

Technology Development for Iron and Cobalt Fischer-Tropsch Catalysts

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Burtron H. Davis

Enrique Iglesia (UC/B Subcontract)

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University of Kentucky Research Foundation

201 Kinkead Hall

Lexington, KY 40506

University of California-Berkeley (Subcontract)

Laboratory for the Science and Application of Catalysis

Department of Chemical Engineering

University of California at Berkeley

Berkeley, CA 94720

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## Abstract

### CAER

A mathematical model has been developed to describe the product distribution of Fischer-Tropsch synthesis, based on the recognition that the termination path to olefin is reversible. The observed product distribution at the reactor outlet consists of the contribution from intrinsic chain propagation on the catalyst surface and the effects of olefin reincorporation. The 2-alpha distribution can be attributed to the effect of vapor liquid separation of hydrocarbon products. The reaction product does not follow ASF single alpha distribution any more even on the catalyst surface. A tight fit between model prediction and experimental data has been demonstrated. Also, the deviation point of the product distribution is precisely predicted to be within carbon number 8-14 under typical FT conditions.

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*In-situ* X-ray absorption spectroscopy (XAS) studies on Fe-Zn-Ru-K oxides indicated that Fe-Zn-Ru-K oxides reduce and carburize to Fe carbides rapidly in synthesis gas at 523 K (<4 h). The oxidation of initially formed Fe carbides to Fe<sub>3</sub>O<sub>4</sub> requires a large CO<sub>2</sub>/CO ratio (>13.0) at the FTS conditions investigated (543 K and 1 atm). The temperature-programmed reduction and carburization of Fe-Zn-Ru-K oxides in H<sub>2</sub> and CO showed that Fe-Zn oxides reduce at lower temperatures than pure Fe<sub>2</sub>O<sub>3</sub> because of the presence of ZnFe<sub>2</sub>O<sub>4</sub> which acts as nuclei for the conversion from Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub>. Ru addition increases Fe oxide reduction by providing H<sub>2</sub> dissociation sites and increases carburization rates by dissociating CO. The addition of K slightly inhibits H<sub>2</sub> and CO reduction but increases carburization rates by assisting CO dissociation. Ru increases FTS rates by increasing reduction and carburization rates and by providing more active sites. Combined with K, Ru-promoted Fe-Zn oxides showed slightly higher initial CH<sub>4</sub> formation

rates and reached steady state values ( $\sim 0.03$  mmol/g-atom Fe s) earlier than the sample without K. Ru-promoted Fe-Zn catalysts appear to have the best performance among all the Fe-based catalysts studied for the FTS reaction. These catalysts had a higher FT activity than both the Fe-Zn-Cu and Fe-Si systems studied previously. Experiments conducted with Fe-Zn-Ru-K showed that the addition of K increased FT rates at low temperatures (235 °C and 220 °C), but decreased them at high temperature (270 °C). However, the other effects usually associated with K-addition such as increase in CO<sub>2</sub> selectivity, decrease in CH<sub>4</sub> selectivity and an increase in  $\alpha$ -olefin/ $n$ -paraffin ratios were observed at all the conditions. In spite of having a selectivity to CO<sub>2</sub> that is as high as that on the Cu-based catalyst, Fe-Zn-Ru-K appears to be the most promising catalyst due to its optimum combination of high FT rates and high selectivity to C<sub>5+</sub> hydrocarbons. A nonlinear multivariate regression program was used to test the validity of two reaction mechanisms proposed for FTS reaction kinetics on Co-based catalysts and both the mechanisms appear to be consistent with the reaction data. After recalibration of the TCD response factors, the hydrocarbon selectivities obtained on a 21.9% Co/SiO<sub>2</sub> appear to be much closer to the ones previously reported and the minor differences that still exist between the data is due to hydrogenation taking place on the wall of the reactor.

## Table of Contents

	<u>Page</u>
Disclaimer .....	1
Abstract .....	2
Table of Contents .....	4
Executive Summary .....	5
Task 1. Iron Catalyst Preparation .....	10
Task 2. Catalyst Testing .....	10
A.    The Formation of Branched Hydrocarbons in the Fe and Co Catalyzed FT Reactions .....	10
Task 3. Catalyst Characterization .....	49
Task 4. Wax/Catalyst Separation .....	49
A.    High-alpha Catalyst Filter .....	49
Task 5. Oxygenates .....	66
Task 6. Literature Review of Prior Fischer-Tropsch Synthesis with Co Catalysts .....	66
Task 7. Co Catalyst Preparation .....	66
Task 8. Co Catalyst Testing for Activity and Kinetic Rate Correlations .....	68
A.    Effect of Water on the Fischer-Tropsch Catalytic Properties of Ruthenium Promoted Co/TiO <sub>2</sub> Catalyst .....	68
B.    Activity of Cobalt Catalysts .....	78
Task 9. Co Catalyst Life Testing .....	85
A.    Deactivation Study of Co-Re-Al <sub>2</sub> O <sub>3</sub> Catalysts .....	85
Task 10. Co Catalyst Mechanism Study .....	96
A.    Product Distribution of Fischer-Tropsch Synthesis .....	96
B.    CO and CO <sub>2</sub> Hydrogenation Over Co/SiO <sub>2</sub> Catalyst .....	115
Task 11. University of California-Berkeley Subcontract .....	124
Task 12. Reporting and Management .....	160