

DIVISION 2: TECHNICAL APPROACH AND CONCEPTS

In this program we have set out to explore the usefulness of new carbon molecular sieving materials with shape-selective properties as low-wax producing catalysts for the Fischer-Tropsch reaction. To do this we first prepared and characterized a variety of Inorganic Oxide-Modified Carbon Molecular Sieves, and then prepared catalysts from these types of materials for activity testing in a fixed-bed high pressure reactor.

We constructed a program comprised of five major tasks to accomplish this :

1. Literature Search
2. Construction and Operation of High Pressure Reactor
3. Preparation of Inorganic Oxide-Modified Carbon Molecular Sieve Catalysts
4. Preparation and Testing of Metal-Modified Carbon Molecular Sieves
5. Final Report

In order to manage our efforts we utilized three simple tools, a project planning summary, a task flow chart, and a time line (see Appendices I, II, and III). Each of these devices was used to track completed work and to plan the execution of future work.

The first working hypothesis to be tested in this work was whether or not we could prepare and characterize new materials which were Inorganic Oxide-Modified Carbon Molecular Sieve (IOM-CMS) materials. We conceptualized three types of IOM-CMS materials, which differ in their preparation, structure, and the type of shape-selectivity that they may display. The materials are shown schematically in Figure 1.

The Type I material was envisioned to be a relatively large particle of an inorganic oxide (e.g. 8 x 18 mesh) on which we would carefully deposit a layer of molecular sieving carbon as an outer shell. This would be done with repetitive cycles of resin adsorption and pyrolysis. Based on its structure we anticipated that a catalyst with this type of structure would display product shape-selectivity.

Type II IOM-CMS materials would be 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.

Type III materials are basically the same as the Type I and II materials except that the inorganic oxide would be first dispersed on the surface of a porous, non-sieving carbon. The oxide-modified carbon is converted into a molecular sieve either by creation of 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 course of this work we prepared all three types of IOM-CMS materials, thus confirming our hypothesis that they could be prepared and with molecular sieving properties. The Type I materials consist of an inorganic oxide particle surrounded by an outer shell of molecular sieving carbon, the Type II materials consist of a dispersion of inorganic oxide crystallites in a matrix of molecular sieving carbon, and the Type III materials are similar to the Type I and II materials except that the oxide is first dispersed on a non-sieving porous carbon particle (see Fig. 1).

The second major hypothesis to test in this work was that the IOM-CMS materials could provide either product or transition state shape-selectivity by virtue of the molecular sieving carbon, and this would lead to a suppression of wax formation in the Fischer-Tropsch reaction.

Type I materials could provide for product shape-selectivity by the imposition of the molecular-sieving carbon shell. This shell would let synthesis gas into the particle for conversion to hydrocarbons, but it would not let the larger undesirable hydrocarbons out. This could lead to gross deactivation via pore clogging but if sites were present for hydrocracking, then it could also lead to conversion of the long chain hydrocarbons to short chain hydrocarbons via a secondary process. Synthesis gas will diffuse through the carbon layer to the inner core containing the Fischer-Tropsch active site and form the usual distribution of short to long chain hydrocarbons. The shorter molecules with sufficiently small critical dimensions will diffuse out of the particle. The longer chain hydrocarbons may find the carbon molecular sieving layer a significant barrier to mass transfer. This barrier may then 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, because of the relationship of the critical dimensions of the products to the pore size of the carbon molecular sieve.

The second operating hypothesis was that the Type II materials might provide for transition state shape-selectivity, provided the region adjacent to the active site was a molecularly sized pore. 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. If a large percentage of the molecular sieving pores terminates at the surface of the oxidic particle, and the rate of reaction at the surface is high enough, then a significant fraction of the reaction will occur at the surface with most of the reactants being consumed prior to their diffusion into the non-sieving interior of the active phase. In this way 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 the inner portion of the porous, non-sieving active phase, then the selectivity of the Type II materials should be similar to that of the Type I materials.

With these working hypotheses in mind we embarked upon a program that had two major and consecutive tasks. The first was the preparation and characterization of the novel carbon molecular sieves. In this we sought to test whether or not the three types of IOM-CMS materials that we had proposed could be prepared, to establish their molecular sieving properties, and to determine how these characteristics were generated. The second task was to prepare and test the IOM-CMS-based catalysts versus their untreated analogues to determine what effect the carbon would have on their activity and selectivity. Results of both of these tasks are described in the sections that follow.