SLURRY PHASE IRON CATALYSTS FOR INDIRECT COAL LIQUEFACTION

Contract No. DE-FG22-95PC95210

to

The University of New Mexico

7/5/94 - 7/4/98

Final Report

Prepared for

U.S. Department of Energy
Federal Energy Technology Center
FETC Project Manager: Richard E. Tischer

Submitted by

Abhaya K. Datye, Professor
Department of Chemical & Nuclear Engineering and
Director, Center for Micro-Engineered Materials
University of New Mexico
Albuquerque, NM 87131
submitted November 19, 1998

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Abstract

This report describes research conducted to support the DOE program in indirect coal liquefaction. Specifically, we have studied the attrition behavior of iron Fischer-Tropsch catalysts, their interaction with the silica binder and the evolution of iron phases in a synthesis gas conversion process. The results provide significant insight into factors that should be considered in the design of catalysts for converting coal based syngas into liquid fuels.

Table of Contents

page

OBJECTIVE	4
EXECUTIVE SUMMARY	4
Task 1:Synthesis of Attrition Resistant Catalysts	5
Task 2:Catalyst-Binder Interactions	5
Task 3:Characterization of working catalysts	5
PUBLICATIONS	7
Appendices	9
Appendix A: Hien N. Pham, Alexander Viergutz, and Abhaya K. Datye, "Improving the Attrition Resistance of Slurry Phase Heterogeneous Catalysts," submitted to Powder Technology.	
Appendix B: Pham, H., Reardon, J. and Datye, A. K., "Measuring the Attrition Resistance of Fe F-T catalysts," Powder Technology, in press.	
Appendix C: Jin, Y. and Datye, A. K., "Phase transformations in Fe F-T catalysts," International Congress of Electron Microscopy, Cancun 1998, vol II, page 391, Institute of Physics Publishing, 1998.	
Appendix D: Jin, Y. and Datye, A. K., "Characterization of Bubble Column Slurry Phase Iron Fischer-Tropsch Catalysts, Natural Gas Conversion V, Stud. Surf. Sci. Catal., vol 119, page 209, 1998.	
Appendix E: Mansker, L. D., Jin, Y., Bukur, D. B. and Datye, A. K., "Characterization of Fe Fischer-Tropsch Catalysts," submitted to the special issue of Applied Catalysis being edited by Prof. Hans Schulz.	

TITLE: Slurry Phase Iron Catalysts for Indirect Coal Liquefaction

PI: Abhaya K. Datye

COLLABORATORS:

Prof. Dragomir Bukur, Texas A&M Univ., College Station, TX.
Dr. Burtron Davis, Center for Applied Energy Research, Univ. of Kentucky, Lexington, Kentucky.
Dr. Nancy Jackson, Sandia National Laboratories, Albuquerque, NM.
Mr. Robert Gormley, DOE-FETC, Pittsburgh, PA.

STUDENTS: Linda Mansker, Hien Pham, Yaming Jin, (all Ph. D. students whose dissertations are in the final stages; partial support for Linda Mansker was obtained from a NSF grant).
Students graduated Mehul Shroff (M. S.) and Aree Hanprasopwattana (Ph. D.)
Undergraduate Students: Ray Griego (funding DOE summer internship), Ralph Brooks, Steve Medd, Alexander Viergutz (all supported by an NSF/REU grant).

INSTITUTION: Center for Microengineered Materials and
Department of Chemical and Nuclear Engineering
University of New Mexico, Albuquerque, NM 87131
(505) 277-0477 FAX (505) 277-1024 email: Datye@unm.edu

GRANT NO: DE-FG22-95PC95210

PERIOD OF PERFORMANCE: July 5, 1995 - July 4, 1998

OBJECTIVE

The objective of this project was to investigate the causes of catalyst attrition in slurry phase iron Fischer-Tropsch catalysts and to synthesize catalysts with improved attrition resistance for this process. Precipitated iron catalysts are being considered by the DOE for conversion of coal-derived syngas where the H_2/CO ratio is around 0.7. The high water-gas shift activity of Fe makes it possible to work at such low H_2/CO ratios, hence Fe catalysts are desirable for the indirect liquefaction of coal.

EXECUTIVE SUMMARY

In this section, we present an overview of the research performed in this DOE-UCR grant. The specific research findings are described in the 10 publications that resulted from this work. Out of

these 10 publications, 5 were published prior to 1997, but the other 5 represent the most recent work and several of them are still in the review process. Therefore, we have included these 5 manuscripts as part of this final report. The work was disseminated widely in the form of 17 presentations at both national and international conferences. This research program also provided fertile training ground for the education and training of students. A total of 5 graduate students were supported with this research grant (4 Ph. D. and 1 M. S.). The grant could not have provided complete support for all these students, therefore partial support was obtained from other sources such as NSF and national laboratories, as well as industry support. In addition, 4 undergraduate students participated in this research as part of their summer internships (supported either by DOE or NSF) and 2 of these students are co-authors on the resulting research publications. The narrative (below) is grouped into three sub-tasks:

Task 1: Synthesis of Attrition Resistant Catalysts

We have synthesized different spray-dried catalyst formulations containing silica as binder. We have evaluated several approaches to measure attrition strength of Fe F-T synthesis catalyst and have concluded that the ultrasonic fragmentation test is most sensitive to differences in strength among these catalysts. Hence, the spray-dried catalysts show improved strength compared to the Fe catalysts that have been previously used in slurry bubble column reactor tests. In future work, we hope to test the activity of these catalysts in a F-T synthesis reactor and to evaluate their attrition strength under working conditions.

Task 2: Catalyst-Binder Interactions

We have completed the temperature programmed reduction studies of model supported and unsupported UCI binderless F-T synthesis catalyst. Model supported catalysts were prepared in our laboratories using Stöber silica spheres as support. We have concluded that the silica binder does not retard the reduction of the iron phase. By TEM, we have seen no evidence of any silicate interfacial phases when the iron was deposited on the silica. However, as described in reference 4, when the iron is co-precipitated with the silica, we do form an unreducible amorphous phase. In our catalysts, the binder does retard the sintering of the carbide phases, and helps to maintain a well-dispersed catalyst with nanophase particle size.

Task 3: Characterization of working catalysts

The working catalyst samples were supplied to UNM by two of our collaborators: Prof. Dragomir Bukur of Texas A&M University, College Station, TX, and Dr. Burtron Davis of the Center for Applied Energy Research, University of Kentucky, Lexington, Kentucky. We have used x-ray diffraction and transmission electron microscopy to study working F-T catalysts. These catalysts had been used in a medium pressure slurry phase CSTR and were discharged during the course of F-T runs at different times on stream. Every step of the catalyst removal and sample preparation steps was examined carefully to eliminate any possible artifacts in the analytical scheme. It was found that removal of hot, catalyst-containing wax from the reactor in air could

potentially cause oxidation of the most reactive components. Hence, wax removal under inert atmosphere was deemed necessary to protect the sample against oxidation. Separation of the catalyst from the F-T wax by Soxhlet extraction has been the most commonly used procedure to obtain a sample suitable for analysis. However, our study showed that this process could also introduce artifacts in sample composition. Hence, we concluded that it was necessary to keep the catalyst in the hydrocarbon wax to preserve its composition.

X-ray diffraction was used to study the types of Fe phases present in the working catalyst. It was found that the scattering efficiencies vary markedly for the different phases, making it necessary to use Rietveld structure refinement to obtain quantitative phase compositions. A simple visual inspection of powder diffraction patterns is very deceptive, because of these differences in x-ray scattering efficiencies. The interference by the wax with the catalyst remains a major problem with using x-ray diffraction, particularly with high α catalysts. We've been exploring separation methods, other than Soxhlet extraction, to provide a reasonable powder sample for analysis, as well as having success in using the Rietveld method, along with a low-density polyethylene crystal structure, to deconvolute the wax diffraction pattern, from that of the catalyst. The XRD analysis was complemented by cross-section TEM, which allows the particle size distribution and morphology of the various Fe phases to be determined. The results to date are very encouraging and, for the first time, provide clues to the nature of the phases responsible for F-T activity. These results help us to understand the activation and deactivation of Fe F-T catalysts.

SIGNIFICANCE TO THE FOSSIL ENERGY PROGRAM

Fischer-Tropsch synthesis represents a commercially viable technology for converting syngas to liquid fuels. While the conversion of coal into liquid fuels is currently being practiced in South Africa, the process is expected to become increasingly attractive in the U. S. as the price of crude oil increases. The DOE is therefore interested in a viable F-T technology for converting coal-derived syngas, for which Fe is the preferred catalyst. This research has provided some of the fundamental information necessary for the design of Fe F-T catalysts.

SPECIFIC ACCOMPLISHMENTS

- Development of a method to determine the attrition strength of precipitated catalysts
- Investigation of the role of particle and binder morphology on attrition strength
- Discovery of the importance of proper catalyst passivation for study of iron catalysts and the development of procedures for catalyst removal from F-T reactors
- Development of new x-ray and TEM analytical protocols for the characterization of the working F-T synthesis catalyst
 - Analysis of the phases present in iron catalysts using x-ray and neutron diffraction data with Rietveld structure methods
 - Analysis of catalyst embedded in the wax, using cross-section TEM

PUBLICATIONS

- (1) Shroff, M. D. and Datye, A. K., "The importance of passivation in Fe catalysts," Catal. Lett. 37, 101 (1996).
- (2) Hanprasopwattana, A., Rieker, T., Sault, A. and Datye, A. K., "Morphology of TiO₂ coatings on silica," Catal. Lett., 45, 165 (1997).
- (3) Datye, A. K., Shroff, M. D., Harrington, M. S., Sault, A. G. and Jackson, N. B., "The Role of Catalyst Activation on the Activity and Attrition of Iron Fischer-Tropsch Catalysts," Stud. Surf. Sci. and Catal., Natural Gas Conversion IV, vol. 107, pg 169, 1997.
- (4) Datye, A. K., Shroff, M. D., Jin, Y., Brooks, R. P., "Nanoscale Attrition of Fe F-T catalysts: Implications for Catalyst Design," Stud. Surf. Sci. Catal., vo. 101, 11th Intl. Congr. Catal., pg 1421, 1996.
- (5) Jackson, N. B., Datye, A. K., Mansker, L., O'Brien, R. J. and Davis, B. H., "Deactivation and Attrition of Fe F-T catalysts," Stud. Surf. Sci. Catal., vol. 111, Catalyst Deactivation 1997, p 501.
- (6) Mansker, L.D., Jin, Y.; and Datye, A. K.; Proceedings of the 1997 Coal Liquefaction & Solid Fuels Contractors Review Conference, Federal Energies and Technologies Center, Pittsburgh, Pennsylvania; 1997; WEB URL : http://www.fetc.doe.gov/events/97conferences/coal_liq/97cl_pdf/datye.pdf/.
- (7) Hien N. Pham, Alexander Viergutz, Robert J. Gormley, and Abhaya K. Datye, "Improving the Attrition Resistance of Slurry Phase Heterogeneous Catalysts," submitted to Powder Technology.
- (8) Pham, H., Reardon, J. and Datye, A. K., "Measuring the Attrition Resistance of Fe F-T catalysts," Powder Technology, in press.
- (9) Jin, Y. and Datye, A. K., "Phase transformations in Fe F-T catalysts," International Congress of Electron Microscopy, Cancun 1998, vol II, page 391, Institute of Physics Publishing, 1998.
- (10) Jin, Y. and Datye, A. K., "Characterization of Bubble Column Slurry Phase Iron Fischer-Tropsch Catalysts, Natural Gas Conversion V, Stud. Surf. Sci. Catal., vol 119, page 209, 1998.
- (11) Mansker, L. D., Jin, Y., Bukur, D. B. and Datye, A. K., "Characterization of Fe Fischer-Tropsch Catalysts," submitted to the special issue of Applied Catalysis being edited by Prof. Hans Schulz.

PRESENTATIONS AT MEETINGS AND CONFERENCES

A total of **17 presentations** were made at meetings and conferences based on the research supported by this grant.

Natural Gas conversion meeting, South Africa (November 95), AIChE meeting (November 95 and November 98), Western States Catalysis Society [March 1996 (2), February 97 (2) and March 1998 (2)], Pittsburgh Coal conference (October 96), Intl. Congr. on Catalysis, Baltimore, MD (July 96), North American Catalysis Society meeting Chicago, IL (May 97), American Crystallographic

Association meeting, St. Louis, MS, (July 97), Southwestern regional ACS meeting, Tulsa, OK (October 97), DOE Contractors meeting (August 97), Catalyst Deactivation symposium in Cancun (November 97) and Natural Gas Conversion meeting in Sicily, Italy (September 98).

Appendices

Appendix A

Improving the Attrition Resistance of Slurry Phase Heterogeneous Catalysts

Hien N. Pham, Alexander Viergutz[†], Robert J. Gormley[‡], and Abhaya K. Datye^{*}

Center for Microengineered Materials and Department of Chemical & Nuclear Engineering,
University of New Mexico, Albuquerque, NM 87131

[†]NSF/REU Summer Student, Department of Chemical Engineering, Cornell University,
Ithaca, NY 14853

[‡]Federal Energy Technology Center, Pittsburgh, PA 15236

^{*}To whom all correspondence should be addressed.

Abstract

Slurry phase heterogeneous catalysts for processes such as Fischer-Tropsch synthesis must exhibit a high degree of attrition resistance. The precipitated Fe-Cu catalyst used for F-T synthesis is quite weak, in its as-prepared state. Spray-drying yields spherical particles which show some improvement in attrition resistance. However, the formation of fines ($< 5\ \mu\text{m}$) in this powder shows that it is not suitable as a slurry phase catalyst. In this paper we report on the use of silica binders to improve the strength of spray-dried agglomerates. The attrition resistance was measured using ultrasonic fragmentation followed by sedigraph particle size analysis. The attrition strength of the iron oxide catalyst agglomerates was compared to that of a commercial alumina powder, which was used as a reference material. The role of calcination (before or after spray-drying) and the method of silica binder addition (before or after spray-drying) was investigated.

Introduction

This work is directed towards synthesis of iron oxide catalysts for Fischer-Tropsch synthesis, a reaction that allows conversion of coal or natural gas into liquid fuels. For coal conversion, Fe catalysts are preferred since they can operate at the lower H_2/CO ratio in coal-derived syngas. These iron oxide catalysts are prepared by co-precipitation of iron and copper salts. Potassium is used as a promoter to improve catalyst selectivity. The preferred reactor type is a slurry phase bubble column which requires spherical catalyst agglomerates 50-70 μm in diameter. Since the products of F-T synthesis are liquid hydrocarbon waxes, separation of product from the catalyst requires that the catalyst agglomerates be attrition resistant.

In a previous study (1), we reported a comparison of two approaches used for measuring the attrition strength of catalyst agglomerates. Ultrasonic fragmentation coupled with particle size distribution measurements was found to be more sensitive to differences in catalyst strength than the conventional approach involving uniaxial compaction. Using the ultrasonic fragmentation approach (2,3), we were able to show that a plate-like kaolin binder did not impart any additional strength to a precipitated iron catalyst, that was otherwise weak and easily susceptible to attrition.

As revealed by TEM, the kaolin and Fe F-T catalyst occurred as two distinct phases, and that both had plate-like structures which did not connect to create strong interlocking forces between them.

We have therefore explored the role of other binder morphologies to provide improved attrition resistance for Fe F-T catalysts. We have worked with silica because it is the preferred choice as a support for obtaining better product selectivity and activity in F-T synthesis. We report here a study of factors that determine the strength of spray-dried agglomerates. When agglomerates are formed, binders are often used for the process. Binders play several roles, such as in controlling the release of drugs via a coating process, or in strengthening brittle materials. For example, Nikolic *et al.* (4) used a sol-gel silica coating (5) to strengthen an alumina substrate.

Several factors can have an effect on the strengths of agglomerates. Horisawa *et al.* (6) found that for their sample powders with polymer binders, the surface polarities of both powders and binders, as well as the degree of polymerization of the binder were important factors in determining the strength of granules. Bortzmeyer *et al.* (7) investigated three different CaCO_3 powders and found that no correlation was observed between the attrition rate and the mechanical properties (tensile strength, fracture energy, etc.). However, a correlation between attrition rate and surface roughness was observed. The factors we have explored in this study include the method of silica addition, and the effect of calcination on the strength of spray-dried agglomerates prepared from precipitated iron oxide.

Experimental

A precipitated Fe-Cu catalyst in its wet form (labeled PRFECU-ED20-124) was used for the experiments. The starting materials were the nitrates of Fe and Cu, and NH_4OH . Solutions of Fe-Cu nitrate and NH_4OH were mixed in a continuous flow through mixer causing the iron hydroxide to precipitate out. The product catalyst was discarded until the pH was between 6.8 and 7.2. The catalyst was then collected in a filter funnel, and the filter cake was pumped down to being wet but not cracked. Samples of the filtrate were obtained; a pH and brown ring test were performed for each sample to ensure that the pH remained near 7.0 and that traces of NH_4OH were removed from the catalyst, respectively. The cake was removed and then resuspended in hot water. After filtering the slurry, samples of the filtrate were obtained for pH and brown ring testings. After the brown ring test was negative, the filter cake was pumped moist. Finally, once the precipitated Fe-Cu catalyst was dry enough to remove it off the filter, the catalyst was suspended in deionized H_2O .

In a typical run, 100 ml of the precipitated Fe-Cu catalyst was ultrasonicated at an amplitude of 20 for 2 min to break up any loose agglomerates. A Tekmar 501 ultrasonic disrupter (20 kHz $\pm$ 50 Hz) equipped with a V1A horn and a 1/2" probe tip was used for the ultrasonication process. The sample was then mixed with 11 ml of potassium silicate solution (KASIL[®]#1; PQ Corp.), with a silica loading of 25 wt%. Dilute Nitric acid (0.1 N; J.T. Baker) was added dropwise while the slurry was stirred until the pH was about 7. The mixture was stirred for a further 20 min and then filtered using a Buchner funnel. Deionized water was then added to prepare 250 ml of slurry. A Buchi 190 Mini Spray Dryer was used to spray-dry the slurry. The inlet temperature of the spray dryer was over 200°C with the outlet being maintained over 100°C. The powder was collected in

a cyclone trap and then analyzed using a Sedigraph 5100 particle size analyzer and scanning electron microscope (SEM).

In another run, 200 ml of PRFECU-ED20-124 was ultrasonicated at an amplitude of 20 for 2 min. Deionized water was then added to prepare 250 ml of slurry. The slurry was spray-dried, and the dried Fe-based catalyst was collected in a cyclone trap. The sample was then mixed with 1 l of potassium silicate solution. The procedure and subsequent analyses were the same as in the previous run.

Other runs involved performing the same procedure from the first run, followed by calcining the sample at 320°C to see if there was any additional strength imparted to the sample, or calcining the SiO₂-containing sample first followed by adding deionized water to prepare 250 ml of slurry, and then spray-drying the slurry to see if there was any additional strength imparted to the sample.

Our synthesized precipitated Fe F-T catalysts were then compared to a VISTA alumina powder (VISTA-B-965-500C). The starting alumina from VISTA was sieved and calcined in air at 500°C. While this alumina is not prepared by spray-drying, it is useful as a reference material since it was being considered as a support for Fe-Cu catalysts in the work of McDonald *et al.* (8).

Results and Discussion

Figure 1 shows a cumulative mass distribution plot of mass finer (%) vs. equivalent spherical diameter for the precipitated Fe-Cu catalyst, as-prepared. Also shown in this plot is the influence of ultrasonic irradiation on the particle size distribution. This catalyst is weak with a broad particle size distribution. Both fracture and erosion occur during ultrasonic fragmentation, and the generation of fine particles below 5 µm may not be acceptable for slurry F-T reactors. Figure 2 shows a cumulative mass distribution plot for the same catalyst which was spray-dried, but without a binder. Spray-drying improves the attrition resistance of the Fe catalyst, and there is a more uniform particle size distribution. However, ultrasonication causes an increase in the fraction of particles below 5 µm, suggesting that the catalyst is still not resistant to erosion.

Figure 3 shows a cumulative mass distribution plot for a precipitated Fe-Cu catalyst/potassium silicate mixture that was directly spray-dried. The addition of the SiO₂ binder further improved the attrition resistance of the catalyst, and now we see little of the fine particles below 5 µm after 25 min of ultrasonic irradiation. Some of the particles between 5 µm and 10 µm may have re-agglomerated, as indicated by the shift in curves within this particle size range. The median particle size (~8 µm) is smaller than that desired for a commercial F-T process (50-70 µm); however, this represents a limitation of our bench-top spray dryer. Figure 4 shows a scanning electron microscope (SEM) image of the spray-dried agglomerates. It was found that the number average particle diameter from this image was smaller than the median size determined by sedigraph particle size analysis. This was traced to a bias in the SEM sampling procedure, which skews the particle size distributions to smaller sizes. Smaller size particles tend to stick to the carbon tape on the SEM stub more favorably than the larger size particles. The larger particles are more likely to come off the carbon tape when the SEM stub is shaken to remove excess particles. To verify the presence of larger particles, the catalyst was first sieved using a standard testing sieve having pore openings of 38 µm, and the remaining large size particles were used for the SEM analysis. Figure 5 shows an SEM image of the same catalyst. Large size particles are seen in Fig. 5 that are not

seen in Fig. 4. The larger particles in Fig. 5 are less spherical than the smaller particles in Fig. 4, probably due to the limitations of our spray dryer.

Figure 6 shows a cumulative mass distribution plot for a precipitated Fe-Cu catalyst/potassium silicate mixture that was spray-dried and then calcined at 320°C. Figure 6 is similar to Fig. 3, suggesting that calcination did not appear to significantly improve the strength of the catalyst. Figure 7 shows an SEM image of the spray-dried/calcined catalyst. These particles have rougher surfaces after calcination than those shown in Fig. 3. The median particle diameter for the spray-dried/calcined catalyst, according to Fig. 6, was smaller than that for the spray-dried catalyst. It is possible that the particles collected after spray-drying were not completely dried. The “wet” particles would lose some water during calcination, shrinking the catalyst particles. Removal of the water present in the catalyst is essential before the Fe F-T catalyst is activated for use in a reaction run. However, it is also important that the calcination temperature be low enough that no adverse chemical reactions (formation of interfacial silicate phases) occur between the Fe F-T catalyst and the SiO₂ support.

Figure 8 shows a cumulative mass distribution plot for a precipitated Fe-Cu catalyst/potassium silicate mixture that was first calcined at 320°C in its dried state before spray-drying. No erosion occurred below 5 µm after 25 min of ultrasonic fragmentation. For particle sizes between 10 µm and 100 µm, the amount (percentage) of fine particles generated were less than those from the other two catalysts, suggesting that the particle size of this catalyst was larger than the other catalysts. For example, the mass % of particle sizes finer than 20 µm was 62% for the catalyst that was calcined before spray-drying, whereas the mass % of particle sizes finer than 20 µm was 94% for the catalyst that was spray-dried without calcination. Figure 9 shows an SEM image of the calcined/spray-dried catalyst. The particles were not spherical after spray-drying, but instead were irregular shaped. The irregular shapes must have resulted when the catalyst was first calcined, with the particle shapes being preserved during spray-drying.

Figure 10 shows a cumulative mass distribution plot for a precipitated Fe-Cu catalyst that was initially spray-dried, potassium silicate solution added, and then spray-dried again. Some erosion was observed in this catalyst, suggesting that SiO₂ addition after initial spray-drying may not be as effective as the silica added before the powder is spray-dried. Figure 11 shows an SEM image of the catalyst. These particles looked similar to those in the catalyst that was spray-dried after SiO₂ addition (Fig. 4). It is clear that examination of the external structure alone is not sufficient for determining the strength of the catalyst.

Figure 12 shows a cumulative mass distribution plot for a VISTA alumina, which was used as a reference sample for comparison with the precipitated Fe F-T catalysts. The strength of this alumina was comparable to the catalyst shown in Fig. 9. However, both the VISTA alumina and the catalyst where silica was added after spray-drying (Fig. 10) were weaker than the other precipitated catalysts.

SEM image (Figure 13) of the VISTA alumina showed that it consisted of irregularly shaped agglomerates, since this alumina did not come from a spray-drying step. The morphology of the calcined catalyst (Fig. 9) is similar to that of the VISTA alumina; however, the calcined catalyst appears to be more attrition resistant than the alumina, since it shows no erosion during ultrasonic fragmentation. It is evident that attrition strength depends on the method of agglomerate

formation, the particle-binder interaction, primary particle size and shape, as well as subsequent processing such as calcination temperature.

Although the calcined/spray-dried catalyst is not spherical, it is comparable in strength to the spray-dried and spray-dried/calcined catalysts. This suggests that the strength does not depend on the shape of the particles. However, particle shape may be very important for other reasons such as slurry hydrodynamics. Furthermore, in a stirred tank reactor, more erosion is likely to occur for non-spherical particles than for spherical particles, and the use of spray-dried particles may be an advantage. In future work, we plan to study the attrition behavior of these precipitated catalysts in various reactor configurations: stirred tank, bubble column, etc.

Table 1 gives surface areas for the precipitated Fe F-T catalysts, using a BET N₂ adsorption analyzer. Of the precipitated catalysts, the calcined/spray-dried catalyst had the highest surface area while the catalyst where silica was added after spray-drying had the lowest surface area. This is reasonable if the silica tends to block access to the interior pores of the catalysts. Catalysts with high surface areas would generally be preferred since the reaction takes place at the gas-solid interface. However, in the case of these iron oxide catalysts, they have to be first transformed into reduced iron phases, such as iron carbide which is thought to be the active phase for this reaction (9). The phase transformations accompanying catalyst activation result in a chemical attrition of the catalyst (10) which needs to be considered when characterizing the attrition properties of these catalysts. This will be the subject of future work.

Summary

The precipitated Fe-Cu catalyst, as-prepared, was weak compared to the same catalyst which was spray-dried. Spray-drying improved the attrition resistance of the Fe F-T catalyst. We have explored the role of silica binder addition and calcination to further improve the attrition resistance of these catalysts. The precipitated catalysts were compared to a VISTA alumina, representing a commercially available reference sample. Our results show that addition of the SiO₂ binder provided further attrition resistance for the Fe F-T catalysts. Cumulative particle size distributions showed that the alumina and the Fe catalyst that was initially spray-dried before addition of SiO₂ were comparable in strength, but both were weaker than the spray-dried, calcined/spray-dried, and spray-dried/calcined catalysts. Calcination of the catalyst after spray-drying did not impart any additional strength to the catalyst.

SEM images of the VISTA alumina support and the calcined/spray-dried catalyst showed that the agglomerates were irregular shaped. However, the calcined/spray-dried catalyst was more attrition resistant than the alumina support. The attrition strength must therefore depend on the method for synthesizing Fe F-T catalysts. Factors which may improve the attrition strength are particle-binder interaction, primary particle shape and size of the precipitated Fe-Cu precursor, type and morphology of binders, and calcination temperature. We found that the attrition strength as measured via ultrasonic fragmentation does not depend on the shape of the Fe F-T catalyst agglomerates being tested. On the other hand, the shape of the catalyst may be important when the catalyst is used in a slurry bubble-column reactor, since it may determine the slurry hydrodynamics.

Acknowledgments

The authors would like to thank the U.S. Department of Energy and the Federal Energy Technology Center (FETC) under contract numbers DE-FG22-95PC95210 and DE-FG26-98FT40110 for their financial support of this project.

References

1. Pham, H.N., Reardon, J., and Datye, A.K., "Measuring the Strength of Slurry Phase Heterogeneous Catalysts", to be published in the journal *Powder Technology*.
2. Thoma, S.G., Ciftcioglu, M., and Smith, D.M., *Powder Tech.*, 68 (1991) 53.
3. Thoma, S.G., Ciftcioglu, M., and Smith, D.M., *Powder Tech.*, 68 (1991) 71.
4. Nikolic, L. and Radonjic, L., *Thin Solid Films*, 295 (1997) 101.
5. Brinker, C.J. and Scherer, J.G.W., Sol-Gel Science, The Physics and Chemistry of Sol-Gel Processing, Acad. Press. Inc., Boston, 1990.
6. Horisawa, E., Komura, A., Danjo, K., and Otsuka, A., *Chem. Pharm. Bull.*, 43 (1995) 488.
7. Bortzmeyer, D. and Goimard, J.C., *Powder Tech.*, 86 (1996) 163.
8. McDonald, M.A., Gormley, R.J., and Zarochak, M.F., "Estimation of Surface Site Density on Iron Fischer-Tropsch Catalysts by Means of a Test Reaction", Proceedings of the 1997 Coal Liquefaction & Solid Fuels Contractors Review Conference, Pittsburgh, PA.
9. Shroff, M.D., Kalakkad, D.S., Coulter, K.E., Kohler, S.D., Harrington, M.S., Jackson, N.B., Sault, A.G., and Datye, A.K., *J. Catal.*, 156 (1995) 185.
10. Kalakkad, D.S., Shroff, M.D., Kohler, S., Jackson, N., and Datye, A.K., *Appl. Catal.*, 133 (1995) 335.

Table 1. BET surface area of the precipitated Fe F-T catalysts.

SAMPLE	BET SURFACE AREA (m²/g)
PRFECU-ED20-124 + SiO ₂ (calcined; spray-dried)	224.3
PRFECU-ED20-124 + SiO ₂ (spray-dried)	127.5
PRFECU-ED20-124 + SiO ₂ (spray-dried; calcined)	158.7
PRFECU-ED20-124 + SiO ₂ (spray-dried PRFECU precursor, addition of binder, spray-dried mixture)	81.3

Figure 1. Sedigraph particle size distribution of a precipitated Fe, Cu catalyst, as-prepared. There is both fracture and erosion of particles after 25 min of ultrasonic fragmentation, indicating that the catalyst is weak. Furthermore, the catalyst has a broad particle size distribution.

Figure 2. Sedigraph particle size distribution of a spray-dried precipitated Fe, Cu catalyst. Spray-drying improves the attrition resistance of the catalyst, and there is a more uniform particle size distribution

Figure 3. Sedigraph particle size distribution of a spray-dried precipitated Fe, Cu catalyst containing silica. No erosion has occurred below 5 μm after 25 min of ultrasonic irradiation.

Figure 4. SEM picture of the spray-dried precipitated Fe catalyst containing silica. Spherical particles are typical for a spray-dried powder, and are smaller than those desired for a commercial F-T process.

Figure 5. SEM image of the spray-dried precipitated Fe, Cu catalyst containing silica. The large size particles were obtained by sieving with a standard testing sieve having pore openings of 38 μm . Also, the larger size particles are less spherical than the smaller size particles.

Figure 6. Sedigraph particle size distribution of a precipitated Fe, Cu catalyst containing silica, which was spray-dried and then calcined at 320°C. Calcination does not appear to impart any additional strength to the catalyst.

Figure 7. SEM picture of a precipitated Fe catalyst containing silica, which was spray-dried and then calcined at 320°C. These particles are roughly spherical in shape, and the median particle diameter is smaller than the spray-dried Fe F-T catalyst.

Figure 8. Sedigraph particle size distribution of a precipitated Fe catalyst containing silica, which was calcined at 320°C in its dried state before spray-drying. No erosion has occurred below 5 μm after 25 min of ultrasonic irradiation.

Figure 9. SEM picture of a precipitated Fe catalyst containing silica, which was calcined at 320°C before spray-drying. These particles are not spherically-shaped, and are larger in size than the spherically-shaped spray-dried particles.

Figure 10. Sedigraph particle size distribution of a precipitated Fe catalyst containing silica. The Fe precursor was spray-dried before adding silica, and then was spray-dried again. This catalyst is weaker than the other precipitated Fe F-T catalysts.

Figure 11. SEM picture of a precipitated Fe catalyst containing silica. The Fe precursor was spray-dried before adding silica, and then was spray-dried again. These particles look similar to the spray-dried catalyst (Fig. 4).

Figure 12. Sedigraph particle size distribution of VISTA-B-965-500C sample. The starting alumina from VISTA was sieved and calcined in air at 500°C. Very little fragmentation occurs after 15 min of ultrasonic irradiation, although some erosion has occurred.

Figure 13. SEM picture of a VISTA alumina support. The alumina is non-spherically-shaped since it is not spray-dried, and is larger in size than the spherically-shaped precipitated Fe F-T catalysts.

Appendix B

Measuring the Strength of Slurry Phase Heterogeneous Catalysts

Hien N. Pham, John Reardon, and Abhaya K. Datye

Center for Microengineered Materials and Department of Chemical & Nuclear Engineering,
University of New Mexico, Albuquerque, NM 87131

Abstract

Fischer-Tropsch (F-T) synthesis is a process used to convert coal-derived syngas to hydrocarbon liquids and waxes. A slurry phase bubble-column reactor (SBCR) is the preferred reactor type due to improved heat and mass transfer and operational simplicity in terms of catalyst loading and discharge. A potential disadvantage in the SBCR versus a fixed-bed reactor is the attrition of the catalyst which can cause difficulty with the catalyst/wax separation, resulting in gradual loss of catalyst from the reactor. In this work, we have evaluated two approaches to measure the strength and attrition resistance of heterogeneous catalysts: uniaxial compaction and ultrasonic fragmentation. A commercial catalyst developed for F-T synthesis was tested along with a sample of an alumina support having a similar particle size distribution. It was found that the cumulative particle size mass distribution plots after ultrasonic fragmentation show significant differences in strength, whereas the same powders show small differences in strength as measured by the uniaxial compaction method. Erosion was found to be the dominant fragmentation mechanism for the alumina support whereas fracture was the dominant mechanism for the F-T catalyst. Ultrasonic fragmentation also was applied to Fe F-T catalysts containing a kaolin binder. The catalyst with the binder was very weak, comparable to the binderless catalyst. Further analysis using TEM showed that kaolin and the Fe F-T catalyst occurred as two distinct phases, with plate-like structures which did not help create strong interlocking forces between them. These results provide clues for the design of attrition resistant catalysts.

Introduction

The Fischer-Tropsch synthesis (1) is a process to convert energy reserves of coal and natural gas into liquid transportation fuels. With dwindling supplies of crude oil, this process is expected to have increasing commercial importance. At present, F-T synthesis is being practiced in South Africa for converting coal-derived syngas ($\text{CO} + \text{H}_2$) into hydrocarbon waxes which are subsequently processed to the desired product slate. The U.S. Department of Energy is also supporting a program of catalyst development (1,2) and pilot plant testing (3) for indirect liquefaction of coal.

SASOL in South Africa first used a tubular fixed-bed reactor for F-T synthesis, where catalyst extrudates were packed in parallel tubes inside a single reactor (4). A fluidized bed reactor was then used because it had a much higher gas throughput than the fixed-bed reactor (4). However, SASOL found many potential advantages in carrying out the F-T reaction in a slurry phase based

on comparisons of all three systems. Hence, work was initially carried out on a small bench scale which later progressed to a pilot plant scale of the slurry reactor. The commercial slurry phase reactor achieved an availability of over 98% in its first year of operation in 1993, and the performance has been maintained ever since.

Currently, the SBCR is used to convert coal-derived syngas to waxy hydrocarbons via Fischer-Tropsch (F-T) synthesis (5,6). Syngas bubbles upwards through a slurry consisting of liquid wax and catalyst particles, diffuses into the slurry, and is converted into more wax by the F-T reaction. The advantages to using a SBCR are: it is simpler and cheaper to construct, it provides better heat transfer and temperature control inside the reactor to improve product yield and quality (7), and it allows the removal and addition of catalyst while the reactor is in operation, thereby improving the overall availability. A fixed-bed reactor for F-T synthesis leads to poor heat of reaction removal capability, nonuniform catalyst loading, low conversion efficiency, and bed plugging due to carbon laydown at high temperatures. Hence, a SBCR is more reliable for F-T synthesis (8).

A potential disadvantage in using a SBCR involves the attrition, or breaking-up, of catalysts. When a SBCR is used to produce lighter products, such as methanol, which are volatile, catalyst attrition may not affect reactor operation. However, attrition becomes a problem with the F-T process where heavy waxy products are being produced, and separation becomes difficult between the wax and smaller catalyst particles. Recent experience comes from the LaPorte plant, using a catalyst prepared by United Catalysts, Inc. (UCI), operated for the DOE by Air Products (3). In the LaPorte SBCR, the filter system was plugged after one day of operation, and there was difficulty with the external catalyst/wax separation resulting in gradual loss of catalyst from the reactor (3).

The requirements for catalyst agglomerates differ from those in other applications; for example, during postprocessing of ceramics, hard agglomerates may counteract compaction, decreasing the shrinkage rate of ceramic powders during sintering (9), hindering densification of ceramic parts, and generating flaws that reduce the strength of the sintered product (10), and degrade the uniformity of products such as paint. Hence, successful dispersion of powders often requires total elimination of agglomerates. On the other hand, agglomeration may be necessary, for example, for ease of handling powders. In applications such as catalysts, excessive attrition of particles, for example, in a fluidized bed could have a strong negative impact on the overall economics of a plant. Unstable fluidization behavior and product contamination also could be caused by unexpectedly high attrition. Other examples include generation of very fine particles (dust) which creates a serious environmental concern, and an explosion hazard if the fines are flammable. Hence, agglomerated products must be capable of resisting attrition during the handling and processing stages.

The importance of the attrition of catalysts is recognized in the catalysis community. ASTM has developed standards for quantifying the attrition of catalysts and catalyst carriers using cylindrical drums, mechanical sieve shaker, or air jets (11-13). Particle shapes for which the attrition test applies include tablets, extrudates, spheres, and irregularly shaped particles. Particle sizes occur in the range of 2-19 mm for the drums, and 10-180 μm for the air jets. However, these tests are not quite applicable to the Fe-catalysts being prepared for bubble column reactors since these catalysts are quite weak. Without an appropriate method to measure

attrition resistance, it is difficult to do research on improving the attrition resistance of these catalysts.

This study describes two approaches we have used to measure the strength or attrition resistance of a heterogeneous catalyst. These methods include uniaxial compaction and ultrasonic fragmentation. The Fe F-T catalyst was compared to a sample of catalyst support that is representative of strong agglomerates. Best-fit lines as well as a mathematical model were used to quantify the strength via uniaxial compaction method, and these results were compared to the qualitative results obtained from ultrasonic fragmentation.

Overview of Attrition Tests

Uniaxial Compaction Method

Uniaxial compaction is a method in which a sample confined in a cylindrical die is compressed uniaxially under a load. This method is an alternative to the conventional method in which individual particles are crushed between two platens (14). Individual particles show a distribution of strengths. To obtain a reliable average strength, many particles must be tested. Hence, uniaxial compaction is often used in place of the conventional method.

Glass *et al.* (15,16) at Sandia National Laboratories showed that compaction generally occurred in two stages (Figure 1). In the first regime, the gradual increase in relative density is due to particles, such as granules and agglomerates, sliding and rearranging without fracture. At this stage little compaction occurs, and only a small percentage of the void space is removed during rearrangement. It is often observed experimentally that this regime has a slope of ≈ 0.003 - 0.005 . In the second regime, a sharp increase in relative density is due to deformation and fracture in conjunction with the sliding and rearrangement of particles (slope ≈ 0.2). At this stage a larger percentage of void space is removed during rearrangement. Beyond the second regime there may be another characteristic slope at higher pressures, but this has not been analyzed because it is still not well understood. The intersection of these slopes in the two regimes is called the breakpoint, which has been used as a semi-quantitative indicator of average strength. If all particles or agglomerates had the same strength and were in regular array, they would start to collapse at the same pressure and the breakpoint would be seen as a sharp discontinuity (17). No discontinuity, however, is observed for most materials due to large variations in strength among particles. This variability was assumed to be attributed to a variation in the flaw size as well as in the size and shape of particles. However, if best-fit lines were drawn through the data in the two linear regimes, an average strength value could be obtained.

Instead of measuring strength based on best-fit lines, average strength could be predicted via mathematical models. For example, Ciftcioglu *et al.* (18) calculated agglomerate strength curves for yttria powders using the Rumpf equation (19). This equation, however, was based on the assumption that the particles were monodispersed and spherical, and that there was instantaneous failure at all points, which contradicted the experimental observations of Glass (15). Adams *et al.* (20) derived a model which correlated pressure to natural strain to obtain an average cohesive strength on a bed of agglomerates. Other models included a theoretical model by Kenkre *et al.*

(21) capable of predicting various powder properties, and a model derived by Song *et al.* (22) to estimate agglomerate tensile strength of ceramic powders.

Glass *et al.* eliminated the effects of shape and size factors by performing uniaxial compaction tests on uniform-size glass spheres. They found that, surprisingly (15), glass spheres with uniform shape and size also exhibited very large variations in strength. One possible reason for the high variability in strength of the glass spheres was that a large range in flaw sizes may be present.

Ultrasonic Fragmentation Method

Thoma *et al.* (23) at the University of New Mexico developed a characterization technique to quantitatively determine agglomerate strength distributions by exposing a powder dispersion to a calibrated ultrasonic field and following the changes via particle size analysis. The ultrasonic disrupter in the calibration study was a 20kHz Tekmar TSD-500 Sonic Disrupter equipped with a V1A horn having a 1/2" tip. The ultrasonic forces were calibrated at various energy level settings for a fixed amount of time via an ultrasonic disrupter using various types of hollow glass bubbles. The bubbles that could not be broken via ultrasound were then crushed in a mercury porosimeter, and hence the effective pressure during ultrasonic excitation could be calibrated. Table 1 gives power output and breakage pressures for a given control setting (24). Determination of the effective breaking pressures involved ascertaining the pressure at which the untreated glass bubble strength distributions merged. Weaker bubbles were used for settings lower than 5, and stronger bubbles were used for settings 5 and above.

Fragmentation Mechanism

Ultrasonic fragmentation of agglomerates (i.e., size reduction) is caused by interaction of cavitation bubbles with adjacent agglomerated particles. Such cavitation causes breakage via the expansion and subsequent violent collapse of these bubbles, creating intense pressures in the vicinity of the collapse (25), which is the primary means of agglomerate comminution (Figure 2).

Two mechanism for particle breakdown have been determined: erosion and fracture. Erosion is a process where primary particles are dislodged from the surface of the agglomerate when the cavitation pressure exceeds the agglomerate strength. Kusters *et al.* reported that the amount of erosion is proportional to the geometric surface area (i.e., external surface) of the parent agglomerate. Fracture is the division of the original agglomerate into several smaller agglomerates, and results from crack propagation through the agglomerate compact. Stresses exerted on the agglomerate cause the initiation and propagation of surface flaws. When the cavitation pressure is below the agglomerate strength of a given powder, then a time lag is observed where crack propagation occurs, weakening the compact, until fragmentation proceeds unhindered. The time lag to unhindered fragmentation will decrease with increasing cavitation stress, and is directly related to agglomerate strength since the time lag will become negligibly small as the cavitation pressure becomes equal to the agglomerate strength. In analogy to mechanical fracture testing (i.e., the Charpy test), the fracture toughness of an agglomerate

powder could be defined by the energy required to achieve a certain amount of product fines given the cavitation pressure is equal to the agglomerate strength. The relative fracture toughness could also be used as a measure of relative agglomerate strength. Such a postulate might be confirmed by using comparing agglomerate fracture by ultrasonication of powders of known strengths by tensile testing methods, e.g., the method of Rumpf, Pietsch *et al.*, and Schubert *et al.* (26-28).

Experimental

Ultrasonic Fragmentation

A 0.5% sodium hexametaphosphate (SHMP; Aldrich Chemicals) solution was prepared by mixing 0.5 g of SHMP with 1 L of deionized water. VISTA-B-965-500C (alumina support) was used as a test sample, representing strong agglomerates, and compared to a UCI-LAPI-COMP-DRUMC catalyst (47.63% Fe, 3.75% Cu, 3.74% K, 5.28% Si by weight), a catalyst used previously in DOE pilot plant tests.

In a typical run, 1 g of catalyst sample was added to 50 ml of the 0.5% SHMP solution which was used as a dispersant. A Micromeritics Sedigraph 5100 analyzer was used to measure the particle size distribution at time 0 min. The suspension was then subjected to ultrasonic energy at an amplitude setting of 20 at 5 min intervals using a Tekmar 501 ultrasonic disrupter equipped with a V1A horn and a 1/2" probe tip (a setting of 20 is equivalent to a setting of 2 for the Tekmar 500 ultrasonic disrupter). After different extents of ultrasonic irradiation, the particle size distribution was analyzed to detect the mode of particle fragmentation.

Uniaxial Compaction

The VISTA alumina support was used for the uniaxial compaction tests. In a typical run, 10 mg were loaded into the cell of a die with a 1/8" opening. A plunger was then placed on top of the filled die, taking great care not to compress the sample. To account for the error due to deformation of the top plunger and to the compliance of the crosshead, the displacement of the empty fixture as a function of load was subtracted from the displacement of the filled die.

Compaction tests were conducted by placing the filled die underneath the crosshead of the Instron 5565 machine. The crosshead was manually lowered such that it was just touching the top plunger. The displacement gauge was zeroed, and the crosshead was then activated at a rate of 1.00 mm/min. Testing was continued until a load of 1000 N was reached. The sample was repeated for reproducibility.

This same analysis procedure was then applied to the UCI catalyst, and compared to the VISTA alumina support.

Results and Discussion

Figure 3 shows semilogarithmic plots of compaction curves for the VISTA-B-965-500C alumina support. The relative density was calculated using the mass of the sample, initial compact height, measured displacement, and theoretical density. No obvious breakpoints in the

compaction curves were observed due to the variability in strengths (17), but if best-fit lines were drawn through the data in the two linear regimes, an average breaking strength value could be obtained. The breaking strength was determined to be 11.97 MPa from Fig. 3a. The test shown in Fig. 3b yielded a curve that was almost identical to that of Fig. 3a, but a lower slope (not shown) at high loads yielded a breaking strength of 6 MPa. Glass *et al.* (15) suggested that as long as the aspect ratio L_t/D was ≤ 1.2 , consistent compaction results would be produced. Although the aspect ratio fit this criterion (0.61 for Fig. 3a vs. 0.74 for Fig. 3b), consistent results were not obtained due to factors such as individual particle sizes and shapes, the place at which the samples were taken from the sample in the bottle, and the disturbance of the sample in the die during placement of the top plunger.

The breaking strength via best-fit lines has been found to be sensitive to how many data points are included in determining the slope of the two linear regimes. Hence, we have explored alternative methods to derive the breaking strength. Figure 4 shows compaction data for the VISTA alumina sample. The data were presented in the form of a plot of $\ln(P)$ vs. natural strain, e , defined as $\ln(h_0/h)$ where h_0 is the initial height and h is the measured height. The results were analyzed using a mathematical model presented by Adams *et al.* (20) which yielded a value for the breaking strength (σ) of the particles within the sample. Except for the data below $e = 0.2$, the model closely fits with the data for e above 0.2. Deviations from the model for $e < 0.2$ may be due to experimental errors based on parameters, such as particle size distribution, during the rearrangement of particles and before the onset of compaction. The breaking strengths determined from the model were 7.44 MPa for Fig. 4a and 4.89 MPa for Fig. 4b. In Figure 3, the breaking strengths differed by about a factor of 2, whereas in Figure 4, they differed by about a factor of 1.5. Although the factors between them do not differ by much, the method using a mathematical model does appear to be less sensitive to variations in the analysis procedure, as is the breakpoint data.

Figure 5 shows a cumulative mass distribution plot of mass finer (%) vs. equivalent spherical diameter for the VISTA alumina sample. According to this plot, there was little attrition after 15 min of ultrasonic irradiation, indicating that erosion was the dominant fragmentation mechanism. Figure 6 shows a cumulative mass distribution plot for the UCI catalyst. According to this plot, fracture was the dominant fragmentation mechanism, along with some generation of fine particles due to erosion. Figure 7 shows compaction data for the VISTA alumina support and the UCI F-T catalyst, fitted with the mathematical model. Figures 5 and 6 showed significant differences in strength by the ultrasonic fragmentation method, while in Figure 7 their strengths differed by about 1.2 MPa via the uniaxial compaction method. Hence, the ultrasonic fragmentation method seems to be more sensitive to the differences between these powders, that are not seen in the compaction method.

We have also explored the use of the ultrasonic fragmentation method for a Fe F-T catalyst that does not contain any silica, and a Fe F-T catalyst containing a kaolin binder. Figure 8 shows a cumulative mass distribution plot for these catalysts. The catalyst containing the kaolin binder was very weak, comparable to the binderless catalyst. Further analysis using transmission electron microscopy (TEM; Figure 9) showed that kaolin and Fe F-T catalyst occurred as two distinct phases, and that both had plate-like structures which did not connect to create strong

interlocking forces between them. Therefore, binders with other morphologies should be explored to provide improved attrition resistance in these catalysts.

Summary

Two methods were explored for their application in measuring the strength or attrition resistance of heterogeneous catalysts: uniaxial compaction and ultrasonic fragmentation. The VISTA alumina support was used to determine the applicability of the uniaxial compaction tests. The breaking strength determined from the breakpoint was found to be sensitive to how many data points were included in determining the slope of the two linear regimes. As an alternative method, average strength was predicted via a mathematical model. However, neither approach provided very consistent results in replicate tests from a given sample. The compaction method was also not able to reveal differences in strength among dissimilar catalysts. The Fe catalyst is considerably weaker than the alumina support, but the strength measured via compaction showed differences in strength of 1.2 MPa, well within the variation seen within a given sample. On the other hand, cumulative mass distribution plots showed significant differences in strength by ultrasonic fragmentation. Erosion was the dominant fragmentation mechanism for VISTA alumina while fracture was the dominant mechanism for the UCI catalyst, both after 15 min of ultrasonic irradiation.

The ultrasonic fragmentation method was used for a Fe F-T catalyst that contained no binder and one that contained a kaolin binder. The results indicate that a plate-like morphology in a binder is not suitable for providing improved agglomerate strength. The role of other binder morphologies on the strength of spray-dried agglomerates is being pursued in our laboratory.

Acknowledgments

The authors would like to thank the U.S. Department of Energy and the Federal Energy Technology Center (FETC) under contract no. DE-FG22-95PC95210 for their financial support of this project. The authors also thank Robert Gormley and his associates at FETC for providing us with the catalysts and support, and for helpful discussions.

References

1. Bukur, D. B., "Development of Precipitated Iron Fischer-Tropsch Catalysts. Quarterly Technical Progress Report", Performer: Texas A&M University, College Station, Department of Chemical Engineering, PR: PC A04/MF A01.
2. Davis, B. H., "Technology Development for Iron Fischer-Tropsch Catalysis. Quarterly Technical Progress Report", Performer: Kentucky University, Research Foundation, Lexington, PR: PC A04/MF A01.
3. Bhatt, B. L., "Liquid Phase Fischer-Tropsch (II) Demonstration in the LaPorte Alternative Fuels Development Unit", Performer: Air Products and Chemicals, Inc., Allentown, PA, PR: PC A07/MF A02.
4. Saxena, S.C., *Catalysis Rev. Sci. Engr.*, 37 (1995) 227.

5. Parkinson, G., *Chem. Engr.* (1997) 39.
6. Raje, A., Inga, J.R., and Davis, B.H., *Fuel*, 76 (1997) 273.
7. Stern, D., Bell, A.T., and Heinemann, H., *Ind. Eng. Chem. Des. Dev.*, 24 (1985) 1213.
8. Bukur, D.B., Nowicki, L., and Patel, S.A., *Canadian J. Chem. Engr.*, 74 (1996) 399.
9. Dynys, F.W. and Halloran, J.W., *J. Am. Ceram. Soc.*, 64 (1981) 596.
10. Lange, F.F. and Metcalf, M., *J. Am. Ceram. Soc.*, 66 (1983) 398.
11. 1996 Annual Book of ASTM Standards, Vol. 05.03, Designation: D4058-92, 979.
12. 1996 Annual Book of ASTM Standards, Vol. 04.02, Designation: C136-95a, 78.
13. 1996 Annual Book of ASTM Standards, Vol. 05.03, Designation: D5757-95, 1064.
14. Bemrose, C.R. and Bridgwater, J., *Powder Tech.*, 49 (1987) 97.
15. Glass, S.J., Ewsuk, K.G., and Readey, M.J., SAMPE Technology Conference, Albuquerque, NM, 1995.
16. Glass, S.J. and Newton, C., ACERS Symposium on Science, Technology, and Commercialization of Powder Synthesis and Shape Forming Processes, Cincinnati, OH, 1995.
17. Ciftcioglu, M., Akinc, M., and Burkhart, L., *Am. Ceram. Soc. Bull.*, 65 (1986) 1591.
18. Ciftcioglu, M., Akinc, M., and Burkhart, L., *Am. Ceram. Soc. Bull.*, 65 (1986) 1591.
19. Rumpf, H., Agglomeration, K.V. Sastry, New York, 1977.
20. Adams, M.J., Mullier, M.A., and Seville, J.P.K., *Powder Tech.*, 78 (1994) 5.
21. Kenkre, V.M., Endicott, M.R., Glass, S.J., and Hurd, A.J., *J. Am. Ceram. Soc.*, 79 (1996) 3045.
22. Song, J-H and Evans, J.R.G., *J. Am. Ceram. Soc.*, 77 (1994) 806.
23. Thoma, S.G., Ciftcioglu, M., and Smith, D.M., *Powder Tech.*, 68 (1991) 53.
24. Thoma, S.G., Ciftcioglu, M., and Smith, D.M., *Powder Tech.*, 68 (1991) 71.
25. Webster, E., *Ultrasonics*, Jan-Mar (1963) 39.
26. Rumpf, H., Agglomeration, Knepper, W.A., (Ed.), New York: Wiley Interscience, 1962.
27. Pietshch, W.B., Hoffman, E., and Rumpf, H., *Ind. Engr. Chem. Prod. Res. Ed.*, 8 (1969) 58.
28. Schubert, H., Herrmann, W., and Rumpf, H., *Powder Tech.*, 11 (1975) 121.

Figure 1 Semilogarithmic compaction curve. Compaction generally occurs in two stages: granule rearrangement and sliding without fracture, and local deformation and fracture with granule rearrangement

Figure 2 Schematic of the cavitation mechanism for agglomerate comminution. The two mechanisms, erosion and fracture, are illustrated.

Fig. 3a

Fig. 3b

Figure 3. Semilogarithmic plots for the VISTA-B-965-500C alumina support. For Fig. 3a, the relative density vs. log P curve can be fit by two linear segments whose intersection determines a nominal breaking strength (11.97 MPa). For Fig. 3b, the compaction curve up to a pressure of 30 MPa is very similar to that of Fig. 3a. However, using linear fits to the data yields a nominal breaking strength of 6 Mpa.

Fig. 4a

Fig. 4b

Figure 4. Compaction data for the VISTA alumina support. A mathematical model presented by Adams *et al.* (20) yields a value for the breaking strength (σ) of the particles within the sample. The model closely fits the data, and the strengths are determined to be 7.4 MPa for Fig. 4a and 4.9MPa for Fig. 4b.

Figure 5 Sedigraph particle size distribution of VISTA-B-965-500C sample. The starting alumina from VISTA was sieved and calcined in air at 500°C. Very little fragmentation occurs after 15 min of ultrasonic irradiation, although some erosion has occurred.

Figure 6 Sedigraph particle size distribution for UCI F-T catalyst UCI-LAPI-COMP-DRUMC, used previously in DOE pilot plant tests. There is considerable particle breakdown and generation of fine particles after 15 min of ultrasonic irradiation.

Figure 7 Compaction data for the VISTA alumina support and the UCI F-T catalyst. A mathematical model presented by Adams *et al.* (20) yields a value for the breaking strength (σ) of the particles within the sample. The strength for the UCI catalyst is determined to be 6.3 MPa, and the strengths between these samples differ by about 1.2 MPa.

Figure 8 Comparison of the breakdown of the binderless catalyst with the kaolin binder containing Fe F-T catalysts. The kaolin binder does not impart any additional strength to the catalyst.

Figure 9 TEM picture of a commercial Fe catalyst with a kaolin binder. Kaolin and Fe catalyst occurs as two distinct phases, and that both have plate-like structures which do not connect to create strong interlocking forces between them.

Table 1. Ultrasonic power output, ϵ , and breaking stress, σ , for a given control setting, N.

Setting, N	Power (W)	Stress (lbs/in ²)	Setting, N	Power (W)	Stress (lbs/in ²)
1.0	1.06	150	6.0	19.25	5,150
2.0	2.13	200	7.0	29.57	6,000
3.0	3.19	350	8.0	55.32	9,950
4.0	5.32	1,250	9.0	79.79	10,200
5.0	13.2	4,350	10.0	100.85	11,500

Thoma, S.G., Ciftcioglu, M., and Smith, D.M., *Powder Tech.*, 68 (1991) 53.

Appendix C

PHASE TRANSFORMATIONS IN IRON FISCHER-TROPSCH SYNTHESIS (FTS) CATALYSTS

Yaming Jin and Abhaya K. Datye

Center for Microengineered Materials and Department of Chemical & Nuclear Engineering,
University of New Mexico, Albuquerque, NM 87131, USA

Iron Fischer-Tropsch synthesis (FTS) catalysts are in the form of Fe_2O_3 as prepared. After activation in H_2 or CO and introduction into the FTS reactor, the catalyst is known to consist of a mixture of iron oxide, reduced iron and carbide phases (1). Previous work has relied on Mössbauer spectroscopy and X-ray diffraction to characterize the phase composition of iron FTS catalysts. These techniques provide information averaged over the sample, and both techniques have difficulty analyzing highly dispersed iron phases having particles less than 5 nm in size (2,3). This has made it difficult to establish the relationship between specific iron phases and overall FTS reactivity (1-4). The active phase(s) responsible for the FTS activity of iron FTS catalysts is still unknown and remains a subject of intense debate and discussion.

Transmission electron microscopy (TEM) allows a study of the spatial distribution and morphology of the various iron phases present in the working catalyst. The difficulty in applying TEM arises because the FTS catalyst is present at a loading of only 5 wt% in a hydrocarbon wax

Figure 1 TEM pictures of SA0706 show phase transformations in the iron carbides in the reaction environment. A) After CO activation the catalyst contains particles of χ -carbide [(CO+ H_2) conversion = 36.1%]. b) After use for 113 hours for F-T-S at a H_2 /CO ratio of 0.67 and a pressure of 100 psig, the χ -carbide has transformed into smaller particles of the ϵ' -carbide with a dramatic increase in activity [(CO+ H_2) conversion = 77.9%].

Figure 2 The particle size distribution of the iron carbides seen A) after initial activation TOS= 0 hour and B) after reaction for TOS=113 hours. The χ -carbide particles have broken up into smaller ϵ' -carbide particles, causing an increase in reactivity for FTS.

of high molecular weight. The wax must first be removed by a process called Soxhlet extraction. We have recently (5) shown that removal of the wax can lead to catalyst oxidation, either during the hot extraction process or during subsequent air exposure. To analyze the catalyst while it is still embedded in the wax, we have used ultramicrotomy to prepare thin sections of the catalyst. In this paper, we describe the nature of phase transformations that occur during activation and as the catalyst is used for F-T synthesis. The samples analyzed here were prepared at Texas A&M University (6) and were used for F-T synthesis in a medium pressure stirred tank reactor. At various times on stream, a sample of the catalyst was removed under a protective inert blanket. The phase composition of these catalysts was studied by Quantitative Rietveld Structure Refinement (5).

Figures 1 shows a cross-section TEM image of the catalyst from run SA-0706 at time on stream TOS = 0 hour, and after use in the F-T synthesis reaction (TOS = 113 hours). After activation for 8 hours at 280 °C in CO, the catalyst has transformed into well defined particles of χ -carbide which is dispersed over a matrix that contains amorphous silica and unreduced iron oxides. During reaction, the χ -carbide transforms into ϵ' -carbide with a break up into smaller particles (see particle size distribution in Fig. 2) and a change in phase. The smaller particles in Fig. 1B can be indexed to the ϵ' -carbide phase based on their lattice fringes of 2.0 Å and from the diffraction pattern (see inset). These phase transformations are key to understanding the remarkable increase in catalyst activity seen on this catalyst over this period.

References

1. Dry, M.E., in *Catalysis Science and Technology*, Vol. 1, ed. Anderson, J.R., and Boudart, M., 1981
2. Shroff, M.D., Kalakkad, D.S., Coulter, K.E., Kohler, S.D., Harrington, M.S., Jackson, N.B., Sault, A.G., Datye, A.K., *J. Catal.*, 156, 185 (1995)
3. Bukur, D.B., Lang, X., and Ding, Y., *J. Amer. Chem. Soc., Div. Fuel Chem.*, 42(2), 623(1997)

4. Rao, K.R.P.M., Huggins, E.E., Huffman, G.F., Gormley, R.J., O'Brien, R.J., Davis, B.H., Energy and Fuels, 10, 540, 1996
5. Mansker, L.D., Jin, Y., Bukur, D.B., and Datye, A.K., Appl. Catal., submitted.
6. We thank Prof. Dragomir Bukur of Texas A&M University for providing these samples, which were prepared as a part of a larger program devoted to synthesis of Fe F-T catalysts.
7. Financial support for this work was provided by the US DOE grant DE-FG22-95PC95210

Appendix D

Characterization of Bubble Column Slurry Phase Iron Fischer-Tropsch Catalysts

Yaming Jin and Abhaya K. Datye

Center for Microengineered Materials and Department of Chemical & Nuclear Engineering,
University of New Mexico, Albuquerque, NM 87131, USA

Abstract

The cross-sectional transmission electron microscopy (XTEM) method and x-ray diffraction (XRD) were used for phase analysis of bubble column slurry phase iron Fischer-Tropsch catalysts. For the deactivated LGX-171, the carbide phase shows mono-dispersion characteristic. The carbide particles have well-defined shape, spherical or rectangular, and give a distinctive c-carbide XRD pattern. The average particle size, 39.4 nm, by XRD was in good agreement with statistical value of 37.5 nm by TEM. On the other hand, two carbide phases are found to coexist in the active catalyst: big twisted particles (20-40 nm) and highly dispersed carbide particles (less than 10 nm). High resolution TEM work shows that the big distorted carbide particles belong to e'-carbide, while the highly dispersed carbide phase is most probably a mixture of e'-carbide and c-carbide. For this particular set of iron catalysts, big faceted magnetite single crystals were found to be present in the catalyst both at the active and deactivated states. From these, we conclude that the e'-carbide must represent the active phase in Fe F-T catalysts.

1. Introduction

Fischer-Tropsch Synthesis is recognized as a viable route for conversion of syngas to liquid fuels (1). This study is directed at understanding mechanisms of catalyst deactivation in Fe catalysts used in a slurry phase reactor. We report here analyses of end-of-run catalysts from two F-T runs. The catalyst reactivity has been reported elsewhere (2), but in the previous work, we were unable to conclusively identify the causes of catalyst deactivation.

It is recognized that loss of surface area of the catalytically active phase and deposition of unreactive carbonaceous deposits must constitute possible mechanisms for catalyst deactivation (2,3). However, there is as yet no consensus on the nature of the active phase in Fe F-T catalysts. Previous work has tried to correlate bulk phase information with catalytic reactivity based on results of analytical methods such as Mössbauer spectroscopy (MS) and X-ray diffraction (XRD) techniques. Besides the intrinsic limitations of these bulk techniques for the quantification of a highly dispersed iron phase (with particles less than 10 nm), there are several other experimental difficulties in determining an accurate phase composition of slurry bubble column F-T catalysts. The catalyst removed from the reactor is dispersed in product wax at a loading of 5 wt%, hence a wax removal step is usually performed prior to analysis. We have recently (4) shown that Soxhlet extraction, the commonly used wax removal procedure, can cause oxidation of the

reduced iron phases. Furthermore, the wax is often crystalline and interferes with the diffraction peaks from the iron carbide phases of interest. We have also found that there are enormous differences in scattering factors for the various iron phases making quantitative analysis based on peak heights completely unreliable (4). We believe that some of these experimental difficulties have resulted in the generally accepted conclusion that there is no clear relationship between catalyst activity and the phase composition of the working catalyst.

In order to get accurate phase information of working FTS catalysts, and to minimize problems with surface oxidation of the reduced iron phases, we feel it is necessary to characterize working iron catalysts protected by the hydrocarbon wax (4). Quantitative Rietveld structure refinement analysis allowed us to obtain useful phase information of the wax-containing iron catalyst sample. Nevertheless, the peak overlaps between the crystalline wax and iron phases of interest, and the low diffraction peak intensities suggested that the XRD analysis be corroborated with other methods. In this paper, we report a cross-section transmission electron microscope (XTEM) study of the phases present in working Fe FTS catalysts. The TEM results along with XRD analysis helps to provide a more comprehensive picture of these catalysts.

2. Experimental

The catalyst sample studied in this paper has a chemical composition of 100Fe/4.4Si/1.0K and was provided to us by Dr. Burtron Davis at the Center of Applied Energy Research (CAER), University of Kentucky, after use in FT synthesis runs. In run LGX-171, the precipitated oxide precursor was pretreated with syngas at 1 atm and 270°C for 24 hours, then underwent FTS at 270°C, 175 psig. The wax-mixed catalyst sample was removed from the slurry reactor after time-on-stream (TOS) 3164 hours. The catalyst activity was high for the first 2800 hours of this run, but over the last few hundred hours there was a rapid deactivation and the catalyst was removed at the end of run where CO conversion was 20%. On the other hand, in run LGX-175, the catalyst precursor was pretreated in CO at 1 atm and 270°C for 24 hours and underwent FTS at the same conditions as LGX-171. The catalyst sample was removed after TOS 1160 hours while its CO conversion was 79%. Detailed reactivity data were reported elsewhere (2,5).

XRD data were obtained on a Scintag PAD-V powder diffractometer using Cu-K α radiation ($\lambda=1.5406$ Å). Scans were taken from 10° to 90° in step-scan mode, 0.04° per step, 0.4° per minute. For cross section TEM, the wax-mixed iron catalysts were first embedded in Spurr's low viscosity epoxy. After curing the epoxy, sections with thickness about 40-60 nm were prepared. The microtomed sample sections were mounted on TEM grids with holey carbon film and examined in a JEOL 2010 HRTEM microscope operated at 200 KeV. These thin sections allow us to get high resolution images that permit detailed phase identification, and also to get particle size distributions for each iron phase.

Figure 1 XRD spectra of LGX-171 (upper) deactivated catalyst and LGX-175 (lower), active catalyst after partial removal of hydrocarbon wax.

3. Results

The XRD spectra of LGX-171 and LGX-175 with wax partly removed are shown in figure 1. Two phases, magnetite and c-carbide, can be clearly identified in the XRD spectrum of LGX-171 (the low activity catalyst). The average particle size estimated by Scherrer's equation is 27.2 nm and 39.4 nm for the two phases respectively. The catalyst from run LGX-175 (high activity) also

Figure 2 XTEM images of LGX-175. **A)** Low mag overview, the large magnetite single crystals are highlighted; **B)** High mag image of one of these faceted particles.

Figure 3 Fig. 3 TEM images showing the complex microstructure of sample LGX-175. **A)** Low mag view of 3 distinct phases: large distorted e'-carbide particles, fine carbide particles (some are highlighted), and highly dispersed magnetite particles. **B)** High mag view showing the coexistence of these 3 phases.

shows pronounced magnetite peaks with an estimated average particle diameter of 30.3 nm. However, the nature of the carbide peaks is very different from those in LGX-171. From the intensity of the (002) diffraction peak of c-carbide at $2\theta=41.45^\circ$ which does not interfere with the other peaks, we can see that very little c-carbide is present in LGX-175. On the other hand, the broad diffraction peaks at $2\theta=44.96^\circ$ and 40.00° match the (121) and (120) diffraction lines of e'-carbide. By using Scherrer's equation, we can estimate the average particle size of e'-carbide to be 19.2 nm.

Figure 2 shows XTEM images of the sample from LGX-175 (figure 2-A). Large (around 50 nm) faceted particles are seen to be sparsely dispersed in this image. By analyzing the high resolution images, we can conclusively identify these particles as magnetite single crystals, as shown in figure 2- B (2.94 Å corresponds to the (220) plane of magnetite). The rest of the catalyst is a complex mixture of iron phases. A typical view is shown in figure 3-A. Closer examination shows three different types of iron phases to be present in this particular sample. There are big distorted particles (20 to 40 nm) always with a surface layer or smaller particles sticking to them (figure 3-A). High resolution images of these iron phases have lattice spacings of 2.26 Å and 2.02 Å correspond to d-values of (120) and (121) planes of e'-carbide. Therefore, we attribute this phase to be e'-carbide. The rest of the catalyst contains highly dispersed particles (usually less than 10 nm) as shown in figure 3-A. Those without a surface layer are identified as fine magnetite particles, shown in figure 3-B (the 2.53 Å spacing corresponds to the d-value of the (311) plane of magnetite). The fact that magnetite lattice fringes are also seen on the surface of the carbide suggests that the highly dispersed magnetite may actually be a passivating oxide formed due to air exposure. The particles with a surface layer marked in figure 3-A are identified

Figure 4 Comparison of carbide phases in LGX-171 (deactivated) and LGX-175 (active). A) Regular shaped c-carbide particles in LGX-171 B) Highly dispersed carbide particles seen in LGX-175 (active catalyst) are missing in sample LGX-171.

as highly dispersed iron carbide. High resolution imaging has revealed that these particles exhibit lattice fringes of e'-carbide as well as c-carbide. These carbide particles do not necessarily coexist with the fine magnetite particles as seen in figure 3-A. In fact this phase was found to be well dispersed everywhere in the sample.

In contrast to sample LGX-175 (the active catalyst), sample LGX-171 (the deactivated catalyst) only showed the presence of c-carbide in addition to the magnetite, both by XRD and TEM. These c-carbide particles had smooth surfaces, and well defined shapes - rectangular or spherical. All of these particles have a uniform surface layer having a thickness of about 3-4 nm (fig. 4-A). The average particle diameter, 39.4 nm by XRD, is consistent with the estimated average diameter of 37.5 nm by TEM. There are also large magnetite single crystals dispersed in this sample similar to those seen in LGX-175. In addition, there is a polycrystalline magnetite phase distributed throughout this catalyst sample. However, unlike the LGX-175 (active) sample, the size of these magnetite particles is larger (about 10 to 20 nm), and those particle always form agglomerates as shown in Figure 4-A.

4. Discussion

In this work, we have analyzed two used FT synthesis catalyst samples by XRD and TEM. The XRD shows e'-carbide to be present in LGX-175 but only c-carbide to be present in LGX-171. It also appears that the e'-carbide peak seen in XRD comes mainly from the distorted, large e'-carbide particles seen in LGX-175 and the highly dispersed carbide particles appear to be missed completely by XRD. However, much of the surface area must come from the highly dispersed carbide phase that is seen in the active catalyst but totally absent from the deactivated catalyst.

Hence, analysis of the active phase must consider this highly dispersed phase. Considering the particle size of this carbide phase, we feel that this phase has most probably been missed by bulk analytical methods such as XRD and Mössbauer (particularly at room temperature where it would be superparamagnetic). This highly dispersed phase is actually a mixture of e'-carbide and c-carbide (as determined from lattice fringe spacings) and it is difficult to quantify the ratio of these two kinds of carbide by TEM alone (which only looks at a small region of the sample). It would be necessary to perform Mössbauer spectroscopy of these samples at liquid He temperatures and correlate with the TEM images to get at the true distribution of these phases. Without this data, we can state that the high activity of catalyst LGX-175 must be related, at least in part, to the presence of the highly dispersed carbide phase. Furthermore, since e'-carbide is the major bulk carbide phase seen in the active catalyst (by XRD), and it is completely absent in the deactivated catalyst, we feel comfortable in stating that the bulk e'-carbide must be more active than the bulk c-carbide.

In the above analysis, we have ignored the presence of the magnetite: the large single crystals as well as the highly dispersed magnetite. With H₂O and CO₂ being by-products of F-T synthesis (their ratio being determined by the extent of water gas shift), we can expect some magnetite to be present as a result of oxidation caused by these molecules. However, in a previous study (4) where the hot wax had been carefully removed under an inert blanket, we found neither the large magnetite crystals nor the dispersed phase. Other recent work (6) involving samples that were not exposed to air before analysis also confirms the absence of magnetite in the catalyst used for F-T synthesis. Hence, we suggest that the magnetite seen here may have two different origins. Since these two samples were both removed from the reactor without an inert protective environment while the slurry was still hot, we think part of the fine magnetite phase could arise due to oxidation of the iron carbide during slurry removal. In the case of LGX-175, we have also seen a magnetite layer on the surface of the iron carbide., analogous to a passivating layer of oxide seen in our previous work on air exposed samples (7). The large faceted magnetite single crystals are present in both the active catalyst (LGX-175) and inactive catalyst (LGX-171). They could not arise from an oxidation of the iron phase during slurry removal. We conclude that these magnetite particles represent unreduced magnetite from the catalyst precursor. Our previous work (8) has shown that magnetite that had a Swiss-cheese (porous) morphology could be readily reduced to iron carbide. The more perfect, faceted magnetite particles must be harder to reduce and hence they persist even after 3000 hours of reaction in syngas, a possibility we will investigate in our future work.

To summarize, we can conclude that the active F-T catalysts consists of a mixture of highly dispersed carbide phase and bulk e'-carbide. In the deactivated catalyst, both e'-carbide and the dispersed carbide were missing. This leaves open the question of how and why the catalyst in run LGX-171 deactivated, since it appeared to run at high conversion for over 2800 hours. Since, no samples are available of the catalyst in its active state, we can only speculate that a process upset may have caused transformation of the active dispersed carbide phase into a mixture of magnetite and c-carbide. It is clear that in its deactivated form the catalyst contains plenty of c-carbide, but show very low activity. Therefore, it appears that the e'-carbide must

represent the active phase in Fe F-T catalysts. Future work will attempt to correlate these observations with Mössbauer spectroscopy which should permit quantification of the phase composition of these working F-T catalysts. We conclude that XTEM provides valuable insight for understanding the microstructure of Fe catalysts used for F-T synthesis.

Financial support for this work from the US Department of Energy, FETC university coal research grant DE-FG-22-95PC95210 is gratefully acknowledged. We thank Dr. Burtron Davis for providing the catalyst samples whose analysis is reported here.

References

1. Xu, L., Bao, S., O'Brien, R.J., Raje, A. and Davis, B.H., ChemTech 47, 1998.
2. Jackson, N.B., Datye, A.K., Mansker, L.D., O'Brien, R.J. and Davis, B.H., in Catalyst Deactivation, (Bartholomew, C.H. and Fuentes, G.A. eds.), Stud. Surf. Catal., 111, 501 (1997).
3. Eliason, S.A. and Bartholomew, C.H., *ibid*, 517 (1997).
4. Mansker, L. D., Jin, Y., Bukur, D. B. and Datye, A. K., submitted to Appl. Catal., 1998.
5. O'Brien, R.J., Xu, L., Spicer, R.L. and Davis, B.H., Energy and Fuels, 10(4), 921 (1996).
6. Mahajan, D., et al., Energy and Fuels, in press
7. Shroff, M.D. and Datye, A.K., Catal. Lett., 37, 101 (1996)
8. Shroff, M.D., Kalakkad, D.S., Coulter, K.E., Kohler, S.D., Harrington, M.S., Jackson, N.B., Sault, A.G., and Datye, A.K., J. Catal., 156(2), 185 (1995).

Appendix E

Characterization of Slurry Phase Iron Catalysts for Fischer-Tropsch synthesis

Linda D. Mansker, Yaming Jin, Dragomir B. Bukur[†], and Abhaya K. Datye[‡]

Center for Micro-Engineered Materials and Chemical and Nuclear Engineering Department
University of New Mexico, Albuquerque, NM 87131-1341, USA

[†] Chemical Engineering Department, MS 3122; Texas A&M University,
College Station, Texas 77843-3122, USA

[‡]To whom all correspondence should be addressed

ABSTRACT

The study of Iron Fischer-Tropsch Catalysts by conventional powder X-ray diffraction (XRD) is complicated by the number and type of phases present (α -Fe, various iron carbides, Fe_xC : $2 \leq x \leq 3$, magnetite, Fe_3O_4), by peak overlap in the diffraction patterns arising from these phases, and by differences in the ability of each phase to diffract x-rays, which directly influences quantitation. This has led to the consensus that activity for Fischer-Tropsch (F-T) synthesis does not correlate with the bulk composition of the iron catalyst, as seen by x-ray diffraction. As we demonstrate in this paper, some of the problems associated with sample analysis of the working F-T synthesis catalyst originate with the difficulty in preserving the microstructures and composition intact, as the sample is separated from the product and prepared for analysis. Other problems can originate with the way diffraction data are commonly collected and interpreted. In this paper, we present a study of an iron F-T synthesis catalyst, used in a stirred tank reactor, where samples have been removed under inert atmosphere and care was taken to preserve the catalyst constituents intact.

We conducted a systematic, careful analysis of a working Fe-based catalyst, used for two F-T synthesis runs. The reactor was operated under conditions similar to those used for commercial F-T synthesis. Using x-ray diffraction with Rietveld Structure analysis, we demonstrate that we can construct a comprehensive picture of this working catalyst, by correlating the results with the kinetics observed with this catalyst after activation with two different pretreatments, CO and H_2 . We conclude that, in its most active form, this Fe catalyst contains the so-called ϵ' -carbide (hereafter designated Fe_7C_3) and alpha-iron (α -Fe), while the so-called χ -carbide (hereafter designated Fe_5C_2), also present in varying amounts during the run, appears to be less active. Our results also show that Soxhlet extraction, a commonly used procedure to remove the wax from a catalyst, can cause changes in catalyst phase composition, and that a separation method based on removal of the wax by warming the sample to reaction temperature and flowing inert gas over it, might present a viable alternative to Soxhlet extraction.

Introduction

The Fischer-Tropsch (F-T) synthesis, which produces high-molecular weight hydrocarbon wax from syngas, is considered an effective solution to the problem of finding suitable substitutes for liquid fossil fuels. The F-T synthesis reaction converts syngas (H_2 / CO, derived from natural gas or coal) to liquid hydrocarbon feed stocks, which can be used for further processing to chemicals, catalytically cracked to various API weight fuels, etc. The choice of catalyst depends upon the syngas ratio (H_2 / CO). The H_2 / CO ratio is dependent, in turn, upon the syngas precursor and the processing method. A reasonable H_2 / CO feed ratio ranges from 1.8 - 2.5, which is typical of natural gas-derived syngas. Coal-derived syngas typically produces an H_2 / CO ratio of 0.5-1.7; therefore the catalyst used must possess adequate water gas shift (WGS) activity (in which F-T synthesis product water and CO from the feed are converted to H_2 and CO_2) to make up the deficit in H_2 for the F-T synthesis. Iron F-T synthesis catalysts effectively promote the water-gas shift (WGS) reaction; however, little is known about the iron catalyst composition, morphology or behavior under typical industrial process conditions. Previous attempts to characterize the iron F-T synthesis catalyst have resulted in a great deal of confusion, some of which may arise from the processing thought to be required to obtain a powder sample suitable for analysis, and from subtleties arising from the catalyst phase composition.

Iron F-T synthesis catalysts are prepared by precipitation of a water-soluble iron species (such as $\text{Fe}(\text{NO}_3)_3$), with or without promoters (such as KNO_3 and $\text{Cu}(\text{NO}_3)_2$) and binders (such as silica). The precipitated powder is then calcined to form hematite (Fe_2O_3) and activated by pretreatment with H_2 , CO, or syngas, outside the reactor or in-situ. Activation alters the catalyst composition to what is thought to be a mixture of iron oxides (Fe_2O_3 , Fe_3O_4), various iron carbides (Fe_xC), and iron metal ($\alpha\text{-Fe}$).

There is no agreement over the nature of the working catalyst and the active phase(s) responsible for F-T synthesis. In the literature, we find studies suggesting that magnetite (Fe_3O_4) may be the active phase (Butt, 1981; Teichner, 1982), while other workers conclude that the iron carbides (Fe_xC) must constitute the active phase(s) (Shroff, et al., 1995, 1996). It is accepted, however, that bulk Fe_3O_4 introduced into the F-T synthesis reactor is inactive for the reaction (Huang et al., 1993) and a careful study of catalysts in a fixed bed reactor has clearly linked deactivation of the Fe catalysts to the transformation into Fe_3O_4 (Coville et al., 1994).

The fully-reduced iron phase ($\alpha\text{-Fe}$) tends to carbide to the Fe_5C_2 phase in syngas; therefore it seems likely that, initially, the Fe_5C_2 carbide would be the active phase. However, as shown in this paper, as well as in a companion paper in this special issue (Bukur et al., 1998), a catalyst activated in CO exhibited very low activity initially, despite having almost completely transformed to the Fe_5C_2 phase, and exhibited a gradual increase in activity to a high steady state value with time, along with significant compositional changes. This implies that the presence of the Fe_5C_2 phase does not guarantee an active catalyst, and some iron phases may be more active than others. However, previous attempts to relate activity to the phase composition have not been successful, and the review paper by Dry (1980) concluded that there is “no reason to relate the amount and nature of iron carbides to F-T synthesis activity.”

In order to gain a better understanding of iron F-T synthesis catalyst, we have systematically examined a working catalyst, using x-ray diffraction as the primary analytical technique, taking special care to ensure that the catalyst morphology is preserved during sample preparation and subsequent analysis. The study was performed as a cooperative effort of two laboratories; the catalyst reactivity study was performed at Texas A&M University (TAMU), while the characterization study was performed at the University of New Mexico (UNM). Specifically, we present an analysis of two runs performed in a stirred tank reactor, using identical catalyst precursor. One of the catalysts was activated in CO at 280° C; the other was activated in H₂ at 250° C. These runs are part of a larger study of catalyst activation treatments conducted at TAMU, as described elsewhere in this issue (Bukur, et al., 1998).

Experimental

The catalyst samples discussed in this paper were obtained from two F-T synthesis runs conducted at Texas A&M University (TAMU). The catalysts were prepared from the same precursor hematite, (Fe₂O₃), doped with potassium (K), copper (Cu), and silica (SiO₂). The first catalyst was pretreated in H₂ at 250°C (run SB-3425, hereafter called the H₂-reduced catalyst); the second catalyst was pretreated in CO at 280°C (run SA-0946, hereafter called the CO-reduced catalyst). The details of catalyst preparation, pretreatment, reaction run conditions, and initial experimental behavior for F-T synthesis in a stirred tank reactor are presented elsewhere in this issue (Bukur, et al., 1998).

Characterization studies were performed at TAMU and at the University of New Mexico (UNM) on two sets of slurry samples (catalyst suspended in the waxy product) removed by dip tube under inert atmosphere from the working reactor, at different times during each run, using the method described by Bukur, et al., 1997. The importance of removing F-T synthesis product slurry under inert atmosphere in order to preserve the composition and morphology of the catalyst has been discussed elsewhere (Datye, et al., 1997).

Each slurry sample was split into two portions. One portion of each sample was provided to UNM by TAMU for detailed X-ray and TEM analysis. Diffraction studies of the slurry samples from both runs and of the Soxhlet-extracted powders prepared at TAMU from the H₂-reduced run (SB-3425) were performed at UNM. X-ray analysis of Soxhlet-extracted powders from the CO-pretreated run (SA-0946) was performed at TAMU. One slurry sample from the H₂-reduced run (SB-3425) was concentrated in our lab by warming the slurry for several days at 150° C under inert atmosphere and letting the catalyst powder concentrate in the bottom portion of the vial. Material was cut from the bottom of the vial and scanned by XRD. The concentrated sample and the remainder of the slurry was then completely stripped of its wax under flowing inert at reaction temperature, for subsequent analysis by x-ray diffraction and high intensity neutron powder diffraction (HIPD), performed at Los Alamos National Laboratory's Manuel Lujan Neutron Science Center (LANSCE).

X-ray diffraction data for slurry and Soxhlet-extracted powder samples from the H₂-pretreated catalyst, and for slurry samples from the CO-pretreated catalyst were collected at UNM, using a Scintag PAD-V powder diffractometer with diffracted beam monochromator, operated in step-

scan mode, using Bragg-Brentano (θ - 2θ) geometry. Data were collected at 15° to 105° , 0.002° per second for the slurry samples and Soxhlet-extracted powders from the H_2 -pretreated catalyst (run SB-3425). Data were collected at 10° to 120° 2θ , 0.005° per second for the slurry samples from the CO-pretreated catalyst (run SA-0946). All scans have an average diffraction scan error on the order of $\pm 0.005^\circ$ ($0.0004 \text{ \AA}$). The x-ray diffraction data for the Soxhlet-extracted powders prepared from the samples of CO-pretreated catalyst slurry (run SA-0946) were collected at TAMU, using a Scintag XDS-2000 series powder diffractometer in fast scan (continuous) mode, Bragg-Brentano (θ - 2θ) geometry, $.0167^\circ$ per second scan rate, with an average diffraction scan error on the order of $\pm 0.05^\circ$ ($0.006 \text{ \AA}$). In this paper, we will report angles to 2 decimal places, and d-spacings to 3 decimal places.

The UNM diffraction data have been used for phase identification and quantitation, structure analysis, minor phase deconvolution, crystallite size analysis, crystallite shape determination, and evaluation of sample preprocessing methods. None of the diffraction data were subjected to background or polarization correction, or $K_{\alpha 2}$ stripping, prior to analysis and interpretation. Slurries, concentrated slurries, and powders were all pack-mounted in a zero-background substrate sample cell, without any preprocessing, addition of solvent, or grinding. Powders in oil were allowed to settle by gravity, then pack-mounted in the same manner as the slurries. Sample volume required was approximately 0.18cc. Selected samples were periodically re-analyzed at UNM. Multiple data collections on selected samples, carefully preserved, from the H_2 -pretreated catalyst synthesis run (SB-3425), were performed 24 hours, 1 month, 4 months, 7 months, and 1 year apart, in order to check sample long-term stability, and to validate UNM's analytical procedures. All phase identifications were verified using the diffraction reference data contained in the International Center for Diffraction Data (ICDD), Joint Committee on Powder Diffraction Standards (JCPDS) powder diffraction data base, sets 1 to 46 (ICDD, 1994), and/or from powder diffraction patterns calculated from the single crystal data for the phase (ref. sections I, III).

High Resolution Transmission Electron Microscopy (HRTEM) of samples from runs SB-3425 and SA-0946 was also performed, and the analysis will be discussed in detail elsewhere (Jin and Datye, 1998). We show a few of the micrographs here, to illustrate the effects of Soxhlet extraction on the composition of the working catalyst in run SB-3425. The slurry sample were embedded in epoxy, and thin slices on the order of 40-50 nm were prepared for HRTEM, by ultramicrotomy. The microtomed sections were mounted on a molybdenum grid coated with an holey carbon film, then coated with amorphous carbon to prevent charging. The samples were examined with a JEOL 2010 HRTEM, operated at 200 KeV.

Results

I. Calculated Absolute Powder X-ray Diffraction Intensities of Major Iron Phases

As an important step in the characterization of the Iron Fischer-Tropsch catalyst, we will consider in detail how some of the commonly observed phases in the working catalyst appear, by x-ray diffraction, and how they may interfere with one another, when mixed. It is well-known that these materials [e.g., alpha-iron (α -Fe), ϵ' -carbide (Fe_7C_3 or $Fe_{2.2}C$), χ -carbide (Fe_5C_2 or $Fe_{2.5}C$), and magnetite (Fe_3O_4)] show overlapping diffraction peaks in the region of interest, $\{25^\circ$

$\leq 2\theta \leq 70^\circ$. However, most previous analyses, including our own (Shroff, et al., 1995), implicitly assume that the absolute or relative intensities from each phase reflect the relative phase abundances. This is, in fact, not the case.

The powder diffraction database (ICDD, 1994) presents the data for each component in terms of relative diffraction intensities as a function of either 2θ or the d-spacing, in Å. The most intense diffraction peak is set to a value of 100 counts or percent, and all other peak intensities are adjusted accordingly. In principle, the powder diffraction database also lists a **relative intensity ratio** (RIR) factor for each phase, listed as I/I_{cor} on the card, which is the ratio of a given compound's 100% relative intensity peak relative to the 100% relative intensity peak for corundum ($\alpha\text{-Al}_2\text{O}_3$), in a 50:50 wt % mixture. The I/I_{cor} value is then used to 'correct' the raw 100% peak intensities of each phase for quantitation purposes, by accounting for differences in elemental and compound x-ray scattering cross-section (Bragg, 1949). The I/I_{cor} (or RIR) is used to quantify phases in a mixture, as follows:

$$\frac{w_i}{w_j} = k \frac{I_i}{I_j} ;$$

$$k = \frac{(I/I_{\text{cor}})_j}{(I/I_{\text{cor}})_i}$$
(1)

where W_i , W_j , I_i and I_j refer to the weight fractions and diffraction peak intensities for phases i and j , respectively, and k is defined as the I/I_{cor} for phase j divided by the I/I_{cor} for phase i .

The use of I/I_{cor} as an empirical correction factor is based on an assumption that weight percents of the phases in a mixture are similar, and that effects such as preferred orientation, extinction, mixing inhomogeneities, and the breadth of the crystallite size distribution are small enough that the changes in the value of I/I_{cor} are minimal. In the case of the Fischer-Tropsch catalysts, the deviation from equal weight percent mixtures can be substantial; intermediate, disordered, defect or distorted structures are common, particles of material for a given phase can deviate significantly from spherical (preferred orientation or growth habit), and significant anisotropy can occur frequently. The only I/I_{cor} listed in the powder diffraction database is that for hematite ($\alpha\text{-Fe}_2\text{O}_3$, card # 33-664), so we simulated powder diffraction patterns for various iron phase mixtures, in order to estimate I/I_{cor} for the phases not listed, and then experimentally verified those of the oxide phases (Fe_3O_4 , and Fe_2O_3).

We first simulated the diffraction pattern for a 50-50 weight % mixture of $\alpha\text{-Al}_2\text{O}_3$ and the isostructural $\alpha\text{-Fe}_2\text{O}_3$, using single crystal structures from the literature (Thompson, et al., 1987 and Antipin, et al., 1985, respectively), then attempted to reproduce the data experimentally by preparing a 50 wt % calcined hematite and calcined corundum mixture (both from Aldrich Chemical Company, 99.995% purity). The constants describing the instrumental parameters, background function, zero-point error, sample transparency and displacement constants, crystal structure, and crystallite sizes were taken from values obtained determined in our laboratory.

Results were encouraging: we obtained a calculated value of 2.39, and an experimental value of 2.49. These both compare favorably with the value of 2.4 in the literature. This shows that either procedure yields a value that differs from the value of 2.4 listed in the powder diffraction database (ICDD, 1994) by no more than 4.5 %. The results are consistent, thus we are assuming that, for the next set of simulations, the error in experimental and calculated I/I_{cor} will be comparable in magnitude. The details of the simulation and experimental verification method will be published elsewhere (Mansker and Datye, in preparation).

The pattern simulations were performed using the DBWS-9411 Rietveld structure analysis program (Young, 1995, Sakthivel and Young, 1995), following the method of phase quantification of Bish and Howard, 1988 and Hill, 1987, 1993. The Rietveld method was developed by Hugo Rietveld in 1967, for crystal structure determination using neutron powder diffraction data (Rietveld, 1967), but its application to x-ray powder diffraction data has become wide-spread in the last decade. The method provides detailed information on the structure, morphology, and phase abundances in a polycrystalline sample from first principles; using this method, quantifications are possible down to hundreds of ppm levels. It can also be used to determine particle size (average and distributions), crystal habit, particle shape (indirectly), particle surface roughness, stress and strain in the powder, the nature of lattice vacancies and defects.

Figure 1a shows the plot of the simulated diffraction data for the 5-phase mixture (20 wt% each of α -Fe, Fe_7C_3 , Fe_5C_2 , Fe_3O_4 , and α - Fe_2O_3) based on single-crystal data from the literature (Wyckoff, 1960; Senczyk, 1993; Herstein and Snyman, 1963; Sénateur, J.P., 1967; Dirand and Afqir, 1983; Fleet, M.E., 1981, 1982, 1984, and Antipin, et al., 1985). The 100% relative intensity peaks for each phase have been labeled. Not only does the figure demonstrate the degree of diffraction peak overlap that is characteristic of these materials in the region, 25° to 70° 2θ , it also illustrates that, when absolute intensities are compared, a mixture of the five Fe phases thought to appear in the F-T catalyst can produce a diffraction pattern which appears visually to be a mixture of mostly α -Fe and Fe_3O_4 , with little or no Fe_7C_3 , Fe_5C_2 , or Fe_2O_3 . An I/I_{cor} is estimated for each of the 5 phases, using $I/I_{cor}|_{hem}$:

$$\frac{I_i}{I_{cor}}(calc) = \frac{I_i}{I_{hem}} \frac{I_{hem}}{I_{cor}} |_{ref}; \quad (2)$$

and the values are listed in Table 1 along with our experimental values of $I/I_{cor}|_{hem}$ and $I/I_{cor}|_{mag}$ determined in this laboratory (Mansker and Datye, in preparation).

For completeness, the powder patterns for each of the phases contributing to the mixture were simulated, and are plotted in figure 1b. Each phase has been normalized to a maximum intensity of 100, so that the details in each diffraction pattern can be seen. Comparison of the estimated I/I_{cor} values and the composite diffraction pattern (figure 1a) demonstrates that large differences in peak intensities can exist, even though the iron phases are combined at equal wt %. Thus it becomes clear that differences in x-ray scattering cross-sections must be considered when

examining mixed the Fe phase catalysts used for F-T synthesis, and that a simple examination of relative peak heights cannot be used to infer the relative amounts of a material present in the working catalyst, without use of the RIR correction factors (I/I_{cor}).

We offer a caveat: the powder patterns shown here for the carbides and magnetite are constructed without accounting for phase disorder or significant distortion, disorder, lattice defects, non-spherical particles, or the bimodal particle size distributions often seen in this catalyst, and should be considered ideal. The kind and number of defects and distortions which can be observed are quite systematic in nature, and will be discussed in detail in another set of papers, in preparation.

II. Influence of Soxhlet Extraction on Catalyst Morphology

X-ray diffraction characterization of the working catalyst samples from the slurry reactor without preprocessing or separation can be problematic, because of interference from the product wax (discussed in section III) and low initial catalyst loading: generally on the order of 10%. Soxhlet extraction is commonly used to concentrate and separate the catalyst from the product wax. Unfortunately, because it employs solvent at its boiling point (on the order of 80°C, Bukur, 1998), Soxhlet extraction may induce undesirable changes in the powder, leading to deceptive results. We examined the H₂-pretreated catalyst sample, unreacted powder in oil (run SB-3425, TOS = 000), and compared it to the Soxhlet-extracted powder from the same sample, using x-ray diffraction (XRD) with quantitative Rietveld structure refinement (QRSR). We performed HRTEM on these two samples, to determine what kinds of morphology changes which might occur on the microscale, during or after extraction.

Figure 2 shows a comparison of the diffraction patterns of the pretreated catalyst suspended in oil, and the pretreated sample after Soxhlet extraction. The oil is of sufficiently low molecular weight that its 1st and 2nd order diffraction peaks show up as broad, diffuse humps, and can be neglected as background. The same is true of the silica contained in the sample.

We make the following observations upon visual inspection: the catalyst in oil contains a prominent peak of α -Fe, along with the characteristic broad, amorphous peaks due to the oil, and the asymmetric, broad peaks with sharper apexes characteristic of amorphous silica. The iron phase appears to have a fairly uniform, large crystallite size (symmetric, nearly Gaussian peak shape, and fairly narrow full-width at half maximum - FWHM). The α -Fe peak in the extracted catalyst is broader, which we attribute to the possible presence of Fe₅C₂ phase overlapping with the α -Fe peak. We also observe Fe₃O₄. The diffraction peaks are very broad at the base, indicating that the Fe₃O₄ may show a bimodal particle size distribution. The height of the α -Fe peak relative to the background is lower than seen in the sample in oil, indicating a smaller wt % of α -Fe in this sample. The α -Fe peak also shows considerable asymmetry with a very broad base which could arise from a bimodal crystallite size distribution, as well as additional overlap with the Fe₅C₂ phase.

We must conclude that the observed composition and morphology in the extracted sample is probably not representative of the material in the reactor. Neither Fe_5C_2 nor Fe_3O_4 should have been present, based on the composition observed in the unreacted catalyst in oil.

The low-magnification micrograph of the Soxhlet-extracted powder, from the H_2 -pretreated catalyst in oil (Figure 3a), shows material with irregularly shaped particles supported on a matrix that contains finer catalyst particles, silica, and some unreduced iron phase. Note the presence of a pronounced surface halo on the particle surfaces, such as that seen on the particles highlighted by arrows in figure 3a. The high-magnification image of one of these haloed particles (figure 3c) clearly shows the thickness of the surface layer (on the order of 5 nm) and the irregular particle shape. The particle's inner core produces lattice fringes of about $2.03\text{\AA}$, which is characteristic of the α -Fe (110) crystal planes. A similar, but thinner, surface oxidation layer was observed by researchers at UNM on carefully passivated samples of α -Fe (Shroff and Datye, 1995).

The micrographs of the pretreated, unreacted catalyst powder in oil (run SB-3425, TOS = 000) are shown in figures 3b and 3d. The overall catalyst microstructure is similar to the extracted catalyst shown in figures 3a and c, but the particles don't show same the thick, pronounced surface halos on their surfaces. The high magnification view of one of the primary particles (figure 3d, examples indicated by arrow in figure 3b) shows a particle of irregular shape, with a much thinner surface halo. Like the Soxhlet-extracted powder, the particle from the unreacted powder in oil also shows lattice fringes of $2.03\text{\AA}$, characteristic of the α -Fe (110) planes.

The samples from the sample at TOS = 000, seemed to indicate that Soxhlet extraction used to separate the catalyst from the product wax induced significant changes in the catalyst, which are detectable by x-ray diffraction and HRTEM, and that both techniques obtain similar information. It wasn't known whether all of the samples subjected to Soxhlet extraction showed the same type of changes. Accordingly, the rest of the samples, slurry and soxhlet-extracted, for both runs, were examined using XRD. The diffraction patterns of the H_2 -pretreated catalyst, run SB-3425, slurry and Soxhlet-extracted sample sets, are shown in figures 4a and b (5 samples each, as a function of TOS). The slurry and Soxhlet-extracted samples for the CO-activated run, SA-0946, are shown in figures 4c (6 samples) and d (6 samples, Bukur, 1998). We will examine them for evidence that the extraction process may have induced changes.

Visual inspection of the slurry diffraction patterns in figure 4a (H_2 -pretreated catalyst) reveals that several peaks remain unchanged with time; these correspond to the wax, α -Fe, and what appear to be trace peaks of carbide, almost too small to identify. While the presence of wax peaks obscures the location of some of the Fe_3O_4 peaks, the most prominent Fe_3O_4 peaks (indicated in Figure 4b) should have been observed if Fe_3O_4 were indeed present in the catalyst slurry. Because they are not observed, we conclude that Fe_3O_4 is not present in the slurry samples in statistically significant amounts.

The extracted catalyst diffraction patterns (figure 4b, H_2 -pretreated catalyst) show the presence of significant amounts of Fe_3O_4 , which is clearly not present in the slurry samples. Note that the α -Fe peak, which appears consistently in the slurry samples, is completely absent in the extracted

samples, except for TOS = 000 hrs. Even in that sample, its intensity is significantly diminished, as shown in figure 2, and discussed earlier.

Having established that the α -Fe seen in the slurry is lost in the Soxhlet-extracted samples, we next examined the α -Fe 100% intensity peak and tail shapes, to ascertain which carbides might be present in the slurry and extracted samples. In the slurry samples, we see evidence of a shoulder on the right of the α -Fe 100% intensity peak, which is indicative of the presence of Fe_7C_3 (100% intensity peak at 44.88°), but no evidence of this phase is seen in the extracted samples. However, the diffraction peaks for Fe_3C_2 (021) and (112) ($\sim 43.39^\circ$ $2\theta/100\%$ and $\sim 42.80^\circ$ $2\theta/51\%$) are seen to be overlapping to form the most prominent peak in all of the extracted samples, which also includes intensity from the Fe_3O_4 (004) diffraction peak ($\sim 43.15^\circ$ 2θ).

For completeness, HRTEM was performed on the Soxhlet-extracted sample from end-of-run, H_2 -pretreated catalyst, TOS=384 (figures 5 a and c) and on a slurry sample near end-of-run, H_2 -pretreated catalyst, TOS=330 (figures 5 b and d). We may make the comparison of a slurry sample from one TOS to the extracted sample of another TOS, because the activity of the catalyst at TOS =330 and 384 did not differ very much (section V), and the XRD patterns of the slurry samples at those TOS were very similar in appearance and composition (section V).

The Soxhlet-extracted sample (H_2 -pretreated run, TOS = 384 hrs, figure 5a) contains primary particles of irregular shape covered with a surface halo. Higher magnification views (figure 5c) illustrate that these surface layers exhibit lattice fringes consistent with Fe_3O_4 . The rough surface layer seems to indicate that oxidation of the particle surface has occurred.

The low-magnification micrograph of the slurry catalyst sample (H_2 -pretreated run, TOS = 330 hrs) is shown in Figure 5b. The particles exhibit morphology similar to that seen after Soxhlet extraction, and also show layers on the surface. Again, we have often observed that samples removed from a working reactor always show a surface layer (Shroff et al., 1995), and, that while a surface oxide formed at room temperature is often amorphous, beam-induced heating during observation by HRTEM transforms it into crystalline magnetite (Fe_3O_4). The high-magnification image of this catalyst (figure 5d), shows that the surface layers observed in the slurry sample remain amorphous, suggesting that the surface layer does not represent a passivating film. The differences between the sample in slurry and after Soxhlet extraction once again indicate that oxidation of the sample occurs either during or after Soxhlet extraction, which is consistent with the diffraction pattern interpretation (section V).

The CO-pretreated catalyst appears to be quite different from the H_2 -pretreated catalyst, which is evident from figure 4. An examination of the diffraction patterns (figures 4c and 4d) reveals that much less change in composition and microstructure appears to have taken place after Soxhlet extraction. Only the last sample in the series (TOS=563) shows significant visual evidence of oxidation and morphological changes upon Soxhlet extraction. The wax appears to interfere much less with the iron phases in the slurry diffraction patterns (figure 4c), which is consistent with the average molecular weights and average wax composition determined as a function of TOS, in the course of the structure analysis (sections IV, V).

Comparing Figure 4c with Figure 4a, one can see clearly that a small amount of magnetite is present in all of the slurry samples from the CO-pretreated catalyst, run SA-0946, while no magnetite is present in the working catalyst slurry from the H₂-pretreated run, SB-3425. The diffraction pattern for the catalyst slurry sample at TOS = 000 (CO-pretreated catalyst) shows that it may consist of Fe₃O₄ and Fe₅C₂, primarily. As the reaction proceeds, some of the Fe₅C₂ in the slurry is transformed to Fe₇C₃ (44.88°), the amount of Fe₃O₄ drops, and some α -Fe is observed in the samples at TOS = {229 and 354} hrs, as indicated in the diffraction pattern over the range, 44° to 45°, where Fe₅C₂, Fe₇C₃, and α -Fe fall clear of the product wax, but overlap with one another and with Fe₃O₄. In all of the slurry samples, the diffraction peak occurring in that region has shoulders on both sides of the maximum, and its multiple apexes are strong evidence of multiple phases.

Examination of the Soxhlet-extracted samples (figure 4d) indicates at first glance that not much change was induced; however, the α -Fe and Fe₇C₃ have disappeared from the samples, and the particle sizes and distribution for Fe₅C₂ and Fe₃O₄ have changed, showing pronounced bimodality. The bimodality in Fe₃O₄ indicates that some material with small particle size, has been oxidized

We will examine one more sample, from the H₂-pretreated catalyst run (SB-3425, TOS = 233 hrs). Figure 6 shows six diffraction patterns on the same plot. From bottom to top, we show filtered product wax (EW), wax stripped from the slurry by warming it to reaction temperature (260 C) under flowing inert (SW), the slurry (SL) as removed from the reactor, concentrated catalyst slurry (CC; concentrated in the wax by warming the slurry to 150° under inert atmosphere for several days, and sampling the bottom of the vial), catalyst powder obtained from of the slurry by Soxhlet extraction (EP), and the powder residue left after stripping the slurry of wax under flowing inert gas, analyzed by XRD one month after first analysis by neutron diffraction (SP). Most remarkable is the difference between the stripped and the Soxhlet-extracted powders (SP and EP, respectively). The α -Fe peak is completely gone from the Soxhlet-extracted powder(EP), which now contains a broad Fe₃O₄ peak. A large Fe₅C₂ peak is seen also in the EP (refer to figure 2, extracted), while the SP appears to contain primarily α -Fe, with trace carbide.

We conclude that Soxhlet extraction of the slurry samples is undesirable, because of possible oxidation of the reduced iron phases which could occur either during extraction or upon subsequent exposure to air. Evidence for slow oxidation of the catalyst in the slurry at room temperature, *despite the protective layer of waxy hydrocarbons*, has been observed in the samples used for quality control and stability checks (see section IV), thus we conclude that the possible oxidation phenomena described here could easily and completely transform highly dispersed α -Fe or carbide phases into Fe₃O₄. Hence we have focused on the study of catalysts in the wax.

III. Interference of the Crystalline Wax with Catalyst in the Slurry

It seems apparent that the high molecular weight, straight-chain hydrocarbon product obtained with an high- α catalyst can be quite crystalline and, its diffraction pattern exhibits significant

overlap with the diffraction patterns of the various Fe phases of interest (refer figure 6). We were concerned that catalyst entrained in the wax was producing the diffraction pattern observed, because the two waxes differed in subtle details and in color, neither being clear nor white. In order to determine if entrainment were a problem, the ‘catalyst-free’ waxes (EW and SW) were examined by AES to determine how much material, if any, remained suspended in them. Consequently, 10 mg each of the extracted wax and inert-stripped wax were digested and analyzed by atomic emission spectroscopy. The extracted wax (EW) showed a total iron content of 80 ppm, and the stripped wax (SW) a total iron content of 207 ppm. Both are well below our detection limit of 350 ppm for XRD, so we concluded that iron entrained in the separated wax does not contribute significantly to the wax diffraction pattern.

The wax diffraction patterns were subsequently analyzed by the Rietveld method, using the low-density polyethylene (LDPE) crystal structure of Hu and Dorsett, 1989. We obtained a very good model for the wax structure, and subsequently used the refined structure parameters, in combination with various iron oxide, metal and carbide single crystal structures, to evaluate the slurry and extracted samples from the two runs. The complete structure analysis results, with quantitation and correlation to reaction kinetics, is discussed in section IV. Because most people who use x-ray diffraction as a tool don’t have the theoretical background required to fully exploit the Rietveld structure method, we also explored physical methods of separating the wax from the catalyst, other than Soxhlet-extraction.

The sample of slurry in which the catalyst was concentrated (CC), when compared with the slurry (SL) and inert-stripped powder (SP), indicates that the concentration and stripping methods do a far better job of maintaining catalyst composition and morphology than does Soxhlet extraction. As additional verification, we analyzed the inert-stripped powder, TOS = 233 hrs, three times, over a period of 4 months, in order to determine if the inert-stripped catalyst remained as stable against oxidation. Neither the neutron diffraction nor the seconde set of x-ray results for the stripped powder (SP) will be presented in detail here; they will be discussed in detail in a separate paper on the samples shown in figure 6, and summarized briefly in the next section.

Comparison of the slurry diffraction pattern (SL) to that of the waxes (EW and SW) shows that the wax accounts for many of the diffraction peaks present in the slurry, and thus wax could be easily misidentified as iron phases, as is evident from the diffraction peak positions listed in Table 2. However, regions of 2θ exist, where no wax peaks interfere with iron phase diffraction peaks. Keeping this in mind, we look for additional detail in the region between 52° and 67° 2θ . Fe_3O_4 has two moderately intense peaks which occur at 57° and 62.5° . α -Fe has peaks at 44.74° and 64.94° . Fe_5C_2 and Fe_7C_3 both have 100% relative intensity peaks which overlap with the α -Fe 100% relative intensity peak, in the range 44° - 45° , at 44.175° and 44.882° 2θ , respectively, but are clear of the wax phase. Fe_5C_2 has a fairly intense peak at about 50.48° ($\sim 12\%$), and Fe_7C_3 at 25.9° ($\sim 12\%$), but, again, the relative intensity ratios with α -Fe and magnetite are such that visual inspection for these phases becomes difficult (ref. Section II).

The catalyst crystallite sizes are small enough (≤ 15 nm) and I/I_{cor} that significant overlap and line broadening can occur in the diffraction pattern (cf. sec. I, table 2, figure 2). In spite of this, presence of either of the iron carbides, in the presence of α -Fe, can be detected visually by

examining the α -Fe peak shape. The α -Fe crystallites in the unprocessed slurry produce a nearly Gaussian peak shape. Asymmetries in the α -Fe 100% intensity peak shape, especially in the tail, are indicative of other phases present, where appearance of a shoulder or 'bumpy' tail to the left suggests Fe_5C_2 , and where the presence of an asymmetry on the right side of the peak indicates Fe_7C_3 . Using these criteria, we have ascertained that Fe C_7 is present in the slurry, but that in this sample (TOS = 233 hrs, H_2 -pretreated catalyst), Fe_5C_2 is not.

In summary, visual inspection of the catalyst in the slurry indicates only the presence of α -Fe and Fe_7C_3 in the slurry. While the α -Fe peaks occur at 2θ values where there is no overlap with the diffraction peaks attributable to the product wax, some of the carbide peaks do overlap with α -Fe, especially with the 100% intensity peak, making it difficult to make a thorough analysis.

IV. Quantitative Rietveld Refinement, and Precision and Accuracy

In the previous section, we concluded that regions of 2θ exist where the catalyst diffraction pattern shows no overlap with that of the waxy product, but that the data may not be enough to permit a reasonable determination of the presence or absence quantity of some phases. Applying structural methods to the wax and to the catalyst can permit us make phase composition determinations, which can be used to evaluate the accuracy of our visual interpretation, and provide an opportunity to test the Mcor values estimated in section I.

Periodically, other samples were re-analyzed to verify the repeatability and accuracy of our analytical technique, and to check sample stability in the slurry. They were from the H_2 -pretreated catalyst (run SB-3425): slurry, TOS = 384 hrs (analyzed twice, 7 months apart), and the inert-stripped powder, TOS = 233 hrs (). The results will not be shown here, but can be found in the electronic document available through FETC (Mansker, Jin, and Datye, 1996). After 7 months, the α -Fe peaks, present in the first scan of the slurry (TOS = 384) at 44.74° and 64.94° 2θ , are not present in the same sample, 7 months later. In fact, the second scan appeared little different than the wax diffraction patterns shown in figure 7. Upon applying quantitative Rietveld structure refinement to the 7-month repeat diffraction pattern, we determined that the only iron phase still present was a very disordered crystalline magnetite, of small crystallite size (Mansker and Datye, 1998). This seems to indicate that the iron catalyst is so reactive, that it undergoes changes over time, even when suspended in the wax matrix, if not well-protected from air.

The inert-stripped powder, H_2 -pretreated catalyst (run SB-3425), was examined 3 times in order to test the separation method (section III) and the compositional/morphological stability of the separated material over time. The powder was analyzed once by neutron diffraction at Los Alamos Neutron Science Center, by x-ray diffraction 1 month later (SP, figure 6), then by x-ray diffraction 4 months after the neutron study. Initial examination of the neutron and the one - month x-ray diffraction pattern indicated that, although the major peak seen in the sample can be easily identified as α -Fe, the phase compositions in the sample could be summarized as a mixture of α -Fe, Fe_7C_3 (ND and XRD) and trace magnetite (XRD). The data from the second x-ray scan seems to indicate that some subtle changes have taken place in the powder, with time. The intensity of the iron peak had diminished somewhat, and some of the minor phase peaks had

become more prominent. All of the peak widths broadened, indicating some crystallite breakup may have occurred. Structural refinement of the diffraction data for the x-ray repeat pattern also indicated that the sample composition had changed: more of the sample had oxidized, the volume average crystallite sizes had decreased (e.g., the peaks widths had increased), and the Fe_7C_3 had completely transformed to the more stable Fe_5C_2 !

The data appear to indicate that, while stripping away the wax and carefully passivating the powder is more effective at preserving the catalyst morphology and composition than Soxhlet extraction, the catalyst remains highly reactive, and changes over time. We concluded that FTS samples, no matter how well protected, are still reactive, even in the waxy product. This is further proof that samples should be analyzed in a timely manner. Again, detailed discussion of the 4 stripped powder diffraction analyses, along with the rest of the samples shown in figure 6, will be discussed in a separate publication.

V. Fischer-Tropsch Reaction Results

Reactivity data for the H_2 -pretreated (SB-3425) and CO-pretreated (SB-3425) catalysts are included here as figure 7 (Bukur, et al., this issue). The plot indicates reactivity as an apparent first order rate constant instead of % conversion, which seems to provide a more accurate picture of the catalyst's intrinsic reactivity. Actual conversions for these runs are shown in the companion paper by Bukur et al., 1998, which were generally high (80%), and are affected by changes in flow rate as well as reaction temperature. Table 3 shows the process parameters during these runs as a function of time and % conversion at selected times on stream. The reaction kinetics for the catalyst activated in CO at 280°C (SA-0946), show a lengthy induction period, in which the activity starts very low, then rises steadily to its steady state value. The run reaches steady state activity near TOS = 113 hrs, where a slurry sample was obtained, and shows stable activity with time, with some fall off in activity towards the end of the run. The catalyst activated in H_2 at 250°C (SB-3425), exhibits high activity at the onset of reaction, which begins to fall at longer run times. The CO-pretreated catalyst shows higher steady state activity than that of the H_2 -pretreated catalyst. In the next section, we will relate these observed variations in catalyst activity with the phase composition and morphology.

VI. Catalyst Evolution with Time on Stream

We have shown that the catalyst in each run undergoes subtle, but definite phase changes, which correlate with the changes in the activity profiles. We will now describe these changes in detail, based on data obtained from the slurry samples (figures 4a and 4c), then discuss what this tells us about this particular catalyst's active components, over time. We will contrast the behavior of the catalyst after activation in CO to that of the same catalyst activated in H_2 . Samples from the CO - activated catalyst (SA-0946) were removed from the reactor at TOS = {0, 113, 229, 354, 427, and 563} hrs. Samples from the H_2 -activated catalyst (SB-3425) were removed from the reactor at TOS = {0, 111, 233, 330, and 384} hrs. The sample compositions were quantified using the Rietveld structure refinement method (Rietveld, 1967), or the estimated I/I_{cor} with the peak intensity, as observed in the diffraction pattern.

Quantitation data from the H₂-activated catalyst (SB-3425) and the CO-activated catalyst (SA-0946) are contained in tables 4 and 5, respectively. Two consistency tests were applied to the H₂-activated catalyst results. First, weight percents at TOS = 111 hrs were calculated using the estimated I/I_{cor} and the 100% peak heights, and then using the more rigorous Rietveld structure method. The results are in good agreement with one another. The second consistency test involved applying the I/I_{cor} and Rietveld quantitation methods to the data from TOS = 233, slurry and inert-stripped powder (SP). Recall, from sections III and IV, that the stripped powder was first subjected to a neutron diffraction study, scanned by XRD 1 month later (SP), then scanned again 3 months after that. Stripping of the wax improved the signal considerably as can be seen in Fig. 6. The high intensity of scattering from the α -Fe phase, as manifested in the I/I_{cor} values reported in table 1, means that the carbide peak will be difficult to see by x-ray, when the α -Fe is present. In spite of this, the quantitation of the slurry data appears consistent with the quantitation obtained from the inert-stripped powder.

Referring the reader back to figure 7 and the data in tables 4 and 5, we will now discuss the activity curve for the H₂-activated catalyst run (SB-3425). Initially, the crystallite size for TOS = 000 hrs, α -Fe, is on the order of 13.5 nm which is in reasonable agreement with the TEM image reported in Fig. 3. Most of the catalyst appears to transform quickly into Fe₇C₃ at TOS = 111 hrs. The Rietveld refinement suggests that it is almost completely transformed into the carbide phase. At this stage, the average crystallite sizes for α -Fe are about 37.9 nm, with Fe₇C₃ at about 5.5 nm. The catalyst is active until approximately TOS = 160 hrs, when a fairly sharp drop-off occurs. Coincidentally, the space velocity of feed gas was decreased, and the system took time to reach a new steady state. While the phase composition of the catalyst remains the same, we observe an increase in crystallite size for Fe₇C₃ (47 nm) and a slight decrease in that for α -Fe (30 nm) in the sample at 233 hours. XRD analysis of the inert-stripped powder from this sample gave comparable crystallite sizes. The data from the sample at TOS=330 hrs. sample indicates that a major change in phase composition has occurred. The catalyst now contains 85.3% Fe₅C₂ and 14.3% Fe₇C₃, with respective crystallite sizes of 37.9 nm for α -Fe, 5.3 nm for Fe₇C₃, and 7.6 nm for Fe₅C₂ (see table 4 and figures 11a, 11b). By TOS=384 hrs, the catalyst appears to have transformed almost completely into the Fe₅C₂, according to the x-ray data, with phase compositions of ~2.5% Fe₇C₃ (4.5 nm particles) and ~97.5% Fe₅C₂ (14.8 nm particles), with trace Fe metal (37.2 nm particles).

The average particle sizes listed above compare favorably with the average particle sizes of seen in the TEM images in figure 3a. The slight differences can be explained by two phenomena. First, XRD determines a volume-average particle size and TEM determines an area-average particle size. Second, XRD is sensitive to the size of the crystalline domains while TEM sees the entire particle, implying that if the particles are polycrystalline aggregates, and not single crystals, the XRD estimate of particle size will be smaller than the TEM size. The TEM image does show that many of the particles in Fig. 3a are not single crystals, and high resolution images, such as the one in Fig. 3c, show the lattice planes in the crystal and allow us to identify the individual crystal phase, and average phase composition is more difficult to estimate from TEM, involving high resolution imaging of numerous crystallites and matching the lattice planes with the expected spacings for each phase. Our limited survey of these particles indicated that the majority of them showed lattice fringes of 2.13 Å, which is consistent with the presence of Fe₅C₂.

Hence, the TEM of the slurry at TOS = 330 hrs. is in good agreement with the phase composition results of the Rietveld structure analysis. The same is true of the sample from TOS = 384 hrs.

The loss of activity in this catalyst appears to be related to the loss of the α -Fe and Fe_7C_3 and concurrent the growth of the Fe_5C_2 phase, by TOS = 330. This behavior seems consistent with a conclusion that α -Fe and Fe_7C_3 are necessary components of an active catalyst, and Fe_5C_2 is less active for F-T synthesis. Although not listed in the table, the relative amounts and volume-average molecular weight of wax were monitored in the sample series, as a function of TOS. Keeping in mind that these are **weight** percents, and that the waxy product distribution could have, on average a molecular weight (MW) of at least 2000 g/mole, Rietveld refinement of the slurries, using two LDPE model structures with MW of 2500 and 1500, respectively, with some disorder, gave a total organic weight percent of 99.98%, for all four samples, TOS = {111, 233, 330, and 384} hrs, with a breakdown of about 35 % material at 2500 g/mole, and 65% material at 1500 g/mole.

The composition and crystallite size data for the CO-activated catalyst run (SA-0946) are listed in table 5. The initial slurry sample (TOS = 000 hrs) consists mainly of Fe_5C_2 , Fe_7C_3 , and trace Fe_3O_4 at wt % of 86.38, 13.41, and 0.22, respectively, giving a carbide ratio (Fe_5C_2 : Fe_7C_3) of ~6.44, with corresponding volume average crystallite sizes of about 26.9 nm, 13.7 nm, and 19.3 nm respectively. By TOS = 113 hrs, the data show that a major phase transformation has occurred: a portion of the Fe_5C_2 carbide has converted to the Fe_7C_3 carbide, with wt% of 52.85, 46.17, and 1 for Fe_5C_2 , Fe_7C_3 , and Fe_3O_4 , respectively. The ratio of these carbides is now 1.14:1, with corresponding crystallite sizes of 11.6 nm, 11.4 nm, and 19.3 nm. This coincides with a maximum in the activity versus time curve for this run. After TOS = 113 hrs, the activity shows a very mild drop, then is relatively constant for a time. The activity begins to drop off again after TOS = 427 hrs. Carbide ratios remain around 1:1, until the sample withdrawn at TOS = 427 hrs, where the ratio decreases to .55:1, then increases to 7.17:1 at TOS = 563 hrs. The Fe_7C_3 carbide crystallite sizes are fairly constant, with the Fe_5C_2 volume average particle size averaging about $\frac{2}{3}$ that of the Fe_7C_3 carbide, until TOS = 427 hrs, when the Fe_5C_2 particle size is now 1.25 times larger than that of the Fe_7C_3 carbide (15.3 nm). At end of run, the Fe_5C_2 particle size is 2.6 times that of the Fe_7C_3 size of 29.5 nm, which is roughly 2 times that observed for this carbide at TOS = 427 hrs. This appears to coincide with a very mild decrease in reactivity. There is only a trace of Fe_3O_4 over the course of reaction and of α -Fe in 3 of the samples {229, 354, and 427 hrs TOS}, although both appear to be present in significant amounts from visual inspection of the XRD patterns (x-ray scattering cross-section effects). The Fe_3O_4 particle sizes grow steadily over the course of reaction. We interpret the data to indicate that the initial low kinetic activity of the CO-activated catalyst can be attributed to the initial phase composition, and that the 'induction period' observed corresponds to the time required for the transformation of some of the Fe_5C_2 carbide into Fe_7C_3 carbide, with a corresponding crystallite size decrease in both phases (increasing surface area). The mild deactivation towards the end of the run seems to be caused by an increase in the $\text{Fe}_5\text{C}_2/\text{Fe}_7\text{C}_3$ ratio, and an increase in crystallite size for the iron carbide phases (decreasing surface area).

Summary

We report a careful, systematic analysis of the diffraction patterns obtained from working Fe-based catalysts used for F-T reaction runs under conditions similar to those used for commercial F-T synthesis. The initial catalyst formulations differ only in the method of activation. We have attempted to quantify the relative amounts and the average crystallite sizes of the iron phases comprising the catalyst a function of time on-stream in the reactor. We have also examined the commonly-used relative intensity ratio (I/I_{cor}) powder x-ray data quantitation protocol, and compared it to the more rigorous Rietveld structure method (Rietveld, 1967). We discovered that the powder diffraction database (ICDD, 1994) does not report I/I_{cor} values for most of the Fe phases of interest to F-T synthesis, thus we developed a method to predict them, and verified it experimentally for the iron oxides. We discovered that the I/I_{cor} for the various phases vary by as much as 3 orders of magnitude because of differences in x-ray scattering cross-sections for the materials. This implies that a simple visual examination of peak heights in this system can be very deceptive: the α -Fe or the Fe_3O_4 peaks will stand out most prominently in an iron F-T synthesis catalyst mixture, while in actuality, the mixture may contain mostly iron carbide phases.

Diffraction studies, used to explore catalyst stability and analytical accuracy and repeatability, indicate that the catalyst is so reactive to oxygen in its reduced state that, unless great care is exercised, the reduced iron species can transform into oxide (Fe_3O_4). Hence, one would expect Fe_3O_4 to be the predominant phase observed in x-ray data, as seen in many of the previous studies. However, Fe_3O_4 is not the major constituent of slurry-phase Fe catalysts: in these runs we found the total Fe_3O_4 content to be less than 1 wt% overall, in a properly protected, used catalyst sample activated in CO. The sample activated in H_2 showed no Fe_3O_4 at all. We have also found that Soxhlet extraction, commonly used to separate the wax from the catalyst, can cause serious composition and morphology transformations in the catalyst, either during extraction, or upon subsequent exposure of the 'clean' material to air. It is also possible that hot solvent may react with the reduced species, particularly with α -Fe, as indicated in the study of the pretreated catalyst sample subjected to Soxhlet extraction from the H_2 -activated run (SB-3425, TOS = 000). In view of these potential complications, we examined the catalysts suspended in the hydrocarbon wax.

Upon examination, we found that the crystalline hydrocarbon wax typically produced from a high- α catalyst overlaps extensively with the iron catalyst diffraction pattern resulting from a slurry. We approached the wax interference problem by exploring an alternate means of separating the slurry components, and testing the use of rigorous structure methods, to deconvolute the wax diffraction pattern from the catalyst diffraction pattern. We tried heating the catalyst slurry to reaction temperature and flowing an inert gas over the material. This caused most of the wax to entrain and flow out with the gas, leaving behind the catalyst powder. The wax diffraction pattern was eliminated by this process, but there remains the concern that the heat treatment may cause changes in catalyst structure.

The Rietveld structure refinement method was applied quantitatively to the wax-catalyst slurry samples from two F-T synthesis runs which used the same catalyst, one activated under CO and

one activated under H_2 , and which showed dramatically different activity profiles. The largest source of uncertainty in the Rietveld refinements of the H_2 -activated catalyst (SB-3425) derived from the degree of crystallinity of the waxy product; the largest source of uncertainty in the Rietveld refinements of the CO-activated catalyst (SA-0946) derive from low catalyst loading (approximately half that used in SB-3425).

The Rietveld method was first tested on ‘clean’ wax samples before use in analysis of the slurries, for verification, then applied to the slurries in order to determine phase compositions, and volume-average particle sizes for each phase. The CO-reduced catalyst, at TOS = 000 hrs, contains Fe_5C_2 , with a small amount of Fe_7C_3 . No graphite is seen by XRD and the TEM images show only a small fraction of the carbide particles to be covered by graphite. This catalyst exhibits a low initial activity, which increases to a steady state value, with a concomitant break up of Fe_5C_2 carbide into *smaller* crystallites and some transformation into the Fe_7C_3 carbide. We speak of this catalyst in terms of a carbide ratio, which we define as the ratio of Fe_5C_2 to Fe_7C_3 carbide. As long as the carbide ratio and crystallite size remains fairly constant *and* small, the activity appears to remain high. Activity appears to decrease with increasing carbide ratio, and with increased crystallite sizes, corresponding to loss of surface area. The H_2 -activated catalyst is completely reduced to α -Fe before reaction. We can state conclusively that this working catalyst has no Fe_3O_4 in it. Our refinements suggest that once reaction begins, the catalyst contains a Fe_7C_3 with a small amount of α -Fe. This sample begins to show significant deactivation which appears to correlate with steady particle growth, and a nearly complete transformation of the Fe_7C_3 carbide to the Fe_5C_2 carbide.

Based on the results from both runs, we postulate that, although not the most active carbide, that a significant amount of the Fe_5C_2 carbide is required in the catalyst to sustain high activity, and that the most active catalyst must contain Fe_7C_3 with a small amount of α -Fe. Further work is necessary to understand the driving force for these phase transformations, and the relative contributions from these phases to overall F-T activity and selectivity. The XRD quantitation needs to be corroborated with TEM, Mossbauer and neutron diffraction to provide an accurate picture of the relative amounts and particle sizes of the different phases present in a Fe F-T synthesis reactor.

This work has also illustrated that ultramicrotomy can be used to prepare thin sections of the working catalyst in wax for analysis by HRTEM. HRTEM data provide some corroboration of the x-ray diffraction results, further detailing the relationship between the microstructure of a working Fe catalyst and its catalytic reactivity. Future work will attempt a correlation of the x-ray diffraction results with Mossbauer and neutron diffraction data, a thorough analysis of the anomalous absorption behavior, and the x-ray, neutron and magnetic scattering behavior of these materials. A detailed HRTEM study of other iron catalyst samples is in progress, and results are presented elsewhere (Jin and Datye, 1998).

Conclusions

We have drawn several conclusions from this study:

- Fe catalysts separated from the product wax by Soxhlet extraction can exhibit significant changes in composition and/or morphology, hence it is preferable to rely on analyses of the catalyst in the hydrocarbon wax or develop less-severe methods of catalyst-product separation.
- Diffraction methods can be used effectively to analyze the reacted catalyst samples suspended in the waxy product, without further processing, when combined with rigorous crystal structure analysis; however, other methods to deal with the interferences arising from the highly crystalline product wax with the catalyst diffraction pattern need to be developed for the novice x-ray analyst.
- The absolute intensities of the 100% diffraction lines from the various iron phases can vary by over three orders of magnitude. This implies that a purely visual examination of an x-ray diffraction pattern resulting from the catalyst cannot always provide clues to the relative abundance of the various phases present, unless one accounts for differences in the x-ray scattering cross-sections.
- Interpretation of XRD patterns can be conducted successfully using the Rietveld structure refinement method. The accuracy of this method can be influenced by the concentration and dispersion of the catalyst in the wax, and the length of time over which the data are taken; hence the development of alternative means of concentrating the catalyst in the wax seems necessary.
- The catalyst activated in CO has an initial composition of mostly Fe_3O_4 and Fe_5C_2 , while the catalyst activated in H_2 has an initial composition of pure $\alpha\text{-Fe}$; however, once F-T synthesis begins, each catalyst readily transforms into a mixture in which significant amounts of Fe_7C_3 and small amounts of $\alpha\text{-Fe}$, are present. In both cases, the catalyst appears to lose activity with a conversion of significant amounts of Fe_7C_3 into Fe_5C_2 and an accompanying growth in crystallite size.
- We suggest that Fe_7C_3 in combination with $\alpha\text{-Fe}$ is associated with the most active catalysts. The behavior of the H_2 -activated catalyst, when compared to that of the CO-activated catalyst, seems also to indicate that the Fe_5C_2 carbide, though less active, must be present in the mixture in significant amounts, in order for high activity to be sustained.

Acknowledgments

This work was supported under the U.S. Department of Energy University Coal Research Grant DE-FG22-95PC95210, with partial support from NSF HRD 93-53208 at the University of New Mexico, and by U. S. Department of Energy Contract DE-AC22-94PC93069 at Texas A&M University. We further acknowledge the X-ray Powder Diffraction Laboratory, Department of

Earth and Planetary Sciences, University of New Mexico, and Los Alamos National Laboratory, Manuel Lujan Neutron Scattering Center.

References

- Amelse, J.A.; Schwartz, L.H.; and Butt, J.B.; *Journal of Catalysis*; **72**, 1981, 95.
- Antipin, M.I.; Tairelson, V.G.; Flugge, M.P.; Gerr, R.G.; Struchkov, Iu. T.; and Oserov, R.P.; *Doklady Akadameii Nauk SSSR*; **281**(4), 1985, 854.
- Baltrus, J.P.; Diehl, J.R.; McDonald, M.A.; and Zarochak, M.F.; *Applied Catalysis*; **48**, 1989, 199.
- Bish, D.L. and Howard, S.A.; *Journal of Applied Crystallography*, **21**, 1988, 86-91.
- Blanchard, F.B.; Raymond, J.P.; Pommier, B.; and Teichner, S.J.; *Journal of Molecular Catalysis*; **17**, 171 (1982).
- Bragg, W.L. and Bragg, W.H., *The Crystalline State: a General Survey*, The Crystalline State, Vol. 1, Bragg, W.L., editor, G. Bell and Sons, Ltd., London (1949).
- Bukur, D.B.; Nowicki, L.; and Lang, X.; *Catalysis Today*; **24**, 1995, 111.
- Bukur, D.B.; Lang, X.; and Ding, Y.; *Preprints of the American Chemical Society Division of Fuels Chemistry*; **42**(2), 1997, 623.
- Bukur, D.B.; Lang, X.; and Ding, Y.; *Applied Catalysis, Journal of Applied Catalysis*, this issue 1998.
- Dictor R.A. and Bell, A.T.; *Journal of Catalysis*; **97**, 1986, 121.
- Dirand, M. and Afqir, L.; *Acta Metallurgica*; **31**(7), 1983, 1089.
- Dorsett, D.L. and Moss, B.; *Polymer*, **24**(3), 1983, 291.
- Dorsett, D.L.; *Acta Crystallographica*, **B51**, 1995, 1021.
- Dorsett, D.L.; *Polymer*, **27**(9), 1986, 1349.
- Dorsett, D.L.; *Polymer*, **38**(2), 1997, 247.
- Dry, M.E.; 'Catalysis - Science and Technology'; J.R. Anderson and M. Boudart, Eds.; Chapter 15, 1980, 160.
- Duvenhage, D.J.; Espinoza, R.L.; and Coville, N.J.; *Studies in Surface Science and Catalysis*; **88**, 1994, 351.
- Dwyer, D.J. and Somorjai, G.A.; *Journal of Catalysis*; **52**, 1978, 291.
- Fleet, M.E.; *Acta Crystallographica*, **B37**, 1981, 917.
- Fleet, M.E.; *Acta Crystallographica*, **B38**, 1982, 1718.
- Fleet, M.E.; *Acta Crystallographica*, **C40**, 1984, 1491.
- Fleet, M.E.; *Journal of Solid State Chemistry*, **62**, 1986, 75.
- Herbstein F.H. and Snyman, J.A.; *Inorganic Chemistry*, **3**(6), 1964, 894.
- Hill, R.J.; and Howard, C.J.; *Journal of Applied Crystallography*, **20**, 1987, 467-474.
- Hill, R.J., in the 'The Rietveld Method'; Young, R.A., ed.; International Union of Crystallography, Oxford University Press, Pub.; 1993, 61-101.
- Hu, H.L. and Dorset, D.L.; *Acta Crystallographica*; **B45**, 1989, 283.
- Huang, C.S.; Xu, L.; Davis, B.H.; *Fuel Science and Technology, International*. **11**; 639 (1993).
- International Center for Diffraction Data (ICDD), Joint Committee on Powder Diffraction Standards (JCPDS) powder diffraction data base, sets 1-42, 1994.
- Jager, B and Espinoza, R.L.; *Catalysis Today*; **23**, 1995, 17.

Jackson, N. B., Mansker, L. D., O'Brien, R. J., Davis, B. H. and Datye, A. K., *Studies in Surface Science and Catalysis*, **111**, 1997, 501.

Jin, Y. and Datye, A. K., *Proceedings of the International Congress on Electron Microscopy; Cancun 1998*, Inst. Of Physics Publishing, **II**, 1998, 379.

Jin, Y. and Datye, A. K., "Characterization of Bubble Column Slurry Phase Iron Fischer Tropsch Catalysts, Natural Gas Conversion V, *Stud. Surf. Sci. Catal.*, vol 119, page 209, 1998.

Kalakkad, D.S.; Shroff, M.D.; Köhler, S.D.; Jackson, N.B.; and Datye, A.K.; *Applied Catalysis A*; **133**, 1995, 335.

Larson, A.C. and Von Dreele, R.B.; "GSAS: General Structure Analysis Program"; Los Alamos National Laboratory, Los Alamos, NM 87545; 1997.

Mansker, L.D., Jin, Y.; and Datye, A. K.; *Proc. Coal Liquefaction and Solid Fuels '97 Conference proceedings, electronic publication, Federal Energies and Technologies Center (FETC), Pittsburgh, Pennsylvania*; http://www.fetc.doe.gov/events/97conferences/coal_liq/97cl_pdf/datye.pdf/; 1997.

Mansker, L.D. and Datye, A.K.; in preparation, 1998.

McCartney, J.T.; Hofer, L.J.E.; Seligman, B.; Lecky, J.A.; Peebles, W.C.; and Anderson, R.B.; *Industrial and Engineering Chemistry*; **57**, 1953, 730.

Moss, B. and Dorsett, D.L.; *Acta Crystallographica*, **A40**, C318 (1984).

Niemantsverdriet, J.W.; van der Kraan, A.M.; van Dijk, W.L.; and van der Baan, H.S.; *Journal of Physical Chemistry*; **84**(25), 1980, 3363.

Niemantsverdriet, J.W.; and van der Kraan, A.M.; *Journal of Catalysis*; **72**, 1981, 375.

O'Brien, R.J.; Xu, L.; Spicer, R.L.; Bao, S.Q.; Milburn, D.R.; and Davis, B.H.; *Catalysis Today*; **36**(3), 1997, 325.

Okudera, H.; Kihara, K.; and Matsumoto, T.; *Acta Crystallographica*, **B52**, 1996, 450.

Rath, L.K. and Longanbach, J.R.; *Energy Sources*; **13**, 1991, 443.

Raupp, G.B. and Delgass, W.N.; *Journal of Catalysis* **58**, 1979, 348.

Rao, V.U.S.; Stiegel, G.J.; Cinquegrane, G.J.; and Srivastava, R.D.; *Fuel Processing Technology*; **30**, 1992, 83.

Rao, K.R.P.M.; Huggins, F.E.; Huffman, G.P.; Gormley, R.J.; O'Brien, R.J.; Davis, B.H.; *Energy and Fuels*; **10**(3), 1996, 546.

Rietveld, H.M., *Acta Crystallographica*, **22**, 151 (1967).

Rietveld, H.M., *Journal of Applied Crystallography*, **2**, 1969, 65.

Sakthivel, A. and Young R.A.; *Rietveld Analysis Program DBWS-9411*, Release 30.03.95, software, 1995.

Sénateur, J.P.; *Annales de Chimie*, **2** 1967, 103.

Senczyk, D.; *Phase Transitions*, **43** 1993, 153.

Shroff, M.D.; Kalakkad, D.S.; Coulter, K.E.; Kohler, S.D.; Harrington, M.S.; Jackson, N.B.; Sault, A. G.; and Datye, A.K.; *Journal of Catalysis*, **156**(2), 1995, 185-207.

Shroff, M.D.; Datye, A.K.; *Catalysis Letters*, **37**(1-2), 1996, 101-106

Thompson, P; Cox, D.E.; and Hastings, J.B.; *Journal of Applied Crystallography*, **20**, 1987, 79.

Withers, R.L. and Bursill, L.A., *Journal of Applied Crystallography*, **13**, 1980, 346.

Wyckoff, R.W.G; New York, 3rd Ed.; Interscience Publishers, 1960.

Young, R.A., ed.; 'The Rietveld Method'; International Union of Crystallography, Oxford University Press, Pub.; 1993.
Young R.A.; Journal of Applied Crystallography, **28**, 1995, 366-367.

Figure Captions

- Figure 1 a: Simulated X-ray diffraction pattern for a 20 wt% mixture of each of these phases: Fe_2O_3 , Fe_3O_4 , $\alpha\text{-Fe}$, Fe_7C_3 , and Fe_5C_2 ;
 b: simulated pattern for each phase plotted at full scale: b) Fe_2O_3 , Fe_3O_4 , $\alpha\text{-Fe}$, Fe_7C_3 , and Fe_5C_2 .
- Figure 2: X-ray diffraction pattern from H_2 -activated run SB-3425, TOS = 000 hrs. Lower curve, sample in the oil, and upper curve: powder after Soxhlet extraction .
- Figure 3 a: Low magnification view of catalyst from the H_2 -activated run SB-3425, TOS = 000 hrs, extracted powder
 b: Low magnification view of H_2 -activated run SB-3425, TOS = 000 hrs, slurry
 c: High magnification view of catalyst from the H_2 -activated run SB-3425, TOS = 000 hrs, extracted powder
 d: High magnification view of catalyst from the H_2 -activated run SB-3425, TOS = 000 hrs, slurry.
- Figure 4 a: X-ray diffraction patterns of samples from catalyst from the H_2 -activated run SB-3425, slurry samples.
 b: X-ray diffraction patterns of catalyst from the H_2 -activated run SB-3425, extracted samples.
 c: X-ray diffraction patterns of catalyst from CO-activated run SA-0946, slurry samples.
 d: X-ray diffraction patterns of catalyst from CO-activated run SA-0946, extracted samples. Note the loss of preferred orientation in the Fe_5C_2 phase, with increasing TOS (*except* in TOS = 563) - this indicates that the particles of a given phase are either breaking up or renucleating. The samples show significant zero-point error, as an S-shaped displacement in the peaks, with TOS. This probably arises from sample prep error, and could not be corrected for directly by UNM, due to lack of access to the raw data. Thus, labeling has been based on the reference angles and/or easily recognizable peak-group shapes.
- Figure 5 a: Low magnification view of catalyst, H_2 -activated run SB-3425, TOS = 384 hrs, extracted powder
 b: Low magnification view of catalyst, H_2 -activated run SB-3425, TOS = 330 hrs, slurry
 c: High magnification view of catalyst, H_2 -activated run SB-3425, TOS = 384 hrs, extracted powder
 d: High magnification view of catalyst, H_2 -activated run SB-3425, TOS = 330 hrs, slurry. Note that figure 5c shows images of the powder, without embedding in epoxy and ultramicrotomy.
- Figure 6 X-ray diffraction pattern of catalyst components, H_2 -activated run SB-3425, TOS = 233 hrs. Original slurry (SL), filtered wax (EW), inert-stripped wax (SW), concentrated catalyst slurry (CC), catalyst after Soxhlet extraction (EP), and catalyst powder obtained after the wax was stripped off in flowing inert (SP). The $\alpha\text{-Fe}$ peak seen in the slurry sample grows in size as the catalyst is concentrated,

while the wax peaks diminish in intensity. Note the remarkable difference between the Soxhlet extracted powder and the inert-stripped powder.

Figure 7: Fischer-Tropsch reactivity curves for H₂-activated run SB-3425, and CO-activated run SA-0946. The results are plotted in the form of a pseudo-first-order rate constant, referenced to 250°C. The rate constant units are in mmol of CO converted per g Fe per MPa pressure per hour. The reactor was operated at temperatures ranging from 260°C to 266°C and varying space velocities. The process conditions and actual conversion at several times on stream are shown in Table 3.

Table 1: I/I_{cor} for iron phase mixture (based on $d_p^{\text{avg}} = 15 \text{ nm}$ for all phases)			
Phase	I_{max}	I/I_{cor}	$I/I_{(\text{Fe5C2})}$
Fe	5750	1526 ± 32	4299
Fe_7C_3	12.19	$3.237 \pm .066$	9
Fe_5C_2	1.34	$0.355 \pm .008$	1
Fe_3O_4	532.2	$141.3 \pm 3 \text{ (c)} / 147 \text{ (e)}$	398
Fe_2O_3	9.191	$2.39 \text{ (c)} \pm .049 / 2.49 \text{ (e)}$	6.7
(c) - calculated (e) - experimental, UNM			

Table 2: d-spacings, angles, and relative intensities in the Wax XRD							
d-spacing, Å	2.986	2.569	2.545	2.485	2.108	1.613	1.444
2θ Angle, °	29.9	34.9	35.24	36.12	42.86	57.04	64.46
% Intensity, extracted	79.96	45.76	48.79	100	98.39	30.18	24.74
% Intensity, stripped	62.58	42.31	42.99	66.87	100	25.84	19.11

TABLE 3: Process Changes with corresponding % Conversion		
TOS, hrs	SA-0946: Change	% conversion
0	Sample; T = 260°C; P = 200 PSIG; H ₂ /CO = 0.67; SV = 2.34 NI/g-cat/h	36.1 (2h)
113	Sample	76.6 (112h)
133	SV=1.8 NI/g-cat/h	76.0 (131h)
229	Sample	80.2 (228h)
231	P = 300 PSIG; SV = 2.64 NI/g-cat/h	76.4 (235h)
354	Sample	81.1 (351h)
427	Sample	81.0 (426h)
443	H ₂ /CO = 0.6; SV = 2.0 NI/g-cat/h	81.5 (442h)
563	Sample	81.9 (561)
TOS, hrs	SB-3425: Change	% Conversion
0	Sample; H ₂ /CO = 0.67; T = 260°C; SV = 2.34 NI/g-cat/h; P = 200 PSIG	75.8 (1.5h)
111	Sample	70.8 (110h)
159	SV = 1.80 NI/g-cat/h	70.2 (157h)
233	Sample	73.5 (230h)
278.5	Power out	71.8 (276h)
279	T = 200°C	---
282	T = 260°C	70.0 (287h)
311	H ₂ /CO = 0.6	69.8 (310h)
330	Sample	65.1 (329h)
330	SV = 1.0 NI/g-cat/h	81.7 (340h)
355	T = 266°C	80.0 (353h)
384	Sample	80.1 (383h)

Table 4: Estimated wt % of iron phases in SB-3425, Slurry samples				
TOS, hrs	α -Fe	Fe_7C_3 (so-called ϵ')	Fe_5C_2 (so-called χ)	Fe_3O_4
0	100	0	0	0
111	0.02 (QRSR) 0.03 (I/I_{cor})	99.98 (QRSR) 98.25 (I/I_{cor})	0	0
233	3.09	96.91	0	0
233 (SP1)	1.76	89.50	---	8.74
330	0.42	14.32	85.26	0
384	.004	2.47	97.52	0
SB-3425, Slurry samples: Particle sizes, nm				
TOS, hrs	α -Fe	Fe_7C_3 (so-called ϵ')	Fe_5C_2 (so-called χ)	Fe_3O_4
0	13.54		---	---
111	37.88	5.27	---	---
233	30.50	47.12	---	---
233 (SP1)	17.54	23.32	---	33.42
330	37.88	5.27	7.63	---
384	37.22	4.49	14.78	---

Table 5: Estimated wt % of iron phases in SA-0946, slurry samples				
TOS, hrs	α -Fe	Fe_7C_3 (so-called ϵ')	Fe_5C_2 (so-called χ)	Fe_3O_4
0	0.00	13.41	86.38	0.22
113	0.00	46.17	52.85	0.99
229	0.01	49.46	49.48	1.05
354	0.01	53.05	46.66	0.28
427	0.02	64.61	35.37	0.01
563	0.00	12.19	87.40	0.41
SA-0946, slurry samples: Particle sizes, nm				
TOS, hrs	α -Fe	Fe_7C_3 (so-called ϵ')	Fe_5C_2 (so-called χ)	Fe_3O_4
0	---	13.67	26.92	19.27
113	---	11.38	11.58	48.195
229	52.12	11.27	7.67	44.16
354	19.1	13.02	7.54	142.1
427	56.77	15.28	19.12	145.86
563	---	29.49	77.34	158.19

Figure 1a

Figure 1b

Figure 2

Figure 3a

Figure 3b

Figure 3c

Figure 3d

Figure 4a

Figure 4b

Figure 4c

Figure 4d

Figure 5a

Figure 5b

Figure 5c

Figure 5d

Figure 6

Figure 7