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# Rate of the Fischer-Tropsch Reaction Over Iron Catalysts

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The rate of the Fischer-Tropsch reaction over triply promoted iron catalyst was studied in a differential reactor at 240°C, in the pressure range 10 to 20 bar with synthesis gases of $H_2/CO$ ratio varying from 1 to 7. The reaction rate was found to be first order with respect to the hydrogen partial pressure and zero order with respect to the carbon monoxide pressure. These findings are in agreement with the relative adsorption characteristics of $H_2$ and CO on reduced magnetite surfaces. Water is a primary product of the Fischer-Tropsch reaction, while $CO_2$ is a secondary product formed via the water gas shift reaction. With a gas ratio $H_2/CO$ of 1.9, the activation energy of the Fischer-Tropsch reaction was found to be 16.8 kcal/mole.

## INTRODUCTION

The kinetics of the Fischer-Tropsch reaction over iron catalysts has been the subject of a considerable number of studies and extensive reviews have been given by Anderson *et al.* (*1–3*). A linear relationship between activity and total synthesis gas pressure has been observed and equations have been proposed in which the rate was controlled by the partial pressures of $H_2$, CO, and $H_2O$ (*1*); or, at lower conversion levels, by $H_2$ alone (*4, 5*).

Previous rate studies were invariably carried out using integral reactors in which changes in gas partial pressures occurred continuously throughout the reactor bed making the interpretation of the results difficult. In the present study it was therefore decided to use a differential reactor. Furthermore, contrary to previously published work, the individual partial pressures of the reactants have been controlled, i.e., the hydrogen partial pressure was varied while keeping the carbon monoxide partial pressure fixed, and vice versa. With such a simplified approach, it was hoped to minimize ambiguities. A drawback of differential reactors is that conversion per pass is necessarily low; and hence the evaluation of activity from the contraction and tail-gas analyses is inaccurate (*6*). If in the Fischer-Tropsch reaction, however, there is a low oxygenated organic product selectivity, then the overall activity is directly related to the production of $H_2O$ and $CO_2$ according to the following reactions:

$$(2n + 1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O, \quad (1)$$

$$2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O, \quad (2)$$

$$H_2O + CO \rightarrow CO_2 + H_2. \quad (3)$$

By combining reaction (3) with reactions (1) or (2), $CO_2$, rather than $H_2O$, would appear as part of the products. From Eqs. (1)–(3), it can be seen that, for every carbon atom appearing in a hydrocarbon molecule, there is 1 mole of $H_2O$ or $CO_2$ produced. Both these products can be trapped out of the tail-gas and the reaction rate can be subsequently determined. For the above to hold, there must of course be minimal $CO_2$ produced from the Boudouard reaction:

$$2CO \rightarrow CO_2 + C. \quad (4)$$

It is normally assumed (*1*) that the $CO_2$ produced in the Fischer-Tropsch reaction comes from the water gas shift [reaction

(3)] and is therefore a secondary product. One of the objectives of the present work was also to confirm this assumption.

## Experimental Methods

### *Catalyst*

The catalyst used was fused magnetite in the form of 4 to 6 mesh spheres. The catalyst was triply promoted with $K_2O$, $Al_2O_3$ and $SiO_2$. The preparation of this type of catalyst has been described previously (7).

### *Reactor*

The reactor is schematically presented in Fig. 1. The steel reactor tube was 90 cm long and 2.5 cm i.d. It was completely surrounded by boiling Dowtherm, the temperature of which was adjusted by varying the pressure above the liquid. 420 $cm^3$ of catalyst was loaded. The temperature of the catalyst bed was read by thermocouples placed at the top, middle, and bottom of the bed. The gas entered the system through a high pressure needle valve and then passed through a high pressure wet gas meter. It entered the reactor via an electrically heated steel coil preheater. On leaving the reactor the tail-gas passed through a steam-heated (2.5 bar steam) wax receiver where wax and some water was trapped out. From there the tail-gas passed through a water-cooled condenser (ca. 20°C), a high pressure receiver maintained at 0°C, a demister (packed with steel rings), a pressure control valve, and finally a low pressure dry gas meter. The reactor was operated on a "once through" basis, no recycle being involved.

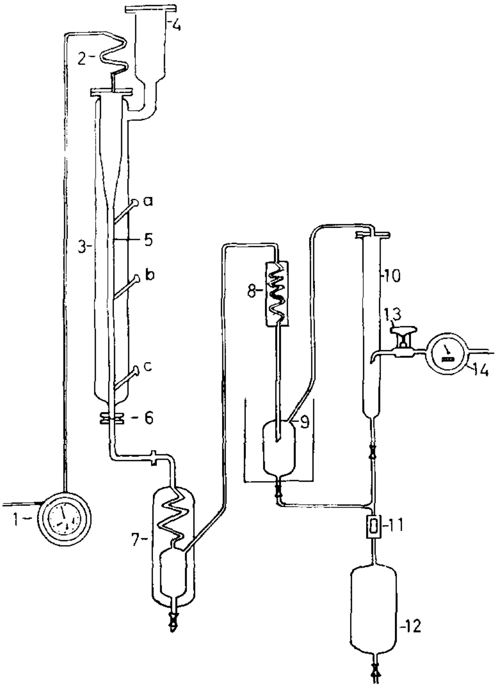

FIG. 1. Reactor: (1) fresh feed gas meter; (2) preheater; (3) Dowtherm jacket; (4) Dowtherm condenser; (5) reactor tube with thermocouples at (a, b, c); (6) stainless steel mesh support; (7) wax receiver; (8) water-cooled condenser; (9) ice-cooled receiver; (10) demister; (11) level glass; (12) low pressure receiver; (13) pressure control valve; (14) tail-gas meter.

### *Reduction and Conditioning*

Hydrogen reduction was carried out in the reactor at 17 bar, ca. 380°C and space velocity 3600 $hr^{-1}$. Full reduction was obtained after 2 days. After reduction, the catalyst was cooled down under hydrogen and the pressure dropped to 4 bar. Conditioning with synthesis gas was commenced at a pressure of 4 bar, room temperature, and space velocity of 3600 $hr^{-1}$. The temperature was increased rapidly to 180°C, then stepwise to 225°C over 2 days. The pressure was then similarily increased to 17 bar over a further 2 days. A conditioning program, as outlined, is of vital necessity if temperature runaways and free carbon formation are to be avoided.

### *Synthesis*

Two synthesis gas streams of $H_2/CO$ ratios (1.9 and 2.3) were used in the study. Both contained about 12% $CH_4$ and 0.7% $CO_2$. Gases of a higher or lower ratio were obtained by blending in $H_2$ or CO, respectively.

Each synthesis step or period was carried out over several days until the daily drainings became consistent.

### Product Analysis

Liquid hydrocarbons, chemicals and water were trapped out in the knockout pots described above. Gaseous hydrocarbons passed out of the system with the tail-gas. To determine the $CO_2$ content of the tail-gas, about 1% of the gas was continually bled off and passed through a dry gas meter, a —80°C trap (to remove water vapor), and finally an Ascarite trap which absorbed the $CO_2$. A similar system on the fresh feed enabled the production of $CO_2$ per day to be calculated from the total fresh feed and tail-gas flows.

The reaction water contained dissolved oxygenated organic products and the drainings for each period were analyzed, thus enabling the moles of $H_2O$ produced to be calculated. The organic content (mainly methanol and ethanol) of the water was typically 3.5% by weight. The amount of oxygen contained in these alcohols was only 2% of that in the water.

After the completed run (60 days) the catalyst was analyzed and the "free carbon" content (i.e., carbon other than that bound as iron carbides or present as wax) was found to be 1.1 g/100 g of Fe. Considering the length of the run, this carbon deposition was negligible; and hence the $CO_2$ produced could not have come from the Boudouard reaction [Eq. (4)].

From the above considerations pertaining to the $CO_2$ and $H_2O$ productions together with the relevant discussion in the introduction, it can be seen that the sum of the moles of $H_2O$ and $CO_2$ produced per unit time reflected the overall Fischer-Tropsch synthesis activity with satisfactory accuracy.

## RESULTS

### The Effect of Constant CO and Variable $H_2$ Partial Pressure Upon Activity

Using gas ratios of $H_2/CO$ between 1.2 and 2.3, the total pressure was adjusted to give a CO partial pressure of 5.4 bar absolute in each case. The temperature was fixed at 240°C and the space velocity was altered to give a constant contact time (i.e., a fixed linear velocity). A space velocity of 3600 $hr^{-1}$ at 17.0 bar was taken as a standard on which the flows were based. The results are given in Table 1.

TABLE 1
THE EFFECT UPON ACTIVITY OF CONSTANT CO AND VARIABLE $H_2$ PARTIAL PRESSURES AT 240°C

| Gas ratio $H_2/CO$ | Pressure (bar) | $H_2$ partial pressure (bar abs) | Produced/day (moles) $H_2O$ | $CO_2$ | $H_2O + CO_2$ |
|---|---|---|---|---|---|
| 1.2 | 12.8 | 6.6 | 15.4 | 10.8 | 26.2 |
| 1.9 | 17.0 | 10.3 | 30.6 | 12.7 | 43.3 |
| 2.3 | 19.7 | 12.3 | 38.1 | 12.6 | 50.7 |

### The Effect of Constant $H_2$ and Variable CO Partial Pressure upon Activity

Using gases of $H_2/CO$ ratios varying between 1.2 and 7.2, the total pressure was adjusted to give a constant $H_2$ partial pressure of 9.0 bar absolute. As above, a fixed linear gas velocity was maintained and the temperature was fixed at 240°C. Results are given in Table 2.

Using the results given in Table 1 and the average activity from Table 2, a graph was plotted (Fig. 2) of activity against $H_2$ partial pressure.

### The Effect of Gas Flow Rate upon the Water Gas Shift Reaction

Results of synthesis carried out at 220°C, 20 bar, with a synthesis gas ratio $H_2/CO$ of 1.9 and at different gas flows are given in Table 3.

TABLE 2
THE EFFECT UPON ACTIVITY OF CONSTANT $H_2$ AND VARIABLE CO PARTIAL PRESSURES AT 240°C

| Gas ratio $H_2/CO$ | Pressure (bar) | CO partial pressure (bar abs) | Produced/day (moles) $H_2O$ | $CO_2$ | $H_2O + CO_2$ |
|---|---|---|---|---|---|
| 1.2 | 17.8 | 7.5 | 23.8 | 14.2 | 38.0 |
| 1.9 | 15.3 | 4.8 | 26.4 | 11.7 | 38.1 |
| 2.3 | 14.3 | 3.9 | 26.8 | 11.0 | 37.8 |
| 3.4 | 11.6 | 2.5 | 30.7 | 8.8 | 39.5 |
| 7.2 | 10.5 | 1.3 | 28.8 | 9.0 | 37.8 |

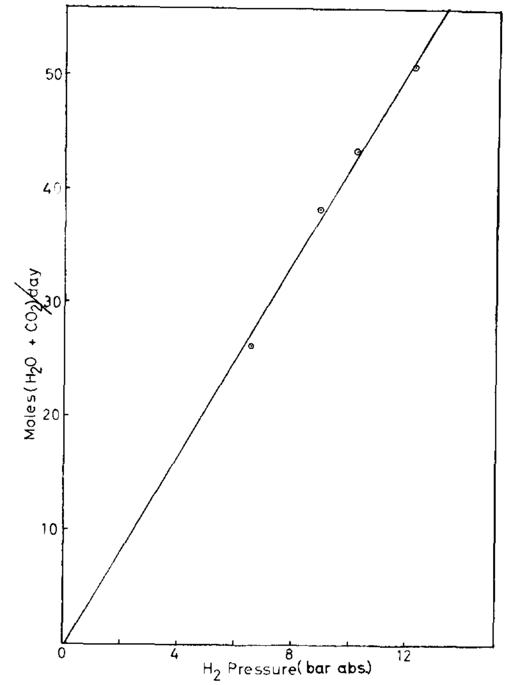

FIG. 2. Activity and hydrogen partial pressure.

### *The Effect of Temperature upon Activity*

Using 1.9 ratio $H_2/CO$ at 17.0 bar and a space velocity of 3600 $hr^{-1}$, synthesis was carried out at a series of temperatures between 225 and 265°C. In each case, a steady performance was observed over several days. The results are given in Table 4. From these results the Arrhenius plot of log[moles $(H_2O + CO_2)$/day] vs $1/T$ gave the activation energy for the Fischer-Tropsch reaction as 16.8 kcal/mole.

## DISCUSSION

TABLE 3
THE INFLUENCE OF GAS FLOW RATE

| Space velocity ($hr^{-1}$) | Produced/day (moles) $H_2O$ | $CO_2$ | $H_2O + CO_2$ |
|---|---|---|---|
| 1050 | 16.2 | 5.8 | 22.0 |
| 9690 | 21.0 | 1.2 | 22.2 |

Table 1 shows that, at a fixed carbon monoxide partial pressure, the activity increased with increasing hydrogen partial pressure. Table 2, on the contrary, shows that, when the hydrogen partial pressure was fixed, a sixfold variation in the carbon monoxide pressure had no effect on activity. The linearity of the plot of activity against hydrogen partial pressure (Fig. 2) together with the results in Table 2 clearly show that under differential conditions the rate of synthesis is first order with respect to the hydrogen partial pressure and zero order with respect to carbon monoxide, i.e.,

$$\text{rate} = Kp_{H_2}, \qquad (5)$$

where $p_{H_2}$ is the partial pressure of hydrogen and $K$ is a constant.

Previous work carried out in this laboratory (*8*) showed that the strength of CO adsorption, as reflected by the heat of adsorption, was stronger than that of hydrogen adsorption on iron. Furthermore, when CO was preadsorbed on the iron surface, no measurable amount of hydrogen could be subsequently adsorbed. These results are readily compatible with the present findings. Under synthesis conditions, the overriding majority of adsorption sites are probably occupied by carbon

TABLE 4
THE EFFECT OF TEMPERATURE UPON ACTIVITY

| Temp (°C) | Produced/day (moles) |  |  | $CO_2/H_2O$ ratio at the reactor exit |  |
|---|---|---|---|---|---|
|  | $H_2O$ | $CO_2$ | $H_2O + CO_2$ | Actual | Equilibrium |
| 225 | 21.9 | 7.0 | 28.9 | 0.78 | 72 |
| 235 | 29.9 | 12.2 | 42.1 | 0.75 | 59 |
| 245 | 35.1 | 18.6 | 53.7 | 0.82 | 49 |
| 255 | 42.6 | 31.5 | 74.1 | 0.98 | 42 |
| 265 | 52.1 | 49.7 | 101.8 | 1.15 | 35 |

monoxide (i.e., surface saturation) thus explaining why the rate of synthesis is zero order with respect to the carbon monoxide partial pressure in the gas phase. If the synthesis mechanism involves the reaction of adsorbed hydrogen with the adsorbed CO then the first order dependence on hydrogen pressure could mean that either the adsorption of hydrogen or the reaction of adsorbed hydrogen molecules with the CO is the rate-controlling step. Alternatively, if an unadsorbed hydrogen molecule is capable of reacting directly with an adsorbed CO molecule then the dependence of the rate on the hydrogen pressure is equally understandable. At present, there is no way of distinguishing between the above-mentioned three possibilities.

Previous findings have shown that alkali increases the heat of adsorption of carbon monoxide and lowers the heat of hydrogen chemisorption (*8*); and hence presumably lowers the amount of hydrogen capable of being adsorbed in the presence of carbon monoxide. This deduction, coupled with the observed first order dependence of synthesis rate on hydrogen partial pressure, might lead to the conclusion that alkali promotion could result in a decrease in activity. It is, however, well established that alkali enhances the rate of synthesis over iron catalysts (*2*, *3*). This conflict need only be an apparent one, however. It has been postulated (*8*) that alkali strengthens the iron–carbon bond and weakens the carbon–oxygen bond in the adsorbed CO molecule thereby making the latter bond more prone to attack by hydrogen. Similar conclusions have been drawn from infrared studies of CO adsorbed on alkali-promoted nickel and cobalt (*9*). As long as the effect of the weakening of the carbon–oxygen bond overrides the lowering of the amount of hydrogen chemisorbed, the overall effect of alkali will be to enhance the reaction rate. If, of course, hydrogen from the gas phase or from the van der Waals layer is capable of reacting directly with chemisorbed CO, then there is no conflict in effects.

The finding that the rate of synthesis is first order with respect to the hydrogen partial pressure and zero order with respect to the carbon monoxide partial pressure is only applicable under the conditions used in the present study. Under circumstances in which the system is not differential, due either to low space velocities, high conversions or extreme gas ratios, the carbon monoxide partial pressure may drop to a level where its concentration also becomes rate determining. In such cases a CO partial pressure term would enter into the rate equation. Studies carried out in this laboratory (*10*) with integral reactors have confirmed Anderson and coworkers' (*1*) findings that water vapor depresses the rate of reaction.

As mentioned in the introduction, $CO_2$ is usually assumed to be a secondary product and the present results support this. Table 3 shows that, while a ninefold increase in gas flow rate had no effect on overall activity (moles of $H_2O + CO_2$ produced), the relative amount of $CO_2$ to $H_2O$ decreased with increasing flow rate. As a higher flow rate must if anything give a lower average residence time, then an increase in flow rate must bring about an increase in the ratio of primary to secondary products. The lowered $CO_2$ production fits the concept that it is the product of a secondary reaction. Table 4 shows that, with increasing temperature, the amount of $CO_2$ produced increased much more rapidly than did the $H_2O$ produced. In all cases, the ratio $CO_2/H_2O$ was much lower than could be expected from the value of the water gas shift equilibrium constant (see last two columns of Table 4). In the studied temperature range, therefore, the rate of the shift reaction was relatively slow. In reactors operating above 300°C, the shift reaction is at equilibrium (*10*). The low values of the $CO_2/H_2O$ ratios obtained in the present study can only mean that $H_2O$ must be the predominant primary product rather than $CO_2$.

## ACKNOWLEDGMENT

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