DIVISION 1: EXECUTIVE SUMMARY

In September of 1984 the Department of Energy granted a two-year contract to the American Cyanamid Company to investigate and develop carbon molecular sieve-based catalysts for the reduction of carbon monoxide with hydrogen. It was speculated that the molecular sieving nature of the carbon might lead to novel shape-selective properties, which with the correct catalyst design and process conditions might lead to a suppression of wax formation and an increase in the gasoline or diesel yield.

At the time that this program was proposed it was generally recognized that a primary thrust of research in the direct reduction of carbon monoxide with hydrogen should focus upon an exploration of shape-selective catalysis.[1] Shape-selective catalysts offered the potential of circumventing the normal polymerization processes evidently operative in the classical Fischer-Tropsch catalysts and which lead to the Anderson-Schulz-Flory statistical distribution of products, including waxes. Precedent for the potential value of this approach came from Mobil Oil Corporation's success in designing a process around H-ZSM5 zeolites for the conversion of methanol to gasoline.[2]

A number of reports have appeared in the patent and open literature claiming catalysts that generate distributions of products that do not follow Anderson-Schulz-Flory statistics, including some with and some without molecular sieving properties. In the former category are catalysts claimed in a series of patents assigned to Ruhrchemie, which produce primarily C_2 to C_4 olefins.[3] Similarly, Kugler has claimed catalysts, comprised of ruthenium supported on manganese-oxide or titania, that yield a high C_2 to C_4 olefin fraction.[4] Madon and coworkers have reported unusual product distributions from sulfided and unsulfided Ru/Al_2O_3.[5] Product distributions were observed to be very sharp, especially between C_5 and C_{25}. A number of other recent reports have claimed shape-

selectivity with zeolite molecular sieves.[6] The common feature in these latter references was that the investigators considered the molecular sieving properties of the catalyst were responsible for the atypical product distributions observed.

Interestingly, relatively little attention had been paid to carbon molecular sieves and their potential for shape-selective catalysis. This was particularly surprising, since the shape-selective properties of catalysts based on carbon molecular sieves had been shown a number of years earlier.[7] In addition carbon molecular sieves with different pore properties had also been demonstrated phenomenologically in terms of their adsorptivity for different sized probe molecules.[8] Recently, Walker and Vannice investigated the use of iron-containing carbon molecular sieves for carbon monoxide reduction with hydrogen.[9] Although it is not claimed, Murchison has reported carbon- supported molybdenum catalysts which produce the theoretical maximum of the C2 to C4 fraction.[10] These catalysts are supported on Saran beads, which are formed by pyrolysis of PVC/PVDC mixtures and are known to have molecular sieving properties.

In general most of the reactions studied with carbon molecular sieve-based catalysts were isomerization or hydrogenation of olefins. Examples were compiled of reactant shape-selectivity, which utilized the molecular discriminatory properties of the carbon. Only those components of reactant mixtures which had critical dimensions smaller than the pore sizes were able to gain entry into the catalyst and react at the active site. Larger molecules were excluded from the internal surface of the catalyst and passed through the catalyst bed unreacted. Only in the later work of Walker and Vannice was the potential for transition state shape-selectivity, through the properties of the carbon molecular sieves considered, and this was for the reduction of carbon monoxide with hydrogen. However, in this report the catalysts were found to have relatively low activity and they produced mostly methane. Hence we found that little or no research on the catalytic properties of carbon molecular

sieves, had been devoted to either transition state or product shape selectivities. It seemed logical then to explore this issue by preparing new carbon molecular sieving materials with structures likely to lead to these types of shape-selectivity, and then to test these for wax-suppression in the Fischer-Tropsch reaction.

In our program we proposed to build novel molecular sieving materials that combine the properties of carbon molecular sieves and inorganic oxides. In this way we hoped to form a new material with both the molecular sieving structures of the carbon and the desirable chemical and physical properties of the oxides. The inorganic oxide would give us improved control of the activity and selectivity of the metal phase over that possible in the pure carbon sieves. Then by placing these catalytic materials in a carbon molecular sieving matrix, the final material would be converted into a molecular sieving form. This novel material in its final form we refer to as an Inorganic Oxide-Modified Carbon Molecular Sieve (abbreviated as IOM-CMS).

We conceptualized three types of IOM-CMS materials, which differ in their preparation, structure, and type of shape-selectivity that they might display. The materials are displayed schematically in Figure 1. The Type I material is a relatively large particle of an inorganic oxide (e.g. 8 x 18 mesh) on which we have carefully deposited a layer of molecular sieving carbon as an outer shell. This is done with repetitive cycles of resin adsorption and pyrolysis. Based on its structure we would anticipate that a catalyst with this type of structure could show product shape-selectivity. Synthesis gas will diffuse through the carbon layer to the inner core containing the Fischer-Tropsch active site. The usual distribution of short to long chain hydrocabons would be formed. The shorter molecules with sufficiently small critical dimensions will diffuse out of the particle. The longer chain hydrocarbons may find that the carbon molecular sieving layer represents a barrier to mass transfer. The mass transfer barrier to the outside may enhance the overall efficiencies of

secondary processes that can occur within the catalyst particle. Therefore if the same or another site is present for secondary hydrocracking of these products, then they may be converted to short chain hydrocarbons which can then diffuse out. Such a scheme is an example of product shape-selectivity, since the relationship of the critical dimensions of the products to the pore size of the carbon molecular sieve, control the selectivity.

Type II IOM-CMS materials are prepared by dispersing ultrafine powders or hydrolytically unstable alkoxide precursors of the inorganic oxide in the resin and then pyrolyzing this mixture. Depending on the nature of the local environment around the catalytically active site, and the intrinsic rate of reaction at the surface of the active phase, one could envision these materials leading to either transition state or product shape-selectivity.

Assuming that a large percentage of the molecular sieving pores terminate on the surface of the oxidic particle, and if the rate of reaction is high enough at the surface so that a significant fraction of the reaction occurs at the surface with most of the reactants being consumed prior to their diffusion into the non-sieving interior of the active phase, then the steric constraints of the molecular sieving pore may exert a transition state shape-selectivity on the growing chain. Alternatively, if the rate of reaction at the particle surface is comparable to or slower than the rate of diffusion into inner portion of the porous and non-sieving catalytically active phase, then the selectivity of the Type II materials should be similar to that of the Type I materials.

Type III materials are basically the same as the Type I and II materials except that the inorganic oxide is first dispersed on the surface of a porous, non-sieving carbon. The oxide-modified carbon is converted into a molecular sieve either by creating a shell of molecular sieving carbon around the surface of large particles of it, as in the Type I

materials, or by mixing fine particles of it with the resin and then pyrolyzing the mixture, as in the Type II materials.

During the last twenty-six months we have produced more than ninety samples of the IOM-CMS materials in the three types of configurations. Inorganic oxides that we have used include silica, alumina, titania, zirconia, titania-zirconia as well as various supported and unsupported catalysts including Fe/SiO_2, $Fe-K/SiO_2$, Ru/SiO_2, C-73, $Fe_2O_3-CuO-K_2O$, and $Fe_2O_3-CuO-K_2O:CoO-MoO_3/Al_2O_3$.

With the Type I materials we have found that generation of molecular sieving properties requires the build-up of a carbonaceous overlayer with successive cycles of resin adsorption and pyrolysis. Our results with the specific adsorption of various sized molecular probes indicates that the onset of molecular sieving properties can begin with as few as two carbon depositions for a low surface area oxide like titania, or may take as many as six for a high surface area oxide like silica. Generally, the full sieving properties of the Type I materials are developed only after eight to twelve cycles of carbon deposition have been completed. The Type I IOM-CMS materials have all displayed 3A molecular sieving properties. This means that they adsorb CO_2, but not n-butane, isobutane, or neopentane.

The Type II IOM-CMS materials are prepared in two different ways and both methods lead to molecular sieves. The Type IIa materials are prepared by adding the metal alkoxides directly to the resin precursor and then pyrolyzing the mixture. This has been done with the precursors to alumina, titania, zirconia, and titania-zirconia. The range of compositions investigated was from 20% to 70% in the oxide. In every case the Type IIa materials were found to display 3A molecular sieving properties in our comparative adsorption test., independent of the amount or composition of the oxide over the range investigated.

Type IIb materials are prepared by mixing ultrafine inorganic oxide powders with the resin precursor in a range of weight ratios from 20% to 70% oxide, and then pyrolyzing this mixture. The inorganic oxides have been prepared by hydrolyzing metal alkoxides and calcining the resultant precipitate. The oxides which have been used include alumina, titania, zirconia, and titania-zirconia. Based on our standard method of comparative adsorption of probe molecules, these materials all display 4A molecular sieving properties (they adsorb CO_2, n-butane, isobutane, and neopentane), at the upper end of the oxide composition range investigated.

The Type III materials have been prepared by first decomposing selected metal alkoxides on the surface of the porous carbon, and then combining these materials with the resin precursor in the Type IIa mode. The results of these investigations are consistent with those that were observed for the Type I and IIa materials.

Catalytic testing of these materials has been with the Type I and IIa IOM-CMS materials. Both supported and unsupported catalyst systems have been formed into Type I and II IOM-CMS materials. These include:

C-73 (a fused metal Ammonia Synthesis catalyst from United Catalysts)

Fe/SiO_2

$Fe-K/SiO_2$

Ru/SiO_2

$Fe_2O_3-CuO-K_2O$

$Fe_2O_3-CuO-K_2O : CoO-MoO_3/Al_2O_3$

The carbon-coated C-73 catalyst showed essentially the same activity and selectivity as the uncoated version. This demonstrated that the carbon molecular sieving overlayer and the

process of forming it, would not poison the catalytically active sites. This was a particularly important finding since C-73 is a fused metal catalyst with low surface area. Therefore the majority of its sites are on the surface and in contact with the carbon overlayer. As a result, any detrimental effect of the carbon would be expected to be more severe in the case of C-73 than with a standard high surface area supported metal catalyst. The latter has a large fraction of its active sites on the internal surface of the support, where they may be inaccessible to the resin and hence unaffected by the carbon or its formation processes.

A series of simple supported metal catalysts including Fe/SiO_2, $Fe-K/SiO_2$, and Ru/SiO_2 were tested. Fe/SiO_2 was found to produce too much methane to be useful in our studies and Ru/SiO_2 was too unstable under process conditions to collect reliable data. The Type-I version of $Fe-K/SiO_2$ tended to produce more of the shorter chain hydrocarbons versus the uncoated catalyst (68% C1-C4 versus 44%). This result was the first evidence that the carbon molecular sieving properties of the IOM-CMS material might affect the selectivity of the catalyst.

The bulk of our testing effort has been expended on the precipitated iron Fischer-Tropsch catalyst Fe_2O_3-CuO-K_2O,(FT), first described by Pichler, [11] and the combination of this catalyst with a hydrocracking catalyst, CoO-MoO_3/Al_2O_3, (HC). IOM-CMS materials have been prepared with just the FT portion, and others have been prepared with both the FT and HC portions combined in various weight ratios. This FT catalyst was a good system to focus upon because it has been shown to produce wax in relatively high yields. In addition this catalyst tends to clog and sinter in the fixed bed mode of operation. Hence, we considered any improvement in the selectivity and on-stream behavior of this catalyst by forming it into a Type I or II IOM-CMS material would be a substantial achievement.

In fact the Type I and II IOM-CMS versions of the FT catalyst displayed both markedly improved on-stream behavior as well as a different product distribution than the untreated FT catalyst. Comparative tests of the Type I and II, IOM-CMS Fischer Tropsch catalysts (C-FT TY-I, C-FT TY-II) with the native FT catalyst show the Type I and II materials are as active as the native FT catalyst. Two runs were attempted with the native FT catalyst, but data could only be collected at 250 psig in one run. The native FT catalyst was very poorly behaved under these 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 340^{0}C. We found this difference to be quite significant. Just as importantly, the IOM-CMS materials tend to produce a higher percentage of the lighter hydrocarbons, and in better yield (> 50% , 170 -180 gm hydrocarbon/m^3 synthesis gas), than the untreated FT catalyst.

Comparative results for IOM-CMS catalysts versus the untreated catalysts, indicate that they make predominantly lighter hydrocarbons and in reasonably high yields. (C1-C4, >80%, ~ 100-170 gm hydrocarbon/m^3 synthesis gas converted). In these catalysts the combined Fischer Tropsch/Hydrocracking (FT/HC) functionalities are in 1:1,3:1, and 6:1 (w/w) ratios, and are in the form of C-FT-HC TY-I, C-FT-HC Non-Sieving, and FT-HC (native). These systems were very well-behaved in the fixed bed mode, operation without clogging or sintering during the course of extended runs (>150 hrs).

In summary, the IOM-CMS materials have been demonstrated with a wide variety of compositions and different adsorptive properties. Catalysts prepared with the IOM-CMS materials showed improved properties relative to the untreated Fischer-Tropsch catalysts. The formation of the carbon molecular sieving function did not deactivate the catalysts. In

fact, the IOM-CMS forms of the catalysts were better behaved, displaying improved resistance to sintering and or clogging. Catalysts tested to-date showed high selectivities to the very short chain hydrocarbons, C1-C4, but not to the gasoline fraction, C5-C11. This may be due to the fact that the pore properties of the materials tested were in the 3A to 4A range. Shifting of this pore size to slightly higher values may produce a concommitant shift in the product distribution.