

Executive Summary

This report covers the fifth six-month period of this three-year grant, under the University Coal Research program. During this period, we have continued the synthesis and analysis of precipitated catalysts, using a bench-top spray dryer. We have also continued studies of the influence of binders on particle strength for doubly promoted iron catalysts on alumina, synthesized by Mr. Robert Gormley, at FETC, and compared those to catalysts synthesized here at the University of New Mexico (UNM) from doubly-promoted hematite with binders, and with a catalyst prepared by a collaborator, Mr. Ralph Brooks, Yale University, using precipitated magnetite with binders. Two methods of deriving catalyst particle breaking stress, ultrasonic fragmentation and uniaxial compaction, were applied to the catalysts, and those results will be discussed briefly. In the next six-month period, the catalysts will be analyzed by TPR in order to determine their ease of reducibility, then tested under typical FTS run conditions, to determine their relative activities and stabilities.

We have completed the preliminary X-ray diffraction analyses and data interpretation for the catalyst samples received from Fischer-Tropsch stirred-tank reactor runs being conducted at Texas A&M University (TAMU). Some of the slurry samples were sealed in epoxy and microtomed for examination by high resolution transmission electron microscopy (HRTEM). The corresponding soxhlet-extracted samples were also analyzed by HRTEM. All of the analyses, results and discussion are attached in the form of paper submitted for publication in the Fall, 1998, special issue of the Journal of Applied Catalysis. In the paper, we show that some of the problems associated with sample analysis of the working F-T catalyst originate with the difficulty in preserving the microstructures and composition intact, as the sample is prepared for analysis. We first discuss how the relative X-ray scattering cross-section differences between Fe, C, and O, can present a deceptive picture of the phase compositions in a working catalyst. We present additional evidence that Soxhlet extraction of a slurry, to obtain a relatively wax-free powder, can cause significant changes in catalyst phase composition. We have made some preliminary quantifications of the phases present in each sample, and related that information to the activity of the catalyst over the course of the run, as a function of time on-stream. We conclude that, in its most active form, the Fe catalyst in a slurry reactor consists of ϵ' -carbide (Fe_7C_3) and alpha-iron ($\alpha\text{-Fe}$), while the χ -carbide which is also present, appears to be less active.

In the coming six-month period, the interpretation of the results presented in the paper will be completed. Additional Neutron diffraction studies of the catalysts will be attempted for comparison to XRD results. The influence of temperature and pressure upon the phase compositions and morphological changes observed by XRD and by Neutron Diffraction in the working catalyst in wax will be explored further, by theoretical modeling as well as experiment, and related to the data from the TAMU samples. The microtomy and analysis of more of the TAMU slurry samples by HRTEM will be completed and discussed in detail.

Technical Objectives

The objective of this research project is to perform fundamental research in support of catalyst development for slurry-phase bubble column reactors for Fischer-Tropsch synthesis. The overall program is divided into several tasks:

Task 1: **Catalyst Particulate Synthesis.** We will first study various factors which determine the attrition resistance of iron catalysts used for slurry-phase Fischer-Tropsch synthesis. The fundamental

insights gained from study of the attrition phenomenon will be used to tailor the preparation of novel precipitated catalysts. In order to determine optimal treatment protocols for these catalysts, it will be necessary to conduct investigations of catalyst microstructure, as a function of treatment method.

Task 2: Catalyst-Binder Interactions. Because the use of binders is considered necessary for synthesis of a catalyst with good attrition resistance, we will perform fundamental studies of catalyst binder interactions. Model catalysts will be studied, ex-situ and in-situ, by high-resolution transmission electron microscopy (HRTEM), in order to determine the nature of interfacial phases at the iron-binder interface. A better understanding of the underlying thermodynamics influencing the catalyst-binder interactions will help provide improved catalyst design criteria.

Task 3: Characterization of used catalysts from reactors operated under typical industrial conditions. Task 3 was not a part of the original proposal. However, we felt that, in order to design a catalyst with improved attrition resistance and high activity, a better understanding of the phenomena affecting a working catalyst's reactivity, life and stability over the course of a reaction run was needed. Consequently, samples from stirred-tank reactors operated at typical industrial FTS conditions, provided by CAER, University of Kentucky and Texas A&M University will be analyzed by X-ray diffraction, neutron diffraction, and HRTEM. The data will help us understand the causes and effects of phase compositions and morphological changes on the catalyst activity under realistic reactor conditions.

Technical Progress

Task 1 - Catalyst Particulate Synthesis

Overview

In the previous semi-annual report, we examined the particle strengths of several catalyst formulations, prepared by Mr. Robert Gormley, Federal Energy Technology Center (FETC), and brought on line a bench-top spray dryer, which is being used to make various catalysts, with and without binder. We have continued our catalyst preparation studies and evaluation of various attrition testing methods. The strengths of the spray-dried catalyst, prepared and treated by various methods, have been investigated by ultrasonic fragmentation and uniaxial compaction. Our results indicate that the method of catalyst preparation, as well as the environment to which the powders are subjected can have a significant effect on catalyst strength.

Ultrasonic Fragmentation Tests

Several catalysts, prepared by Mr. Robert Gormley, of FETC, have been analyzed for agglomerate strength by ultrasonic fragmentation. Experimental details for the ultrasonic fragmentation testing method have been described in detail in our previous reports. One gram of catalyst is dispersed in 50 ml of deionized water. A Sedigraph particle size analyzer is used to determine the particle size distribution of the suspension. The suspension is ultrasonicated, using a Tekmar high-intensity probe. After ultrasonication for varying periods of time, the suspension is reanalyzed by Sedigraph, in order to determine the mode of particle fragmentation. The results are also used to derive a quantitative measure of agglomerate strength, as explained previously in our progress reports.

Figures 1 and 2 show fragmentation results from two samples of the FETC catalyst, prepared from Fe_2O_3 promoted with K and Cu and deposited in different ways onto preformed alumina granules. These samples are

designated as AQFE/CU/K/AL-ED1-24 and AQFE/CU/K/AL-FH1-137, respectively. The first catalyst sample, -ED1-24 (figure 1), appears to be much stronger than sample -FH1-137 (figure 2), but is comparable to the Vista alumina powder discussed in the August, 1997, semi-annual report. We attribute these results to differences in treatment conditions. Figures 3 and 4 show fragmentation results from two samples of precipitated, Cu-promoted Fe catalyst, calcined at 350°C in air, prepared under different conditions. These are designated as PRFECUAL/4K-ED10-58 and as PRFECUAL/4K-ED11-117, respectively. The results show that -ED10-58 (figure 3), appears to be much stronger than -ED11-117 (figure 4), but is comparable to the Vista alumina powder discussed in the August, 1997, semi-annual report. It was stated in the August, 1997, report that calcination did not appear to significantly improve the strength of the agglomerates; therefore these results may also be attributed to differences in treatment conditions.

Next, spray-dried catalysts were prepared at UNM from Fe_2O_3 precursor with varying amounts of binder, using a Buechi mini spray dryer. These samples were compared to similar ones using a Fe_3O_4 precursor, prepared by Mr. Ralph Brooks, Yale University. The Fe_3O_4 catalyst was synthesized as follows: A slurry of 6.5 ml, 5 weight % silica (PSA), 106 ml, 5 weight % silica (deionized Ludox SM-30), and 50 g magnetite (Fe_3O_4), was spray-dried, using a Yamato DL-41 spray dryer under the following drying conditions: atomizing air at 3 kgf/cm², aspirator at 0.8 m³/min, pump at 3.5 (approximately 30 cm³/min), drying chamber temperature of 240°C, and collecting chamber temperature of 95°C.

Figure 5 shows fragmentation results for the Fe_3O_4 catalyst. As expected, particle fragmentation is comparable to that observed in our spray-dried catalysts, as shown in the February, 1997, report. However, the Fe_3O_4 catalyst may not be active for FTS (Huang, et al., 1993). Hence, the known catalytic activity of the precursor could be an important issue to consider when preparing catalysts; therefore the activity of these two precipitated catalysts will be explored in the near future.

Uniaxial Compression Testing

The catalysts tested in the previous section were also examined using an Instron 5565 uniaxial compaction test apparatus. Experimental details, as well as a detailed discussion of the uniaxial compression method, have been described in our previous reports. Figures 6 and 7 show compaction data for the FETC catalyst shown in Figure 2, and for the Fe_3O_4 catalyst, respectively. The data are presented as a plot of $\ln(P)$ vs. natural strain, e . The results were analyzed using a model presented by Adams, et. al., 1994, which yields a value for the breaking strength, σ (in Mpa), of the particles within the powder sample. According to these data, the catalyst prepared by depositing doubly-promoted Fe_2O_3 on preformed alumina granules is much stronger than the spray-dried Fe_3O_4 catalyst. In contrast, the ultrasonic fragmentation results imply that the spray-dried Fe_3O_4 catalyst is stronger than the doubly-promoted Fe_2O_3 on alumina. We concluded that the catalyst powder strength is affected by its environment, as well as treatment conditions.

Future Work

The effects of catalyst environment in the fluid suspension will continue to be investigated. The behavior of the two types of precipitated, spray-dried catalysts, using Fe_2O_3 and Fe_3O_4 precursors, in a model reactor, operated at typical industrial conditions will be explored. We hope to determine conclusively which of the two particle strength testing methods more accurately predicts catalyst behavior in a slurry-bubble column. Our work over the next six months will continue to explore the effectiveness and performance of the spray-dried precipitated catalysts and the effect of metal-support interactions on the attrition resistance of these catalysts.

ask 2 - Catalyst Binder Interactions

Task 3 - Characterization of used catalysts from reactors operated under typical industrial conditions

Tasks 2 and 3 are addressed together, for the purposes of this report. The progress on these two tasks is summarized in the draft publication, included as attachment A, submitted for publication in the Journal of Applied Catalysis, special issue on Fischer-Tropsch catalysis, edited by Prof. Hans Schulz.

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References

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