Synthesis of Gaseous Hydrocarbons from Carbon Monoxide and Hydrogen over Transition Metal Catalysts (Part 4)

The Effect of Pretreatment on the Composition and the Catalytic Activity of Reduced Lamellar Compound of Graphite with Ferric Chloride

Takashi INO*, Naoyuki ITO*, Eiichi KIKUCHI* and Yoshiro MORITA*

A lamellar compound of graphite (LCG) with FeCl_3 was treated in flowing Ar or H_2 in the temperature range from 400 to 800°C. The FeCl_3 in the layers was reduced to FeCl_2 or to metallic Fe whose contents changed depending on the conditions of treatment. Hydrogenation of carbon monoxide was investigated at 400°C and 20 atm using these LCG catalysts. Although the active site of the LCG catalyst was the metallic Fe located between the graphite layers, it was shown that the content of FeCl_2 in the layers was important for controlling catalytic activity of the LCG. The catalytic activity of the LCG increased with increasing FeCl_2 content up to 0.9 mmol/g-catalyst. However, FeCl_2 itself showed no catalytic activity at 400°C. As is known, the interlayer spacing of graphite enlarged by FeCl_2 is larger than that enlarged by Fe, and the FeCl_2 in the LCG catalyst probably behaves as the spacer.

1. Introduction

In our previous work¹⁾ it was shown that metallic Fe found between the graphite layers, which was produced by reduction of a lamellar compound of graphite (LCG) with FeCl_3 in flowing H_2 at 400°C, was catalytically active for hydrogenation of carbon monoxide. The reaction products found on the LCG catalyst consisted mainly of C_1 – C_4 hydrocarbons, and the selectivity for hydrocarbon production was outstanding (more than 90% at 400°C) compared with Fe catalyst merely supported on graphite and this catalyst produced a considerable amount of CO_2 with hydrocarbons. The constituents in the intercalated layers of catalytically active LCG were FeCl_2 and metallic Fe. It will be shown in the present study that concentrations of these components in the layers are varied by treating FeCl_3 –LCG under various conditions. Furthermore, the correlation observed between catalytic activity and composition in the intercalated layers will be described.

2. Experimental

2.1 Apparatus and Procedure

Hydrogenation of carbon monoxide was carried out in a flow system with a fixed bed of catalyst

at 400°C and 20 atm. The composition of feed gas was $3\text{H}_2 + \text{CO}$. Details of the reactor were given earlier¹⁾. The amount of catalyst (W) and the feed rate of carbon monoxide (F) were 1.00 g and 4.46×10^{-4} mol/min, respectively, and the reciprocal space velocity of CO (W/F) was 2,240 g-catalyst·min/ CO -mol. The composition of effluent gas from the reactor was determined by means of a gas chromatography, as mentioned previously¹⁾.

Thermal gravimetric analyses of LCG catalyst were performed under atmospheric pressure by use of Shimadzu Thermal Analyzer DP-30. The amounts of FeCl_2 in used LCG catalysts were determined from the weight losses during the heating to 800°C in flowing He ¹⁾. The total amount of Fe in a used catalyst was determined by heating the catalyst with concentrated sulfuric acid and weighing the Fe_2O_3 residue after burning off the graphite. The difference between the amount of total Fe and that of FeCl_2 was defined as the amount of metallic Fe in the LCG catalyst.

2.2 Materials

A pulverized natural graphite was used in the present work for catalyst preparation. It was designated as "Spectroscopic Powder" and supplied by Union Carbide Corp. A LCG with FeCl_3 was prepared according to the method of Croft²⁾: 20 g of anhydrous ferric chloride and 6 g of dried graphite were placed in a sealed Pyrex tube, which was evacuated at room temperature, then they were heated to 300°C and held at that temperature

Received March 15, 1980.

* Department of Applied Chemistry, School of Science and Engineering, Waseda University (3-4-1, Okubo, Shinjuku-ku, Tokyo 160)

for 4 hr. When intercalation was complete, the resulted compound was washed with a 5 N aqueous solution of hydrochloric acid and pure water to free excess FeCl_3 . The LCG thus obtained was dried overnight at 110°C and stored in a desiccator. The FeCl_3 concentration in the LCG was 62% by weight. The X-ray study showed that interlayer spacing of this compound was $9.42 \text{ \AA}$ which was in good agreement with a previously reported value for stage 1 structured $\text{FeCl}_3\text{-LCG}^9$. Before using it as catalyst, the resulted $\text{FeCl}_3\text{-LCG}$ was treated in flowing Ar or H_2 . During this treatment FeCl_3 in the layers was partly eliminated. On the other hand, the remaining FeCl_3 was reduced to FeCl_2 or metallic Fe. After the treatment, the LCG was washed with a 5 N aqueous solution of hydrochloric acid to remove metallic Fe which deposited on the outer surface of the graphite.

A cylindered mixture of carbon monoxide and hydrogen (H_2/CO) was used in the catalytic study after removing the iron carbonyl impurities in a column charged with activated charcoal. The oxygen impurity in the cylinder hydrogen was removed in a Deoxo unit, dried with a molecular sieve drier, and then it was used for catalyst reduction. High purity helium (better than 99.995%) was used for thermal gravimetric studies.

3. Results and Discussion

Hydrogenation of carbon monoxide was performed at 400°C and 20 atm using the LCG catalyst. The reaction products consisted of $\text{C}_1\text{-C}_7$ hydrocarbons, carbon dioxide and water. The catalytic activity was represented in terms of X_{HC} which is the percentage of CO converted to hy-

drocarbons.

Variations in the catalytic activities of the LCGs treated at various temperatures in flowing Ar are shown in **Fig. 1** as a function of time on stream. When LCG catalyst was treated in Ar in the temperature range from 400 to 600°C , its catalytic activity increased with time on stream during the initial period of about 6 hr and then it attained a steady state. On the other hand, the activity of the catalyst treated at 700°C was rather low and it did not change remarkably. As mentioned in a previous paper¹⁾ the main component in the intercalated layers of the LCG catalyst treated in flowing He was FeCl_2 , which was partly reduced to metallic Fe by subsequent reduction in flowing H_2 at 400°C . Thus, it is considered that the increase in the catalytic activity with time on stream resulted from the increase in number of active sites due to the reduction of FeCl_2 to metallic Fe in the graphite layers.

As shown in **Fig. 2**, when LCG catalyst was reduced in flowing H_2 , the activity increased with time on stream, but to a less extent compared with the catalyst treated in flowing Ar. Reduction at higher temperatures reduced the extent of increase in the catalytic activity with time on stream.

Table 1 lists product distribution, catalytic activity, and composition in the intercalated layers observed at the steady state. The LCG catalysts treated under the conditions shown in **Table 1** showed high selectivity for production of hydrocarbons against CO_2 , which is expressed by (*S*) in **Table 1**. Concentrations of FeCl_2 and metallic Fe in the catalyst treated in Ar decreased with increasing treatment temperature. The catalytic

Treatment conditions : Period = 1 hr, Temperatures = 400°C (●), 500°C (○), 600°C (△), 700°C (●)
Reaction conditions : Temperature = 400°C , Pressure = 20 atm, W/F = 2, 240 g-cat·min/CO-mol

Fig. 1. Effect of Ar Treatment on Activity of LCG Catalyst

Reduction conditions : Period = 1 hr, Temperatures = 400°C (●), 500°C (○), 550°C (△), 600°C (△)
Reaction conditions : Temperature = 400°C , Pressure = 20 atm, W/F = 2, 240 g-cat·min/CO-mol

Fig. 2. Effect of H_2 Reduction on Activity of LCG Catalyst

Table 1 Effects of Pretreatment on Catalyst Composition, Activity and Selectivity
Reaction Conditions : Temperature = 400°C, Pressure = 20 atm, W/F = 2, 240 g-cat·min/CO-mol

Pretreatment			Composition in the layer		X_{HC} (%)	S (%)	Hydrocarbon Distribution (mol %)				
Temperature (°C)	Period (hr)	Atmosphere	FeCl ₂	Metallic Fe (mmol/g)			C ₁	C ₂	C ₃	C ₄	C ₅ +
500	1	Ar	0.93	1.92	54	92	60.4	14.8	13.1	6.5	5.2
600	1	Ar	0.77	2.06	50	92	60.1	13.7	13.3	6.9	6.0
650	1	Ar	0.75	1.79	47	91	62.0	14.2	12.9	6.3	4.5
670	1	Ar	0.07	0.59	24	93	79.6	11.6	5.9	1.9	1.0
700	1	Ar	0.02	0.64	11	89	86.4	8.5	3.6	1.0	0.5
800	1	Ar	0.00	0.64	2	100	96.3	2.8	0.7	0.2	0.0
800 ^{a)}	1	Ar	0.00	2.35	8	86	84.0	8.9	4.5	1.6	0.9
400	1	H ₂	1.36	2.33	30	96	63.3	14.0	12.6	5.9	4.3
400	8	H ₂	1.11	2.31	38	93	62.0	15.3	11.4	6.0	5.3
500	1	H ₂	0.93	2.20	47	93	61.7	14.7	12.2	6.2	5.2
500	24	H ₂	0.45	1.91	28	87	67.0	14.2	10.2	4.6	4.0
550	1	H ₂	0.36	1.43	22	96	75.6	13.3	7.3	2.5	1.3
600	1	H ₂	0.20	1.50	11	95	84.1	9.9	4.3	1.2	0.5

activity of the LCG treated in flowing Ar decreased with decreasing concentrations of FeCl₂ and metallic Fe.

The LCG when treated in H₂ at 400°C for 8 hr and then treated in Ar at 800°C for 1 hr was low in catalytic activity though relatively large amounts of metallic Fe existed in the graphite layers. The X-ray diffraction measurements of used LCG catalysts showed no diffraction peaks attributed to α -Fe, indicating that metallic Fe in these catalysts is highly dispersed in the graphite layers. The catalytic activity of the LCG treated in H₂ above 500°C was correlated with FeCl₂ concentration more directly than with the concentration of metallic Fe. Consequently, it seems that FeCl₂ in LCG catalysts plays an important role for determining the catalytic activity as well as concentration of metallic Fe.

Liengme et al.⁴⁾ pointed out from their Mössbauer study of FeCl₂-LCG that there is no direct interaction between FeCl₂ and graphite. When a commercial reagent of FeCl₂ was used as catalyst in hydrogenation of carbon monoxide, no hydrocarbon was formed and the reduction of FeCl₂ to metallic Fe did not occur at 400°C. Therefore, it is considered that FeCl₂ in LCG catalysts is inactive for hydrocarbon synthesis. Vol'pin et al.^{3),5)} reported that interlayer spacing of FeCl₂-LCG (9.51 Å) determined from their X-ray study is larger than that of Fe-LCG (5.9 Å). This may

mean that FeCl₂ in LCG catalysts behaves as the spacer which enlarges the interlayer spacing of graphite.

As a general trend, LCG catalysts treated in flowing Ar were more active than those treated in flowing H₂ at the same temperature while the concentrations of FeCl₂ and metallic Fe in the former catalysts were smaller than those in the latter. The activity of LCG catalyst increased with increasing FeCl₂ content up to about 0.9 mmol/g-catalyst and exceeding it the catalytic activity decreased with increasing FeCl₂ content. Although it is still uncertain why the activity of LCG catalyst behaves opposite directions at FeCl₂ contents below and above 0.9 mmol/g-catalyst, it seems that diffusion of feed gas to the active sites in the layer is retarded when the graphite layer of the catalyst is occupied by FeCl₂ too closely.

References

- 1) Kikuchi, E., Ino, T., Morita, Y., *J. Catal.* **57**, 27 (1979).
- 2) Croft, R. C., *Aust. J. Chem.* **9**, 181 (1956).
- 3) Vol'pin, M. E., Novikov, Yu. N., Lapkina, N. D., Kasatochkin, V. I., Struchkov, Yu. T., Kazakov, M. E., Stukan, R. A., Povitskij, V. A., Karimov, Yu. S., Zvarikina, A. V., *J. Am. Chem. Soc.* **97**, 3366 (1975).
- 4) Liengme, B. V., Bartlett, M. W., Hooley, J. G., Sams, J. R., *Phys. Letters* **25A**, 127 (1967).
- 5) Novikov, Yu. N., Vol'pin, M. E., Prusakov, V. E., Stukan, R. A., Gol'danskij, V. I., Semion, V. A., Struchkov, Yu. T., *Strukt. Khim.* **11**, 1039 (1970).

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4報)

還元した塩化第二鉄・グラファイト層間化合物の組成および活性におよぼす前処理の影響

井野 隆*, 伊藤 直之*, 菊地 英一*, 森田 義郎*

FeCl_3 -グラファイト層間化合物 (LCG) を種々の条件で処理した後, Fischer-Tropsch (F-T) 合成の触媒として用い, その触媒活性におよぼす層間内の Fe 量および FeCl_2 量の影響について検討した。反応は固定床流通反応装置を用いて 400°C , 20 atm にて行った。生成物は C_1 - C_7 炭化水素, 二酸化炭素および水であった。触媒活性は原料 CO の炭化水素への転化率 X_{HC} (%) で示した。 FeCl_3 -LCG を Ar 中 400 – 700°C で処理した後これを触媒として反応に用いたところ **Fig. 1** に示すように活性は経時変化した。 700°C で処理した触媒を除いていずれも経時時間とともに活性上昇を示した。これは Ar 処理によって生じた層間内の FeCl_2 が合成ガス気流中で徐々に金属鉄に還元されたためと考えられる。**Fig. 2** は H_2 中 400 – 600°C で処理した時の触媒活性の経時変化を示したものである。Ar 処理の場合と同様に活性は, 経時時間とともに増加したが, 処理温度が高い程活性の経時変化は少なかった。

これら種々の前処理を施した LCG 触媒の定常状態における触媒活性, 炭化水素分布および層間内の組成を, **Table 1** に示した。層間内の FeCl_2 量および金属鉄量は処理温度の上昇

とともに減少した。 H_2 中 400°C , 8 時間処理し, その後 Ar 中 800°C で処理した触媒では, 金属鉄量が比較的多いにもかかわらず低活性であった。これらの LCG 触媒の X 線回折測定を行ったところ, いずれの触媒の場合も α -Fe に帰属する回折ピークは認められなかった。このことは LCG 触媒中の金属鉄は層間内で高分散状態に保たれていることを示している。 H_2 中 500°C 以上で処理した触媒の活性は金属鉄量よりむしろ FeCl_2 量と良い相関関係を示した。LCG 触媒の活性点は層間内の金属鉄であることを前報¹⁾で示したが, これらの結果から LCG 触媒中の FeCl_2 は金属鉄と同様, LCG 触媒の活性に対して重要な役割を果しているものと思われる。

しかしながら, FeCl_2 の市販品試薬を触媒として用いても炭化水素の生成はみられず, 一方層間内の FeCl_2 とグラファイトの間には相互作用がないことが知られていることから LCG 触媒中の FeCl_2 も F-T 合成に対して不活性であると考えられる。Vol'pin ら^{2),3)}によると FeCl_2 -LCG の層間距離 (9.51 Å) は Fe-LCG のそれ (5.9 Å) よりも広く, LCG 触媒中の FeCl_2 は層間距離を広げるスペーサーの作用をしているものと思われる。

* 早稲田大学理工学部応用化学科 (160 東京都新宿区大久保 3-4-1)

Keywords

Carbon monoxide, Hydrogenation, Iron catalyst, Lamellar compound, Graphite