Synthesis of Gaseous Hydrocarbons from Carbon Monoxide and Hydrogen over Transition Metal Catalysts (Part 2)

The Activity and Selectivity of Graphite-Supported Iron Catalysts

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The activity and selectivity of various Fe catalysts for hydrocarbon synthesis from a mixture of carbon monoxide and hydrogen were investigated under atmospheric pressure at 400°C. When the catalytic activity was compared on the basis of hydrocarbon production rate per weight of Fe, the graphite-supported catalysts were found most active among the catalysts studied. Methane was the main constituent of the hydrocarbon products on all the Fe catalysts investigated under these conditions. The selectivity for the production of C₂-C₄ hydrocarbons varied from catalyst to catalyst. Some of the graphite species tested were effective as supporting materials for the catalysts to produce C₂-C₄ hydrocarbons with relatively high selectivity.

The addition of K₂CO₃ promoted the activity of graphite-supported catalysts. As the carbon deposition was more remarkably enhanced by the addition of K₂CO₃, however, the selectivity for hydrocarbon production decreased.

1. Introduction

For the Fischer-Tropsch synthesis Fe has long been recognized as one of the most active catalysts and various modification has been made to improve the catalytic properties of Fe in this reaction. It has well been known that the catalytic activity of Fe is promoted by the addition of a certain amount of alkali oxide or salts¹⁾ such as carbonate or silicate. The alkali enhances the rate of synthesis and also shifts the product spectrum towards the heavier hydrocarbons. As alkali does not increase the total effective surface area of Fe, its promoter effect is, no doubt, chemical in nature and it has been postulated that the alkali compound influences the electronic state of the Fe atom²⁾⁻⁵⁾.

In our previous study⁶⁾ on catalytic hydrogenation of carbon monoxide over the Group VIII transition metals, it has been shown that the specific activity and the selectivity of graphite-supported Rh catalyst is quite different from those of alumina- or activated charcoal-supported catalysts. This difference may be attributed to the metal-support effect involving the electron transfer from graphite to metal: the high work function of the transition

metals relative to graphite leads to a significant negative charging of the metals. Thus, it is considered that the action of graphite for the transition metals is similar in nature to that of alkali. Therefore, such effect of graphite seems to be favorable for the Fe catalysts in the Fischer-Tropsch synthesis.

The purpose of the present work was to investigate the activity and selectivity of graphite-supported Fe catalysts and to compare them with those of other types of Fe catalysts.

2. Experimental

2.1 Apparatus and Procedure

Experiments were carried out in a circulating flow system with a fixed bed of catalyst. Details of the reactor have been given earlier⁶⁾. The catalyst was pretreated in air or hydrogen at a desired temperature (350~500°C) for 1 hr and then brought to the reaction temperature in a stream of argon. At this temperature a mixture of carbon monoxide and hydrogen in a composition fixed at 3H₂+1CO was introduced. The product analysis was achieved by means of gas chromatography, as mentioned previously⁶⁾.

The BET surface areas of the graphites used were determined by measuring the adsorption isotherms of nitrogen at liquid nitrogen temperature. Measurements were made in a conventional glass

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adsorption system.

The mean crystallite size of graphite was calculated from the X-ray diffraction pattern using the breadth at half height, according to the Debye-Scherrer Eq. (1):

$$L = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where L is the mean dimension of the crystallite perpendicular to the set of planes giving a diffraction line at glancing angle θ , λ is the wave length of the X-ray, β is the true half maximum line breadth, and K is the shape factor. Corrections of the observed line breadths for instrumental broadening and $K\alpha$ -doublet broadening were made with the use of the curves given by Klug and Alexander⁷⁾. X-ray measurements were made by use of Rigaku Denki D3F counter-diffractometer employing Fe $K\alpha$ radiation filtered by Mn. The instrumental broadening itself was determined using a Si reference sample of size greater than 1,000 Å. K is nearly 0.9 for ordinary three-dimensional lattice, while 1.84 for two-dimensional lattice⁸⁾. As proposed by Akamatsu⁹⁾ the L_c -dimension was determined from (002) line using $K=0.9$, while the L_a -dimension was from (110) line using the following equation:

$$K = 0.9 + (1.84 - 0.9)P \quad (2)$$

where P is the fraction of disoriented layers. The values of P can be calculated according to the following equation proposed by Franklin:¹⁰⁾

$$d(002) = 3.44 - 0.086(1 - P^2) \quad (3)$$

where $d(002)$ is the inter-layer spacing of graphite and is calculated from the diffraction angle of the (002) diffraction of graphite.

2.2 Materials

The catalysts were prepared by individually impregnating graphite, alumina, silica, and activated charcoal with an aqueous solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. After impregnation, the sample was dried overnight at 110°C and stored in a desiccator. The graphites used as catalyst supports are described in the following:

- G-1: "4 inch square SMG" supplied by Showa Denko Ltd., containing less than 20 ppm of impurities. Graphitized by heating petroleum coke at 3,000°C and subsequently purified by chlorine at 3,000°C.
- G-2: "8 inch square SMG". The others are the same as G-1.
- G-3: Spectroscopic electrodes supplied by Nippon Carbon Co.

- G-4: Supplied by Showa Denko Ltd. Graphitized by heating needle coke at 3,000°C.
- G-5: Same as G-2 except no purification by chlorine.
- G-6: Supplied by Showa Denko Ltd. Prepared by heating petroleum coke at 1,000°C.
- G-7: Natural graphite "Spectroscopic Powder SP-1" supplied by Union Carbide Corp.
- G-8: "KS-75" supplied by Lonza Ltd. Graphitized by heating anthracite at 2,800°C.
- G-9: "T-44" supplied by Lonza Ltd. Graphitized by heating petroleum coke at 2,800°C.

G-1~G-6 were crushed to 70~350 μ prior to impregnation. The other graphites were used in the form of powder less than 150 μ in size. The $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was obtained from Wako Pure Chemical Industry Ltd. The Fe catalysts supported on γ -alumina and activated charcoal were reduced in H_2 at 400°C for 1hr. The γ -alumina and charcoal used were Alon G from Cabot Co. and a coconut charcoal from Takeda Chemical Industries Ltd., respectively. A precipitated Fe catalyst, whose composition was $75\text{Fe}^{2+} - 25\text{Fe}^{3+} - 20\text{Cu} - 1\text{K}_2\text{CO}_3$, was prepared according to the following method¹¹⁾: Solution 1 contained 134 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O} + 61$ g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O} + 26$ g $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 2 l of H_2O . Solution 2 contained 200 g Na_2CO_3 dissolved in 2 l of H_2O . Solution 1 was heated to 70°C and Solution 2 to boiling. Precipitation was effected by adding Solution 2 to Solution 1 rapidly until the solution became alkaline. The precipitate was washed until free from alkali, then alkalinized with 0.5 g K_2CO_3 dissolved in 100 ml H_2O . The mixture was evaporated and dried at 110°C.

Cylinder hydrogen was used after it was purified in a Deoxo unit to remove the oxygen impurity, and dried through a molecular sieve drier. Carbon monoxide was supplied by Matheson Co., Inc.

3. Results and Discussion

3.1 Comparison of Various Fe Catalysts

The hydrogenation of carbon monoxide was performed under atmospheric pressure at 400°C, using the precipitated Fe catalyst and supported Fe catalysts. Graphite, γ -alumina, silica, and activated charcoal were used as the catalyst supports. The reaction products consisted of C_1 - C_5 hydrocarbons, carbon dioxide, and water.

The experimental results were represented in terms of X and X_{HC} which were % CO reacted and % CO converted to hydrocarbons, respectively.

The plots of typical time dependency of X_{HC}

Catalyst is 5% Fe/G-2 pretreated in air at 350°C for 2 hr.

Reaction conditions : Temperature = 400°C, W/F = 8,960 g-cat·min/CO-mol

Fig. 1 Variation of X_{HC} and Hydrocarbon Distribution with Time

Catalyst is precipitated iron (75Fe²⁺+25Fe³⁺+20Cu-1K₂CO₃) pretreated in air at 350°C for 2 hr.

Reaction conditions : Temperature = 400°C, W/F = 8,960 g-cat·min/CO-mol

Fig. 2 Variation of X_{HC} and Hydrocarbon Distribution with Time

and hydrocarbon distribution over a graphite-supported Fe catalyst are shown in **Fig. 1**. The X_{HC} increased with time on stream during the initial period of about 5 hr and reached a steady state value. The hydrocarbon distribution showed no considerable change during this period. The other supported Fe catalysts showed a similar trend. On the other hand, the precipitated Fe catalyst required reaction time 10 times longer than that of the supported catalysts to reach a steady state as shown in **Fig. 2**.

The catalytic activity and product distribution at the steady state are summarized in **Table 1** where the olefin contents in the C₂ and C₃ hydrocarbons are also shown. The catalytic activity was defined as the reaction rate per weight of Fe (r) which was calculated according to Eq. (4). The selectivity for the production of hydrocarbons against CO₂ (S) was calculated according to Eq. (5):

$$r = \frac{X_{\text{HC}}}{W/F} \cdot \frac{1}{\text{weight \% of Fe in the catalyst}} \quad (4)$$

$$S (\%) = \frac{X_{\text{HC}}}{X} \times 100 \quad (5)$$

Here W/F is the reciprocal space velocity of feed CO (g-cat·min/mol).

The activity (hydrocarbon production rate per weight of Fe) and selectivity to produce C₂ hydrocarbons of the graphite-supported Fe catalyst were the highest among these Fe catalysts used. The other catalysts were almost of the same order of activity except the charcoal-supported catalyst which was less active. It was also found that the graphite-supported catalyst was more selective for the production of hydrocarbons as opposed to carbon dioxide than the other catalysts. The C₂ and C₃ hydrocarbons produced on these catalysts were highly olefinic except

Table 1 Catalytic Activity and Selectivity of Various Iron Catalysts

Catalyst	5%Fe/Al ₂ O ₃	30%Fe/Al ₂ O ₃	5%Fe/SiO ₂	5%Fe/G-2	5%Fe/C	Precipitated Fe
X (%)	3.1	24.5	14.2	9.9	3.6	60.9
X_{HC} (%)	1.0	5.9	1.0	7.3	0.1	17.5
S (%)	32	24	7	74	3	29
$r \times 10^6$ (mol/g-Fe·min)	22	22	22	160	2	23
Hydrocarbon Distribution (mol%)						
C ₁	78.2	80.1	78.9	71.1	88.5	84.7
C ₂	15.8(0.74)	14.0(0.59)	15.3(0.83)	19.1(0.66)	11.5(0.10)	9.4(0.57)
C ₃	5.4(1.00)	5.3(0.88)	4.7(1.00)	8.2(1.00)	0.0	4.5(0.77)
C ₄	0.6	0.6	1.1	1.4	0.0	1.1
C ₅	0.0	0.1	0.0	0.2	0.0	0.3

() : Olefin content, olefin/(paraffin + olefin)

Reaction temperature = 400°C, W/F = 8,960 g-cat·min/CO-mol

Table 2 Effect of Pretreatment

Pretreatment	at 350°C in Air	at 500°C in Air	at 500°C in H ₂	No Pretreatment
X _{HC} (%)	7.2	7.3	5.2	8.0
r × 10 ⁴ (mol/g-Fe·min)	1.6	1.6	1.2	1.8
Hydrocarbon Distribution (mol%)				
C ₁	70.5	71.1	82.6	81.4
C ₂	19.1(0.66)	19.1(0.66)	12.6(0.64)	13.2(0.53)
C ₃	9.0(1.00)	8.2(1.00)	4.4(1.00)	5.0(0.86)
C ₄	1.4	1.4	0.4	0.4
C ₅	0.0	0.2	0.0	0.0

() : Olefin content, olefin/(paraffin+olefin)
Catalyst is 5% Fe/G-2. Reaction temperature=400°C, W/F=8, 960 g-cat·min/CO-mol

the charcoal-supported catalyst.

3.2 Effect of Pretreatment on the Catalytic Properties of Fe Supported on Graphite

The distribution of hydrocarbons produced on graphite-supported catalysts was found to change considerably depending on the atmosphere of gas in which they were pretreated whereas their catalytic activity was scarcely influenced. **Table 2** shows the effect of the type of pretreatment on the catalytic activity and product distribution. The catalyst pretreated in air showed the highest selectivity for the production of C₂ hydrocarbons. The temperature of air pretreatment in the range from 350 to 500°C had minor influence on the catalytic selectivity. Graphite in alkali containing or high metal-loading catalysts, however, burnt out during the pretreatment in air at 500°C. Thus, the pretreatment temperature was fixed at 350°C in the subsequent experiments.

3.3 Effect of Fe Content in Graphite-Supported Catalyst

The effect of Fe content on the catalytic behavior of Fe supported on graphite was investigated in the range of Fe content between 1.0 and 30 wt%. The variations of X_{HC} and hydrocarbon distribution on these catalysts are shown in **Fig. 3**. The selectivity for the production of C₂ or C₃ hydrocarbons decreased with increasing Fe content whereas the X_{HC} increased. The hydrocarbon distribution on almina-supported catalysts, however, scarcely changed with Fe content as shown in **Table 1**.

Figure 4 shows the variation of hydrocarbon distribution on the 10% Fe/G-2 catalyst as a function of X_{HC} which was varied by changing W/F. The hydrocarbon distribution was almost independent of X_{HC}. Accordingly, the variation of hydrocarbon distribution with Fe content may not be due to the variation of X_{HC} but probably due to the different degree of dispersion of Fe on graphite.

Catalysts are Fe/G-2 pretreated in air at 350°C for 2 hr.
Reaction conditions : Temperature=400°C, W/F=8, 960 g-cat·min/CO-mol

Fig. 3 Effect of Fe Content in Graphite-Supported Catalysts on X_{HC} and Hydrocarbon Distribution

Catalyst is 10% Fe/G-2 pretreated in air at 350°C for 2 hr.
Reaction temperature=400°C

Fig. 4 Relation between X_{HC} and Hydrocarbon Distribution

3.4 Effect of Alkali Addition on the Catalytic Behavior of Graphite-Supported Fe Catalysts

In the Fischer-Tropsch synthesis, alkali is known as a significant promoter for Fe catalysts and the

role of alkali is assumed to improve the electronic state of the Fe^{2+} atom. The effect of alkali on the catalytic behavior of Fe-graphite system was investigated by adding various amounts of K_2CO_3 to the 5% Fe/G-2 catalyst. **Figure 5** shows the variation of X and X_{HC} as a function of the amount of alkali added. Up to 1 wt%, X_{HC} increased and reached a maximum which was 3 times larger than that of the unpromoted catalyst. However, carbon deposition was more drastically enhanced by the addition of K_2CO_3 , resulting in the decrease in the selectivity for hydrocarbon production. The mechanism of disproportionation of CO on Fe has been recognized by many studies^{12)~14)} to proceed via carbide above its temperature of decomposition, e.g.,

It is well known that alkali promotes the carburization of Fe shown by Eq. (6) during the Fischer-Tropsch synthesis. Thus, it is natural that carbon deposition is remarkable on alkaliized Fe catalysts at 400°C which is above the decomposition temperature of the carbide. The hydrocarbon distribution, however, was unchanged by alkali addition.

Catalysts are alkali-promoted and unpromoted 5% Fe/G-2 pretreated in air at 350°C for 2 hr.
Reaction conditions : Temperature=400°C, W/F=8,960 g-cat·min/CO-mol

Fig. 5 Effect of Alkali Addition on X and X_{HC}

3.5 Comparison of Graphite Species as Support for Fe Catalyst

The structural and physical properties of artificial graphites depend considerably on the nature of raw materials or the thermal history during their production. The results of X-ray diffraction measurement on these graphites and the natural graphite are summarized in **Table 3** in terms of the P-value, L_a , L_c , and L_a/L_c . Their BET surface areas are also shown in **Table 3**. From the P-value, which is the fraction of disoriented

Table 3 Physical Properties of Various Kinds of Graphite

Graphite	P-Value	L_a (Å)	L_c (Å)	L_a/L_c	BET Surface Area (m ² /g)
G-1	0.36	569	260	2.19	1.9
G-2	0.34	632	230	2.75	2.1
G-3	0.34	560	298	1.88	2.1
G-4	0.20	517	425	1.22	1.5
G-5	0.34	628	308	2.04	1.9
G-6	0.99	41	29	1.41	2.1
G-7	0.00	470	628	0.75	1.6
G-8	0.14	709	633	1.12	8.8
G-9	0.14	937	503	1.86	12.4

Catalysts are 5% Fe/Graphite pretreated in air at 350°C for 2 hr.

Reaction conditions : Temperature=400°C, W/F=8,960 g-cat·min/CO-mol

Fig. 6 Correlation between L_a/L_c and Selectivity for C_2 and C_3 Hydrocarbons

layers, it is evident that the natural graphite (G-7) is of completely ordered structure while G-6 is nearly amorphous. The P-values of the other artificial graphites lie between these two extremes. The dimension of graphite lattice, measured as L_a or L_c , of G-6 was smaller by one order of magnitude than the others. The BET surface areas of these graphites were almost of the same magnitude except for those of Lonza Graphites (G-8 and G-9).

The effect of graphite species as catalyst support on the activity and selectivity of Fe catalysts was investigated at 400°C using catalysts with 5 wt% of Fe. The activity could not be correlated to any of these structural and physical properties of the graphites. When the selectivities for the production of C_2 and C_3 hydrocarbons were plotted against the ratio of L_a/L_c , however, fairly good linear relationships were obtained between them, while no relationships were found between the selectivity and the P-value. The results are shown in **Fig. 6**.

Graphite shows an anisotropy for electric resis-

tance. The electric resistance in the direction perpendicular to the graphite layers is 100 to 1,000 times larger than that in the direction parallel to the graphite layer. The increase in the ratio L_a/L_c may increase the degree of interaction between graphite and Fe, resulting in the enhancement of selectivity for the production of C_2 or C_3 hydrocarbons. However, exceptions were encountered in **Fig. 6** with the catalysts using G-6, G-8, and G-9 graphite supports. The BET surface areas of G-8 and G-9 were about 4 times larger than those of the other graphites. Although it is still uncertain why these graphites give catalysts with higher selectivity for the production of C_2 or C_3 hydrocarbons, the dispersion factor seems to be important and relevant for the Fe-graphite system.

References

- 1) Anderson, R. B., "Catalysis", Emmet, P. H. Ed., Vol. 4, 123 (1956), Reinhold, New York.

- 2) Love, K. S., Brunauer, S., *J. Am. Chem. Soc.*, **64**, 745 (1942).
- 3) Dry, M. E., Oosthuizen, G. J., *J. Catal.*, **11**, 18 (1968).
- 4) Bokhoven, C., Van Heerden, C., Westrik, R., Zwiering, P., "Catalysis", Emmet, P. H., Ed., Vol. 3, 265 (1955), Reinhold, New York.
- 5) Kölbl, H., Actes Congr. Intern. Catalyse, 2e, Paris, **2**, 2075 (1960).
- 6) Kikuchi, E., Ino, T., Ito, N., Morita, Y., *Bull. Japan Petrol. Inst.*, **18**, (2) 139 (1976).
- 7) Klug, H. P., Alexander, L. E., "X-ray Diffraction Procedures", Chap. 9, (1954), John Wiley, New York.
- 8) Warren, B. E., *Phys. Rev.*, **59**, 693 (1941).
- 9) Akamatsu, H., Inokuchi, H., Takahashi, H., Matsunaga, Y., *Bull. Chem. Soc. Japan*, **29**, 574 (1956).
- 10) Franklin, R. E., *Acta. Cryst.*, **4**, 253 (1951).
- 11) Pichler, H., "Advances in Catalysis", Frankenburg, W. G., and Komarewsky, V. I., Eds., Vol. 4, 271 (1952), Academic Press., New York.
- 12) Akamatsu, H., Sato, K., *Bull. Chem. Soc. Japan*, **22**, 127 (1949).
- 13) Ruston, W. R., Warzee, M., Hennaut, J., Watz, J., *Carbon*, **7**, 47 (1969).
- 14) Walker, Jr. P. L., Rakszawski, J. F., Imperial, G. R., *J. Phys. Chem.*, **63**, 133, 140 (1959).

要 旨

遷移金属触媒上での一酸化炭素の水素化による気体炭化水素の合成 (第2報)

グラファイト担持鉄触媒の活性と選択性

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種々の鉄触媒を用いて合成ガスからの炭化水素合成反応を行い, その触媒活性と選択性につき検討した。反応は固定床流通循環反応装置を用いて行った。リアクターの詳細は引用文献 6) に示されている。実験条件はすべて常圧, 400°C, 原料組成 $H_2/CO=3$ (mol/mol) である。

シリカ, アルミナ, 活性炭およびグラファイトに担持した鉄触媒と沈殿鉄触媒の活性, 選択性を調べた結果, **Table 1** に示す結果を得た。ここで X , X_{HC} はそれぞれ CO の反応率と CO の炭化水素への転化率であり, 反応速度 r および炭化水素への選択性 S は Eqs. (4), (5) のように定義される。

$$r = \frac{X_{HC}}{W/F} \cdot \frac{1}{\text{触媒中の鉄の重量百分率}} \quad (4)$$

$$S (\%) = \frac{X_{HC}}{X} \times 100 \quad (5)$$

ここで反応速度 r を触媒活性と定義した。いずれの触媒においても主成物はメタンであるが, グラファイト担持鉄触媒ではメタンに加え C_2 , C_3 炭化水素も比較的高い選択率で合成された。これらの触媒の中では, 鉄重量あたりの反応速度はグラファイト担持鉄触媒が最も高く活性炭担持鉄触媒が最も低い。他の触媒はほぼ同じ活性であった。

グラファイト担持鉄触媒は前処理の条件により選択性が大き

く影響され, 350~500°C で空気焼成した場合, C_2 , C_3 炭化水素への選択性が最も高くなった。しかし活性には大きな変化は見られなかった (**Table 2**)。

一般に, 鉄触媒はアルカリ酸化物のような電子供与性化合物の添加により触媒活性が促進されることが知られている¹⁾。ところで, グラファイト担持鉄触媒の活性は少量のアルカリ (K_2CO_3) を添加することにより著しく促進され, アルカリ添加量 1 wt% のとき X_{HC} は最大となり無添加触媒の 3 倍となった (**Fig. 5**)。しかしアルカリ添加触媒では炭素析出が激しく無添加触媒に比べて炭化水素への選択性は低下した。CO の不均化による炭素析出反応に対して触媒活性をもつ金属では, 炭素析出は金属カーバイドを経由して進行するとされている^{12)~14)}。すなわち,

したがってアルカリ添加した触媒を用いたとき炭素析出が著しいのはアルカリが Eq. (7) のカーバイド化を促進しているためと思われる。

グラファイト担持鉄触媒において, その担体であるグラファイトの種類を変えることにより, 触媒の選択性が変化し, 生成物分布に影響を与えることが見いだされた。人造グラファイトの物理的性質および構造はその原料あるいはグラファイト生成過程の熱履歴に大きく依存する。X線回折より求めた種々のグ

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ラファイトの P-値, L_a , L_c , L_a/L_c をその BET 表面積とともに **Table 3** に示した。ここで P-値とは不規則的に積み重なったグラファイト層の割合であり, L_a および L_c はそれぞれグラファイトの a 軸および c 軸方向の平均結晶子径である。これらのグラファイトに鉄を 5 wt% 担持した触媒を用いて反応を行った結果, 活性とグラファイトの物理的性質との間には相関性は見られなかったが, C_2 , C_3 炭化水素への選択性と L_a/L_c

値との間には良い直線関係が認められた。グラファイトの電気抵抗は異方性であり, グラファイト層に対して垂直方向の電気抵抗は平行方向のそれよりも 100~1,000 倍大きい。したがって L_a/L_c 値の変化はグラファイトと鉄の相互作用の程度を変化させることが予想され, それによって炭化水素分布も変化するものと考えられる。

Keyword

Carbon monoxide, Graphite support, Hydrocarbon, Hydrogenation, Iron catalyst