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| 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

Four slurry reactor tests have been performed during the last year. Initial activity of silica-supported catalyst prepared from organic solution was higher than that of TAMU's precipitated catalysts, and was fairly stable during 300 h of testing. However, its methane selectivity was significantly higher than that of the precipitated catalysts. The other silica and alumina supported catalysts deactivated slowly with time on stream, and their methane selectivity was relatively high . For the silica supported catalyst prepared by organic impregnation, it was found that the effect of potassium promotion on catalyst activity and selectivity was negligible.

Reduction behavior of a large number of catalysts has been characterized. The effect of different supports, metal loading and synthesis procedure has been investigated. Temperature programmed reduction (TPR) in hydrogen showed two reduction peaks for all catalysts; one at 300-400°C and the other at 550-650°C. The first peak corresponds to a degree of reduction of ca. 20%, while the total degree of reduction varied between 80 and 100% for temperatures up to 800°C. No clear trends in the reduction behavior of different catalysts were found. Isothermal

reduction in hydrogen at 280°C showed that most catalysts were completely reduced after 8 hours. The exceptions were the catalysts on Vista B alumina support, HP 14 alumina support and unpromoted catalyst on Davison 948 silica support. Degree of reduction for these catalysts was only to ca. 55% after 8 hours of reduction, increasing to ca. 60% after 16 hours.

The results so far show that Davison 948/952 silica and Puralox HP 14-150 alumina are the most promising supports. Further effort should be directed towards improvements in synthesis procedures: support calcination, organic impregnation and promoters (type and precursor).

In parallel with this effort, Prof. Bartholomew and his student have synthesized silica-supported Fe catalysts doped with small amounts of Pt, using a non-aqueous evaporative deposition technique. These catalysts have been tested for F-T activity in a fixed-bed reactor, and have been characterized using Mössbauer spectroscopy for studies of pretreatment effects and catalysts after fixed-bed runs. The results indicate a CO conversion of ca. 97 % after 100 hours, a $CO_2$ conversion of ca. 40%, and a methane selectivity of ca. 10%. In addition, hydrothermal stability tests and statistical design analyses of these catalysts have been investigated.

Novel catalyst microstructures have been prepared at UNM via spray drying that encapsulate the Fe oxide phase in a mesoporous silica shell. These catalysts have been characterized using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM), and ultrasonic fragmentation has been used to determine the extent of attrition. The results indicate that these catalysts provide attrition resistance while minimizing Fe-silica interactions, and that the iron oxide nanoparticles are encapsulated inside the silica shell.. The reducibility of these novel catalysts has also been investigated via TPR and X-ray Diffraction (XRD). The results indicate that the encapsulated Fe F-T catalyst containing ca. 40 wt.% iron oxide could be completely reduced to $\alpha$-Fe under hydrogen at 300°C. Furthermore, the encapsulated catalyst particles remain intact after reduction.

## 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.

## ARTICLES, PRESENTATIONS AND STUDENT SUPPORT

Journal Articles & Conference proceedings


1. 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).
2. 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).
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9. 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.
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11. H. N. Pham, A. Viergutz, R. J. Gormley and A. K. Datye, “Improving the Attrition Resistance of Slurry Phase Heterogeneous Catalysts”, “Powder Technology”, 110, 196-203, (2000).
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13. Jin, Y. M. and Datye, A. K., Phase transformations in iron Fischer-Tropsch catalysts during temperature-programmed reduction, Journal of Catalysis ;, **196**, #1, 8-17, (2000).
14. Bukur, D. B. and Lang, X. S., "Highly Active and Stable Iron Fischer-Tropsch Catalyst for Synthesis Gas Conversion to Liquid Fuels", Ind. Eng. Chem. Res., 38, 3270-3275 (1999).
15. Bukur, D. B., Ding, Y. and Sivaraj, C., "Supported Iron Catalysts for Fischer-Tropsch Synthesis ", Prep. Pap.-Am. Chem. Soc., Div. Petr. Chem., **45**(2), 218-220, 2000.

Journal Articles and Conference proceedings (in preparation and in press)

1. Pham, H.N., Bergroth, M., Datye, A.K., “Synthesis of Attrition Resistant Heterogeneous Catalysts Using Templated Mesoporous Silica”, to be submitted.
2. Bukur, D.B., Hanssen, K.F., Sivaraj, C., "Supported Iron Catalysts for Slurry Phase Fischer-Tropsch Synthesis ", AIChE Meeting, Houston, April 22-26, 2001.

Conference Presentations

1. 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.
2. N. B. Jackson, L. Evans and A. K. Datye, “Attrition Determining Morphology Changes on Iron Fischer-Tropsch Catalysts"” presented at the Proceedings of the 5t$^{h}$ International Natural Gas Conversion Symposium, Italy, 1998.
3. Y. Jin and A. K. Datye, “Characterization of Bubble Column Slurry Phase Iron Fischer-Tropsch Catalysts”, presented at the Proceedings of the 5$^{th}$ International Natural Gas Conversion Symposium, Italy, 1998.
4. 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.
5. 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.
6. L. D. Mansker and A. K. Datye, “Quantitative Diffraction Methods Applied to the Characterization of Working Iron Fischer-Tropsch Catalysts”, presented at the 13$^{th}$ Annual Western States Catalysis Club Meeting, Albuquerque, 1999.
7. Y. Jin, L. Mansker and A. K. Datye, “The Nature of the Active Phase in Iron Fischer-Tropsch Catalysts”, presented at the 13$^{th}$ Annual Western States Catalysis Club Meeting, Albuquerque, 1999.
8. H. N. Pham and A. K. Datye, “The Synthesis of Attrition Resistant Slurry Phase Iron Fischer-Tropsch Catalysts”, presented at the 13$^{th}$ Annual Western States Catalysis Club Meeting, Albuquerque, 1999.
9. H. Pham and A. K. Datye, “The Synthesis of Attrition Resistant Slurry Phase Iron Fischer-Tropsch Catalysts”, presented at the 217$^{th}$ National Meeting, American Chemical Society, Symposium of Syngas Conversion to Fuels and Chemicals, Anaheim, 1999.
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