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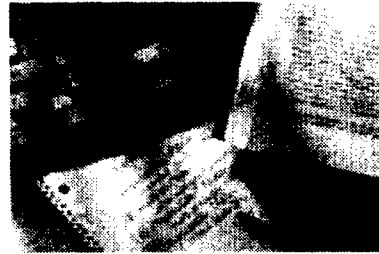
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Conversion of Low H_2/CO Ratio Synthesis

Gas to Hydrocarbons

MASTER

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ABSTRACT

The influence of the reduction procedure on free carbon formation over iron catalysts has been examined. Based on an analysis of the partial pressure dependence of the rates of hydrocarbon and carbon dioxide formation after different reduction procedures, it is suggested that as the severity of reduction conditions increases, the rate of carbon formation and the rate of the water gas shift reaction increase. The synthesis reaction rate also increases, but appears to reach an upper limit.

The kinetic rate expressions for the formation of Fischer-Tropsch products over iron were determined after following two different reduction procedures. These experiments were carried out to examine the influence of reduction procedure on the product distribution and rate of carbon formation.

Results from two experiments, referred to as Experiments 1 and 2 will be discussed. In Experiment 1, the catalyst was reduced under 10 at H_2 at 325°C for 120 hrs. In Experiment 2, the catalyst was exposed to hydrogen at 300°C and 10 atm for 24 hrs. Then, syngas was introduced, and the synthesis rate was measured. This procedure was repeated twice more. After the third reduction, the product distribution and rate of reaction were measured as a function of temperature and partial pressures.

The rate of free carbon formation can be calculated using a balance on oxygen:

$$R_{CO_2} + R_{H_2O} = R_{HC} + R_C \qquad (1)$$

where R_{CO_2} is the rate of CO_2 formation, R_{H_2O} is the rate of water production, R_{HC} is the rate at which CO is converted to hydrocarbons, and R_C is the rate of free carbon formation. If $R_C = 0$, then $R_{CO_2} + R_{H_2O} = R_{HC}$ and R_T, the rate of consumption of CO and H_2, is given by $R_T = 3R_{HC}$. R_{CO_2} can be measured directly, and R_{HC} can be estimated from measured values of alpha along with information on the rate of formation of lower hydrocarbons.

For the purpose of analyzing the data obtained in Experiments 1 and 2 it is useful to define the quantity R_d as follows:

$$R_d = R_c - R_{H_2O} - R_{HC} \tag{2}$$

R_d is the difference between the rate of carbon formation and the rate of water formation, and can be determined from measured rates of CO_2 and hydrocarbon production. The analytical system used in these experiments does not allow quantitative measurement of H_2O concentrations. If R_d is negative, R_{H_2} exceeds R_c. When the water-gas-shift (WGS) activity is low $R_{HC} = R_{H_2O}$. If, in addition, R_c is zero, R_d/R_{HC}, and $R_d = 0$. Thus, if R_d/R_{HC} is close to -1, the WGS activity is low and carbon formation does not occur. Increases in R_d/R_{HC} can result from increasing carbon formation or increasing WGS activity. If R_d is positive, R_C exceeds R_{H_2O}, and R_d is now a lower estimate of R_C.

On Schulz-Flory plots observed during Experiment 1, shown in Fig. 1, the lines that fit the higher carbon numbers do not intersect the vertical axis at $R_{c_n}/R_{CH_4} = 1$; this trend is more pronounced at low CO pressure and high H_2 pressures. Note also that alpha changes with carbon number. Figure 2 shows R_d as a function of H_2 and CO partial pressures. R_d is a strong function of CO partial pressure, and becomes negative at 1 atm. This results from the high rate of H_2O production at low CO partial pressures. However, R_d is a weak function of hydrogen partial pressure.

Table 1 shows R_{HC}, R_d, alpha, and R_{CO} after each reduction in Experiment 2. R_{CO} is the total rate of CO consumption. R_d is always negative, in sharp contrast to the values measured in Experiment 1. The second reduction produced the largest change in alpha, R_d, and R_{HC}. There was a smaller increase in alpha and R_{HC} after the third reduction, but R_d/R_{HC} increased significantly.

Figure 3 shows Schulz-Flory plots observed during Experiment 2. As in Experiment 1, the intercept at the ordinate is less than one, and the same trend with partial pressures is observed. Figure 1 shows R_d as a function of P_{CO} and F_{H_2O} after the third reduction. The dependence on CO partial pressure is similar to that observed in Experiment 1, but the H_2 dependence is drastically different. As P_{H_2O} increases, R_d decreases dramatically.

Table 2 shows values of R_d, R_{CO}, R_{HC}, and alpha at 260°C, 10 atm, with $H_2/CO = 1$ for Experiments 1 and 2. Note that although R_{HC} is roughly the same in the two experiments, Experiment 1 shows much higher values of R_{CO} and R_{CO_2}. Note also that the value of alpha is much lower in Experiment 1. Table 3 compares power law dependencies of R_{CO}, R_{CO_2}, R_{CH_4}, R_{HC}, and alpha for Experiments 1 and 2. The kinetic parameters determined at 250 °C in Experiment 1 are similar to those determined in Experiment 2 at 260 °C. The parameters determined in Experiment 1 at 206°C differ considerably from the other values listed. Table 4 lists R_d as a function of temperature at 10 atm, $H_2/CO = 1$, for Experiments 1 and 2. The activation energies are calculated to be 59 and 76 kcal/mole.

DISCUSSION

It can be hypothesized that the behavior of the y-intercept in the Schulz-Flory plots observed in both experiments results from the existence of two types of carbon: one that participates in chain growth, and one that eventually forms free carbon. The second type of carbon can be hydrogenated only to methane, while the first type of carbon can produce higher hydrocarbons.

The different H_2 dependencies of R_d seen in Experiments 1 and 2 result from differences in dependencies of R_{HC} and R_{CO_2} on P_{H_2}, as shown in Table 3. In agreement with measurements of total syngas consumption reported in many other studies, the order with respect to H_2 measured for hydrocarbons is close to unity in both experiments. However, the order with respect to H_2 for CO_2 production and CO consumption is higher in Experiment 1 at 260 °C than at 250 °C or in Experiment 2. This may be related to the WGS activity. If the WGS reaction goes to completion, and no carbon is formed, the oxygen mass balance requires that the rate of conversion of CO to hydrocarbons be matched by the rate of CO_2 production. In this case, the partial pressure dependence of R_{CO_2} and R_{HC} must be the same. Measurements of the WGS reaction rate (Bohlbro, H., "An Investigation of the Kinetics of the Conversion of Carbon Monoxide by Water Vapor over Iron oxide Based Catalysts," 2nd edition, Haldor Topsoe, 1969) show that the WGS reaction rate decreases at P_{H_2} increases. Thus, the rate of CO_2 production will exhibit a partial pressure dependence between that the synthesis reaction and that of the WGS reaction. The lower H_2 dependnce of R_{CO_2} observed in Experiment 2 indicates that the WGS activity is low.

The high activation energy for R_d results from the fact that R_d is a difference between two rates: $R_d = R_c - R_{H_2O}$. The water gas shift rate and the carbon formation rate change with T. As T increases, R_c increases and R_{H_2O} decreases. The high activation energies, then, are another indication that R_d is not a direct measure of R_c, but depends on both the carbon formation rate and the WGS reaction rate.

Although the partial pressure dependence for methane production is the same in both experiments, the order with respect to CO for hydrocarbon

production is higher in Experiment 2 and at 250°C in Experiment 1. The difference in kinetics of hydrocarbon production results from differences in the kinetics of production of higher hydrocarbons. These differences are reflected in different partial pressure dependenices of alpha. It seems that while the activity for hydrogenation of carbon in the two experiemtns is the same, the probability of chain growth (and its variation with pressure) is different.

From the preceeding discussion, it is apparent that there are three main differences between Experiment 1 and Experiment 2 . One of the differences between Experiment 1 and Experiment 2 may be the ability of the catalyst to dissociate CO. The rate of hydrocarbon formation is roughly the same in the two experiments, but R_d is positive in Experiment 1 and negative in Experiment 2. This leads us to suggest that the rate of CO dissociation is significantly higher in Experiment 1, and that the carbon that is not hydrogenated is converted to free carbon.

A second difference between the two experiments is the lower WGS activity in Experiment 2 at 260°C and at 250°C in Experiment 1. This in turn influences the partial pressure dependence of the rate of CO_2 production.

A third difference between the two experiments is the lower chain growth probability observed in Experiment 1.

CONCLUSIONS

1)   As the severity of reduction conditions increases, the tendency of the catalyst to form free carbon increases. This tendency seems to be related to the rate of CO dissociation.

2) The rate of the water gas shift reaction also increases as the severity of the reduction conditions increases.

3) Cycling between reduction and reaction increases alpha as well as the activity of the catalyst. This procedure has been used to produce a catalyst characterized by low carbon formation rates and high selectivity to higher hydrocarbons.

4) R_d, defined as the difference between the rate of carbon formation and the rate of H_2O formation, increases dramatically with temperature. This results from the fact that R_d is a difference between two rates. The activation energies measured are much higher than those reported in the literature for carbon formation over nickel catalysts.

5) Partial pressures of H_2 and CO also influence R_d. It is difficult to separate changes in the rate of carbon formation from changes in the rate of water formation. It is likely, though, that the partial pressure dependencies measured in Experiment 1 at 260°C reflect changes in the rate of carbon formation alone. In this experiment, a weak positive order dependence on P_{H_2} was observed. The dependence of R_d on P_{H_2} measured in Experiment 2 reflects the rate of the water-gas-shift reaction as well as the rate of carbon formation.

NOMENCLATURE

P_{CO} CO partial pressure, atm.

P_{H_2} H_2 partial pressure, atm.

R_C Rate of free carbon formation, moles/g-min.

R_{CH_4} Rate of methane formation, moles/g-min.

R_{CO} Rate of CO consumption, moles/g-min.

R_{CO_2} Rate of CO_2 production, moles/g-min.

R_{C_n} Rate of formation of products containing n carbon atoms, moles/g-min.

R_d $R_{CO2} - R_{hc}$ (see equation 2)

R_{HC} Rate of conversion of CO to hydrocarbons, moles CO/g-min.

R_{H_2O} Rate of water formation, moles/g-min.

Table 1

Number of Reductions	P_{H_2}	P_{CO}	R_{HC}	R_{CO}	R_d	α	$\dfrac{R_d}{R_{HC}}$
1	5.74	4.26	5.21×10^{-5}	8.28×10^{-6}	-2.14×10^{-6}	0.69	-0.41
2	5.56	4.44	2.28×10^{-5}	3.49×10^{-5}	-10.7×10^{-6}	0.73	-0.47
3	5.45	4.55	3.16×10^{-5}	5.51×10^{-5}	-8.16×10^{-6}	0.74	-0.26

Each reduction at 300°C, in 10 atm H_2, for 24 hrs.

Rates measured at 250°C

All rates are in $\dfrac{moles}{g\text{-}min}$

Table 2

Experiment	R_{HC}	R_d	R_{CO}	
1	5.93×10^{-5}	5.48×10^{-5}	2.28×10^{-4}	0.70
2	5.48×10^{-5}	-4.30×10^{-6}	1.06×10^{-4}	0.78

$T = 260°C$
$P = 10$ atm
$H_2/CO = 1.0$

Table 3

Experiment	T, °C	R_{CH_4}		R_{CO_2}		R_{CO}		R_{HC}		α	
		a	b								
1	260	-0.23	1.14	0.58	0.75	0.58	0.75	0.15	0.84	0.04	-0.05
2	260	-0.34	1.28	0.60	0.49	0.52	0.55	0.42	0.74	0.10	-0.05
3	250	-0.20	1.50	0.60	0.43	0.60	0.43	0.48	1.05	-	-

Experiment 1: 120 hrs reduction at 325°C in 10 atm H_2

Experiment 2: 3 cycles of reduction for 24 hrs at 300°C in 10 atm H_2, followed by treatment in syngas.

Table 4

T_d vs. T for Experiments 1 and 2

R_d, $\dfrac{moles}{min-g}$	T,°C	Experiment
1.96×10^{-5}	250	1
5.48×10^{-5}	260	1
-4.10×10^{-6}	250	2
2.17×10^{-6}	250	2
1.29×10^{-5}	270	2
2.91×10^{-5}	280	2

P_{CO} P_{H_2}
(atm)

5	2
5	5
2	5
1	5
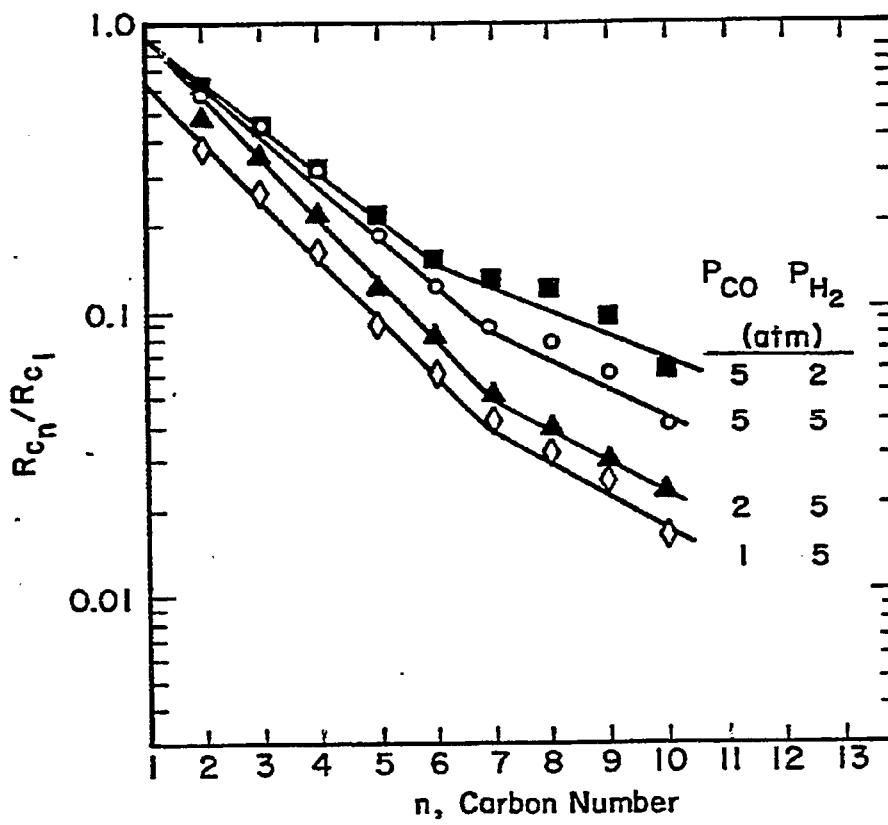
Fig. 1

R_d vs. P_{H_2}, P_{CO} in Experiment 2

T= 260° C
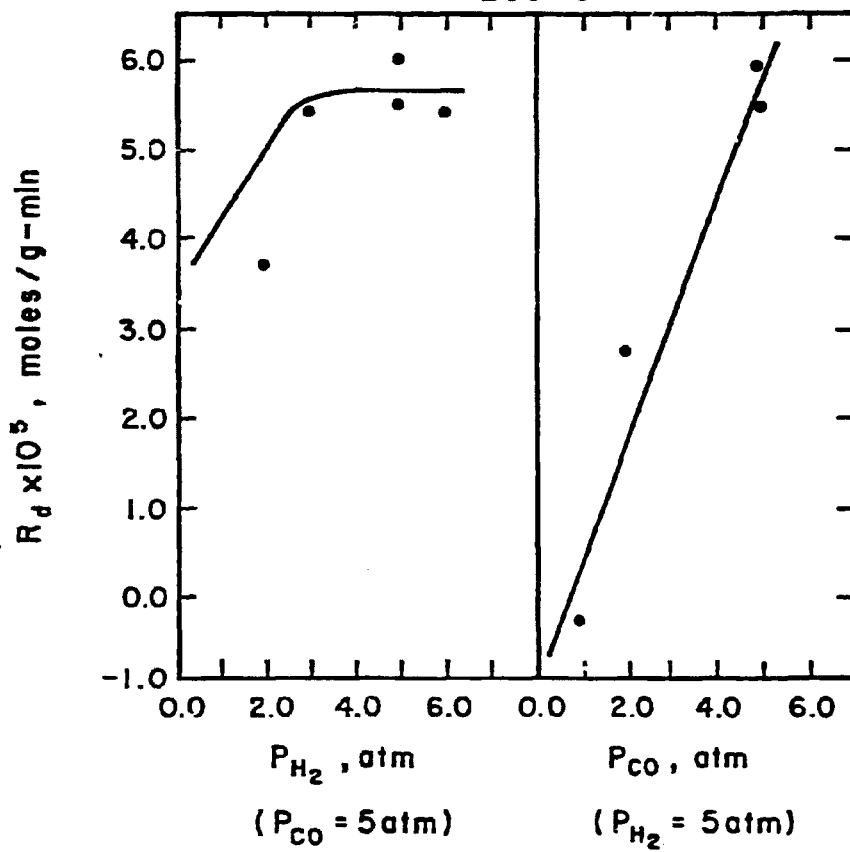
Fig. 2

R_d vs. P_{H_2} , P_{CO} in Experiment 1

T = 260° C
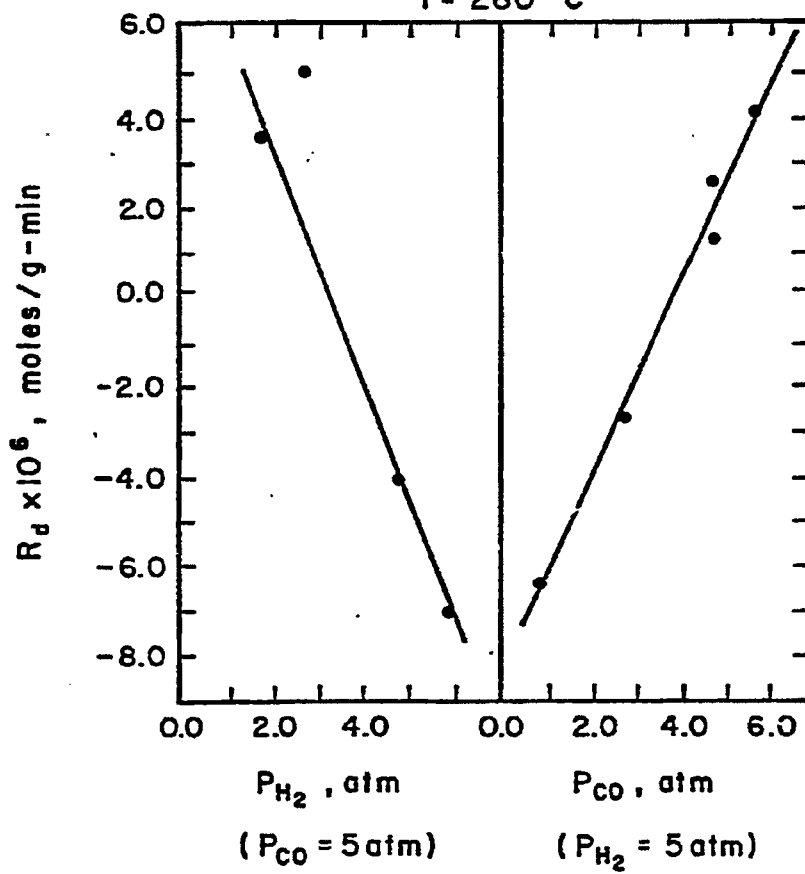
Fig. 4

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