

DIVISION 6. Discussion

Section A. IOM-CMS Materials. The first goal of this research was to determine if and how the different types of proposed IOM-CMS materials could be prepared. By preparing over 92 samples in three different types we have shown not only that indeed the different types of proposed IOM-CMS materials can be made, but also they can be made with a wide variety of inorganic-oxide bases with variable properties.

We have demonstrated the Type I, IOM-CMS material with three types of silica, silica-alumina, titania, titania-zirconia, silica-supported iron, potassium-promoted iron, and ruthenium. The amount of carbon needed to produce the maximum sieving effect depends upon the physical nature and possibly the chemical properties of the inorganic oxide. With the relatively low surface area titania the amount of carbon needed is approximately 30 wt%, while with the higher surface area silica the level of carbon needed to induce sieving is over 55 wt%. The majority of the carbon deposition on titania occurs in the first three steps. Subsequent steps lead to less carbon deposition, but these small additional amounts of carbon seem to be the ones critical for the generation of the molecular sieving properties. Likewise in the silica case the majority of the carbon to be deposited is deposited after the first six steps. After this the subsequent steps also lead to less deposition but this smaller amount of additional carbon is more important to the development of the sieving properties. The difference between the two inorganic oxides is presumably due to their different physical properties.

These results suggest a model for the formation of the sieving properties in which the surface of the oxide must first adsorb a saturation level of carbon before the sieving carbon can be formed. Once all the oxidic surface area available for carbon deposition is full, then subsequent carbon deposition can occur on the carbon already present, and begin to close

off the pores of the oxide. A simple calculation illustrates the point. If we assume a simple, close-packed array for the deposited carbon as zeroth order structural approximation, and if we take the Bragg-Slater atomic radius of 0.70 \AA for the carbon,³⁸ then we can calculate the approximate weight percentage of carbon necessary to cover the surface of the silica sample that we studied in detail.

$$C_{\text{radius}}^{\text{Bragg-Slater}} = 0.70 \text{ \AA}$$

{ [1 carbon atom / Unit Area (m^2)] x [1 mole carbon / $6.02 \text{ E}23$ atoms] x [12 gm / 1 mole carbon] x [300 $\text{m}^2/\text{gm SiO}_2$] } = { gm Carbon / gm SiO_2 } (to give an approximate monolayer of carbon)

$$\{ [1 / 3.14 \times (0.7 \text{ \AA} \times 1 \text{E-}10 \text{ m}^2/\text{\AA})] \times [1 \text{ mole} / (6.02 \text{ E}23)] \times [12 \text{ gm/mole}] \times [300 \text{ m}^2/\text{gm silica}] \} = 0.388 \text{ gm carbon / gm silica}$$

wt% carbon for 1 monolayer of carbon on silica

$$= \{ 0.39 / (1.00 + 0.39) \} \times 100$$

$$= 28 \% \text{ carbon (72\% silica)}$$

This very approximate calculation indicates that the silica is capable of holding enough carbon to amount to 28% of the total composite weight. Our results indicate that molecular sieving occurs at about twice that level or at about 53 wt%.

Interestingly, if we take the density of the molecular sieving carbon as that of amorphous carbon, $2.0 \text{ cm}^3/\text{gm}$,³⁹ and given the pore volume of the silica is $1.0 \text{ cm}^3/\text{gm}$, then we find 33 wt% carbon corresponds to the amount of carbon needed to just fill the available pore volume of the silica.

$$(1 \text{ gm SiO}_2) \times (1 \text{ cm}^3/1 \text{ gm SiO}_2) \times (1 \text{ gm carbon}/ 2.0 \text{ cm}^3) = 0.5 \text{ gm carbon}$$

$$(0.5 \text{ gm carbon}/ (0.5 \text{ gm carbon} + 1.0 \text{ gm SiO}_2)) = 0.33 \text{ --->>> } 33 \text{ wt\% carbon to fill the pores in 1.0 gm of silica}$$

In both calculations the amount of carbon to cover the available surface area or to fill the available pore volume of carbon is very close, 28 wt% for the former and 33 wt% for the latter. Both calculations suggest that the pores and available surface of the silica are filled with the carbon and then an additional amount of carbon, approximately 20 wt% must be added to complete the encapsulation and render the inner pores inaccessible to the gaseous outer phase.

Since the numbers used are gross approximations to the true area of the carbon atom and the density of these polymer derived-carbons, we can only use them qualitatively to guide us in the structural model. Thus a large portion of the 20 wt% difference between the amount of carbon found by experiment to correspond to the sieving limit and the amounts of carbon calculated to fill the pore volume or available surface area, may partially reflect on the crudeness of these approximations.

Similar arguments and calculations can be made for the build-up of carbon on the titania IOM-CMS material.

Our model for the carbon build-up that leads to the formation of molecular sieving properties in the Type 1, IOM- CMS materials, is a filling of the available surface area and porosity of the inorganic oxide by carbon followed by some additional fraction of carbon deposited over the pore filling carbon to close off any remaining fissures or structural

defects that would let small molecules diffuse into the particle. This model seems to fit the sum of our experimental data and observations the best. The implications of this model on the catalytic applications we have explored will be discussed below.

We have prepared the Type II, IOM-CMS materials by two different methods. The addition of the metal alkoxides in the PFA resin leads to materials that we call the Type IIa materials. In this preparation we envision the metal alkoxide molecules dissolving in the resin and decomposing to give a molecular dispersion of the oxide precursors. Since the metal alkoxides are readily decomposed by hydrolysis, and since a by-product of the resin pyrolysis is water, we expect that in the carbonization of the resin-alkoxide mixture the alkoxide is decomposed to the corresponding oxide accompanied by the formation of carbon.

All the Type IIa materials prepared in this way have 3A sieving properties independent of the amount of the alkoxide added. This is particularly interesting in view of the range of inorganic oxide content (up to 63 wt%) that we have covered. The further exploration of these type of materials seems warranted, especially since they may have not only the structural properties of molecular sieving carbon, but also the chemical properties, such as acidity of the added inorganic oxides. It is worth noting that the water adsorption on the Type IIa, sample is not the same as the Type I materials, but is reminiscent of the 3A zeolite, although to a lesser degree.

The Type IIb materials are prepared by the addition of the ultrafine inorganic oxide powders formed by the hydrolysis of the corresponding alkoxides. The interesting feature of these materials is that they have adsorptive properties approaching that of a 4A molecular sieve. Namely, not only do these materials adsorb CO₂, but they also adsorb significant and measurable amounts of n-butane. This may be due to the formation of interstices between

the particles of the added inorganic oxide. Since the particles were not sieved in any way we would expect a distribution of particle sizes for the inorganic oxide. If the 4Å pores really do arise through interstices between the particles, then the diameters of particles involved in this, must be very small because of simple geometric constraints. It is likely that only a fraction of the particles of the added inorganic oxide actually fall in this range, (probably something much less than 17.5%, 2 sigma, assuming a normal distribution around a median particle diameter typically resulting from this hydrolysis of the alkoxides). Therefore, if we could skew the distribution of the particle sizes toward the small diameter tails, then we could in principle increase the fraction of pores in the 4Å region. This approach, in principle, might also be extended to tailor the pore sizes of the Type IIb IOM-CMS materials to any region of interest.

Reinforcing this concept of micropore control through the control of the chemical and physical properties of the additives, are our results with the Type III materials. The preparation of these materials followed that of the Type IIb materials. The molecular probe data indicate that the Type III samples can be made to behave as 4A or 3A sieves, simply by controlling the ratio of resin to added surface-modified carbon. In fact these Type III materials have even more 4A-like properties than the Type IIb materials, because they have an even higher specific adsorptivity of n-butane, close to that of the carbon dioxide.

The sum of these results indicate that we can readily modify the properties of the carbon molecular sieves, by the addition of inorganic oxides. We have demonstrated that all three of the proposed types of IOM-CMS materials can be made, and are sieving. We have also noted that the sieving properties of the IOM-CMS materials can be modified by the nature, both chemical and physical, of the additives, and the way in which they are introduced into the resin. Certainly, some aspects of these results are similar to those that have been observed with all-carbon based molecular sieves, but they had not been previously

demonstrated with inorganic oxide-modified carbon molecular sieves. It is reassuring and important that preparation of the IOM-CMS materials and the properties that result from these preparation techniques, follow the general trends observed for the pure carbon molecular sieves. This implies that we have not disrupted the pyrolysis chemistry for the formation of the sieving properties, by addition of the oxides or their precursors. This is important to our original hypothesis of preparing new materials with the best properties of both the carbon molecular sieve and the inorganic oxide. A disruption of the resin pyrolysis chemistry, had it occurred, would have been undesirable, because it may have lead to a loss in the carbon sieving properties.

Section B. Catalytic Properties of IOM-CMS Materials. The first set of catalyst testing results were gathered on the Type-I materials with carbon-coated C-73, silica-supported iron, potassium-promoted iron, and ruthenium. These test results indicated that after conversion of these catalysts into their carbon-coated forms, they still had activity comparable to their uncoated forms. Prior to having these results, we considered it possible, that the chemistry of and/or the temperatures used for the resin pyrolysis process, or even the deposited carbon itself, could lead to either chemical, or physical poisoning (or both) of the underlying active metals. The case of C-73 would represent a worst case in this scenario, because its sites are localized on the relatively low geometric surface area of the particles. The absence of apparent poisoning of this catalyst by the carbon overlayer was necessary but not sufficient evidence that the carbon would not poison active metal sites. It was insufficient evidence, because we considered it possible that the carbon overlayer could be imperfect in its coverage, and catalysis could occur at these uncovered or accessible sites. The activity of the carbon-coated silica- supported iron catalysts, closed this loop, because in this system we could show that the carbon-coating was complete by the molecular probe analysis, an option we did not have with the low surface area C-73

sample. Hence, the combined results were both necessary and sufficient to show that neither the carbon nor the process of its formation would lead to catalyst poisoning.

The Rh-Mo/Al₂O₃ system is of interest because it shows a remarkable propensity to form oxygenated products and from hydrogen-poor synthesis gas. The onstream activity and selectivity of the catalyst were relatively high. The catalyst produced nearly 60% dimethyl ether at 13% CO and H₂ conversion levels, for an extended period of time, with no decrease in activity or selectivity. The XPS results on the catalyst indicate that the rhodium and molybdenum do not agglomerate (sinter). The molybdenum remains in the + VI oxidation state even after forcing reduction, and the rhodium is reduced nearly to the zero oxidation state, but the final valence state may indicate that it is still slightly electropositive relative to rhodium metal. This slightly electropositive nature may be related to the catalyst tendency to make oxygenated products and not exclusively methane, as does rhodium metal.

The tests of the Type I and II, IOM-CMS versions of the precipitated iron catalysts have shown that the carbon has an effect on the catalyst, especially with respect to its onstream materials behavior. In our hands the precipitated iron catalyst rapidly clogged and sintered, resulting in a sizable pressure drop (~ 150 psig) across the catalyst bed, and the formation of wax in the reactor itself. For this reason we were able to generate only limited data for the catalyst, and it was of relatively low quality, since we were not able to recover the products quantitatively (carbon balance = ~ 30%). In contrast, the carbonized versions of the catalyst were all remarkably well-behaved under a variety of different conditions of temperature, and pressure. There was no evidence of gross wax formation and our recoveries of the products were as a result, uncomplicated and relatively high. The carbon-coated catalysts also displayed a pronounced shift of the products toward the light hydrocarbons, and the overall yields of hydrocarbon per unit volume of synthesis gas

converted were reasonably high. It was particularly interesting to note that we were able to obtain these beneficial characteristics even after only one carbon coating cycle. Our interpretation of this is that due to the very low surface area of this catalyst, even one carbon coating cycle is enough to fill pores and cover the surface. This view is supported by our observations with the carbon coating of high surface area silica, and low surface area titania, and the model that we proposed based on these results.

The FT-HC catalysts also behaved well on-stream, showing no signs of waxing or clogging, and no formation of a pressure drop, similar to the carbonized FT catalysts. The addition of the hydrocracking catalyst to the FT catalyst in addition to the molecular sieving carbon, further accentuated the trend toward the production of light hydrocarbons. At 250°C, and 500 psig (1:1CO:H₂) the C-FT:HC(1:1), Type I; C-FT:HC(1:1), non-sieving; FT-HC(1:1) uncoated catalyst, C-FT:HC(6:1), Type I; and the C-FT:HC(3:1), Type I catalysts each produced 67, 64, 81, 76 and 86 wt% respectively in the C₁ to C₄ fraction. The ASF plots for all these catalysts show a break suggesting a double alpha mechanism is operative. However, at the 1:1 weight ratio of the FT:HC components the hydrocracking activity is so active that this dominates the selectivity. Therefore, there is relatively little apparent contribution from the carbon in these catalysts. At the higher ratios of FT:HC the products begin to shift back out toward the heavier hydrocarbons, but the hydrocracking activity still seems to dominate the overall selectivity. With the 3:1:FT:HC catalyst we also tested the effect of higher hydrogen to carbon monoxide ratios, namely 3 to 1. Somewhat surprisingly this variable had little effect on the selectivity.

Section C. Summary and Perspective.

In summary the IOM-CMS materials show improved properties relative to the untreated precipitated iron Fischer-Tropsch (FT) catalysts. The formation of the carbon molecular

sieving function did not grossly deactivate any of the catalysts. In the IOM-CMS form the FT catalysts were very resistant 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 allow for a shift in the product distribution.

The concept of combining a standard wax-producing Fischer Tropsch catalyst with a hydrocracking component and then surrounding these with a carbon molecular sieving shell as a barrier to mass transfer has been tested, and basically we have found that it works. All the catalysts tested produce primarily C1 to C4 products whereas the pure Fischer Tropsch catalyst produces far more waxes. However, we have also shown that at the 1:1:FT:HC level the HC component dominates the selectivity of the catalyst. However by lowering the amount of the hydrocracking component to ratios of 6:1 and 3:1 FT:HC the catalysts begin to behave with more intermediate selectivities, making far less of the higher hydrocarbons than the pure Fischer Tropsch catalyst but also less of the C1 to C4 fraction. It seems reasonable that the composition and amounts of these components could be balanced to provide the optimum selectivity to a desired range of products such as the gasoline or diesel range. Further investigations should focus on the balancing of these components and then substituting the hydrocracking catalyst with a hydrogenolysis catalyst like rhodium on silica or alumina. In addition we should test the FT-HC combination in a Type II configuration.

Finally, the Type III IOM-CMS materials have intriguing molecular sieving properties, and offer even more design flexibility. Therefore some future effort should be devoted to testing the Type III IOM-CMS materials in this application.