DE85017180

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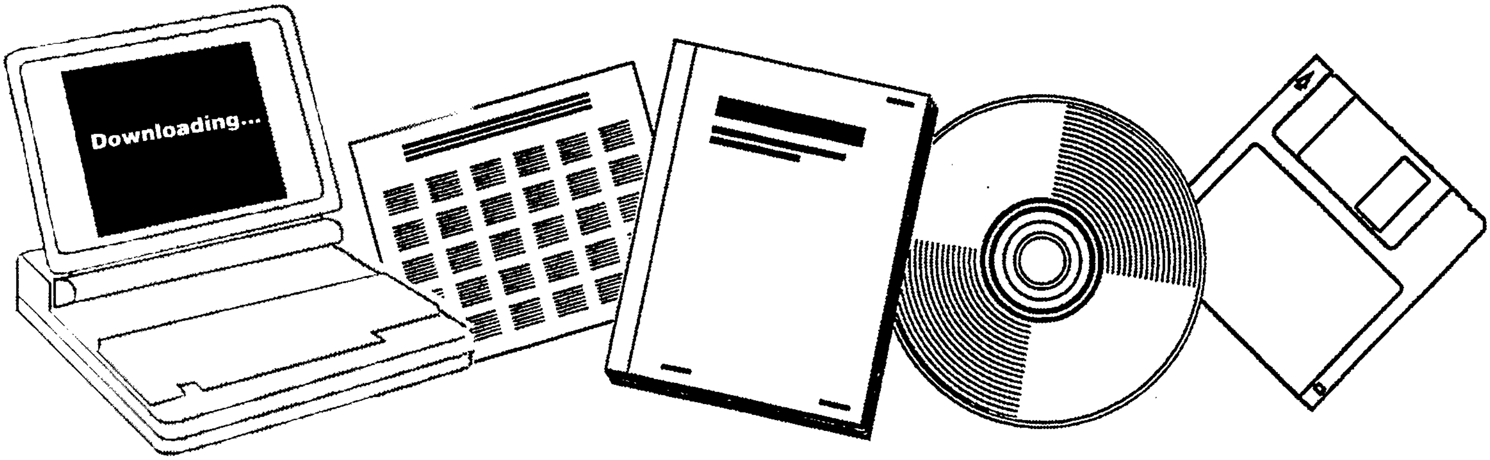

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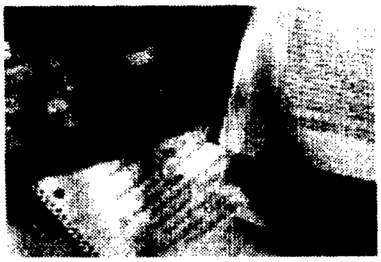

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DOE/PC/40795--T10

DE85 017180

Quarterly Progress Report
April 1 to June 30, 1982

Conversion of Low H_2/CO Ratio Synthesis Gas to Hydrocarbons

Grant No. DE-FG22-81PC40795

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ABSTRACT

The first goals of this project are: 1) to understand the influence of mass transfer on the performance of Fischer-Tropsch slurry reactors, and 2) to determine the nature of carbon formed during reaction. In reaching this second goal, knowledge of the catalyst composition will be useful.

Work during the current quarter, using both an experimental bubble column slurry reactor and a well-stirred slurry reactor has shown considerable differences in the observed partial pressure dependencies on H_2 and CO. For both types of reactor, the rate of product formation can be represented by the expression $r = kP_{CO}^{a}P_{H_2}^{b}$. The magnitude of the exponent b is close to unity in all cases. The value of a is ~ −0.4 to −0.2 for the stirred slurry reactor, but is more positive for the bubble column reactor. This suggests that the bubble column may be operating in a regime in which the mass transfer of CO has a strong influence on the rate of CO consumption.

Experimental Work and Discussion

The partial pressure dependence of the rate of the Fischer-Tropsch synthesis was measured in a differential-operated, slurry-column reactor at 250°C. The experiment proceeded as follows. After reduction for four days in 3600 NTP cm^3/min H_2 at 10 atm and 325°C, reaction was initiated with $P_{CO} = P_{H_2} = 5$ atm. After about 24 hrs., when steady state had been achieved, the partial pressures were changed. After 3 hours, the effluent gas was sampled, and the reactor was returned to its original state. After some time, the reaction rate was measured, and the partial pressures were set at new values. After three hours, the reaction rate was measured, and the catalyst was again returned to original conditions. This sequence of steps was repeated until the rate had been measured at a range of partial pressures for each reactant. The above procedure was followed to ensure that the composition of the catalyst did not change.

The activity of the catalyst (at original conditions) remained constant for 4 days, at which time the activity declined by a factor of two over the course of 36 hours. The partial pressure-rate experiments were then repeated at the lower activity.

The rate could, for both cases, be described by an expression of the form:

$$r = kP_{CO}^{a}P_{H_2}^{b} ,$$

a and b are listed in Table 1 for the two activities observed, as well as for the same catalyst under the same conditions in a stirred slurry reactor (R. Dictor, and A. T. Bell, unpublished results). a is much more positive in the bubble column slurry reactor than in the stirred slurry reactor. In addition, a is less positive when the activity of the catalyst is lower. It is possible that these trends result from mass transfer effects. If the resistance to mass transfer of CO is high, the CO concentration at the catalyst surface may become low enough to make the reaction positive order in CO. In the stirred slurry, however, the resistance due to mass transfer is low enough that the concentration at the catalyst surface is identical to that at the gas-liquid interface, and the true kinetics are measured.

The concentraton of CO at the catalyst surface can be estimated using literature values for $k_{L,CO}$ and the interfacial area, a. Using our previous estimates of $k_{L,CO} = 0.0185$ cm/s and a = 4.0 cm^{-1} (D. Stern, A. T. Bell, and H. Heinemann, submitted to Chem. Eng. Sci.), the concentration difference between the liquid-gas interface and the catalyst is estimated to be roughly 10 percent of the CO concentration at the liquid-gas interface. Clearly, the estimated concentration drop is not large enough to account for the observed kinetics. However, there is some indication that the estimated value for the interfacial area is high. Shah, et al. (AIChE J., 28, 353 (1982)) indicate that with non-Newtonian fluids, slugging can occur at conditions (column diameter, flow rate), such as used in this study. Since slurries behave as non-Newtonian fluids, these authors suggest that these results apply to slurry reactors. In our glass column, large diameter (1-2 cm) bubbles can be seen in a slurry of hexane and iron catalyst at a catalyst loading and gas flow rate comparable to those used in the steel reactor. The interfacial area of 4 cm^{-1}, which was measured in the absence of solids, corresponds to a bubble diameter of .15 cm. Thus, the interfacial area may be lower than 4 by a factor of 6.7-13.4, and the concentration of CO at the catalyst surface may indeed be low enough to explain the observed kinetics.

Table 1

Power Law Rate Parameters

	a			b		
Compound	"Active" Catalyst	"Less Active" Catalyst	Stirred Slurry	"Active Catalyst	"Less Active Catalyst	Stirred Slurry
CO_2	0.876	0.569	0.35	0.416	0.414	0.35
CH_4	0.052	−0.54	−0.4	1.03	1.03	1.1
C_4H_8	0.570	−0.141	−0.2	0.851	0.733	1.0

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* From the expression: $r = kP_{CO}^{a}P_{H_2}^{b}$

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