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Factors Influencing the Formation of Carbon on Iron Fischer-Tropsch Catalysts

II. The Effect of Temperature and of Gases and Vapors Present During Fischer-Tropsch Synthesis

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The influence of small amounts of different gases or vapors on the rate of carbon monoxide decomposition to carbon over an iron carbide catalyst was studied. Hydrocarbons, both saturated and unsaturated, had no effect on the rate. Hydrogen, water, acetic acid, ethyl alcohol, and methyl ethyl ketone enhanced the rate of the Boudouard reaction. In all cases in which enhancement occurred molecular hydrogen was shown to be present within the catalyst bed. It is postulated that the hydrogen enhanced the strength of adsorption of carbon monoxide thereby increasing its rate of decomposition. While ammonia acted as a poison for the Boudouard reaction, molecular nitrogen was found to have no effect. The activation energy of the reaction over the temperature range 285 to 338°C was 27 kcal/mole.

INTRODUCTION

During Fischer-Tropsch synthesis over iron catalysts it is important to minimize the formation of carbon as this leads to swelling of the catalyst particles. The effect of promoters on the Boudouard reaction over iron catalysts has been described in part I of this series (*1*). In this paper, part II, the influence of various gases and vapors which are normally in contact with the catalyst during Fischer-Tropsch synthesis are considered.

Berry, Ames, and Snow (*2*) working at temperatures between 400 and 760°C showed that the addition of 3% water vapor increased the formation of free carbon, from the decomposition of carbon monoxide, on ferric oxide. The further addition of 4% hydrogen again increased free carbon formation while the addition of small amounts of ammonia or hydrogen sulfide inhibited the decomposition. Meroc and Boullé (*3*) also found that water vapor had an effect on free carbon formation on iron catalysts.

As hydrogen and nitrogen (and hence possibly ammonia) as well as water vapor are present during Fischer-Tropsch synthesis it was of interest to re-investigate the influence of these gases on the Boudouard reaction over promoted iron catalysts, as well as to extend the investigations to the other gases also present in the reactors, e.g., hydrocarbons, alcohols, acids, etc.

As several of the possible side reactions of the gaseous additives were exothermic and conceivably could therefore raise the temperature of the catalyst bed, it was considered desirable to study the influence of temperature on the rate of the Boudouard reaction over the catalyst used in these studies. Cohn *et al.* (*4*) working on Hägg carbide, which was doubly promoted with 0.56 g Cu and 0.18 g K_2CO_3/100 g Fe, found the activation energy for free carbon deposition to be 23.5 kcal/mol. However, this cannot be looked upon as an absolute value for the reaction because as Rozovskii and Savel'ev (*5*) have shown the activation energy is dependent upon the alkali promoter.

EXPERIMENTAL

The catalyst used throughout this work was a sample of doubly promoted fused magnetite. The K_2O content was ca 0.5 g/100 g Fe. For the fixed bed runs the hydrogen reduction and Boudouard reaction procedure was as is described in part I (*1*) except where otherwise stated. In some runs the catalyst bed was kept in circulation (i.e., partially fluidized) by using a 17 mm pyrex reactor tube with a sintered glass disc in the center acting as bed support and gas distributor. Gas was passed in at the bottom of the reactor tubes and by using 12 g of magnetite and a carbon monoxide flow of 400 ml/min the catalyst bed was kept in motion. Reduction was carried out for twenty hours at 400°C using a hydrogen flow of 400 ml/min.

Vapors of ethyl alcohol, acetic acid, propionic acid, methyl ethyl ketone, and water were added to the carbon monoxide stream, respectively, by passing the gas through U-tubes containing silica gel saturated with the particular liquid. Different amounts of vapor were added to samples in the same run by maintaining the U-tubes at different temperatures. The gases ethylene, hydrogen, and nitrogen were either bled directly into the carbon monoxide stream or else cylinders of the appropriate gas mixtures were made up. Traces of ammonia were added by passing the carbon monoxide over ammonium carbonate, the carbon dioxide which was also released being removed by ascarite before the gas entered the reactor tubes. *n*-octane, 1-octene, *n*-decane, and 1-decene were pumped over the sample using a micropump at 1 ml/hr.

Dry ice traps were placed between the exit of the reactor tubes and the ascarite traps hence stopping contamination of the latter with water or organic vapors. Frequent checks of the free carbon content of the catalysts were made by chemical analysis of the latter and the results were always in good agreement with those obtained by weighing the carbon dioxide evolved. The actual weight gain of the reaction tubes, which corresponded to the amount of carbon deposited, was also in good agreement with the values obtained from the evolved CO_2.

Unless otherwise stated, the Boudouard reaction was studied at a catalyst bed temperature of 325°C.

RESULTS

The Effect of Temperature

Several runs were carried out at catalyst bed temperatures between 285 and 338°C. There was almost a ten-fold difference in rate of carbon deposition between these temperatures and an Arrhenius plot (Fig. 1) gave an activation energy of 27 kcal/mol for the sample used.

The Effect of CO Flow Rate

To investigate whether fluctuations in the flow rate had any effect on the rate of carbon deposition the flow was deliberately varied between 25 and 100 ml/min per 5 g sample. No change in the rate of deposition was observed. In the fluidized bed experiments with a flow equivalent to 167 ml/min per 5 g sample the rate of deposition was also the same as for the above runs.

As the CO flow rate, and hence the linear velocity through the catalyst bed, varied by a factor of ca seven without influencing the rate of the Boudouard reaction it is presumed that the removal of the heat of reaction from the catalyst bed was not a controlling parameter in these experiments.

The Effect of Ethylene and Other Hydrocarbons

It is well known that in the catalytic hydrogenation of ethylene, ethylene acts as an autopoisoning agent (*6*, *7*, *8*, *9*). In view of the fact that large amounts of ethylene are present during Fischer-Tropsch synthesis, it was of interest to see whether ethylene had any effect on the rate of the Boudouard reaction.

The catalyst was exposed to ethylene in

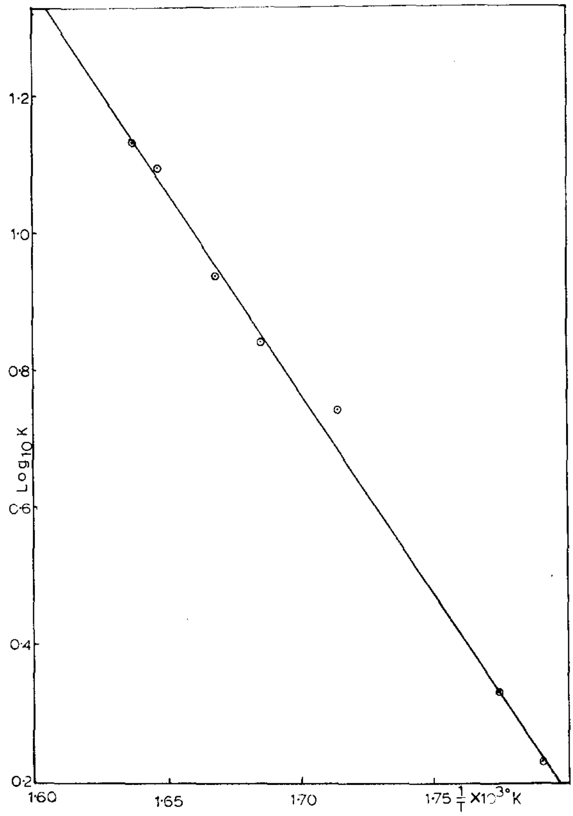

FIG. 1. Arrhenius equation plot for the Boudouard reaction.

three different ways. Firstly, pure ethylene was passed over the catalyst at 325°C after the formation of Hägg carbide and before the deposition of free carbon. Secondly, the deposition reaction was stopped midway through and pure ethylene was passed over the catalyst for two hours and, lastly, ethylene (2% and 5%) was constantly bled into the carbon monoxide stream. In all these cases ethylene was found to have no effect whatsoever on the rate of carbon formation. Similarly the addition of the hydrocarbons *n*-octane, 1-octene, *n*-decane and 1-decene to the CO gas stream had no effect on the rate of the Boudouard reaction.

The Effect of Water Vapor and Hydrogen

The percentage water vapor added to the carbon monoxide stream varied from 0.5 to 4.1%. As the water gas shift reaction occurs rapidly at 325°C over the catalyst used in this work allowance was made for the carbon dioxide liberated in this reaction. A summary of these runs along with those in which hydrogen was added is given in Table 1. From the table it can be seen that in the fixed bed runs, although the amount of water vapor added varied by as much as a factor of six, the effect in all cases was much the same in that carbon formation was increased ca 1.4-fold. In the fluidized runs, while the blanks were the same as in the fixed bed, the effect of water vapor was more pronounced to give an average increase for several runs of 2.4 times the blank (Fig. 2). As was the case in the fixed bed runs an increase in the percentage of water in the CO had little if any additional effect.

In fixed bed runs the effect of adding hydrogen was much the same as the effect of adding water vapor in that free carbon formation was increased by a factor of ca 1.3 irrespective of the amount of H_2 added. From run 4 Table 1 it can also be seen that the increase in the rate of carbon formation

TABLE 1
THE EFFECT OF WATER VAPOR AND HYDROGEN ON CARBON FORMATION

Run	Catalyst bed	Length of run (hr)	% Vapor or gas added	Rate of carbon formation (mgC/gFe/hr)
1	Fixed	20	Zero	9.2
			0.7 H_2O	12.8
			1.5 H_2O	13.8
			3.1 H_2O	13.2
2	Fixed	20	Zero	9.8
			0.5 H_2O	12.7
			1.5 H_2O	13.5
			2.7 H_2O	13.3
3	Fixed	16	Zero	7.7
			2.0 H_2	10.1
			7.0 H_2	9.5
			Zero	7.7
4	Fixed	14	Zero	9.4
			4.1 H_2O	12.9
			6.0 H_2	13.7
			3.5 H_2O + 6.0 H_2	13.9
5	Fluidised	30	Zero	9.9
			2.9 H_2O	22.9
6	Fluidised	27	Zero	9.6
			4.4 H_2	16.7

is very much the same no matter whether hydrogen and water vapor are added separately or together. From run 6 Table 1 it is seen that once again with a fluidized run, while the blank was the same as in fixed bed runs, the increase due to hydrogen is greater (the increase being a factor of 1.7 as against 1.3 for the fixed bed runs). The increase was, however, less than in the cases in which water was added (run 5). The influence of hydrogen in the fluidized bed is depicted in Fig. 3.

The Effect of Oxygenates

The influence of three different oxygenates namely acetic acid, ethyl alcohol and methyl ethyl ketone on the rate of the Boudouard reaction was investigated. The results are summarized in Table 2. In both runs 1 and 2 it was found that addition of the oxygenates enhanced the rate of the carbon deposition. Furthermore, even though different amounts of oxygenates were passed over the catalyst samples, the measured increase in the rate of carbon deposition was much the same for the different oxygenates in each run. In run 2 the exhaust gas was analyzed by mass spectrometry and in the case of the oxygenate additions hydrogen was found to be present as is shown in Table 2.

Gas chromatographic analysis were carried out on the liquid products trapped out in the —80°C traps immediately after the reactor vessels. In the case of the acetic acid runs the liquid product contained no acetic acid but only acetone. All the acetic acid was hence converted, the main reaction apparently being the decarboxylation of the acid to acetone. In support of this it was found that when allowance was made for the CO_2 evolved in the above decarboxylation reaction the balance of the CO_2 trapped by the ascarite corresponded exactly to the weight gain of the catalyst sample. In the rate data pertaining to the acetic acid runs in Table 2, allowance has in fact been made for this additional evolution of CO_2. The fact that iron acts as a catalyst for the decomposition of fatty acids to ketones has been known for many years (*10*). The fact that hydrogen and

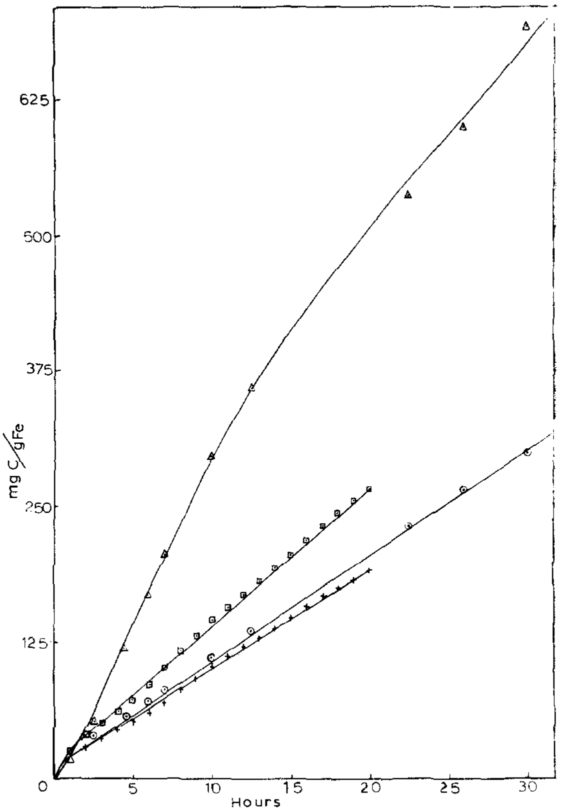

FIG. 2. The effect of water vapor on the Boudouard reaction. ⊙ Fluidized bed blank; △ Fluidized bed with 2.9% water vapor added; + Fixed bed blank; ⊡ Fixed bed with 2.9% water vapor added.

methane were also detected in the exhaust gas indicates that further decomposition reactions were also taking place. A more detailed investigation of the reactions of acetic and other organic acids and oxygenates over promoted iron catalysts is at present under way in this laboratory. Preliminary results have indicated that both propionic and butyric acids (as well as acetic) are converted to the relevant ketones over fused iron catalysts.

In the case of the ethyl alcohol run the liquid product was found to contain both ethyl alcohol and acetaldehyde.

The Effect of Ammonia

When traces of ammonia were added to the CO gas stream (0.25 to 0.5%) the

TABLE 2

THE EFFECT OF OXYGENATES ON CARBON FORMATION

Run	Length of run (hr)	% Vapor added to CO	% H_2 in Exhaust gas	Rate of carbon formation (mgC/gFe/h)
1	18	Zero		11.3
		2.5 CH_3COOH		13.2
		6.4 C_2H_5OH		12.9
		11 $C_2H_5COCH_3$		13.2
2	22	Zero	0.0	10.6
		4.4 CH_3COOH	1.8	18.4
		9.7 C_2H_5OH	1.0	18.5

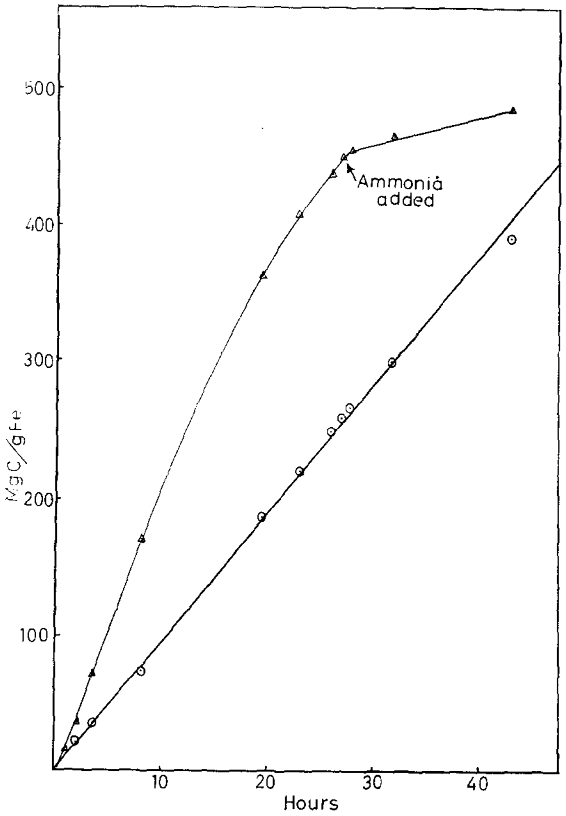

FIG. 3. The effect of hydrogen and ammonia on the Boudouard reaction. ⊙ Fluidized bed blank; ⊡ Fluidized bed with 4.4% hydrogen added (and after 27 hr traces of ammonia also added).

Boudouard reaction was immediately affected and became almost completely inhibited after a few hours. Even in a fluidized run in which hydrogen was also present the decomposition of carbon monoxide was virtually stopped (see Figure 3). Upon removing the source of ammonia and then continuing with pure carbon monoxide, the Boudouard reaction slowly recovered showing that ammonia is a reversible poison for the reaction.

The Effect of Nitrogen

Carbon monoxide is known to be a poison in the synthesis of ammonia over iron catalysts and it was therefore of interest to ascertain if the reverse was true in that nitrogen was a poison for carbon monoxide adsorption and decomposition.

Mixtures of 1:1 nitrogen and carbon monoxide deposited carbon at the same rate as pure carbon monoxide showing that in no way does nitrogen hinder the Boudouard reaction.

DISCUSSION

From the results obtained it appears that the presence of hydrocarbons, whether saturated or unsaturated have no effect on the rate of decomposition of CO to carbon over promoted iron carbide. Water vapor, small amount of hydrogen and aliphatic acids, alcohols and ketones, however, all enhanced the reaction rate. In some cases, in particular when water vapor was present, the bed temperature was observed to be one or two degrees higher than the sample through which pure CO only was flowing. The reaction of H_2O with CO to give H_2 and CO_2, which occurs rapidly under the present experimental conditions, is exothermic and it was considered possible that the observed increase in the rate of the Boudouard reaction was simply due to the higher bed temperature. From the direct determination of the influence of temperature on reaction rate (reported on in the "Results" section) the expected increase in rate as a result of the observed higher bed temperatures were calculated. It was found, however, that this was not sufficient to account for the observed rises in reaction rate. Furthermore, as already mentioned, the fact that the linear velocity of the CO through the catalyst bed had no influence on reaction rate indicated that dissipation of heat within the catalyst bed was not a relevant factor in these studies. It was therefore concluded that the observed enhancement was due to some chemical interaction of the gaseous additives with the catalyst. It is significant that in all cases in which the rate of carbon deposition was enhanced molecular hydrogen was present within the catalyst bed (due either to its direct introduction as such or to its formation as a result of reaction of the gaseous additives). Hydrogen is capable of enhancing the rate by the creation of more reaction sites, or of more active sites or could result in some form of mutual enhancement of adsorption. Mutual enhancement in adsorption has been proposed by several workers in systems in which hydrogen is present (*11*, *12*, *13*, *14*, *15*). In a recent publication by this laboratory (*16*), it was postulated that when CO adsorbs on iron catalysts it tends to withdraw electrons from the surface. Contrary to this hydrogen on adsorption tends to donate electrons to the iron surface. Such an electron enrichment of the iron adsorption sites would strengthen the metal to carbon bond and subsequently weaken the carbon to oxygen bond of the adsorbed carbon monoxide (*16*) thus enhancing the rate at which the latter bond is broken, *i.e.*, enhancing the rate of carbon formation from CO. An alternative explanation is that hydrogen reduces the surface iron carbide to metallic iron in which chemical state it is a more active catalyst for carbon monoxide decomposition.

The finding (in parallel runs) that the enhancement effect of water or of hydrogen was apparently independent of the amount of these gases added to the CO is of interest, but no satisfactory explanation of this observation can be offered unless it is assumed that there are only a small limited number of sites which are capable of responding to activation by the hydrogen. The concept that in catalysis only a small fraction of the surface sites are actually active in synthesis is an old one. It is also not clear why the influence of water and of hydrogen was greater in fluidized beds than in fixed beds (see Table 1).

Ammonia was shown to be an effective, but temporary, poison while nitrogen had no effect on the Boudouard reaction. The fact that ammonia did act as a poison implies that it must have adsorbed fairly strongly on the active sites. It is not known in which form the poison is present, whether as adsorbed N-H radicals or atomic nitrogen. The fact that molecular nitrogen had no effect shows that as such it is not capable of competing with the carbon monoxide for the active adsorption sites.

An interesting feature of this work, although not particularly concerned with carbon formation, is that in the decomposition of fatty acids the main and indeed the only non-gaseous product is the corresponding ketone. This suggests the possibility that in Fischer-Tropsch synthesis ketones are secondary products resulting from the decomposition of fatty acids. In view of this it is perhaps of significance that in Fischer-Tropsch synthesis the ratio of acetic acid to propionic acid produced is about the same as that of acetone to methyl ethyl ketone (*17*).

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