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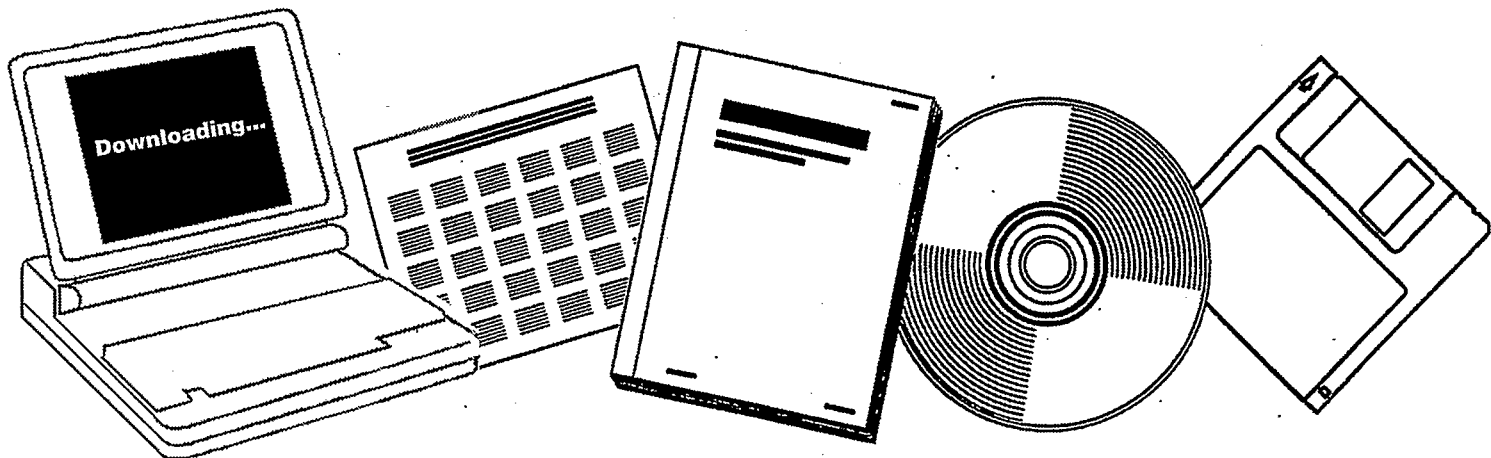
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# RATE AND SELECTIVITY ENHANCEMENT IN FISCHER TROPSCH SYNTHESIS. FINAL TECHNICAL REPORT

MICHIGAN UNIV., ANN ARBOR. DEPT. OF  
CHEMICAL ENGINEERING

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## **RATE AND SELECTIVITY ENHANCEMENT IN FISCHER TROPSCH SYNTHESIS**

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### Introduction :

One of the most frustrating aspects of indirect coal liquefaction by the Fischer Tropsch Synthesis has been the inability of the researchers to find highly selective catalysts. Commercially, the most valuable products are the liquid fuels ( gasoline C<sub>5</sub>-C<sub>11</sub>, diesel fuel C<sub>12</sub>-C<sub>18</sub> ) and chemical feedstocks (C<sub>2</sub>-C<sub>5</sub> ). In addition to the selectivity problem the optimum hydrogen to CO ratio for the group VIII metal (Fe, Co, Ru ) based catalysts is greater than 3 for high activity. This last problem makes it necessary to add significant amounts of hydrogen to the syngas coming out of the coal gasifiers having a hydrogen to CO ratio of approximately 0.8 . Our objective in this research project was to test the feasibility of a novel method ( one that looks at the engineering side ) of improving the selectivity and activity of the existing FTS catalysts. Our approach was based on controlled unsteady state operation of FTS reactors : namely forced concentration cycling of the feed between hydrogen rich and poor feed streams . The basic idea is to change the gas phase composition periodically in order not to allow the catalyst surface to operate at steady state and thus escape the limitations imposed by the kinetics of the rate determining step.

A second goal of the research project was to investigate the fundamental mechanism of FT synthesis and the surface phenomena responsible for rate enhancements or the observed selectivity.

### Highlights of the Research :

Overall this project was very successful in proving that one could in fact change the selectivity of a complex reaction such as Fischer Tropsch Synthesis through forced concentration cycling.

With charcoal supported molybdenum catalysts concentration cycling improved both the reactivity and selectivity of the catalysts. In addition to being able to manipulate the carbon number selectivity we were also able to manipulate the olefin to paraffin selectivity of the catalyst.

With alumina supported ruthenium catalysts concentration cycling improved the activity of the catalysts much more than the molybdenum based catalysts. The changes in selectivity however were much more complex . We were successful in enhancing the

selectivity to several of the carbon numbers . Moderate pressure studies showed that the relative rate enhancement and selectivity enhancement increased with pressure.

In order to understand the complex behavior of the ruthenium catalyst we also performed in depth transient response studies. Our transient response studies enabled us to measure the changes in the selectivity of the catalyst during concentration cycling .

Irrespective of the catalyst we also observed that concentration cycling decreased the rate of catalyst decay very significantly.

### Details of the Results:

Part of our results have already appeared in print and reprints are attached. The following is a brief summary of our findings.

#### Results obtained with the molybdenum catalysts

1. " Molybdena on Titania : II. Thiophene Hydrodesulfurization Activity and Selectivity ", K. Y.S. Ng and E. Gulari , Journal of Catalysis , 95, 33-40 (1985) , Copy attached .

This manuscript reports part of the work on titania supported molybdenum as a potential FTS and HDS ( hydrodesulfurization ) catalyst. In general we observed that titania supported molybdena is a very good HDS catalyst . The activity of the pure molybdenum catalyst is a factor of three to five higher than the best commercial catalyst. One of the surprise findings was the less than a factor of two increase observed when cobalt was used as a promoter. This increase in activity is much less than what is observed with alumina supported catalysts. Another important finding was that the monolayer to sub-monolayer catalysts have the highest activity per mole of molybdenum on the catalyst.

2. " Rate and Selectivity Modification in Fischer-Tropsch Synthesis Over Charcoal Supported Molybdenum by Forced Concentration Cycling ", J. W. Dun and Erdogan Gulari , The Canadian Journal of Chemical Engineering , 64,260-266 (1986) , Copy attached .

This paper reports on one of the major feasibility demonstrations of this research project, the feasibility of rate and selectivity enhancement in FTS . Forced concentration cycling between pure CO and H<sub>2</sub> was used to successfully change both the selectivities and reactivities of promoted and unpromoted charcoal supported molybdenum catalysts. It was found that with the unpromoted catalyst the rate enhancement increases with temperature and selectivity shifts towards methane. At lower temperatures concentration cycling increases the selectivity to the higher hydrocarbons to levels only achievable with

promoted catalysts. Concentration cycling with the potassium promoted catalyst results in small rate enhancements but the olefin to paraffin ratio is dramatically changed without changing the carbon number distribution.

3. " Effect of Pretreatment Conditions on the Activity and Selectivity of Molybdenum Catalysts " , J. W. Dun and Erdogan Gulari , Chemical Engineering Communications . In Press

This paper reports the results of our work on the preparation of high activity molybdenum catalysts for FTS . It was determined that the minimum reduction temperature and time were four hours at 450 °C . Longer reduction resulted in slight loss of activity . Shorter reduction times were found to lead to very low activity catalysts. It was also found that the best method of loading molybdenum was through the equilibrium adsorption method . With this method of loading the activity of the catalyst on a per unit basis stays constant over the whole loading range. In comparison the commonly used incipient wetness technique results in catalysts that are only half as active for the same loading .

#### Results obtained with the ruthenium catalysts

1. "Modification of Product Distribution Through Periodic Operation : Fischer Tropsch Synthesis over Ru/Al<sub>2</sub>O<sub>3</sub> " , Y. Barshad and Erdogan Gulari , Chem. Eng. Comm. **43**, 39-51 (1986 ) , Copy attached .

This paper reports on one of the major feasibility demonstrations of this research project, the feasibility of rate and selectivity enhancement in FTS . Forced concentration cycling was used to show that it is possible to increase the time averaged rate of reaction by several hundred percent over that of steady state. The improvements in selectivity were more complex. Significant selectivity enhancements were observed for ethane propane and butane .

2. "Selectivity of Ru/ Al<sub>2</sub>O<sub>3</sub> Under Transient Conditions " , X. Zhou and Erdogan Gulari, IN Press .

This paper reports the results of our fundamental studies of FTS synthesis in order to design our concentration cycling experiments better. By combining a mass spectrometer and a GC in a novel way we were able to determine the concentrations of C<sub>1</sub>-C<sub>12</sub> hydrocarbons during the transient response experiments . A combination of CO and hydrogen step up and

pretreatment transient experiments revealed that the chain growth step of FTS on ruthenium is much faster than the carbon deposition and termination steps. Some of the surprising and important findings were: i- Hydrogenation of carbidic carbon ( $C_{\alpha}$ ) is more selective towards linear chain alkanes and hydrogenation of surface carbon,  $C_{\beta}$  associated with hydrogen is much more selective towards the branched chain products; ii- Chemisorbed CO appears to block the hydrogenation of  $C_{\beta}$ ; iii- There is no difference between the carbidic  $C_{\alpha}$  deposited by exposure to CO alone or in the presence of hydrogen. iv- Even in the presence of CO the catalyst contains large amounts of CO but this hydrogen appears to be not available for the FTS reaction. Our preliminary results indicate that majority of the hydrogen is diffused into the bulk of the catalyst crystallites. v- Olefins are formed only from the carbidic carbon  $C_{\alpha}$ .

We are in the process of incorporating these findings into the design of better concentration cycling experiments.

3. "Rate Enhancement and in Phase Separation of Products", X. Zhou and Erdogan Gulari, To be submitted to AIChE journal.

Our previous studies with ruthenium and molybdenum catalysts have shown that the product distribution changes periodically during each cycle. In this work we explored the possibility of separating the product stream into several product groups and taking advantage of the periodic changes in the selectivity of the product stream. By phase locking the switching valves on the product stream we were able to achieve significant separation between methane and the higher hydrocarbons and between olefins and paraffins. This method has significant commercial implications if FTS ever becomes commercial on a large scale.

#### CO Oxidation Results

During this project we also continued the research we had started on cyclic operation of CO oxidation reactors. The following is a list of manuscripts in this area that acknowledge support from this contract.

1. "Carbon Monoxide Oxidation Under Transient Conditions: A Fourier Transform Infrared Transmission Spectroscopy Study", Y. Barshad, X. Zhou and Erdogan Gulari, J. Catalysis, 94, 128-141(1985), Copy Attached.

This paper reports the results of our fundamental studies on the mechanism of CO

oxidation. In this study we showed that concentration cycling leads to the formation of surface intermediates that are not present on the catalyst surface in detectable amounts under steady state conditions. The rate enhancements observed were found to be directly correlated with the concentration of the surface CO adsorbed on Pt atoms sharing a chemisorbed oxygen atom.

2. " CO Oxidation on Pd/Al<sub>2</sub>O<sub>3</sub> . Transient Response and Rate Enhancement Through Forced Concentration Cycling " , X. Zhou. Y. Barshad and Erdogan Gulari, Chemical Engineering Science,

41, 1277-1284 (1986) , copy attached .

This manuscript describes the enormous rate enhancements achieved through forced concentration cycling of the feed between CO and O<sub>2</sub> with a supported palladium catalyst. This reaction shows rate enhancements ( compared to steady state operation) of as much as two orders of magnitude .

3. " CO Oxidation and Adsorption on Pd/Al<sub>2</sub>O<sub>3</sub> Under Transient Conditions", X. Zhou and Erdogan Gulari , Langmuir , in press .

In this study we discuss the surface phenomena responsible for the enormous rate enhancements observed on Pd during concentration cycling between CO and oxygen . We present IR evidence that there are at least two different mechanisms of CO oxidation on Pd . One of these mechanisms is only active under transient conditions . The surface concentration of one of the surface intermediates is shown to be linearly proportional to the rate of CO<sub>2</sub> production. Other transient response evidence is discussed to show the similarities between the results obtained with polycrystalline catalysts and single crystal .

4. " Kinetic Phase Transitions in Irreversible Surface Reactions " , R. M. Ziff , Erdogan Gulari and Y . Barshad , Phys Rev Lett , 56,2553 (1986) .

This manuscript describes the results of some of our theoretical simulations of surface reactions and concentration cycling.

#### List of Scientific Presentations:

The following is a list of Scientific presentations resulting from this research project:



1. K.Y.S. Ng and Erdogan Gulari , " Thiophene HDS activity of Mo/ Titania Catalysts " , Catalysis Soc. Meeting , Houston , 1985 .
2. X.Zhou, Y.Barshad and Erdogan Gulari, " An FTIR Study of CO Oxidation on Palladium under Transient Conditions " , Catalysis Soc. Meeting , Houston , 1985 .
3. K.Y.S. Ng, X. Zhou and Erdogan Gulari " Raman and IR Characterization of Molybdenum Oxalate in solution and on Alumina , Catalysis Soc. Meeting , Houston , 1985 .
4. Y. Barshad, R. Ziff , and Erdogan Gulari " Monte Carlo type model of catalytic CO oxidation", Michigan Catalysis Society spring symposia , East Lansing , May 1985 .
5. Y. Barshad, X. Zhou, J.W. Dun and Erdogan Gulari , " Rate and Selectivity Enhancement in FTS " , Michigan Catalysis Society spring symposia , East Lansing , May 1985 .
6. Erdogan Gulari " Rate and Selectivity Enhancement In FTS " , DOE Contractors Conference , July 24 , Pittsburgh Penn. 1985 .
7. X. Zhou and Erdogan Gulari " Transient and Periodic Response of Ru/ Al<sub>2</sub>O<sub>3</sub> in FTS " , ACS Annual Meeting , Chicago, Sept. 1985 .
8. Erdogan Gulari and X. Zhou " Periodic Operation of a Catalytic FTS Synthesis Reactor " AICHE Annual Meeting , Chicago, Nov. 1985 .
9. X. Zhou and Erdogan Gulari, " Transient Response Study of FT synthesis on Ru/ Alumina", Michigan Catalysis Society Annual Symposia , May 27 , 1986 .
10. Erdogan Gulari and X. Zhou , " Periodic Operation of a CO Oxidation reactor " , ISCRE 9 , Philadelphia , May 19 , 1986 .

#### Seminars Presented at Universities:

Caltech , October 1985 .  
Carnegie Mellon , September 1985 .  
USC , February 1986 .  
UC. Davis , April 1986 .

#### Concluding Remarks

As is evident from the above publications and meeting presentations this project was very successful in terms of meeting both its scientific goals and being productive . We are

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**continuing the research we have started with this contract and will pursue the new and promising leads we have developed in indirect coal liquefaction .**

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