Syngas Conversion on Calcined Fe-Ti-Zn-K Catalysts (Part 2)

Direct Conversion of Synthesis Gas to Light Olefins in the Slurry Phase[†]

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Roles of calcination temperature of Fe-Ti-Zn-K catalysts in the Fischer-Tropsch reaction were investigated in the slurry phase under a pressure of 10 atm at a temperature in range from 300 to 325°C and H₂/CO ratio of 1. A stable activity with selectivity for ethylene and propylene of 24–25% was obtained when the catalyst was calcined at a higher temperature than 800°C, and deactivation took place below this temperature. Changes in bulk component of the catalysts by calcination, reduction and reaction were followed by X-ray diffraction. The surface concentration of titanium on the catalyst determined by XPS increased with calcination temperature, although the bulk composition determined by X-ray fluorescence spectroscopy hardly changed. It was deduced from these findings that the catalysts calcined at higher temperature than 800°C was covered with hardly reducible shell containing titanium, which stabilized the active sites on the surface by prevention of carburization. And it was suggested that magnetite (Fe₃O₄) phase stabilized by the irreducible shell was responsible for the reaction at stationary state.

1. Introduction

It is well known that the product distribution of the Fischer-Tropsch (FT) reaction in most cases obeys the Schulz-Flory polymerization rule, which makes it difficult to obtain a certain range of hydrocarbons selectively, although many efforts have been made to find a catalyst with high selectivity.^{1),2)} Selective FT catalysts for light olefins include:

- 1) Chemical modification of conventional FT catalysts³⁾,
- 2) Regulation of metal particle sizes in the catalysts⁴⁾, and
- 3) Combination of a FT catalyst and a support with shape selective properties such as a zeolite.⁵⁾

A calcined Fe-Ti-Zn-K catalyst developed by

Ruhrchemie A.G.,⁶⁾ which belongs to category (1) mentioned above, is reported to be one of the most selective FT catalysts for light olefins. The catalyst is prepared by sintering a homogeneous mixture of iron oxide, titanium oxide, zinc oxide and potassium carbonate in the weight ratio of Fe: Ti: ZnO: K₂O of 100: 10–50: 5–15: 3–5 at 1,050°C for several hours, followed by reduction at 500°C for several hours. Ethylene and propylene are obtained with more than 50% selectivity in hydrogenation of carbon monoxide on the catalyst at 340°C, 10 atm and GHSV = 500 hr⁻¹ with CO conversion of 87%. The catalyst is, however, not described in detail in the patent.

It is of interest to characterize the catalyst, which is supposed to have complicated chemical structure and various phases of oxides which are difficult to be defined unequivocally. The purpose of the present investigation is to elucidate the effects of calcination on the properties of the catalyst. Changes in the bulk and surface composi-

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tion of the catalyst by calcination, reduction and reaction were tracked by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and X-ray fluorescence spectroscopy (XRF). In order to evaluate such a complicated catalyst appropriately, hydrogenation of carbon monoxide was carried out in a slurry reactor, by which reaction temperature on the catalyst surface is precisely controlled.^{7)~9)}

2. Experimental

2.1 Preparation of Catalysts

A mixture of Fe₂O₃, TiO₂, ZnO and K₂CO₃ in the weight ratio of Fe: Ti: ZnO: K₂O=100: 25: 10: 4 was thoroughly homogenized by using a kneader and a ball mill, and was pressed into pellets. The pellets were calcined at a temperature from 600 to 1,200°C, for 15 hr, and used as a catalyst after being crushed into fine powder passing 60 mesh.

2.2 Procedure

Fifteen ml of the catalyst was reduced at 450°C for 10 hr, and suspended in a 250 ml of paraffin liquid (bp. 330–390°C) into a slurry under an oxygen free atmosphere. A semi-batch type slurry reactor (flow type for gas phase) was charged with the slurry of the catalyst prepared above. A reaction gas mixture of H₂: CO: Ar=45: 45: 10 was bubbled into the slurry from the bottom of the reactor, and was mixed with it sufficiently by compulsive stirring. Reaction conditions were as follows; $T=300\text{--}325^\circ\text{C}$, $P=10$ atm, GHSV=2,000 hr⁻¹. Reaction temperature was raised stepwise, and kept for 24 hr, respectively. Effluent gaseous products at the reaction condition was introduced into a gas-liquid separator held at 100°C and 2 atm. The gas phase was automatically analyzed by an on-line gas chromatograph (purchased from Yanagimoto Mfg., model AG 1000 TFH). All of hydrocarbons with carbon number less than 6 and light alcohols in the product gas were determined with an accuracy of $\pm 0.01\text{--}0.1\%$.

Conversion and carbon-based selectivity were calculated on the basis of argon concentration in the reaction gas as an internal standard. CO conversion is expressed by the following equation,

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

where $[\text{Ar}]$ and $[\text{CO}]$ are the concentration of Ar and CO in the effluent gas, and $[\text{Ar}]^\circ$ and $[\text{CO}]^\circ$ are the initial concentration of Ar and CO in the reaction gas. In this manner, CO conversion can

be accurately evaluated, even though all of the carbonaceous products are not determined. Yield of the product with carbon number n (C_n yield) is expressed by the following equation,

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

where $[C_n]$ is the concentration of the product with carbon number n in the effluent gas. Carbon based selectivity for the C_n product (excluding CO₂) is consequently given from the above equations as follows,

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

In order to evaluate decomposition of paraffin liquid at the reaction conditions, a blank test on the catalyst was performed in which hydrogen instead of syngas was used as reaction gas. Any appreciable amount of gaseous hydrocarbons was not detected at all.

2.3 Analysis of Catalysts

Fresh and used catalysts were identified by using an X-ray diffractometer (Rigaku Electric Co., Ltd., model Geigerflex RAD). Elemental analysis of the catalysts was performed with an X-ray fluorescence spectrometer (Philips, model PW1410). Surfaces of the catalysts were analyzed by an X-ray photo-electron spectrometer (Shimadzu Mfg., model ASIX). A scanning electron microscope (SEM) was employed for observation of the catalyst surfaces. Surface areas of the catalysts were determined by adsorption of argon at liquid nitrogen temperature by using a full-automatic surface area analyzer (Shimadzu Mfg., model Micromeritics 2200).

3. Results

3.1 Hydrogenation of Carbon Monoxide

Figure 1 shows time course of hydrogenation of carbon monoxide at 325°C, 10 atm and GHSV=2,000 hr⁻¹ on catalysts calcined at a temperature of 600–1,200°C, after the reaction at 300°C for 24 hr. A time course of the reaction in a fixed bed at GHSV=5,000 hr⁻¹ on a catalyst calcined at 1,000°C is also illustrated in the same figure for comparison. Although a slight deactivation was observed at the earliest stage, the activity on the catalyst in the slurry phase was generally stable during the time on stream, except for the catalyst calcined at 600°C, in comparison with the reaction in the fixed bed reactor. Further, the conversion at stationary state decreased monotonously with increasing calcination temperature, except for the catalyst calcined at 600°C.

Table 1 Results of CO Hydrogenation in the Slurry Phase on Fe-Ti-Zn-K Catalysts Calcined at Various Temperature

Calc. Temp. (°C) React. Temp. (°C)	600		800		900		1,000		1,200	
	300	325	300	325	300	325	300	325	300	325
CO Conv. (%)	42.1	32.1	32.0	36.5	18.8	30.3	14.9	16.7	1.3	3.3
CO ₂ Yield (%)	20.4	15.7	14.9	17.3	7.6	14.2	5.7	7.3	0.5	1.5
Selectivity (C-%)										
CH ₄	5.4	14.6	9.2	14.8	7.5	14.4	6.2	11.2	—	9.8
C ₂ H ₄	6.8	6.4	7.5	8.4	5.6	8.3	5.0	9.0	—	9.6
C ₂ H ₆	1.1	1.7	6.6	5.8	4.9	8.2	1.2	2.7	—	0.0
C ₃ H ₆	5.6	6.2	13.3	16.0	11.6	16.8	7.9	14.6	—	10.4
C ₃ H ₈	0.6	1.0	2.3	2.0	1.9	2.7	0.9	1.6	—	2.2
C ₄ H ₈	4.3	4.3	10.2	12.2	8.3	11.9	6.2	12.4	—	4.8
C ₄ H ₁₀	0.6	0.8	1.6	1.4	1.3	1.6	0.8	1.4	—	2.4
C ₅ H ₁₀	3.2	2.8	6.0	6.9	4.5	5.9	4.8	7.6	—	—
C ₅ H ₁₂	0.7	0.5	1.2	1.0	1.0	1.1	0.4	0.9	—	—
Total	28.3	38.3	57.9	68.5	46.5	70.9	33.4	61.4	—	39.2
Carbon Residue on Used Catal. (wt%)	19.1		5.3				1.9		1.6	
Surface Area of Fresh Catal. (m ² /g)	5.2		3.5		2.2		1.2		0.1	

$P=10$ atm, $GHSV=2,000$ hr⁻¹, $H_2/CO=1$

○, calcined at 600°C; ◐, calcined at 800°C
 ○, calcined at 900°C; ●, calcined at 1,000°C
 △, calcined at 1,200°C;
 ▼, calcined at 1,000°C (reaction in a fixed bed,
 $GHSV=5,000$ hr⁻¹).

Fig. 1 Time Course of CO Hydrogenation on Fe-Ti-Zn-K Catalysts at 325°C, 10 atm and $GHSV=2,000$ hr⁻¹ in a Slurry Reactor (Except for ▼)

Detailed reaction results at stationary state are given in **Table 1**. As for conversion, it is noticed that a decrease on the catalyst calcined at 600°C was observed when reaction temperature was raised from 300 to 325°C, which clearly indicates that a deactivation occurred on the catalyst at higher reaction temperature. Selectivity for light hydrocarbons (C₁–C₅) at reaction temperature of 325°C was generally higher than that at 300°C. The selectivity on the catalyst calcined at 600°C was low even when the reaction temperature was raised to 325°C. Selectivity for ethylene and propylene at 325°C was almost constant within a

range of 24–25% on the catalysts calcined at a temperature higher than 800°C, except for the case in that the conversion was too low to be worth discussing the selectivity.

Residual carbon on the used catalysts were determined after the catalysts were rinsed with *n*-hexane, THF and ethyl ether, and dried in air. A remarkable amount of carbon was detected on the used catalyst calcined at 600°C, as listed in **Table 1**.

The catalysts before and after hydrogen treatment at 450°C were observed with a scanning electron microscope. The shapes of catalyst particles were almost unchanged by reduction. The particle sizes increased with the calcination temperature. A remarkable sintering was also tracked by BET areas of the catalysts as given in **Table 1**.

3.2 X-Ray Powder Diffraction (XRD) of the Catalysts

X-Ray powder diffractograms of the catalysts before and after reduction as well as after reaction are illustrated in **Fig. 2**. The main peaks of as-made catalysts (before reduction) corresponded to those of hematite (Fe₂O₃) regardless of the variation of calcination temperatures (**Fig. 2-a**). Minor peaks of pseudobrookite (Fe₂TiO₅) were also observed in the catalysts calcined at higher temperatures, of which intensity increased with the temperature. Besides these peaks, small peaks of rutile (TiO₂) were detected.

Peaks corresponding to magnetite (Fe₃O₄) were observed in every reduced catalyst (**Fig. 2-b**). Peaks of metallic iron were intensified in the catalyst when calcination temperature was low.

Although peak intensity of magnetite in used

Fig. 2-a X-Ray Diffractograms of As-Made Fe-Ti-Zn-K Catalysts calcined at (1), 600°C; (2), 800°C; (3), 1,000°C and (4), 1,200°C

Fig. 2-b X-Ray Diffractograms of Reduced Fe-Ti-Zn-K Catalysts Calcined at (1), 600°C; (2), 800°C; (3), 1,000°C and (4), 1,200°C

catalysts were almost identical to that in the corresponding fresh catalysts (after reduction), peaks of metallic iron disappeared with being replaced by those of iron carbides (**Fig. 2-c**). The intensity of the carbide peaks in the used catalysts corresponded to that of disappeared peaks of metallic iron in the fresh one, semiquantitatively.

A spacing distance $d(311)$ of magnetite contained in the used catalysts (the corresponding peak was at about $2\theta=35.5^\circ$ in **Fig. 2-c**) was precisely determined by X-ray diffraction by using silicon powder as an internal standard. Spacing

Fig. 2-c X-Ray Diffractograms of Used Fe-Ti-Zn-K Catalysts Calcined at (1), 600°C; (2), 800°C; (3), 1,000°C and (4), 1,200°C

Fig. 3 Effect of Calcination Temperature on Spacing Distance $d(311)$ of Magnetite in Used Catalysts

distances were plotted against the calcination temperatures as shown in **Fig. 3**. The distance tended to increase with temperature with a correlation factor of 0.71, although some scatter might be seen in the data.

3.3 Bulk and Surface Composition of the Catalysts

Bulk composition of the catalysts before and after calcination determined by X-ray fluorescence spectroscopy are listed in **Table 2**. Bulk composition scarcely changed by calcination. Only the amount of potassium tended to decrease a little with increasing calcination temperature.

On the contrary, the surface composition, determined by XPS, largely changed with calcination temperature, as listed in **Table 3**, where

Table 2 Bulk Composition of Calcined Fe-Ti-Zn-K Catalysts

Calc. Temp. (°C)	—	600	800	1,000	1,200
Fe ₂ O ₃ (wt%)	71.8	72.8	72.2	72.8	72.5
TiO ₂	21.0	20.5	20.9	20.6	21.1
ZnO	5.1	4.7	4.8	4.7	4.8
K ₂ O	2.1	2.0	1.9	1.8	1.6

Table 3 Surface Composition of Calcined Fe-Ti-Zn-K Catalysts after Reduction

Calc. Temp. (°C)	—	600	800	1,000	1,200
Fe	100	100	130	120	80
Ti	100	210	250	280	380
Zn	100	100	60	40	5
K	100	60	40	50	60

Relative amount based on un-calcined catalyst

the values are relative to those of the catalyst before calcination. Surface concentration of zinc decreased by calcination, and it was almost diminished when the catalyst was calcined up to 1,200 °C. The amount of iron on the surfaces did not change so much, although that of titanium increased monotonously with calcination temperature. Surface concentration of potassium by calcination was almost unchanged.

4. Discussion

4.1 CO Conversion and Surface Area of Catalysts

A good correlation between surface area of the catalysts and CO conversion was observed at reaction temperature of 300°C, as shown in **Fig. 4**. On the contrary, the catalyst calcined at 600°C was deactivated during reaction at 325°C, in succession to the reaction at 300°C for 24 hr. As illustrated in **Fig. 2-b**, intensive peaks of metallic iron were observed in the diffractograms of the fresh catalysts calcined at 600°C and 800°C, respectively. Peaks of iron carbides were observed in place of metallic iron in the diffractograms of the used catalysts. These results suggest that most of the metallic iron in the fresh catalysts were turned to iron carbides during reaction. It is well known that, at the reaction conditions studied, iron carbides are easily decomposed into metallic iron and carbonaceous material, which leads to a deactivation of the catalyst. A large quantity of metallic iron in the fresh catalyst calcined at 600°C is supposed to be a main reason for the deactivation at 325°C, which corresponded to the remarkable amount of residual carbon on the used catalyst. Although a large amount of heat can be evolved during reac-

Fig. 4 CO Conversion at 300°C (●) and at 325°C (○) against Surface Area of Fe-Ti-Zn-K Catalysts Calcined at Various Temperature

tion at high conversion on the catalyst with high surface area, local heating, which often leads to deactivation, is negligible in the present case because a slurry reactor was employed.

4.2 Selectivity

Selectivities for ethylene and propylene, for total C₂+C₃ (ethylene+ethane+propylene+propane) and for methane were plotted against selectivity for total gaseous hydrocarbons (C₁-C₅) in **Figs. 5-a** and **5-b**. Results on the catalyst calcined at 1,200°C were omitted in the figure because the conversion was too low to be worth discussing selectivity. Results in the reaction at 300°C show that selectivity for the gaseous hydrocarbons was varied from 30 to 60% with the calcination temperature of the catalysts. Although conversion was smoothly varied with calcination temperature as shown in **Fig. 4**, product distribution changed obviously on these catalysts. In the reaction at 325°C, results on the catalysts calcined at 800°C, 900°C and 1,000°C were almost identical whereas selectivity for the gaseous hydrocarbons was much lower on the catalyst calcined at 600°C than on the others.

When a line connecting each point and the origin in **Fig. 5-a** is extrapolated to 100% of the gaseous hydrocarbon, the intercept indicates the selectivity in the gaseous hydrocarbons. Points in **Fig. 5-a** are mostly aligned in 3 lines respectively. The selectivity for total C₂+C₃, for methane and for ethylene and propylene in the gaseous hydro-

Fig. 5-a Selectivity for Methane (Δ), for Ethylene and Propylene ($\bullet$) and for Total C_2+C_3 ($\circ$) against Selectivity for the Total Gaseous Hydrocarbons in the Reaction at 300°C on Fe-Ti-Zn-K Catalysts Calcined at Various Temperature

Fig. 5-b Selectivity for Methane (Δ), for Ethylene and Propylene ($\bullet$) and for Total C_2+C_3 ($\circ$) against Selectivity for the Total Gaseous Hydrocarbons in the Reaction at 325°C on Fe-Ti-Zn-K Catalysts Calcined at Various Temperature

carbons are about 50%, 15% and 37%, respectively. Since olefins such as ethylene and propylene are easily converted into paraffins, the selectivity for the olefins are slightly scattered in **Fig. 5-a**. Methane selectivity and total C_2+C_3 selectivity without such an unstable factor are in-

dependent of the calcination temperature. From these results, only selectivity for the total gaseous hydrocarbons changed at various calcination temperature, and each selectivity in the gaseous hydrocarbons could not be distinguished by the reaction at 300°C.

The results at reaction temperature of 325°C were analyzed in the same way. It is noticed that the selectivity for the gaseous hydrocarbons increased to 62% with an increase of selectivity for ethylene and propylene and for total C_2+C_3 in the reaction at 325°C on the catalyst calcined at 1,000°C. Although the results on the catalyst calcined at 600°C seemed to resemble those on the catalyst calcined at 1,000°C in the reaction at 300°C, the character of these catalysts were distinct from each other, by considering the reaction results at 325°C. Methane selectivity in the gaseous hydrocarbons on the catalyst calcined at 600°C increased when reaction temperature was raised from 300 to 325°C. Methane selectivity on the catalysts calcined at 800°C and 900°C increased slightly and that on the catalyst calcined at 1,000°C was almost unchanged, with increasing reaction temperature. Selectivity for total C_2+C_3 in the gaseous hydrocarbons tended to decrease to some extent on these catalysts, with increasing reaction temperature.

These results can be explained as follows: In the reaction at 300°C, majority of products other than C_1-C_5 on the catalyst calcined at 600°C were proved to be carbonaceous materials such as graphitic carbon and iron carbides, whereas those on the catalyst calcined at 1,000°C were hydrocarbons with high boiling points and oxygenates. When the reaction temperature was raised to 325°C, desorption rate of light hydrocarbons from the catalyst calcined at 1,000°C increased to give rise to an increase in selectivity for light hydrocarbons. On the catalyst calcined at 600°C, however, the methanation was promoted on surface iron carbides by an increase in reaction temperature, since the heavier materials on the catalyst were mainly graphitic carbon. By increasing reaction temperature from 300 to 325°C, a small increase in methane selectivity in the gaseous hydrocarbons on the catalyst calcined at 800°C was observed. This increase can be explained in connection with the fact that metallic iron phase was observed in **Fig. 2-b** (2). The results at 325°C clearly indicate that the character of the active sites depend on the calcination temperature,

although the difference could not be clarified by the reaction at 300°C.

4.3 Catalyst Composition and Stability

The peaks corresponding to $\text{Fe}_3\text{O}_4(311)$ were not split in the X-ray diffractograms of the used catalysts, as shown in **Fig. 2(c)**. From this fact, the shift of the peaks in **Fig. 3** indicates that the lattice constant increased with calcination temperature, and that titanium oxides were dissolved to magnetite (Fe_3O_4) phase to some extent in the catalyst calcined at a temperature higher than 800°C.

XPS results show that surface composition of the catalyst depends on the calcination temperature, though bulk composition determined by X-ray fluorescence spectroscopy was almost identical. In comparison with the catalyst calcined at 600°C, the catalyst calcined at 1,000°C is characterized by the surface concentrations rich in titanium and poor in zinc.

By taking these results into consideration, hardly reducible oxide containing titanium on the surface as well as in the bulk of the catalyst prevents iron oxides from over-reduction, which is supported by the fact that metallic iron phase was hardly found in X-ray diffractograms of freshly reduced catalysts calcined at 1,000°C and 1,200°C (**Fig. 2-b**

(3) and (4)). These results are in good agreement with the changes in selectivity of the catalysts. The catalyst of present investigation is characterized by calcination at a high temperature which decreases the content of free iron oxides in the catalyst by solid state reaction. By prevention of formation of free iron oxides, or metallic iron, a possibility of increasing selectivity for gaseous hydrocarbons containing $\text{C}_2 = + \text{C}_3 =$ with depression of methane formation can be seen.

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要 旨

焼結 Fe-Ti-Zn-K 触媒による合成ガス転化反応 (第2報)
スラリー法による合成ガスから軽質オレフィンへの直接転化反応

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合成ガスから低級オレフィンを直接合成する反応において、高転化率で高い選択率を示す触媒として、Ruhrchemie 社が開発した焼結 Fe-Ti-Zn-K 触媒⁹⁾ が知られている。しかし、この触媒は複雑な組成を有するのでその詳細は不明である。そこで、本報告ではこの触媒の焼成温度の効果をX線回折 (XRD) および XPS 法で検討した。併せて、反応温度制御が容易なスラリー法^{7)~9)} で反応を行った。

Fe : Ti : ZnO : K₂O の重量比が 100 : 25 : 10 : 4 となるようにそれぞれの酸化物あるいは炭酸塩を混合し、600~1,200°C の所定の温度で 15 時間焼成したものを触媒として用いた。触媒を粉碎し、450°C で 10 時間還元した後、流動パラフィンに懸濁させて、高圧流通式スラリー反応管を用いて反応を行った。反応条件は、300~325°C, 10 atm, GHSV=2,000 hr⁻¹, H₂/CO=1 とした。生成物は装置に直結したガスクロマトグラフで自動分析した。反応前後の触媒は、XRD, XPS 等で検討した。

800°C 以上で焼成した触媒では、スラリー法で反応を行うと、反応温度 325°C でも安定した活性と 24~25% のエチレン・プロピレン選択率が得られた。(Fig. 1, Table 1) 転比率は、一般に、焼成温度の高い触媒ほど低かった。600°C で焼成した触媒では、反応温度 325°C において活性劣化が見られ、また、このとき、低級炭化水素への選択率は低かった。

走査型電子顕微鏡を用いて、還元前後の触媒を観察したところ、還元による形状の変化は認められなかったが、高温焼成による粒子径の増大が見られた。

焼成時の触媒の X 線回折像は、主に、ヘマタイト相に対応するものであり、高温焼成のときには、このほかチタン酸鉄 (Fe₂TiO₅) 相の生成も認められた。(Fig. 2-a) 還元後の触媒では、いずれの場合もマグネタイト相が認められ、また、800°C 以下で焼成した触媒では金属鉄相が生成した。(Fig. 2-b) 反応後の触媒では、マグネタイトに対応するX線回折像はそのまま認められたが、金属鉄相のものは消失し、代わって炭化鉄が生成した。(Fig. 2-c) このとき、金属ケイ素を内部標準として、マグネタイトの *d* (311) に対応する面間隔を精密に測定したところ、800°C 以上で焼成すると面間隔の増大が認められた。(Fig. 3)

蛍光X線を用いて、焼成後の触媒のバルク組成を測定したところ、焼成温度による各成分濃度の変化は認められなかった。(Table 2) これに対して、XPS で測定した触媒の表面組成は

焼成温度により変化した。高温で焼成すると、チタン濃度が増大し、亜鉛濃度が減少した。(Table 3)

反応温度 325°C における、600°C 焼成触媒の活性劣化は、還元時に生じた金属鉄相と関連付けて理解できる。還元時に金属鉄相が生じた触媒では反応後に炭化鉄が生じることから、遊離の金属鉄は反応中に炭化し、さらに炭素質を遊離するので活性が劣化したものと思われる。

エチレン・プロピレンへの選択率、全 C₂, C₃ への選択率およびメタンへの選択率を、気相炭化水素 (C₁~C₅) への選択率に対してプロットすると、300°C の反応では、焼成温度によらず、それぞれの選択率はそれぞれ同一の直線に乗り、気相成分中に占める割合は、それぞれ約 37%, 50% および 15% であることがわかる。(Fig. 5-a) これに対して、325°C の反応では、同様のプロットをすると、600°C 焼成の触媒のみメタン生成の割合が高く、また、気相炭化水素への選択率が低いことがわかる。(Fig. 5-b) このように、300°C の反応では、一見、同じような結果を与える 600°C 焼成の触媒と 1,000°C 焼成の触媒ではあるが、325°C で反応を行うと、その性質が明らかに異なることがわかる。これは次のように説明できる。すなわち、300°C での反応生成物のうち 600°C 焼成の触媒では、気相炭化水素以外の生成物はほとんどグラファイトのような炭素質であり、一方、1,000°C 焼成触媒のそれは高沸点炭化水素であると仮定する。反応温度を 325°C に上げると、600°C 焼成の触媒上では、グラファイトや炭化鉄が生じているため、メタン生成反応が増大するものと思われる。一方、1,000°C 焼成の触媒上では、反応温度の上昇に伴って低級オレフィンの脱離が促進され、結果的に、低級オレフィン選択率が増大したものと思われる。

800°C 以上で焼成した触媒では、反応後の触媒に含まれるマグネタイト相の *d* (311) 面間隔が増大していることから、チタン成分が固溶しているものと思われる。また、触媒の表面およびバルクの組成分析の結果、高温で焼成した表面はチタンに富む層で覆われているものと思われる。この難還元性の表面層の形成は、バルクにおけるチタン成分の固溶とあいまって、触媒中の鉄成分が過度に還元することを抑制し、マグネタイトとして安定に保つのに寄与しているものと思われる。このため、高温で焼成した触媒は、高い反応温度においても炭化鉄を生成せず、安定な活性を維持するものと理解される。

Keywords

Carbon monoxide, Fischer-Tropsch synthesis, Hydrogenation, Iron catalyst, Light olefin, Slurry process