DIVISION 4: Experimental Methods

Our experimental methods revolved around two problems:

(1)   phenomenological characterization of the new IOM-CMS materials by molecular probe molecule adsorption

(2)   catalytic testing of the new IOM-CMS based materials for Fischer-Tropsch activity and selectivity

In both cases not only did we have to construct the adsorption instrumentation, and the test reactor, but we also had to develop the proper methods to carry out these investigations, and then process the data. In the following sections we describe the instrumentation and techniques we have used throughout this research program.

Section A. Characterization of Carbon Molecular Sieves by Molecular Probe Analysis.

Molecular sieving materials are capable of separating molecules on the basis of their molecular cross-section or volume. These materials contain pores with dimensions close to those of the critical dimensions of small molecules. Adsorption of a molecule occurs if the critical kinetic dimensions of the molecule are smaller than the minimum cross sectional area of the pore opening.

Zeolites are the largest single class of molecular sieving materials. These materials contain super cages comprised of silicon, aluminum, and oxygen atoms. The molecular-sized pores and channels between these super cages give the zeolites their molecular sieving properties and distinguish them from simple porous inorganic oxides such as silica, alumina, titania,

zirconia, or mixed phases of these materials. The various types and properties of these materials are described thoroughly in the monograph by D.W. Breck[35] Critical dimensions of various zeolites are given in Table 2. A comparison of pore structure dimensions and the critical dimensions of small molecules of interest is also given in Table 3.

The zeolites are crystalline materials so that their pore dimensions can be determined directly with X-ray diffraction, making it possible to predict what size molecules will or will not gain entry to the internal surface. The pore size can also be determined phenomenologically by measuring the extent of adsorption of a series of different size molecules with critical dimensions less than, equal to, and greater than those expected for the actual pore. Typical probe molecules for these adsorption experiments include CO_2, n-butane, isobutane, and neopentane. Critical dimensions for these molecules are collected in Table 4. By adsorbing these molecules, the molecular sieving characteristics of molecular sieves with non-crystalline structures, like the carbon based systems, can also be evaluated and compared to the zeolitic sieves. Hence materials that adsorb only CO_2 and smaller molecules are referred to as 3A type sieves. Similarly, those that adsorb n-butane, CO_2, and smaller molecules are termed 4A, and 5A type sieves distinguished by the extent of isobutane adsorption.[8a-d]

Since carbon molecular sieves , and the IOM-CMS materials prepared herein, are both multicrystalline and amorphous, we have characterized their sieving properties phenomonologically by molecular probe adsorption. The probe molecules that we have utilized are the classic ones: CO_2, n-butane, isobutane, and neopentane. The samples were characterized by comparing the specific adsorption of each of these molecules on both the untreated inorganic oxides, which were non-sieving, and their IOM-CMS versions which

had differing degrees of molecular sieving properties depending upon the amount of carbon present.

The IOM-CMS materials had not been prepared before, so we anticipated preparing large numbers of samples, and the molecular probe apparatus in which we conducted the adsorption studies, had to be able to generate data with high throughput. A system was constructed based on a Cahn electrobalance (see Figure 4). A high vacuum chamber was attached to the balance, and it contained a carousel capable of holding up to six samples. (In December, 1986 this was modified to hold up to ten samples.) The carousel was attached to a heater block, which contained cartridge heaters and a thermocouple. The temperature of the carousel was set and maintained with a Wizard programmable controller.

The carousel could also be rotated so that each sample could be picked up and hung on the balance to gravimetrically measure adsorptive uptake of the probe molecules. By having the six samples in the carousel, they were all conditioned, and then exposed to the adsorbate simultaneously. The individual samples were then weighed separately. After an analysis with one probe molecule, the samples were heated in vacuo to reconditon them, and then exposed to the next molecular probe molecule. This cycle was repeated until all four probe molecules had been exposed to all of the samples. In this way a large number of samples were characterized fairly rapidly. The detailed procedure used to carry out these analyses is displayed in Appendix IV. The results of these molecular probe analyses on the IOM-CMS materials are described in the next division of this report.

Section B. IOM-CMS Materials Preparation. Preparation of the IOM-CMS materials differed according to the Type of sieve we were preparing. In the following we describe the preparation of the Type I , IIa, and IIb materials.

C-SiO$_2$(beads), Type I. 50 gm of microporous silica beads (Aldrich, No. 25,562-9, 3mm. diam., N$_2$BET S.A.= 600 m^2/gm, P.V.=0.39 cm^3/gm, pore diam. = 25Å.) were immersed in polyfurfuryl alcohol (Occidental Chemical Corporation, No. 16470, Durez Resin , Lot No. 57VIBIA), and then drained of the excess. The beads with adsorbed PFA were heated in a tube furnace under flowing nitrogen with the following heat cycle: 100-300°C, in 50°C increments every 30 mins; 300°C for 2hr. These steps were repeated up to twelve times. In addition during the fourth, eighth, and last heating cycles the sample was raised to 500°C and soaked for 6hr. After this the furnace was cooled down to room temperature in flowing nitrogen and the sample removed, and stored in a capped vial.

C-SiO$_2$ (large pore silica), Type-I. 50 gm of large pore silica (Alfa Products, No. 89346, Lot No. 081781, N$_2$BET S.A.= 300 m^2/gm, P.V. = 1.0 cm^3/gm, 8 x 12 mesh) were converted into a Type I, IOM-CMS material following the same methods as above.

C-SiO$_2$-Al$_2$O$_3$ (pellets), Type-I. 50 gm of silica-alumina pellets were converted by the same procedures, as described above, into a Type I, IOM-CMS material.

C-TiO$_2$, C-ZrO$_2$, C-TiO$_2$:ZrO$_2$, Type-I. Titania, zirconia, and titania:zirconia were prepared by hydrolysis of the alkoxide precursors. An appropriate amount of Ti(IV) butoxide (Alfa Products No. 77124, Lot No. 011684) was added to deionized water at 25°C with rapid stirring. The precipitate, which was formed immediately, was filtered away from the liquor, and washed with deionized water, and air dried at 25°C. The oxidic powder was then calcined in air at 500°C for 2 hr. The calcined powder was ball-milled for >16 hr, and then pelletized. The same procedures were followed for the zirconia, and titania:zirconia binary oxide.

After pelletization the oxides were each converted into Type I IOM-CMS materials using the methods previously described.

C-Fe/SiO$_2$ and C-Fe-K/SiO$_2$ Type-I. Two catalysts were made on Davidson silica (N$_2$BET S.A.= 273 m^2/gm, P.V. = 1.1 cm^3/gm, 8 x 12 mesh, pore diameter= 45Å). The first was 20 wt% iron on (80 wt%) silica, and the second was 20 wt%Fe, 30 wt%K, and 50 wt% SiO$_2$. Both were made by a standard technique: impregnation of the support with a ferric nitrate, potassium nitrate and hexamineruthenium (III) chloride solution to incipient wetness, followed by calcination in air.

As in the previous examples, these catalysts were converted into Type I IOM-CMS materials by repetitive adsorption of polyfurfuryl alcohol and pyrolysis cycles.

C-Fe$_2$O$_3$:CuO:K$_2$O. Type-I. The Fischer-Tropsch catalyst (FT) that we have tested and modified is the precipitated Fe$_2$O$_3$-CuO-K$_2$O prepared by the methods of Pichler. The metals are Fe, Cu, and K each precipitated from their corresponding chloride salts. In our preparation we prepared 150 gm batches of this material by combining 134 gms of Fe(II)Cl$_2$·4H$_2$O, 61 gms of Fe(III)Cl$_3$·6H$_2$O, 26 gms of CuCl$_2$·2H$_2$O in 2.0 L of H$_2$O (T= 70 $^\circ$C) and precipitating these with 200 gms of Na$_2$CO$_3$ in 2.0 L of H$_2$O (T= 70 C). The resultant precipitate was filtered and washed with 0.5 gms K$_2$CO$_3$ in 100 cm^3 of H$_2$O. The catalyst cake was calcined at 105 $^\circ$C for 10 hours in flowing air. The catalyst was then ball-milled for 16 hours to reduce the particle size to less than 200 mesh.

The raw catalyst was formed into pellets approximately 13/16" O.D. x 1/8" L. This material was reduced in-situ after loading in the reactor. 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).

$C\text{-}Fe_2O_3CuO\text{:}K_2O\text{-}CoO\text{:}MoO_3/Al_2O_3$, Type-I. The trifunctional catalysts (C-FT:HC) were prepared by ball-milling the precipitated iron catalyst with a 3% CoO-15% MoO_3/Al_2O_3 hydrocracking catalyst (American Cyanamid). This powder was then formed into pellets to prepare the control catalyst, the Type I version, and the Type II version. These catalysts were prepared in the same way as were the samples based on the iron catalyst alone.

The Type IIa samples were prepared by mixing the polyfurfuryl alcohol with metal alkoxides and then pyrolyzing the mixture in a tube furnace under flowing nitrogen.

$C\text{-}TiO_2$, Type IIa. Titanium (IV) butoxide was mixed with PFA in seven different weight ratios to obtain theoretical ratios of TiO_2 to carbon of 1:2, 1:1, 2:1, 4:1, 10:1, 15:1, and 20:1. These mixtures were heated by the cycle: 100°C for 1 hr., 30 min. each in 100°C intervals from 200-600°C, soak at 600°C for 3 hr.

$C\text{-}ZrO_2$, Type IIa. Zirconium (IV) n-propoxide was mixed with PFA in three different weight ratios to obtain ratios of ZrO_2 to carbon of 1:2, 1:1, and 2:1. These mixtures were heated in flowing nitrogen utilizing the following cycle: 100°C for 1 hr, ramped to 600°C at 3°C/min., and soaked at 600°C for 2 hr.

$C\text{-}Al_2O_3$, Type IIa. Aluminum (IV) s-butoxide was mixed with PFA in three different weight proportions to obtain theoretical Al_2O_3 to carbon ratios of 1:2, 1:1, and 2:1. These mixtures were heated for 1hr at 100°C, then from 100 to 600°C in 100°C intervals of 30 min. each, and finally for 3 hr at 600°C.

C-TiO$_2$:ZrO$_2$, Type IIa. Equimolar amounts of the titanium (IV) n-butoxide, and the zirconium (IV) n-propoxide were mixed with PFA in the proper weight proportions to obtain oxide to carbon ratios of 1:2, 1:1, and 2:1. The heating cycle was like that used above.

The Type IIb IOM-CMS samples were prepared by mixing the metal oxide powders, formed by the hydrolytic precipitation of the alkoxides and calcination of the precipitate, with the PFA and then pyrolyzing.

C-TiO$_2$, Type IIb. Titania powder was mixed with PFA in these weight ratios: 1:2, 1:4, and 1:8. The samples were heated at 100°C for 1hr, 200°C for 1hr, 300°C for 2 hr, and finally 500°C for 6 hr.

C-ZrO$_2$, Type IIb. Zirconia powder was mixed with PFA in the same weight ratios as the C-TiO$_2$, Type IIb sample, and the pyrolysis cycle used was also the same.

C-TiO$_2$:ZrO$_2$, Type IIb. Titania-Zirconia powder was mixed with PFA in the same weight ratios as the C-TiO$_2$, Type IIb sample, and the pyrolysis cycle was also the same.

C-TiO$_2$, C-ZrO$_2$, Type III. Wide-Pore carbon(American Cyanamid) was first ball-milled for 16 hrs. and then functionalized by contacting it with Ti(IV) n-butoxide, dissolved in isopropyl alcohol, and in a volume sufficient to fill the pore volume of the carbon. In order not to exceed the pore volume of the carbon the contacting step was repeated three times, with heating cycles of 200°C in air after each contacting step. This resulted in 20 wt% titania on the carbon. The same process was followed to prepare titania-modified and zirconia-modified (using Zr(IV) propoxide) Raven 8000 carbon beads, also at the 20 wt% level.

Three samples of Type III materials were prepared with each of the three surface-modified porous carbons. These were prepared by separately mixing 20 gm of the modified carbon base with 20, 80, and 160 gm of PFA. The mixtures were then heated in flowing nitrogen at 20ºC/min to 500ºC, soaked at 500ºC for 2 hr, then heated again at 20ºC/min to 600ºC, and soaked for 5 hr.

In all, this gave rise to 9 Type III, IOM-CMS samples. Three based on titania-modified wide-pore carbon, three based on titania-modified Raven 8000 carbon beads, and three based on zirconia-modified Raven 8000 carbon beads.

Section C. Catalyst Testing. Catalyst testing was conducted in a fixed-bed, down-flow reactor. Carbon monoxide and hydrogen were metered to the reactor with separate mass flow controllers, and the streams were mixed prior to entry into the reactor. The reactor consisted of a stainless steel tube (1/2" I.D. x 12" L) fitted with reducers and valves to match the 1/4" inflow and outflow tubes. This was heated with a tight-fitting oven. Temperature was measured with three thermocouples two in the oven and one placed in the reactor bed. The signal from these was sent back to a fully programmable solid state temperature controller. Pressure was set with a standard back pressure regulator placed in line after the trap-train. Total pressure was monitored with a standard mechanical pressure gauge. Two in-line trap trains were used to condense products. These consisted of three traps in series held at 50, 0, and 0ºC respectively. Non-condensible products from the reactor were sampled by an automated valve which fed two on-line gas chromatographs, for product identification and quantitation. One gas chromatograph used a thermal conductivity detector and was used for H_2, CO, and CO_2 analyses. The other gas chromatograph utilized a flame ionization detector for hydrocarbon analyses.

In the course of an experiment the catalyst sample was reduced in-situ in flowing hydrogen or synthesis gas. The synthesis gas composition was set by first flowing it through a bypass around the reactor and then monitoring the carbon monoxide and hydrogen compositions with the on-line g.c. With the synthesis gas composition fixed at the desired level, the reactor temperature was set and allowed to stabilize (in hydrogen), then the synthesis gas was introduced into the reactor and the pressure was adjusted to the necessary level. The carbon monoxide and hydrogen conversions, and the production of light hydrocarbons C_1 to C_7, and CO_2 were monitored throughout the experiment. The concentrations of hydrogen, carbon monoxide, and carbon dioxide were determined on a 1000 ul (1 atm., 150°C) sample of the reactor effluent with a gas chromatograph utilizing a thermal conductivity detector.

The concentrations of the hydrocarbons were determined on a 250 ul (1 atm., 150°C) sample of the reactor effluent with a gas chromatograph fitted with a flame ionization detector. At any given set of conditions the run was allowed to occur sufficiently long to reach near steady state conversions for more than 24 hrs and to collect gram quantities of product. Typical run times ranged from 50 to over 150 hours. When conditions were changed, the reactor effluent was generally swung from one set of three traps to the other, in order to keep the products from each set of conditions separate. At the end of a run, the products were removed from the traps, and mixed with carbon disulfide. The soluble organic layer was separated and analyzed by off-line gas chromatography. Individual components in both the on-line analysis and the off-line analyses were identified and quantitated by analyzing standard samples. Product distributions were compiled from the raw data with software written by us for this application (see Appendix 5).