surface areas, macro- and mesopore structures, metal support interactions, acidities and basicities. In contrast the polymer-derived carbon molecular sieves had the ultramicroporosity needed to provide for molecular sieving but are relatively inert and offered little in the way of variable acidity/basicity or metal support interactions. Therefore it seemed logical that a combination of the two materials into one composite sieve could offer the best aspects of both and possibly synergistic properties uncharacteristic of either alone.

With the potential features in mind, we proceeded to conceptualize three separate types of IOM-CMS materials.

Type I IOM-CMS Materials. The Type I material would be comprised of a large (8x18 mesh) particle of the inorganic oxide surrounded by a shell-coating of the molecular sieving carbon. In this way the inner non-sieiving particle would be surrounded by a molecular sieving gate of carbon. Molecular communication to the inorganic oxide would then be regulated by the pore restrictions of the carbon. However once through the gate the reactants or adsorbates would experience the same catalytic environment present in the untreated inorganic oxide. In many respects the structure of the Type I material is similar to that of the all-carbon composite molecular sieves first prepared and characterized by Walker and Metcalfe, in which a molecular sieving overlayer of polymer-derived carbon was deposited on particles of porous active carbon, rendering the combination a molecular sieve.[8 b,c]

The Type I materials are prepared by building a carbon overlayer in a series of successive steps. The steps involve contacting the particle of the inorganic oxide with polyfurfuryl alcohol, draining off the excess, heating in a flowing inert gas to convert the resin to carbon. These steps are repeated until a sufficient amount of carbon has been added to produce the desired molecular sieving properties. The latter are diagnosed phenomenologically by adsorption of various sized molecules.

In order to investigate the preparation of the Type I, IOM-CMS materials we included the following support and catalytic materials : silica, spheres and 8x18 mesh particles, alumina, silica-alumina, silica-supported iron, silica-supported potassium-promoted iron, titania, titania-zirconia, ruthenium/silica, precipitated iron Fischer-Tropsch (FT) catalyst (Fe_2O_3:CuO:K_2O), combined precipitated iron FT catalyst and hydrocracking catalyst (3% CoO-15% MoO_3/ Al_2O_3). The specific details of the preparations of these materials are described in the experimental section.

The results of the molecular probe analyses on these materials are displayed in Table 5, as a function of the number of cycles of carbon coating that they were given. The first two entries are for the silica spheres and the large pore, 8x18 mesh silica particles. In both of the materials in their untreated states the specific adsorption of all the probe molecules is quite high. By coating with the carbon the adsorptivities of the probe molecules dropped with coating step. After twelve carbon coating cycles both materials adsorb CO_2, in reasonably high quantities comparable to that of the untreated oxide itself, but the adsorptions of the larger hydrocarbon molecules are negligible. We also note that the CO_2 surface area increases with carbon content. This is not surprising since the added carbon contains ultramicroporosity that provides very high surface area, and the potential for capillary condensation of the carbon dioxide.

Based on these results the materials behave similarly to a 3A zeolite, adsorbing only the CO_2. Similar results were observed with the other samples of inorganic oxides, with differences in the number of carbon coating cycles necessary for the material to be converted to a molecular sieve and the extent of the sieving produced (see Table 5). It is interesting to note that the alumina sample in the form of Trilobes (Cyanamid Trade Mark) did not become sieving, to any appreciable extent, even after ten cycles of carbon coatings (see Table 5). We also noted that the measured N_2 BET surface area of the carbon coated samples dropped considerably compared to the untreated inorganic oxide. It is likely that the actual measurable surface area did not drop, but because of the molecular sized pores in the carbon, the kinetic rate of adsorption is effectively lowered and the process may have become activated, as is often the case for microporous carbons. It is likely, then, that the time-frame and temperature regime used for these nitrogen adsorption experiments is inadequate for the full adsorption to occur, and as a result the measured adsorption is considerably lower than the real value. As a way to estimate the effective N_2 BET surface

area of the carbon coated samples, we plotted the known, and verified N_2 BET surface area against the CO_2 specific adsorption for the untreated inorganic oxides (see Figure 5). With this plot we can estimate the BET surface area that the IOM-CMS material would have from its measured CO_2 adsorption.

These results indicate that a wide variety of inorganic oxides with markedly different chemical compositions, physical properties and forms can be converted into IOM-CMS materials. We also noted that for the majority of the inorganic oxides used, the onset of molecular sieving began after 8 carbon coating cycles. This suggested that a relationship existed between the weight percent of carbon present and the molecular sieving properties of the materials. Furthermore it seemed likely that the amount of carbon needed to bring about the sieving properties, might depend to some extent on the surface area and pore structure of the particular inorganic oxide.

In this investigation we sought to determine how the carbon content of the IOM-CMS materials changed with each successive carbon-coating step. It was important to relate this to the way in which the specific adsorption of the probe molecules changed with the additional carbon. We also obtained the nitrogen adsorption isotherms on each sample after the successive coating and pyrolysis steps.

In order to address the question of how the physical properties of the inorganic oxide influenced the onset of molecular sieving, we chose to focus upon two samples that had very different surface areas and porosities. We focused on titania pellets (approximately 1/8" diam. x 3/16" L, 60 m^2/gm) and large-pore silica particles (8 x 12 mesh, 300 m^2/gm). We prepared the titania by hydrolysing titanium(IV) butoxide (Alfa Products, # 77124) and then calcining this at 500°C for two hours in air. The titania powder was then pelletized. The large pore silica was use as purchased (Alfa Products, #89346, 8 x 12 mesh).

The oxides in these forms were then successively immersed in polyfurfuryl alcohol resin, drained, and carbonized by pyrolysis at 550°C in flowing nitrogen. These steps were repeated twelve times. After each step the new material was weighed and the amount of carbon added in that step was calculated by difference. Representative samples were saved from each step. A portion was then burned in flowing air, and the residual oxide was carefully isolated and weighed. The difference in weight before and after burning gave the total amount of carbon present on the sample at that point in the preparative cycle. With both of these methods the amount of carbon produced in each carbon-coating and pyrolysis step could be calculated. The data from these experiments for the titania and silica materials are collected in Tables 6 and 7. Clearly, there is good agreement between the percent carbon calculated by the two different methods for each of the samples.

The next part of the study was to determine the change in the specific adsorptivities of these probe molecules on each of the samples as a function of the carbon content and coating number. These results are plotted in Figures 6 and 7 for titania and silica, respectively. In both cases the carbon dioxide adsorption increases with the addition of carbon. This is because the added carbon is microporous and has surface area accessible for carbon dioxide adsorption. As the carbon content increases the adsorption of the larger probe molecules drops.

In general we have noted that eight coatings were usually needed to induce molecular sieving properties in the Type I IOM-CMS materials. These data show that at the eighth coating the carbon dioxide adsorption becomes larger than that for the other probe molecules. These two observations seem to correlate well. However, with titania the eighth coating step corresponds to only 30% carbon, while on silica it corresponds to 43-49% carbon. Our interpretation of these data is that the carbon deposits on the surface of

the oxidic particle and it must reach a minimum value before it can begin to cover the inner pores of the inorganic oxide. Above this minimum value of carbon content the inner inorganic oxides are rendered inaccessible to adsorbate molecules larger than the pore size of the deposited carbon.

In order to gain further insight into the formation of the Type I IOM-CMS materials we obtained nitrogen adsorption isotherms on the titania and silica samples. Figures 8a- e and 9a-f show the nitrogen adsorption isotherms as a function of carbon coating step, i.e. carbon content, for the titania and silica samples, respectively. These data show that as the carbon content increases on the individual oxides the nitrogen isotherm shows more historesis between the adsorption and desorption loops. After twelve coatings the separation between the adsorption and desorption cycles is large for both of the samples. It is noticable that the titania sample shows this effect after the second coating with carbon, while the silica shows no effect even after the third coating. This may be explained as follows: the titania has larger pores and lower surface area than the silica by more than a factor of six. This means that less carbon is needed to cover this area, and it can begin to cut-off the inner pores sooner than it can with the silica.

Finally, we also investigated the time dependencies of CO_2 adsorption and desorption on a Type I, IOM-CMS material in this case the C-FT:HC(1:1) catalyst. The data in Figures 10 and 11 show the adsorption and desorption data respectively for the uncoated and coated (8 cycles) versions of the catalyst. The data indicate that the adsorption and desorption kinetics are slower for the IOM-CMS sample than for the raw catalyst.

Type II IOM-CMS Materials.

Type II materials were conceptualized as a dispersion of very fine inorganic oxide particles, distributed throughout the carbon matrix. This is in contrast to the form of the Type I

material in which the inorganic oxide particle is large and in effect supports the carbon molecular sieving shell. We have found that the Type II materials can be prepared in two different ways. In the first method a hydrolytically unstable metal alkoxide compound, used as a precursor to the inorganic oxide, was mixed with the polyfurfuryl alcohol resin. The mixture was then pyrolyzed under flowing nitrogen in a tube furnace using the following heating cycle: 100°C for 1 hr, 30 min each in 100°C increments from 200°C to 600°C, 600°C for 3 hr. Following the heat treatment the samples were crushed and screened to retain the 40x80 mesh particles for molecular probe analysis.

In order to determine the composition of the Type IIa materials the samples were oxidized in air. This was done to burnoff the carbon and leave behind the oxide generated from the hydrolytically unstable alkoxide precursor in the pyrolysis step. By careful weighing before and after the oxidation process, the amounts of carbon and inorganic oxide could be calculated for each sample. The results of these analyses, as well as the metal alkoxide and polyfurfuryl acohol conversions, are collected in Table 8 for the Type IIa materials. The titania series ranged in oxide content from 9 to 63 wt%, the zirconia series: from 12 to 30 wt%, the alumina series from: 13 to 40 wt%, and the titania-zirconia series: from 10 to 26 wt%. We noted in the course of this analysis that the carbon yield from polyfurfuryl alcohol improved in the presence of the metal alkoxide versus that for the pure resin. In the case of Ti(IV) butoxide, the carbon yield was observed to go as high as 50 % (weight carbon produced/ weight resin used), versus typical yields of about 25 % for the resin alone. With the other alkoxides used the effect was not as great, leading to yields of about 30-35 %. This enhanced carbon yield may be catalysed by the metal alkoxides, possibly causing either more efficient dehydration or crosslinking of the resin, or both.

Molecular probe analyses of the Type IIa materials demonstrated that all of these materials were molecular sieves (see Table 5). They all adsorbed nearly as much CO_2 as the pure

carbon alone, but nearly zero amounts of the larger probe molecules. Based on this we would classify these materials as 3A type sieves. It was somewhat surprising to discover that we could increase the metal oxide content to over 60 wt% and still find the same molecular sieving properties as in the pure carbon sieve. This result suggests that the metal oxides are in the form of very highly dispersed particles.

The Type IIb IOM-CMS materials were prepared by mixing fine powders of the metal oxides with PFA. The metal oxides were prepared by hydrolysis of the same metal alkoxides used in the preparation of the Type IIa sieves. The powders were mixed in different weight ratios with the polfurfuryl alcohol and then pyrolyzed in the usual way following either of these heating cycles: 100°C for 1 hr, 200°C for 1 hr, 300°C for 2 hr, 500°C for 6 hr; or ramp at 20°C/min to 500°C, 500°C for 2 hr, ramp at 20°C/min to 600°C, 600°C for 6 hr.

Carbon burnoff experiments were also used with the Type IIb samples to determine the carbon and inorganic oxide contents of these materials. The same analyses were performed as with the Type IIa materials (see Table 9). In the titania series the metal oxide content ranged from 46 to 61 wt%, the zirconia series: 32 to 60 wt%, the titania-zirconia series: 38 to 44 wt%. As expected the addition of the oxidic powders did nothing to improve the yield of carbon from the resin.

Molecular probe analyses of the Type IIb materials adsorb significant quantities of CO_2 and n-butane, but nearly zero amounts of the two larger probe molecules (see Table 5). At the first level this could imply that these materials behave similarly to the 4A molecular sieves. To verify this more rigorously further testing with these samples would have to be done. However it is remarkable that these Type IIb materials adsorb more of n-butane than the Type IIa materials. It may be that the addition of the fine oxidic particles leads to interstices

that can adsorb these larger molecules and which do not form in the preparation starting with the metal alkoxides.

To further describe the properties of these IOM-CMS materials, the adsorption of water was determined on various samples , including Type I, IIa and IIb samples. It is important to know the water adsorption isotherms, since the IOM-CMS materials can also be viewed as new adsorbent materials and water adsorption is a standard method of comparison between adsorbents.

The water adsorption data are displayed in Figure 12 for IOM-CMS materials, their native oxide bases and zeolite 3A. Clearly the zeolite is the best adsorbent, showing the characteristic nonlinear adsorption of water even at the low partial pressures. The three Type I samples, SiO_2-Al_2O_3, SiO_2 beads, and large pore SiO_2, carbon-coated 10, 12, and 12 times each, adsorbed water similarly to the carbon alone. (This pure carbon sample was plasma-treated, but we found that this had no effect on its adsorptive properties.) The most interesting sample is the Type II IOM-CMS Al_2O_3- carbon sample. This material has a distinctly different water adsorption isotherm than the Type I materials, with some non-linear adsorption at the lower partial pressures. Although much lower on an absolute scale this is reminiscent of the zeolite sample. The water adsorption behavior of the IOM-CMS materials, especially of Type II, deserves further scrutiny.

The Type III materials were conceptualized to be like the Type I, and Type IIb materials, except that the inorganic-oxide was first dispersed on a porous carbon support. Then this surface-modified carbon was to be either shell-coated with polymer-derived carbon, mimicking the Type I system, or mixed with the resin as a fine powder, following the Type IIb approach. In the experiments that we were able to conduct with the Type III materials,we followed the latter approach of dispersing the powder in the resin.

The molecular probe analyses of the nine Type III samples are very interesting (see Table 5). The three sets of samples each show the same trends. At the lowest ratio of polymer resin to surface-modified porous carbon the materials all behave as 4A type molecular sieves, adsorbing relatively large quantities of CO_2 and n-butane, but nearly zero amounts of the isobutane and neopentane. This holds for the both the titania-modified wide pore carbon and the Raven 8000 beads, and the zirconia-modified Raven beads. At the middle ratio of polymer resin to base material, the two titania-modified samples display 3A type molecular sieving properties, adsorbing CO_2 in large quantities, but only negligible amounts of the other, larger probe molecules. The zirconia-modified Raven 8000 beads, behave more like the 4A sieve even at this middle ratio of polymer resin to surface-modified carbon base. At the highest ratio of polymer resin to surface-modified carbon base, all three of the samples display the 3A sieving properties.

These Type III results, combined with those obtained for the Type IIa and b samples, further reinforce our contention that by proper control of the inorganic oxide precursor chemistry, and the physical properties of solid additives we may be able to control the molecular sieving properties of the IOM-CMS materials with good precision.

Section B. Preparation and Testing of Metal-Modified Carbon Molecular Sieves Catalysts.

In this phase of the work we applied the information and techniques gained in the research devoted to the preparation and characterization of the IOM-CMS materials, to prepare new catalysts for testing in the Fischer-Tropsch reaction. The IOM-CMS catalysts tested were Type I and II materials, formed from suitable catalyst bases. The bases included fused iron (C-73), supported metals (Fe/SiO_2, $Fe-K/SiO_2$, Ru/SiO_2, $Rh-Mo/Al_2O_3$) and precipitated iron catalysts ($Fe_2O_3:CuO:K_2O$, $Fe_2O_3:CuO:K_2O-CoO-MoO_3/Al_2O_3$).

By preparing the catalysts first and then converting them into the IOM-CMS materials, we were always able to test the untreated catalyst against the carbon-coated catalysts. By carefully reproducing the conditions and monitoring the products, we were able to access to what extent the carbon affected the selectivity of the catalysts.

C-73 (United Catalysts) is a fused iron catalyst, with very low surface area, limited largely to the geometric surface area of the catalyst particles. The carbon-coated C-73 samples were prepared to ascertain whether or not the carbon overlayer and the process of forming this layer would affect the catalytic activity deleteriously. This was a good experiment because the C-73 sample has most of its active sites on the surface of the catalyst, where they are accessible to the resin precursor, and a large percentage would likely be covered by the carbon. Hence any chemically- or physically- induced poisoning of these sites by the carbon, would be expected to produce a more drastic effect in this catalyst than in one in which the active sites were buried in pores and not covered by the carbon.

The difficulty in this experiment is that there is no way to prove whether or not the carbon overlayer continuously covers the surface of the C-73 particles. In the case of the IOM-CMS materials prepared from high surface area supports, the molecular probe analysis is useful because a sufficient amount of adsorption occurs to determine the degree of sieving. With the low geometric surface area of C-73 this does not occur (5 mg/gm CO_2).

Therefore we have no way to determine the actual degree to which the surface is covered with the carbon. This leaves open the possibility that the synthesis gas may react on uncovered sites. Yet the experiment still provides important insight because if the covered sites were poisoned then we would expect activity to be correspondingly lower. Our

approach was to build up the carbon in a series of steps to try and insure complete coverage, and then test. The test results are given in Table 10.

It is evident from the data that the carbon-shell coating on C-73 does not lead to any major dimunition in activity. Under a variety of conditions the carbon-coated catalysts gave high conversions comparable to that of the uncoated sample. At 350°C, and 500 psig with 1:1 synthesis gas flowing at 50 sccm, the two carbon-coated C-73 samples gave CO and hydrogen conversions of 83%, and 39%, and 84%, and 72%, respectively. Under the same conditions the uncoated C-73 sample gave conversions of 72%, and 42%. The overall hydrocarbon yields were also comparable. Anderson-Schulz-Flory plots were constructed from the data (see Figures 13 a,b) for selected runs of the C-73 and carbon-coated C-73 catalysts (runs No. 10, C-73, and Nos.12-15, carbon-coated C-73). The plots are virtually the same indicating that the carbon has not affected the selectivity.

This result indicates that the carbon coating did not lead to any dimunition in activity or a change in the selectivity. This suggests that all the sites are evenly covered by carbon and the synthesis gas can migrate through the carbon overlayer to the active sites beneath it.

In the C-73 samples the possiblity of fissures leads to some question regarding the result. We thought the next experiment to complement the C-73 experiment would be to carbon-coat a simple supported metal catalyst. With this system we would be able to prove if the sample were a molecular sieve after numerous carbon coatings, by the simple molecular probe analysis. Also the contacting or adhesion of the carbon to a porous oxidic support like silica seemed more likely to be more robust than to the fused iron catalyst.

We prepared a 20 wt% Fe/SiO_2 catalyst in the usual way by contacting the support with a salt solution of the iron to just fill the available pore volume. The catalyst was dried, and

calcined at 300°C in air. The batch was split in half. The first half was retained as a control; the second half was carbon-coated to produce a Type I IOM-CMS catalyst. Molecular Probe analysis indicated that the sample was a molecular sieve (see Table 5).

The control and IOM-CMS catalysts were run in two separate but equivalent runs. The results are collected in Table 11. The results of these runs indicate that the IOM-CMS version of the catalyst was as active and under some conditions more active than the control catalyst. This combined with the results from the C-73 catalyst runs show that the process of carbon-coating does not have an effect on the activity of the catalysts. However, since this catalyst base made mostly methane we could not access the effect of the carbon on the selectivity.

The next step with the supported metal catalysts was to try and extend the product distribution out to a molecular weight region where the carbon might have an effect on the selectivity. To do this we prepared Fe-K/SiO$_2$, and Ru/SiO$_2$. Both of these catalysts were expected to produce more of the long chain hydrocarbons than the Fe/SiO$_2$.

Both catalysts were prepared by pore volume saturation of the supports with suitable solutions of the metal salts, air drying, and calcination at 300°C. The metal loadings on the two catalysts were: 20 wt% Fe, and 20 wt% K, and 3.5 wt% Ru, respectively. (The iron catalyst was prepared on the Aldrich large pore silica; the ruthenium catalyst was prepared on Aldrich silica gel spheres).

In both cases a portion of the catalyst was retained as the control and a portion was carbon coated to produce the Type I, IOM-CMS materials. These samples were found to have molecular sieving properties in the molecular probe analysis.

The Fe-K/SiO$_2$ system was tested first. The uncoated control catalyst was run at four different combinations of temperature and pressure. The test catalyst was then run under equivalent conditions. Data for runs 18-2-1, and 19-2-1 were analyzed and are collected in Table 12.

Here again, we observe that the cataysts are of nearly equal activity, converting CO and H$_2$ at approximately 15-16%, and 5-6% respectively.The Anderson-Schulz-Flory plots for these two runs are displayed in Figures 14a and b. The deviations from linearity suggest a double alpha mechanism like that described by Satterfield may be operative.[36] It is clear in this example that the ASF plots are essentially the same over the wide product distribution for the uncoated and IOM-CMS versions of the catalyst. Some slight deviations in selectivity are noted at the lighter end of the product spectrum. The control catalyst produces 18% C1, 38% C2-C7, and 44% >C7, as gram fractions of the total hydrocarbon products. The IOM-CMS version of the catalyst produces 26% C1, 56% C2-C7, and 18% >C7 (see Figures 15a and b).

Since the catalysts were prepared from the same materials and were tested under conditions that were kept as equivalent as possble, this may be evidence for some small change in selectivity, to favor the light hydrocarbons, due to the carbon molecular sieving layer. However differences this small can also arise due to actual differences in apparently equivalent conditions, or from slight mishandling of the products during workup or analysis.

The 3.5 wt% Ru/SiO_2 catalyst system was also tested. Unfortunately both the Type I, IOM-CMS version and the control were extremely poorly behaved, with low and unstable conversions, and surprisingly high methane yields. Since ruthenium is a good FT metal, behaving like potassium-promoted iron but with more activity, we expected that this catalyst would be a good choice. The support was a very high surface area silica gel bead with a nominal N_2 BET surface area of >600 m^2/gm. Even though we calcined the catalyst after impregnation with the metal salt solution, it may be that the silica gel had not yet become thermally stabilized. Thus further physical changes of the support during the test may have been, all or partially responsible for the poor behavior.

The last supported metal catalyst tested was 3 wt% Rh-2.8 wt%Mo/ Al_2O_3.The catalyst was prepared by chemisorbing $Mo(CO)_6$ onto the alumina, from degassed, and refluxing heptane solution. The material was filtered and dried in air at room temperature, then this was added to fresh degassed heptane. The mixture was brought up to reflux again and $Rh(CO)_2(acac)$ was added to the mixture. Uptake of the rhodium was rapid as evidenced by the loss of the dark green color in solution, and the change of color in the catalyst solids from white to dark red. The resultant material was again separated and air-dried on a suction filter. The powder was then pelletized, and stored without further treatment.

The catalyst was tested in hydrogen-poor synthesis gas (1:1.3: H_2:CO) at 250°C and at different pressures from 250 to nearly 1000 psig. The results of these runs and the conditions used are collected in Table 13. Conversions of carbon monoxide and hydrogen varied with pressure (see Figure 16). The drop in activity between 250 and 500 psig may be due to the second reduction that was done at 450°C, versus the first done at 350°C. The higher temperature may have lead to sintering of the metal, manifested by a drop in activity.

Above 500 psig the conversion levels increased nearly linearly to 13% at 970 psig. Each of these conversions was taken after the activity had leveled out.

Comparison of the product distributions at 250 and 970 psig shows that a change in selectivity has occurred, even though the activities are nearly equivalent (see Figures 17a and b). At the lower pressure the major products were: methane-30.1 mole%, and dimethyl ether-35.9 mole%. At the higher pressure the major products were: dimethyl ether- 58.5 mole%, and methane 18.5 mole%. In a similar way the minor products also showed some reversal in yields.

A plot of the ratio of the micromoles of dimethyl ether divided by those of methane as a function of pressure, shows that the dimethyl ether/ methane yield ratio varied linearly with increasing pressure. At 250 psig the ratio was just above 1, and at 970 psig it was over three. Since the dimethyl ether is a product of the acid dehydrolysis of methanol, the data indicate that at 970 psig the catalyst was actually making six times as much methanol as methane (see Figure 18).

Similarly, the overall oxygenate efficiency, taken as the ratio of the (total gms. oxygenate product/ total gms. hydrocarbon product), increases linearly with pressure from approximately one at 250 psig to over five at 970 psig (see Figure 19).

In order to understand the electronic and physical factors involved in the selectivity of this catalyst, we investigated it briefly with X-ray photoelectron spectroscopy. These data were collected on a sample of the 3 wt% Rh-2.8 wt% Mo/Al_2O_3 (see Table 14). The fresh sample displayed a Rh 3d 5/2 binding energy of 309.0 ev, and a molybdenum energy of 232.5 ev. Upon reduction in flowing hydrogen at 450°C the Rh levels dropped to 307.7 ev, and the Mo remained unchanged. Further reduction led to a final Rh level of 307.4 ev,

and again no change in the Mo levels. Exposure to carbon monoxide did not shift the levels of any of the metals. It is also noteworthy that the atom ratios did not change during reduction, indicating that no gross agglomeration occurred.

Although technologically and scientifically interesting, the decision was made to forgo any further testing of this catalyst unless time permitted at the end of the contract, since its product slate was not appropriate to the focus of this program.

The Fischer-Tropsch catalyst that we have tested and modified is the precipitated Fe_2O_3-CuO-K_2O prepared by the methods of Pichler.[37] The metals are Fe, Cu, and K each precipitated from their corresponding chloride salts.

The raw catalyst was formed into pellets approximately 1/8" O.D. x 1/4" L.
These pellets were converted into the Type I IOM-CMS versions of this catalyst by carefully building up a carbon molecular sieving layer with successive coating and pyrolysis cycles with polyfurfuryl alcohol (Durez resin). The method was previously discussed. The Type II IOM-CMS versions were prepared by mixing the powdered catalyst with the polyfurfuryl alcohol resin in specific weight ratios and then carbonizing. This material was reduced in-situ after loading in the reactor.

The trifunctional catalysts were prepared by ball-milling the precipitated iron catalyst with a 3% CoO-15% MoO_3/Al_2O_3 hydrocracking catalyst. This powder was then formed into pellets to prepare the control catalyst, the Type I version, and the Type II version in the same way as were the samples based on the iron catalyst alone. This resulted in two IOM-CMS versions of the catalyst with molecular sieving properties, and one version which was only carbon-coated only once, and the uncoated control of the FT catalyst.

Testing was conducted in the usual way. The IOM-CMS catalysts were tested at 250ºC and 250 , 500, 800 psig (1:1:CO:H$_2$). The raw catalyst was tested only at 250ºC, and 250 psig. The C-FT sample which was coated only once was tested over a range of temperatures from 250 to 340ºC, but at only 500 psig. Comparative results for Type I and II, IOM-CMS Fischer Tropsch catalysts (C-FT TY-I, C-FT TY-II) with the native FT catalyst and the C- FT catalyst that was coated only once (C-FT Non-Sieving) are collected in Table15 and Figures 20(a), (b), and (c).

The results show the Type I and II materials are as active as the native FT catalyst or the non-sieving C-FT catalyst. At 250 psig, and 250ºC, the CO and H$_2$ conversions are 23%, and 2.5% respectively for the Type I catalyst, 24.9 and 7.7% respectively for the Type II catalyst, and 36% and 15.1% respectively for the untreated FT catalyst. Hence as in the cases already reported for the carbon coated supported and unsupported catalysts, the carbon coating did not harm the catalyst's activity.

Not shown, however, is the fact that two previous runs were attempted with the native FT catalyst at 500 psig, but data could only be collected at 250 psig in a third run, and even under these conditions the experimental problems noted at the higher pressure were not completely overcome. The native FT catalyst was very poorly behaved at the high pressure conditions. It rapidly clogged and sintered, which led to a large pressure drop across the bed in excess of 150 psig. In contrast, the IOM-CMS materials were very well-behaved in the fixed bed mode under these conditions. They did not sinter, or clog, and could be run for extended periods over a wide range of conditions from 250 to 1000 psig, and from 250 to 340C. We found this difference to be technologically significant.

We note also that the IOM-CMS materials tend to produce lighter, C$_1$ to C$_4$, hydrocarbons (see Figure 21), in good yield (> 45%-54%), in comparison to the untreated FT catalyst

(less than or equal to 31%). Note that, in fact, the untreated FT catalyst probably, actually makes somewhat less C1-C4 hydrocarbon, because the value reported is based on the hydrocarbons recovered. Since the experiment was difficult to conduct with the catalyst clogging and waxes depositing in the reactor, it is likely that we lost a significant fraction of the heavier products. The low carbon balance (30%) supports this. Hence, the light products are actually over-accounted for in this product distribution and the difference between the IOM-CMS version and the uncoated version is even larger than it appears. The catalysts also have good overall activity for hydrocarbon production (170-180 gm hydrocarbon/m^3 synthesis gas).

The polymerization probabilities and degrees of polymerization reported in Table 15 are calculated from a linear least squares fit of the weight fractions of products from C_2 - C_6. (This is used throughout the data workups.) The IOM-CMS versions of the catalyst have polymerization probabilities in this carbon number region, which are nearly identical to those of the uncoated FT catalyst, ASF plots displayed in Figures 22 (a) and (b). Here, too, the same caution, previously mentioned, must be exercised when comparing to the results of the pure FT catalyst.

Of particular interest are the results obtained with the C-FT sample which was carbon-coated only once. The single coating of carbon leads to the same well-behaved, on-stream activity as displayed by the Type-I and Type-II, IOM-CMS samples. The activites, and selectivities are also very nearly the same as those for the IOM-CMS materials as well, (see Table 15, and Figures 21, and 22).

This is significant because it implies that the level of carbon necessary for the beneficiation of the FT catalysts behavior is relatively low, and thus less of the costly, polymer-derived carbon can be used to get the same effect.

At first this seems quite surprising. However, on further consideration we realize that the precipitated iron catalyst is a very low surface area material, even lower in surface area than the titania pellets that we converted to Type I, IOM-CMS materials. In the case of the titania we noted from the nitrogen adsorption isotherm that even after just two carbon-coating cycles, the adsorption/desorption isotherms showed marked historesis. This is evidence of a large amount of ultramicroporosity introduced by the carbon, and it dominates the adsorptive properties of the titania alone.

In the case of the precipitated iron catalyst the surface area is just as low (7 m^2/gm). Therefore, even after one carbon coating which has added as much as 30 wt% carbon to the system, may already be nearly as encapsulated in the molecular sieving carbon as the Type-I, sample that underwent at least 8 carbon coating cycles. Based on these arguments it is not surprising that the catalysts labelled Type I, IOM-CMS and the one labelled non-sieving actually behave so similarly.

We tested the trifunctional catalysts that combined the molecular sieving carbon with the Fischer-Tropsch and Hydrocracking functions. The concept is that the synthesis gas molecules can enter through the carbon molecular sieving core, and are converted on the FT sites to the usual distribution of products including long chain hydrocarbons. However, because of the barrier to mass transfer imposed by the carbon shell, these molecules cannot leave the interior of the particle. This effectively increases the probability of the long chain hydrocarbon encountering a hydrocracking site, where it can be converted into a short chain hydrocarbon, prior to diffusing out of the catalyst particle. In this way, each catalyst particle behaves like a mini-reactor with a Fischer-Tropsch and Hydrocracking zone. This concept is illustrated in Figure 23 and is distinguished from the mode of operation for the Type II materials.

The catalysts prepared and tested with the trifunctional design include the following:

C-FT-HC (1:1); Type I IOM-CMS

C-FT-HC (3:1); Type I IOM-CMS

C-FT-HC (6:1); Type I IOM-CMS

C-FT-HC (1:1); Nonsieving

FT-HC (1:1); No carbon

In each of these materials the FT portion is the Fe_2O_3-CuO-K_2O catalyst, first described by Pichler, and then by R.B. Anderson.[37] The hydrocracking portion is a 3% CoO-15% MoO_3/18%SiO_2-64%Al_2O_3 catalyst prepared by American Cyanamid. The catalysts were prepared by mixing the two powders in the correct weight ratio and then ball-milling these for 24 hrs. Next the powders were pelletized (3/16" D x 1/8" W). These were then carbon-coated with repetitive adsorption and pyrolysis cycles with polyfurfuryl alcohol. This led to three Type I IOM-CMS samples with 1:1, 3:1, and 6:1 FT:HC weight ratios. Another sample,1:1 FT:HC, was carbon-coated only once to test the effect of the formation and presence of a partial carbon coating, and one sample, also 1:1 FT:HC, was left uncoated to determine what effect the lack of a carbon coating would have on the catalyst's activity and selectivity.

In the first test 16.7 gms of the Type I, 1:1 FT:HC, IOM-CMS catalyst [C-FT-HC(1:1) TY-I] were loaded into the reactor and reduced in flowing synthesis gas (1:1:CO:H_2, 1 atm., 80 sccm.) at 325°C for 24 hrs. The reactor was pressurized to 500 psig with synthesis gas (1:1:CO:H_2), and the temperature was lowered to 250°C. Products were collected for 69.3 hrs. The temperature was raised in steps to 280, 295, 310, 325, 340°C,

and the condensible products were collected for 69.6, 69.3, 71.0, 72.0, 79.0 and 88.8 hrs., respectively and then analyzed. The data from this run are collected in Table 16.

The %CO conversion rose linearly from approxomately 5% at 500 psig and 280°C to almost 50% at 340°C (see Figure 24). The data indicate that over the temperature range tested the catalyst produced from 67 to 86% of its product between C1 and C4, from 29 to 10% between C5 and C11, from 1 to 2% between C12 and C19, and less than 4% above C19 (see Figure 25). From 123 to a maximum of 198 gms (at 295°C) of hydrocarbon were produced per cubic meter of synthesis gas converted. The ASF plots for four of the runs are plotted in Figure 26. The plots show a fairly linear drop between C1 and C7, then the curve falls less sharply between C7 and C11; it drops again between C11 and C14, then it falls very slowly above C14. However, above C11 the weight fraction falls below 10E-3. A linear least squares fit to the points between C2 and C6 yields a range of polymerization probabilities from 0.56 to 0.34.

In the next two tests we kept the 1:1FT:HC base constant, and varied the amount of carbon present on the catalysts. The first catalyst, C-FT-HC(1:1) Non-Sieving, was prepared by coating the base once with a carbon overlayer. This may not completely convert the catalyst to a molecular sieve, and that is why we refer to it as "Non-Sieving". However, the 1:1FT-HC catalyst has15% carbon after one coating, a level very close to that of the titania sample after one coating. The surface area and particle size distribution of 1:1FT-HC is probably close to that of the carbon-titania Type-I sample. Adsorption of enough PFA to yield 14% carbon on the first coating of the titania, produces a significant change in its pore properties (see the N_2 adsorption isotherms, Figure 8a-f). Additional carbon further affects the pore properties of the titania but the major change is due to the first carbon-coating. Based on this, and the fact that the FT-HC base has even lower surface area than the titania, we might expect that first carbon coating on 1:1FT:HC would also greatly affect the pore properties

and, hence, the selectivity of the catalyst to nearly the same extent as the heavily coated Type I, 1:1 FT:HC, IOM-CMS catalyst. If it does, then this would imply that less of the expensive carbon coating could be used on low surface area catalysts, such as this one, to get the desirable effects of multiple coatings.

We tested the C-FT-HC(1:1) Non-Sieving and also the FT-HC (1:1) Native sample, which did not have carbon on it. The reduction and test conditions were kept the same as those used with the C-FT-HC(1:1) TY-I catalyst. In each run the amount of active catalyst, not including the weight of carbon, was kept constant. The data for these two catalysts are collected in Tables 17 and 18.

The C-FT-HC(1:1) Non-Sieving catalyst gave a 10% CO conversion at 250°C and this rose to 60% at 340°C (see Figure 27). The FT-HC (1:1) Native also gave an initial CO conversion of 10% at 250°C, but this rose to nearly 80% at 340°C (see Figure 28). The latter catalyst is nearly twice as active as the C-FT-HC(1:1) TY-I catalyst at every temperature, while the former is about 10 to 15% more active at points above 250°C. All three of the catalysts display similar selectivities above 250°C with 70 to 85% of the product falling in the range from C1 to C4 (see Figures 29 and 30). At 250°C the C-FT-HC(1:1) TY-I and C-FT-HC(1:1) Non-Sieving catalysts yield 64 to 67% from C1 to C4, 26 to 29% from C5 to C11, while the native sample yields 81% C1 to C4 and 16% C5 to C11. At the higher temperatures any effect of the carbon is apparently swamped out by the activity of the hydrocracking catalyst, which in essence tends to level their selectivity. However, at the lower temperature the samples with either one or multiple carbon coatings tend to give the same selectivity. Interestingly, at 250°C the carbon-coated materials yield less of the very short chain hydrocarbons than the uncoated material, at nearly the same conversion levels. At this point we can only speculate that this occurs through a different

global mechanism for long chain hydrocarbon formation with the carbon-coated samples versus the uncoated samples.

The C-FT-HC(1:1) Non-Sieving produces from 104 to 145 gms hydrocarbon per cubic meter of syngas converted, a value consistently lower than the C-FT-HC(1:1) TY-I catalyst. In the same way the FT-HC (1:1) Native produces 111 to 169 gm hydrocarbon per cubic meter of syngas converted but at consistently higher CO conversion levels. The ASF plots for these two catalysts are very similar to the plots for the C-FT-HC(1:1) TY-I (see Figures 31 and 32). Based on the sum of these data we decided to prepare catalysts with higher ratios of the FT:HC portions.

C-FT-HC(6:1), TY-I and C-FT-HC(3:1), TY-I were prepared for testing. The catalysts were pretreated as before, and the mass of total active phase was kept constant, relative to the uncoated catalyst. The data for these two systems are collected in Tables 19 and 20. The CO conversion activity of the C-FT-HC(6:1), TY-I catalyst started at 10% at 250°C and rose to 70% at 310°C, but then it fell back to 50% at 340°C (see Figure 33). This may have been due to a physical deactivation process. Hydrocarbon production varies from 124 to 171 gms hydrocarbon per cubic meter of syngas converted. The selectivity is different than that of the other FT:HC catalysts. The formation of higher hydrocarbons is shown in the gram fraction charts (see Figure 34), but it is still at a relatively low level. The ASF plots for this catalyst are displayed in Figure 35. There is a small difference evident in the plot versus the other FT-HC catalysts, namely with respect to the weight fraction of the higher hydrocarbons.

The final catalyst tested was the C-FT-HC(3:1) TY-I, which was of an intermediate composition. Due to operator error this catalyst was probably slightly reoxidized after its initial reduction. Hence if we look at the data for the first temperatures tested up to 340°C

(see Table 20 and the first four points of Figure 36), the catalyst was particularly low in activity at 250 and 280°C, and then rose rapidly to over 50% CO conversion at 340°C. The gram fractions and ASF plots of these runs are displayed in Figures 37 and 38, respectively. Deviations in the ASF plot were noted in this data, especially at 280°C. However due to the reoxidation question the catalyst was rereduced and the run repeated. The CO conversion data for these points are collected in Figure 36. The activity of the catalyst was markedly better after the second reduction. Clearly the fraction of products between C1 and C4 (see Figure 37) is less than that observed with the 1:1FT:HC series of catalysts. The ASF plots for the second set of data points (see Figure 38) indicate that the higher hydrocarbons are being cracked more efficiently than on the 6:1:FT:HC catalyst. After C9 the weight fractions fall off to less than 0.001.

We were also curious about what effect a higher hydrogen to carbon monoxide ratio would have upon the activity and selectivity of the catalyst. As can be seen from the last four points in Figure 36, the CO conversion activity is actually slightly lower in the hydrogen-rich feed. As would be expected the products are shifted substantially toward the C1 to C4 fraction at the lower temperatures (from 55-65% at 1:1:CO:H2 to 70% at 1:3:CO:H2, see Figure 37). ASF plots are included for the products of this feed for 250 and 265°C (see Figure 39).