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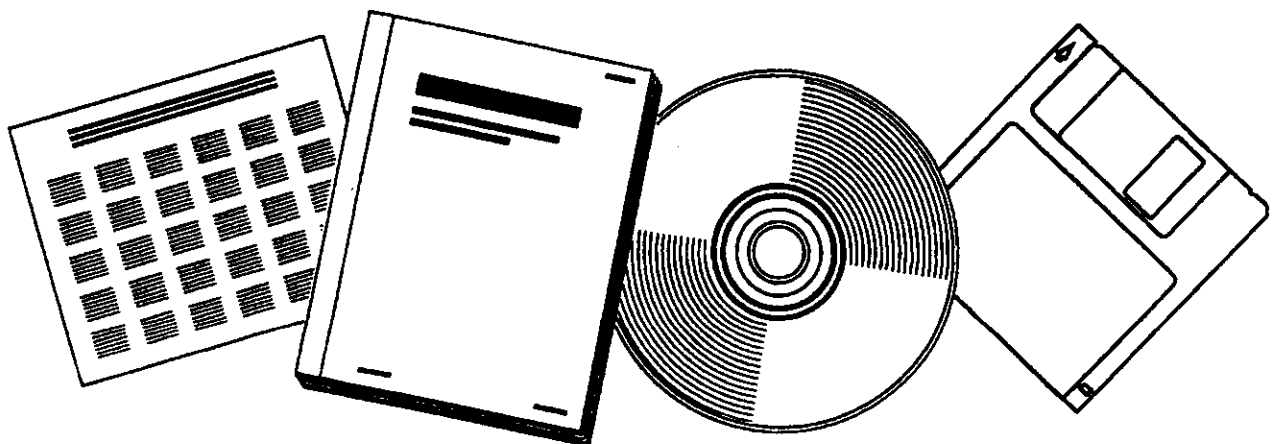
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# RATE AND SELECTIVITY ENHANCEMENT IN FISCHER TROPSCH SYNTHESIS. QUARTERLY RESEARCH REPORT

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

20 MAR 1986



U.S. DEPARTMENT OF COMMERCE  
National Technical Information Service

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DEFG 00 8690

RECEIVED BY OST APR 07 1986

March 20 , 1986

Quarterly Research Report

To

Department of Energy

University Coal Research

Pittsburgh Energy Technology Center

**MASTER**

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

DE-FG 22-84PC70785

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### Highlights of Research During This Quarter

Our research during this quarter continued to be concentrated on investigating the fundamental surface processes occurring on the alumina supported ruthenium catalysts. We were successful in measuring the product selectivities of the surface species under transient conditions. Perhaps the most important finding during this quarter was that on ruthenium the chain propagation step in Fischer-Tropsch synthesis is much faster than the initiation and termination steps. Also an important finding was that most of the surface carbon does not participate as active intermediates in the presence of chemisorbed CO.

### Details of the Research Performed During This Quarter

In order to be able to predict and understand the fundamental reasons for the changes in activity and selectivity during concentration cycling we undertook a detailed investigation of the selectivity of the surface species on ruthenium/ alumina. Our work with the ruthenium catalysts shows that there are three different kinds of surface carbon on the catalyst surface. Carbidic carbon,  $C_{\alpha}$ , carbon chains that contain hydrogen,  $C_{\beta}$ , and inactive carbon.  $C_{\alpha}$  is the most active form, followed by alkylic carbon  $C_{\beta}$  and inactive (possibly graphitic) carbon. We find that  $C_{\alpha}$  species deposited by pure CO pretreatment or pretreatment by CO and hydrogen are identical terms of activity, amount and selectivity. Perhaps the most surprising finding of this phase of the research was that even during a transient the product distribution resulting from hydrogenation of  $C_{\alpha}$  obeys the Schultz-Flory distribution extremely well. Thus chain growth process by CH insertion is either very rapid and is in equilibrium all the time or the carbon backbones on the surface already have the Schultz-Flory distribution before the hydrogenation step. This second possibility implies that there is no need for hydrogen to have chain growth. In order to decide which one of these mechanisms is the actual one we measured the  $C_1$ - $C_7$  product distribution during one complete hydrogen titration transient of the surface species. A representative transient for ethane is shown in figure 1. Combining all the transients we were able to fit Schultz-Flory Plots to the the product distribution data as a function of time during the transient. The quality of all the fits were very high ( $R = 0.99$  or better). The results are shown in figure 2. We see that the chain growth probability starts from a value very close to one and decreases to approximately 0.35. This curve is strong evidence that the chain propagation probability changes with the availability of hydrogen. At the beginning of the transient the surface is deficient in hydrogen but there is plenty of carbidic

carbon and thus the high chain growth probability. The fact that the quality of all the fits along the transient is very high proves that the chain propagation step is much faster and is in equilibrium with the initiation and termination steps.

If the Schultz-Flory distribution is established in the absence of hydrogen then the chain growth probability should not change during the transient. The large change observed is evidence that chain growth occurs only in the presence of hydrogen. This finding also supports the chain growth model with methylene insertion.

Selectivity and activity transients with  $C_{\beta}$  show that the products resulting from the hydrogenation of this surface species do not obey Schultz Flory distribution at all. An equally interesting observation was the relative contribution of  $C_{\beta}$  and  $C_{\alpha}$  to linear and branched chain hydrocarbons. Figure 3 illustrates the difference between the iso-butane and n-butane dramatically. We see that there is very little n-butane produced by hydrogenation of  $C_{\beta}$ . This figure implies that for the high molecular weight branched hydrocarbons  $C_{\beta}$  may be the major source rather than  $C_{\alpha}$ .

#### Presentations

" Transient Response Investigations of CO hydrogenation on Ru/Al<sub>2</sub>O<sub>3</sub> ." University of Southern California, February 18, 1986.

" CO Hydrogenation on Ruthenium / Alumina catalyst ", University of California Berkeley, March 14, 1986.

# C<sub>2</sub>H<sub>6</sub> Transient

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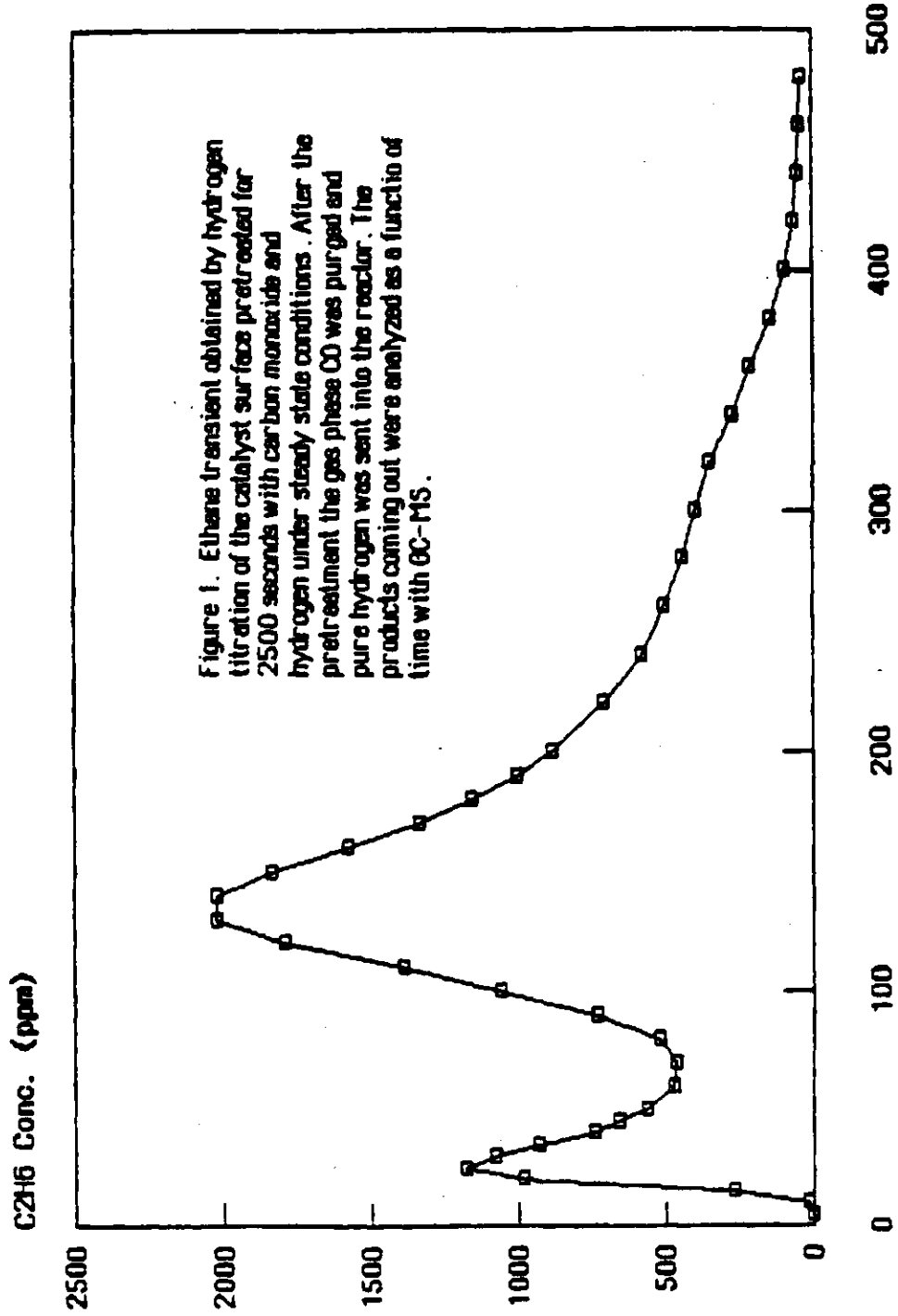
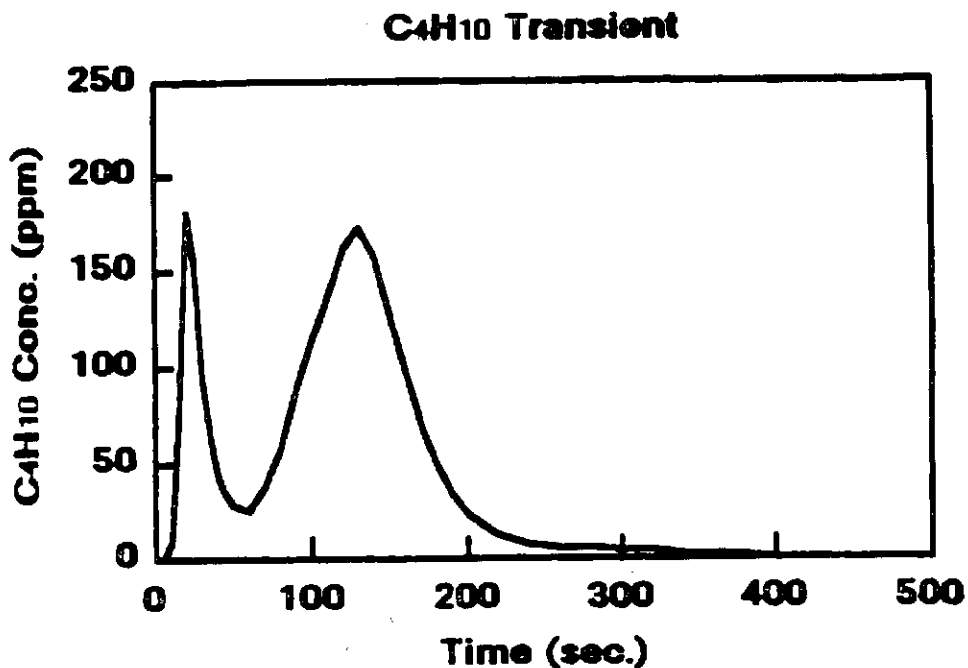
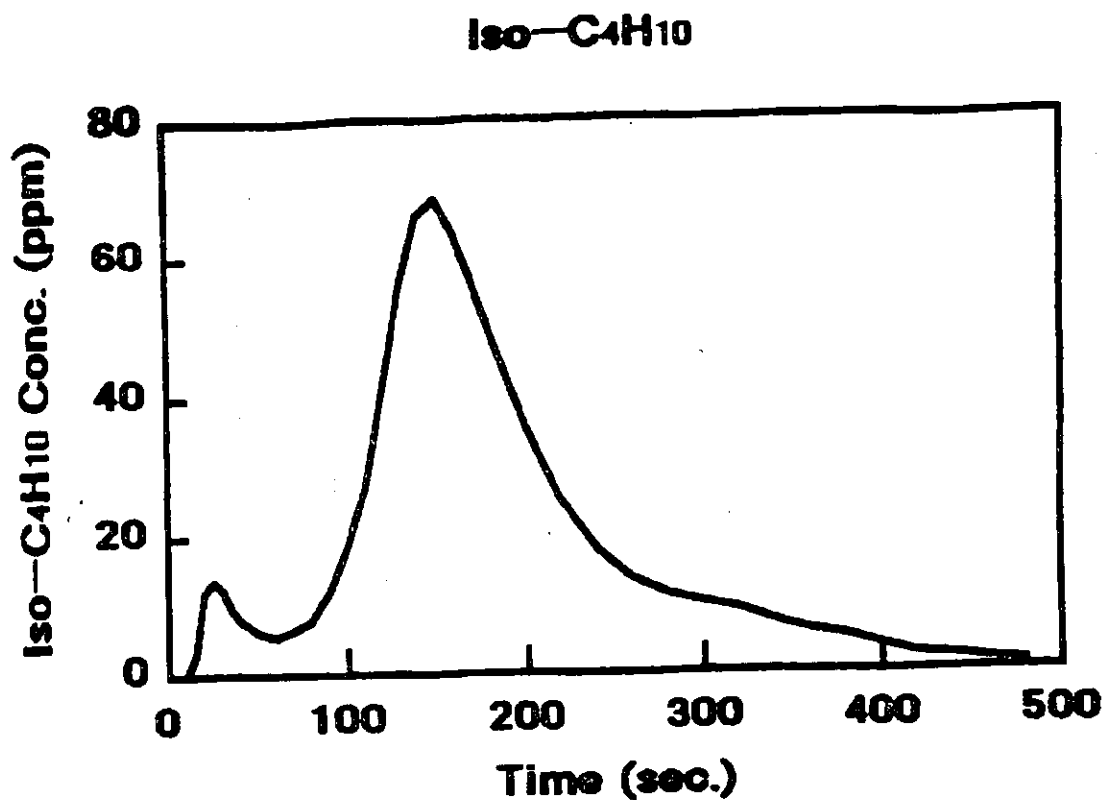


Figure 1. Ethane transient obtained by hydrogen titration of the catalyst surface pretreated for 2500 seconds with carbon monoxide and hydrogen under steady state conditions. After the pretreatment the gas phase CO was purged and pure hydrogen was sent into the reactor. The products coming out were analyzed as a function of time with GC-MS.

Time (sec.)

T=138 °C, P= atm, FR=125 ml/min

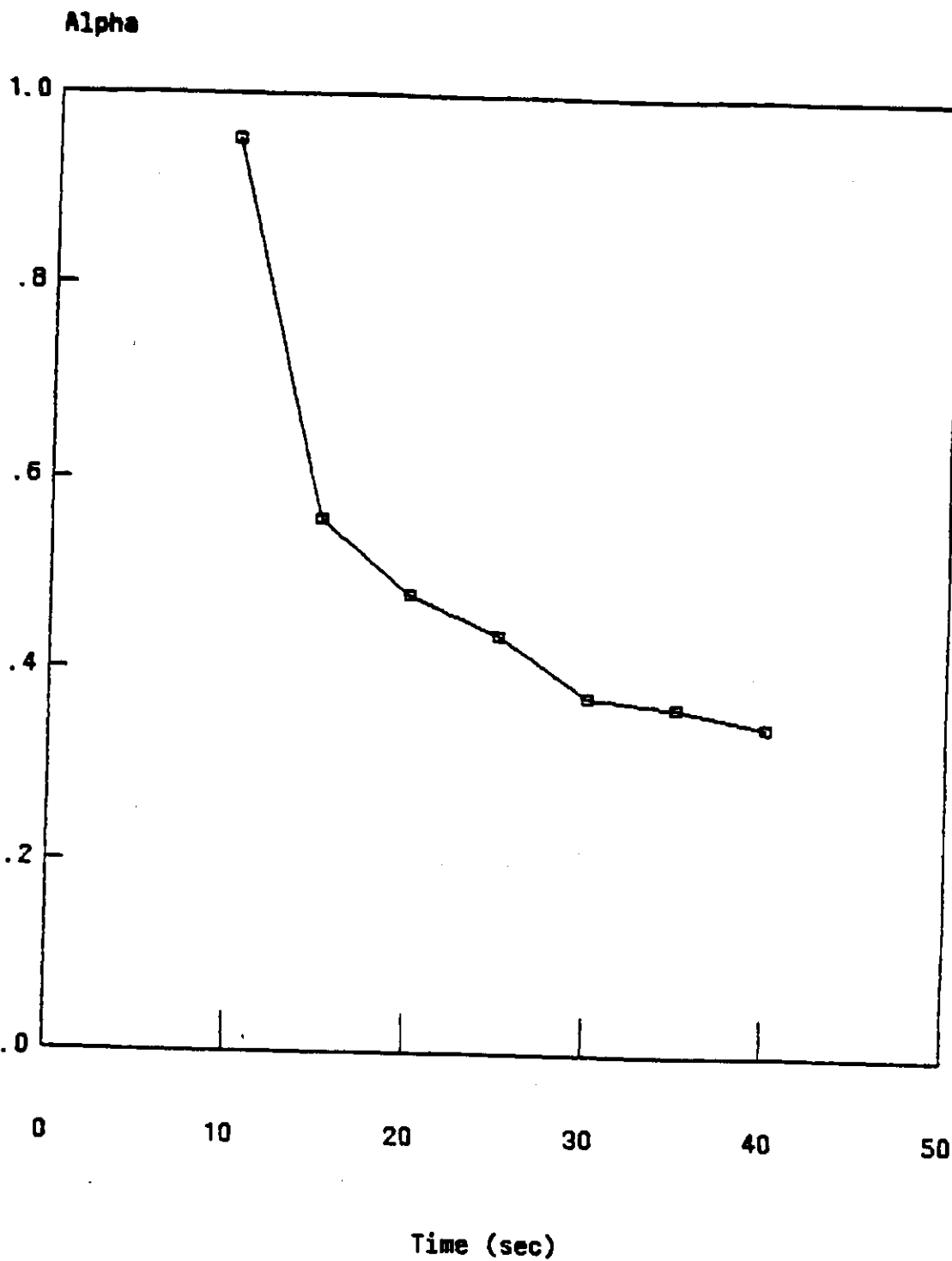


**T=138°C, P=atm, FR=125 ml/min**

**CO+H<sub>2</sub>: 2500 sec, He: 80 sec, H<sub>2</sub>: 500 sec**

Figure 2. Concentrations of iso-butane (top) and n-butane (bottom) in the product stream as a function of time during the hydrogen titration transients of surface carbon. The first peak is the active carbon C<sub>α</sub> peak and the second peak is the C<sub>β</sub> peak. Note the dramatic difference in the relative concentrations in the C<sub>α</sub> peak.

Figure 3. Chain growth probability of Schultz-Flory distributions fitted to the products during the  $C_{\alpha x}$  hydrogen titration transient. The peak in the rate of hydrocarbon production (as shown in figures 1 and 2) is reached around 17-18 seconds. The large decrease shows that the chain growth probability is a strong function of  $C_{\alpha x}$  on the catalyst surface.



T=138°C, p=atm, FR=125 ml/min