RATE AND SELECTIVITY ENHANCEMENT IN FISCHER TROPSCH SYNTHESIS. QUARTERLY RESEARCH REPORT

MICHIGAN UNIV., ANN ARBOR. DEPT. OF
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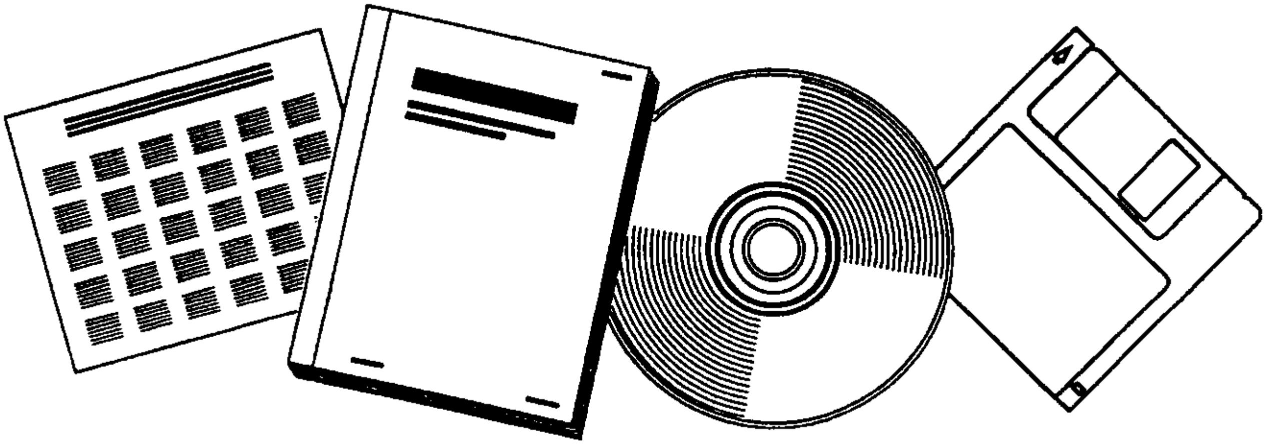

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QUARTERLY RESEARCH REPORT

TO

DEPARTMENT OF ENERGY

UNIVERSITY COAL RESEARCH

PITTSBURGH ENERGY TECHNOLOGY CENTER

RATE AND SELECTIVITY ENHANCEMENT IN FISCHER TROPSCH SYNTHESIS

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Highlights of Research During this Quarter

We successfully demonstrated that concentration cycling improves selectivity and reactivity of Ruthenium / Alumina catalyst at moderate pressures (50 psig). Rate of reaction was improved by more than a factor of two compared to the equivalent steady state. We were also able to observe the reactive intermediate responsible for the enormous rate enhancements we had previously observed during CO oxidation on palladium. The surface concentration of this intermediate was found to correlate extremely well with the instantaneous rate of reaction. We have assembled a fast response quadrupole mass spectrometer for online selectivity measurements during the next phase of our research.

Our efforts during this quarter were concentrated on three areas:

1. Forced concentration cycling of the feed with a Ruthenium catalyst at above atmospheric pressure.
2. Determining the surface intermediates responsible for the enormous rate enhancements observed during CO oxidation on Pd / Al_2O_3.
3. Assembling a quadrupole mass spectrometer for achieving high mass resolution during concentration cycling studies.

The details are as follows:

Forced concentration cycling of the feed with a Ruthenium catalyst at above atmospheric pressure : This portion of our research was undertaken to determine the benefits of concentration cycling at high pressures. Due to temporary experimental limitations with our IR cell the maximum pressure was limited to 50 psig. The results we have so far indicate that the rate of hydrocarbon production is improved on the average by a factor of two to three. Just as importantly we find that concentration cycling moves the region of maximum rate to higher CO to H_2 ratios, typically doubling that of steady state ratio. Selectivity enhancement towards higher hydrocarbons is best at CO to H_2 ratios of 0.3 or higher. We have also assembled a reactor which can be used at higher pressures (up to 150 psig). A transmission IR single pellet reactor is also under construction in order to detect the surface hydrocarbon intermediates during concentration cycling.

Determining the surface intermediates responsible for the enormous rate enhancements observed during CO oxidation on Pd / Al_2O_3 : With palladium we had observed that concentration cycling between CO and oxygen streams resulted in CO oxidation rates that were close to 100 times more than the steady state rates. These rate enhancements are even higher than those observed with platinum. Our research this term was aimed at understanding the reason for this. We were successfull in detecting a surface intermediate that exists on the surface under reaction conditions only if the surface is oxygen covered before introducing CO into the system. This surface intermediate is the very active CO species adsorbed into a surface structure with $\theta_{CO} = \theta_{O} = 0.5$. The existence of this species was predicted by high vacuum studies but our observation is the first experimental detection of this species under realistic atmospheric conditions. The surface concentration of this species was measured quantitatively by IR spectroscopy and was found to be linearly correlated with the rate of carbon dioxide concentration.

Assembling a quadrupole mass spectrometer for achieving high mass resolution during concentration cycling studies.

One of the major problems we have been facing in analysing our data has been the speed of GC analysis for the higher hydrocarbons. With a GC the analysis process is never fast enough to follow the initial transients which we have found to be very useful in deciding the reactor operating parameters. Also during steady periodic operation selectivity information for one data point takes as much as one hour, thus seriously limiting our ability to gather data. To solve this problem we purchased (with funds from NSF) a Balzers QMG 112 quadrupole mass spectrometer with a computer interface, making it plug to plug compatible with our current computer. This will enable us to get instantaneous mass distribution information. Another instrumentation development we now have is a transmission IR single pellet reactor which makes detection of surface intermediates possible. We are planning on using these two new pieces of equipment extensively during in the immediate future.

Papers Submitted for Publication During This Quarter:

1. "CO Oxidation on Pd/ Al_2O_3 Transient Response and Rate Enhancement Through Forced Concentration Cycling", X. Zhou, Y. Barshad and Erdogan Gulari, Chemical Engineering Science.
2. "Rate and Selectivity Enhancement in FTS Synthesis Over Charcoal Supported Molybdenum Catalysts", J. W. Dunn and Erdogan Gulari, Canadian Journal of Chemical Engineering.

Meeting Presentations During this Quarter

1. " CO Oxidation on Pd/ Al_2O_3 Under Transient Conditions an IR Study " , X. Zhou, Y. Barshad and Erdogan Gulari , paper # C2 ,North American Catalysis Society Biennial Meeting , Houston , March 1985.

2. "Spectroscopic and Activity Characterization of Mo, Mo-Co / Titania Catalysts ", K.Y.S. Ng and Erdogan Gulari , paper # C11 , North American Catalysis Society Biennial Meeting , Houston , March 1985.

3. " Spectroscopic Characterization of Molybdenum Oxalate Based Catalysts " , K. Y. S. Ng, X. Zhou and Erdogan Gulari , paper # P11 , North American Catalysis Society Biennial Meeting , Houston , March 1985.