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# Effects of Various Gas-Pretreatments of the Fe Powder, Prepared by the Reduction of $FeI_2$ with Potassium Metal, on the Catalytic Properties in Fischer-Tropsch Synthesis

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Fischer-Tropsch (F-T) synthesis was carried out on the Fe powder catalyst prepared by the reduction of $FeI_2$ with potassium metal in refluxing tetrahydrofuran (THF). 1-Butene was obtained with 37 wt% selectivity and a rather high conversion of 12 wt% by an autoclave system at 553 K. After $H_2$-pretreatment of the Fe powder at 573 K, propylene was produced as the major product (15 wt% selectivity) under otherwise the same experimental conditions. In a conventional flow system with a stream of $H_2$, $H_2/CO$, and CO during a heat-up period of the reactor to 533 K, $C_3$, $C_4$, and $C_5$ olefins were produced as major products, respectively. The synthesized Fe powder contains 1.6 wt% of carbon, which may be produced by the decomposition of THF in preparation of the catalyst. During the gas-pretreatment of the Fe powder in the flow reactor, evolution of $CH_4$ $CO_2$, and CO was observed. The amount of carbon on the Fe powder produced after the gas-pretreatment varied with the pretreatment gas in the order, $CO > H_2/CO > H_2$. Quantitative X-ray photoelectron spectroscopy (XPS) analysis of the Fe powder surfaces indicates that a significant amount of carbonaceous species is accumulated during the F-T reaction, and that the accumulation of such species can be avoided by the $H_2$-pretreatment of the Fe powder. The change in surface properties by the gas-pretreatments is discussed in relation to the corresponding change of the product distribution in the F-T synthesis.

One of the most important research objects in Fischer-Tropsch (F-T) synthesis is the development of catalysts that primarily make it possible to obtain economically valuable products, such as low-molecular-mass olefins. Many noteworthy efforts have been made for this purpose, e.g., the encapsulation of active metal species into support cages[1,2] and the use of ultrafine metal powders.[3,4] In the previous reports,[5,6] we have demonstrated that the F-T reactions over Fe and Fe-Co powder catalysts, prepared by the reduction of metal halides with potassium metal in refluxing tetrahydrofuran (THF), yield 1-butene with more than 35 wt% selectivity and a rather high conversion of over 10 wt% in a batch autoclave system at 533—553 K. On the other hand, a Co powder catalyst, prepared by a similar procedure in THF, showed the ordinary Schulz-Flory type hydrocarbon distribution.[6]

This paper reports the effects of different gas-pretreatments of the Fe powder catalyst on the product distribution in the F-T reactions conducted in a conventional medium-pressure flow reactor and an autoclave system. We have examined also the change in the amount of carbonaceous materials on the catalyst surface upon the gas-treatments, which was analyzed by X-ray photoelectron spectroscopy (XPS).

## Experimental

**Preparation of Fe Powder.** The Fe powder catalyst was prepared in a three-necked flask by the reduction of $FeI_2$ ($5.1 \times 10^{-3}$ mol) with excess molten potassium metal ($2.1 \times 10^{-2}$ mol) in refluxing THF for 5 h under a flowing argon atmosphere. After completion of the reduction, methanol was added dropwise to the resulting THF solution to decompose the remaining potassium. The black Fe powder formed was stirred in purified methanol (250 mL) for 30 min under a dry nitrogen atmosphere to remove KI incorporated into the Fe powder. The Fe powder thus purified was dried at 383 K under vacuum overnight, prior to the use as a catalyst. Details of the preparation procedures were described elsewhere.[5,6]

**F-T Synthetic Conditions.** A typical procedure for the F-T synthesis in a flow reactor is as follows. The Fe powder catalyst (0.2 g) was wrapped with silica wool and placed in a stainless-steel basket which was set in the center of a stainless-steel reactor ($\phi$ 16 mm×250 mm). The reactor was heated at 5 K $min^{-1}$ up to reaction temperature (533 K) in flowing $H_2$, $H_2/CO$ (2/1 molar ratio), or CO at 1 atm and with the flow rate of 6 L $h^{-1}$. When the temperature of the reactor reached 533 K, the pretreatment gas was switched to $H_2/CO$ (2/1 molar ratio) to proceed the F-T process at 533 K under 8 kg $cm^{-2}$. The weight-flow ratio was fixed at 6 g-cat · h $mol^{-1}$. An exit line, which connected the reactor with a trap cooled by dry ice-acetone, was heated at 373 K using a ribbon heater.

The F-T process was carried out in a 100 mL autoclave containing the Fe powder catalyst (0.2 g) and a mixture of $H_2$ and CO ($H_2/CO=2.0$) at 553 K and 20 kg $cm^{-2}$. The detailed procedures for the F-T synthesis in the autoclave[5,6] and flow[10] systems have been described previously.

Gaseous products from the flow reactor were sampled intermittently from a sampling valve set just below the reactor and analyzed by GLC.[5,6] The condensed products in the trap and reactor, the latter of which was recovered by pentane washing, were analyzed by GLC.[5,6] The products from the autoclave system were recovered and analyzed by a similar manner to that described previously.[5,6]

**XPS Measurements.** XPS measurements were conducted with Mg$K_\alpha$ radiation (8 kV×30 mA) under $1 \times 10^{-6}$ Pa using a Shimadzu ASIX-1000 instrument. The XPS peak intensity was corrected by considering the photo-ionization cross section.[11] The detailed conditions for the XPS measurements were given previously.[12] Gas-treatments of Fe powder sample were conducted in a microreactor directly attached to the XPS instrument, by flowing $H_2$ and $H_2$/CO (2/1 molar ratio) at 573 K for 30 min and at 553 K for 1 min, respectively.

## Results and Discussion

**F-T Synthesis in the Autoclave System.** Table 1 shows the results of the F-T syntheses by the autoclave system with Fe powder catalysts at 553 K. The high selectivity for $C_4$ hydrocarbons (42 wt%) and the rather high total hydrocarbon yield (12 wt%) were attained over the Fe powder catalyst without $H_2$-pretreatment. Furthermore, $C_2$—$C_5$ hydrocarbons were produced with 79 wt% selectivity, which consisted mostly of 1-alkenes (over 83% selectivity). When Fe powder was pretreated in a stream of $H_2$ gas at 573 K for 1 h, a significant change in the hydrocarbon product distribution was observed (Table 1). The major fraction between $C_2$ and $C_5$ hydrocarbons was $C_3$ (18 wt% selectivity) and the selectivity for $C_2$—$C_5$ hydrocarbons and olefins decreased considerably, although the total hydrocarbon yield (11 wt%) was nearly the same and the olefins consisted of 1-alkenes.

**F-T Synthesis in the Flow System.** The results of the F-T synthesis in the flow reactor are summarized in Table 2. The values of the selectivity for $C_2$—$C_5$ hydrocarbons (over 72 wt%) and the total hydrocarbon yield (8—13 wt%) were approximately the same as those obtained by the autoclave system shown in Table 1. The major products varied with the pretreatment gas in the flow system; $C_5$, $C_4$, and $C_3$ hydrocarbons became the major products by the pretreatment of the catalyst with CO, $H_2$/CO, and $H_2$, respectively. These results were reproducible as regards to the product distribution and the hydrocarbon yield. The pretreatments with $H_2$/CO and $H_2$ in the flow system seem to correspond to the experimental conditions in the autoclave system without any pretreatment (heated under $H_2$/CO atmosphere) and with $H_2$-pretreatment, respectively. Thus, the same hydrocarbons are produced as the major products in the autoclave system with and without $H_2$-pretreatment as those in the flow system pretreated with $H_2$ and $H_2$/CO gases, respectively. However, the selectivity of $C_3$ hydrocarbons (33 wt%) and olefins in the flow system with the $H_2$-pretreatment are higher and lower than those in the corresponding autoclave system, respectively, although the reason of such differences has not been definite.

In order to examine the optimum experimental conditions for the selective production of $C_3$ hydrocarbons in the flow system, the reaction temperature was changed from 533 K to 573 K (Table 3). The higher temperature leads to an increase in the hydrocarbon yield (from 13 to 24 wt%) accompanied by decreased $C_3$ selectivity (from 33 to 23 wt%), while the selectivity for $C_2$—$C_5$ hydrocarbons remained high value at around

Table 1. F-T Synthesis in an Autoclave System[a]

| $H_2$ pretreatment[b] | Hydrocarbon yield/wt% | Hydrocarbon distribution/wt%[c] | | | | | |
|---|---|---|---|---|---|---|---|
| | | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6^+$ |
| No | 11.7 | 15 | 13 | 13 | 42 | 11 | 6 |
| | | | (88) | (88) | (88) | (83) | |
| Yes | 11.0 | 20 | 12 | 18 | 16 | 14 | 20 |
| | | | (83) | (86) | (84) | (74) | |

a) F-T reaction conditions: 553 K; $H_2$/CO (=2.0); 20 kg cm$^{-2}$. b) 573 K for 1 h in a flowing $H_2$ atmosphere. c) Value in parentheses is olefin selectivity (wt%).

Table 3. Effects of Temperature on F-T Products in a Flow System[a]

| Reaction temp/K | Hydrocarbon yield/wt% | Hydrocarbon distribution/wt%[b] | | | | | |
|---|---|---|---|---|---|---|---|
| | | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6^+$ |
| 533 | 12.8 | 10 | 10 | 33 | 18 | 11 | 18 |
| | | | (77) | (85) | (46) | (tr.) | |
| 553 | 15.6 | 12 | 13 | 27 | 19 | 15 | 14 |
| | | | (87) | (93) | (74) | (50) | |
| 573 | 24.3 | 16 | 14 | 23 | 20 | 14 | 13 |
| | | | (84) | (91) | (86) | (55) | |

a) $H_2$ was streamed during the heat-up period of the reactor. Other reaction conditions were the same as in Table 2. b) Value in parentheses is olefin selectivity (wt%).

Table 2. F-T Synthesis in a Flow System[a]

| Gas streamed[b] | Hydrocarbon yield/wt% | Hydrocarbon distribution/wt%[c] | | | | | | C content of Fe/wt% | |
|---|---|---|---|---|---|---|---|---|---|
| | | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6^+$ | E.A.[d] | Gas A.[e] |
| CO | 8.2 | 11 | 12 | 18 | 13 | 25 | 21 | 2.5 | 3.8 |
| | | | (89) | (85) | (85) | (49) | | | |
| $H_2$/CO | 12.4 | 11 | 14 | 20 | 22 | 17 | 16 | 1.6 | 2.5 |
| | | | (84) | (90) | (78) | (75) | | | |
| $H_2$ | 12.8 | 10 | 10 | 33 | 18 | 11 | 18 | 1.5 | 1.5 |
| | | | (77) | (85) | (46) | (tr.) | | | |

a) F-T reaction conditions: 533 K; $H_2$/CO (=2.0); 8 kg cm$^{-2}$; W/F=6 g-Fe h mol$^{-1}$. b) Gas streamed during heat-up period of a reactor at 5 K min$^{-1}$ to 533 K. c) Value in parentheses is olefin selectivity (wt%). d) Estimated by elemental analysis. e) Estimated by accumulated amounts of evolved gases (see Fig. 2).

70 wt%. With an increase in temperature, the selectivity of light fractions ($C_1$ and $C_2$ hydrocarbons) and heavy fractions ($C_6^+$ hydrocarbons) increased and decreased, respectively, in agreement with catalytic behavior reported for many F-T catalysts.[13] For $C_3$—$C_5$ hydrocarbons, however, selectivity of $C_3$ hydrocarbons decreased and that of $C_4$ and $C_5$ hydrocarbons remained almost constant. Such a unique product distribution of $C_3$—$C_5$ hydrocarbons demonstrates the character of the Fe powder catalyst.

Figure 1 shows the profiles of the total hydrocarbon yield and hydrocarbon product distribution with respect to the reaction time at 553 K. The hydrocarbon yield decreased to half of the initial value in 7 h and thereafter it remained constant. The hydrocarbon product distribution is essentially constant over the whole time period examined, as far as the following points are concerned; the $C_3$ hydrocarbons are produced as the major products and rather low selectivity for $CH_4$ and high selectivity for $C_2$—$C_5$ hydrocarbons are sustained.

**Presence of a Carbonaceous Overlayer on the Fe Powder.** The synthesized Fe powder was found to contain 1.6 wt% of carbon by elemental analysis. During the heat-treatment of Fe powder in an $H_2$-atmosphere at 573 K for 1 h, $CH_4$, $CO_2$, CO, and $C_2H_6$ were evolved with the amount of 40, 65, 28, and 0.07 $\mu$mol g-Fe$^{-1}$, respectively. Klabunde et al.[14] previously observed the evolution of $CH_4$, $CO_2$, $C_3H_8$, and small amounts of other hydrocarbon gases during the heat-treatment of Ni powder prepared by the condensation of Ni vapor in pentane. The gas evolution has been reported to result from a carbonaceous over layer formed by the decomposition of pentane used as a condensation solvent of Ni vapor.[14] Thus, a carbonaceous overlayer will also be produced by the decomposition of THF in the preparation of the Fe powder, because metal powders by the present procedures are known to be very reactive.[15]

The amount of carbon produced on the Fe powder after various gas-pretreatments in the flow system was estimated by elemental analysis (Table 2). The amount of carbon varied with the gas in the order, CO (2.5 wt%)>$H_2$/CO (1.6 wt%)>$H_2$ (1.5 wt%).

Profiles of gases evolved during those pretreatments are shown in Fig. 2. Carbon dioxide was mainly evolved during heat-treatments with CO and $H_2$/CO and the amount increased with an increase in temperature. Such profile of gas evolution suggests that accumulation of carbonaceous materials on Fe surfaces occurs by the Boudouard reaction ($2CO=C+CO_2$). At a high temperature around 523 K, a small amount of $CH_4$ was also detected even with pure CO-pretreatment in the absence of $H_2$, suggesting the presence of hydrocarbon species on the Fe surfaces. In the $H_2$ stream, CO was evolved at a rather low temperature region around 473 K and small amounts of $CO_2$ and $CH_4$ were detected at a high temperature region around 523 K. Evolution of CO and $CO_2$ indicates the presence of oxygen-containing carbonaceous species on Fe surfaces, which may be produced by the decomposition of THF during the preparation of the Fe powder catalyst and/or the oxidation of carbonaceous species by iron oxides during the heat-treatment (vide infra). The amount of carbon on Fe surfaces with various gas-pretreatments was also estimated by the accumulated amounts of evolved gases and listed in Table 2, where the same order is obtained as that estimated by the elemental analysis. The variation of the amount of carbon with the gas-pretreatment indicates carbon accumulation occurs by

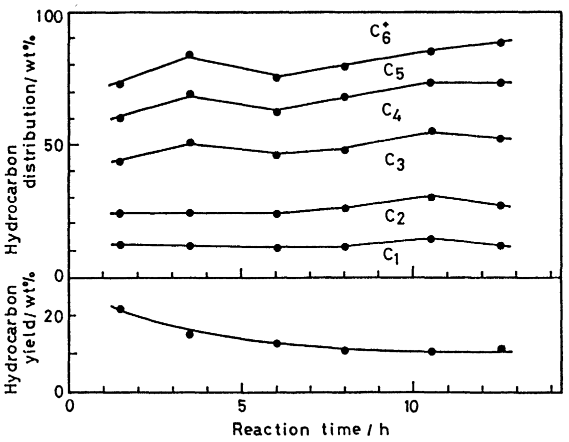

Fig. 1. Changes in the hydrocarbon yield and product distribution depending on F-T reaction time on a Fe powder catalyst. F-T reaction conditions: 553 K; $H_2$/CO (=2.0) 8 kg cm$^{-2}$; W/F=6 g-Fe·h mol$^{-1}$.

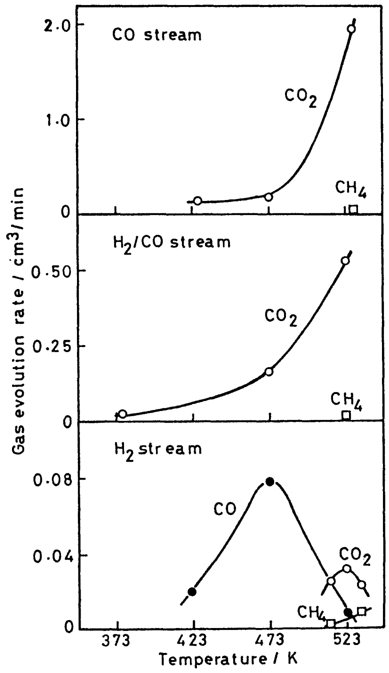

Fig. 2. Profile of gas evolved from Fe powder during the heat-up period of a reactor.

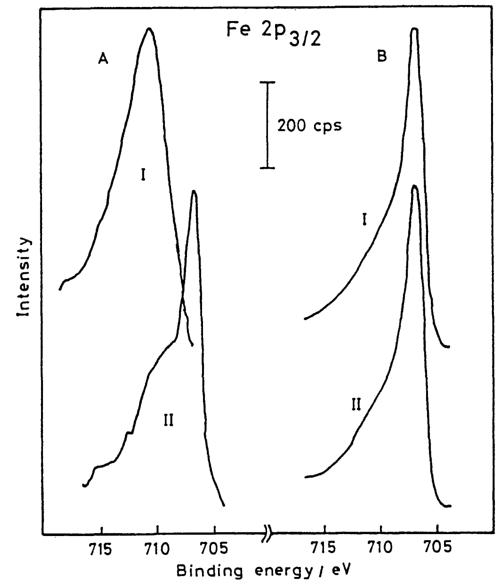

Fig. 3. Fe $2p_{3/2}$ XPS spectra of a Fe powder sample. A, a sample without $H_2$-pretreatment; B, a sample with $H_2$-pretreatment. I, a sample before exposure to $H_2$/CO; II, a sample after exposure to $H_2$/CO.

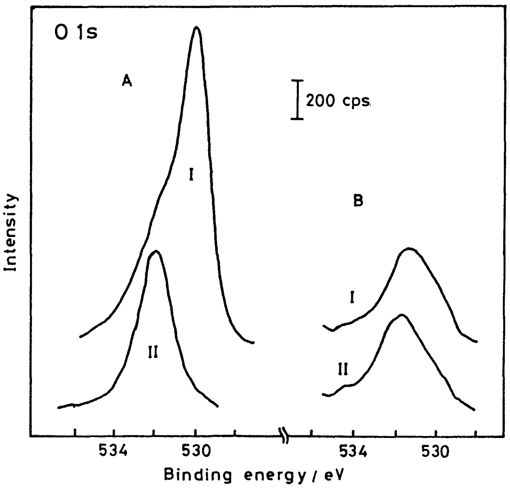

Fig. 4. O 1s XPS spectra of a Fe powder sample. Notations are the same as in Fig. 3.

the CO-pretreatment, whereas a part of the carbonaceous materials can be removed by the $H_2$-pretreatment.

**XPS Analyses of Fe Powder Surfaces.** The Fe $2p_{3/2}$ XPS spectra of the Fe powder catalyst before and after gas-pretreatments are shown in Fig. 3. The sample before the gas-treatment gives the Fe $2p_{3/2}$ line at 710.7 eV (Fig. 3 A-I), which agrees well with the reported binding energy values of $Fe_2O_3$ at 710.7 eV[9,16] and 710.8 eV,[17] indicating the presence of $Fe_2O_3$ layer on Fe powder surfaces. Such $Fe_2O_3$ layer has also been reported for fresh Fe powder prepared by the reduction of $Fe_2O_3$ by $H_2$ at 675 K for 24 h.[16] After treatment of the original Fe powder with $H_2$/CO up to 553 K (conditions comparable to the F-T synthesis in the autoclave system without $H_2$-pretreatment), the intensity of $Fe_2O_3$ peak decreased significantly and a new peak appeared at 706.9 eV (Fig. 3 A-II), which agrees well with those of iron carbides, such as $Fe_5C_2$.[16-18] Formation of iron carbides is well known to occur during F-T syntheses on various Fe catalysts.[7,9,16-20] When the original Fe powder is treated with $H_2$ at 573 K (similar conditions for the autoclave system), the Fe $2p_{3/2}$ line appeared at 706.7 eV, which agrees with the reported value (706.6 eV) of metallic iron,[16,18] and no peak attributed to $Fe_2O_3$ was observed (Fig. 3 B-I). The consecutive treatment of the $H_2$-pretreated Fe powder with the $H_2$/CO gas resulted in a slight shift of the Fe $2p_{3/2}$ peak position from 706.7 to 706.8 eV (Fig. 3 B-II), that suggests the presence of iron carbides.

Figure 4 shows the O 1s XPS spectra. The O 1s peak of the original Fe powder before the gas-treatment was observed at 529.9 eV with a shoulder in the high binding energy region around 532 eV (Fig. 4 A-I). This main peak position coupled with the

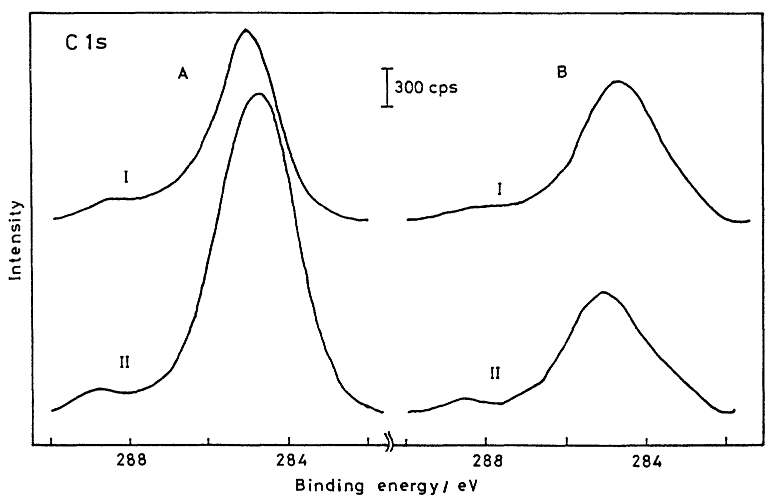

Fig. 5. C 1s XPS spectra of a Fe powder sample. Notations are the same as in Fig. 3.

Table 4. Quantitative XPS Analysis of Fe Powder Surface

| Sample | C 1s peak area/cps • eV | Fe $2p_{3/2}$ peak area/cps • eV | Ratio of C 1s area to Fe $2p_{3/2}$ area |
|---|---|---|---|
| Original | 3380 | 2880 | 1.2 |
| After exposure to $H_2$/CO[a] | 6660 | 1120 | 6.0 |
| With $H_2$ pretreatment[b] | 3010 | 5080 | 0.6 |
| After exposure to $H_2$/CO[a] | 2560 | 4630 | 0.6 |

a) At 553 K for 1 min. b) At 573 K for 30 min.

result of the Fe $2_{3/2}$ peak analysis (Fig. 3 A-I) supports the presence of $Fe_2O_3$ (530 and 529.7 eV have been reported in Refs. 21 and 16, respectively). After the exposure to $H_2$/CO, the $Fe_2O_3$ peak disappeared, but the shoulder peak around 532 eV remained unchanged (Fig. 4 A-II). The remaining peak is ascribed to those of various oxygen-containing carbonaceous and hydrocarbon species adsorbed on Fe; CO (530.1—531.4 eV),[21,22] $CH_3OH$ (532.0 eV),[23] and $CH_3COOH$ (532.0 eV).[24] The similar peak appeared after the treatment of the original Fe powder with $H_2$ (Fig. 4 B-I), followed by the exposure to $H_2$/CO (Fig. 4 B-II). This observation is compatible with the evolution of CO and $CO_2$ during heat-treatment of the Fe powder as described above (Fig. 2).

Figure 5 shows the C 1s XPS spectra. The Fe powder samples both before and after the gas-treatments show wide C 1s peaks ranging from 282 to 290 eV, suggesting the presence of various types of carbonaceous species on Fe powder surfaces.

**Change in C 1s and Fe $2p_{3/2}$ Peak Intensity upon Gas-treatments.** The results of quantitative XPS analyses, using the C 1s (Fig. 5) and Fe $2p_{3/2}$ (Fig. 3) peak areas and photo-ionization cross section,[11] are summarized in Table 4. The ratio of the C 1s to the Fe $2p_{3/2}$ speak areas (C/Fe) clearly indicates the presence of large amounts of carbonaceous species on the original Fe powder surfaces. When the original Fe powder was exposed to $H_2$/CO, the C/Fe value increased from 1.2 to 6.0, indicating the accumulation of carbonaceous species on Fe surfaces under the F-T conditions, as reported for various types of Fe catalysts.[7-9,16-22] After the treatment of the original Fe powder with $H_2$ at 573 K, the C/Fe value was reduced to 0.6, about half of the value of the original Fe powder. Thus, the $H_2$-treatment considerably removed the carbonaceous overlayer on the Fe powder. These XPS results are consistent with the change in the amount of carbon estimated after the $H_2$/CO- and $H_2$-pretreatments in the flow system (Table 2). Interestingly, after the exposure of the $H_2$-pretreated catalyst to $H_2$/CO, the C/Fe ratio remained unchanged (0.6). Thus, once the Fe powder catalyst is treated with $H_2$, no accumulation of carbonaceous species occurs.

**Detailed XPS Analyses of C 1s Peaks.** In order to get further insight into the carbonaceous species on Fe powder surfaces, the C 1s peaks shown in Fig. 5 were separated into 4 or 5 components by the curve resolution technique: A typical example is shown in Fig. 6. The results of the peak separation are summarized in Table 5, where C 1s peaks are divided into 4 components; 283.0—283.3 eV (group 1), 284.6—285.0 eV (group 2), 285.6—287.0 eV (group 3), and 287.5—288.8 eV (group 4). These groups were assigned to carbonaceous species according to the literatures as follows.

Table 5. Separated C 1s XPS Peaks Measured for Fe Powder

| Sample[a] | Respective peak area/cps • eV[b] | | | |
|---|---|---|---|---|
| | Group 1 (283.0—283.3 eV) | Gruop 2 (284.6—285.0 eV) | Gruop 3 (285.6—287.0 eV) | Group 4 (287.5—288.8 eV) |
| Original | —[c] | 2650<br>(0.78) | 370<br>(0.11) | 360<br>0.11) |
| After exposure to $H_2$/CO | —[c] | 5180<br>(0.77) | 1240<br>(0.19) | 240<br>(0.04) |
| With $H_2$ pretreatment | 230<br>(0.08) | 2330<br>(0.77) | 150<br>(0.05) | 300<br>(0.10) |
| After exposure to $H_2$/CO | 250<br>(0.10) | 1400<br>(0.54) | 790<br>(0.31) | 120<br>(0.05) |

a) Treatment conditions are the same as in Table 4.
b) Value in parentheses is ratio to total C 1s peak area.
c) Not detected.

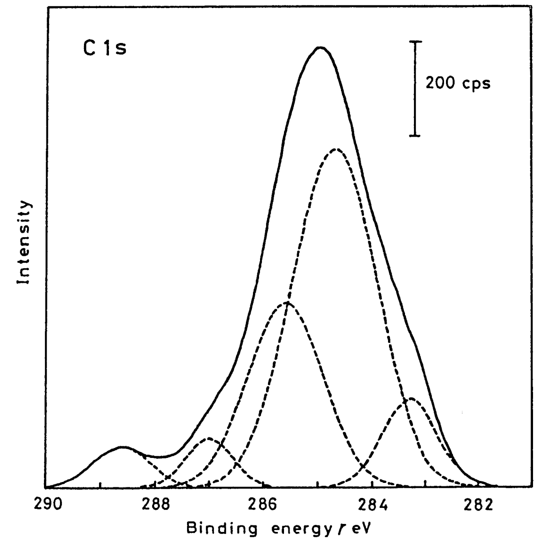

Fig. 6. Separated peaks from C 1s XPS spectrum obtained from a Fe powder sample with $H_2$-pretreatment followed by exposure to $H_2$/CO.

The group 1 peak region corresponds to that of iron carbides (283.2—283.5 eV).[9,16–18,21,22] The disappearance of the group 1 peak upon treatment of the original Fe powder with $H_2/CO$ may be caused by the accumulation of a large amount of carbonaceous species over carbide layer (see Table 4), because the corresponding Fe $2p_{3/2}$ peak position agrees well with that of iron carbides (Fig. 3 A-II).

The group 2 peak region corresponds to that of graphite (284.5—285.3 eV),[8,9,17,18,21,22,25] adsorbed $C_2H_4$,[24] or polymethylene[21] on Fe. It has been reported that graphite is difficult to be removed by $H_2$-pretreatments.[25] However, the carbonaceous species originally present on Fe powder surfaces is removed at least partially, as shown in Fig. 3 and Tables 2 and 4. Thus, the carbonaceous species in group 2 of the original Fe powder catalyst could be assigned to $C_mH_n$ species which can be removed by the $H_2$-pretreatment. The group 2 is the main component of the C 1s spectra for all samples. The change in the group 2 peak area by various gas-treatments is essentially consistent with that of the total carbon shown in Table 4.

The group 3 peaks are attributed to oxygen-containing species adsorbed on Fe, such as carbon monoxide (285.6—285.9 eV)[22,25] and $\alpha$-carbons of hydroxyl and carbonyl groups (285.4—285.7).[23] The group 4 peaks are ascribed to highly oxygenated species, such as carboxylates (288.3—288.8 eV)[24] and carbonates (289.0 eV).[21] The O 1s XPS peaks observed in Fig. 4 as well as the evolution of CO and $CO_2$ during the $H_2$-pretreatments (Fig. 2) support the presence of oxygen-containing carbonaceous species on the original Fe powder catalyst.

The change of Fe catalyst surfaces during the F-T synthesis estimated by XPS is summarized as follows: The original Fe catalyst surfaces are covered with $Fe_2O_3$ (Fig. 3) together with hydrocarbon and oxygen-containing carbonaceous species (Table 5). Under the F-T conditions, the $Fe_2O_3$ layer is converted to iron carbides (Fig. 3) and large amounts of hydrocarbon and oxygen-containing carbonaceous species are accumulated on the iron carbides (Table 5). The $H_2$-pretreatment of the original Fe catalyst results in the reduction of the surface $Fe_2O_3$ layer to metallic iron (Fig. 3), accompanied by partial removal of carbonaceous species on the original catalyst. Under the F-T conditions, the $H_2$-pretreated Fe catalyst is also converted to iron carbides (Fig. 3). In this case, however, accumulation of hydrocarbon species will be little in comparison with the case of the original catalyst which already contains carbonaceous species. This will be the reason why the $H_2$-pretreatment results in the change in the major products from $C_4$ to $C_3$ hydrocarbons in both the autoclave (Table 1) and flow (Table 2) systems.

The gas-pretreatment could cause sintering of Fe powders. However, such a change in the Fe powders will be unlikely to occur, because neither decrease in the total hydrocarbon yield after the $H_2$-pretreatment (Table 1) nor deterioration in the yield of respective hydrocarbon products after repeated reaction over the same Fe catalyst[5] was observed in the autoclave system, and also because only small change in the total hydrocarbon yield and the $C_2$—$C_5$ selectivity was observed for the flow system by various gas-pretreatments (Table 2).

Carbonaceous overlayers have previously been reported[26,27] to affect the selectivity and activity of catalytic reactions. For example, Somorjai[27] reported that the presence of an ordered overlayer is responsible for the formation of benzene during the dehydrogenation of cyclohexane on Pt catalyst, whereas cyclohexene becomes the major product in the presence of a disordered overlayer. Thus, the presence of hydrocarbon over layer on the Fe powder surfaces demonstrated in this study may play an important role in the unique F-T catalytic property of the Fe powder.

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