TITLE	NOVEL SLURRY PHASE DIESEL CATALYSTS FOR COAL-DERIVED SYNGAS
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ABSTRACT

OBJECTIVE

The primary objective of this research program is to develop attrition resistant catalysts that exhibit high activities for conversion of coal derived syngas (H_2/CO ratio of ~ 0.7). The specific objective is to develop novel catalysts for synthesis of clean diesel fuels from coal.

ACCOMPLISHMENTS TO DATE

We have completed evaluation of commercially available catalyst supports to determine which among these would be most suitable for use for preparing diesel catalysts. The method used was ultrasonic irradiation, which provides a rapid screening test to determine the extent of fracture and erosion in these materials. The most promising among these were then subjected to a long term, simulated slurry reactor test where N_2 gas was bubbled in a CSTR with the support suspended in a hydrocarbon oil. A supported iron catalyst was prepared using this support and subjected to a long term test in a CSTR where it was first stirred under N_2, then activated in CO. Samples were withdrawn at periodic intervals and washed free of hydrocarbon. These samples are currently being analyzed for the extent of attrition suffered during these simulated CSTR tests. Based on these results, a catalyst will be formulated that will then be subjected to fixed bed reactor test to determine its catalytic activity and a slurry reactor test to determine performance and attrition resistance.

In parallel with this effort, Prof. Bartholomew and his student have synthesized silica-supported Fe catalysts doped with small amounts of Pt. These catalysts have been characterized using H_2 chemisorption and Mössbauer spectroscopy and tested for F-T activity. The results indicate a marked improvement in catalytic reactivity for Pt-promoted Fe/silica relative to unpromoted Fe/silica which is correlated with a higher chi carbide content for the Pt-promoted catalyst. The potential for use of Pt as a promoter is being investigated.

Novel catalyst microstructures have been prepared at UNM via spray drying that encapsulate the Fe oxide phase in a templated silica shell. These catalysts provide attrition resistance while minimizing Fe-silica interactions. The reducibility of these novel catalysts is being investigated via TPR and XRD. Over the next year, we plan to test the catalytic reactivity of these catalysts.

Further investigation of the nature of the active phase in Fe F-T catalysts was continued with a collaborative effort with Prof. Neil Coville at the Univ. of Witwaterstrand in South Africa. Mössbauer analysis of Fe catalysts after CO activation and after F-T synthesis was performed. Working Fe Fischer-Tropsch (F-T) catalysts were studied using Transmission Electron Microscopy (TEM), X-ray Diffraction (XRD) and Mössbauer spectroscopy. The catalysts were removed from a slurry phase Fischer-Tropsch reactor. Instead of using Soxhlet extraction, which may expose the highly reactive catalyst to atmospheric oxidation, we have used an alternative pretreatment involving room temperature extraction that allows us to concentrate the catalyst, but at the same time protect it against atmospheric oxidation. Catalysts from two slurry reactor F-T runs were analyzed, one in its active state and the other after deactivation. Major changes in phase composition as well as in particle size can be seen in the deactivated catalyst relative to the active catalyst. In its active state, the Fe F-T catalyst contains highly dispersed carbide particles of χ-Fe_5C_2 and Fe_7C_3. The deactivated catalyst, on the other hand, shows a different carbide structure that is indexed by Mössbauer as the ε' carbide.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAMS

The Fischer-Trospch synthesis is a vital technology for converting natural gas and coal into premium liquid fuels. Most current interest in this field is directed at natural gas conversion and the catalyst of choice appears to be cobalt based. However, Fe catalysts have several advantages, namely they are cheap, they can tolerate a range of H_2:CO ratios, and they provide high reactivities. The disadvantage is that the high iron loadings make these catalysts friable and susceptible to attrition during their use in a slurry bubble column reactors. Hence, the synthesis of novel attrition resistant catalysts is very important for further development of alternative fuel sources to meet our nation's transportation needs.

PLANS FOR THE COMING YEAR

- Continue synthesis of novel attrition resistant catalysts at the bench scale
- Continue testing of the most promising catalysts in fixed bed reactors
- Continue simulated slurry bubble column runs to establish attrition behavior
- Continue characterization studies to improve understanding of support and promoter effects

ARTICLES, PRESENTATIONS AND STUDENT SUPPORT

Journal Articles & Conference proceedings

- Mansker, L.D., Y. Jin, D.B. Bukur, and A.K. Datye, “Characterization of slurry phase iron catalysts for Fischer-Tropsch synthesis.” Appl. Catal., A, 1999. 186(1,2): p. 277-296.
- S. A. Eliason and C. H. Bartholomew, "Reaction and deactivation kinetics for Fischer-Tropsch synthesis on unpromoted and potassium-promoted iron catalysts," Applied Catalysis A: General 186, 229-243 (1999).
- Bartholomew, C.H., M.W. Stoker, L. Mansker, and A. Datye, “Effects of pretreatment, reaction, and promoter on microphase structure and Fischer-Tropsch activity of precipitated iron catalysts.” Stud. Surf. Sci. Catal., 1999, 126, p. 265-272.
- H. N. Pham, J. Reardon and A. K. Datye, "Measuring the strength of slurry phase heterogeneous catalysts," Powder Technol., 103, p. 95-102 (1999).
- H. Pham and A. K. Datye, “The Synthesis of Attrition Resistant Slurry Phase Iron Fischer-Tropsch Catalysts”, Preprints of the Div. Of Petr. Chem., Amer. Chem. Soc., vol. 44, pg 115-118 (1999).
- Y. Jin, L. Mansker and A. K. Datye, “The Nature of the Active Phase in Iron Fischer-Tropsch Catalysts”, Preprints of the Div. Of Petr. Chem., Amer. Chem. Soc., vol. 44, pg 97-99 (1999).
- Y. Jin and A. K. Datye, “ Phase Transformations in Iron-Fischer Tropsch Synthesis (FTS) Catalysts”, Proc. Intl. Congr. Electron Microscopy, Cancun 1998, vol. II, pg 379 – 380.
- Y. Jin and A. K. Datye, “Characterization of Slurry Bubble Column Iron Fischer-Tropsch Catalysts”, “Natural Gas Conversion V, Stud. Surf. Sci. Catal., 199, pg 209-214 (1998).
- N. B. Jackson, L. Evans and A. K. Datye, “Attrition Determining Morphology Changes in Iron Fischer-Tropsch Catalysts,” Natural Gas Conversion V, Stud. Surf. Sci. Catal., 199, pg 137-142 (1998).

Journal Articles and Conference proceedings (submitted)

- A. K. Datye, Y. Jin, L. Mansker, R. T. Motjope, T. H. Dlamini and N. J.Coville, “The nature of the active phase in iron Fischer-Tropsch catalysts,” Proc. International Congress on Catalysis, Granada, Spain, July 2000, in press.
- H. N. Pham, A. Viergutz, R. J. Gormley and A. K. Datye, “Improving the Attrition Resistance of Slurry Phase Heterogeneous Catalysts”, “Powder Technology”, in press.
- H. N. Pham and A. K. Datye, “The Synthesis of Attrition Resistant Slurry Phase Iron Fischer-Tropsch Catalysts”, “Catalysis Today”, in press.

Conference Presentations

- J. Xu, C. G. Guymon, G. Huber, C. H. Bartholomew, Activity and Characterization of a Supported Iron-Platinum Fischer-Tropsch Synthesis Catalyst, paper presented at the Western States Catalysis Club Meeting, February 25, 2000.

- Y. Jin, L. Mansker and A. K. Datye, "The Genesis of Iron Fischer-Tropsch Catalysts for Coal to Liquids Conversion," presented at the North American Catalysis Society meeting, Boston, MA, May 1999.
- H. Pham and A. K. Datye, "The Synthesis of Attrition Resistant Slurry Phase Iron Fischer-Tropsch Catalysts", presented at the North American Catalysis Society meeting, Boston, MA, May 1999.
- L. D. Mansker and A. K. Datye, "Quantitative Diffraction Methods Applied to the Characterization of Working Iron Fischer-Tropsch Catalysts", presented at the 13th Annual Western States Catalysis Club Meeting, Albuquerque, 1999.
- Y. Jin, L. Mansker and A. K. Datye, "The Nature of the Active Phase in Iron Fischer-Tropsch Catalysts", presented at the 13th Annual Western States Catalysis Club Meeting, Albuquerque, 1999.
- H. N. Pham and A. K. Datye, "The Synthesis of Attrition Resistant Slurry Phase Iron Fischer-Tropsch Catalysts", presented at the 13th Annual Western States Catalysis Club Meeting, Albuquerque, 1999.
- H. Pham and A. K. Datye, "The Synthesis of Attrition Resistant Slurry Phase Iron Fischer-Tropsch Catalysts", presented at the 217th National Meeting, American Chemical Society, Symposium of Syngas Conversion to Fuels and Chemicals, Anaheim, 1999.
- Y. Jin, L. Mansker and A. K. Datye, "The Nature of the Active Phase in Iron Fischer-Tropsch Catalysts", presented at the 217th National Meeting, American Chemical Society, Symposium of Syngas Conversion to Fuels and Chemicals, Anaheim, 1999.
- Y. Jin and A. K. Datye, " Phase Transformations in Iron-Fischer Tropsch Synthesis (FTS) Catalysts", presented at the International Congress of Electron Microscopy, Cancun, 1998.
- N. B. Jackson, L. Evans and A. K. Datye, "Attrition Determining Morphology Changes on Iron Fischer-Tropsch Catalysts"" presented at the Proceedings of the 5th International Natural Gas Conversion Symposium, Italy, 1998.
- Y. Jin and A. K. Datye, "Characterization of Bubble Column Slurry Phase Iron Fischer-Tropsch Catalysts", presented at the Proceedings of the 5th International Natural Gas Conversion Symposium, Italy, 1998.

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- Hien Pham (Ph. D.) student in chemical and nuclear engineering, Univ. of New Mexico
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- Alec Klinghoffer (Ph. D) student in chemical engineering, Texas A&M university
- J. Xu (Ph. D.) student in chemical engineering at Brigham Young University
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