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Catalytic Synthesis of Hydrocarbons from Carbon Monoxide and Hydrogen on Lamellar Compound of Graphite Intercalated by Ferric Chloride

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From the thermal gravimetric studies of a lamellar compound of graphite (LCG) intercalated by ferric chloride, it was shown that $FeCl_3$ in the intercalated layers was reduced to $FeCl_2$ and partly to metallic Fe in flowing H_2 at 400°C: The main constituent in the LCG treated in H_2 for 1 hr was $FeCl_2$, and with an increasing period of H_2 treatment some part of the $FeCl_2$ was further reduced to metallic Fe between the graphite layers. The catalytic activity and selectivity of the reduced LCG for hydrocarbon synthesis from CO and H_2 were investigated at 300 to 500°C and 1 to 20 atm. The catalytic activity of the LCG increased with increasing degree of reduction of the $FeCl_2$, suggesting that the activity is attributed to metallic Fe. The main reaction products were C_1–C_4 hydrocarbons and the formation of higher hydrocarbons or organic oxygenated compounds was negligible. The LCG catalyst gave hydrocarbons in outstandingly high selectivity (more than 90% at 400°C) compared with an Fe catalyst merely supported on graphite which gave considerable amount of CO_2 with hydrocarbons.

INTRODUCTION

It is well known that iron is one of the most active catalysts for the Fischer–Tropsch synthesis. Although the Fischer–Tropsch synthesis means the production of gasoline in the narrow sense, this reaction exhibits many possibilities: production of methane, paraffin wax, other chemicals such as olefins, or oxygenated compounds. The purpose of the present study was focused on the production of C_1–C_4 hydrocarbons, e.g., ethylene or propylene. It is economically attractive to produce selectively short-chained olefins as organic raw materials directly from carbon monoxide and hydrogen. In our previous study (*1*) on the hydrogenation of carbon monoxide on supported iron catalysts, it was found that the catalytic properties of iron were significantly altered by the kind of support dispersing the Fe and that graphite gave the most selective catalyst for our purpose. The present study was intended to investigate the catalytic properties of Fe located between the graphite layers. For this aim, a lamellar compound of graphite (LCG) with ferric chloride was used after reduction.

The catalytic synthesis of hydrocarbons from carbon monoxide and hydrogen over LCG catalysts was studied by Ichikawa *et al.* (*2*) and Mashinskii *et al.* (*3*) who described that the addition of an alkali metal was necessary to activate the LCG with transition metal chlorides. Ichikawa *et al.* explained the role of the alkali metal through the formation of an electron donor–acceptor complex. On the other

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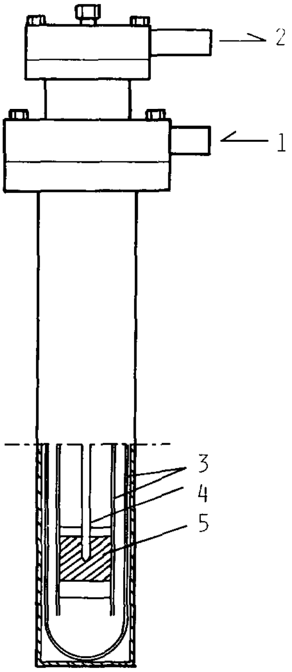

FIG. 1. Reactor: 1, inlet; 2, outlet; 3, Pyrex glass tube; 4, thermocouple well; 5, catalyst bed.

hand, Mashinskii *et al.* showed that alkali metal was required to reduce the metal chloride to metal. It will be shown in the present study that the LCG containing metallic Fe can be prepared by the reduction of the LCG with ferric chloride in flowing hydrogen at 400°C. Furthermore, the catalytic properties of the reduced LCG will be described.

EXPERIMENTAL

Materials. The LCG with $FeCl_3$ was prepared according to the method of Croft (*4*): A mixture of weighed amounts of anhydrous ferric chloride and dried graphite was placed in a sealed Pyrex tube which was evacuated at room temperature, subsequently heated to 300°C, and held at that temperature for 4 hr. When the reaction was completed, the resulted compound was washed with a 5 *N* aqueous solution of hydrochloric acid and pure water to free excess $FeCl_3$. The amount of unreacted $FeCl_3$ was determined by titrating the filtrate with a standard solution of potassium dichromate. The LCG thus obtained was dried overnight at 110°C and stored in a desiccator. The graphite used was a pulverized natural graphite designated as "Spectroscopic Powder" which was supplied by Union Carbide Corp. Prior to use as catalyst, the LCG was pretreated in flowing hydrogen at 400°C and subsequently washed with a 5 *N* aqueous solution of hydrochloric acid in order to remove α-Fe which deposited on the catalyst surface through the reduction of $FeCl_3$ eluted from graphite layers during the pretreatment. The LCG catalyst obtained contained 13% of Fe by weight. A graphite-supported Fe catalyst was prepared by impregnating the graphite with an aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$. The catalyst was calcined at 350°C for 2 hr and reduced in flowing hydrogen at 400°C for 4 hr.

A mixture of carbon monoxide and hydrogen ($H_2/CO = 3$) in cylinder was used in the catalytic study after removing the iron carbonyl impurity in an activated charcoal column. Cylinder hydrogen, after the removal of the oxygen impurity in a Deoxo unit and drying with a molecular sieve drier, was used for the catalyst reduction and thermal gravimetric study. High purity helium (better than 99.995%) was used for the thermal gravimetric study.

Apparatus and procedure. The hydrogenation of carbon monoxide was carried out in a flow system with a fixed bed of catalyst. The details of a reactor are shown in Fig. 1. The diameters of inner and outer pyrex tubes were 17 and 26 mm, respectively. A weighed amount of catalyst was retained between plugs of quartz wool near the bottom of the inner tube. A thermocouple enclosed in a 5-mm-o.d. Pyrex tube was inserted in the center of the catalyst bed.

The amount of catalyst (W) and the feed rate of carbon monoxide (F) were varied in the range 0.20 to 1.00 g and 3.33×10^{-4}–5.71×10^{-3} moles/min, respectively. The time factor was defined by the conventional reciprocal space velocity W/F. The reaction pressure and temperature were varied in the range 1 to 20 atm and 300 to 500°C, respectively. The reaction temperature was high relative to the ordinary Fischer–Tropsch synthesis since this study was aimed to synthesize gaseous hydrocarbons.

The effluent gases from the reactor were monitored by a gas meter after the removal of water in an ice trap. Reaction products consisted of hydrocarbons, carbon dioxide, and water. The formation of organic oxygenated compounds was negligible under the reaction conditions studied. Concentrations of H_2, CO, CO_2, and CH_4 in the off-gases were determined by means of a TCD gas chromatography. Chromatographic separations were made with an activated charcoal column at 90°C using argon as a carrier gas. The distributions of hydrocarbon products were determined by gas chromatography with use of a flame ionization detector and two columns of "Chromosorb 102" and squalane supported on Cellite 545.

Thermal gravimetric analyses of the LCG with $FeCl_3$ were performed by use of Shimazu thermal analyzer DP-30. Measurements were carried out under atmospheric pressure. The sample was heated at a rate of 10°C/min to a desired temperature in a stream of He or H_2. The substances eliminated from the LCG during the measurements were quantitatively collected and analyzed. The amounts of chlorine and hydrogen chloride were determined by titration using standard solutions of sodium thiosulfate and sodium hydroxide, respectively. Ferric and ferrous chlorides were titrated with potassium dichromate using stannous chloride as a reducing reagent.

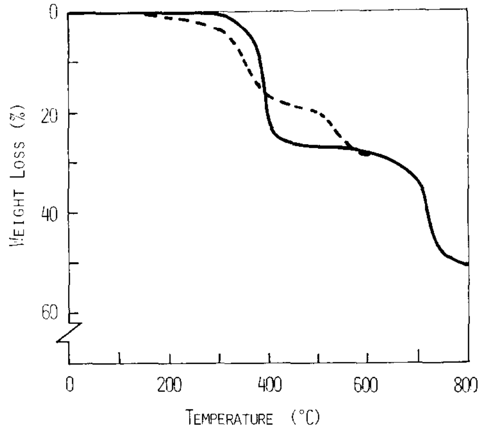

Fig. 2. Thermal gravimetric diagrams of the LCG with $FeCl_3$ in flowing He (solid line) and H_2 (dotted line).

RESULTS AND DISCUSSION

Figure 2 shows typical diagrams of thermal gravimetric analyses of the LCG with $FeCl_3$. On heating the LCG, the weight loss took place in two steps: at 300 to 410°C and 670 to 750°C in flowing He, and at 300 to 390°C and 520 to 580°C in flowing H_2. When the LCG was heated to 400°C in flowing H_2 and held at that temperature for 6 hr, the first weight loss was almost completed during the period of temperature rising to 400°C but the weight of the LCG continued to decrease slowly for about 4 hr after the temperature had reached 400°C as shown in Fig. 3. After the sample was kept at 400°C for 6 hr in H_2, it was heated in a stream of He. The weight loss at 670 to 750°C was observed again.

Table 1 gives the results on analyses of the compounds removed from the LCG during the thermal gravimetric measurements. On heating to 800°C in He, $FeCl_3$, $FeCl_2$, and Cl_2 came out of the LCG, while only $FeCl_3$ and Cl_2 were removed up to 500°C. The first two results given in Table 1 show that the weight loss at 300 to 410°C is attributed to the escape of $FeCl_3$ and Cl_2 and the second weight loss at 670 to 750°C due to $FeCl_2$. Here,

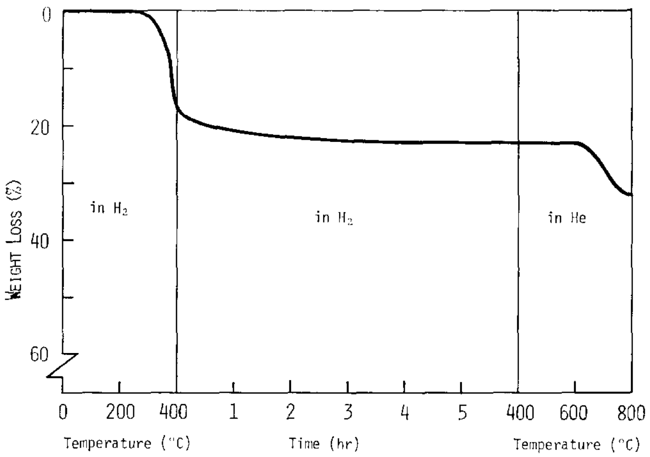

FIG. 3. Thermal gravimetric diagram of the LCG with $FeCl_3$ in flowing H_2 (room temperature to 400°C) and subsequently in flowing He (400 to 800°C).

$FeCl_2$ may be formed during the catalyst preparation and heating periods by the decomposition of $FeCl_3$:

$$2FeCl_3 \rightleftarrows 2FeCl_2 + Cl_2.$$

On the other hand, when the LCG was heated in flowing H_2, HCl was formed. And when pretreated once in H_2 at 400°C for 8 hr, only $FeCl_2$ was eliminated on the subsequent heating to 800°C in He. The amount of $FeCl_2$ eliminated, however, was reduced by the H_2 pretreatment at 400°C. The results in Table 2 show how the amounts of $FeCl_2$ and total Fe changed with the period of H_2 pretreatment. The amount of $FeCl_2$ decreased with pretreatment time up to 4 hr, while the total amount of Fe in the compound did not change considerably. This shows that the reduction of $FeCl_2$ to Fe metal proceeded during the pretreatment period.

The catalytic activity and selectivity of the reduced LCG for the hydrogenation of carbon monoxide were investigated at 300 to 500°C and 1 to 20 atm. Experimental results were expressed in terms of X and X_{HC} which were percentage CO reacted and percentage CO converted to hydrocarbons, respectively. These were calculated from the effluent gas composi-

TABLE 1

Results of Quantitative Analysis of the Compounds Removed from the LCG with $FeCl_3$ during Thermal Treatment

Treatment conditions				Compounds removed from the LCG (mmoles/g)		
Atmosphere	Temperature (°C)		Period (hr)	Cl_2 (HCl)	$FeCl_2$	$FeCl_3$
	From	To				
He	25	800	1	0.4	1.4	1.8
He	25	500	1	0.4	0.0	1.8
H_2	25	400	8	(4.5)	Nil	0.6
He	400	800[a]	1	0.0	0.7	0.0

[a] After pretreated in H_2 at 400°C for 8 hr.

tions according to the following equations:

$$X(\%) = \frac{(CO_2) + \sum i\,(Ci)}{(CO) + (CO_2) + \sum i(Ci)} \times 100 \quad (1)$$

$$X_{HC}(\%) = \frac{\sum i(Ci)}{(CO) + (CO_2) + \sum i(Ci)} \times 100. \quad (2)$$

Here (Ci) is the molar concentration of the hydrocarbon whose carbon number is i, and (CO) and (CO_2) are those of CO and CO_2, respectively.

When the LCG was reduced by H_2 for 8 hr, its catalytic activity scarcely changed with time on stream, as shown in Fig. 4. On the contrary, the activity of the catalyst reduced for only 1 hr increased initially with time on stream, as shown in Fig. 5. The hydrocarbon distributions on both of these catalysts were similar and almost independent of the time on stream. As the major difference in the structural composition of these catalysts as identified by thermal gravimetry was the degree of reduction of $FeCl_2$ in the graphite layers, their activity seems to be attributed to metallic Fe. Furthermore when these catalysts were treated with a 5 *N* HCl solution after use, only a negligible amount of iron was washed out. Such HCl treatment did not change the catalytic activity and selectivity at all.

TABLE 2

Variation in the Composition of the Intercalated Substances with the Period of Reduction Time at 400°C

Period of reduction time (hr)	Amount (mmoles/g) of	
	$FeCl_2$	Total Fe
1	3.0	4.0
2	2.1	4.1
4	1.2	4.2
6	1.2	4.2

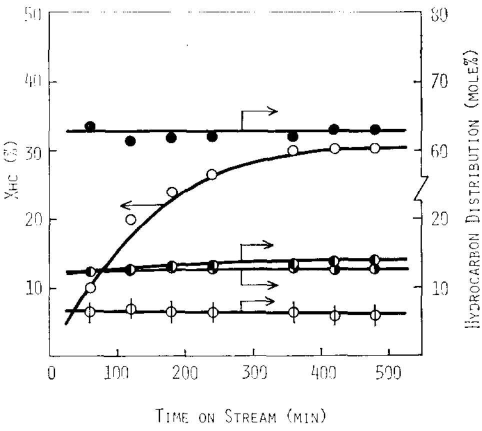

FIG. 4. Variation in X_{HC} and hydrocarbon distribution with time on stream on the LCG catalyst treated in H_2 at 400°C for 1 hr: ○, X_{HC}; ●, methane; ◐, C_2; ◑, C_3; ⦶, C_4. Reaction conditions: temperature = 400°C; pressure = 20 atm; W/F = 2240 (g-catalyst·min/CO-mole).

These results show that the active sites are located in the graphite layers.

Effects of reaction temperature on CO conversion and product distributions are given in Table 3. The reaction products mainly consisted of C_1–C_4 hydrocarbons with a minor formation of higher hydrocarbons over the temperature range studied.

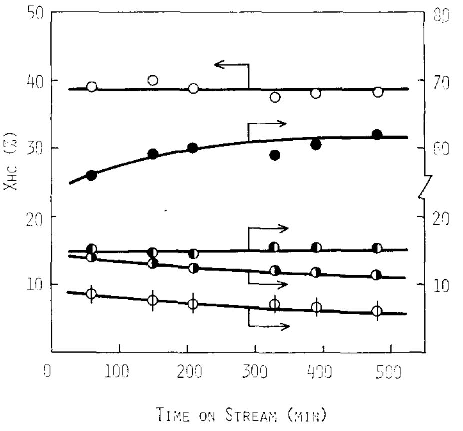

FIG. 5. Variation in X_{HC} and hydrocarbon distribution with time on stream on the LCG catalyst treated in H_2 at 400°C for 8 hr: ○, X_{HC}; ●, methane; ◐, C_2; ◑, C_3; ⦶, C_4. Reaction conditions: temperature = 400°C; pressure = 20 atm; W/F = 2240 (g-catalyst·min/CO-mole).

TABLE 3

Effect of Reaction Temperature on CO Conversion[a]

	Temperature (°C)				
	300	350	400	450	500
X (%)	1	6	41	72	85
X_{HC} (%)	1	6	38	63	68
S (%)	100	100	93	88	80
Hydrocarbon distribution (mole%)					
C_1	86.2	71.8	62.0	72.1	87.6
C_2	5.9 (0.17)[b]	13.0 (0.36)	15.3 (0.32)	12.1 (0.44)	7.0 (0.24)
C_3	4.9 (0.24)	9.5 (0.67)	11.4 (1.00)	9.1 (1.00)	3.9 (0.71)
C_4	2.0	3.6	6.0	4.0	1.1
C_5+	1.0	2.1	5.3	2.7	0.4

[a] Reaction conditions: pressure = 20 atm, W/F = 2240 (g-catalyst·min/CO-mole).

[b] Values in parentheses refer to fractions of olefin: olefin/(paraffin + olefin).

Both X and X_{HC} increased with reaction temperature. However, the formation of CO_2 was more enhanced than hydrocarbon synthesis at higher temperatures, resulting in the decrease in the selectivity for hydrocarbon formation (S), which was defined as:

$$S(\%) = \frac{X_{HC}}{X} \times 100. \qquad (3)$$

Reaction pressure was also an important factor that influenced the conversion of CO, as shown in Fig. 6. At 400°C, X_{HC} increased remarkably as reaction pressure increased and it began to level off at about 20 atm. The carbon number distribution of product hydrocarbons was almost independent of the pressure if compared at the same level of CO conversion, as illustrated in Table 4. The fraction of ethylene in C_2 hydrocarbons, however, decreased with increasing reaction pressure.

The selectivity of the reduced LCG catalyst, especially the distribution of product hydrocarbons, was sensitive to the degree of CO conversion. Figure 7 shows the relations between them obtained by varying the time factor W/F. At lower levels of CO conversion, methane was predominantly formed and the selectivity for the formation of C_2–C_4 hydrocarbons increased with increasing CO conversion up to 30%. This phenomenon may account for the low selectivity for the formation of C_2–C_4 hydrocarbons at 300 and 350°C as given in Table 3. The observed variations of selectivity against conversion could be explained by considering the effect of steam produced to enhance the formation of higher hydrocarbons. A detailed kinetic explanation for such behavior of this cata-

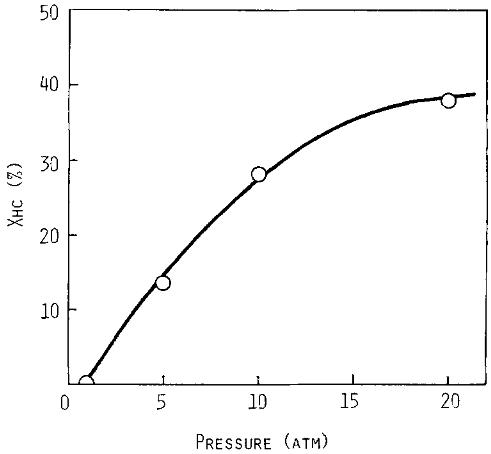

FIG. 6. Variation of X_{HC} at 400°C with reaction pressure.

TABLE 4

Effect of Reaction Pressure on CO Conversion at 400°C

Pressure (atm)	5	10	20
W/F	2240	2100	1250
X (%)	14	21	21
X_{HC} (%)	14	20	20
S (%)	100	95	95
Hydrocarbon distribution (mole%)			
C_1	70.4	67.4	67.8
C_2	15.4 (0.76)[a]	14.7 (0.56)	14.0 (0.38)
C_3	8.6 (1.00)	10.4 (1.00)	9.7 (1.00)
C_4	3.2	4.6	4.8
C_5+	2.4	2.9	3.7

[a] Values in parentheses refer to fractions of olefin.

lyst against steam will be given in a separated paper.

The selectivity of the LCG catalyst was compared with a graphite-supported Fe catalyst. The distribution of hydrocarbons produced on the graphite-supported catalyst depended slightly on conversion, as shown in Fig. 8. The formation of C_2–C_4 hydrocarbons was more selective on the LCG catalyst than on the Fe catalyst merely supported on graphite. The property more characteristic of the LCG catalyst was found in the remarkably high efficiency of CO conversion to hydrocarbons. It is generally recognized that the formation of CO_2 is inevitable for Fe catalysts in the Fischer–Tropsch synthesis because of their high activity for the water–gas shift reaction. Therefore, it is interesting to note that the nature of Fe in the intercalated layers is different from that in the usual Fe catalysts.

The results of the present study on the catalytic properties of the LCG show that there is a peculiar interaction between Fe and graphite. Vol'pin *et al.* (*5*) made magnetic and X-ray studies on LCGs with the metal obtained by reducing the

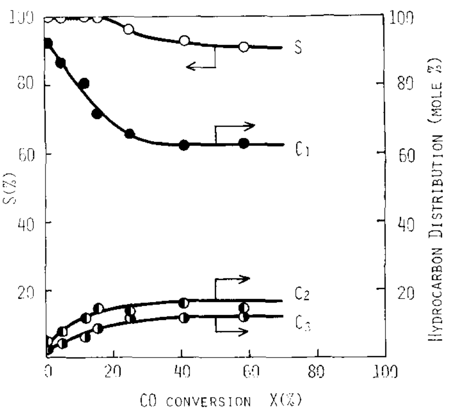

Fig. 7. Variation in hydrocarbon distribution and the selectivity of hydrocarbon production (S) with degree of CO conversion on the LCG catalyst at 400°C and 20 atm.

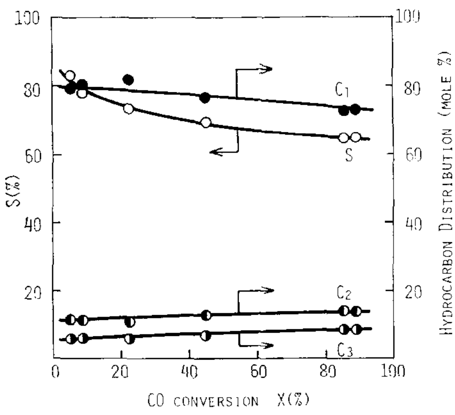

Fig. 8. Variation in hydrocarbon distribution and the selectivity of hydrocarbon production (S) with degree of CO conversion on the graphite-supported Fe catalyst at 400°C and 20 atm.

corresponding LCGs with a metal chloride using a reducing reagent such as sodium borohydride. According to their results, the intercalated Fe interacts with graphite only weakly. And it was argued by Liengme *et al.* (*6*) that $FeCl_2$ in the LCG was weakly held by graphite layers than by $FeCl_3$. Thus, it is considered that the interaction between the intercalated substances and graphite in the LCG catalyst of the present study is not as significant as it is in the LCG with alkali metals where alkali metals have been shown to activate graphite layers through the formation of electron donor–acceptor complexes (*7*). The X-ray diffraction analysis of the spent LCG catalyst showed no diffraction peaks attributed to α-Fe. This seems to show that metallic Fe in this catalyst is highly dispersed in the graphite layers. Thus, we speculate that the characteristic selectivity of the Fe–LCG catalyst is associated with highly dispersed Fe in the intercalated layers of graphite.

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