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QUARTERLY TECHNICAL PROGRESS REPORT
(Jan-March, 1995)

CONTRACT TITLE: MÖSSBAUER SPECTROSCOPY STUDIES OF IRON-CATALYSTS USED IN FISCHER-TROPSCH (FT) PROCESSES

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Objectives: To carry out Mössbauer spectroscopy study of Iron-based catalysts used in FT synthesis to identify iron phases present and correlate with water gas shift and FT activities.

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Mössbauer Spectroscopy Studies:

The U.S. Department of energy has currently a program to develop Fischer-Tropsch catalysts which are active at low H_2/CO ratio of 0.7. Dr. Burt Davis has been developing Fischer-Tropsch catalysts which are active at a low H_2/CO ratio. It is of interest to find out any relationships that may exist between the iron phases that are produced during activation and FT synthesis and the activity of the catalysts.

Mössbauer spectroscopy investigations were carried out on 14 iron-based catalysts during the period under review. The catalyst $100Fe/4.4Si/0.71K$ (all atomic ratios) was subjected to activation first in syngas and subsequently in CO gas atmosphere. Fischer-Tropsch (FT) synthesis was carried out on the above catalyst. Another catalyst $100Fe/4.4Si/2.6Cu/0.71K$ (all atomic ratios) activated in syngas and subjected to FT synthesis was also studied to understand the effect of added Cu on the phase distribution and its effect on the FT activity. These samples were sent by Dr. Burt Davis, Center for Applied Energy Research, University of Kentucky.

The following trends were observed:

- (1) Activation of the catalyst in syngas, H_2/CO lead to the formation of Fe_3O_4 and no carbides were formed. The FT activity was found to be low at 9-12% (H_2+CO) conversion.
- (2) Activation of the catalyst in CO for 22hrs lead to the formation of 33% of χ -carbide and the FT activity was found to be high at 88% maximum.
- (3) Addition of copper to the catalyst has improved the FT activity for those catalysts pretreated in syngas at elevated pressures.

Summary of Technical Progress:

During the period under review only the scheduled Task 2 was carried out.

Mössbauer spectroscopy measurements of the following iron FT catalysts, received from Dr. Burt Davis, Center for Applied Energy Research, University of Kentucky, Lexington, KY were carried out. The catalysts were subjected to Mössbauer measurements as received without any cleaning of any wax coating present on the surface of the catalysts.

Conditions of activation and FT synthesis are given below:

Catalyst: 100Fe/4.4Si/0.71K (atomic ratios)
Initial Activation in: Syngas for 93hrs and subsequently co activated for 22hrs at 270 °C, C, C, 175psig, 2.0 nL/hr-g(Fe)
Synthesis conditions: 270°C, 175 psig, 3.4nL/hr-g(Fe), H₂/CO=0.7

Catalyst: 100Fe/4.4Si/2.6Cu/0.71K (atomic ratios)
Activation in: Syngas at 270 °C,175psig,3.4nL/hr-g(Fe), H₂/CO=0.7
Synthesis conditions: 270°C, 175 psig, 3.4nL/hr-g(Fe), H₂/CO=0.7

The iron-phases present in the two catalysts are shown in the following Tables I and II: The spm phase shown in the Tables refers to the superparamagnetic particles of either oxides or carbides. Low temperature measurements are yet to be done to identify the phase.

Results:

The catalyst 100Fe/4.4Si/.71K gets converted to 100% Fe₃O₄ after the catalyst was activated in syngas and subjected to FT synthesis for 93hrs. No carbide was formed. The FT activity was low at 12.2% of (H₂+CO) conversion. When the catalyst was subsequently activated in CO for 22hrs, 33% of χ -carbide was formed and the FT activity increased. It reached a maximum of 88% (H₂+CO) conversion after TOS=77.5hrs and subsequently it drops to 81% at TOS=341hrs.

It is observed that as the carbide content decreased from 33% to 19% , the FT activity increased from 25% to 88%. On the other hand, when the carbide content is increased from 19% to 26%, the FT activity is decreased from 88% to 81% of (H₂+CO) conversion.

The catalyst with added Cu and activated in syngas gave rise to slightly better FT activity with 51% (H₂+CO) conversion at the end of 214hrs FT synthesis as compared to the catalyst without any Cu. The activity is relatively low as compared to the activity of the catalyst activated in CO.

The above results indicate that the χ -carbide is involved either directly or indirectly in the FT synthesis.

Table I

Catalyst: 100Fe/4.4Si/0.71K (atomic ratios)
Initial Activation in: Syngas for 93hrs and subsequently co activated for 22hrs at 270 °C, C, C, 175psig, 2.0 nL/hr-g(Fe)
Synthesis conditions: 270°C, 175 psig, 3.4nL/hr-g(Fe), H₂/CO=0.7

| | Catalyst | Spm-phase | Fe ₃ O ₄ | χ-Fe ₅ C ₂ | % Conversion* |
|--------|------------------------------|-----------|--------------------------------|----------------------------------|---------------|
| 1 | TOS=6.33h syngas | 75 | 25 | - | 9.2 |
| 2 | TOS=24.0h syngas | 31 | 69 | - | 9.7 |
| 3 | TOS=46.0h syngas | 11 | 89 | - | 11.5 |
| 4 | TOS=93.0h syngas | - | 100 | - | 12.2 |
| 5 → | TOS=22h CO- pretreated | 9 | 58 | 33 | 25 |
| 6 | TOS=26.5h syngas | 15 | 60 | 25 | 59 |
| 7 | TOS=77.5h syngas | 18 | 63 | 19 | 88 |
| 8 | TOS=198.0 h syngas | 13 | 67 | 20 | 86 |
| 9 | TOS=341h syngas | 11 | 63 | 26 | 81 |

*Catalyst preparation and FT runs were carried out at CAER, University of Kentucky

Table II

Catalyst: 100Fe/4.4Si/2.6Cu/0.71K (atomic ratios)
Activation in: Syngas at 270 °C, 175psig, 3.4nL/hr-g(Fe), H₂/CO=0.7
Synthesis conditions: 270°C, 175 psig, 3.4nL/hr-g(Fe), H₂/CO=0.7

| | Catalyst | Spm-phase | Fe ₃ O ₄ | χ-Fe ₅ C ₂ | % CO Conversion * |
|---|-------------|-----------|--------------------------------|----------------------------------|-------------------|
| 1 | TOS=4.33h | 19 | 81 | - | 26 |
| 2 | TOS=21.0h | 10 | 90 | - | 26 |
| 3 | TOS=45.0h | 14 | 86 | - | 32 |
| 4 | TOS=113.75h | 3 | 82 | 15 | 43 |
| 5 | TOS=214.5h | 4 | 76 | 20 | 51 |

*Catalyst preparation and FT runs were carried out at: CAER, University of Kentucky