Hydrogenation of Carbon Monoxide to Light Olefins over Chlorine-Containing Magnetite Catalysts in Slurry Phase[†]

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Hydrogenation of carbon monoxide was carried out at $P=10$ atm, $T=325^{\circ}\text{C}$, and GHSV=1,000–5,000 h^{-1} over chlorine-containing magnetite catalysts in the slurry phase. High selectivities to light olefins ($\text{C}_2=\text{C}_4$) of 48% with suppression of methane formation to 11% were obtained with these catalysts. Carbon dioxide, a by-product of the reaction, was hardly produced over the catalysts. The chlorine content in the used catalysts, determined by X-ray fluorescence spectrometry, was in the atomic ratio range of $\text{Cl}/\text{Fe}=0.002\text{--}0.01$. The XPS results of the catalysts showed that the surface concentration of chlorine was in the range of $\text{Cl}/\text{Fe}=0.1\text{--}0.2$, and that the chlorine on the surface was more negatively charged than that of the iron chloride. The chlorine prevented over-reduction of the surface to metallic iron during the reaction. These effects were explained in terms of electron attraction of the chlorine on the surface.

1. Introduction

We have suggested that, under high pressures and at high temperatures, practical iron-based Fischer-Tropsch (FT) catalysts with high selectivity to olefins are in the form of magnetite-like species.¹⁾

Various promoters are often added to the FT catalysts to enhance the selectivity to light olefins. Potassium salts have been most commonly used for this purpose.²⁾ A small amount of potassium, indeed, enhances olefin selectivity, and depresses methane and paraffin formations by reducing the hydrogenation activity of the catalyst. At the same time, however, the distribution of hydrocarbons shifts toward higher molecular weights. Consequently, the selectivity to light olefins cannot be improved so much by use only of alkaline salt promoters.

We have reported previously that high selectivity to ethylene and propylene was obtained over the magnetite catalysts prepared from iron chlorides

when CO hydrogenation was carried out in a fixed-bed reactor³⁾, while, due to its ineffective heat removal, deactivation of the catalyst occurred to some degree.

The purposes of the present paper are : examination of this type of catalysts more in detail, and application of the catalysts to CO hydrogenation in a slurry type reactor, with which the intrinsic characteristics of the catalysts could probably be more precisely evaluated, because the heat of reaction is effectively dissipated in the slurry phase.

2. Experimental

2.1 Preparation of Catalysts

2.1.1 Magnetite Prepared by Reflux

Chlorine-containing magnetite was obtained by reflux of an aqueous solution of ferric chloride in the presence of metallic iron powder at 100°C for 1 week.⁴⁾ The magnetite was treated in a H_2 flow at 400°C for 10 h to remove part of the chlorine from it. The treatment was carried out outside the reactor. The magnetite is henceforth called "magnetite by reflux" and abbreviated as $\text{Cl}/\text{Fe}_3\text{O}_4$.

[†] A part of this study was presented at "The 54th Shokubai Toronkai", (1984).

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2.1.2 Magnetite Prepared by Ammonium Co-precipitation

Magnetite was obtained from an aqueous solution of ferrous and ferric chlorides (1 : 2) by co-precipitation with ammonia water. This magnetite is abbreviated as $\text{NH}_3 \downarrow \text{Fe}_3\text{O}_4$.

2.1.3 Chloridized Magnetite

Ferric oxide hydrate ($\alpha\text{-FeOOH}$) was mechanically mixed with ferric chloride. The mixture ($\text{Cl}/\text{Fe} = 0.1$) was treated in a H_2 flow at 350°C for 10 h to be reduced partially to magnetite. This magnetite is henceforth called "chloridized magnetite" and abbreviated as $\text{Cl-Fe}_3\text{O}_4$.

2.1.4 Magnetite from Akaganeite

Akaganeite ($\beta\text{-FeOOH}$), which is known to contain chloride ion in its micropore, was obtained from an aqueous solution of ferric chloride⁵⁾, and was treated in a H_2 flow at 350°C for 10 h to be reduced to magnetite. This magnetite is abbreviated as $\beta\text{-FeOOH}$.

2.1.5 Magnetite without Chlorine (control)

Magnetite without chlorine, as a control, was obtained from chlorine-free ferrous hydroxide by air-oxidation.⁶⁾

2.2 Procedure

Each magnetite catalyst prepared above was crushed into a fine powder which was suspended in a 250 ml of liquid paraffin (bp. $330\text{--}390^\circ\text{C}$) to form a slurry of the catalyst. Hydrogenation of carbon monoxide was carried out with the slurry catalyst in a semi-batch slurry type reactor (flow type for gas phase). Reaction conditions were as follows : $T = 325^\circ\text{C}$; $P = 10$ atm ; $\text{GHSV} = 1,000\text{--}5,000$ h^{-1} . The reaction gas had the following composition : H_2 : CO : $\text{Ar} = 45 : 45 : 10$. By using argon concentration in the reaction gas as an internal standard, conversion and carbon-based selectivity were expressed by the following equations :

$$\text{CO conv.} = \left(1 - \frac{[\text{CO}]}{[\text{Ar}]}\right) \times \frac{[\text{Ar}]_0}{[\text{CO}]_0} \times 100 \quad (1)$$

$$C_n \text{ yield} = \frac{[C_n]}{[\text{Ar}]} \times n \times \frac{[\text{Ar}]_0}{[\text{CO}]_0} \times 100 \quad (2)$$

$$C_n \text{ selectivity} = \frac{C_n \text{ yield}}{(\text{CO conv.}) - (\text{CO}_2 \text{ yield})} \quad (3)$$

where $[\text{Ar}]$ and $[\text{CO}]$ are the concentrations of Ar and CO in the effluent gas, $[\text{Ar}]_0$ and $[\text{CO}]_0$ are the initial concentrations of Ar and CO in the reaction gas, and $[C_n]$ is the concentration of the product of which carbon number is n , respectively. In this manner, the CO conversion can be accurately evaluated even though all of the carbonaceous

products are not determined. Detailed procedures and analyses of the products were described previously.⁷⁾

2.3 Analyses of Catalysts

Fresh and used catalysts were identified using an X-ray diffractometer (Rigaku ; Geigerflex RAD). Chlorine in the catalysts was determined using an X-ray fluorescence spectrometer (Philips ; PW 1410). Surfaces of the catalysts were analyzed with an X-ray photoelectron spectroscope (Shimadzu ; ASIX).

3. Results

3.1 Blank Test

A blank test was carried out by using hydrogen instead of syngas to evaluate the decomposition of the liquid paraffin used as the slurry medium. When the reaction temperature was raised to 350°C , a trace amount (below 0.01 vol %) of C_4 and C_5 was detected only in the effluent gas over the magnetite catalyst prepared by reflux ($\text{Cl}/\text{Fe}_3\text{O}_4$). The amount was almost equivalent to the limit of accuracy of the gas chromatograph employed.

3.2 Reaction Results

Hydrogenation of carbon monoxide was carried out at $P = 10$ atm, $T = 325^\circ\text{C}$, and $\text{GHSV} = 1,000\text{--}5,000$ h^{-1} in the slurry phase. The results are given in **Table 1**. Both conversion and selectivity were almost invariable during 20 h.

Carbon monoxide conversion after H_2 pretreatment was 8.6% over the $\text{Cl}/\text{Fe}_3\text{O}_4$ catalyst (Run 1). However, CO conversion was less than 2% over the $\text{Cl}/\text{Fe}_3\text{O}_4$ catalyst without H_2 pretreatment (Run 2). Methane and $\text{C}_2\text{--C}_4$ olefin ($\text{C}_2^+ \text{--} \text{C}_4^+$) selectivities were 11% and 48%, respectively. Only a small amount of CO_2 was detected as a by-product (Run 1).

High CO conversion of about 20% was obtained over the chlorine-free magnetite catalyst (Fe_3O_4 ; Run 3). Substantial amount of methane, $\text{C}_2\text{--C}_5$ paraffins, and CO_2 were produced.

The results over other chlorine-containing magnetite catalysts are also summarized in **Table 1** (Run 4—6). Since the activity of each catalyst was different, GHSV was adopted in such a manner that the conversion, excluding CO_2 could be adjusted in the range of 5—20%. Lower selectivity to light olefins and higher selectivity to methane were observed over the magnetite catalyst prepared by ammonium co-precipitation ($\text{NH}_3 \downarrow \text{Fe}_3\text{O}_4$; Run 4) and over the catalyst prepared from akaganeite ($\beta\text{-FeOOH}$; Run 6) than those over the $\text{Cl}/\text{Fe}_3\text{O}_4$

Table 1 Hydrogenation of Carbon Monoxide over Chlorine-Containing Magnetite Catalysts in Slurry Phase

Run	1	2	3	4	5	6
Catalyst Preparation	Cl/Fe ₃ O ₄ reflux	Cl/Fe ₃ O ₄ reflux	Fe ₃ O ₄ air-oxidation	NH ₃ ↓Fe ₃ O ₄ ammonium coprecipitation	Cl-Fe ₃ O ₄ chloridized	β-FeOOH akaganeite
H ₂ Treatment ^{a)} (°C)	400	—	—	—	350	350
GHSV (hr ⁻¹)	2,000	2,000	2,000	2,000	1,000	5,000
CO Conv. (%)	8.6	1.6	19.6	21.1	6.0	8.7
CO ₂ Yield (%)	0.4	0.1	4.8	3.8	0.1	1.5
Selectivity (C-%)						
CH ₄	11.1	— ^{b)}	21.5	16.5	11.3	22.5
C ₂ H ₄	10.9	—	4.8	7.7	10.5	7.6
C ₂ H ₆	3.5	—	11.9	5.3	1.4	8.7
C ₃ H ₆	20.6	—	16.5	16.4	17.0	15.8
C ₃ H ₈	1.4	—	5.2	1.6	0.9	3.0
C ₄ H ₈	16.8	—	9.0	10.5	11.6	7.7
C ₄ H ₁₀	1.1	—	1.8	1.0	0.7	1.6
C ₅ H ₁₀	8.5	—	3.7	5.5	5.7	3.6
C ₆ H ₁₂	0.8	—	1.0	2.8	1.5	3.2
total	74.7	—	75.3	67.2	60.6	73.6
C ₂ -C ₄ Olefin	48.3	—	30.3	34.6	39.1	31.1
Paraffin/Olefin (C ₂ -C ₅)	0.12	—	0.59	0.27	0.10	0.48
Residual Cl in used Catal. (Cl/Fe)	0.002	0.07 ^{c)}	<0.001	0.01	0.01	0.003
BET Area (m ² /g)	32	32	37	15	18	14
Bulk Composition of used Catalyst Identified by XRD ^{d)}	⬤	⬤(s) ⬤(w)	⬤(s) ⬤(m)	⬤	⬤(s) ⬤(w)	⬤(s) ⬤(w)

Reaction conditions : $P=10$ atm, $T=325^{\circ}\text{C}$, $\text{H}_2/\text{CO}=1$.
a) The pretreatment was carried out outside the reactor.
b) The conversion was too low to calculate selectivity.
c) Chlorine content in the fresh catalyst.
d) ⬤, Fe₃O₄; ●, Fe-carbide; ⊕, FeOOH; s, strong; m, medium; w, weak.

catalyst. Over these catalysts the formation of CO₂ was generally depressed.

3.3 Analysis of Used Catalyst

The chlorine contents in the used catalysts were determined by X-ray fluorescence spectrometry, and the Cl/Fe atomic ratios of them are listed in **Table 1**. The chlorine content in the fresh Cl/Fe₃O₄ catalyst was found to be Cl/Fe=0.07 (Run 2). A trace amount of chlorine of Cl/Fe=0.002 still remained after the H₂ pretreatment followed by CO hydrogenation (Run 1). The residual chlorine contents in the other used catalysts (Run 4–6) were in the range of Cl/Fe=0.003–0.01.

The BET areas of the fresh catalysts were in the range of 14–37 m²/g.

The Cl/Fe₃O₄ catalyst was confirmed by XRD to maintain the magnetite structure even after H₂ pretreatment and CO hydrogenation (Run 1). The NH₃↓Fe₃O₄ catalyst and the chloridized catalyst (Cl-Fe₃O₄) were also found to maintain the magnetite structure after reaction (Runs 4 and 5). On the contrary, small peaks corresponding to iron carbides were detected by XRD in the used chlorine-free (Fe₃O₄ ; Run 3) and β-FeOOH (Run 6) catalysts.

3.4 XPS of Cl/Fe₃O₄

The XPS results corresponding to Fe 2p and Cl

2p bands of fresh and used Cl/Fe₃O₄ catalysts as well as of ferrous chloride, for comparison, are summarized in **Table 2**. The binding energies of Fe 2p_{3/2} and Cl 2p_{3/2} bands were corrected by using the C 1s band of adsorbed carbon on the samples as an internal standard at 285.0 eV. The binding energies of ferrous chloride were almost identical to those reported in literature^{9),10)}. The binding energies of Fe 2p_{3/2} of fresh and used catalysts indicate that the valency of Fe on the catalysts was approximately 3. The Cl 2p_{3/2} bands of these catalysts, on the other hand, shifted toward lower binding energy side than the band of ferrous chloride by 0.6–0.9 eV. This shift suggests that the valence state of chlorine on the catalysts was almost the same as that of alkali halides¹¹⁾, and that the chlorine was more negatively charged than that of iron chlorides.

From the peak intensity ratio (Cl/Fe), the surface concentration of chlorine of the Cl/Fe₃O₄ catalyst is estimated to be Cl/Fe=0.1–0.2 (atomic ratio) including the experimental errors, as shown in **Table 2**. The value was higher than the chlorine contents determined by X-ray fluorescence spectrometry. After H₂ pretreatment and reaction, the surface concentration did not change so much as the inside concentration, which decreased from

Table 2 Binding Energy and Surface Concentration of Chlorine on Cl/Fe₃O₄ Catalysts

	Binding Energy*		Cl/Fe		Literature
	Fe 2p _{3/2}	Cl 2p _{3/2}	peak intensity ratio	surface concentration (atomic ratio)	
Fresh Catalyst (before H ₂ pretreatment)	711.4 eV	198.4 eV	0.06	0.16±0.05	
Used Catalyst FeCl ₂ (this study)	711.4	198.7	0.05	0.13±0.05	
	710.5	199.3	0.89	2.3 ±0.6	
FeO	710.3				8)
Fe ₂ O ₃	711.4				8)
	711.5				9)
FeOOH	711.0				8)
FeCl ₂	710.8	199.0			9), 10)
FeCl ₃	711.5	199.2			9), 10)
LiCl		198.7			11)
NaCl		198.4			11)
KCl		198.3			11)

* Values referenced to adsorbed carbon with C 1s=285.0 eV.

Fig. 1 Selectivity to Methane (●) and to C₂-C₄ Olefins (○) against Selectivity to the Total Gaseous Hydrocarbons over Magnetite Catalysts in Table 1

Cl/Fe=0.07 to 0.002, as mentioned above.

4. Discussion

4.1 Product Pattern

When the selectivities to methane and C₂-C₄ were plotted against the selectivity to gaseous hydrocarbons (C₁-C₅), the results in Table 1 could be depicted as shown in Fig. 1. As for the results over Cl/Fe₃O₄ and Cl-Fe₃O₄ (Runs 1 and 5, Fig. 1), each point was almost aligned on the same line extrapolated to 100% of gaseous hydrocarbons, the intercepts at 15% and 65% indicated the selectivities to methane and C₂-C₄ in the gaseous hydrocarbons, respectively.

By applying the same analysis to other catalysts, deviations from the lines indicated that the product patterns on the catalysts were different from the

pattern on the Cl/Fe₃O₄ catalyst¹²⁾, and that the selectivity to methane was higher, and the selectivity to C₂-C₄ was lower for the other catalysts than for the above two catalysts.

Thus, by this analysis, the catalysts could be classified into two groups, Runs 1 and 5 (group 1), and Runs 4 and 6 (group 2). The hydrogenation activity was higher for group 2 than for group 1.

In any case, the selectivity over the chlorine-containing magnetite catalysts was characterized as follows :

- 1) Only a trace amount of CO₂ was produced as a by-product.
- 2) Methane formation was suppressed.
- 3) Selectivity to gaseous hydrocarbons was high. Consequently,
- 4) Relatively high selectivity to light olefins was accomplished.

And these characteristics were distinctive over the Cl/Fe₃O₄ catalyst. The lower selectivity to olefins for group 2 catalysts indicated that chlorine might not be distributed uniformly on the surface of the catalyst, and the chlorine distributed inside catalyst was not so effective for improving the olefin selectivity as group 1 catalysts.

4.2 Oxidation State of Catalyst and Olefin Selectivity

Iron carbides were scarcely detected by XRD in the used catalysts belonging to group 1. On the other hand, some of the catalysts of group 2 were carburized during the reaction. It is suggested that, based on this result and the product pattern, paraffin selectivity correlates to the carburization of the catalyst. It is reported that metallic iron is rapidly carburized during the reaction, and that methane selectivity is high on

The lines are predicted by the Schulz-Flory polymerization law at $\alpha=0.6$, 0.65 and 0.7 , respectively.

Fig. 2 Schulz-Flory Plot over $\text{Cl}/\text{Fe}_3\text{O}_4$ Catalyst

the surface.⁷⁾

The XPS results of the $\text{Cl}/\text{Fe}_3\text{O}_4$ catalyst showed that the chlorine on the catalyst surface was more negatively charged than that of iron chloride, and that the electron density of Fe on the surface decreased. The $\text{Cl}/\text{Fe}_3\text{O}_4$ catalyst was not easily reduced to metallic iron by H_2 treatment. These results indicate that the surface of the catalyst was maintained by chlorine to be oxidative.

Carbon dioxide, a by-product, was hardly produced over the catalyst. It is implied that the water gas shift reaction (WGSR) was prevented by chlorine. It is reported that WGSR can proceed only when the surface iron can be partially reduced by CO .¹³⁾ Low yield of CO_2 supports the fact that over-reduction of the surface is prevented.

The same effect of halogen is also reported on Rh catalysts in CO hydrogenation to acetic acid, where Rh was not metallic but in a low valence state ($+1\sim 2$) maintained by halide ion. These catalysts improved selectivity to acetic acid to 76% and suppressed the formation of highly hydrogenated products, such as methane, ethanol and acetaldehyde.¹⁴⁾ This suppression is considered stemming from reduction in the hydrogenation activity of the catalysts.

Basing on these results, the high selectivities to olefins of the chlorine-containing magnetite catalysts reflect their low hydrogenation activities brought about by their surface chlorine. The suppression of methane formation may be explained in the same way. Fujimoto et. al. proposed the same

explanation for the increase in olefin selectivity by silica-supported Rh catalysts by addition of halides to or HCl treatment of the catalysts.¹⁵⁾

4.3 Molecular Weight Distribution

The product distribution over $\text{Cl}/\text{Fe}_3\text{O}_4$ catalyst was depicted in Fig. 2. The selectivity to C_3 and C_4 deviated upward from the line predicted by the Schulz-Flory distribution rule. Since the cracking of the slurry solvent was almost negligible, the deviation cannot be attributed to cracking. Such high selectivity could not be realized in a fixed-bed reactor, as reported earlier.³⁾ The uniform surface temperature of the catalyst in the slurry phase is considered to be the main reason for such high selectivity. Hot spots in fixed-bed system may induce partial desorption of the surface chlorine to reduce selectivity.

The $\text{Cl}/\text{Fe}_3\text{O}_4$ catalyst was hardly carburized during the reaction in the slurry phase as shown in Table 1. This result suggests that the surface of the catalyst is maintained unchanged and side reactions scarcely occurred. Thus, the high selectivity of the $\text{Cl}/\text{Fe}_3\text{O}_4$ catalyst was attained in the slurry phase.

The reaction temperature in this study was higher than the conventional FT reaction over iron type catalysts.²⁾ It is reported that high temperatures are desirable for increasing the selectivity to light hydrocarbons.¹⁶⁾ Metallic iron catalysts are, however, unstable at high temperatures, and they are rapidly converted into carbides and lose their FT activity.¹⁾ On the contrary, magnetite catalysts can be used at high temperatures provided the iron in the catalysts is maintained to be oxidative.⁷⁾ The role of the chlorine in the catalysts is, then, to maintain the oxidation state of the catalyst surface.

Another role of the chlorine may be assumed in limiting the product distribution. The electronic effect, which was ascertained by XPS, of the chlorine is in the opposite direction to that of potassium promoters as is generally accepted.¹⁷⁾ Potassium promoters are electron donative, whereas chlorine is electron attractive. It is well known that the product distribution shifts toward higher molecular weights by the addition of potassium salts to FT catalysts. For a similar reason, the selectivity to light hydrocarbons might increase in the opposite direction over the $\text{Cl}/\text{Fe}_3\text{O}_4$ catalyst. The increase in the light hydrocarbon selectivity is also reported in some patents when easily decomposable halides were added to syngas¹⁸⁾ or when the catalysts were

treated with chlorides.^{19),20)}

Thus, high selectivity to C₃–C₄ over the catalysts was accomplished by the two effects of chlorine (the limitation of product distribution and the suppression of methane formation), as mentioned above. The detailed characterization of the chlorine on the surface of the catalyst is now in progress, and it will be reported in another paper.

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要 旨

スラリー法による塩素含有マグネタイト触媒上での
一酸化炭素の軽質オレフィンへの水素化

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金属鉄の存在下で塩化第二鉄水溶液を還流することによって得られるマグネタイト⁴⁾を 400°C で水素処理したもの(以下, Cl/Fe₃O₄ と略)を触媒として用い, スラリー法で Fischer-Tropsch (FT) 反応を行った。反応条件は, $T=325^{\circ}\text{C}$, $P=10\text{ atm}$, $\text{GHSV}=1,000\sim5,000\text{ hr}^{-1}$, $\text{H}_2/\text{CO}=1$ とし, 前報⁷⁾で述べた方法により, 生成物の分析を行った。反応気体に添加した Ar を内部標準として, CO 転化率および炭素数基準の選択率を求めた (Eqs. (1)~(3))。また, 他の方法で調製した塩素含有マグネタイト触媒とも比較した。

触媒に含まれる塩素の酸性により, スラリー媒体のクラッキングが起り, 反応結果に影響することが懸念されるが, ブランク試験の結果, 反応条件の範囲内では, この影響はほとんど無視できることがわかった。

塩化鉄から還流法で調製したマグネタイトには, 原料に起因する塩素の残留が認められ, その量は Fe に対する原子比で 0.07 程度であった。このままのマグネタイト触媒は残留塩素の毒作用によってほとんど活性を示さないが, 400°C で水素処理することにより触媒中の塩素が 0.002 程度にまで除かれ, 活性が得られた。この触媒上では, 他の方法で調製した塩素含有マグネタイト触媒よりも高い低級オレフィン (C₂~C₄) 選択率 (48%) が得られた。また, CO₂ の副生がほとんどなく, メタンの生成が 11% にまで抑制され, 気相炭化水素選択率が高かった。なお, 反応後のこの触媒のバルクの組成は, Fe₃O₄ のままであった (Table 1)。

反応前後における Cl/Fe₃O₄ 触媒の Fe 2p および Cl 2p に対応する XPS の測定結果から, 反応前後とも, 触媒表面の塩素の電子密度は塩化鉄よりも大きく, Fe の電子密度を減少させていることが示唆された。また, 水素処理および反応の前

後で触媒バルクの塩素量は大きく変化するにもかかわらず, 触媒表面の塩素濃度はほぼ一定で, Cl/Fe=0.1~0.2 程度と推定された。この値は, バルクの塩素量よりはるかに大きいといえる (Table 2)。

メタン選択率あるいは C₂~C₄ 選択率を気相炭化水素選択率に対してプロットするという解析法¹²⁾を用い, 生成物パターンを比較した。その結果, 塩素化したマグネタイト触媒 (Cl-Fe₃O₄) は Cl/Fe₃O₄ 触媒と類似した生成物パターンを有するが, 他の塩素含有マグネタイト触媒は異なるパターンを示すことが見いだされた (Fig. 1)。

塩素含有マグネタイト触媒では, 水性ガス転化反応がほとんど進行しないこと, および, 400°C の水素処理でも触媒が金属鉄まで還元されないこと, さらに, XPS の結果等から, 塩素の電子吸引効果により, 触媒表面が金属的になりやすく, 水素化能が低下して, メタンをはじめとするパラフィン生成が抑制されたものと思われる。

Cl/Fe₃O₄ 触媒では Schulz-Flory 則から予測される値よりも高い C₃ および C₄ 選択率が得られた (Fig. 2)。その原因として, まず, スラリー法で反応を行ったため触媒層温度が均一に保たれ, 副反応や塩素の部分的な脱離が防止できたことが考えられる。さらに, 残留塩素の効果により触媒表面が金属的になりやすく, 高温での反応が可能で, そのために, 生成物分布が低分子側に偏ったものと思われる。また, 塩素の電子的効果はカリウムとは逆方向であり, したがって, 分子量分布が低分子側に偏ったものと思われる。その上, 残留塩素に起因する水素化能抑制によりメタン生成が抑制されたため, 高い低級オレフィン選択率が得られたのであろう。

Keywords

Carbon monoxide, Chlorine, Fischer-Tropsch synthesis, Light olefin, Magnetite, Slurry phase